Electronic Spin States in Fullerides and Endohedral Fullerenes

Von der Fakultät Mathematik und Physik der Universität Stuttgart zur Erlangung der Würde eines Doktors der Naturwissenschaften (Dr. rer. nat.) genehmigte Abhandlung

Vorgelegt von

Jürgen Rahmer

aus Böblingen

Hauptberichter:	Prof. Dr. M. Mehring
Mitberichter:	Prof. Dr. D. Schweitzer
Eingereicht am:	12. Mai 2003
Tag der mündlichen Prüfung:	16. Juli 2003

2. Physikalisches Institut der Universität Stuttgart

2003

Preface

The proposal of a spherical shape for the carbon cluster C_{60} in the middle of the 1980s triggered a number of fundamental discoveries. At the outset, these were the clarification of the singular structural and electronic properties of the "Buckminster fullerene" C_{60} and the larger members of the family of carbon cage molecules. With the availability of greater amounts of fullerenes thanks to the Krätschmer arc burning synthesis, the interest shifted from molecular to solid state properties of C_{60} . Crystalline C_{60} , also referred to as "fullerite", exhibited new astonishing phenomena, like the three-dimensional rotation of C_{60} within the crystalline structure and the light-or pressure-induced formation of one- and two-dimensional intra-crystalline fullerene polymers.

The incorporation of alkali atoms into the large interstitial spaces in solid C_{60} brought yet another new discovery: the formation of fullerene charge-transfer salts, so-called "fullerides". Depending on the magnitude of the charge transfer, these materials are insulating, semiconducting, or metallic, and even superconductivity with critical temperatures as high as 40 K has been observed. Furthermore, reversible structural phase transitions between monomer and $(C_{60})_2$ -dimer as well as $(C_{60})_n$ -polymer phases were discovered. The use of counter ions other than the alkali elements led to further interesting materials, like the organic ferromagnet TDAE- C_{60}^{-1} with a Curie temperature of 16 K.

On the molecular level, research soon focussed on "endohedral fullerenes", i.e., carbon cages that were found to enclose atoms or clusters of atoms. These materials allow intrinsic doping of fullerenes, while at the same time the dopants are shielded and stabilized by the carbon shell of the cage.

The award of the 1996 Nobel prize in chemistry to Kroto, Curl, and Smalley for the discovery of the fullerenes marked both the peak and the end of this initial phase of fullerene research. At this time, the focus started to shift towards carbon nanotubes, which were discovered in 1991 as a by-product of the fullerene production process.

¹TDAE is tetrakis(dimethylamino)ethylene [1].

Due to their unique electronic and mechanical properties, carbon nanotubes promise a number of applications in the fields of nano-electronics and materials' science. The present phase of fullerene research is therefore characterized by a lower level of activity, but a drive towards the realization of new unconventional materials by combining building blocks from classical chemistry with fullerene cages. Typical research aims are the creation of magnetic materials by combining transition metal elements with fullerenes, the improvement of the endohedral fullerene production methods towards high yields to eventually enable the synthesis of endohedral fullerene solids, the synthesis of C_{60} cation salts ("fullerenium salts"), and the inclusion of fullerenes into carbon nanotubes ("peapods").

This thesis reports on investigations of classic fullerene materials typical for the initial research phase as well as new materials. Several fullerene salts and one endohedral system were studied by means of electron spin resonance (ESR) at standard and high fields corresponding to X-band (9.5 GHz) and W-band (95 GHz) frequencies. In part, supplementary nuclear magnetic resonance (NMR), magnetic susceptibility, x-ray, and Raman measurements were performed.

The alkali fullerides \mathbf{RbC}_{60} and \mathbf{CsC}_{60} are classic fullerene materials, which exhibit a number of structurally different phases. Among them, the metallic polymer phase has attracted considerable attention. The existence of one-dimensional polymer chains in this phase led to the proposal of a quasi-one-dimensional metallic character. In contrast, band structure calculations suggested a rather isotropic electronic system. This contradiction motivated ESR investigations at standard and high-fields, which are presented in chapter 4.

Bis(arene)chromium fullerides belong to the more recently synthesized compounds, which combine C_{60} with transition metals in order to create new magnetic materials. Chapter 5 presents a complete characterization of bis(toluene)chromium fulleride including the clarification of a phase transition to a dimer phase below 250 K. This chapter furthermore presents investigations of bis(mesitylene)chromium fulleride and bis(benzene)chromium fulleride.

An interesting group of fulleride materials which has not received much attention to date are the **mixed alkali/alkaline-earth fullerides**. In comparison to alkali fullerides, the higher charge transfers achieved with alkaline-earth dopants allow higher doping levels without the need to increase the number of dopant atoms. In this way, structural effects which depend on the number of counter ions per C_{60} can be separated from the influence of the magnitude of the charge transfer to the molecule. Two protagonists of this group of fullerides, namely $CsBaC_{60}$ and $KCsBaC_{60}$ are presented

in chapter 6.

Another modern system are **fullerenium salts**, which result from the combination of C_{60} with strong oxidants. These materials address the question whether the wealth of solid state phenomena observed in the electron-doped fullerenes can also be realized with hole-doped C_{60} . ESR measurements of fullerenium arsenic hexafluoride are presented in chapter 7.

The last research topic addressed in this work concerns the classic low-yield endohedral system $\mathbf{Sc_3}@\mathbf{C_{82}}$. Although the discovery of this substance dates back to 1991, temperature-dependent ESR studies and the availability of ¹³C enriched material allowed new insights into this fascinating compound. Chapter 9 presents the investigations of $\mathbf{Sc_3}@\mathbf{C_{60}}$ in solution. In order to enable a better assessment of the obtained results, chapter 8 discusses other group III (Sc, Y, La) endohedral materials. Furthermore, by way of a general introduction to fullerenes, chapter 1 reviews molecular properties of $\mathbf{C_{60}}$ and higher fullerene cages, while chapter 2 gives a brief report on relevant solid state properties of $\mathbf{C_{60}}$ and the fullerene salts.

Chapter 3 briefly discusses the experimental methods used in this work. Right from the beginning of fullerene research, electron spin resonance (ESR) played an important role in the elucidation of electronic properties of fullerene-based materials. It helped to identify and discriminate the first paramagnetic endohedral fullerene, $La@C_{82}$, from diamagnetic empty cages. Moreover, solid state properties like metallicity, magnetic-order phenomena, or superconductivity can be directly accessed by ESR. Temperature-dependent studies furthermore supply information about electronic dynamics in molecules as well as in the solid state. Finally, hyperfine coupling between the electronic spin and neighboring nuclear spins provides information on the degree of delocalization of the electronic wave function.

ESR signal analysis is greatly facilitated by the comparison of spectra obtained at different frequency bands. The availability of a 95 GHz (W-band) ESR spectrometer in addition to standard 9.5 GHz (X-band) spectrometers was thus a crucial prerequisite for the thorough ESR analysis of fullerene materials presented in this work.

As mentioned above, in addition to ESR other methods have been applied. Among those were x-ray diffraction, magnetic susceptibility (SQUID) measurements, Raman spectroscopy, and nuclear magnetic resonance (NMR), all of which are briefly introduced and discussed in view of their role in fullerene research in chapter 3.

As a tribute to new dissertation regulations, a German abstract is appended to this work in chapter "Zusammenfassung".

6_____

Contents

Pr	reface	e	3	
\mathbf{Li}	st of	Abbreviations	11	
1	Full	erenes – Carbon in 3D	13	
	1.1	A New Form of Carbon	13	
	1.2	Buckminsterfullerene C_{60}	16	
		1.2.1 Structure and Symmetry	16	
		1.2.2 Electronic Properties	18	
	1.3	Higher Fullerenes	20	
	1.4	Endohedral Fullerenes	21	
		1.4.1 The First "Endohedrals" \ldots \ldots \ldots \ldots \ldots	22	
		1.4.2 The Family of Endohedral Fullerenes	23	
2	2 Solid State Fullerene Compounds 25			
	2.1	Fullerite – C_{60} in the Solid State	25	
		2.1.1 Structure	25	
		2.1.2 Electronic Properties	27	
		2.1.3 Polymerized Fullerite	28	
	2.2	Fullerides – C_{60} Forms Salts $\ldots \ldots \ldots$	29	
		2.2.1 Alkali Fullerides	29	
		2.2.2 Mono-Alkali Fullerides AC_{60} (A =K,Rb,Cs)	30	
		2.2.3 A_3C_{60} – A Medium T_c Superconductor	37	
		2.2.4 Mixed Alkali/Alkaline-Earth Fullerides	38	
		2.2.5 Transition Metal Fullerides	39	
	2.3	Fullerenium Salts	40	
3	Cha	racterization Methods in Fullerene Research	41	
	3.1	Electron Spin Resonance	41	

	3.1.1	Resonance Condition	41
	3.1.2	g Anisotropy	42
	3.1.3	Hyperfine Coupling	43
	3.1.4	Exchange Averaging	44
	3.1.5	Elliott Theory	46
	3.1.6	Paramagnetic Susceptibility	46
	3.1.7	Pauli Paramagnetism	47
	3.1.8	X-Band and W-Band ESR	48
	3.1.9	Fullerenes from the Perspective of ESR	48
3.2	NMR		49
	3.2.1	NMR Line Shifts	49
	3.2.2	$^{13}\mathrm{C}$ NMR Line Shifts in Fullerenes $~$	49
	3.2.3	Relaxation	50
3.3	SQUII	O Measurements	50
3.4	Rama	n Spectroscopy	51
ESI	R Inves	stigations of the Polymer Phase of RbC_{60} and CsC_{60}	53
4.1	High-I	Field ESR of a RbC_{60} Crystal	54
	4.1.1	Sample Preparation	54
	4.1.2	ESR Measurements	55
	4.1.3	Discussion	58
4.2	Scatte	ring Rates in Metallic RbC_{60} and CsC_{60}	59
	4.2.1	Sample Preparation	59
	4.2.2	Elliott Theory	59
	4.2.3	Measurements and Data Analysis	60
	4.2.4	Discussion	63
4.3	Pressu	$ure-Aligned \ RbC_{60} \ Powder \ . \ . \ . \ . \ . \ . \ . \ . \ . \ $	64
	4.3.1	W-Band ESR in the Metallic Phase	64
	4.3.2	W-Band ESR in the Insulating Phase	65
4.4	Summ	ary	67
Bis	Arene)Chromium Fullerides	69
5.1	Chron	´ nium Complexes	70
5.2	Fulleri	de Synthesis	71
5.3	Bis(To	oluene)Chromium Fulleride	72
	5.3.1	X-Ray Diffraction	72
	5.3.2	Magnetic Susceptibility Measurements	74
	 3.2 3.3 3.4 ESF 4.1 4.2 4.3 4.4 Bis(5.1) 5.2 5.3 	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3.1.1 Resonance Condition 3.1.2 g Anisotropy 3.1.3 Hyperfine Coupling 3.1.4 Exchange Averaging 3.1.5 Elliott Theory 3.1.6 Paramagnetic Susceptibility 3.1.7 Pauli Paramagnetism 3.1.8 X-Band and W-Band ESR 3.1.9 Fullerenes from the Perspective of ESR 3.2.1 NMR 3.2.2 ¹³ C NMR Line Shifts 3.2.2 ¹³ C NMR Line Shifts in Fullerenes 3.2.3 Relaxation 3.4 Raman Spectroscopy ESR Investigations of the Polymer Phase of RbC ₆₀ and CsC ₆₀ 4.1 High-Field ESR of a RbC ₆₀ Crystal 4.1.1 Sample Preparation 4.1.2 ESR Measurements 4.1.3 Discussion 4.2 Elliott Theory 4.2.4 Discussion 4.2.5 Amesurements and Data Analysis 4.2.4 Discussion 4.3.1 W-Band ESR in the Metallic Phase 4.3.2 W-Band ESR in the Insulating Phase 4.4 Summary Bis(Arene)

		5.3.3	ESR of $Cr(C_7H_8)_2C_{60}$	76
		5.3.4	13 C NMR	81
		5.3.5	1 H NMR	83
		5.3.6	Discussion	84
	5.4	Bis(M	esitylene)Chromium Fulleride	86
		5.4.1	X-Ray Diffraction	86
		5.4.2	Magnetic Measurements	87
		5.4.3	ESR of $Cr(C_9H_{12})_2C_{60}$	91
		5.4.4	13 C NMR	94
		5.4.5	Discussion	95
	5.5	Bis(Be	enzene)Chromium Fulleride	95
		5.5.1	ESR of $Cr(C_6H_6)_2C_{60}$	96
	5.6	Summ	ary	97
6	Mix	ed All	kali/Alkaline-Earth Fullerides	99
	6.1	The "	Azide Route" to Fullerides	100
	6.2	CsBa	\mathbb{C}_{60}	101
		6.2.1	Raman Measurements of $CsBaC_{60}$	101
		6.2.2	X-Ray Diffraction Measurements of $CsBaC_{60}$	103
		6.2.3	X-Band ESR of $CsBaC_{60}$	104
		6.2.4	W-Band ESR of $CsBaC_{60}$	106
		6.2.5	Discussion	108
	6.3	KCsB	aC_{60}	108
		6.3.1	Raman Measurements of $KCsBaC_{60}$ (#1)	109
		6.3.2	X-Ray Diffraction Measurements of KCsBaC_{60} (#1)	110
		6.3.3	X-Band ESR of KCsBaC ₆₀ (#1)	110
		6.3.4	¹³³ Cs NMR of KCsBaC ₆₀ (#1)	113
		6.3.5	¹³ C NMR of KCsBaC ₆₀ (#1)	116
		6.3.6	Characterization of $KCsBaC_{60}$ (#2)	118
		6.3.7	W-Band ESR of KCsBaC ₆₀ (#2) $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	119
		6.3.8	SQUID Measurements of KCsBaC_{60} (#2)	122
		6.3.9	Discussion of the Superconducting State	124
	6.4	Summ	ary	125
7	Full	ereniu	m Salts	127
	7.1	Synthe	esis and Characterization of $(AsF_6)_n C_{60}$	128
	7.2	ESR o	of $(AsF_6)_n C_{60}$, Batch #3	129

		7.2.1	X-Band ESR	129
		7.2.2	W-Band ESR	132
	7.3	ESR (Comparison of Different Batches	134
	7.4	Concl	usion	135
8	Gro	up III	Metallofullerenes: $M_n@C_{82}, M = Sc, Y, La$	137
	8.1	Mono	metallofullerenes $M@C_{82}$, $M = Sc, Y, La$	138
		8.1.1	La@C ₈₂	138
		8.1.2	$Y@C_{82}$	140
		8.1.3	$Sc@C_{82}$ (and $Sc_2@C_{84}$)	141
	8.2	$Sc_3@C$	\mathbb{D}_{82}	142
9	ESI	R Inve	stigations of $Sc_3@C_{82}$	147
	9.1	Synth	esis and Sample Preparation	147
	9.2	$Sc_3@C$	C_{82} with ¹³ C in Natural Abundance	148
		9.2.1	X-Band ESR at Room Temperature	148
		9.2.2	Temperature-dependent X-Band Measurements	151
		9.2.3	X-Band Measurements After Sample Transfer	158
		9.2.4	Temperature-dependent W-Band Measurements	159
	9.3	^{13}C E	nriched $Sc_3@C_{82}$	161
		9.3.1	X-Band ESR at Room Temperature	161
		9.3.2	Temperature-dependent X-Band ESR	169
		9.3.3	W-Band Measurements	172
		9.3.4	SQUID Measurements	174
		9.3.5	Summary	176
Sı	ımm	ary		179
Zι	usam	menfa	ssung	183
Bi	ibliog	graphy		206

Abbreviations

1D/2D/3D	one-/two-/three-dimensional
AC	alternating current
bcc	body-centered cubic
BCS	Bardeen-Cooper-Schrieffer
bct	body-centered tetragonal
CDW	charge-density wave
CESR	conduction-electron spin resonance
cw	continuous wave
DC	direct current
Decalin	decahydronaphtalene $(C_{10}H_{18})$
DFT	density functional theory
EELS	electron energy loss spectroscopy
ESR	electron spin resonance
FC	field cooled
fcc	face-centered cubic
FWHM	full width at half maximum
hfc	hyperfine coupling
HOMO	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
HWHM	half width at half maximum
IPR	isolated pentagon rule
IUPAC	International Union of Pure and Applied Chemistry
LDA	local density approximation
LUMO	lowest unoccupied molecular orbital
MAS	magic angle spinning
MEM	maximum entropy method
MPI	Max-Planck-Institut
MPMS	magnetic properties measurement system
MRI	magnetic resonance imaging
NMR	nuclear magnetic resonance

PP	peak to peak
ppm	parts per million (10^{-6})
sc	simple cubic
\mathbf{SC}	superconducting
SDW	spin-density wave
SNR	signal-to-noise ratio
SQUID	superconducting quantum interference device
TCB	trichlorobenzene $(C_6H_3Cl_3)$
TMS	tetramethylsilane $(Si(CH_3)_4)$
UPS	ultraviolet photoelectron spectroscopy
UV	ultraviolet
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
ZFC	zero-field cooled

Constants and Factors

$A_{\rm iso}$	isotropic hyperfine	coup	ling	constant	
g	electronic g factor				
g_n	nuclear g factor				
h	Planck's constant:	h	=	$6.626076\cdot 10^{-34}~{\rm Js}$	
ħ	$\hbar = h/2\pi$				
k	Boltzmann factor:	k	=	$1.380658 \cdot 10^{-23} \text{ JK}^{-1}$	1
$\mu_{ m B}$	Bohr magneton:	$\mu_{ m B}$	=	$9.274015 \cdot 10^{-24} \text{ Am}^2$!
$\mu_{ m n}$	nuclear magneton:	$\mu_{ m n}$	=	$5.050787 \cdot 10^{-27} \text{ Am}^2$!

Chapter 1

Fullerenes – Carbon in 3D

This introductory chapter gives a brief account of the discovery of C_{60} and discusses its basic molecular properties. Furthermore "higher fullerenes" as well as "endohedral" systems are introduced.¹

1.1 A New Form of Carbon

"A rather esoteric interest in quantum dynamics led to the discovery of long chains in space and subsequently the discovery of C_{60} [...]" – H. Kroto [4]

The story of the fullerenes began long before their discovery, namely in the 1940's and 50's, when the architect Buckminster Fuller devised light and stable buildings, the so-called "geodesic domes". A representative model of this architecture is displayed in Fig. 1.1. The domes' basic building units are triangles, which form hexagons interspersed with a few pentagons. While an array of hexagons leads to a 2D planar structure like in graphene sheets, pentagons introduce strain and thus lead to the curvature needed for the construction the typical dome-like buildings.

When in 1985 Kroto *et al.* investigated carbon clusters as possible causes of diffuse interstellar IR absorption lines, they were struck by the unusual stability of clusters containing 60 carbon atoms [5]. The sole explanation for the extraordinary inertness of these clusters could be that all sp^2 valences were satisfied – a requirement that can only be met by a spheroidal structure. The group resolved the puzzle by suggesting

¹For a complete overview of the field of fullerenes and fullerene-based materials, starting from the discovery of C_{60} until about 1996, the book of Dresselhaus *et al.* [2] is a recommendable read. A more specialized, but also more up-to-date compendium has been published by Kadish and Ruoff in 2000 [3].



Figure 1.1: Typical geodesic dome construction by Buckminster Fuller. Two of the pentagons needed to obtain the curvature of the two-dimensional hexagonal lattice are marked by thick lines (one at the top, the other one, slightly deformed, at the entrance of the construction).

the highly symmetric soccer-ball structure depicted in Fig. 1.2 for the C_{60} cluster. The resemblance of this C_{60} spheroid to the domes of Buckminster Fuller led to the name "Buckminster Fullerene". Today the term "fullerene" is used to refer to carbon cage structures in general.

For the synthesis of carbon clusters, Kroto and his group used a laser ablation technique. Thereby, the application of short laser pulses on a rotating graphite target vaporizes small graphite fragments into a helium gas stream. After supersonic expansion of the carrier gas, the carbon particles are ionized and directed into a time-of-flight mass spectrometer. With this setup, the famous spectra displayed in Fig. 1.2 were recorded. An increase in the time delay between vaporization of the graphite and expansion of the gas improves the yield of C_{60} with respect to other carbon clusters substantially.

In the following years, theoretical considerations [4] as well as optical and photoelectron spectroscopy [6] produced growing evidence for the cage structure of C_{60} . However, investigations suffered from the fact that only minute quantities of fullerenes were available. The carbon cages were only observable while passing through a timeof-flight mass spectrometer.

This situation changed rapidly, when in 1990 Krätschmer et al. presented a method



Figure 1.2: Left: C_{60} viewed along one of its five-fold symmetry axis. Right: Timeof-flight mass spectra of carbon clusters formed in a laser ablation process under varying conditions. Only clusters with an even number of carbon atoms are observed (c). When the time allowed for the cluster formation is increased (b,a), the yield of C_{60} , and to a lesser degree of C_{70} , is strongly enhanced (from [5]).

which allowed the production of gram quantities of fullerenes [7]. The "Krätschmer method" is based on the production of graphitic carbon soot by evaporating graphite electrodes in an arc discharge under a helium atmosphere. The soot contains C_{60} to several weight percent. C_{60} dissolves in benzene and thus can be extracted from the soot. Once dried, it forms a black crystalline powder, which Krätschmer named "fullerite".

The large quantities of fullerenes provided by the Krätschmer method enabled the application of many well-established methods of characterization and thus quickly promoted a deeper understanding of the cage molecules.



Figure 1.3: ¹³C NMR single line proof for the icosahedral symmetry of C_{60} , which implies the equivalence of all 60 carbon positions [8]. The shift of 142.5 ppm is in the range for non-protonated aromatic carbons, namely 120-150 ppm [9].

¹³C NMR measurements, for instance, became feasible and delivered a very elegant proof for the soccer-ball structure of C_{60} : The soccer-ball is a regular truncated icosahedron in which all vertices, i.e., carbon atoms, are equivalent. Consequently, for an icosahedral C_{60} cluster only one single ¹³C NMR line is expected. In fact, C_{60} films prepared by the Krätschmer method exhibit one single NMR line with a chemical shift of 142.5 ppm [8], as shown in Fig. 1.3.

At this point the evidence for the existence of a new form of carbon was convincing. The field quickly diversified into many branches, dedicated to topics like higher fullerenes (C_n with n > 60), endohedral fullerenes (which enclose one or more atoms), heterofullerenes (where carbon cage atoms are substituted by other elements), fullerene solids, or elongated fullerenes (nanotubes).

In 1996, H. W. Kroto, R. F. Curl, and R. E. Smalley were awarded the Nobel Prize in chemistry for the discovery of the fullerenes and the early experiments which verified the closed cage structure.

1.2 Buckminsterfullerene C₆₀

1.2.1 Structure and Symmetry

Euler's network closure requirement states that a polyhedron consisting only of hexagons and pentagons has to have exactly 12 pentagon faces to form a closed structure [4]. The number of hexagons can freely be chosen. Accordingly the smallest possible fullerene cage, C_{20} , consists only of pentagons. Adding two carbon atoms to the cage creates a hexagon. Thus by the addition of hexagons, cages of arbitrary size can be constructed. This implies that only even-numbered cages occur, which then have closed electronic shells. The first mass spectra already revealed the absence of odd-numbered cages, as shown in Fig. 1.2, diagram (c). However, mass spectra under varying conditions showed, that within the family of closed carbon shells, C_{60} , and to a lesser degree C_{70} , are by far the most stable structures. What is their advantage over the other cages?

It turns out that icosahedral C_{60} is the smallest possible arrangement that avoids fused pentagons. Neighboring pentagons are energetically unfavorable because of the large curvature and strain they induce. The cages are stabilized if the pentagons are surrounded by hexagons. This observation has been formulated as the "isolated pentagon rule" (IPR). Thus it is reasonable that C_{70} , being the second-smallest cage to satisfy the IPR, is also quite stable, while C_{20} , where all pentagons are fused, is very unstable. Empty carbon cages with fused pentagons are generally not stable.

Among the carbon cages that satisfy the IPR, the case of C_{60} is again very special, since the soccer-ball structure has the highest symmetry.² The almost spherical shape allows the molecule to distribute the strain that arises from warping a carbon sheet into a closed cage more homogeneously than the ellipsoidal C_{70} or any other cage of lower symmetry. This property is also reflected in the fact that C_{60} has only one type of carbon site, as discussed in Fig. 1.3 above, whereas C_{70} already hosts 5 distinct sites.

In fact, C_{60} exhibits the highest known molecular symmetry. The molecule belongs to the icosahedral symmetry group I_h , with 6 five-fold rotational axes through the centers of the 12 pentagonal faces, 10 three-fold axes through the centers of the hexagonal faces, and 15 two-fold axes through the center of the hexagon-hexagon fusions.

Despite the high symmetry, the atoms of C_{60} are interconnected by two different types of carbon bonds. From the dipolar coupling of neighboring nuclei, ¹³C NMR revealed that the bonds between carbons at hexagon-pentagon fusions are with 1.46 Å slightly longer than the bonds between neighboring hexagons with only 1.40 Å bond length [10]. The resulting cage diameter of 7.10 Å relates to an average bond length of 1.44 Å, which is slightly longer than the bond length of 1.42 Å observed in graphite.

 $^{{}^{2}}C_{80}$, C_{180} , C_{240} , and many larger fullerenes have the same symmetry as C_{60} , but due to their large size, their formation is less probable.

1.2.2 Electronic Properties

A first approximation to obtain electronic energy levels for the C₆₀ molecule considers the 60 π electrons as free electrons on a sphere. Choosing the energy E_0 as a point of reference, then with the conversion factor γ , the energy levels E_l can be written in terms of the angular momentum quantum number l:

$$E_{l} = E_{0} + \gamma l (l+1).$$
(1.1)

With the *l*th shell having the multiplicity 2(2l + 1), the 60 π electrons completely fill the levels up to l = 4 and partially fill the l = 5 level. However, an open shell compound is not expected to be very stable.



Figure 1.4: Level sequence for the π orbitals as obtained from a Hückel calculation [11]. The angular momentum quantum number l results from the simple model of 60 electrons confined to a sphere. The splitting within one quantum-number larises from the reduction of the spherical symmetry to the icosahedral symmetry of the cage. For quantitative results, e.g. the HOMO-LUMO gap, LDA calculations have been employed [12].

This problem is solved when the symmetry is reduced from spherical to icosahedral. The orbitals then decompose into the irreducible components of the icosahedral group and the 22-fold degeneracy of the l = 5 shell is lifted. Fig. 1.4 shows the resulting levels. It is obvious that the splitting of the l = 5 level into a 10-fold degenerate h_u level and two 6-fold degenerate t_u levels leads to a stable closed shell species.

The succession of molecular π levels in Fig. 1.4 has been obtained from a Hückel calculation [11, 13]. However, in the case of C₆₀ this is only an approximation, because the curvature of the sphere partially mixes σ and π bonds. Furthermore the existence of two different bond lengths goes along with an inhomogeneous π electron distribution over the bonds. Nonetheless, a local-density approximation (LDA) calculation using the density-functional approach gives only marginal corrections to this level scheme [12]. The left part of Fig. 2.2 in chapter 2 shows the levels resulting from such a calculation. Energy levels lying 6 eV and more below the HOMO are attributed to σ bonds, whereas levels close to the Fermi energy arise from π electrons. The HOMO-LUMO gap is calculated to be about 1.9 eV.

C ₆₀ – Molecular Properties	
Bond length on a pentagon	1.46 Å
Bond length on a hexagon	1.40 Å
C_{60} mean diameter	7.10 Å
HOMO-LUMO gap	$1.92~{\rm eV}$
Electron affinity	$2.65 \ \mathrm{eV}$
First ionization potential	$7.6~{\rm eV}$
Second ionization potential	11.5 eV

Table 1.1: Summarized molecular properties of C_{60} . Structural information is taken from [10], electronic data from [12, 14–17].

To further characterize C_{60} , the ionization potentials have been determined using ultraviolet photoelectron spectroscopy (UPS) of thin films of C_{60} [14] and singlephoton ionization with synchrotron radiation [15,16]. Table 1.1 shows that both the ionization energies and the electron affinity [17] are rather large,³ a fact that renders C_{60} a very good electron acceptor, but a poor electron donor. This is a fundamental property of C_{60} that also influences the stability of solid state fullerene compounds, as discussed in chapter 2.

Table 1.1 summarizes the relevant structural and electronic properties of the C_{60} molecule.

Concerning the magnetic properties of C_{60} , it is clear that the closed shell leads to a diamagnetic non-degenerate ground state (J=0). However, it has been found that

³For comparison: Oxygen and fluorine have electron affinities of 1.47 and 3.45 eV and first ionization potentials of 13.7 and 17.5 eV, respectively.

the diamagnetism is much less pronounced than in graphite. Calculations exhibit that the diamagnetism of the hexagon ring currents is partly cancelled by a paramagnetic contribution from pentagon ring currents, so that a rather small diamagnetic susceptibility of $-0.35 \cdot 10^{-6}$ emu/g at room temperature results.⁴

1.3 Higher Fullerenes

 C_{70} and all larger cages with an even number of carbon atoms have at least one isomer that satisfies the isolated pentagon rule (IPR). However, while C_{70} is a stable and rather abundant species, the yield of higher fullerenes in the Krätschmer process is generally low. In addition, with increasing size, the fullerenes diversify in to a large number of IPR satisfying cage isomers. While for C_{70} , C_{72} , and C_{74} only one IPR isomer is possible, C_{76} , C_{78} , C_{80} , C_{82} , and C_{84} allow for 2, 5, 7, 9, and 24 IPR isomers, respectively [18].

Since not all IPR isomers are stable, only part of the possible structures has been isolated. Characterization by ¹³C NMR, which is sensitive to the number of inequivalent carbon positions on the cage, proved the existence of IPR isomers for C₇₆ [19], C₇₈ [20], C₈₀ [21], C₈₂ [22], and the even numbered cages from C₈₄ to C₉₆ [23, 24].



Figure 1.5: C_{70} has only the one IPR-satisfying structure depicted here. The molecule has D_{5h} symmetry. The figure displays the molecule with its five-fold symmetry axis aligned horizontally in the drawing plane.

⁴Graphite: $-21.1 \cdot 10^{-6}$ emu/g for $H \parallel c$ and $-0.4 \cdot 10^{-6}$ emu/g for $H \perp c$.



Figure 1.6: All 9 IPR isomers of C_{82} , numbered according to the Atlas of Fullerenes [18]. The isomers with symmetries C_2 , C_{3v} , and C_{2v} are aligned with their rotational symmetry axes perpendicular to the drawing plane, whereas for the isomers with C_s symmetry the mirror plane is parallel to the drawing plane.

The symmetry of most higher fullerenes is reduced with respect to the icosahedral C_{60} . For illustration, Fig. 1.5 shows the structure of the only IPR isomer of C_{70} , while Fig. 1.6 displays all 9 IPR isomers of C_{82} .

In general, higher fullerenes have a lesser degree of curvature and thus are closer related to graphite.

1.4 Endohedral Fullerenes

Fullerenes which enclose atoms inside the cage are referred to as "endohedral fullerenes". Smalley *et al.* suggested the notation $M@C_n$ for a metal atom M encaged

in a fullerene C_n , which is widely used today.⁵

1.4.1 The First "Endohedrals"

Already in 1985, the year in which C_{60} was discovered, Smalley's group succeeded in enclosing lanthanum atoms inside carbon cages. This was achieved by impregnating the graphite disk, which is used as the carbon source in the laser ablation process [5], with lanthanum. Time-of-flight mass spectroscopy revealed that beside the evennumbered empty carbon shells, even-numbered clusters with one lanthanum atom each were produced. Interestingly, except for the case of C_{60} and C_{70} , these clusters proved to be more stable under laser irradiation than their empty relatives [25]. Although this unusual stability of the lanthanum-containing clusters suggested the inclusion of lanthanum into the cage, the assumption was heavily debated for a long time.

Six years later the Smalley group greatly increased the yield of metallofullerenes by transferring the laser ablation process to a temperature of 1200 °C in an oven or alternatively by using the Krätschmer arc discharge method [26]. In both cases the starting material was a mixture of graphite and La₂O₃ and mass spectroscopy revealed that large amounts of La@C₆₀, La@C₇₄, and La@C₈₂ cages were produced. However, after sublimating the carbon clusters and dissolving the material in hot toluene, beside the empty cages C₆₀, C₇₀, C₈₄, and C₉₆, only La@C₈₂ persisted. The fact that La@C₈₂ is more stable than C₈₂ alone, suggested that the C₈₂ cage is stabilized by a charge transfer from the lanthanum atom to the cage.

Evidence for the endohedral character of the lanthanum ion came from photofragmentation studies [28]. Under intense laser irradiation, pairs of carbon atoms were removed from the cage, so that smaller cages which still enclosed lanthanum were produced. In the case of exohedral lanthanum, the removal of the metal ion would be expected long before the cage is damaged.

Today, the structure of endohedral La@C₈₂ is known from synchrotron radiation studies [27]. Fig. 1.7 shows the molecular structure, which has D_{2v} symmetry.

The C_{82} cage, and to a lesser degree C_{80} and C_{84} , proved to be well-suited for hosting one or more group III transition metal atoms (scandium, yttrium, lanthanum). These systems are reviewed separately in chapter 8, as an introduction to the investigations of $Sc_3@C_{82}$ presented in chapter 9.

⁵However, IUPAC has introduced the name "incar fullerenes" for endohedral fullerenes and proposes the notation " iMC_n " for a metal atom M inside a C_n cage.



Figure 1.7: Structure of La@C₈₂. The cage has D_{2v} symmetry and the lanthanum atom is shifted from the center towards a hexagon by about 2 Å [27].

1.4.2 The Family of Endohedral Fullerenes

Beside lanthanum itself, a large number of lanthanides are known to form stable endohedral mono- and dimetallofullerenes, mainly with C_{82} , C_{84} , and C_{80} cages [29]. In addition to the group III transition metals and the related lanthanides, incorporation of alkaline earth metal atoms also leads to stable components: Ca, Ba, and Sr in C_{82} and C_{84} cages have been isolated and characterized [30]. Since these elements are divalent, a two-fold electron transfer to the cage occurs, which results in diamagnetic systems.

Even so-called "missing" cages like C_{72} and C_{74} , which cannot be isolated in macroscopic amounts as long as they are empty, have been shown to be stabilized by endohedral calcium [31]. Again this stabilizing effect results from the charge transfer to the cage.

Furthermore alkali atoms like lithium, sodium, and potassium have been introduced into C_{60} by ion implantation [32]. However, not only metals, but also some non-metallic elements like helium [33] and nitrogen [34] have been implanted into C_{60} .

A new endohedral species, $Sc_3N@C_{80}$ has been discovered recently [35]. The Sc_3N cluster forms an equilateral triangle with nitrogen at the center. Obviously the nitrogen atom has a strong stabilizing effect on the scandium cluster and thus also on the fullerene. A relative of this compound, namely $Sc_3N@C_{68}$ even manages to stabilize the non-IPR C_{68} cage [36]. Meanwhile a number of other fullerenes based

on the metal-nitrogen "template" have been synthesized, among them $Y_3N@C_{80}$ and $Ho_3N@C_{80}$ [37]. The C_{80} cage of these materials belongs to the symmetry group I_h , which is also observed for C_{60} . The parameters in the arc-burning synthesis for the metal-nitrogen fullerenes can be chosen such that these materials are by far the most abundant product in the soot, even more abundant than C_{60} itself. This allows high yields which are to date impossible to achieve with the nitrogen-free endohedral species.

Up to now a considerable part of the periodic table has been enclosed in fullerene cages. Depending on the charge transfer, these systems allow the doping of fullerene cages from the inside. As soon as larger quantities of these materials become available, the synthesis of solids with unusual properties is expected. Moreover, endohedral systems shield their guest atoms against chemical attack, which thus can be transported or studied in reactive environments. This effect has been exploited with $Gd@C_{82}$, a variant of which is used as an MRI contrast agent which is injected into the human blood stream [38].

Chapter 2

Solid State Fullerene Compounds

This chapter gives a short introduction to the field of solid state fullerene compounds. It focusses on solids based on C_{60} , which, from the solid state physics' point of view have proven to be far more interesting than solids based on C_{70} and other higher fullerenes. The properties of solid fullerene materials are strongly determined by the molecular properties of C_{60} discussed in the previous chapter. For this reason, solids based on C_{60} are often called "molecular solids".

The following sections are supposed to lay the foundation for the investigations of RbC_{60} and CsC_{60} , bis(arene)chromium fullerides, mixed alkali/alkaline earth fullerides, and fullerenium salts presented in chapters 4, 5, 6, and 7, respectively.

2.1 Fullerite $-C_{60}$ in the Solid State

2.1.1 Structure

 C_{60} forms a black, crystalline solid for which Krätschmer introduced the term "fullerite" [7]. Synchrotron powder diffraction measurements revealed that the C_{60} spheres are arranged in a face-centered cubic (fcc) array, with a lattice constant of a=14.17 Å. This corresponds to an intermolecular center-to-center distance of about 10 Å [39]. Considering the diameter of 7.1 Å of the fullerene sphere, the distance is too large to allow the formation of covalent bonds between the spheres. Consequently the material is held together only by van-der-Waals forces.

The unit cell of a C_{60} crystal is depicted in the left part of Fig. 2.1. An important property of the fcc structure is the existence of one octahedral and two tetrahedral interstitial sites per C_{60} , with radii of 2.06 Å and 1.12 Å [40], respectively. These sites are displayed as spheres in the right part of Fig. 2.1. For clarity, the tetrahedrons



Figure 2.1: Left: Fcc unit cell of a C_{60} crystal. The unit cell accommodates four C_{60} molecules. The spaces between the spheres are classified as octahedral (O) and tetrahedral (T) interstitial sites. Right: Illustration of the interstitial sites. The large red spheres represent the space available in the octahedral sites whereas the small green spheres represent the tetrahedral positions. The black lines indicate the eight tetrahedral environments and the central octahedral environment of the unit cell. Altogether there are two T sites and one O site per C₆₀.

and the central octahedron enclosing the spheres are also shown. As discussed later in this chapter, the interstitial sites can host dopant atoms.

The crystal symmetry of fullerite at room-temperature is $Fm3m^1$ [40]. Since C₆₀ has no 4-fold rotational symmetry axis but only 2-, 3- and 5-fold axes, the highest possible crystal symmetry with all molecules in the same orientation would be $Fm3^2$. Only if the molecules randomly assume one of two standard orientations, which are related by a 90 degree rotation about any of the twofold symmetry axes, a non-local measurement like x-ray diffraction yields the observed Fm3m symmetry. This random distribution about different, symmetry-equivalent positions has been named "merohedral disorder"³. In fact, NMR measurements show that at ambient temperatures the spheres not only adopt the two above-mentioned standard orientations, but rotate rapidly with three degrees of rotational freedom and with correlation times in the

¹short for $F4/m\overline{3}2/m$

²short for $F2/m\overline{3}$

³From merohedron (German: "Teilflächner"): Crystal whose surfaces do not display all symmetries of the crystal system.

order of 9 to 12 ps [41]. Therefore this high-temperature phase is also called "rotor phase" [42].

The rotational dynamics change drastically when the material is cooled and a phase transition at about 260 K lowers the lattice symmetry to $Pa\overline{3}^{4}$, which corresponds to a simple cubic system with a=10.04 Å [39,43]. The quasi-free rotation of the spheres is then reduced to a jump-rotation among symmetry equivalent and other nearly degenerate orientations. The rotational jump motion of this so-called "ratchet phase" occurs mainly around the [111] direction. At temperatures below 90 K rotational motion is completely frozen, leaving the C₆₀ molecules locked in differing orientations, which has been described in terms of a "rotational glass" [44]. The underlying reason for this behavior is the attempt of the molecules to minimize their energy by orienting the electron-rich carbon-carbon bonds towards the electron-deficient pentagon or hexagon faces of the neighboring molecules. This can be achieved in many nearly degenerate orientations which are separated by large energy barriers, so that upon cooling the molecules are prevented from adopting the orientation which is lowest in energy [45], hence the name "locked phase".

In summary, rotational disorder is a characteristic attribute of solid C_{60} which affects the electronic and transport properties of fullerene solids [46].

2.1.2 Electronic Properties

In the room-temperature fcc arrangement the electronic overlap between neighboring fullerene molecules is rather small. Therefore only narrow electronic bands develop, which are closely related to the molecular orbitals. This is illustrated by the results of band-structure calculations shown in Fig. 2.2. Accordingly, the bandgap $\Delta E \approx 1.5 \text{ eV} [12]$ is of the same order as the molecular HOMO-LUMO gap (1.9 eV). The gap size positions the material at the borderline between a poor semiconductor and an insulator ($\sigma = 1.7 \cdot 10^{-8} \ (\Omega \text{ cm})^{-1}$ at room-temperature [46]). Due to the highly correlated electronic system and the narrow electronic bands, C₆₀ is often called a "molecular solid".

Table 2.1 summarizes relevant solid state parameters of C_{60} .

⁴The symmetry element 'a' denotes an axial glide plane parallel to the lattice vector **a** with a translation of $\mathbf{a}/2$.



Figure 2.2: The close relation between the C_{60} molecular levels (left) and the crystalline energy bands (right) shows that C_{60} to a large degree retains its molecular nature in the solid. The energies are obtained from a local density approximation calculation [12].

C_{60} – Solid State Properties			
Fcc lattice constant	14.17 Å		
Intermolecular distance	10.02 Å		
Tetrahedral site radius	1.12 Å		
Octahedral site radius	$2.07 \ { m \AA}$		
Density	$1.72 \mathrm{~g/cm^3}$		
Cohesive energy	1.6 eV		
Bandgap ΔE	1.5 eV		
Electrical conductivity (300 K)	$1.7\cdot 10^{-8}~\mathrm{S/cm}$		

Table 2.1: Summarized solid state properties of C_{60} fullerite. Structural information is taken from [39, 40], band gap and cohesive energy from [12], and conductivity from [46].

2.1.3 Polymerized Fullerite

The van-der-Waals bonded C_{60} spheres in the fullerite can be forced to interconnect via chemical bonds. This is achieved by the application of high pressure at elevated temperatures [47] or by irradiating C_{60} films with ultraviolet light at roomtemperature [48]. At temperatures below 260 K, the restricted ability of the molecules to reorient prevents the bond formation process. Both laser and pressure treatment lead to a polymerization, either one-dimensional or two-dimensional, depending on temperature as well as the magnitude of the applied pressure or photocurrent. Naturally, polymerization goes along with a change in the crystal structure, which is transformed to orthorhombic body-centered in the 1D case and various lower symmetry arrangements in the 2D case. In contrast to fcc C_{60} , polymerized C_{60} is not soluble in common organic solvents like toluene.

The intermolecular bonds form via [2+2] cycloaddition, where the π -type bond between two adjoining hexagons on a sphere breaks up and makes two bonds with the respective π electrons on the neighboring molecule. Thus the molecules are interconnected by a four-membered carbon ring, as illustrated in the right part of Fig. 2.5, where the polymer chain found in RbC₆₀ and CsC₆₀ is depicted.

2.2 Fullerides $-C_{60}$ Forms Salts

The interstitial spaces in C_{60} fullerite can be used to intercalate the lattice with atoms or small molecules, as indicated in the right part of Fig. 2.1. This was particularly successful with alkali and alkaline-earth metal atoms, which have the appropriate sizes to fit into the interstices. The ionic radii of theses elements are listed in Tab. 2.2. Once introduced to the lattice, they transfer their valence electron(s) to the electrophilic fullerene molecule. Hybridization between the dopant and the carbon levels remains weak and the resulting system essentially is an ionic salt. The fullerene plays the anionic part, therefore this group of materials was termed "fullerides". Since the dopants occupy the spaces between the C_{60} spheres, this method is referred to as "exohedral" doping, in contrast to "endohedral" doping, where the dopant is located inside the fullerene cage.

The following overview starts with the alkali fullerides, which first displayed all the astonishing properties that were later also found in more complex fullerene salts.

2.2.1 Alkali Fullerides

With alkali metal dopants, electron transfers of up to 12 electrons onto C_{60} have been achieved [3]. This corresponds to a filling of the LUMO and "LUMO+1" of C_{60} , both of which can accommodate 6 electrons, as it was shown in Fig 1.4. While very high doping levels can only be attained with small alkali atoms, e.g., in Na₁₁C₆₀ [49] and

alkali metal	r_i (Å)	alkaline earth	r_i (Å)
Li^+	0.76	Be^{2+}	0.30
Na^+	1.02	Mg^{2+}	0.65
K^+	1.38	Ca^{2+}	1.00
Rb^+	1.52	Sr^{2+}	1.13
Cs^+	1.67	Ba^{2+}	1.34
Fr^+	1.75	Ra^{2+}	1.37

Table 2.2: Radii of the alkali and alkaline-earth metal ions. The radii of the tetrahedral and octahedral sites in the fcc lattice of C_{60} are 1.12 and 2.06 Å, respectively [40].

 $Li_{12}C_{60}$ [3], moderate doping up to A_6C_{60} is easily accomplished with the larger alkali atoms A = K, Rb, and Cs. For these atoms, stable charge transfer compounds of the type A_nC_{60} exist for n = 1, 3, 4, and 6 [50]. Doping levels in-between these values lead to phase separation [51].

Intercalation, i.e., doping, is usually achieved by exposing C_{60} powder or single crystals to the vapor of the respective alkali metal. Subsequent tempering at temperatures above 300°C is applied over the course of several days in order to homogenize the alkali distribution. Since in fcc C_{60} three interstitial sites are available, the crystal can retain its symmetry up to a doping level of n=3. Thus KC_{60} , RbC_{60} , CsC_{60} , K_3C_{60} , and Rb_3C_{60} have fcc phases. Only Cs_3C_{60} forms a body-centered cubic (bcc) structure, because the fcc tetrahedral sites are too small to accommodate the Cs^+ cation. Fullerides with n=6 also prefer the more open bcc structure, while for n=4the symmetry is lowered to body-centered tetragonal (bct).

As in the case of solid C_{60} , the electronic properties of alkali fullerides show a close relation to the electronic configuration of molecular C_{60} . Conductivity measurements revealed that the A_6C_{60} , in which the LUMO of C_{60} is completely filled, are as insulating as C_{60} itself. For a partially filled LUMO, semiconducting (n=1,4), metallic (n=1,3), and even superconducting behavior (n=3) is observed [52].

The following sections focus mainly on mono-alkali fullerides AC_{60} and give a short introduction to the superconducting A_3C_{60} .

2.2.2 Mono-Alkali Fullerides AC_{60} (A=K,Rb,Cs)

The most interesting structural properties have been observed in AC_{60} with A = K, Rb, and Cs. Above roughly 350 K, these materials share an isostructural fcc hightemperature phase. Slow cooling to ambient temperatures results in a phase transition to a polymer phase, where covalent bonds between the fullerenes create long chains within the solid. While the three compounds at first seemed to have an isostructural polymer phase, differences in the relative chain orientations have been discovered. These lead to a metal-to-insulator transition below 50 K in RbC₆₀ and CsC₆₀ on the one hand, while KC₆₀ on the other hand remains unchanged at low temperatures. Furthermore, RbC₆₀ and CsC₆₀ exhibit additional phases, which can be reached by shock cooling (quenching) the samples from 500 K to liquid nitrogen temperatures. The following sections briefly review the different phases.

AC_{60} (A = K, Rb, Cs) – The fcc High-Temperature Phase



Figure 2.3: The fcc structure of AC_{60} (A = K, Rb, Cs) hosts the dopant atoms in the octahedral sites. This phase, also known as "rocksalt" phase, is stable at temperatures above roughly 350 K.

At temperatures above 350–400 K, the mono-alkali fullerides retain the fcc symmetry of the C_{60} fullerite lattice. As shown in Fig. 2.3, the dopant ions selectively occupy the octahedral sites [53]. The electron transfer from the alkali atoms to the fullerene spheres leads to an ionic Coulomb attraction, which results in a slight contraction of the lattice. The lattice constants are summarized in Tab. 2.3.

NMR investigations revealed that the high-temperature phase is paramagnetic, with exchange coupled electrons that are rather localized on the C₆₀ spheres [54]. From IR-transmission experiments, a resistivity of $\rho = 18 \text{ m}\Omega \text{ cm}$, i.e., semi-conducting behavior, has been determined [55].

AC_{60} – Structural Properties			
Compound	Phase	Lattice constant(s) $(Å)$	
C_{60}	fcc $(Fm3m)$	14.17	
KC_{60}	fcc $(rocksalt)$	14.06	
RbC_{60}	fcc $(rocksalt)$	14.08	
CsC_{60}	fcc (rocksalt)	14.13	
KC_{60}	orthorhombic $(Pmnn)$	9.11, 9.95, 14.32	
RbC_{60}	orthorhombic $(I2/m)$	9.14,10.11,14.23	
CsC_{60}	orthorhombic $(I2/m)$	9.10, 10.22, 14.17	

Table 2.3: Structure and lattice constants of different AC_{60} phases. The fcc phase is stable above 350 K and transforms to the orthorhombic room-temperature phase if the sample is cooled slowly. Data taken from [53, 56, 57].

AC_{60} (A = K, Rb, Cs) – The Metallic Polymer-Phase

Slowly cooling the fcc AC_{60} fullerides to ambient temperatures leads to the formation of a body-centered orthorhombic phase [58]. In the course of the structural transition the C_{60} molecules approach their neighbors along the fcc [110] direction, which becomes the *a* direction of the orthorhombic lattice. Fig. 2.4 shows the relation between the high-temperature fcc structure and the orthorhombic arrangement. The center-to-center separation of the C_{60} spheres along the *a* axis becomes as small as $a \approx 9.1$ Å, which is close enough to allow the formation of bonds by [2+2] cycloaddition [56]. Thus along the *a* direction, polymer chains of C_{60} molecules are formed within the crystal. Fig. 2.5 illustrates the polymer bonding for the case of RbC₆₀. Upon heating the material to more than 350–400 K, the polymer bonds break up again. The monomer-polymer transition is thus a true thermal phase transition, driven by the reversible formation and breaking of covalent bonds in the solid [56]. However, the exact transition temperature depends on the precise doping level and the thermal treatment of the material [51]. The dependence on doping and thermal treatment is characteristic for many properties of the alkali fulleride materials and

should be kept in mind, when differing results on nominally identical materials appear.



Figure 2.4: Relation between the high-temperature fcc lattice and the orthorhombic structure. The orthorhombic phase occurs when fcc AC_{60} is slowly cooled to ambient temperatures. The polymer bonds form along the *a* axis.

With a resistivity of $\rho = 9 \text{ m}\Omega \text{ cm}$ for RbC₆₀, the polymer phase of the AC₆₀ is considered as metallic [55]. Below 50 K, RbC₆₀ and CsC₆₀ undergo a metal-to-insulator transition into a magnetically ordered phase [59–61]. This transition is not observed in KC₆₀ and it is interesting to note that this difference results from structural dissimilarities between the seemingly isostructural KC₆₀ on the one hand and RbC₆₀ and CsC₆₀ on the other hand.

X-ray diffraction revealed that in RbC₆₀ and CsC₆₀ the plane spanned by the intermolecular bonds is parallel between neighboring polymer chains, a fact which has been called "ferrorotational coupling" of the chains. In contrast, the chains in KC₆₀ are arranged in an "antiferrorotational" fashion [63]. The rotational alignment of the chains is promoted by the quadrupolar interaction between the C₆₀⁻ ions on neighboring chains. Two competing types of this interaction occur: a direct quadrupolar interaction which favors antiferrorotational alignment and an indirect quadrupolar interaction via the polarized alkali ions which promotes ferrorotational coupling. In the case of the larger Rb and Cs cations, their higher quadrupolar polarizability results in a ferrorotational chain alignment [57,64]. This leads to a symmetry reduction



Figure 2.5: Body-centered orthorhombic unit cell (left) and polymer chain formed by [2+2] cycloaddition along the *a* direction (right). Ball-to-ball separation and bond length apply to RbC₆₀ [56].

to I2/m, so that the lattice structure actually is monoclinic for RbC₆₀ and CsC₆₀. However, x-ray measurements show no deviation from right angles [63] so that this phase is nonetheless referred to as orthorhombic.

Polymer Phase in RbC_{60} and $CsC_{60} - 1D$ versus 3D

The unusual short interfullerene spacing of $a \approx 9.1$ Å within the polymer chain in comparison to the interchain fullerene distance of 9.85 Å soon led to the proposal of a one-dimensional conductivity in the polymer phase [58]. Although the same situation exists in KC₆₀, the 1D assumption was used to interpret the low-temperature metalto-insulator transition in RbC₆₀ and CsC₆₀ as an instability of a 1D system against the formation of spin-density waves. This is a typical phenomenon observed in quasione-dimensional organic conductors like the Bechgaard salt (TMTSF)₂PF₆ [65,66]. The controversy about dimensionality has led to numerous publications on this subject. While the advocates of one-dimensional conductivity interpret results from NMR [67,68], ESR [58,69], and static susceptibility measurements [70] in their favor, the supporters of a three-dimensional picture rely on the same methods [71–75] but come to different conclusions. On the side of theory, the notion of three-dimensional, but slightly anisotropic electronic and magnetic properties finds wide support [76–78],



Figure 2.6: Phases of RbC_{60} and CsC_{60} . The polymer phase is a stable phase which is related to the high-temperature phase by heating and slow cooling. A quench of the fcc high-temperature phase to liquid nitrogen temperatures results in the metastable low-temperature monomer phase. Heating this phase eventually leads to the polymer phase via a metastable dimer phase and a transitional return to the high-temperature monomer phase at about 270 K [62].

with the exception of one group [70] which favors the one-dimensional spin-densitywave picture.

In order to help to resolve this controversy, ESR and high-field ESR measurements of RbC_{60} and CsC_{60} samples have been performed in the framework of this thesis.

These experiments and resulting conclusions are discussed in chapter 4.

Beside the polymer phase, metastable phases of the AC_{60} exist. Fig. 2.6 gives an overview of all phases which occur in RbC₆₀ and CsC₆₀. KC₆₀ behaves slightly different: the metal-to-insulator transition below 50 K in the polymer phase does not occur and also the metastable monomer quench phase has not been reported. The two metastable structures of RbC₆₀ and CsC₆₀ are reviewed in the following sections.

RbC_{60} and CsC_{60} – The Metastable Monomer Phase

This phase is reached by shock-cooling the high-temperature fcc phase from 500 K to liquid nitrogen temperatures. The structure of this phase is reported to be simple cubic [79] with monomeric C_{60} entities. This phase is a three-dimensional metal which transforms irreversibly into a dimer phase upon heating to 125 K and 150 K for RbC₆₀ and CsC₆₀, respectively.

RbC_{60} and CsC_{60} – The Metastable Dimer Phase

The dimer phase is formed either by heating the low-temperature sc phase or by directly quenching the fcc high-temperature phase to temperatures in the range from about 150 K to 250 K [79]. The dimerization has been inferred from IR and Raman measurements [80]. X-ray investigations supported this picture by finding a monoclinic structure with a doubled unit cell. Finally Rietveld refined data led to a scenario with singly bonded $(C_{60})_2^{2-}$ pairs [81,82]. The fullerene center-to-center distance is 9.34 Å which relates to a separation of 1.54 Å. Further proof of the dimer bond came from ¹³C NMR: The electron spins of the C_{60}^- cancel in the dimer bondingorbital and therefore the substantial paramagnetic shift of the ¹³C line vanishes. This has been observed as a line shift from 179 ppm versus TMS for C_{60}^- to 146 ppm for $(C_{60})_2^{2-}$, which is close to the typical position of the likewise diamagnetic neutral C_{60} at 143.5 ppm [83]. ¹³C NMR also verified the notion of a single bond (in contrast to the twofold bond in the polymer phase) by assessing the relative intensity of the sp^3 carbons involved in the bonding in comparison with the sp^2 carbons on the other cage positions [84].

A Word on Sample Quality

Finally it should be noted that many properties of the alkali fullerides are strongly susceptible to small changes in the doping level or the thermal treatment. This means that in spite of long tempering periods usually applied, the investigated materials
normally have areas with non-stoichiometric doping. This problem led to publications about coexisting phases in the low-temperature polymer phase [85] as well as the monomeric quench phase [86]. Furthermore, while KC_{60} consistently has been reported to be metallic down to very low temperatures, one group recently found a metal-to-insulator transition at 50 K, similar to the one observed in RbC_{60} and CsC_{60} [87]. The discrepancies are ascribed to differences in the thermal treatment of the samples.

2.2.3 A_3C_{60} – A Medium T_c Superconductor

Superconductivity in fullerides was first observed at temperatures below 18 K in K_3C_{60} [88]. Soon it was found that in the fcc fullerides, T_c increases almost linearly with the lattice constant, as shown in the left part of Fig. 2.7. Thus higher transition temperatures can be obtained using larger alkali ions, such as rubidium and cesium [89]. The highest transition temperature for a stable fulleride was found with $T_c = 33$ K in RbCs₂C₆₀.⁵ By the application of a pressure of 12 kbar, bcc Cs₃C₆₀ can be transformed into a different structure which is superconducting at temperatures below $T_c = 40$ K [93].

Fulleride superconductors are BCS-type. The increase in lattice constant using larger counter ions reduces the overlap between neighboring molecules and thus decreases the bandwidth, which results in a higher density of states at the Fermi level. This can be shown using a simple BCS estimate for T_c :

$$k_{\rm B} T_{\rm c} = 1.13 \,\overline{\omega}_{\rm ph} \, e^{-\frac{1}{N(E_F)V}} \,.$$
 (2.1)

 $\overline{\omega}_{\rm ph}$ is the average phonon frequency for mediating the electron pairing, $N(E_F)$ is the density of states at the Fermi level, and V is the superconducting pairing interaction. The product $N(E_F)V$ is equal to $\lambda_{\rm ep}$, the electron-phonon coupling constant. Typical parameters are $\overline{\omega} \approx 225 \cdot 10^{12} \, {\rm s}^{-1}$, $V \sim 50 \, {\rm meV}$, $N(E_F) \sim 9 \, {\rm states/eV/C_{60}/spin}$, which lead to $T_c \sim 18 \, {\rm K}$. The typical LUMO band width in K₃C₆₀ or Rb₃C₆₀ is about 0.5–0.6 eV [2].

The effect of the lattice constant on the superconducting transition temperature is nicely illustrated by the comparison between Na₂CsC₆₀ with a = 14.13 Å, which has

⁵In the years 2000 and 2001, J. H. Schön, B. Batlogg, and co-workers published a series of reports on field-induced doping of C_{60} crystals in a field-effect transistor setup. Thereby a transition temperature of $T_c = 52$ K was reported for hole doped C_{60} [90] and a T_c of even 117 K for lattice expanded C_{60} [91]. However, these results were never reproduced and the authors withdrew their publications after the accusation of fraud and the evidence of scientific misconduct furnished by an independent investigation committee in 2002 [92].



Figure 2.7: Left: The transition temperature in superconducting alkali fullerides depends linearly on the fcc lattice constant a_0 [89]. Right: The phase diagram T_c versus chemical doping level shows that in cubic fullerides superconductivity is restricted to doping levels between 2.5 and 3.5 electrons per C₆₀ [94].

a T_c of 11 K, and its lattice-expanded relative $(NH_3)_4Na_2CsC_{60}$ with a = 14.47 Å and $T_c = 29.6$ K.

2.2.4 Mixed Alkali/Alkaline-Earth Fullerides

The use of alkaline-earth metal atoms allows the transfer of two electrons per dopant atom onto C_{60} . Thus quite high charge transfers can be achieved. This has been demonstrated with the alkaline-earth fullerides Ca_5C_{60} , Ba_4C_{60} , and Sr_6C_{60} . These materials superconduct with transition temperatures below 10 K without having a half-filled LUMO or an fcc structure, which were the two prerequisites for superconductivity in alkali fullerides [95, 96].

Furthermore, alkaline-earth doping can be used to completely fill the C₆₀ LUMO without changing the fullerite fcc structure. This permits the separation of charge effects from the structural effects of doping. A good example is the case of Sr₃C₆₀, where the single octahedral and the two tetrahedral sites of fcc C₆₀ are occupied by strontium ions and an fcc structure with a=14.14 Å results [97]. Due to the completely filled LUMO, the material is insulating like C₆₀ itself.

Beside the alkaline-earth fullerides, mixed alkali/alkaline-earth fulleride have been

synthesized. Again, the motivation was to change the charge transfer to C_{60} without changing the structure by substituting alkali ions with alkaline-earth ions. For this purpose, the solid solution compound $K_{3-x}Ba_xC_{60}$ with $0 \le y \le 2$ has been synthesized by Yildirim *et al.* [94]. Furthermore, KCsBaC₆₀ and NaCsBaC₆₀ have been prepared, which are characterized by a fourfold electron transfer onto C_{60} ; these materials are not superconducting. Mixed alkali/alkaline-earth fullerides enabled the construction of the phase diagram shown in Fig. 2.7. The bottom line of the this diagram is, that for cubic alkali or alkaline-earth fullerides superconductivity is restricted to systems with triply charged C_{60} anions.

Other interesting mixed alkali/alkaline-earth fullerides are $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$, for which the molecular orbital above the LUMO, i.e., the "LUMO+1", is half filled and which show superconductivity at 5.6 K and 2.0 K, respectively [98].

Two members of the group of mixed alkali/alkaline-earth fullerides, namely $CsBaC_{60}$ and $KCsBaC_{60}$, have been investigated in collaboration with F. Rachdi from the Université de Montpellier. Thereby possible superconductivity in $CsBaC_{60}$ and the elucidation of the electronic properties of $KCsBaC_{60}$ were the driving forces behind the inquiries. Results are presented in chapter 6.

2.2.5 Transition Metal Fullerides

The combination of fullerenes with transition metals is seen as a promising path towards new interesting solids. In particular, one expects new conducting and magnetic materials. However, while it has been shown that the rare earth elements europium and samarium form fullerides similar to the alkali fullerides [99, 100], with Eu₆C₆₀ even having a ferromagnetic phase below 12 K, the like has not been achieved for lighter transition metal elements. Here, direct intercalation of C₆₀ with metal vapor leads to non-stoichiometric, poorly defined materials. Hg_xC₆₀, for instance, can be formed with x < 1, but no charge transfer to the fullerene molecule is found [101]. On the other hand, XPS measurements of Ti_{2.1}C₆₀ and Ti_{3.6}C₆₀ indicate a partial charge transfer to the C₆₀ and possible hybridization between metal and fullerene orbitals, but this has only been achieved in thin films [102].

A different route to transition metal fullerides makes use of transition metal complexes. These offer a wide variability in size, magnetic and electronic properties and thus facilitate the design of stable fullerides. By these means, cobalt has been cocrystallized with C_{60} using Co^{II}-containing porphyrin rings (tbp) [103]. However, these complexes are rather large, so that a very dilute, non-ionic solid results.

In the case of chromium, well-defined transition metal fullerides can be synthesized

using the compact bis(arene)chromium complexes. This has been demonstrated by Broderick *et al.* for the arenes benzene, toluene, and mesitylene [104]. These fullerides are stabilized by a charge transfer from the complex to C_{60} and offer very interesting solid state physics, which has been investigated in the framework of this thesis. Chapter 5 presents investigations of this new type of organometallic fullerene salt.

2.3 Fullerenium Salts

The wealth of phenomena encountered in fulleride materials soon raised the question whether fullerenium salts, i.e., salts with C_{60} cations, are also feasible. The main problem is certainly the electrophilic nature of C_{60} and its high ionization potential (see Tab. 1.1), so that very strong oxidants have to be applied.

It was found that C_{60} forms stable compounds with iodine, but the material does not exhibit a charge transfer and thus is insulating. It is a clathrate, i.e., a mixture of neutral C_{60} and I_2 , with iodine occupying the interstitial sites of the C_{60} lattice [2]. Obviously, iodine is too weak an oxidant as to remove electrons from C_{60} .

In contrast to iodine, fluorine is strong enough to oxidize C_{60} . The intercalation of C_{60} with AsF₅ is reported to lead to a charge transfer [105]. Thereby AsF₅ dissolved in liquid SO₂ is reacted with C_{60} powder. The resulting material has approximately the stoichiometry $(AsF_6)_2C_{60}$, so that C_{60}^{2+} cations should be formed [106]. However, structure, stoichiometry, and charge transfer of the reported materials are not well defined. In order to improve this situation, $(AsF_6)_nC_{60}$ has been synthesized by the group of Prof. Jansen at the MPI für Festkörperforschung in Stuttgart and was studied by ESR in the framework of this thesis. Chapter 7 reports the results obtained on different samples of this type.

Chapter 3

Characterization Methods in Fullerene Research

This chapter briefly presents techniques which are relevant for the fullerene investigations presented within the scope of this thesis. Since most measurements reported in this work were performed using electron spin resonance (ESR) at standard and high fields, it starts out with an introduction to ESR and shortly describes the spectrometers used. Later on, the roles of ¹³C nuclear spin resonance (NMR), static susceptibility measurements, and Raman spectroscopy in the field of fullerenes are explained.

3.1 Electron Spin Resonance

Electron spin resonance is a well-established technique and there is abundant literature on the underlying principles of this method [107–109]. Therefore the following sections highlight only aspects which are necessary for this work.

3.1.1 Resonance Condition

The spin \boldsymbol{S} of the charged electron results in a magnetic moment

$$\boldsymbol{\mu} = \gamma \boldsymbol{S} = -g \, \frac{\mu_{\rm B}}{\hbar} \boldsymbol{S} \,. \tag{3.1}$$

Hereby γ denotes the magnetogyric ratio, which can be expressed by the g factor, the Bohr magneton $\mu_{\rm B}$, and \hbar , which is the Planck constant divided by 2π . In a magnetic field \boldsymbol{B} , the magnetic moment $\boldsymbol{\mu}$ has the energy $E = -\boldsymbol{\mu} \cdot \boldsymbol{B}$, which leads to the

Hamiltonian of the Zeeman interaction

$$\mathcal{H} = g \,\frac{\mu_{\rm B}}{\hbar} \boldsymbol{B} \cdot \boldsymbol{S} \,. \tag{3.2}$$

If the Cartesian z axis points along the field direction, only the S_z component of the spin is relevant. Using the eigenvalue relation $S_z |\varphi\rangle = \hbar m_S |\varphi\rangle$ for the electron wave function φ , one arrives at the quantized energy levels

$$E = g \,\mu_{\rm B} \,B \,m_S \,. \tag{3.3}$$

The energies are determined by the magnetic quantum number $m_S = -S, ..., S - 1, S$, so that 2S + 1 energy levels occur. The energy difference between these levels corresponds to frequencies in the GHz range for magnetic fields from a few Milliteslas to several Teslas. Thus microwaves are used to induce transitions between electronic Zeeman levels. The selection rule $\Delta m_S = \pm 1$ leads to the ESR resonance condition

$$h\nu = \Delta E = g\,\mu_{\rm B}\,B\,.\tag{3.4}$$

 ν is the transition frequency and *h* the Planck constant. For the free electron, the *g* value is $g_e = 2.0023$. In atoms, molecules, and solids this value can be modified by spin-orbit interaction, but in organic materials (light nuclei) and solids (quenching of the orbital contribution) it is often found close to g_e .

3.1.2 g Anisotropy

The modification of the free electron g factor by spin-orbit coupling can introduce an orientational dependence to the Zeeman interaction. To account for this, the Zeeman Hamiltonian is written as follows:

$$\mathcal{H} = \mu_{\rm B} \, \boldsymbol{B}^{\rm T} \cdot \mathbf{g} \cdot \boldsymbol{S} \,. \tag{3.5}$$

Hereby, g anisotropy is represented by the second rank tensor \mathbf{g} . In order to calculate the orientational dependence of the Zeeman splitting, the following has to be considered: the quantization axis of the spin occurs along the effective magnetic field $\boldsymbol{B}_{\text{eff}} = \boldsymbol{B}^{\text{T}} \cdot \mathbf{g}/g_{\text{e}}$. g_{e} is the free electron g value and thus the magnitude of the effective field is given by

$$|\boldsymbol{B}_{\text{eff}}| = \frac{1}{g_{\text{e}}} \sqrt{\boldsymbol{B}^{\text{T}} \cdot \mathbf{g} \cdot \mathbf{g} \cdot \boldsymbol{B}}$$
(3.6)

$$= \frac{B}{g_{\rm e}} \sqrt{\boldsymbol{n}^{\rm T} \cdot \mathbf{g}^2 \cdot \boldsymbol{n}}$$
(3.7)

with \boldsymbol{n} being the normal vector along the field direction.¹ If one expresses the field direction in the reference frame of the g tensor by $\boldsymbol{n} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)^{\mathrm{T}}$ and introduces the g tensor based on the principal values g_{xx}, g_{yy} , and g_{zz} ,

$$\mathbf{g} = \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix},$$
(3.8)

then the g factor for a specific field orientation can be calculated by

$$g(\vartheta,\varphi) = \sqrt{\boldsymbol{n}^{\mathrm{T}} \cdot \mathbf{g}^{2} \cdot \boldsymbol{n}}$$
(3.9)

$$= \sqrt{g_{xx}^2 \sin^2 \vartheta \cos^2 \varphi + g_{yy}^2 \sin^2 \vartheta \sin^2 \varphi + g_{zz}^2 \cos^2 \vartheta}.$$
(3.10)

The g anisotropy can also be described in terms of the isotropic value g_{iso} , the axial anisotropy Δg , and the non-axiality parameter η . These quantities are related to the Cartesian parameters in the following way:

$$g_{\rm iso} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz}) \tag{3.11}$$

$$\Delta g = g_{zz} - g_{\rm iso} \tag{3.12}$$

$$\eta = (g_{xx} - g_{yy})/\Delta g.$$
 (3.13)

3.1.3 Hyperfine Coupling

The Hamiltonian in the presence of hyperfine coupling between the electron spin S and a nucleus with spin I can be written as:

$$\mathcal{H} = \mu_{\rm B} \, \boldsymbol{B}^{\rm T} \cdot \mathbf{g} \cdot \boldsymbol{S} + \boldsymbol{S}^{\rm T} \cdot \mathbf{A} \cdot \boldsymbol{I} - \mu_{\rm n} \, \boldsymbol{B}^{\rm T} \cdot \mathbf{g}_{\rm n} \cdot \boldsymbol{I} \,. \tag{3.14}$$

The first term is the electron Zeeman term as introduced above. The second term describes an anisotropic hyperfine coupling via the second rank coupling tensor **A**. The third term is the nuclear Zeeman interaction, which is roughly three orders of magnitude smaller that the electron Zeeman contribution.

In order to simplify the calculation of eigenvalues, one can employ some approximations. In the first place, the electron spin is quantized along the effective field which is a superposition of the external field B and the hyperfine field. In the following it is assumed that the hyperfine field is small compared to the external field and thus Sis quantized along B. Secondly, the nuclear spin is quantized along the effective field

¹The g tensor is assumed to be symmetric: $\mathbf{g} = \mathbf{g}^{\mathrm{T}}$.

which results from the hyperfine interaction and the nuclear Zeeman contribution. Often one can assume that the nuclear Zeeman effect is negligible compared to the hyperfine coupling. The energy then reads as follows [107]:

$$E = g(\vartheta, \varphi) \,\mu_{\rm B} \, B \, m_S + \sqrt{\boldsymbol{n}^{\rm T} \cdot \mathbf{A} \cdot \mathbf{A}^{\rm T} \cdot \boldsymbol{n}} \, m_S \, m_I \,. \tag{3.15}$$

 $\boldsymbol{n} = \boldsymbol{B}/B$ is the normal vector pointing along the field direction. With the $(AA)_{ij}$ being the elements of the matrix product $\mathbf{A} \cdot \mathbf{A}^{\mathrm{T}}$ and the normal vector given by $\boldsymbol{n} = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)^{\mathrm{T}}$, the hyperfine coupling for a particular field orientation is defined by

$$A(\vartheta,\varphi) = \sqrt{\mathbf{n}^{\mathrm{T}} \cdot \mathbf{A} \cdot \mathbf{A}^{\mathrm{T}} \cdot \mathbf{n}}$$

$$= \left[(AA)_{xx} \sin^{2} \vartheta \cos^{2} \varphi + 2(AA)_{xy} \sin^{2} \vartheta \cos \varphi \sin \varphi + (AA)_{yy} \sin^{2} \vartheta \sin^{2} \varphi + 2(AA)_{xz} \cos \vartheta \sin \vartheta \cos \varphi + (AA)_{zz} \cos^{2} \vartheta + 2(AA)_{yz} \cos \vartheta \sin \vartheta \sin \varphi \right]^{\frac{1}{2}}.$$
(3.16)

For the case of axial symmetry $(A_{xx} = A_{yy} = A_{\perp}, A_{zz} = A_{\parallel})$ this simplifies to

$$A^{2}(\vartheta) = A_{\perp}^{2} \sin^{2} \vartheta + A_{\parallel}^{2} \cos^{2} \vartheta .$$
(3.17)

Often it is helpful to describe the anisotropy in terms of the isotropic value $A_{iso} = 1/3 (A_{xx} + A_{yy} + A_{zz})$, the uniaxiality parameter $\Delta A = A_{zz} - A_{iso}$, and the asymmetry parameter $\eta = (A_{xx} - A_{yy})/2$.

3.1.4 Exchange Averaging

Exchange coupling between two different spin species results from an overlap of the electronic wave functions. The energy in case of an isotropic exchange coupling between two spins S_1 and S_2 can be obtained from the Heisenberg Hamiltonian

$$\mathcal{H} = -2J\boldsymbol{S_1} \cdot \boldsymbol{S_2} \,. \tag{3.18}$$

Thereby J denotes the exchange coupling constant, which is positive in the case of ferromagnetic coupling and negative for antiferromagnetic coupling. Using the operators $S_{\pm} = S_x \pm iS_y$, the Hamiltonian can be reformulated as

$$\mathcal{H} = -2J \left(S_{1x} S_{2x} + S_{1y} S_{2y} + S_{1z} S_{2z} \right)$$

= $-J \left(S_{1+} S_{2-} + S_{1-} S_{2+} + 2S_{1z} S_{2z} \right).$ (3.19)

The first two terms represent flip-flop processes, which lead to an exchange of the spin orientation between neighboring spins. In a cluster or a solid, the spin state can thus be transported or be delocalized over several paramagnetic centers. If this process is fast, i.e., if the spin exchange rate is comparable to the ESR line separation in frequency units, it leads to an averaging of the individual signals of the spin species S_1 and S_2 into a single resonance line.

The position of the averaged line is obtained from the following center-of-mass formula, where the individual line positions B_1 and B_2 are weighted with their respective ESR susceptibilities χ_1 and χ_2 :

$$B_{\rm avg} = \frac{B_1 \chi_1 + B_2 \chi_2}{\chi_1 + \chi_2} \,. \tag{3.20}$$

If the initial line separation is small compared to the absolute g values, this relation holds for the g-factors also:

$$g_{\rm avg} = \frac{g_1 \chi_1 + g_2 \chi_2}{\chi_1 + \chi_2} \,. \tag{3.21}$$

For slower exchange rates $1/\tau$, when the separated lines begin to shift towards their common center, the shift is given by

$$\sqrt{\delta B_0^2 - \delta B_e^2} = \frac{\sqrt{2}}{\gamma \tau} \,. \tag{3.22}$$

 δB_0 denotes the separation of the undisturbed lines, whereas δB_e is the separation under the influence of exchange coupling. $\gamma = g\mu_{\rm B}/\hbar$ is the magnetogyric ratio. It is also interesting to look at the linewidth in dependence of the exchange rate $1/\tau$. For a rate well below the frequency separation of the lines ("slow interconversion"), the linewidth ΔB is given by

$$\Delta B = \Delta B_0 + \frac{1}{2\tau\gamma}. \tag{3.23}$$

 ΔB_0 is the linewidth in the absence of exchange coupling [107]. Consequently, in the limit of slow interconversion, the initial lines are broadened by the exchange coupling. With increasing coupling strength, the lines coalesce into one signal, until the limit of strong exchange coupling is reached. In this case of "fast interconversion" the linewidth is determined by

$$\Delta B = \Delta B_0 + \gamma \frac{\tau \delta B_0^2}{4} \,. \tag{3.24}$$

This implies that with increasing exchange rate, the width of the averaged line is reduced to the initial linewidth ΔB_0 found in the absence of exchange coupling.

3.1.5 Elliott Theory

Elliott's theory [110], which was extended by Yafet [111], allows to relate conduction electron spin resonance (CESR) linewidth and g factor to the conduction electron scattering rate in a metallic system.

Conduction electron scattering on impurities or phonons leads to spin relaxation if the subbands for the two spin orientations are mixed by spin-orbit coupling. Elliott showed that the admixture of one subband to the other can be estimated by the ratio $\lambda/\Delta E$, where λ is the spin-orbit coupling constant and ΔE is the separation of the respective band and its neighbor bands having the same transformation properties. Thus, when switching on spin-orbit coupling, the wave function connected to the Zeeman state $|\uparrow\rangle$ becomes

$$(a_{\mathbf{k}}|\uparrow\rangle + b_{\mathbf{k}}|\downarrow\rangle)e^{i\mathbf{k}\cdot\mathbf{r}}$$

The ratio b/a is determined by the strength of the mixing, i.e., by $\lambda/\Delta E$. Elliott demonstrated that the admixture leads to a g shift $\Delta g = g - g_e$ versus the freeelectron g value $g_e = 2.0023$. Since the shift is also proportional to the magnitude of the mixing, experimental determination of Δg gives a measure of the influence of spin-orbit coupling on the band structure.

The probability that an electron scattering process leads to a spin flip is proportional to the square of the mixing strength which, following the above reasoning, can be expressed by the g shift Δg . Hereby Elliott established the relation between the scattering rate $1/\tau$ and the metallic spin-relaxation rate $1/T_1$:

$$\frac{1}{T_1} = \alpha \frac{\Delta g^2}{\tau},\tag{3.25}$$

where α is a material-dependent parameter of order unity [111]. Because of the equivalence of transverse and longitudinal relaxation rates $1/T_2 = 1/T_1$ in metallic systems, the above expression can be related directly to the ESR linewidth:

$$\Delta B_{\rm HWHM} = \frac{1}{\gamma T_2} = \frac{\alpha}{\gamma} \frac{\Delta g^2}{\tau}, \qquad (3.26)$$

where ΔB_{HWHM} is the half width of the resonance and $\gamma = g \frac{\mu_{\text{B}}}{\hbar}$ is the magnetogyric ratio.

3.1.6 Paramagnetic Susceptibility

The paramagnetic contribution to the magnetization for a system with total spin J is given by

$$M_{\text{para}} = n_0 g \mu_{\text{B}} J B_J(\alpha) , \qquad (3.27)$$

where the B_J is the Brioullin function, which in this case depends on the ratio between magnetic and thermal energy $\alpha = g\mu_{\rm B}JB_0/kT$. It is given by

$$B_J(\alpha) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}\alpha\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}\alpha\right).$$
(3.28)

For the case of W-band ESR with a typical field of $B_0 = 3.4$ T and a spin of J = S = 1/2, the parameter α is equal to unity for T = 2.29 K. But already at 6 K, it is only 0.38 and thus the Brillouin function is well approximated with first two terms of the hyperbolic cotangent expansion²:

$$B_J(\alpha) = \frac{J+1}{J}\frac{\alpha}{3}.$$
(3.29)

Using this approximation, one arrives at the Curie law for the susceptibility:

$$\chi_{\text{para}} = \mu_0 \frac{M}{B_0} = \frac{C}{T}, \text{ with } C = n_0 \frac{\mu_0 (g\mu_{\text{B}})^2 J(J+1)}{3k}.$$
 (3.30)

Thus for Curie spins, a plot of $1/\chi$ over T yields straight lines through the origin with a slope of 1/C.

If one includes electronic correlations such as exchange coupling, a modified Curie law results:

$$\chi = \frac{C}{T - \Theta} \,. \tag{3.31}$$

This is the Curie-Weiss law that describes the paramagnetic susceptibility of an antiferromagnet ($\Theta < 0$) or a ferromagnet ($\Theta > 0$) above its respective paramagnetic ordering temperature $|\Theta|$.

3.1.7 Pauli Paramagnetism

Pauli paramagnetism is observed in metallic systems and results from the polarization of conduction electrons close to the Fermi energy $E_{\rm F}$. The paramagnetic contribution to the susceptibility is given by

$$\chi = \frac{1}{V} \mu_0 \mu_{\rm B}^2 \rho(E_{\rm F}) \,. \tag{3.32}$$

 $\rho(E_{\rm F})$ is the density of states at the Fermi energy $E_{\rm F}$. Often, this energy is specified by the Fermi temperature $T_{\rm F} = E_{\rm F}(0 \text{ K})/k$. For classical metals it can be as high as several ten thousand Kelvin. In principle, the Pauli susceptibility is independent of temperature, but due to its dependence on the density of states at the Fermi level, it is susceptible to changes in lattice constant.

 $^{2} \operatorname{coth} x = \frac{1}{x} + \frac{x}{3} - \frac{x^{3}}{45} + \dots$

3.1.8 X-Band and W-Band ESR

Standard ESR is performed at the classic radar frequency band at 9.5 GHz (X band). For the investigations presented in this work, two continuous wave (cw) Bruker spectrometers (*ESP 300* and *ER 200 D-SRC*) with a rectangular TE_{102} cavity *ER 4102* were put to use. By helium cooling with an Oxford *ESR 900* continuous flow cryostat, a temperature range from 6 K to 350 K is accessible.

This work is also strongly based on investigations performed with the commercial highfield ESR spectrometer *Elexsys 680* by Bruker. This machine operates at a frequency of 95 GHz (W band), which is generated in a heterodyne setup by mixing an X-band intermediate frequency with the output of a stabilized oscillator that works at 85 GHz. Maximum microwave power at 95 GHz is roughly 8 mW. At W-band frequencies the wave length amounts to mere 3 mm and thus high filling factors can be achieved, which increase sensitivity. The Bruker system uses a cylindrical cavity which is driven in the TE₀₁₁ mode. W-band ESR sensitivity is further increased by the higher spin polarization which results from a ten-fold larger field with respect to X band. The system allows fields up to 6 T, which are achieved with a superconducting split pair magnet. Field variations up to 700 G can be performed with a pair of resistive roomtemperature coils, whereas for larger field variations the superconducting magnet has to be swept. An Oxford *CF935* helium flow cryostat allows temperature variations between 6 K and roughly 320 K.

Beside a substantial increase in sensitivity, the main advantage of W-band ESR is the increase in g resolution by a factor of ten with respect to X band. Since most other interactions, hyperfine coupling for instance, are independent of the applied field, comparison between X- and W-band spectra allows a clear separation of g anisotropy from other contributions.

Finally it should be noted that the W-band spectrometer is also equipped for pulsed ESR. Detection via the fast transient recorder *SpecJet* offers a time resolution of 2 ns.

3.1.9 Fullerenes from the Perspective of ESR

Naturally, the whole spectrum of ESR techniques has been applied to molecular and solid state fullerene materials. Beside the very successful application of ESR to the paramagnetic endohedral fullerenes, which is discussed in detail in chapter 8, the study of radical C_{60} ions in solution yielded important information. In particular it was found that C_{60}^- has a g value close to 1.999 [112], well below the free electron value of 2.0023. From the anisotropy of the spectra, a Jahn-Teller distortion of C_{60} was

inferred. Consequently, the low g value is generally explained by spin-orbit coupling to unquenched angular momentum of the Jahn-Teller distorted $(t_{1u})^1$ configuration [113]. C_{60}^{3-} in liquid solution behaves quite similarly to C_{60}^- , but has a slightly higher g value of 2.001 [112].

 C_{60}^+ cations on the other hand were found to have g values close to 2.003, i.e., larger than the free electron value. Therefore, g factors can be used to discriminate differently charged C_{60} ions. Since C_{60} retains a large part of its molecular properties in the solid, with appropriate caution this reasoning can also be applied in solid fullerene materials.

3.2 NMR

NMR has been applied only sporadically in the framework of this thesis. Therefore, merely a brief introduction is presented here.

3.2.1 NMR Line Shifts

Important information is gained by the evaluation of the NMR line shift relative to a reference material. A line shift can arise from diamagnetic shielding currents of closed shells or from an averaged hyperfine coupling to the electron spins, typically of a metal. The former is referred to as chemical shift and can be described by a second rank tensor $\boldsymbol{\sigma}$, while the latter is the so-called Knight shift described by the tensor **K**. The shift energy is given by

$$\mathcal{H} = -\mathbf{B}^{\mathrm{T}} \cdot (\boldsymbol{\sigma} + \mathbf{K}) \cdot \mathbf{I} \,. \tag{3.33}$$

The Knight shift in metals can be related to the conduction-electron susceptibility χ and the hyperfine coupling tensor **A** by

$$\mathbf{K} = \frac{\chi}{\mu_0 \, g_{\mathrm{e}} \mu_{\mathrm{B}} \, g_{\mathrm{n}} \mu_{\mathrm{n}}} \, \mathbf{A} \,. \tag{3.34}$$

3.2.2 ¹³C NMR Line Shifts in Fullerenes

In general, ¹³C NMR is able to discriminate different bonding states by their line shift. For instance, sp^2 and sp^3 hybridized carbon atoms have well separated isotropic shift ranges of 120 - 150 ppm and 34 - 40 ppm, respectively [9]. Neutral C₆₀ in the solid as well as in solution has a ¹³C NMR isotropic shift value of about 143 ppm. This reflects the almost pure sp^2 nature of its bonds. The formation of sp^3 dimer or polymer bonds in solid fullerenes can therefore be evidenced by the occurrence of sp^3 signals in the ¹³C NMR.

In the case of charged C_{60} anions, additional line shifts arising from the effect of the extra charge on the one hand, and the effect of the electron spin on the other hand, have to be distinguished.

From investigations of alkali fullerides, the effect of additional charges has been determined to be a downfield chemical shift of about 2 ppm per electron and carbon atom [114]. In addition, in the case of an odd number of electrons on the cage, the paramagnetic shift due to the unpaired electron spin has to be considered. Thereby one has to discriminate between localized electron spin density which causes a paramagnetic shift and the delocalized spin density which leads to a Knight shift. In general, the molecular paramagnetic shift in C₆₀ anions dominates over solid state effects [113]. The influence of an electron spin localized on the fullerene is an additional downfield shift of about 40 ppm. Combining chemical and paramagnetic shift contributions, one arrives at a shift of 185 ppm for C₆₀ and 189 ppm for C₆₀³⁻. These values are in fact close to the measured ¹³C shifts of C₆₀ anions in solution as well as in the solid state.

3.2.3 Relaxation

Hyperfine interaction in metals not only causes a Knight shift, but also opens a relaxation path. The respective spin-lattice relaxation rate $1/T_1$ can be expressed in terms of the isotropic Knight shift K using the Korringa relation:

$$\frac{1}{T_1} = \frac{4\pi}{\hbar} kT \left(\frac{g_\mathrm{n}\mu_\mathrm{n}}{g_\mathrm{e}\mu_\mathrm{B}}\right)^2 K^2 \,. \tag{3.35}$$

In principle, this form of the Korringa relation holds only for a free non-interacting electron gas. However, in this context, it should suffice to give an impression of how electrons cause nuclear relaxation.

3.3 SQUID Measurements

A superconducting quantum interference device (SQUID) allows the detection of minute magnetic flux changes by the combination of two Josephson junctions. This technique is put to use in magnetic properties measurement systems (MPMS). For this thesis a Quantum Design MPMS was available, which allows magnetization measurements at applied fields of 0 to 7 T in the temperature range between 2 K and 400 K.

Thereby two operating modes are available: a DC mode in which the magnetization is measured at a constant field and an AC mode which records the absorptive and dispersive response of an oscillating magnetization which is driven by a modulation of the external magnetic field.

According to

$$\chi = \frac{M}{H} = \mu_0 \frac{M}{B_{\text{ext}}}, \qquad (3.36)$$

the static susceptibility can be derived from the magnetization. The temperaturedependence of the total susceptibility often allows the separation of diamagnetic and paramagnetic contributions. Furthermore Curie and Pauli paramagnetism can be discerned by their different temperature behavior. If the number of paramagnetic centers is known, the spin quantum number of a Curie system can be determined according to Eqn. 3.30. Low-temperature saturation measurements, where the magnetization is driven into saturation by the application of high external fields, also allow the determination of the spin quantum number as well as the number of spins according to the Brillouin function introduced in Eqn. 3.28.

Furthermore, the diamagnetism of a superconducting phase or the fingerprint magnetization curves of magnetically ordered states can be clearly identified in SQUID measurements.

3.4 Raman Spectroscopy

 C_{60} and its salts can be viewed as molecular solids, thus a clear distinction between intermolecular and intramolecular vibrational modes can be made. Intermolecular acoustic and optical phonons as well as librational modes exhibit wave numbers³ below roughly 200 cm⁻¹, whereas the intramolecular modes peak about 700 cm⁻¹ for radial or "breathing modes", and around 1400 cm⁻¹ for tangential modes [2]. Vibrational modes are mainly studied by Raman and infrared spectroscopy, partly also by inelastic neutron scattering (preferably with single crystals) and electron energy loss spectroscopy (different selection rules than IR and Raman). In general Raman spectroscopy couples to induced dipoles, i.e., depends on the polarizability, whereas IR spectroscopy couples to permanent dipoles and hence depends on the dipole moment of

a vibration. Raman transitions do not change parity, the selection rule is $\Delta l = 0, \pm 2$. Of the molecular modes of C₆₀, ten are Raman active $(2A_g + 8H_g)$ and four are IR active $(4F_{1u})$ in first order. The Raman active modes with the highest symmetry

³Unit conversion: 1 meV = 8.0668 cm⁻¹ = 11.606 K = 0.24184 THz and 1 THz = 33.356 cm⁻¹, or, easier to memorize, 290 K \approx 25 meV \approx 200 cm⁻¹.



Figure 3.1: $A_g(2)$ pentagonal pinch mode used to determine the doping level of C₆₀. The tangential movement indicated for the front pentagon proceeds in phase for all pentagons on the cage.

are the $A_g(1)$ radial "breathing" mode (492 cm⁻¹) and the tangential $A_g(2)$ "pentagonal pinch" mode (1469 cm⁻¹). The latter mode is characterized by a contraction/expansion of the pentagons as indicated in Fig. 3.1. Due to weak van der Waals bonds in fullerene solids, intramolecular mode frequencies are not altered compared to the free molecule.

In negatively charged C_{60} , the population of antibonding orbitals leads a softening of the $A_g(2)$ pinch mode. The resulting frequency downshift depends linearly on the charge n in the following way [42]:

$$\bar{\nu} = 1469 \text{ cm}^{-1} - n \cdot 6.1 \text{ cm}^{-1}$$
. (3.37)

Thus the $A_g(2)$ mode can be used to determine the charge state of C_{60} at the molecular level. Furthermore, polymerization and dimer formation can detected by a broad peak at about 1458 cm⁻¹, which rises at the expense of the undisturbed $A_g(2)$ mode. The dependence of the $A_g(2)$ mode on the charge level has also been exploited in this work to determine the charge states of fulleride materials. Raman measurements were performed by H. Vogt at the Max-Planck-Institut für Festkörperforschung in Stuttgart. For excitation, a helium-neon laser (wavelength 632.8 nm) has been used, which deposits a power of 0.4 mW at the location of the sample. The resolution of the Raman spectrometer at the frequency of the $A_g(2)$ pinch mode is about 1.8 cm⁻¹.

Chapter 4

ESR Investigations of the Polymer Phase of RbC₆₀ and CsC₆₀

 RbC_{60} and CsC_{60} are the fullerides with the largest number of stable and metastable phases. Among those, the polymeric orthorhombic phase has attracted most attention. It forms at about 350 K when the temperature is lowered from the hightemperature face-centered cubic phase. As discussed in chapter 2, the nature of the ground state of this phase below the metal-to-insulator transition at around 50 K is still under debate. The polymer bonds formed by [2+2] cycloaddition result in sp^3 hybridized bonding atoms and an unusually short spacing of the fullerene molecules along the *a* axis of the orthorhombic unit cell. This situation has led to the proposal of quasi-one-dimensional conductivity and a corresponding transition to a lowtemperature spin-density-wave (SDW) state [58] as observed in Bechgaard salts like $(TMTSF)_2 PF_6$ [66]. The conjecture was supported by the observation of ESR line broadening below the metal-to-insulator transition, which was interpreted in terms of antiferromagnetic resonance (AFMR) as the typical fingerprint of a SDW [69]. Since only powder samples were investigated up to then, the characteristic features of AFMR were only partially resolved. Others therefore issued a note of care concerning the interpretation of ESR data [115]. If one assumes the AFMR interpretation to be correct, it is still open whether the low-temperature phase is a SDW or 3D antiferromagnetic (AFM) state.

This chapter presents ESR results on different types of RbC_{60} and CsC_{60} samples, in order to resolve the question of dimensionality of the electronic system in the polymer phase of these materials.

4.1 High-Field ESR of a RbC₆₀ Crystal

Chauvet *et al.* [58] proposed a one-dimensional metallic state which may suggest itself due to the polymeric structure and more importantly by comparing the ESR linewidth with the cubic fulleride Rb_3C_{60} . According to the Elliott theory [110] presented in chapter 3, the large conduction electron scattering rate in a 3D metal is expected to lead to much broader ESR lines than in a 1D system, as long as the spin-orbit interaction is comparable between the two metals. The much narrower ESR linewidth observed in orthorhombic RbC_{60} thus was seen as a hint at decreased conductionelectron scattering as the consequence of a reduced dimensionality.

The following sections present a detailed ESR investigation which shows that also g tensor anisotropy contributes to the ESR linewidth in RbC₆₀ samples, in particular at high fields, and more importantly, that the observed anisotropy is consistent with a 3D metallic state. In order to separate g tensor line shifts from dynamic broadening, a high field (95 GHz) single crystal ESR investigation has been performed.

4.1.1 Sample Preparation

The RbC₆₀ crystal samples were prepared by sealing single crystals of pristine C_{60} together with a stoichiometric amount of rubidium in an evacuated quartz tube. The tube is heated to 400 °C for a couple of days and then cooled to ambient temperatures. Since the polymer phase is the only insoluble phase in organic solvents, all unwanted phases can be removed by dissolving the crystal in toluene. A detailed description of this procedure can be found in [116]. The dimensions of crystals used for ESR measurements are in the range from 0.3 to 0.5 mm.

It has to be noted that the above procedure does not lead to homogeneous single crystals. The volume change during the phase transition from the fcc high-temperature phase to the orthorhombic phase at room-temperature introduces a considerable amount of strain on the crystal, which thereby breaks into smaller single "minicrystals" or domains. A scanning-electron microscopy picture of the surface of such a crystal is shown in Fig. 4.1.

As the phase transition leads to six possibilities to assign the fcc axes to the orthorhombic a, b, and c axes, one has to assume that these six respectively orthogonal orientations are randomly distributed over the domains. This situation will be dealt with in the ESR analysis.



Figure 4.1: Scanning-electron microscopy exposure showing the morphology of RbC_{60} crystals made by the method described in the text. One can clearly see that the pristine crystal breaks into small "mini-crystals". Picture taken from [117].

4.1.2 ESR Measurements

 RbC_{60} single crystal samples were investigated using ESR at X- and W-band frequencies, i.e., at 9 and 95 GHz, in order to determine the *g* anisotropy. As already mentioned in chapter 3, at W-band frequencies the resolution of *g* anisotropies is improved by a factor of 10 in comparison with X band. Measured *g* values have been corrected by comparison to a Li:LiF standard sample [118].

ESR measurements performed at X-band frequencies show a single Lorentzian line in the temperature range from about 40 K to room temperature, as plotted in the inset of Fig. 4.2. Its width is related to the electronic dynamics which are governed by conduction electron scattering [110], which will be discussed later on in this chapter. At 50 K a linewidth of $\Delta B_{\rm FWHM} = 3.52$ G is observed with an isotropic g factor of $g_{\rm iso} = 2.0015$. Towards higher temperatures, the linewidth increases due to increased electron-phonon scattering, while towards lower temperatures, the linewidth also increases in the course of the metal-to-insulator transition. Thus a minimal dynamic linewidth is observed at around 50 K. This facilitates the determination of the g anisotropy and therefore the following ESR measurements have been conducted at 50 K.

The W-band spectrum is a set of overlapping Lorentzian lines arising from the different unit cell orientations of the crystal with respect to the magnetic field. Rotation of the sample reveals an orientational dependence of the line pattern, as displayed in



Figure 4.2: Comparison of W-band and X-band spectrum (inset) at 50 K. Both signals are plotted over a field range of 50 G. While at 95 GHz, the g anisotropy is partially resolved, at 9 GHz it is hidden within the linewidth of the Lorentzian signal.

Fig. 4.3. The series of spectra was obtained by rotating the sample in steps of 30° . In order to determine the full g tensor, which describes the electronic anisotropy of the unit cell, the single crystal spectrum is analyzed for the orientations displayed in Fig. 4.3. The analysis is complicated by the abovementioned domain structure of the crystals.

All differently oriented domains are assumed to have the same g tensor. According to the orthorhombic structure one can expect six different domain orientations. Correspondingly the simulation uses a weighted sum of six different g tensor orientations. In its local frame, the g tensor is characterized by $g_{iso} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$, $\Delta g = (g_{zz} - g_{iso}), \eta = (g_{xx} - g_{yy})/\Delta g$. Since the weight of each of the domains is unknown, it is introduced as fitting parameter. For simplicity, the same orientationindependent ESR linewidth for all individual lines is assumed. Altogether, 13 parameters determine the model spectrum: six weight factors, the linewidth, the three principal values of the g tensor, and three Euler angles describing the orientation of the crystal with respect to the magnetic field.

A combined fitting procedure was used, which tried to match the model with all seven spectra at the same time. This was achieved with a simulation program written in C/C++ which calculates a set of single crystal spectra using the Gamma library [119], determines the standard deviation with respect to the set of experimental spectra and uses a genetic algorithm to minimize the aberration by varying the abovementioned



Figure 4.3: Orientational dependence of the line structure in W-band ESR at 50 K. The sample was rotated about an axis perpendicular to the static field in steps of 30° degrees. Dashed lines represent simulated spectra obtained from a genetic fitting procedure described in the text.

parameters. Several thousand steps are required to achieve a reasonable agreement between simulation and data. A typical example of a fit is represented by the dashed lines in Fig. 4.3. For this fit the relative weights (1.00,1.02,0.19,1.80,2.06,0.12) of the six domains were obtained.

In order to increase the confidence level of the fitting procedure, the genetic algorithm was started from random initial parameter sets several times. The resulting Euler angles vary strongly from one fit to the other, because there is a high degree of degeneracy among the different orientations for the domains with respect to the sample frame. Nonetheless, the g tensor values show only slight variations. Table 4.1 lists the average value of the parameters extracted from ten different runs of the simulation, together with the standard deviation for these ten sets.

g tensor values			
	$g_{ m iso}$	Δg	η
Average Value	2.0015	0.00038	0.61
Error	0.0001	0.00004	0.12
	g_{xx}	g_{yy}	g_{zz}
Average Value	2.00143	2.00119	2.00188
Error	0.00013	0.00016	0.00014

Table 4.1: g tensor values and their standard deviation resulting from ten runs of the simulation: the different tensor elements are defined as $g_{iso} = \frac{1}{3}(g_{xx} + g_{yy} + g_{zz})$, $\Delta g = (g_{zz} - g_{iso})$, and $\eta = (g_{xx} - g_{yy})/\Delta g$. g_{iso} was determined at X band by comparison with a standard; its error is the experimental accuracy.

4.1.3 Discussion

From Fig. 4.3 it is obvious that the simulation does match the spectra quite well although not completely. Regarding the sample morphology shown in Fig. 4.1, this is most probably due to small contributions from unoriented and disordered interdomain material. Nevertheless the standard error for the values found is rather small, so that within the limits of the model one can be quite optimistic about the accuracy of the results. As shown in Tab. 4.1, a non-axial g tensor for the orthorhombic polymer phase of RbC₆₀ is found, with principal values $g_{xx} = 2.00143$, $g_{yy} = 2.00119$, and $g_{zz} = 2.00188$, corresponding to an isotropic g factor of $g_{iso} = 2.0015$.

How does this g tensor relate to the electronic structure? Band structure calculations which include the calculation of the g tensor are unfortunately not available. Thus one has to resort to symmetry arguments. It follows from symmetry that the principal axes must correspond to the a, b, c axes of the orthorhombic unit cell. Because of the domain structure of the sample one cannot determine the relation between the g tensor principal axes (x, y, z) and the (a, b, c) crystal axes from the experimental data alone. However, the conduction electron spin density distribution as determined from NMR data [74,120] has the polymer axis (a) as its unique axis. One can therefore infer that the same axis corresponds to the unique axis of the g tensor (z axis). The anisotropy in the plane perpendicular to the a axis (b, c, or x, y axes) is appreciable but much less than between the z axis and the x, y axes, consistent with the orthorhombic bandstructure as calculated by Erwin et al. [76].

In conclusion, the g tensor parameters reflect the orthorhombic structure of the polymer phase. However, the small anisotropy of the g tensor is consistent with a rather isotropic electronic structure of orthorhombic RbC₆₀. It should be noted that the 3D nature of the electronic state suggests an antiferromagnetic ground state rather than a SDW ground state.

4.2 Scattering Rates in Metallic RbC₆₀ and CsC₆₀

Beside the extraction and interpretation of the full g anisotropy presented in the previous sections, one can gain additional information by studying the temperature-dependent dynamic conduction-electron-spin-resonance (CESR) linewidth. For this reason, the temperature-dependent CESR linewidths of RbC₆₀ and CsC₆₀ powder samples at standard (X band) and high fields (W band) are measured and analyzed using the Elliott theory. The standard explanation of the narrow ESR linewidth in RbC₆₀ in comparison to the large width in cubic Rb₃C₆₀ in terms of a reduced conduction electron scattering rate implicitly assumes a comparable spin-orbit coupling for both systems. Instead it seems more reasonable that the presence of three rubidium ions per C₆₀ in Rb₃C₆₀ will lead to a larger spin-orbit coupling compared with RbC₆₀. The same scattering rate would then naturally translate into an increased spin relaxation and hence broader CESR line for Rb₃C₆₀.

4.2.1 Sample Preparation

 RbC_{60} and CsC_{60} powder samples have been prepared by K.-F. Thier¹ using the standard method with subsequent slow cooling of the samples from 400 K to room temperature. Characterization was done by ¹³C NMR [121]. The samples, sealed in quartz tubes, were investigated using ESR at X- and W-band frequencies, i.e., at 9 and 95 GHz.

4.2.2 Elliott Theory

Elliott theory [110] presented in chapter 3 allows to relate observed CESR linewidths to intrinsic conduction electron scattering rates in a metallic system. The link between linewidth and scattering rate is the g factor, whose deviation from the free electron value serves as a measure of the spin-orbit coupling.

¹during his time as a PhD student at the 2. Physikalisches Institut

The metallic character of RbC_{60} and CsC_{60} has been shown by optical measurements [59]. Besides, there are two strong indications that the Elliott theory can be applied to the metallic phase of RbC_{60} and CsC_{60} . One is the monotonic increase in linewidth with rising temperature, which hints at a coupling of the spin relaxation to the electron-phonon scattering. The other one is the fact that the resonance observed for CsC_{60} is considerably broader than that for RbC_{60} (see Fig. 4.4). As one expects the heavier cesium atom to cause a larger spin-orbit coupling, this effect demonstrates the importance of spin-orbit coupling for spin relaxation in these materials.

4.2.3 Measurements and Data Analysis



Figure 4.4: X-band spectra of RbC_{60} and CsC_{60} powder samples at 200 K. The CsC_{60} resonance is considerably broader than that of RbC_{60} . This effect can be attributed to larger spin-orbit coupling of the conduction electrons caused by the heavier cesium atom.

Fig. 4.4 displays spectra taken at 200 K at X band. For both materials a Lorentziantype resonance is observed. The signals arise from the conduction electrons of the polymer phase, which is metallic in the temperature range from about 50 K to 350 K. Going from X- to W-band frequencies, g anisotropy leads to a broadening of the lines for both materials. If one fits all spectra with Lorentzian lines, the temperature dependences displayed in Fig. 4.5 are obtained. For RbC₆₀, however, W-band measurements reveal a slight asymmetry of the ESR line which is due to the partial resolution of g anisotropy. The g anisotropy of RbC₆₀ single crystals has been determined in section 4.1.2 [122]. The resulting g tensor is used to simulate a powder pattern, which is then convolved with a Lorentzian fit function in order to match the spectra. The Lorentzian then contains the dynamic linewidth, whereas the influence of g anisotropy is taken account of by the powder simulation. Assuming the same spin dynamics at 9 and 95 GHz, X-band and W-band dynamic linewidths should be the same. However, the same dynamic width for both frequency bands could only be obtained by reducing the g anisotropy from [122] by roughly 20 %, which, on the other hand is within the errors assumed for the g tensor determination. The dynamic linewidths obtained by this method are displayed in Fig. 4.6.



Figure 4.5: Temperature dependence of the full ESR linewidth of RbC_{60} (left) and CsC_{60} (right) powder samples at X- and W-band frequencies, as obtained from Lorentzian fits to the resonance lines. The solid lines in the right figure correspond to the model function described in the text.

In contrast to the linewidth, the g factor for both materials changes only very slightly in the temperature range of interest ($\delta g < 2 \cdot 10^{-4}$). RbC₆₀ has a g factor of 2.0015 (±0.0001), while the value for CsC₆₀ is g = 2.0026 (±0.0001).

The temperature-dependent linewidth data has been modeled using the following relation:

$$\Delta B_{\rm FWHM} = \frac{\hbar}{\mu_{\rm B}} \frac{\Delta g^2}{g} \frac{2}{\tau} + \frac{\Delta g_{\rm aniso}}{g} B_0 \,. \tag{4.1}$$

The first term contains all contributions which are attributed to spin relaxation via spin-orbit coupling. This term corresponds to the Elliott Eqn. (3.26) with $\alpha = 1$. The second term is only applied for CsC_{60} , where no g-anisotropy information is available. It allows the determination of the g anisotropy Δg_{aniso} from the difference in linewidth between X and W band. As described above, for RbC_{60} the g anisotropy is already taken account of by the convolution of an anisotropic powder pattern with a Lorentzian line.

Concerning the first term, the determination of the g shift Δg raises some questions:



Figure 4.6: Temperature dependence of the dynamic part of the ESR linewidth of RbC_{60} powder samples at X- and W-band frequencies. The solid line corresponds to the model function described in the text.

In Elliott theory, Δg is the deviation of the g factor from the free electron value. Now it is a well-known fact that the g factor of discrete C_{60}^- ions is found in the range from 1.994 to 2.001 [112], resulting from an intrinsic spin-orbit coupling of the C_{60} anion. In the fulleride salt there is additional spin-orbit coupling due to the electronic bandstructure formation and admixture of the counter ion wavefunctions. One might conceive the case that the two contributions shift the g factor in opposite directions; then the total g shift with respect to the free electron value is not a good measure of the strength of the spin-orbit coupling of the conduction band.

Applying the reasonable assumption that in CsC_{60} the electrons are subject to a larger spin-orbit coupling than in RbC_{60} (heavy atom effect), one would expect that the spinorbit contribution to Δg is larger in CsC_{60} than in RbC_{60} . However, experimental values are $\Delta g = 2.0015 - 2.0023 = -0.0008$ for RbC_{60} and $\Delta g = 2.0026 - 2.0023 =$ 0.0003 for CsC_{60} . One can therefore conclude that the proper reference for the spinorbit contribution to the relaxation rate is not the free electron value $g_e=2.0023$, but rather the C_{60}^- ion value, for which $g_{\text{C}_{60}}=1.9999$ is used in the following [112].

The scattering rate can be expressed by the sum $\tau^{-1} = \tau_{\rm ph}^{-1} + \tau_{\rm res}^{-1}$ with a temperaturedependent phonon part $\tau_{\rm ph}(T)^{-1}$ and a temperature-independent residual part $\tau_{\rm res}^{-1}$. The phonon part is modeled by a power law as $\tau_{\rm ph}(T)^{-1} = \tau_{\rm ph}^{-1}(300 \text{ K}) \cdot (T/300 \text{ K})^{\beta}$, with the scattering rate $\tau_{\rm ph}^{-1}(300 \text{ K})$ at room temperature (300 K). The temperature independent rate $\tau_{\rm res}^{-1}$ represents scattering of conduction electrons from lattice defects and impurities.

	$ m RbC_{60}$	CsC_{60}
Δg	$16 \cdot 10^{-4}$	$27 \cdot 10^{-4}$
$\tau_{\rm ph}^{-1}(300\ K)\ ({\rm s}^{-1})$	$3.29 \cdot 10^{13}$	$7.54 \cdot 10^{13}$
$\tau_{\rm res}^{-1}~({\rm s}^{-1})$	$2.27 \cdot 10^{13}$	$3.42 \cdot 10^{13}$
$\Delta g_{ m aniso}$	$3.0 \cdot 10^{-4}$	$17.0 \cdot 10^{-4}$

Table 4.2: Parameters obtained from modeling the linewidth data for RbC₆₀ and CsC₆₀ with Δg referenced against the value of C⁻₆₀ ($g_{C_{60}}=1.9999$). The parameters are further explained in the text.

In order to exclude the influence of line-broadening caused by the low-temperature phase below 50 K, the model function is only applied in the temperature range from 60 to 300 K. The exponent β is assumed to be the same for both materials and set to $\beta = 2$, which is close to the values obtained from an unrestricted fit of this parameter. The resulting model functions, without the g anisotropy term for RbC₆₀ but including the g term for CsC₆₀, are plotted as solid lines in Fig. 4.6 and the right part of Fig. 4.5, respectively. One should note that X- and W-band data are fitted with a single parameter set; the resulting parameters are summarized in Tab. 4.2.

4.2.4 Discussion

With $\tau \approx 10^{13} \text{ s}^{-1}$ at room temperature, the scattering rates are found to be roughly the same as those found for classical 3D metals like copper ($\tau = 3.7 \cdot 10^{13} \text{ s}^{-1}$) or silver ($\tau = 2.4 \cdot 10^{13} \text{ s}^{-1}$) [123]. On the other hand, for quasi-one-dimensional systems like (fluoranthenyl)₂PF₆ or related compounds, the linewidth corresponds to interchain scattering rates which are in the range $10^{10} - 10^{11} \text{ s}^{-1}$ [124]. The Elliott relation (3.26) implies, that this also holds for 1D systems which exhibit a large ESR linewidth, like (TMTSF)₂PF₆ with about 200 G at ambient temperatures [125]. The reason is the strong spin-orbit coupling, in the case of (TMTSF)₂PF₆ induced by the substantial electron density at the heavy selenium atoms, which leads to a large g shift and therefore to large ESR linewidths, even for small scattering rates.

Hence, the magnitude of the scattering rates found in RbC_{60} and CsC_{60} leads to the conclusion that the electronic conduction in the metallic polymer phase of these materials is rather isotropic. The narrower linewidths in comparison with Rb_3C_{60} are the consequence of a reduced spin-orbit coupling, which might result from the smaller number of alkali ions in RbC_{60} . No indication of a reduced scattering rate due to dimensionality effects has been found. Therefore the low temperature phase transition is not likely to be viewed as an instability of a quasi-1D system against the formation of a spin-density-wave. On the contrary, the 3D nature of the electronic state favors a 3D antiferromagnetic ground state.

It should be noted that the impurity scattering is rather large and reflects the fact that this type of materials suffers from finite polymer chain lengths. Also the expected orientational disorder of the orthorhombic domains will introduce severe grain boundary scattering so that the large residual broadening can be rationalized. In fact this also explains why it is difficult to observe long range magnetic order in the low temperature phase [115].

Comparing CsC_{60} with RbC_{60} one finds a much larger g anisotropy for CsC_{60} , which indicates an appreciable admixture of cesium orbitals to the conduction-band wave function.

In summary, it has been shown that the scattering rates of conduction electrons in RbC_{60} and CsC_{60} in the temperature range from 60 K to 300 K can be extracted from the temperature-dependent ESR linewidths at X- and W-band frequencies by applying the Elliott theory. The observed scattering rates are consistent with a 3D metallic character of the conduction electrons and therefore challenge the conjecture of quasi-1D-electronic state in these materials.

4.3 Pressure-Aligned RbC₆₀ Powder

The insulating ground state of RbC_{60} and CsC_{60} powder samples has been studied by ESR in the author's diploma thesis [126]. From these investigations it was concluded, that the low-temperature ESR spectra are dominated by defect signals and does not show a clear sign of antiferromagnetic resonance (AFMR) [127]. In the framework of this PhD thesis, a new type of RbC_{60} powder sample has been investigated. In this material, the direction of polymer formation was influenced by uniaxial pressure exerted on the sample during the phase transition from the cubic to the orthorhombic phase [128]. The ESR investigations of this material are briefly discussed in the following.

4.3.1 W-Band ESR in the Metallic Phase

Oriented RbC_{60} powder samples were supplied by B. Renker who slowly cooled the powder through the fcc-to-orthorhombic phase transition at about 400 K under the

application of uniaxial pressure of 12 kbar. This procedure enhances the formation of polymer chains in the crystal axes close to the direction of the applied pressure and thus leads to a partial alignment of the samples [128].



Figure 4.7: Orientational dependence of the CESR signal of a pressure-aligned RbC₆₀ powder sample obtained at 50 K. The line structure is due to g anisotropy and its orientational variation proves the partial alignment of the domains. The dashed lines indicate the outer limit for a g anisotropy.

Fig. 4.7 displays four W-band spectra taken at different angles in the metallic phase of a pressure-aligned RbC₆₀ powder. The clear orientational dependence is due to g anisotropy and proves the partial alignment of the polymer chains. The dashed lines roughly indicate the outer limits of the g anisotropy. Their distance corresponds to a δg of 0.00119, which is larger than the the maximum g difference determined in section 4.1.2 for the crystal sample, namely $g_{zz} - g_{yy} = 0.00069$. As the latter value refers to the true crystal g tensor, whereas the width of the spectrum of the pressure aligned sample gives only an upper limit for the g anisotropy, this difference can be rationalized.

4.3.2 W-Band ESR in the Insulating Phase

With the partial alignment of the material visible in the ESR of the metallic phase, one can take a look at the insulating ground state. It has been reported to be magnetically ordered, but it is not clear whether an antiferromagnet or a spin-density-wave order is realized.

Both a spin-density-wave and an antiferromagnetic ground state show a distinctive ESR behavior, known as antiferromagnetic resonance (AFMR) [129]. In an antiferromagnet neighboring spins are aligned by the exchange coupling which can be expressed by the exchange field $B_{\rm E}$. The orientation of the spins with respect to the lattice occurs along the so-called "easy axis", which is determined by any interaction that couples the spins to the anisotropy of the (non-cubic) lattice. This interaction can in general be described by a molecular field $B_{\rm A}$.

In an ESR experiment, the alignment of the spins leads to a very strong dependence of the resonance field on the orientation of the easy axis with respect to the applied field. Thus for single crystal or a partially aligned material, a strong orientational dependence of the signal should result.



Figure 4.8: W-band signal of different RbC_{60} samples at 6 K. None of the signals exhibits an orientational dependence. The spectra are attributed to overlapping signals of polymeric chain ends, isolated C_{60}^- ions, and remnants of the high-temperature CESR signal [122, 126, 130].

Upon cooling below 50 K, the ESR signal of the pressure-aligned RbC_{60} sample changes significantly. Fig. 4.8 compares the W-band spectra of this sample with the low-temperature signal of the RbC_{60} crystal and the powder sample. In spite of the orientational dependence found in the metallic phase for the crystal (Fig. 4.3) and the aligned (Fig. 4.7) material, all three low-temperature spectra are independent of the sample orientation with respect to the field. This is also true for the X-band measurements (not shown) and thus is in clear contrast to the characteristics of AFMR, which predicts a strong orientational dependence.

The investigation of pressure-aligned RbC_{60} thus corroborates the notion that the low-temperature ESR is dominated by defect signals and does not show AFMR behavior. A detailed analysis of the low-temperature signal using pulsed ESR and a more detailed discussion of AFMR can be found in [122, 126, 130].

4.4 Summary

X- and W-band measurements of different RbC_{60} and CsC_{60} samples have been performed with the aim of acquiring new information about the dimensionality of the electronic system in the polymer phase of these fullerides. Main results on the different samples are:

• RbC₆₀ Crystal

High-field ESR of a RbC₆₀ crystal sample for the first time allowed the resolution of a g anisotropy of the polymer phase. The determination of the g tensor was complicated by the domain structure of the material. Nonetheless, it was possible to extract the principal g tensor values $g_{xx} = 2.0014$, $g_{yy} = 2.0012$, and $g_{zz} = 2.0019$ by fitting the complete angular dependence of the ESR signal with a model.

The g anisotropy is rather small and has no pronounced axiality. It reflects the orthorhombic structure of the metallic polymer phase without giving an indication of enhanced conductivity along the polymer chains. This result is in tune with ¹³C NMR investigations which find sp^3 hybridization for the bonding atoms [84] and an increased spin density at the equator of the fullerenes, away from the bonds [74].

• RbC₆₀ and CsC₆₀ Powder Samples

Comparative temperature-dependent ESR studies at X and W band have been performed on RbC₆₀ and CsC₆₀ powder samples. From the frequency dependence of the ESR linewidth, the influence of g anisotropy was determined and thus the dynamic contribution to the linewidth was accessible. The dynamic information contained in the temperature-dependent linewidths was related to conduction electron scattering rates using the Elliott model. Resulting rates for electron-phonon scattering at room-temperature are $\tau_{\rm ph}^{-1} = 3.29 \cdot 10^{13} \, {\rm s}^{-1}$ and $\tau_{\rm ph}^{-1} = 7.54 \cdot 10^{13} \, {\rm s}^{-1}$ for RbC₆₀ and CsC₆₀, respectively. These rates are in the same order of magnitude as rates in classical 3D metals. Since in metals with reduced dimensionality of the electronic system reduced scattering rates are expected, this result confirms the notion of a rather isotropic electronic system. This is also the picture favored by theory [76].

Beside electron-phonon scattering, large contributions from scattering at domain walls and defect sites are found. These result from small domains and finite polymer chain lengths. This important information is also relevant for the interpretation of magnetic low-temperature phase investigations.

• Pressure-Aligned RbC₆₀

A g anisotropy was resolved in the metallic phase of pressure-aligned RbC₆₀ powder samples. Cooling to temperatures below the metal-to-insulator transition led to a significant change in the signal, with a low-temperature spectrum that is independent of the sample orientation. This reproduces the behavior previously found in the low-temperature phase of the RbC₆₀ crystal [126] and contradicts expectations for antiferromagnetic resonance (AFMR). Thus ESR does not prove the existence of magnetic order, but also cannot exclude it. Imperfect magnetic order due to small domain sizes can possibly suppress long-range magnetic phenomena.

In summary, the ESR investigations of RbC_{60} and CsC_{60} support the picture of a metallic polymer phase in which conductivity results from the overlap of fullerene orbitals along all three crystal axes. The insulating polymer bonds along the orthorhombic *a* axis do not contribute to conductivity. For this reason a magnetic ground state results most probably from 3D antiferromagnetic order. Against this background, the formation of a spin-density-wave, which depends on a quasi-1D electronic system, can be ruled out.

Chapter 5

Bis(Arene)Chromium Fullerides

Even after more than a decade of fullerene research, new combinations of well-known atoms and molecules with carbon cage molecules still promise the discovery of new unconventional materials. A strong motivation is the prospect of creating "magnetic materials", whose magnetically ordered states can be used for several applications, among which data storage is only the most salient. Principle building blocks for those materials are transition metals, which by the overlap of their partially filled d orbitals experience the ordering force of an exchange interaction.

However, transition metals do not easily combine with carbon cages. So far, transition-metal fullerides similar to the alkali fullerides, i.e., of the type $A_n C_{60}$ (A=transition metal), are limited to few, poorly characterized materials [102]. On the other hand, if the metal ion is incorporated in an organometallic complex, the probability of aggregation with fullerenes is greatly enhanced. This has been shown by Broderick *et al.* for bis(arene)chromium complexes with the arene molecules benzene, toluene, and mesitylene [104]. All three complexes form charge-transfer salts with C_{60} . Broderick et al. report only few selected x-ray, conductivity, UV-vis, near-IR, and ESR measurements, which do not give a comprehensive picture. Therefore, in collaboration with the group of Prof. Jansen at the MPI für Festkörperforschung in Stuttgart, a complete characterization and investigation of the electronic and magnetic properties using x-ray diffraction, magnetic (SQUID) measurements, ESR, ¹³C NMR, and ¹H NMR has been performed in the framework of this thesis [131]. On the side of ESR, electronic properties have been studied by standard (9 GHz) and high-field (95 GHz) ESR [132].

This chapter presents the investigation of the three fulleride materials $Cr(C_6H_6)_2C_{60}$, $Cr(C_7H_8)_2C_{60}$, and $Cr(C_9H_{12})_2C_{60}$. Synthesis and characterization were carried out at the Max-Planck-Institut, while the author contributed ESR investigations and the

SQUID-data analysis in the case of bis(mesitylene)chromium fullerides.

5.1 Chromium Complexes

Atomic chromium has an electronic configuration of $3d^54s^1$, i.e., a half-filled *d*-orbital. It forms stable complexes with the arene ring-molecules benzene, toluene (methylbenzene), and mesitylene (1,3,5-trimethylbenzene). Thereby a partial charge transfer of about $\delta = 0.7$ electrons from the metal atom to the rings occurs [133].



Figure 5.1: Bis(arene)chromium complexes formed with benzene, toluene, and mesitylene, i.e., C_6H_6 , C_7H_8 , and C_9H_{12} .

Fig. 5.1 depicts the respective bis(arene)chromium "sandwiches". The distance between the two ring planes amounts to 3.2 Å for bis(benzene)chromium [134].

The three complexes are diamagnetic and constitute good electron donors. Fig. 5.2 shows the energies of the molecular orbitals for bis(benzene)chromium. The HOMO derives from the *d*-orbitals of the chromium atom.

¹³C NMR measurements find that the π -electron system is essentially quenched. Although there is a net electron transfer from the chromium atom to the ring molecules, the quenching is attributed to a donation of π -electron density into vacant metal orbitals [133]. For future reference it should be noted that liquid benzene has a chemical shift of 128.7 ppm versus TMS [9]. With respect to liquid benzene, the complexed rings experience an upfield shift of 53.9 ppm, so that a shift of $\delta_{iso}=74.8$ ppm versus TMS results.

The complexes have been synthesized using the Fischer-Hafner method [135] by A. Hönnerscheid at the MPI für Festkörperforschung in Stuttgart. He also synthesized the fullerides discussed in the following.



Figure 5.2: Molecular energy levels and orbitals for the bis(benzene)chromium complex, from [134]. The HOMO derives from the chromium *d*-orbitals and hosts two electrons.

5.2 Fulleride Synthesis

Bis(arene)chromium fullerides are synthesized by adding a solution containing the chromium complexes to a solution containing C_{60} . The fulleride immediately precipitates and can be filtered off. After washing the material with clean solvent and drying it under vacuum, a black microcrystalline powder¹ remains [131]. The bis(arene)chromium fullerides are air-sensitive and have to be treated under inert conditions. Usually, toluene is used as a solvent. Application of other solvents like decalin and benzene showed that the products of the reactions of bis(toluene)chromium and

¹There have been efforts to grow single crystals, but so far they have not been successful.

bis(mesitylene)chromium with C_{60} are independent of the solvent. However, in the case of bis(benzene)chromium fulleride, the crystal structure depends on the solvent used. Solvent molecules are built into the lattice which is in turn not very well defined. For this reason, the following report focusses on the toluene and mesitylene variants of the fulleride, which are solvent-free, whereas the benzene derivative is discussed only very briefly.

5.3 Bis(Toluene)Chromium Fulleride

Bis(toluene)chromium fulleride $Cr(C_7H_8)_2C_{60}$ is the most interesting material of this group of organometallic fullerides, because it undergoes a reversible first order phase transition at 250 K and furthermore has a well-defined structure.

This section presents the investigation of the structural and electronic changes occurring during the phase transition using x-ray powder diffraction, static susceptibility (SQUID) measurements, standard and high-field ESR, as well as ¹³C and ¹H NMR.

5.3.1 X-Ray Diffraction

X-ray powder diffraction patterns have been recorded at a wavelength of $\lambda = 1.54$ Å. The diffractograms plotted in Fig. 5.3 show different reflection patterns at room-temperature and at 180 K. The crystal structure determined from the room-temperature spectrum is simple cubic with a lattice constant of a = 9.984 Å. The chromium/fullerene ratio is 1 and the ions are arranged in the CsCl-type fashion depicted in Fig. 5.4.

Rietveld refinement of this structure gives best results for the space group $Pm\bar{3}m$, which implies rotational disorder of both chromium complex and C_{60} . The rotating complexes occupy a sphere with a radius of about 3.3 Å, which is comparable to the radius of C_{60} with 3.55 Å. Due to its large size, the dopant cannot occupy interstitial sites of the fcc fullerite lattice (NaCl-type), but enforces the more spacious CsCl structure. Thus the material can be regarded as a rare case of non-interstitial doping of C_{60} .

Upon cooling below 250 K, the compound undergoes a transition into a triclinic phase with lattice parameters a=13.641 Å, b=13.834 Å, c=13.855 Å, $\alpha=91.83^{\circ}$, $\beta=116.78^{\circ}$, and $\gamma=119.33^{\circ}$. These values have been determined by an additional synchrotron investigation which allowed higher resolution at a wavelength of $\lambda = 0.7$ Å [136]. In the low-temperature phase, the unit cell is doubled and the symmetry is strongly


Figure 5.3: X-ray powder diffraction patterns of $Cr(C_7H_8)_2C_{60}$. The hightemperature spectrum reflects the high symmetry of a cubic phase, while the lowtemperature spectrum belongs to a triclinic phase. Spectra were recorded using copper radiation at $\lambda = 1.54$ Å.

reduced to $P\overline{1}$. The new axes a, b, and c correspond to diagonals of the cubic faces of the high-temperature cell.

The structural transition can be pictured more easily if one derives the lowtemperature indexing directly from high-temperature cubic cell. Then the cubic a axes become a' = 9.9 Å, b' = 9.6 Å, c' = 10.0 Å, with $\alpha' = 92.5^{\circ}$, $\beta' = 92.3^{\circ}$, and $\gamma' = 89.9^{\circ}$. This means that along the b' direction the interfullerene distance is considerably reduced. The volume per formula unit decreases from V = 995.2 Å³ above the transition temperature to V' = 962.4 Å³ below. The doubling of the unit cell goes along with a pairing of C₆₀ molecules along the b' axis, which results in an interfullerene distance of only 9.23 Å within the pair.

Fig. 5.5 depicts the triclinic cell. Strong peak overlap in the x-ray diffractogram and the large number of free parameters rendered the determination of molecular orientations impossible. However, in order to have space for the bulky toluene rings, the complexes most probably orient along the body diagonals of the former cubic cell.



Figure 5.4: CsCl-type unit cell of the simple-cubic room-temperature phase of $Cr(C_7H_8)_2C_{60}$. The lattice constant is a = 9.984 Å, which leads to a unit cell volume of V = 995.2 Å³. Both fullerene and chromium complex rotate freely.

5.3.2 Magnetic Susceptibility Measurements

SQUID measurements were performed at a field of 5 T. In order to assess the diamagnetic signal contribution, the educts have been measured separately and their diamagnetic contribution has been subtracted from the fulleride signal. Temperaturedependent magnetic measurements reveal that the two phases are separated by a narrow reversible phase transition at 250 K. Fig. 5.6 plots the static paramagnetic susceptibility (left) and its inverse (right) versus temperature. For Curie spins, straight lines through the origin are expected for the inverse susceptibility.²

The inverse susceptibility plot shows that at low temperatures the spins behave almost perfectly Curie-like. The number of formula units can be determined from the weight of the sample and thus the magnetic moment per formula unit can be inferred from the slope of the line. A moment of $\mu = 1.72 \ \mu_{\rm B}$ is obtained, which is equivalent to one spin S = 1/2 per formula unit. In the high-temperature range, $1/\chi$ is slightly curved, so that a range of magnetic moments $\mu = 2.2 - 2.7 \ \mu_{\rm B}$ is possible. The lower dashed line in Fig. 5.6 represents a moment of $\mu = \sqrt{2} \cdot 1.72 \ \mu_{\rm B} = 2.43 \ \mu_{\rm B}$, i.e., two independent spins S = 1/2. The data points approach this line and therefore it is reasonable to assume the existence of two spins S = 1/2 per formula unit in the hightemperature phase. Since the constituent molecules are diamagnetic, upon formation of the compound an electron transfer must have occurred. With C₆₀ being a good

²For further explanation see chapter 3, Eqn. (3.30)



Figure 5.5: Triclinic low-temperature cell of $Cr(C_7H_8)_2C_{60}$. The new crystal axes correspond to the face diagonals of the cubic high-temperature cell. While the cubic cell contains one formula unit, this doubled cell contains two. Parameters are a =13.641 Å, b = 13.834 Å, c = 13.855 Å, $\alpha = 91.83^{\circ}$, $\beta = 116.78^{\circ}$, $\gamma = 119.33^{\circ}$, and volume V = 1924.8 Å³ [136].

electron acceptor and $Cr(C_7H_8)_2$ a good reducing agent, a transfer of one electron to C_{60} is most plausible. Consequently $Cr(C_7H_8)_2C_{60}$ does not co-crystallize, but is in fact a salt and thus is correctly termed a "fulleride". The charge transfer has also been proven by near-IR absorption studies, which find absorption bands typical for C_{60}^- anions. Furthermore, UV-VIS studies find a characteristic band of $Cr(C_7H_8)_2^+$ cations [104]. Thus, the electronic configuration in the high-temperature phase is well-understood; the 'hole' on the chromium complex and the additional electron on C_{60} constitute the two observed spin species.

However, the situation in the low-temperature phase is not clear. If only one spin species is observed, which of the two species of the high-temperature phase has disappeared? How does this happen? In the following the first question is addressed by means of ESR.



Figure 5.6: SQUID-measurements of $Cr(C_7H_8)_2C_{60}$ at a field of 5 T. The plots show the temperature dependence of the molar paramagnetic susceptibility of $Cr(C_7H_8)_2C_{60}$ (left) and its inverse (right). In the inverse plot, straight lines through the origin reflect Curie behavior. The dashed lines represent Curie behavior for one spin S = 1/2 per unit cell (upper line) and two independent spins S = 1/2 (lower line), respectively.

5.3.3 ESR of $Cr(C_7H_8)_2C_{60}$

ESR experiments at standard (9 GHz, X band) and high frequencies (94 GHz, W band) have been performed in order to clarify the spin configuration at temperatures below the phase transition.

X-Band ESR

X-band ESR in both phases shows a single Lorentzian resonance line. Fig. 5.7 compares the high- and low-temperature signal. At the phase transition, linewidth and line position change. This is clearly visible in Fig. 5.8, where g value and linewidth are plotted versus temperature. The values are obtained from Lorentzian fits to the spectra.

The low-temperature g factor is quite small for a fulleride system and hints at a strong influence of the chromium ion. In order to verify this assumption, a $Cr(C_7H_8)_2I$ reference sample was investigated. In this material, the chromium complex has the same electronic configuration as in the fulleride, but a diamagnetic counterion I⁻. In this case ESR probes only the spin on the chromium complex. The measurement yields a temperature-independent g factor of 1.9868, close to g = 1.9870 observed for $Cr(C_7H_8)_2C_{60}$ at around 200 K. One can therefore assume that the low-temperature signal originates in the spin S = 1/2 of the $Cr(C_7H_8)_2^+$ complex.



Figure 5.7: X-band spectra of $Cr(C_7H_8)_2C_{60}$ above and below the phase transition. In the high-temperature phase, linewidth and g factor are larger than in the low-temperature regime.



Figure 5.8: Temperature-dependent g factor (left) and X-band linewidth $\Delta B_{\rm FWHM}$ (right) of $\rm Cr(C_7H_8)_2C_{60}$ as extracted from Lorentzian fits to the spectra.

The high-temperature g value is in-between the chromium value and the range from 1.9940 to 2.0010, where C_{60}^- is usually observed [112]. Therefore the signal cannot be assigned easily. In order to gain more information, W-band measurements have been performed.

W-Band ESR

The temperature-dependent W-band ESR signal of $Cr(C_7H_8)_2C_{60}$ is displayed in Fig. 5.9. While the high-temperature signal still has Lorentzian lineshape, in the low-temperature phase a g anisotropy can be resolved. Fig. 5.10 directly compares



Figure 5.9: Temperature-dependent W-band spectra of $Cr(C_7H_8)_2C_{60}$. The spectrum at 300 K has Lorentzian line-shape with width of $\Delta B_{\rm FWHM}=70.6$ G. Upon cooling through the transition range at around 250 K, the line shifts and develops an anisotropic shape. The spectra are scaled to the same peak-to-peak amplitude.

the spectra above and below the phase transition. The dotted line represents a fit to the anisotropic spectrum at 240 K. An anisotropic powder pattern convolved with a Lorentzian line has been used to match the spectrum. The fit yields a quasi-axial g tensor with $g_{xx} = 1.9910$, $g_{yy} = 1.9907$, and $g_{zz} = 1.9793$, and a Lorentzian linewidth of $\Delta B_{\rm FWHM} = 76.4$ G.

From the assignment of the low-temperature signal to the chromium complex in a triclinic environment, a g anisotropy is indeed to be expected. Its magnitude of



Figure 5.10: Comparison between the W-band spectrum of $Cr(C_7H_8)_2C_{60}$ above and below the transition temperature of 250 K. At 260 K the Lorentzian line is located at g = 1.9916 with a linewidth of $\Delta B_{\rm FWHM} = 66.8$ G (dashed line). The dotted line represents a fit to the low-temperature spectrum. From the fit a g anisotropy with principal values $g_{xx} = 1.9910$, $g_{yy} = 1.9907$, and $g_{zz} = 1.9793$, and a Lorentzian linewidth of $\Delta B_{\rm FWHM} = 76.4$ G have been extracted.

 $\Delta g = g_{\perp} - g_{\parallel} \approx 0.012$ would be unusually large for a spin on C₆₀ and thus confirms the attribution of the signal to the Cr⁺ complex.³

At high temperatures, both the spin on the chromium complex and the spin of the C_{60} anion should be observed. However, W-band measurements, like the X-band results, show only one isotropic line. The vanishing anisotropy can be understood in terms of the onset of an averaging molecular rotation in the cubic phase. But the existence of only one line, which is shifted with respect to the chromium signal, has to be the result of an exchange averaging process between the two different spin species. Thereby the chromium signal and the signal of C_{60}^- coalesce into a single resonance line, due to an exchange coupling rate that is larger than the line separation (in frequency units). As discussed in section 3.1.4, the resulting line position can be obtained from a center-of-mass-type formula, in which the positions of the undisturbed lines are weighted with their respective ESR susceptibilities:

$$g_{\rm avg} = \frac{g_{\rm Cr} + \chi_{\rm Cr} + + g_{\rm C_{60}^-} \chi_{\rm C_{60}^-}}{\chi_{\rm Cr} + \chi_{\rm C_{60}^-}} \,. \tag{5.1}$$

According to the stoichiometry, equal susceptibilities for both spin species can as-

³In orthorhombic RbC₆₀, for instance, as reported in the previous chapter, $\Delta g = 0.0004$ was found [122].

sumed and thus from the low-temperature value $g_{Cr^+} = 1.9870$ and the hightemperature value $g_{avg} = 1.9916$, a g factor of $g_{C_{60}^-} = 1.9962$ results for the C_{60} anion. This is a typical value for C_{60}^- , for which g factors in the range from 1.994 to 2.001 have been reported [112].

Due to the exchange mechanism, the linewidth has to be of dynamic origin. This is confirmed by the observation that the high-temperature linewidth is almost independent of the applied field; it amounts to $\Delta B_{\rm FWHM} = 52.3$ G at X band and $\Delta B_{\rm FWHM} = 66.8$ G at W band, both at 260 K.

Finally, the question has to be addressed, why no hyperfine coupling to the chromium nucleus is observed. With a natural abundance of 9.55 %, chromium has a nuclear spin of I = 3/2. At high temperatures one can expect that possible hyperfine coupling is averaged due to the observed exchange coupling of the electron spins. At low temperatures, however, a hyperfine coupling could be detectable.

For comparison, a report by Orera *et al.* on chromium defects in SrCl₂:Cr is reviewed [137]. In that investigation, chromium was ionized by x-irradiation at liquid nitrogen temperatures, so that Cr⁺ ions were formed. ESR resolves both the center line due to the I = 0 nuclei and the weaker four-line pattern due to the I = 3/2 fraction. An isotropic hyperfine splitting of 22.5 G is observed.

With an X-band linewidth of around $\Delta B_{\rm FWHM} = 25$ G in the low-temperature phase, a splitting of this magnitude should be resolved. However, as stated above, in the bis(arene) complexes, a partial electron transfer of 0.7 *e* from the metal to the aromatic rings occurs. Therefore one can expect a reduced electron spin density at the chromium nuclear site and thus reduced hyperfine coupling. In this scenario the hyperfine satellites would be hidden within the linewidth of the I = 0 signal.

In summary, ESR investigations revealed that the high-temperature signal results from an exchange averaging between the spin on the cationic chromium complex and the spin of the C_{60} anion. The low-temperature signal is produced solely by the spin of the bis(toluene)chromium cation.

However, the question remains, why the spin of C_{60}^- is not observed in the lowtemperature phase. Possible scenarios known from the alkali fullerides include dimer or polymer formation between the fullerene cages [56,81,138]. In a dimer phase, two doublet electron spins on neighboring fullerenes can pair in an interfullerene bonding orbital. In case of a polymer chain, the short distance between the C₆₀ cages can lead to substantial exchange interaction and an ordering of the spins. The dimer and the polymer scenario can be discriminated by looking at the magnetic surrounding of the carbon nucleus using ¹³C NMR.

5.3.4 ¹³C NMR

¹³C NMR investigations of $Cr(C_7H_8)_2C_{60}$ have been performed in order to obtain information about the bonding state of C_{60} in the low-temperature phase. In particular, the idea of dimer or polymer formation is to be verified. If the electron spins on C_{60} cancel with spins on neighboring molecules by forming dimer bonds, the paramagnetic shift of the ¹³ C NMR signal induced by the electron spins has to vanish. This should lead to an observable line shift. If, on the other hand, a polymer is formed, the uniaxial strain put on the C_{60} molecule should render the carbon positions on the cage inequivalent, so that the isotropic C_{60}^- line would turn into a complex line pattern.

Fig. 5.11 shows ¹³C-MAS-NMR spectra at temperatures above and below the phase transition. The spectra have been obtained on a 400 MHz spectrometer⁴ with a magic-angle-spinning (MAS) frequency of 10 kHz by L. van Wüllen at the MPI für Festkörperforschung in Stuttgart.



Figure 5.11: ¹³C-MAS-NMR spectra of $Cr(C_7H_8)_2C_{60}$ at different temperatures. The main lines between 100 and 200 ppm arise from the fullerene, whereas the small peaks in the room-temperature spectrum at negative shift values and at 392 ppm are due to the sp^2 and sp^3 toluene carbons, respectively.

 $^{^{4}}$ For 13 C this translates into a resonance frequency of 100 MHz at a field of 9.4 T.

The room-temperature spectrum is dominated by the fullerene peak at a shift of 185 ppm (vs. TMS). This is a typical shift value for C_{60}^- , which in the solid state has been observed at positions ranging from 179 ppm to 188 ppm [113]. The 42 ppm down-field shift with respect to pristine C_{60} at 143 ppm [8] is explained by the paramagnetic shift induced by the unpaired electron on the cage. The influence of the additional charge is generally assumed to be small [113]. The absence of spinning sidebands hints at a small linewidth in consequence of the rapid rotation of the fullerenes.

The tiny peaks in the room-temperature spectrum arise from the toluene carbons. Hereby, the group of 4 peaks at around -50 ppm is attributed to the sp^2 ring carbons, whereas the single peak at 392 ppm arises from the sp^3 methyl carbon. The lines are vastly shifted in comparison with the pure neutral complex, where the sp^2 carbons signals are found at about 80 ppm and the methyl carbon is at 20.2 ppm. The reason is the different charge state of the complex and, even more important, the strong paramagnetic shift induced by the neighboring electron spins. Besides, at room-temperature the huge chemical shift anisotropies which are typical for aromatic ring carbons ($\Delta \delta > 200$ ppm) are completely averaged. This confirms the notion of a rapid three-dimensional rotation of the bis(toluene)chromium complexes.



Figure 5.12: Temperature-dependent position of the fullerene peaks in the ¹³C-MAS-NMR spectra. The high-temperature shift is typical for C_{60} mono-anions, whereas the low-temperature values are found both for neutral C_{60} and $(C_{60})_2^{2-}$ dimers.

At the phase transition, the strong fullerene signal at 185 ppm disappears and a new line at 145 ppm appears. The shift values versus temperature are plotted in Fig. 5.12. The observed low-temperature shift value is not only close to neutral C_{60} , but has also

been observed in the $(C_{60})_2^{2-}$ dimer phases of KC_{60} and RbC_{60} [71,83]. Considering the above results from XRD, magnetic measurements, and ESR, a dimer formation is the most convincing scenario. In this case, the 2 ppm downfield shift with respect to neutral C_{60} can be attributed to the charge on $(C_{60})_2^{2-}$.

The toluene signals disappear at low temperatures, because the rapid threedimensional rotation of the complexes is slowed down or completely hindered in the triclinic cell. Thus the motional narrowing effect is reduced and the lines broaden beyond detectability.

In summary, ¹³C NMR clearly validates the notion of dimer formation. The existence of an isotropic low-temperature signal, which is shifted upfield with respect to the high-temperature signal in consequence of the disappearing paramagnetic shift contribution from the electron spin, is a clear indication of $(C_{60})_2^{2-}$ dimer formation. In contrast, oligomer or polymer bonds would deform the C_{60} cages and lead to an anisotropic multiline spectrum.



Figure 5.13: ¹H-MAS-NMR spectrum of $Cr(C_7H_8)_2C_{60}$ at room temperature. The strong signal which is shifted to negative values is due to methyl protons. The less intense line complex at around 260 ppm belongs to the five remaining ring protons. Hereby, the small peak belongs to the proton opposite to the methyl group, while the overlapping peaks result from the remaining two pairs of ring protons.

Fig. 5.13 shows the ¹H-MAS-NMR spectrum of $Cr(C_7H_8)_2C_{60}$ at room temperature. The signal of the methyl protons appears at negative values (vs. TMS). The less intense line complex at around 260 ppm belongs to the 5 remaining ring protons. The magnified view at the center of the diagram shows that the large peak is formed by two lines, each of which has about twice the intensity of the small peak to the right. From the symmetry of the toluene ring it follows that the small peak arises from the proton opposite to the methyl group, while the overlapping peaks results from the remaining two pairs of ring protons.

In comparison to typical chemical shift values of several ppm observed for protons in aromatic systems, the lineshifts in the fulleride are enormous. As in the case of ¹³C NMR, these values result from the close vicinity of electron spins which induce strong paramagnetic shifts.

5.3.6 Discussion

The notion of C_{60} - C_{60} dimer formation in the low-temperature phase of $Cr(C_7H_8)_2C_{60}$ is supported by all of the above measurements. Table 5.1 compares the experimental

	Dimer Phase	Monomer Phase
	$T < 250 {\rm ~K}$	$T>250~{\rm K}$
lattice type	triclinic (doubled cell)	cubic
lattice parameters	a=13.641 Å, $b=13.834$ Å, $c=13.855$ Å, $\alpha=91.83^{\circ}$, $\beta=116.78^{\circ}$, $\gamma=119.33^{\circ}$	a=9.984 Å
closest C_{60} - C_{60} distance	9.23 Å	$9.984~{\rm \AA}$
magnetic moment (per formula unit)	$1.72 \ \mu_{\rm B}$	$2.2-2.7~\mu_{\rm B}$
spins per formula unit	$1 \times S = 1/2$	$2 \times S = 1/2$
isotropic g factor	1.9870	1.9916
g anisotropy	$g_{xx} = 1.9910, \ g_{yy} = 1.9907,$ $g_{zz} = 1.9793$	-
13 C NMR shift	145 ppm	185 ppm

Table 5.1: Summary of results obtained for the two phases of $Cr(C_7H_8)_2C_{60}$.

findings above and below the phase-transition temperature.

It is useful to compare the situation with the dimer phase occurring in KC_{60} and RbC_{60} . The interfullerene distance of 9.23 Å observed for the dimer in bis(toluene)chromium fulleride is close to the values of 9.34 Å reported for RbC_{60} [81]. In the alkali fullerides, the dimer bond has been found to be a single bond. To allow for an sp^3 hybridization, the bonding carbon atoms are slightly pulled out of the spheres. The resulting bond length of 1.54 Å [82] is tune with the situation in $\text{Cr}(\text{C}_7\text{H}_8)_2\text{C}_{60}$, where this bond length requires a dislocation of the bonding atoms by



Figure 5.14: Triclinic low-temperature structure including the dimer bonds. The triclinic unit cell of Fig. 5.5 and its continuation in [011] direction are shown. The carbon atoms involved in the bonds are pulled out of the spheres by 0.3 Å. The dimer bond length is about 1.5 Å [136].

0.3 Å [136]. The dimer-phase structure is displayed in Fig. 5.14. The perspective is the same as in Fig. 5.5, but the unit cell is repeated along the [011] direction and the dimer bonds as well as the dislocation of the binding atoms are included in the image.

5.4 Bis(Mesitylene)Chromium Fulleride

Bis(mesitylene)chromium fulleride $Cr(C_9H_{12})_2C_{60}$ has a well-defined crystal structure independent of the solvent used in its synthesis. Despite its close relationship to the bis(toluene)chromium fulleride, it shows no first-order phase transition. This section presents the observations made on a $Cr(C_9H_{12})_2C_{60}$ powder sample precipitated from toluene.

5.4.1 X-Ray Diffraction



Figure 5.15: X-ray powder diffraction pattern of $Cr(C_9H_{12})_2C_{60}$ at room temperature. The spectrum was taken with copper radiation at $\lambda = 1.54$ Å.

The room-temperature XRD pattern shown in Fig. 5.15 reveals a primitive rhombohedral structure which is closely related to the primitive cubic cell found in bis(toluene)chromium fulleride. The lattice constant a = 10.124 Å is larger due to the larger volume occupied by the mesitylene molecules. The cell is subject to a small rhombohedral distortion with an angle $\alpha = 92.44^{\circ}$ close to 90° , so that the primitive cell is almost cubic, as shown in Fig. 5.16.



Figure 5.16: Primitive rhombohedral structure of bis(mesitylene)chromium fulleride. The lattice constant at room temperature is a = 10.124 Å, with $\alpha = 92.44^{\circ}$, which leads to a unit cell volume of V = 1034.8 Å³.

5.4.2 Magnetic Measurements

SQUID measurements of $Cr(C_9H_{12})_2C_{60}$ have been performed at a field of 5 T. The diamagnetism of the educts has been determined separately and has been subtracted



Figure 5.17: SQUID-measurement of $Cr(C_9H_{12})_2C_{60}$ at a field of 5 T. The plots show the temperature dependence of the paramagnetic part of the total sample magnetization (left) and its inverse (right). The dashed lines represent Curie fits to the inverse magnetization in the temperature ranges from 5 K to 15 K and 180 K to 360 K, respectively. The slopes are in tune with the notion of two spins S=1/2 per formula unit above about 180 K, and one spin S=1/2 below 15 K. The fit to the upper part (T > 180 K) of the inverse magnetization can be improved by using a Curie-Weiss law. Then a Curie-Weiss temperature of $T_N \approx 26$ K is found. For simplicity the plot only displays the Curie fit.

from the magnetization of the product. The resulting paramagnetic part of the magnetization of the fulleride and its inverse are displayed in Fig. 5.17. Usually the paramagnetic susceptibility is displayed, but at a temperature of 5 K and a field of 5 T saturation effects can occur and it is therefore advisable to work with the magnetization. However, for simplicity the following analysis does not consider saturation effects, but the singlet-triplet model introduced towards the end of this section is formulated without high-temperature approximations.

The magnetization behaves roughly Curie-like, but in the inverse plot deviations from the straight-line behavior are found. A fit to the slope of the inverse magnetization in the range from 180 K to 360 K yields a straight line that does not go through the origin. This is the typical Curie-Weiss behavior of exchange coupled spin species. A Curie-Weiss fit yields a magnetic moment of roughly 2.5 $\mu_{\rm B}$ and a paramagnetic Néel-temperature of 26 K. In the low-temperature range between 5 K and 15 K, a Curie fit can be applied, which yields a magnetic moment of about 1.9 $\mu_{\rm B}$.

From the magnetic moments one can infer that below 20 K roughly one spin per formula unit (which would correspond to a magnetic moment of $\mu = 1.73 \ \mu_{\rm B}$) and above 180 K two spins (corresponding to $\mu = 2.43 \ \mu_{\rm B}$) are observed. If one interprets this result in analogy to bis(toluene)chromium fulleride, then above 180 K both the charged chromium complex and C_{60}^- carry a spin S=1/2, whereas below 15 K the spins of the C_{60}^- are cancelled in dimer bonds. In the following, this picture will be referred to as **dimer-formation model**.

In this model, the temperature dependence of the magnetization implies that the number of spin-carrying C_{60}^- anions decreases continuously in the temperature range between 180 K and 15 K. Under the simplifying approximation of Curie behavior (instead of Curie-Weiss) for two spins above 180 K and one spin below 15 K, one can deduce the number of C_{60}^- spins from the temperature dependence of the magnetization in the intermediate temperature range. The validity of the Curie approximation is demonstrated by the dashed lines in the right part of Fig. 5.17. They represent a combined fit for the magnetization of one spin S=1/2 below 15 K and two spins S=1/2 above 180 K, with the number of spins N of one species being the only fit parameter. As the number N of spins on the chromium complexes in the sample does not change, their contribution to the magnetization can be subtracted. The remaining function then is the magnetization due to the C_{60}^- spins. Assuming Curie behavior, their number can be extracted from the temperature-dependent magnetization. The result is plotted in Fig. 5.18. Starting from the number of C_{60}^- spins decreases



Figure 5.18: Temperature-dependent number of spin-carrying C_{60}^- anions, as extracted from the measured magnetization shown in Fig. 5.17. The solid red line corresponds to a fit which models the thermally activated breaking up of dimer bonds as further explained in the text.

continuously as spins pair in $(C_{60})_2^{2-}$ dimer bonds. The solid red line in Fig. 5.18 corresponds to an attempt to fit the temperature dependence of the spin number N by a thermal activation law

$$N = N_0 \cdot e^{-\Delta E/kT} \,. \tag{5.2}$$

The fit yields an activation energy of $\Delta E/k = 62.5$ K.

Thus it has been shown that the temperature dependence of the magnetization can be modelled by assuming a $(C_{60})_2^{2-}$ dimer formation over the broad temperature range from about 180 K to 15 K. However, in comparison with the clear first-order phase transition observed in bis(toluene)chromium fulleride, the thermally activated breaking up of dimer bonds over such a large temperature range seems very unusual for a solid. Therefore an alternative model is introduced: if one assumes that a pairing or dimer formation of the fullerene anions exists over the whole temperature range, then the temperature dependence of the magnetization can be the result of singlettriplet excitations on the dimers. This **singlet-triplet model** assumes that electrons on the two cage molecules of a pair are exchange coupled with coupling strength J. The pair Hamiltonian using Heisenberg exchange can be written as

$$\mathcal{H} = -2J\mathbf{S_1} \cdot \mathbf{S_2} - g\mu_{\rm B}B_0(S_{1z} + S_{2z}).$$
(5.3)

This can be solved to yield the pair magnetization [139, 140]:

$$M_{\text{pair}} = 2g\mu_{\text{B}} \frac{\sinh\left(g\mu_{\text{B}}B_{0}/kT\right)}{1 + 2\cosh\left(g\mu_{\text{B}}B_{0}/kT\right) + e^{-2J/kT}}.$$
(5.4)

The hyperbolic functions arise because at a field of 5 T and at low temperatures the usual approximation that the magnetic energy is much smaller than the thermal energy is not valid. Under the assumption that the spins on the bis(mesitylene)chromium cation complexes are independent, but the fullerene spins form pairs, the total magnetization can be written as

$$M = Ng\mu_{\rm B} \left\{ \frac{\sinh\left(g\mu_{\rm B}B_0/kT\right)}{1 + 2\cosh\left(g\mu_{\rm B}B_0/kT\right) + e^{-2J/kT}} + \frac{1}{2}B_{\frac{1}{2}}\left(g\mu_{\rm B}B_0/2kT\right) \right\}, \quad (5.5)$$

where N is the number of formula units and $B_{\frac{1}{2}}$ is the Brillouin function introduced in chapter 3, which is now used instead of its high-temperature Curie approximation.



Figure 5.19: SQUID-measurement of $Cr(C_9H_{12})_2C_{60}$ at a field of 5 T. The dots show the measured paramagnetic component of the magnetization (left) and its inverse (right). The solid red lines correspond to a model that assumes independent spins on the chromium complexes and exchange coupled spin pairs on neighboring fullerenes, as further explained in the text.

Fig. 5.19 models the magnetization and its inverse using Eqn. 5.5. Aside from slight deviations, the model matches the data quite well. Fitting parameters are the number of formula units $N = 15.8 \cdot 10^{18}$ and the exchange coupling constant J/k = -74.5 K. As expected, the coupling is antiferromagnetic, so that a singlet pair ground-state results.

At this point the dimer picture is only a speculation, which, however, serves well in explaining the temperature-dependent susceptibility. The following section presents ESR measurements which were carried out with the aim of acquiring additional information on the temperature-dependent spin configuration in $Cr(C_9H_{12})_2C_{60}$.

5.4.3 ESR of $Cr(C_9H_{12})_2C_{60}$

In order to obtain more information on a possible fullerene pair or dimer formation, ESR measurements at X band and W band have been performed.

X-Band ESR

Fig. 5.20 shows that the X-band signal at all temperatures consists of a single Lorentzian line. At temperatures above 180 K, where the SQUID results propose the existence of two spin species, this can only be explained if a substantial exchange coupling between the two spin species exists. In this case, as described above for $Cr(C_7H_8)_2C_{60}$, the signals of $Cr(C_7H_8)_2^+$ and C_{60}^- merge into a single line.



Figure 5.20: X-band spectra of $Cr(C_9H_{12})_2C_{60}$ at 300 K and 10 K, scaled to the same amplitude.

The left part of Fig. 5.21 displays the g values obtained from Lorentzian fits to the data. Starting at about 180 K, a clear decrease in the g factor is observed. The reason for this g shift is the decreasing paramagnetic contribution of the fullerene ions, which in both of the above models pair in a singlet ground state. This results in a decreasing ESR susceptibility of the fullerene ions. According to Eqn. 5.1 the exchange-averaged ESR signal then shifts towards the g value of the chromium complex.

Using the temperature-dependent number of C_{60}^- spins as obtained from the magnetization measurement with the *dimer-formation model*, the g shift can be modelled by adjusting the g factors for $Cr(C_9H_{12})_2^+$ and C_{60}^- according to Eqn. 5.1. The black solid line shown in the left part of Fig. 5.21 represents this approach for $g_{Cr^+}=1.9888$



Figure 5.21: Temperature-dependent g factor (left) and X-band linewidth $\Delta B_{\rm FWHM}$ (right) of $\rm Cr(C_9H_{12})_2C_{60}$ as extracted from Lorentzian fits to the spectra. A g shift below about 180 K is clearly visible. The black solid line represents the g-shift expected for an exchange-averaged signal of the chromium complex and $\rm C_{60}$, when the number of $\rm C_{60}^-$ spins decreases according to the dimer-formation model described in the text. The red line results from the singlet-triplet model, which assumes triplet excitations on $(\rm C_{60})_2^{2-}$ pairs.

and $g_{C_{60}}=1.9966$. Comparing these values with the ones obtained for $Cr(C_7H_8)_2C_{60}$, namely $g_{Cr^+}=1.9870$ and $g_{C_{60}}=1.9962$, one can conclude that they are characteristic of the chromium-complex cation and the fullerene anion, respectively. The deviation between the two g values of the chromium complexes can be attributed to the different arene rings in bis(toluene)chromium and bis(mesitylene)chromium.

The red line in the g value plot corresponds to the singlet-triplet model describing a triplet excitation on a $(C_{60})_2^{2-}$ pair. Using the respective susceptibilities in Eqn. 5.1, $g_{Cr^+} = 1.9898$ and $g_{(C_{60})_2^{2-}} = 1.9961$ are obtained for the chromium and the triplet signal, respectively. These values can also be reconciled with the values obtained in the case of bis(toluene)chromium fulleride.

The right part of Fig. 5.21 shows that the ESR linewidth increases with increasing admixture of fullerene spins to the signal. This is qualitatively the same behavior as observed in $Cr(C_7H_8)_2C_{60}$.

W-Band ESR

In the case of bis(mesitylene)chromium fulleride, X-band ESR yields only isotropic signals. For the assessment of exchange averaging, resolved g anisotropies would be helpful. Therefore high-field ESR at W-band frequencies has been performed.

Temperature-dependent W-band measurements of $Cr(C_9H_{12})_2C_{60}$ are displayed in Fig. 5.22. At ambient temperatures an almost isotropic signal is found. Upon cooling



Figure 5.22: Temperature-dependent W-band spectra of $Cr(C_9H_{12})_2C_{60}$. The spectra are scaled to the same peak-to-peak amplitude. The dashed line is just a guide to the eye.

below about 200 K, a strong g anisotropy develops, which also shifts the center of the signal to higher fields, i.e., lower g values. The g shift is in tune with X-band observations and accordingly can also be explained in the picture of exchange averaging. By spin pairing in $(C_{60})_2^{2-}$ dimers, the number of fullerene spins is strongly diminished with decreasing temperature, so that the unaveraged anisotropic powder pattern of the chromium complex is found. The leftmost hump at the dashed line in the spectrum at 6 K is probably a residual fullerene signal. With rising temperature, its weight increases and at the same time the exchange interaction between the appear-

ing fullerene spins and the chromium spins narrows the total line pattern to the almost isotropic signal observed above 180 K.

In conclusion, W-band ESR further supports the notion of a spin-singlet dimer state of the fullerenes at low temperatures.

5.4.4 ¹³C NMR



Figure 5.23: ¹³C-MAS-NMR spectrum of $Cr(C_9H_{12})_2C_{60}$ at room temperature. The signal of C_{60}^- at 186 ppm dominates the spectrum. At around -40 ppm the mesitylene ring carbons appear, while the methyl carbons are shifted to 382 ppm.

¹³C-MAS NMR has been performed on $Cr(C_9H_{12})_2C_{60}$ from room-temperature down to about 200 K. The spectrum does not change significantly in this temperature range. Therefore in Fig. 5.23 only the spectrum at 295 K is displayed. The dominant signal has a shift of 185 ppm, which is the fingerprint signal for C_{60}^- anions. Two small humps towards negative shift values arise from the two types of mesitylene ring carbons, whereas the methyl carbons appear at 382 ppm. These strong shifts results from the paramagnetism of both the chromium complexes and the fullerenes.

5.4.5 Discussion

Results from magnetization and ESR measurements of $Cr(C_9H_{12})_2C_{60}$ indicate that the behavior of this material can be understood in the picture of C_{60} - C_{60} -dimer formation at low temperatures. However, the transition is not sharp, but extends over a temperature range from 180 K to 15 K. Two models have been introduced to explain this behavior; both imply a spin-singlet dimer ground state. The *dimer-formation model* considers the formation and breaking of dimer bonds as the responsible mechanism for the changes in magnetic properties. From the viewpoint of solid state physics, the *singlet-triplet model* seems more appropriate since it naturally explains the broad temperature range over which the changes occur by the excitation of triplet spin states.

5.5 Bis(Benzene)Chromium Fulleride

While bis(toluene)chromium and bis(mesitylene)chromium complexes have the appropriate sizes to form stoichiometric lattices with C_{60} , bis(benzene)chromium seems to be too small. This can be deduced from the fact that the XRD spectrum of $Cr(C_6H_6)_2C_{60}$ precipitated from a toluene solution is completely different from the spectrum of $Cr(C_6H_6)_2C_{60}$ precipitated from a benzene solution. Considering the stability of the bis(arene)chromium complexes, it is highly improbable that ring molecules exchange with the solvent. Therefore one can assume that the sandwich molecules stay intact, but solvent molecules are built into the lattice and thus account for the different structures.

Beside the solvent-dependent character, $Cr(C_6H_6)_2C_{60}$ material made from toluene changes its structure over the course of several weeks into a presumably more stable modification. Thus there are at least three different structures of $Cr(C_6H_6)_2C_{60}$: a metastable and a stable modification resulting from the synthesis in toluene, and a stable structure resulting from the synthesis in benzene.

While the complexes with toluene and mesitylene form rather large crystals, the chromium-bis-benzene fulleride powder is very fine. The bad crystallinity leads to broad overlapping peaks in the powder diffraction data, which do not allow a reliable structure determination for any of the three $Cr(C_6H_6)_2$ fullerides.

Due to a lack of well-defined materials, SQUID, ESR, and NMR measurements do not give a conclusive picture. Furthermore, the phase which has formed in the sample made from toluene after several weeks has not yet been investigated by these methods. Therefore, the following subsection reviews only the ESR measurements of the metastable phase of $(C_6H_6)_2C_{60}$ made from toluene and the phase obtained from benzene. For additional information on other measurements of the $Cr(C_6H_6)_2$ fullerides the reader should consult the PhD thesis of A. Hönnerscheid [141].

5.5.1 ESR of $Cr(C_6H_6)_2C_{60}$



Figure 5.24: Left: Room-temperature and low-temperature X-band spectra of $Cr(C_6H_6)_2C_{60}$ precipitated from toluene. The spectra are scaled to the same peak-to-peak amplitude. Right: As a measure of the anisotropy, the temperature dependence of the peak-to-peak (PP) distance is displayed.

X-band measurements of $Cr(C_6H_6)_2C_{60}$ as precipitated from toluene reveal a strong axial g anisotropy that increases with decreasing temperatures. As a measure of the anisotropy the peak-to-peak (PP) distance is plotted in Fig. 5.24. The isotropic g factor is independent of temperature with $g_{iso}=1.9924$, the anisotropy increases from $\Delta g \approx 0.0095$ at 300 K to $\Delta g \approx 0.016$ at 10 K. The smooth increase in PP-linewidth and the constant isotropic g value do not give a hint at a phase transition.

The left part of Fig. 5.25 shows that $Cr(C_6H_6)_2C_{60}$ which was synthesized using benzene as a solvent has an isotropic ESR signal which narrows with decreasing temperatures. The g factor plotted in the right figure shows a slight shift at around 240 K. This might be indicative of a phase transition.

Since the materials are not well defined, further analysis of the measurements was considered to be fruitless.



Figure 5.25: Left: X-band spectra of $Cr(C_6H_6)_2C_{60}$ as precipitated from benzene. The spectra are scaled to the same peak-to-peak amplitude. No *g* anisotropy is observed. Right: Isotropic *g* factor as obtained from a Lorentzian fit.

5.6 Summary

Although bis(arene)chromium fullerides do not meet the expectation of magnetic ordering, they have proven to be interesting solid-state charge-transfer systems. In fact, the exchange coupling necessary for a magnetically ordered state is present in the room-temperature phase of both bis(toluene)chromium fulleride and bis(mesitylene)chromium fulleride. However, these systems avoid a low-temperature spin ordering by reducing the density of available spins. The formation of chemical bonds between the paramagnetic C_{60}^- anions leads to diamagnetic $(C_{60})_2^{2-}$ dimers. The remaining spins on the chromium complexes are thus separated by diamagnetic fullerenes and their exchange coupling is drastically reduced so that no magnetic ordering is observed down to 5 K.

The results for the different variants of bis(arene)chromium fullerides are:

• $Cr(C_7H_8)_2C_{60}$

Bis(toluene)chromium fulleride is a well-defined material that at 250 K shows an abrupt reversible phase transition from a cubic high-temperature phase to a triclinic low-temperature phase. While the cubic phase is characterized by the presence of monomeric C_{60}^- anions and bis(toluene)chromium cations, the triclinic low-temperature phase goes along with the formation of $(C_{60})_2^{2-}$ dimers. The doubling of the unit cell associated with the dimer formation has been corroborated by synchrotron powder investigations of the low-temperature phase. Magnetically, the cubic high-temperature phase is characterized by the two exchange coupled spin species of the chromium complex cations and C_{60} anions, respectively. In the low-temperature phase, the fullerene spins pair in dimer bonds while the chromium spins remain unaffected.

• $Cr(C_9H_{12})_2C_{60}$

Bis(mesitylene)chromium fulleride does not exhibit a first-order phase transition, but a slow transformation in the temperature range between 180 K and 15 K. Magnetization measurements as well as ESR and ¹³C NMR show that the rhombohedral room-temperature structure is characterized by exchange coupled spins on both types of counterions, a situation similar to the one observed in bis(toluene)chromium fulleride. The combination of magnetization measurements and ESR at standard and high fields reveals that the number of spins associated with the fullerene anions diminishes strongly below 180 K. This can be explained by the formation of $(C_{60})_2^{2-}$ pairs with spin singlet ground state. The singlet-triplet model, one of two models which have been introduced to fit the temperature-dependent magnetization data, explains the broad transition range naturally by assuming thermal singlet-triplet excitations on existing $(C_{60})_2^{2-}$ dimers. The exchange coupling strength between the spin pair amounts to J/k = -74.5 K.

• $Cr(C_6H_6)_2C_{60}$

Bis(benzene)chromium fullerides have been precipitated from benzene and toluene solution, respectively. As the bis(benzene)chromium complex is too small to form a stoichiometric lattice with C_{60} , solvent molecules are incorporated into the crystal structure. This makes the materials unstable, hard to reproduce and characterize. Therefore the bis(benzene)chromium variant of these fullerides has not been studied in detail.

Chapter 6

Mixed Alkali/Alkaline-Earth Fullerides

In fulleride materials, substitution of alkali ions with alkaline-earth ions allows higher charge transfers to C_{60} without the need to increase the number of dopant atoms per fullerene. In this way, the charge transfer can be varied without changing the lattice structure. Alkaline-earth dopants allowed Yildirim *et al.* to map out the superconducting transition temperature versus the doping level of C_{60} [94], as already mentioned in chapter 2. In general, alkaline-earth dopants permit new combinations of structure and charge transfer in fullerides and thus potentially enable the synthesis of new materials.

An interesting question which can be addressed with mixed alkali/alkaline-earth fullerides is whether fullerides of the type $ABaC_{60}$, where 'A' stands for an alkali atom, are superconducting. These systems should exhibit a three-fold electron transfer to C_{60} and thus have the same electronic configuration as the superconducting alkali fullerides A_3C_{60} . However, structural differences will occur, whose effect on possible superconductivity is hard to assess. In order to find out about electronic and structural aspects of the $ABaC_{60}$ materials, $CsBaC_{60}$ has been synthesized and studied in collaboration with F. Rachdi from the Université de Montpellier, France.

Furthermore, fcc fullerides with a transfer of four electrons onto C_{60} have been investigated only sparsely. These materials are not superconducting and supposedly are weakly metallic [142]. For the investigation of a system of this type, KCsBaC₆₀ samples have been prepared in the abovementioned collaboration.

The following sections report on synthesis and characterization of the mixed alkali/alkaline-earth materials $CsBaC_{60}$ and $KCsBaC_{60}$. For characterization, x-ray diffraction, Raman as well as ESR spectroscopy, and in the case of $KCsBaC_{60}$ also

NMR and SQUID measurements have been applied.

6.1 The "Azide Route" to Fullerides

The "azide route" to fullerenes has been proposed by Yildirim, Rachdi *et al.* as a method to prepare fullerides with various different dopant atoms from the first two groups of the periodic table [94, 142]. The standard method, which uses the vapor of pure alkali and alkaline-earth metals, is impractical in this case, because of the large differences in vapor pressures among these metals. Thus the fullerides have been prepared from the alkali and alkaline-earth azides of the respective metals. The azides were synthesized from the carbonates or hydroxides according to the following reactions:

$$K_2CO_3 + 2 \text{ HN}_3 \rightarrow 2 \text{ KN}_3 + \text{H}_2O + CO_2$$

 $Cs_2CO_3 + 2 \text{ HN}_3 \rightarrow 2 \text{ CsN}_3 + \text{H}_2O + CO_2$
 $Ba(OH)_2 + 2 \text{ HN}_3 \rightarrow Ba(N_3)_2 + 2 \text{ H}_2O$.

Hydrazoic acid, HN_3 , used in these reactions is prepared from sodium azide with sulphuric acid:

$$H_2SO_4 + NaN_3 \rightarrow HN_3 + HNaSO_4$$
.

Azides form microcrystalline white powders, which are stable in air and easy to handle. In order to prepare the fullerides, these powders are mixed with C_{60} powder, put into cleaned copper tubes and then sealed in glass tubes. These tubes are put into a furnace with temperatures well above 400 °C so that the azides decompose and the metal atoms intercalate homogeneously into the fullerite. Azide decomposition temperatures are listed in Tab. 6.1. Afterwards the material is tempered for several days above 400 °C.

Azide	decomposition temperature (°C)
KN_3	355
CsN_3	390
$\mathrm{Ba}(\mathrm{N}_3)_2$	160

 Table 6.1: Decomposition temperatures of azides used for the fulleride preparation.

Yildirim *et al.* suggested a two-step intercalation of C_{60} : in order to avoid the formation of the very stable Ba_3C_{60} , in a first step only the alkali azides are intercalated and in a second step the resulting material is tempered in the presence of barium azide. However, in our collaboration F. Rachdi suggested and applied the one-step method, where all azides are mixed with C_{60} right from the start.

6.2 CsBaC₆₀

In this material, C_{60} should be loaded with three additional electrons, a configuration in which in the alkali fullerides A_3C_{60} become superconducting. However, the fullerite fcc lattice has three interstitial sites per fullerene, two tetrahedral and one octahedral. If only the tetrahedral sites were occupied, the lattice symmetry could be retained. If, in contrast, the small barium ions occupy the smaller tetrahedral sites and the larger cesium ions the octahedral ones, only every other tetrahedral site would be occupied and the lattice symmetry would be reduced. For this reason it is interesting to study $CsBaC_{60}$ as an example of fullerides of the type $ABaC_{60}$.

 $CsBaC_{60}$ has been synthesized via the azide route as described above. The material is a black microcrystalline powder, which is typical for fulleride salts. The powder was transferred to x-ray and ESR sample tubes in the argon atmosphere of a glove box. In order to evaluate the quality of the newly synthesized material, x-ray diffraction experiments were carried out. After this confirmation of good crystallinity, ESR experiments were started. However, the absence of superconductivity motivated Raman measurements in order to determine the charge state of C_{60} in this fulleride. These measurements show that the expected homogenous charge distribution is not realized. The following report starts with this important Raman result.

6.2.1 Raman Measurements of CsBaC₆₀

As discussed in section 3.4, the pentagonal pinch mode $A_{\rm g}(2)$ of C_{60} exhibits a characteristic frequency shift that depends linearly on the number of additional electrons on C_{60} . Thus Raman measurements allow the determination of the charge state of C_{60} anions in a fulleride crystal.

Raman measurements were performed by H. Vogt at the Max-Planck-Institut für Festkörperforschung in Stuttgart. For excitation, a helium-neon laser (wavelength 632.8 nm) has been used, which deposits a power of 0.4 mW in the sample. Fig. 6.1 shows the pentagonal pinch mode of CsBaC_{60} together with a scale that indicates the number n of additional electrons on C_{60} at a given frequency, according to the empirical relation $\overline{\nu} = 1469 \text{ cm}^{-1} - n \cdot 6.1 \text{ cm}^{-1}$, which was introduced in chapter 3. The resolution of the Raman spectrometer as this frequency is about 1.8 cm⁻¹. The



Figure 6.1: Pentagonal pinch mode $A_g(2)$ of C_{60} in $CsBaC_{60}$. The upper scale represents the number of additional electrons on C_{60} which corresponds to the respective wave number. Instead of a single Raman mode expected at 1450.7 cm⁻¹ for three electrons, two modes corresponding to roughly five and one electrons per C_{60} are observed. The solid line represents a fit function consisting of two Lorentzian lines.

expected Raman mode for three electrons is obviously split into two modes corresponding to roughly one and five electrons per C₆₀. These modes can be fitted very well using Lorentzian lines. The fit shown in Fig. 6.1 finds that the areas under the two Lorentzians are about equal. Thus one has to infer that the material separates into two phases, which can only be CsC_{60} and $CsBa_2C_{60}$. As stated in chapter 2, pure CsC_{60} forms polymer chains that cause a splitting of the $A_g(2)$ Raman mode [143], which is not observed here. For this reason one can assume that the different charge states exist on a local scale, i.e., that a charge disproportionation has taken place.

In the pristine C_{60} crystal, there are two tetrahedral and one octahedral interstitial sites per C_{60} . On the average one barium and one cesium atom have to be distributed over the three sites. Thereby, the Ba²⁺ is smaller than the Cs⁺ ion (see Tab. 2.2) and will thus prefer the tetrahedral coordination. In principle one can assume that every other tetrahedral site is occupied by barium, while the rather large cesium ion preferentially occupies the more spacious octahedral site. Under these assumptions the charge disproportionation can only be understood if the charge from the barium atoms is not transferred equally to the four C₆₀ neighbors that are positioned at the corners of a tetrahedron. It is possible that due to polarization effects the barium ion does not sit at the center of the tetrahedral site but is shifted towards a vertex or an edge of the tetrahedron and thus a preferential charge transfer to one or two molecules out of the four can occur. If this process happens in an ordered fashion, a reduced crystal symmetry and a doubling of the unit cell would be expected. If on the other hand the disproportionation happens statistically, then on the average no effect should be visible. These assumptions are tested in the following using x-ray powder diffraction.

6.2.2 X-Ray Diffraction Measurements of CsBaC₆₀



Figure 6.2: X-ray diffractogram of $CsBaC_{60}$ powder and a simulation for an fcc cubic cell $(Fm\bar{3}m)$ with lattice constant a=14.18 Å. The simulation assumes that all barium and 30 % of the cesium ions are located in tetrahedral sites, while the remaining 70 % of the cesium ions populate the octahedral sites.

X-ray diffraction measurements were performed by H. Thurn at the Institut für Anorganische Chemie of the Universität Stuttgart using a powder diffractometer with monochromatic copper radiation at $\lambda=1.54$ Å. The diffractograms were taken in a Debye-Scherrer scan mode. Figure 6.2 shows the diffractogram and a simulation to the data.

The reflections visible at large angles in the diffractogram proof the good crystallinity of the microcrystals. The simulation for an fcc cubic unit cell with symmetry $Fm\bar{3}m$ matches best for a lattice constant a=14.18 Å. There are only two small reflections (at roughly 22 and 24 degrees) which do not appear in the simulation, thus the material is supposed to be almost pure. The simulation assumes that all barium ions occupy the smaller tetrahedral sites of the fcc lattice, which is rationalized by the fact that the barium ions are smaller (ion radius $Ba^{2+} 1.34 \text{ Å}$) than the cesium ions (radius $Cs^+ 1.67 \text{ Å}$) and due to their higher charge prefer the close vicinity to the negatively charged C_{60} ions. For the cesium ions a distribution with 30 % in the tetrahedral and 70 % in the octahedral sites matches the intensity distribution of the diffractogram quite well [144]. It has to be added that Ba^{2+} and Cs^+ are isoelectronic and cannot be discerned by x-ray diffraction. The increase in lattice constant in comparison with the fullerite crystal (a=14.16 Å [89]) is attributed to the fact that the barium ions are larger than the space provided by the fullerite tetrahedral sites.

The data does not indicate a doubling of the unit cell which might occur due to the charge disproportionation observed in the Raman measurements. Therefore one can assume that the C_{60}^{-} and C_{60}^{5-} are distributed statistically over the lattice.

6.2.3 X-Band ESR of CsBaC₆₀

A one- or fivefold charge onto C_{60} results in paramagnetic fullerene ions. The question arises, whether the C_{60} anions act as localized Curie-like spins or whether the band structure results in metallic behavior, like in the $A_3@C_{60}$. In order to gain information about the electronic system, ESR measurements were performed at X-band frequencies (9 GHz).



Figure 6.3: Left: Low-temperature X-band spectrum of $CsBaC_{60}$. The Lorentzian fit represented by the dashed line does not match the spectrum completely. This deviation only occurs at temperatures lower than 50 K. Right: Temperature dependence of the X-band ESR peak-to-peak (PP) linewidth. For comparison, the PP linewidth obtained from a Lorentzian fit is plotted. Deviations are due to a non-Lorentzian lineshape. The solid line represents a linear fit to the PP data.

The spectrum of $CsBaC_{60}$ powder shows one single ESR line at a g value of 2.0033,

as displayed in the left part of Fig. 6.3. Measurements in the temperature range from 6 K to 350 K revealed that the g value is temperature-independent, while the peakto-peak linewidth of the ESR signal strongly depends on temperature. It increases almost linearly with temperature, as shown in the right part of Fig. 6.3. This indicates metallic behavior; an analysis of the temperature-dependent linewidth follows in the section on W-band measurements.

The lineshape is Lorentzian in the temperature range from 350 K to 50 K, but below 50 K deviations appear. The low-temperature spectrum displayed in Fig. 6.3 has broader wings than expected for a Lorentzian line. This indicates a distribution of linewidths, which in the case of $CsBaC_{60}$ can result from the existence of different local environments, depending on the distribution of C_{60}^- and C_{60}^{5-} fullerenes in the vicinity of the electron spin. The signal can be matched perfectly using a sum of two or more Lorentzian lines with the same g factor.



Figure 6.4: Temperature dependence of the ESR susceptibility (left) and its inverse (right). The solid line represents the function a/T^n , with a = 290 a.u.Kⁿ and n = 0.22.

Fig. 6.4 displays the temperature dependence of the X-band ESR susceptibility, as obtained from a double integration of the measured spectra. The low-temperature increase in susceptibility is not very pronounced and thus cannot be explained by a Curie behavior. Since the material is assumed to be metallic, a modified Pauli susceptibility is the most probable explanation for the observed temperature dependence. Just to give a guide to the eye, the solid line representing the function a/T^n with a = 290 a.u.Kⁿ and n = 0.22, has been introduced. The right part of Fig. 6.4 shows the inverse ESR susceptibility. It should be noted that the temperature-dependence of the susceptibility has been confirmed in a SQUID measurement (not shown).

6.2.4 W-Band ESR of CsBaC₆₀

In order to clarify the composition of the X-band ESR signal by the possible resolution of a g anisotropy, W-band measurements were performed.



Figure 6.5: Left: Comparison of the W-band (solid line) and X-band signal (dashed line) of $CsBaC_{60}$ powder at 295 K. Right: Temperature-dependent linewidth obtained from Lorentzian fits to the W-band spectra, compared to the X-band linewidth. The line through the X-band data represents the fit used for the Elliott analysis explained in the text.

W-band ESR also exhibits one structure-less resonance signal. At room temperature, no significant line-broadening in comparison with the X-band spectrum, i.e., no g contribution to the linewidth is observed, as it is evident from the spectra shown in Fig. 6.5. The lineshape is perfectly Lorentzian at all temperatures. Therefore one can infer that the signal is a homogeneous line, not a superposition of different components.

A fit to the spectra yields the linewidth, which is plotted as the half width at half maximum in Fig. 6.5. The high-temperature discrepancy between X- and W-band linewidths can be attributed to a large error for the W-band fits, which is caused by a very small signal-to-noise ratio above 300 K. Concerning the low-temperature deviation of the W-band width, one can assume that unresolved g anisotropy explains the offset. With rising temperature, the linewidth then goes from an anisotropy-dominated to a relaxation-dominated regime.

Elliott Analysis

In metallic systems, the temperature-dependent conduction-electron-spin-resonance (CESR) linewidth can be related to the electronic scattering rate. This concept, first formulated by Elliott [110], has been introduced in chapter 3 and has been employed

	CsBaC_{60}	CsC_{60}
$\Delta g_{\rm so}$	$34 \cdot 10^{-4}$	$27 \cdot 10^{-4}$
$\tau_{\rm ph}^{-1}(300~{\rm K})~({\rm s}^{-1})$	$1.32 \cdot 10^{14}$	$7.54 \cdot 10^{13}$
$\tau_{\rm res}^{-1} \; ({\rm s}^{-1})$	$9.80 \cdot 10^{12}$	$3.42 \cdot 10^{13}$
β	1.0	2.0

Table 6.2: Phononic and residual scattering rates obtained from the Elliott analysis of the $CsBaC_{60}$ ESR linewidths. For comparison, results on CsC_{60} are listed in the right column.

successfully with RbC_{60} and CsC_{60} in chapter 4. In the following it is applied to the X-band data of $CsBaC_{60}$, because the strong linear increase of the linewidth with temperature hints at a metallic behavior of this material. Furthermore, from the comparison with the W-band linewidths, it is reasonable to assume that at X-band, g anisotropy contributions to the linewidth are negligible. Thus the linewidth directly reflects spin dynamics. Applying the Elliott relation for the dynamic ESR linewidth

$$\Delta B_{\rm dyn} = \frac{\hbar}{\mu_{\rm B}} \frac{\Delta g_{\rm so}^2}{g} \frac{2}{\tau_{\rm e}} \tag{6.1}$$

with g = 2.0033 and $\Delta g_{so} = 2.0033 - 1.9999 = 0.0034$, one can relate the electronic scattering rate $1/\tau_e$ to the full linewidth ΔB_{dyn} . The reference g=1.9999 is the value observed for C_{60}^- anions in solution [112]. There is no report on isolated C_{60}^{5-} ions, but their electronic properties should be quite similar to C_{60}^- due to the electron-hole analogy in the partially occupied LUMO. Therefore the same reference g value can be applied.

In a first approximation the scattering rate contains two contributions

$$\tau_{\rm e}^{-1} = \tau_{\rm ph}^{-1} + \tau_{\rm res}^{-1} \,, \tag{6.2}$$

namely scattering from phonons and a residual rate describing scattering from lattice defects, for instance. Assuming the residual scattering rate $\tau_{\rm res}^{-1}$ to be temperature-independent and using the following temperature dependence for the phonon part

$$\tau_{\rm ph}(T)^{-1} = \tau_{\rm ph}(300 \text{ K})^{-1} \cdot (T/300 \text{ K})^{\beta}, \qquad (6.3)$$

the fit in the right part of Fig. 6.5 yields the parameters displayed in Tab. 6.2. The law residual containing rate hints a small number of lattice defects. The

The low residual scattering rate hints a small number of lattice defects. The high phononic scattering rate indicates a three-dimensional metallic character.

6.2.5 Discussion

The existence of one homogeneous ESR line implies that the spins on C_{60}^- and C_{60}^{5-} contribute to the same signal and thus are not independent. In fact, as derived from the temperature-dependent ESR linewidths, the electrons can move within a metallic band structure and therefore only experience an average of the two charge states. However, differently charged fullerene molecules found in the Raman measurements and their statistical distribution according to the x-ray results should disturb the translational symmetry on which the band structure is based. The low residual scattering rates found from the Elliott analysis, on the other hand, indicate that the disorder does not lead to strong electron scattering.

6.3 KCsBaC₆₀

KCsBaC₆₀ was provided by F. Rachdi from the Université de Montpellier, France. Initial Raman, X-band ESR, and ¹³C MAS NMR data on this material have already been published by his group [145, 146]. The following sections present new Raman, x-ray, X-band ESR, and ¹³³Cs as well as ¹³C NMR measurements of this sample, which is referred to as sample #1. Later on, Raman measurements as well as W-band ESR and SQUID results of a new KCsBaC₆₀ sample are presented. This material was synthesized in Stuttgart together with F. Rachdi and in the following is referred to as KCsBaC₆₀ #2.

All measurements presented in the following were carried out in Stuttgart. It should be noted that ESR and NMR investigations have been conducted under the assumption of well-defined materials. This assumption was based on a publication by Rachdi *et al.* [145] which reported the Raman characterization of sample #1. The Raman results were presented as a verification of the proper stoichiometry. However, after the occurrence of inconsistent results, x-ray and further Raman investigations have been performed in Stuttgart, which revealed that the sample quality is not good enough to allow a clear assignment of the observations to a phase with the stoichiometry KCsBaC₆₀. Nonetheless the author has decided to present the investigations, partly because there are enough interesting aspects to be reported, and partly as an example of the pitfalls that have to be considered when working with fullerides.

In order to have a clear picture of the sample quality right from the start, the report begins with the Raman results.
6.3.1 Raman Measurements of $KCsBaC_{60}$ (#1)



Figure 6.6: Pentagonal pinch mode of C_{60} in KCsBaC₆₀. The upper scale represents the number of electrons on C_{60} that corresponds to the respective wave number. Instead of a single Raman mode for four electrons on C_{60} at 1444.6 cm⁻¹, several modes are observed (dots). For comparison, data on KCsBaC₆₀ from Yildirim *et al.* [142] is also shown (circles).

Raman measurements have been conducted in order to check the charge transfer in KCsBaC₆₀. Measurements were performed by H. Vogt at the MPI für Festkörperforschung in Stuttgart. Parameters are the helium-neon laser wavelength of 632.8 nm with a power of 0.4 mW at the location of the sample. Since alkali atoms form mono-cations and barium forms a di-cation, a fourfold electron transfer to C₆₀ is expected. However, Fig. 6.6 reveals that the material contains C₆₀ anions with a broad range of charge states. There is a broad component peaked at around C₆₀⁶⁻, which is superimposed with distinct narrow peaks roughly at electron transfers of 1, 3, and 5. Most probably the sixfold electron transfer occurs in a Ba₃C₆₀ configuration, which according to Yildirim *et al.* forms easily and is very stable [142]. For the other charge states, most probable candidates are KBa₂C₆₀ and CsBa₂C₆₀, KCs₂C₆₀ and K₂CsC₆₀ as well as KC₆₀ and CsC₆₀, for charge transfers of five, three, and one electron, respectively. For comparison, Fig. 6.6 also shows a Raman measurement published by Yildirim *et al.* [142]. Clearly their KCsBaC₆₀ fulleride is better defined, with a range of only 4 to 5 electrons on C₆₀.

6.3.2 X-Ray Diffraction Measurements of $KCsBaC_{60}$ (#1)



Figure 6.7: X-ray powder diffraction pattern of KCsBaC₆₀. The simulation (not shown) yields an fcc lattice with a lattice constant of a=14.29 Å. There are several small peaks which cannot be assigned to this structure and furthermore the main peak at 20° has a shoulder which hints at inhomogeneous doping.

The x-ray powder diffraction spectrum displayed in Fig. 6.7 is compatible with an fcc structure with lattice constant a=14.29 Å. However, shoulders in the main peaks as well as small reflections that do not belong to the cubic structure evidence non-homogeneous doping and the existence of differently structured regions. These findings are in line with the Raman results. For comparison, Yildirim *et al.* report a lattice constant of a = 14.22 Å for their KCsBaC₆₀ material from synchrotron powder diffraction measurements [142]. The difference in lattice constants may arise from another distribution of the differently sized ions to the tetrahedral and octahedral sites.

6.3.3 X-Band ESR of KCsBaC₆₀ (#1)

From the Raman results it follows that beside C_{60}^{6-} , which has a filled LUMO and thus is assumed to be diamagnetic, C_{60} anions with one, three, and five negative charges exist in KCsBaC₆₀ #1. In other fullerides, this combination of the fcc structure and odd numbers of electrons on C_{60} led to metallic behavior and for the threefold charge transfer even to superconductivity. Both properties can in principle be identified by ESR. X-band ESR of the KCsBaC₆₀ sample from F. Rachdi yields a composite signal, which consists of a narrow and a broad component, both centered at almost the same position. Fig. 6.8 gives an overview of the temperature-dependence of the X-band signal. The signal can be fitted reasonably well using two Lorentzian line functions.



Figure 6.8: X-band ESR signal of the $KCsBaC_{60}$ sample from F. Rachdi at various temperatures. Two line components at almost the same position make up the signal.

This allows the extraction of the ESR parameters for the two components. Fig. 6.9 presents the temperature-dependent linewidths and susceptibilities obtained from this fit procedure. The left part of Fig. 6.9 shows what is already apparent in Fig. 6.8: The broad line component narrows considerably as the temperature declines from 300 K to 50 K. As discussed previously in the framework of the Elliott mechanism 3.1.5, this is the typical behavior of a metallic system.

The narrow line component narrows linearly in the complete temperature range from 300 K to 23 K. The broad line component on the other hand broadens below 50 K



Figure 6.9: Left: Temperature dependence of the X-band linewidth for the two line components as extracted from a fit using two Lorentzian lines. Right: Total X-band susceptibility (open circles) as well as susceptibility of the broad (squares) and narrow (triangles) component as obtained from the Lorentzian fit. The dots represent the ESR susceptibility obtained from a double integration of the spectra. The difference between the total susceptibility from the fits and the susceptibility obtained from the double integration shows that below room temperature the Lorentzian fit is not perfect.

and becomes undetectable at temperatures of 23 K and below. This seems to be a precursor effect to a phase transition occurring at 23 K.

A look at the ESR susceptibility plotted in the right part of Fig. 6.9 clearly indicates the existence of such a phase transition below 30 K. The ESR susceptibility for the two line components is obtained from Lorentzian fits to the data, whereas the total susceptibility results from a double integration of the ESR spectra. The rather flat progression of the susceptibilities indicates a Pauli-like behavior, an observation that confirms the assumption that at least the broad line component belongs to a metallic phase.

Thus from the temperature dependence of the susceptibility and from the linewidth one can infer that the system is metallic, with the broad peak corresponding to a conduction-electron-spin-resonance (CESR) signal, while the narrow peak might correspond to a different metallic phase or as well be a localized defect signal.

As stated above, the ESR parameters indicate a phase transition at low temperatures. In fact, upon cooling the sample below 23 K the broad signal component vanishes. The narrow component broadens slightly. Fig. 6.10 shows that furthermore a striking new feature appears in the spectrum: a strong non-resonant microwave absorption which depends on the sweep direction of the magnetic field. This is a common feature found in superconducting powder samples [147] and thus proves the existence of



Figure 6.10: X-band modulated microwave absorption in the superconducting phase of $KCsBaC_{60}$ at a temperature of 10 K.

superconductivity with a transition temperature of about 23 K in this material. The microwave absorption arises from losses at the intergrain boundaries, so-called weak links, which act as Josephson junctions with a parallel resistive path. In the superconducting state the incident microwave evokes high-frequency shielding currents which are subject to dissipation at the weak links. Thereby the absorption also depends on the sweep direction. More information on this effect can be found in the publications of Dulčić *et al.* [147–149].

The fact that the broad signal vanishes below 23 K can be related to the pairing of the quasi-particles in the superconducting state. This implies that the broad ESR signal and superconductivity arise from the same electrons.

6.3.4 133 Cs NMR of KCsBaC₆₀ (#1)

In order to further characterize the superconducting transition, temperaturedependent ¹³³Cs NMR measurements have been performed on the KCsBaC₆₀ sample from F. Rachdi. ¹³³Cs NMR is quite common since the isotope has a nuclear spin of I = 7/2 with a natural abundance of 100 %.

Measurements were performed at a field of 9.08 T which corresponds to a cesium resonance frequency of about 50.7 MHz. Fig. 6.11 shows the room-temperature spectrum obtained from the Fourier transformation of a spin echo signal. The shift is given relative to a $CsBr_{aq}$ standard. The spectrum is fitted well by a Lorentzian line. As the lineshape remains unchanged down to low temperatures, a temperature-dependent



Figure 6.11: Left: ¹³³Cs NMR spectrum at a field of 9.08 T and a temperature of 275 K. The fit with a Lorentzian line (dashed line) yields a full linewidth of 2.0 kHz. The shift on the upper scale is given relative to $CsBr_{aq}$. Right: Temperature dependence of the ¹³³Cs NMR linewidth. The linewidth was obtained from Lorentzian fits to the spectra.

linewidth as plotted in the right part of Fig. 6.11 can be obtained from Lorentzian fits to the spectra.

The linewidth shows a substantial increase below 250 K. In cubic fulleride materials at this temperature the three-dimensional rotation of the fullerene molecules turns into a jump-motion. Thus rotational averaging effects disappear and the line broadens due to unaveraged anisotropies. The slight broadening at temperatures below 23 K is related to the transition to the superconducting state and is probably caused by the formation of a vortex lattice.

The phase transition is more clearly visible in the temperature-dependent shift of the ¹³³Cs NMR line which is displayed in Fig. 6.12. Between 25 K and 350 K the line shifts linearly with temperature to negative shift values, which corresponds to a diamagnetic shift. Since the material is metallic, this has to be a Knight shift, which is in principle paramagnetic, but can change signs when the hyperfine coupling of the nuclei to the conduction electrons is negative. As shown in chapter 3, the Knight shift is proportional to the electronic susceptibility and the hyperfine coupling. In the ESR it was found that the susceptibility is rather constant. The hyperfine coupling, however, might increase as the lattice constant shrinks upon cooling and thus might account for the observed line shift.

In the superconducting state, conduction electrons pair and the Knight shift disappears. The low-temperature shift with respect to the linear extrapolation of the Knight shift (solid line) amounts to roughly 8 kHz. Since the shift is much larger than



Figure 6.12: Temperature-dependent ¹³³Cs line shift relative to CsBr_{ad}.

the line broadening below 23 K, one can assume that all cesium atoms experience the phase transition.

T_1 measurements

In order to obtain information about relaxation dynamics in the system, the spinlattice relaxation time T_1 has been determined. In the temperature range from 100 K to 350 K, this has been done by inversion-recovery spin-echo measurements. Below 100 K slow spin relaxation requires the use of the saturation-recovery technique which allows higher repetition rates. Fig. 6.13 displays the temperature dependence of the T_1 relaxation rate as well as $1/(T_1T)$. For metals, nuclear relaxation is determined by the hyperfine coupling to the conduction electrons. According to the Korringa relation presented in chapter 3, relaxation should be proportional to the temperature as well as to the square of the Knight shift [109]. The rather flat progression in the $1/(T_1T)$ plot shows that relaxation in fact increases linearly with temperature. However, the slight increase of $1/(T_1T)$ with temperature is in contrast to the decreasing (negative) shift shown in Fig. 6.12. Thus other mechanisms may also contribute to the T_1 relaxation. Due to extremely slow relaxation at very low temperatures, only one measurement below 23 K has been performed, namely at 10 K. This measurement indicates a reduced relaxation in the $1/(T_1T)$ plot. At this temperature, the opening of the superconducting gap leads to a pairing of the electron spins. Thus reduced T_1 relaxation can be understood in terms of a strongly reduced hyperfine relaxation.



Figure 6.13: Left: Temperature dependence of the longitudinal relaxation rate of the ¹³³Cs spins in KCsBaC₆₀. Right: Plot of $1/(T_1T)$ over temperature. According to the Korringa relation, the rather constant value above 25 K indicates metallic behavior.

6.3.5 ¹³C NMR of KCsBaC₆₀ (#1)

The question arises whether the phenomena observed in the 133 Cs NMR are also visible in carbon NMR. Carbon has spin 1/2 in a natural abundance of 1.11 %. The applied magnetic field amounts to 9.08 T, which corresponds to a 13 C resonance frequency of 97.3 MHz.



Figure 6.14: ¹³C NMR spectrum at 275 K. The dashed line corresponds to a fit with two Lorentzian lines. The narrow line is centered at 181.4 ppm and has a full width of 1.06 kHz (10.9 ppm), while the broad component is centered at 100.6 ppm with a width of 1.50 kHz (15.2 ppm). Both components cover approximately the same area. The shift on the upper scale is given with reference to tetramethylsilane (TMS).

Fig. 6.14 displays the spectrum obtained from a spin echo sequence at 275 K. The spectrum consists of two signals, a narrow component centered at 181 ppm and a broad component at 101 ppm. As stated in section 3.2, neutral C_{60} has a chemical shift of 143 ppm. For C_{60} anions, one usually observes an additional chemical shift of about 2 ppm for each charge on C_{60} and a paramagnetic shift of roughly 40 ppm in case of an unpaired spin. This implies that the narrow line component is shifted due to an unpaired electron spin. This line can therefore be attributed to one of the C_{60} anions with an odd number of charges. However, the relation between charge and chemical shift is only a rule of thumb and thus the exact charge state cannot be inferred from the line shift. The broad line component extends to the range of shift values which are typical for diamagnetic C_{60} anions. Thus one can infer that this line component results from C_{60}^{6-} , which was found to be present in the Raman investigation, as well as molecules which have formed chemical bonds. The large width of this line component probably results from the fact that bonded fullerenes cannot rotate and thus the signal cannot be motionally narrowed.



Figure 6.15: Left: Temperature-dependent shift of the narrow signal component in the ${}^{13}C$ spectrum. Right: Full linewidth of the narrow component. Line shift and width have been obtained from Lorentzian fits to the spectrum.

As shown in the left part of Fig. 6.15, the narrow line component undergoes a slight diamagnetic shift as the temperature is lowered. In this process, the line broadens substantially, as displayed in the right part of Fig. 6.15. The temperature dependence is very similar to the one observed in the ¹³³Cs NMR, i.e., the signal broadens as the fullerene rotation stops at the transition from the rotor phase to the ratchet phase below 250 K. Below the phase transition to the superconducting state at 23 K, the line narrows slightly.

Relaxation measurements have also been performed using the saturation recovery echo technique. For that purpose, the recovery of the integrated intensity of the Fourier-



Figure 6.16: Left: Temperature dependence of the longitudinal relaxation rate of the ¹³C spin in KCsBaC₆₀. The kink at about 230 K results from the freezing of the 3D rotation of the fullerene spheres. Right: Plot of $1/(T_1T)$ over temperature. Due to Korringa relaxation $1/(T_1T)$ is almost constant.

transformed echo signal has been analyzed. Over the whole temperature range from 6 K to 350 K the recovery is biexponential, with both contributions having about equal intensity at the beginning of the recovery. The left part of Fig. 6.16 displays the temperature dependence of the slower of the two relaxation rates. The kink at around 230 K shows that it is also sensitive to the changing rotation rate of the fullerene molecules. The right part displays the rate divided by the temperature; the rather constant value at temperatures above the superconducting transition implies that the relaxation follows the Korringa relation.

For the component with the larger relaxation rate (not shown), the relaxation time is decreased by a factor of 3-9 with respect to the component plotted in Fig. 6.16. Except for the kink at 230 K this component shows the same temperature dependence as the slowly relaxing component. The existence of a second relaxation rate is probably related to the existence of differently charged C₆₀ anions which thus are subject to different relaxation rates.

6.3.6 Characterization of $KCsBaC_{60}$ (#2)

In 2001, a new batch of KCsBaC₆₀ samples has been prepared at our institute in collaboration with F. Rachdi and the Jansen group from the MPI für Festkörperforschung. In the following, material from this batch is referred to as KCsBaC₆₀ #2.

In order the characterize this fulleride and compare it with the old material, x-ray, Raman, and X-band ESR measurements have been conducted. The x-ray investigation (not shown) reveals that part of the material has the same structure as the old



Figure 6.17: Left: The Raman measurement reveals that the new KCsBaC₆₀ material (dots) is differently doped than the old material (circles). However, phases with C_{60}^{-} and C_{60}^{3-} ions are present in both materials. Right: Comparison of the X-band signal of the old (#1) and new (#2) KCsBaC₆₀ sample at ambient temperatures. The narrow signal is less pronounced or simply broader in the old sample, whereas the linewidth of the broad component is slightly smaller in the new sample.

sample, but there are also strong reflections that probably belong to BaCO₃ [144]. This would imply that part of the barium does not contribute to the doping process. Raman measurements shown in the left part of Fig. 6.17 indicate that in comparison with the expected stoichiometry the material is in fact underdoped and a charge transfer of slightly more than one electron per C₆₀ dominates. However, there is also a contribution at a wave-number corresponding to C_{60}^{3-} .

Although the x-ray and Raman measurements are markedly different for KCsBaC₆₀ #1 and #2, the ESR spectra shown in the right part of Fig. 6.17 are almost identical for the two materials. The ESR signal consists of a broad and a narrow component, which appear at the exactly the same positions for both materials. The mere difference between the spectra are small deviations in linewidth. This is a very astonishing result which indicates that the ESR signal must be due to C_{60}^- and C_{60}^{3-} anions, because according to the Raman measurements, only these two charge states occur in both materials.

From the new material, samples have been made for the following W-band ESR and SQUID investigations.

6.3.7 W-Band ESR of KCsBaC₆₀ (#2)

The left part of Fig. 6.18 compares the X- and W-band spectrum of the new KCsBaC₆₀ material. The linewidths of the broad component are identical, thus they are not affected by g broadening. This implies that the linewidth is determined purely by



Figure 6.18: Left: Comparison of the X- (dashed line) and W-band (solid line) spectra of KCsBaC₆₀ (#2). Right: The W-band linewidths as obtained from a free fit of two Lorentzian lines to the data (filled symbols). The open symbols correspond to the X-band data of the old sample (#1). Although the linewidth of the broad component of this material is slightly larger, the temperature-dependences are identical.

dynamics, which complies with the expectation for conduction electrons in a cubic system. The narrow component, on the other hand, broadens at W band and thus is hard to discriminate from the broad signal. This leads to an uncertainty in the determination of its linewidth.

In the right part of Fig. 6.18 the W-band linewidth of the two signal components is plotted with filled symbols. For both components an almost linear increase in linewidth is found above about 50 K. Below 50 K, towards the superconducting phase transition, a strong increase in linewidth is found for the broad component. This is exactly the temperature behavior that was found at X band for the old material, plotted for comparison with open symbols. Although the Raman and x-ray results indicate that the fullerides #1 and #2 are markedly different, ESR, aside from a small scaling factor in the linewidths, shows identical behavior for both materials. This finding suggests that at least the paramagnetic phases of both materials are comparable.

A look at the superconducting phase transition confirms the similarity between the old and the new material. Fig. 6.19 shows that at W band the broad line component also vanishes at low temperatures. The onset of non-resonant microwave absorption, which is a clear indication of superconductivity, appears between 25 K and 20 K, compared to 23 K for sample #1 at X band.

It is interesting to take a closer look at the microwave absorption phenomenon at W band. Fig. 6.20 compares an up-sweep with a down-sweep of the magnetic field at



Figure 6.19: Low-temperature W-band spectra of KCsBaC_{60} (#2). As the sample is cooled through the transition to the superconducting phase, the broad signal component broadens and disappears while the narrow component remains unchanged.



Figure 6.20: W-band ESR spectra of KCsBaC_{60} at 8 K. Non-resonant microwave absorption depending on the sweep direction is visible. The right figure enlarges the baseline shown in the rectangle of the left figure. The baseline oscillations are reproducible.

8 K. Again the typical sweep-direction dependent absorption described previously is visible (left). In addition, a reproducible oscillation of the baseline is observed (right). Its frequency does not depend on the sweep velocity. These oscillations probably result from phase jumps when flux quanta that are trapped in the superconducting grains are released.

6.3.8 SQUID Measurements of KCsBaC₆₀ (#2)

ESR investigations of KCsBaC₆₀ #1 and #2 indicate that both materials become superconducting below roughly 23 K. In order to get a more precise picture of the superconducting state, magnetic measurements of the static susceptibility have been performed using a SQUID magnetometer.



Figure 6.21: Left: Comparison of the field-cooled (FC) and zero-field-cooled (ZFC) DC magnetization of KCsBaC₆₀ powder (#2) measured at an external field of 30 G. The onset of superconductivity appears at 22 K. Right: Dispersive part of the AC magnetization, measured at 30 G and the W-band field of 33600 G, respectively. Parameters were a modulation frequency of 1 kHz and a modulation amplitude of 50 mOe. Since only changes in magnetization are detected, the difference between field-cooled and zero-field-cooled measurements disappears.

A DC SQUID measurement determines the total sample magnetization in an applied external field B_{ext} . According to $\chi = \mu_0 \frac{M}{B_{\text{ext}}}$, the static susceptibility χ can be obtained. The DC SQUID measurement of KCsBaC₆₀ (#2) in the low-temperature range yields the magnetization and susceptibility shown in the left part of Fig. 6.21. The applied field is 30 G. When an ideal superconductor is cooled through T_c in a low magnetic field, the magnetic field is completely expelled from the inside of the superconductor. This effect, also known as the Meissner effect, leads to a diamagnetic susceptibility of χ =-1. However, in the field cooled (FC) case of a granular superconductor, vortices are included in the powder and cannot be expelled due to pinning effects and loop currents. These effects lead to a reduced diamagnetism. In the zero-field-cooling (ZFC) case the field is switched on when the material is already superconducting; magnetic flux then cannot intrude into the material and therefore a stronger diamagnetism results.

For our sample, the ZFC susceptibility reaches a value of $\chi = M/H = -0.139$ at 2 K. Assuming perfect diamagnetism $\chi = -1$ for the superconducting phase, no shielding of non-superconducting crystallite centers by a superconducting surface, and furthermore negligible contributions from non-superconducting regions, this corresponds to a shielding fraction of 13.9 %, i.e., 13.9 % of the material are superconducting.

As already mentioned in chapter 2, from the present knowledge of fulleride materials one can assume that in fcc structures superconductivity only occurs with triply charged C_{60} anions. The Raman measurement shown in Fig. 6.17 indicates that only a small fraction of roughly 10 to 20 % of KCsBaC₆₀ #2 has triply charged fullerenes. That means that all of this fraction must be superconducting in order to account for the diamagnetism observed in the SQUID measurement.

The right part of Fig. 6.21 displays the dispersive signal contribution of an AC SQUID measurement of the same material. In an AC measurement, the response of the magnetization to a small oscillating external field is detected. A typical oscillation frequency is 1 kHz. The detection in phase with the field oscillation and 90° phase shifted to it, yields a dispersive and an absorptive magnetization signal, respectively. In our case, the modulation amplitude was too small to get an absorptive contribution, thus only the dispersive part is displayed in Fig. 6.21. It differs from the DC results in the fact that the offset magnetization of pinned vortices and superconducting loops in the FC measurement does not show up, so that the difference between ZFC and FC vanishes.

From the low-temperature magnetization at low fields, the shielding fraction can be determined in an analogous way to the calculation in the DC case, only that now the magnetic field is the field modulation amplitude, which is 50 mOe in our case. With an AC magnetization of $M = -3.59 \cdot 10^{-6}$ emu a susceptibility of $\chi = -0.151$ or a shielding fraction of $x_{sh} = 15.1$ % follows, which is in line with the 13.9 % obtained from the DC measurements.

The AC SQUID measurements at the W-band field of 33600 G show that in this case the shielding currents already reduce the transition temperature from 22 K to about 19 K. In other words, at 19 K the critical field is 33600 G.

6.3.9 Discussion of the Superconducting State

From the above results it is clear that both samples of KCsBaC_{60} are superconducting with a transition temperature of about 22 K. Since superconductivity in cubic fullerides is commonly observed only in the case of a threefold electron transfer to C_{60} , one has to assume that only that subphase of KCsBaC_{60} with triply charged fullerenes becomes superconducting. According to Raman measurements, in both samples this subphase constitutes less than a quarter of the sample material.

It is interesting to find out whether this phase is a known superconductor, K_3C_{60} for instance, or if the peculiar mixture of alkali and alkaline-earth ions makes up a new member of the group of superconducting fullerides. As reported in chapter 2, a linear relation has been found between lattice constant and transition temperature for the cubic superconductors. From the left part of Fig. 2.7 one would expect a lattice constant of 14.3 Å for a superconducting transition temperature of 22 K. This matches exactly the lattice constant of 14.29 Å found in the x-ray investigations.

Compound	Structure	Lattice Const. (Å)	T_c (K)
C_{60}	fcc	14.17	_
$\mathrm{K}_{3}\mathrm{C}_{60}$	fcc	14.25	19.5
K_2CsC_{60}	fcc	14.29	24
$\mathrm{KCs}_2\mathrm{C}_{60}$	unstable	_	—
$\mathrm{Cs}_3\mathrm{C}_{60}$	—	_	40 (12 kbar)
CsBaC_{60}	fcc	14.18	—
$K_{3-x}Ba_xC_{60}$	fcc	_	15 (x=0.25)
$\mathrm{K_{3}Ba_{3}C_{60}}$	bcc	11.24	5.6
$\mathrm{Ba}_4\mathrm{C}_{60}$	bco	—	7

Table 6.3: Fulleride superconductors containing K, Cs and/or Ba, according to [3] and our own measurement on $CsBaC_{60}$.

Table 6.3 lists possible subphases that might lead to the superconductivity observed in KCsBaC₆₀. The most promising candidate is definitely K_2CsC_{60} . Probably subphases of this stoichiometry exist in the samples. Furthermore, since CsBaC₆₀ is not superconducting, it makes sense that barium is not involved in the superconducting phase.

6.4 Summary

Investigations of the two barium-containing fullerides $CsBaC_{60}$ and $KCsBaC_{60}$ were presented in this chapter.

• $CsBaC_{60}$

The fulleride $CsBaC_{60}$ has not been reported in the literature so far. The reason might be the disproportionation of $CsBaC_{60}$ into CsC_{60} and $CsBa_2C_{60}$, which is observed in the Raman measurements. Consequently, the fullerene molecules are not triply charged like in the alkali fulleride superconductors and therefore the absence of superconductivity probed by ESR and SQUID measurements is easily understood. The CsC_{60} fraction of the sample could be expected to polymerize like in pure CsC_{60} . However, no splitting of the respective Raman mode due to polymerization has been found. One can therefore infer that the material does not contain macroscopic domains with different doping levels, but that the charge disorder only exists on the scale of a few lattice constants.

This picture is supported by x-ray results which find good crystallinity and a cubic symmetry with lattice constant a=14.18 Å. If larger regions of CsC₆₀ existed, orthorhombic domains would occur. On the other hand, x-ray investigations show no sign of unit cell doubling, which would be expected in case of a spatially ordered disproportionation. Thus the two different charge states must be distributed statistically on a local scale.

Although two differently charged C_{60} cations exist in $CsBaC_{60}$, ESR finds one homogeneous signal. The temperature-dependence of the linewidth and the ESR susceptibility indicate that the material is metallic and thus the conduction electrons experience an average of the different environments.

In conclusion, superconductivity, which might have been expected due to the formal transfer of three electrons to C_{60} , does not occur in CsBaC₆₀. Although the system is cubic like the superconducting A_3C_{60} fullerides, a charge disproportionation prevents the occurrence of triply charged C_{60} . However, from what is known to date, the half filled LUMO is a prerequisite for superconductivity in the cubic fullerides. Since only one sample of CsBaC₆₀ was produced, one cannot assess the influence of the parameters used in the synthesis of the material. Instead of intercalating C_{60} with the azides of both dopants at the same time, one can also offer them sequentially, as suggested by Yildirim *et al.*. Furthermore, the influence of tempering time and temperature has not been studied systematically. • KCsBaC₆₀

Two materials from different batches of KCsBaC₆₀ have been investigated. Although they differ strongly in the Raman spectra, their magnetic properties are governed by the subphases they share: namely a phase with a onefold electron transfer and a phase with a threefold transfer to C₆₀. The phases with electron transfers of five or six as found for sample #1 have no influence on the magnetic properties observed in the ESR. At least from the C₆₀⁶⁻ ions one can expect that they are diamagnetic and thus are not relevant in magnetic measurements.

Lineshifts and T_1 relaxation observed in the ¹³³Cs and ¹³C NMR of sample #1 are compatible with metallic behavior. However, a broad background signal in ¹³C NMR confirms the existence of differently doped subphases.

ESR finds two signals which are both indicative of metallic behavior. Furthermore the superconducting state is detected by its fingerprint non-resonant microwave absorption. SQUID measurements confirm the existence of a superconducting state with a transition temperature of 22 K. The transition temperature allows an assignment of this phase to K_2CsC_{60} .

In conclusion, one has to be aware of the fact that the synthesis of KCsBaC_{60} as it was done in collaboration with F. Rachdi has not led to materials with correct stoichiometry. Instead, as evidenced by Raman and x-ray investigations, multiphase materials have been prepared, whose magnetic properties are somewhat similar, but too complicated to allow a complete assignment to the different subphases.

Concerning mixed alkali/alkaline-earth fullerides it has to be noted that their synthesis demands a high level of scrutiny and experience. The investigated materials, however, were the first mixed alkali/alkaline-earth materials synthesized in the abovementioned collaboration. While, the phase separation in $CsBaC_{60}$ seems to be a real effect which may not be related to the details of the synthesis, for $KCsBaC_{60}$ the literature has examples of better defined materials. However, in spite of these problems, the investigations yielded a wealth of phenomena which made research on these materials rewarding.

Chapter 7

Fullerenium Salts

Fullerenium salts, i.e., materials containing C_{60}^{n+} cations, are desirable substances to synthesize in order to find out about their solid state properties. The most interesting question is whether these materials show similar phenomena as their fulleride counterparts with C_{60}^{n-} anions. Possible phenomena include metallicity, dimer- or polymer formation, and superconductivity.¹

Unfortunately, due to the electrophilic nature of C_{60} , chemical oxidation is very hard to achieve. There are reports on fullerenium salts of the type $(AsF_6)_2C_{60}$, but the crystallinity of the materials is not very good [105]. However, the existence of a charge transfer has been shown by the identification of AsF_6^- in IR measurements [150]. Furthermore a semiconducting behavior with a gap of 0.22 eV and a room-temperature resistivity of $10^6 \ \Omega \text{ cm}$ have been reported. ¹³C NMR shows an anisotropic spectrum with an isotropic shift value of 143 ppm for the C_{60}^{2+} cation [105, 106]. This is close to the value for neutral C_{60} and suggests that the C_{60}^{2+} ions are diamagnetic.

The group of Prof. Jansen at the Max-Planck-Institut für Festkörperforschung also synthesized several batches of fullerenium arsenic hexafluoride of the type $(AsF_6^-)_n C_{60}^{n+}$, using different ratios of AsF_5 to C_{60} in the synthesis. Thereby an oxidation of C_{60} in the range of n=1-2 has been achieved. Characterization and ESR investigations of these materials are presented in the following, with the focus put on the material with best crystallinity which is referred to as batch #3.

¹As already mentioned in chapter 2, Schön *et al.* reported superconductivity in crystalline C_{60} at a doping level of about 3.4 holes per C_{60} using field-induced doping [90]. However, these results have never been reproduced and were found to be fraudulent by an investigation committee [92].

7.1 Synthesis and Characterization of $(AsF_6)_nC_{60}$

For the synthesis, a large excess of arsenic pentafluoride AsF_5 is dissolved in liquid SO_2 and then reacted with C_{60} powder. The excess amount is needed in order to react all C_{60} . Thereby the following reaction takes place [150]:

$$3AsF_5 + 2C_{60} \rightarrow 2AsF_6^- + 2C_{60}^+ + AsF_3$$

With an excess of AsF₅ available, a further oxidation of C_{60}^+ to C_{60}^{2+} can in principle be achieved. After a reaction time of about three hours the solution adopts a green color which indicates that C_{60} has been oxidized. The solvent SO₂ and AsF₃ are then removed by drying the material and a greenish powder remains. AsF₆ intercalates the C_{60} crystal so that crystallites with stoichiometry $(AsF_6^-)_n C_{60}^{n+}$, n=1-2, are formed.



Figure 7.1: X-ray powder diffraction pattern of $(AsF_6)_nC_{60}$, batch #3, at room-temperature.

Characterization by x-ray diffraction finds crystalline order, but it is not possible to assign the reflections to a single structure. Fig. 7.1 displays the x-ray diffraction pattern obtained for the material from batch #3. This batch has been prepared with a ten-fold excess of AsF_5 with respect to the amount of AsF_5 necessary following the above equation of reaction. According to the x-ray investigation, this material has the best crystallinity of the five batches produced. Besides, the x-ray pattern indicates a much better sample crystallinity than reported in the literature by Datars *et al.* and one can clearly exclude the structure indexing presented there [105, 151]. The diffractogram furthermore shows no trace of crystalline C_{60} , so that one can assume that all pristine C_{60} crystals have reacted with the oxidant.

The failure of the structure determination indicates the existence of differently structured subphases. Probably the size ratio between the two counter ions is not optimal for crystallization. While C_{60} is a sphere with a radius of 3.55 Å, the AsF₆⁻ can be represented by a sphere of radius 3.0 Å. In the simplistic picture of hard spheres, this size ratio should lead to a CsCl structure with a coordination number of eight. However, the size difference between the two ions might be large enough to have a competition with NaCl order which has a coordination of six.² Another explanation for the poor crystallization might be the susceptibility of C₆₀ to Jahn-Teller distortions. The possible coexistence of C₆₀⁺ and C₆₀²⁺ cations which are subject to different Jahn-Teller distortions might prevent a long-range crystalline order.

In order to exclude fluorination of C_{60} , an IR investigation has been performed, which finds no evidence for C–F bond modes [151].

7.2 ESR of $(AsF_6)_nC_{60}$, Batch #3

ESR of different batches of $(AsF_6^-)_n C_{60}^{n+}$ in general shows the same trends, but also exhibits some differences. As mentioned above, according to the x-ray investigation batch #3 has the best crystallinity [151]. Therefore ESR measurements of this compound are reported as an exemplary case.

7.2.1 X-Band ESR

At X-band frequencies, the fullerenium salt exhibits a narrow Lorentzian roomtemperature signal, as plotted in Fig. 7.2. The full width of the ESR line is $\Delta B_{\rm FWHM}$ =7.5 G. The resonance is positioned at a g value of 2.0024. A rough estimate of the number of spins from the signal intensity indicates that a large fraction of the material contributes to the ESR.

Since the arsenic-fluoride compounds that take part in the synthesis are all diamagnetic, the signal can be attributed to C_{60} cations. Furthermore, C_{60}^{2+} is expected to be diamagnetic and the third oxidation step is very unlikely to be achieved in this compound. Thus one can infer that the signal is due to the mono-cations C_{60}^+ . The g value is in tune with the range of g factors from 2.0020 to 2.0030 which has been reported for C_{60} radical cations in solution [113].

For the investigation of electronic dynamics in this material, temperature-dependent ESR measurements have been performed. Fig. 7.3 displays the evolution of the spectrum with decreasing temperatures. In this process, the signal remains at a constant

 $^{^{2}}$ In comparison, the rotating Cr(C₇H₈)₂ molecule in bis(toluene)chromium fulleride presented in chapter 5 has a radius of 3.3 Å. This is large enough to allow good crystallization in the CsCl structure.



Figure 7.2: X-band ESR signal of $(AsF_6^-)_n C_{60}^{n+}$ (#3) at ambient temperatures. The lineshape is perfectly Lorentzian, with a full width of $\Delta B_{FWHM}=7.5$ G. The g value amounts to 2.0024.



Figure 7.3: Temperature-dependent X-band ESR signal of $(AsF_6^-)_n C_{60}^{n+}$ (#3). At low temperatures the narrow dynamic linewidth allows the resolution of an anisotropy.

field position, which corresponds to the abovementioned g factor of 2.0024. The dynamic linewidth, however, decreases continuously upon cooling, so that below roughly 180 K anisotropies are resolved. As a measure of the linewidth, the peak-to-peak (PP) distances have been extracted from the spectra. These are plotted in Fig. 7.4. At



Figure 7.4: Temperature-dependent peak-to-peak (PP) X-band linewidth of $(AsF_6^-)_n C_{60}^{n+}$. The solid line is a fit to the dynamic high-temperature broadening of the signal. When at low temperatures the dynamic part becomes small in comparison with the anisotropy, a constant anisotropy-determined PP linewidth remains.

temperatures above roughly 180 K, the dynamic contribution to the linewidth dominates the signal. It increases linearly with temperature and thus is compatible with a metallic behavior of the material. Using the Elliott model introduced in section 3.1.5, a room-temperature conduction electron scattering rate of $1/\tau=2.1\cdot10^{14}$ s⁻¹ is obtained. This is a very rough estimation, based on the linear fit shown in Fig. 7.4 and a g shift measured with respect g=2.0030 for the C⁺₆₀ ion.³ The scattering rate is by a factor of 2–6 larger than the phononic scattering rates found for metallic RbC₆₀ and CsC₆₀.

At 100 K and below, the PP width is determined by the temperature-independent anisotropy of the signal.

Further information on the spin system is given by the temperature-dependent ESR susceptibility, which has been determined by a twofold integration of the X-band spectra. The susceptibility and its inverse are plotted in Fig. 7.5. The solid lines in both

³The g value of C_{60}^+ cations in solution is found between 2.0020 and 2.0030. The reference chosen here was taken with the aim of obtaining a reasonable scattering rate. For g=2.0024 the rate would diverge.



Figure 7.5: Left: The ESR susceptibility can be matched by the modified Curie behavior of an antiferromagnet (solid line), as explained in the text. The resulting paramagnetic Néel temperature is $T_{\rm N}=76.5$ K. Right: The inverse susceptibility follows a straight line which does not go through the origin. The solid line is a plot which uses the fit values obtained from the fit displayed in the left figure.

plots correspond to a fit using the modified Curie behavior of an antiferromagnetic system, namely $\chi_{\text{ESR}} = \frac{C}{T-T_{\text{N}}}$, with T_{N} being the paramagnetic Néel temperature. The parameters extracted from the fits are C = 766.7 a.u.K and $T_{\text{N}}=76.5$ K. Obviously the fit matches the susceptibility very well, thus one has to assume the existence of a correlated electronic system. However, despite the observed correlations, no signs of magnetic order are found down to temperatures of 6 K.

7.2.2 W-Band ESR

In order to acquire more information about the anisotropy of the signal, W-band measurements have been performed.

Fig. 7.6 compares the low-temperature W-band signal with the X-band signal. Clearly, the W-band signal is strongly broadened. This implies that the low-temperature anisotropy observed at X band is g anisotropy. From the signal shape one can deduce that the anisotropy is non-axial. One can therefore assume that the C₆₀ cations experience a non-cubic environment of low symmetry.

However, as displayed in Fig. 7.7, the spectrum cannot be matched using the powder distribution of only a non-axial g tensor convolved with a Lorentzian line. One could assume that deviations arise from hyperfine coupling to the fluorine nuclei, which have spin I=1/2. However, the hyperfine contribution at X- and W-band frequency should be the same. Since in comparison to the W-band signal, the X-band resonance is very narrow at all temperatures, the influence of hyperfine coupling can be assumed



Figure 7.6: Comparison of the W-band and X-band signal of $(AsF_6^-)_n C_{60}^{n+}$ (#3) at 20 K. The high-field signal is dominated by g anisotropy.



Figure 7.7: Comparison of the ESR-signal at 6 K with a fit based on a nonaxial g tensor convolved with a Lorentzian line. Fit parameters are $g_{xx}=2.0036$, $g_{yy}=2.0027$, $g_{zz}=2.0010$, and a full Lorentzian linewidth of $\Delta B_{\rm FWHM}=11.8$ G.

to be negligible. This leaves g anisotropy as the only cause for the line-broadening observed at high fields. The deviation between the spectrum and the fit then implies that the material cannot be described by only one g tensor and therefore different electronic environments must exist. This finding is in tune with the fact that the x-ray diffraction spectra did not allow a proper determination of the structure.

Finally, temperature-dependent W-band spectra plotted in Fig. 7.8 reveal that the high-field signal at all temperatures is dominated by anisotropy.



Figure 7.8: Temperature-dependent W-band spectra of $(AsF_6^-)_n C_{60}^{n+}$ (#3). The main features of the spectra are determined by g anisotropy and do not change with temperature. The dashed lines indicate a separation of 33 G. However, at low-temperatures, the shape of the powder pattern changes slightly and a shoulder develops on the low-field side of the signal.

7.3 ESR Comparison of Different Batches

Different batches of $(AsF_6^-)_n C_{60}^{n+}$ differ mainly in the excess of AsF_5 used in the synthesis. An excess in the range between 2 and 10 was applied for different batches. Nonetheless in all compounds C_{60} is expected to give away one or two electrons. Thus the spectra for all compounds are quite similar in terms of the overall magnitude of the g anisotropy and the temperature evolution of the spectra. However, the detailed line patterns differ. This is illustrated by the comparison of the low-temperature W-band spectra of batch #3 and #4 in Fig. 7.9. The slight differences in the ESR are in tune with the fact that the crystal structure is not well defined and differently ordered phases exists, whose distribution and extension varies from sample to sample. However, the spectra are similar enough to allow the conclusion that the electronic structure is quite similar in the different subphases.



Figure 7.9: Comparison of the W-band signal of $(AsF_6^-)_n C_{60}^{n+}$ batch #3 (left) and #4 (right) at 6 K. The magnetic field sweep width is the same for both spectra.

7.4 Conclusion

In summary, ESR investigations of $(AsF_6^-)_n C_{60}^{n+}$ find a signal with a g value that is characteristic of C_{60}^+ mono-cations. Thus a charge transfer has taken place and paramagnetic C_{60}^+ mono-cations are formed. Since C_{60}^{2+} ions are diamagnetic, ESR does not give information about their existence and possibly the material simply has the composition $[AsF_6]^-[C_{60}]^+$.

The monotonic increase in ESR linewidth with temperature indicates metallic behavior. Although dynamic linewidths are rather narrow in comparison with alkali fulleride linewidths, due to the weak spin-orbit coupling high conduction electron scattering rates are necessary to account for the broadening. The magnitude of the spin-orbit coupling can be deduced from the deviation of the g value from the C₆₀ cation value, which is very small in these materials.

At W-band fields, the ESR signal is dominated by g anisotropy. Since x-ray investigations indicate the existence of different subphases, a sum of their signal contributions is observed and no single g tensor can be assigned to the data. The existence of g anisotropy results from a non-cubic environment of the spin-carrying C_{60}^+ ion. A comparison between the ESR signal of different batches shows that the magnitude of the g anisotropy is comparable for these materials.

The weakness of the explored material is certainly the poorly defined crystalline structure. For the future, the use of counter ions other than AsF_6^- might be desirable in order to find materials with better crystallization properties.

Chapter 8

Group III Metallofullerenes: $M_n@C_{82}, M = Sc, Y, La$

This chapter reviews the group III endohedral fullerenes in order to give a frame of reference for the investigations of $Sc_3@C_{82}$ presented in chapter 9. The focus is put on paramagnetic compounds which are accessible by ESR.

The first and most stable metallofullerenes resulted from the combination of C_{82} cages with the group III transition-metal elements scandium, yttrium, and lanthanum, also referred to as group IIIB elements. Table 8.1 summarizes electronic and nuclear properties of these trivalent elements. All three elements have small ionization energies, comparable to those of the alkali-metal elements.

	$^{45}\mathrm{Sc}$	⁸⁹ Y	139 La
Atomic number	21	39	57
Electronic configuration	$4s^23d^1$	$5s^24d^1$	$6s^25d^14f^0$
Ionic radius $(3+)$	0.75 Å	0.90 Å	1.03 Å
Natural abundance	100~%	100~%	99.91~%
Nuclear spin I	7/2	1/2	7/2
Nuclear g factor	1.3591	-0.2748	0.7952
Ionization potentials $I/II/III$ (eV)	6.6/12.8/24.8	6.2/12.2/20.5	5.6/11.1/19.2

Table 8.1: Important properties of the group III transition metal elements Sc, Y, and La. Ionic radii are listed for the triply charged cations. Ionization potentials are taken from [152].

The three elements have equivalent electronic configurations, but differ in size and ionization potentials. The size determines the number of atoms which fit into a C_{82}

cage, which is largest for scandium, whereas the ionization potential determines the charge transfer per atom to the cage, which is largest for lanthanum.

8.1 Monometallofullerenes $M@C_{82}$

La@C₈₂ was the first endohedral fullerene to be isolated [26]. The homologous systems $Sc@C_{82}$ and $Y@C_{82}$ are also stable. Group III transition-metal atoms have been incorporated in numerous carbon cages of different sizes and symmetries [153, 154]. Nonetheless, highest yields are still achieved with the C₈₂ cage.

8.1.1 La@C₈₂

As discussed in chapter 1, photofragmentation experiments revealed that the lanthanum ion is in fact located inside the C_{82} cage [28]. However, further characterization measurements, which were performed on toluene extracts from the soot produced by the Krätschmer method, suffered from the fact that only a tiny fraction of the extracted fullerenes was endohedral. At this point electron spin resonance (ESR) proved to be a very valuable tool, since it is only sensitive to the paramagnetic metallofullerenes while all empty carbon cages are ESR silent.

Thus an ESR spectrum of La@C₈₂ was obtained by Johnson *et al.* although the weight fraction of the endohedral material was only about 2 % of the solved fullerenes. The lowest trace in Fig. 8.1 shows a typical X-band spectrum of La@C₈₂. The 8 main lines arise from the isotropic hyperfine coupling to the nuclear spin I=7/2. Anisotropies are averaged due to rotational motion of the almost spherical molecule in liquid solution. The hyperfine splitting amounts to $A_{\rm iso}=1.25$ G. Comparison of this value with $A_{\rm iso} \approx 60$ G for $5d^1$ La in CaF₂ [156] led to the assumption that the spin density on the lanthanum cation must be reduced with respect to La²⁺ and thus the formal charge state is La³⁺@C³⁻₈₂. A charge transfer of three electrons onto the C₈₂ cage was further corroborated by photoemission spectroscopy experiments [157, 158] and theoretical calculations [159].

The small satellite lines in the ESR spectrum result from hyperfine coupling to ¹³C atoms on the cage. ¹³C has a nuclear spin of I=1/2 and occurs with a natural abundance of 1.1 %. The rather complex satellite spectrum arises from inequivalent carbon sites with differing hyperfine coupling strengths. Modelling the satellite lines shown in the left part of Fig. 8.2 allows the extraction of the ¹³C coupling constants [155]. At least seven electronically different groups of carbon atoms have been identified.



Figure 8.1: X-band spectra of the group III metallofullerenes at room temperature. The first endohedral fullerene to be investigated by ESR was La@C₈₂ (lowest trace). The splitting into 8 main lines arises from the isotropic hyperfine coupling to ¹³⁹La with I=7/2. Several satellite lines are split off as a consequence of hyperfine coupling to ¹³C atoms with I=1/2, which occur with a natural abundance of 1.1 % on the cage. The same holds for Sc with I=7/2 (upper trace) and Y (center trace) with I=1/2. Note the different field scaling for the three spectra. Data taken from [155].

The ${}^{13}C$ hyperfine coupling constants assigned to these groups have values between 0.4 G and 1.8 G.

If the fullerenes are extracted from the soot under anaerobic conditions, a second ESR pattern with lower intensity appears [153]. This has been ascribed to a less stable isomer of La@C₈₂ which exhibits a reduced isotropic hyperfine coupling and a slightly smaller g value, as shown in Tab. 8.2. For both isomers theory predicts an off-center position of the lanthanum ion, with a shift towards the center of a hexagon and possible bonding to the cage carbons [158, 159].

Recently the structure of La@C₈₂ (I) has been determined by synchrotron powder diffraction [27]. Hereby the diffraction data was analyzed using a combination of the maximum entropy method (MEM) and Rietveld refinement. The resulting electron density distribution confirms the formal charge state $La^{3+}@C_{82}^{3-}$ as well as the off-



Figure 8.2: ¹³C satellite lines. The small linewidth allows the resolution of ¹³C hyperfine couplings although carbon occurs with a natural abundance of only 1.1 %. From fitting a model function to the spectra, more than seven different ¹³C coupling constants were extracted by Seifert *et al.* [155].

center position of the ion, close to a hexagon face (closest La-C distance: 2.56 Å, distance La to cage center: 1.97 Å). The structure is shown in Fig. 1.7 in chapter 1. Furthermore, from the synchrotron measurements, the cage symmetry was determined to be C_{2v} and a partial delocalization of the lanthanum ion along the carbon cage wall has been observed.

The C_{2v} symmetry of La@C₈₂ (I) has been confirmed by ¹³C NMR on the diamagnetic monoanion [160]. Similar experiments revealed that the less stable isomer La@C₈₂ (II) has C_s symmetry [161] and thus allows for 3 different IPR isomers, as shown in Fig. 1.6.

8.1.2 Y@C₈₂

The results for Y@C₈₂ are very similar to those for La@C₈₂. Again two isomers are reported which show different hyperfine couplings. ESR parameters are listed in Tab. 8.2. The main difference with respect to the La@C₈₂ ESR is the existence of only two main signals according to the nuclear spin I=1/2 of yttrium, as shown in the center trace in Fig. 8.1.

A formal charge transfer of three electrons was determined by x-ray photoemission spectroscopy (XPS) [157]. MEM/Rietveld analysis of synchrotron powder data shows that the yttrium ion is located off-center (distance center to Y: 3.14 Å) and is probably strongly bound to the cage (distance C-Y: 2.9 Å) [162]. The cage symmetry has not been determined experimentally, but calculations favor a C_{2v} cage for Y@C₈₂ as well as for $La@C_{82}$ and $Sc@C_{82}$ [163].

Due to the smaller size of the yttrium ion in comparison with lanthanum, the formation of $Y_2@C_{82}$ is possible and in fact yields a stable compound. It is not accessible to ESR because of its diamagnetic nature.

8.1.3 Sc@ C_{82} (and Sc₂@ C_{84})

Scandium is the smallest of the group III transition metals and therefore up to three scandium ions fit into a C₈₂ cage. The monoendohedral Sc@C₈₂ behaves very similar to La@C₈₂ and Y@C₈₂. Again, ESR reveals the existence of two isomers. X-ray diffraction with MEM analysis shows that (at least in the dominating isomer) the scandium ion is located close to a six-membered ring, with a Sc–C distance of 2.54 Å, which is in tune with theoretical predictions [164]. The cage symmetry for the dominating isomer (I) is C_{2v} [165]. However, in contrast to the above-mentioned systems, these measurements indicate a rather divalent charge state with an electron transfer of only 2.2. This would imply that an unpaired electron is localized on the scandium ion.

	$A_{\rm iso}$	g factor	Width (G)	Sym.	Charge state
La@C ₈₂ (I)	1.15 - 1.25	1.9997 – 2.0012	0.049 - 0.125	C_{2v}	$La^{3+}@C_{82}^{3-}$
$La@C_{82}$ (II)	0.83	1.9989 - 2.0006	0.052 - 0.13	C_s	$La^{3+}@C^{3-}_{82}$
$Y@C_{82}$ (I)	0.48 - 0.49	1.9999 - 2.0006	0.10 - 0.12	C_{2v}	$Y^{3+}@C^{3-}_{82}$
$Y@C_{82}$ (II)	0.32 - 0.36	1.9998 - 2.0001	0.11	—	$Y^{3+}@C^{3-}_{82}$
$Sc@C_{82}$ (I)	3.80 - 3.83	1.9998 - 2.0002	0.036 - 0.045	C_{2v}	$Sc^{<3+}@C^{<3-}_{82}$
$Sc@C_{82}$ (II)	1.16 - 1.74	2.0002 - 2.0009	0.019	—	$Sc^{<3+}@C^{<3-}_{82}$
$Sc_3@C_{82}$	6.22 - 6.25	1.9985 - 1.9986	0.78	C_{3v}	$(\mathrm{Sc}_3)^{(3-6)+} @\mathrm{C}_{82}^{(3-6)-}$

Table 8.2: Summary of ESR parameters of the paramagnetic group III endohedrals with a C_{82} cage. Taken from [27, 28, 153, 157, 161, 166–171]. The linewidth depends on the viscosity of the solvent and the temperature. Since different groups used different solvents and measured at various temperatures, a range of observed widths is given. The same holds for the isotropic hyperfine coupling, which is also temperature-dependent. The *g*-value ranges arise from experimental error.

ESR results (see Tab. 8.2) show that indeed the hyperfine coupling is by about a factor of three larger than in La@C₈₂ [170,171], which is only partly due to the larger nuclear g factor of scandium and thus indicates an increased spin density on the scandium ion. On the other hand, the observed hyperfine coupling is still very small compared to couplings of about 60 G for Sc^{2+} in Sc-doped CaF₂ [172]. Thus the assumption of a formal three-fold charge transfer with no significant charge density in the 3*d* orbitals of scandium seems more plausible. This notion is further supported by the small nuclear quadrupole interaction determined from ESR experiments [173].

Similar to yttrium, scandium also forms dimetallofullerenes which are ESR-silent. Sc₂C₈₄ is one of the most abundant and stable metallofullerenes known to date [174]. The absence of an electron spin allows ⁴⁵Sc NMR experiments which find two lines at ambient temperatures that coalesce into a single line at elevated temperatures. This is explained by a model which assumes that the two scandium ions occupy inequivalent positions at low temperatures, but exchange their positions rapidly at high temperatures and thus average the NMR signal [175]. As for the case of the monoscandium system, synchrotron/MEM experiments favor a divalent scandium charge state for the discandium fullerene, i.e., $(Sc^{2+})_2@C_{84}^{4-}$ [176].

The C_{82} variant of discandium fullerenes also exists, but it is not as abundant as $Sc_2@C_{84}$ and therefore has not received much attention.

8.2 Sc₃@C₈₂

 $Sc_3@C_{82}$ was the first trimetallic endohedral system to be discovered. It was characterized by ESR of the toluene extract of soot produced in the arc burning process with scandium metal mixed into the graphite rods. The resulting spectra were a superposition of the above-mentioned $Sc@C_{82}$ 8-line spectrum and a 22-line spectrum [170, 171], as shown in trace (a) of Fig. 8.3. The 22 lines arise from hyperfine coupling to n=3 equivalent scandium nuclei, each with spin I=7/2. The different hyperfine components have different statistical weight, namely the intensity ratio 1:3:6:10:15:21:28:36:42:46:48:48:46:42:36:28:21:15:10:6:3:1.

ESR parameters are listed in Tab. 8.2. The fact that only 2nI+1=22 ESR lines and not $(2I+1)^n=512$ lines appear implies the equivalence of the three ⁴⁵Sc nuclei on the time scale of the ESR. This requires, at least on the average, that the scandium ions form an equilateral triangle. In the eighties, this configuration of a scandium trimer was observed in rare gas matrices at low temperatures [177]. The threefold symmetry of the scandium triangle makes it very likely that the cage also has C_3 symmetry, although the equivalence of the scandium nuclei could also be achieved by a rapid averaging motion in a cage with lower symmetry. However, from ESR it is highly probable that the cage is one of the two C_{3v} cage isomers displayed in Fig. 1.6.

The ESR linewidth of $Sc_3@C_{82}$ was found to be substantially larger than in the mo-



Figure 8.3: First ESR spectrum obtained from $Sc_3@C_{82}$ (a). It is a superposition of the spectra of $Sc_3@C_{82}$ and $Sc@C_{82}$, as shown in trace (c) and (d), respectively. (b) is the superposition of the two simulations (c) and (d). From [170].

noendohedral Sc@C₈₂. The lineshape is Lorentzian, thus it is presumably determined by dynamic effects. Different authors attributed the large linewidth to a jump motion of the scandium atoms inside the cage [178], to a rotation of the triangle [179], and to a dynamic distortion of the triangle [180], respectively.

Recently a synchrotron powder diffraction measurement with MEMS/Rietveld analysis has been published [181]. Fig. 8.4 shows the resulting structure. The scandium trimer sits at an off-center position with a closest Sc-C distance of 2.52 Å. Although the method seems to give a clear picture of the structure, the results are heavily debated:

• The synchrotron data yields a Sc–Sc distance of 2.3 Å. This is shorter than calculated distances in Sc₃ and Sc₃⁺ trimers [182]. It is not plausible that a positively charged trimer is able to substantially reduce its size inside a negatively charged cage. Furthermore, theoreticians argue that electrons are removed from the bonding orbitals of scandium and thus calculations arrive at much larger



Figure 8.4: Top, side, front, and bottom view of $Sc_3@C_{82}$, based on structural results from synchrotron radiation powder diffraction. The three scandium ions form an equilateral triangle which is located off-center on the three-fold rotational axis of the C_{82} cage.

Sc–Sc distances of about 3.4 Å [183].

- According to the suggested structure, the scandium trimer is shifted about 0.85 Å along the symmetry axis from the center towards the narrower part of the cage. A large Sc–Sc distance due to Coulomb repulsion should lead to a preferential residence in the wider part of the fullerene. This may be a small effect since the cage is almost spherical, with an average radius of 4.1 Å.
- From the integration of the charge map, a formal charge state of (Sc₃)³⁺@C₈₂³⁻ is obtained from the synchrotron measurements. On this point all publications disagree: DFT calculations favor (Sc²⁺)₃@C₈₂⁶⁻ [183] whereas extended Hückel calculations arrive at (Sc₃)⁴⁺@C₈₂⁴⁻ [184]. Voltammetry measurements also derive an electronic configuration of (Sc₃)⁴⁺@C₈₂⁴⁻ [185].
• The cage isomer obtained from the charge map is isomer number 7 according to the numbering shown in Fig. 1.6 [18]. The bottom of this cage consists of a corannulene molecule, i.e., a hexagon surrounded by six hexagons, as shown in Fig. 8.4. On this point there is also disagreement between different theoreticians. DFT calculations lead one group to the results that isomer number 7 is in fact the more stable one [186], whereas others report that isomer number 8 should be much more stable [183]. The bottom hexagon of the latter cage is surrounded by alternating hexagons and pentagons.

In summary, it is clear that the electronic state as well as the dynamics and position of the scandium cluster are not fully understood. The ESR investigations presented in the following chapter were undertaken in order to gain new insights to answer these questions.

For completeness it shall be noted that an ESR spectrum of a non-equivalent scandium trimer, presumably inside a carbon cage, has been published [187]. Unfortunately, the type of the cage could not be determined.

Chapter 9

ESR Investigations of Sc₃@C₈₂

ESR measurements of $Sc_3@C_{82}$ at standard and high fields were performed with the aim of acquiring information on electronic as well as structural and dynamic properties. Two samples of $Sc_3@C_{82}$ were available:

- 1) $Sc_3@C_{82}$ with ¹³C in natural abundance, solved in 1,2,4-trichlorobenzene (TCB).
- 2) $Sc_3@C_{82}$, ¹³C enriched to about 10 %, solved in Decalin.

After a brief review of the synthesis of $Sc_3@C_{82}$, this chapter at first presents ESR investigations of the non-enriched material (1) and afterwards the work on the ¹³C enriched material (2).

9.1 Synthesis and Sample Preparation

 $Sc_3@C_{82}$ is produced in a Krätschmer arc discharge process, with graphite rods that are mixed either with metallic scandium particles or scandium oxide Sc_2O_3 . The arc discharge takes place in a helium atmosphere and produces a fullerene-containing soot. The cage molecules are then extracted from the soot using a solvent like toluene or CS_2 . The fraction of endohedral scandium systems, which amounts to only a few percent of the solved fullerenes, is then separated from other solved carbon structures by two-stage high-performance liquid chromatography (HPLC). The HPLC allows the separation of molecules according to molecular weight, size, and shape [170,171,188]. $Sc_3@C_{82}$ was synthesized by the group of L. Dunsch at the IFW Dresden. The material contains ¹³C atoms in natural abundance. The ESR sample consists of $Sc_3@C_{82}$ dissolved in 1,2,4-TCB, which was sealed under vacuum in a 4 mm glass tube. From the comparison of the ESR susceptibility of the $Sc_3@C_{82}$ sample with a ruby standard, the number of spins was calculated to be roughly $6 \cdot 10^{14}$. After a first series of X-band measurements, the sample was divided into two fractions used for measurements at W-band and X-band frequencies. This procedure was done under a constant argon flow. Suprasil tubes of outer diameter 0.9 mm and 4.0 mm were used for the W-band and X-band sample, respectively.

According to L. Dunsch [189] the sample consists to 95 % of Sc_3C_{82} . The remainder are diamagnetic empty cages as well as ESR-silent di-scandium systems. $Sc_3@C_{82}$ is stable in air, so that air contact is not a problem as long as oxygen is expelled afterwards by degassing the sample. TCB, which is used as the solvent, has a higher viscosity than the widely-used carbon disulfide. Due to its π -electron system it also has a high polarizability.

The 10 % ¹³C enriched $Sc_3@C_{82}$ sample was synthesized by the group of H. C. Dorn at Virginia Tech. The material is dissolved in Decalin and sealed in a 5 mm ESR tube. The sample contains more material and thus gives rise to a stronger ESR signal than the specimen from the Dunsch group. Since the large sample volume does not fit completely into the resonator and furthermore strongly disturbs the cavity mode, the measured ESR susceptibility can only give a lower limit to the number of spins. The comparison to a ruby standard yields a limit of about 10¹⁵ spins, but from the color and volume of the sample number of spins is estimated to be close to 10¹⁶ spins. After the acquisition of X-band data, a W-band sample was prepared in a glove box under continuous nitrogen flow.

9.2 $Sc_3@C_{82}$ with ¹³C in Natural Abundance

This section presents the ESR results obtained with the $Sc_3@C_{82}$ material from the Dunsch group. At first, the room-temperature spectrum is discussed. Then the temperature-dependent X-band spectra before and after the sample transfer from the original glass tube to a quartz tube are discussed. Finally, temperature-dependent high-field ESR measurements are presented.

9.2.1 X-Band ESR at Room Temperature

The X-band ESR spectrum at room temperature is displayed in Fig. 9.1. The 22-line spectrum arises from the hyperfine coupling of the electron spin to three equivalent 45 Sc nuclei with I=7/2, as already discussed in section 8.2.

In order to model the spectrum, a Lorentzian line function $\mathcal{L}(B; A, \Delta B, B_0)$ depending on the magnetic field *B* is introduced. The line is determined by the parameters



Figure 9.1: Room-temperature X-band spectrum of Sc₃@C₈₂ solved in TCB (left). The spectrum is fitted using a model function of 22 Lorentzians as explained in the text. Only four parameters (amplitude, linewidth, g factor, and hyperfine splitting) determine the fit. With the parameter values $\Delta B_{\rm FWHM}=1.78$ G, g=1.9987, and $A_{\rm iso}=6.27$ G one finds an almost perfect fit, as shown in the magnified comparison (right) between model function (line) and data (dots).

amplitude A, linewidth ΔB , and resonance field B_0 . The total spectrum then is constructed according to

$$\mathcal{S}(B) = \sum_{M_{I_1}=-I}^{I} \sum_{M_{I_2}=-I}^{I} \sum_{M_{I_3}=-I}^{I} \mathcal{L}(A, \Delta B, B - B_0 - (M_{I_1} + M_{I_2} + M_{I_3})A_{\text{iso}}).$$
(9.1)

The three sums are over the spin orientations of the three scandium nuclei. Hereby the isotropic hyperfine coupling strength A_{iso} is assumed to be equivalent for all three scandium atoms. The actual position of a hyperfine component is determined by the product of A_{iso} with the sum over the nuclear magnetic quantum numbers M_{I_i} of the three ⁴⁵Sc nuclei.

The right part of Fig. 9.1 shows that with these 4 parameters an almost perfect fit to the spectrum is possible. More sophisticated fitting routines, which include a linear and quadratic M_I dependence of the linewidth and/or the isotropic hyperfine coupling, do not give a relevant improvement of the fitting result. Thus linewidth ΔB and hyperfine coupling A_{iso} are both considered to be independent of M_I .

The observed linewidth of $\Delta B_{\rm FWHM}$ =1.78 G is slightly larger than reported for Sc₃@C₈₂ in other solvents [190].

Origin of the ESR Linewidth of Sc₃@C₈₂

In comparison with the monoendohedral $Sc@C_{82}$, the ESR linewidth in $Sc_3@C_{82}$ is about one order of magnitude larger. This result has motivated several ESR investigations [178, 179, 190]. The liquid environment and the Lorentzian lineshape suggest that the broadening is homogeneous. Hereby the following dynamic mechanisms have been considered:

• Line-broadening effects arising from incomplete motional averaging of a hyperfine anisotropy in solution show a linear or quadratic dependence of the linewidth on M_I [107]. The degree of averaging depends on the relation between magnitude of the splitting and tumbling frequency of the molecule in the solvent. The latter depends on the viscosity η of the solvent and on temperature, so that for the linewidth the following dependence results:

$$\Delta B \propto \eta / T \,. \tag{9.2}$$

As stated above, the linewidth observed in the $Sc_3@C_{82}$ spectrum at room temperature does not exhibit a M_I dependence, thus a complete averaging of anisotropies can be assumed.

• If a paramagnetic molecule has a permanent electric dipole moment, then upon rotation, **spin-rotational coupling** can occur. Hereby the changing electric field creates a magnetic moment which couples to the electron spin moment via dipole-dipole coupling. This mechanism broadens all lines equally. In a solvent of viscosity η , the linewidth varies linearly with temperature according to

$$\Delta B \propto T/\eta \,. \tag{9.3}$$

However, investigations in solvents of vastly different viscosity showed no strong effect on the linewidth [179, 190]. Therefore spin-rotational coupling is assumed to be negligible in this system.

• As the relaxation does not depend strongly on the type of solvent used, it has been concluded that the line-broadening results from a motion of the scandium trimer inside the cage. Theoretical calculations predict an almost concentric electrostatic potential inside the cage and therefore low activation energies for a rotational motion of the trimer [183]. The rotation of the charged trimer leads to a field modulation which relaxes the electron spin and thus results in **relaxational broadening** of the ESR.

One can hence conclude that the increased relaxation in comparison with monoendohedral $Sc@C_{82}$ must be related to an internal motion of the scandium ions. This explains the larger ESR linewidth in comparison with the monoendohedral materials, where the ions are bound to the cage walls and cannot move.

9.2.2 Temperature-dependent X-Band Measurements

Temperature-dependent measurements have been performed to gain more information on possible internal dynamics of $Sc_3@C_{82}$. Fig. 9.2 shows the evolution of the spectra



Figure 9.2: Left: $Sc_3@C_{82}$ X-band spectrum upon cooling. Right: Fit function using the 22-line hyperfine pattern plus one Lorentzian line at the center of the spectrum.

as the sample is cooled down from room temperature. It is interesting to note that the solvent TCB freezes already at 289 K. This has no effect on the signal – all anisotropies are still averaged. This means that either the rotation of the almost spherical molecule is not affected by the freezing of TCB or the averaging results only from internal motion of the scandium ions in the cage.



Figure 9.3: Left: Upon cooling, the ESR susceptibility lost in the hyperfine pattern appears in the center line. The total ESR susceptibility roughly follows a Curie behavior (dashed line). Right: Upon heating, the transformation takes place at higher temperatures.

Below about 240 K the 22-line hyperfine pattern significantly loses intensity, while a signal at the center of the spectrum develops. The right part of Fig. 9.2 shows that the total signal can be modelled using a 22-line hyperfine pattern and one additional Lorentzian line, which is located exactly at the center of the pattern. The temperature-dependent ESR susceptibility and linewidth obtained from the fit are displayed in Fig. 9.3 and Fig. 9.4, respectively. The g factor is independent of temperature.

The susceptibility plot in Fig. 9.3 shows that upon cooling, the sum of all signal components (total χ) roughly follows a Curie behavior (dashed line). The susceptibility which is lost in the hyperfine pattern appears in the center line. Hence, the system clearly goes from a state with resolved isotropic hyperfine coupling to a state with unresolved hyperfine coupling. It was not possible to track the hyperfine pattern quantitatively below 180 K, thus it is not clear whether the transformation is completed at lower temperatures. Below 140 K the background signal from the glass tube dominates the signal.

Upon heating, the transformation takes place at higher temperatures. This hysteresis behavior indicates that after 20 to 30 minutes spent at one temperature, the system still has not reached equilibrium. Aside from the hysteresis behavior, the transformation is completely reversible.

Fig. 9.4 shows that the widths of both the center line and the hyperfine components increase at low temperatures. The lineshape is Lorentzian and thus hints at a dynamic line-broadening mechanism. A reason for the broadening at low temperatures could



Figure 9.4: Left: Linewidth of the hyperfine components. The discrepancy between cooling and heating data results from the hysteresis behavior of the sample. Right: Linewidth of the center line from a Lorentzian fit. Above 260 K the fit is unreliable due to the small intensity of the center line.

be incomplete motional averaging of anisotropies due to a slowing down of motions in the cold sample.

None of the early publications on $Sc_3@C_{82}$ have reported the emergence of a center line in the spectrum. Only recently, aside from the Dunsch group [191], the Shinohara group reported this effect on $Sc_3@C_{82}$ solved in toluene [192].

There are three possible explanations for the disappearance of the hyperfine coupling (hfc):

- 1) The hfc is averaged. A possible scenario would be that the Sc₃@C₈₂ molecules in solution form clusters. The close intermolecular distance would then lead to an exchange interaction that could average the hyperfine coupling [107]. A strong argument against this explanation is the fact that the solvent TCB freezes at 289 K, whereas the transformation takes place at 220 K, long after the solution is frozen. At this stage, a clustering of the molecules is very improbable. Furthermore different cluster sizes and therefore a smooth transition between the two signals would be expected.
- 2) The hfc is strongly reduced. A reduction of the coupling by roughly a factor of 10 would conceal the hyperfine splitting within the ESR linewidth. For this to happen, the electron density at the scandium nuclei has to be strongly diminished. Therefore the electron distribution on the molecule and/or its total structure have to change. Bartl *et al.* favor a structural change induced by the chemical pressure of TCB [191].

3) At low temperatures the hfc has a large axial anisotropy with $A_{\perp} = 0$ and $A_{\parallel} = 3A_{\rm iso}$. This is expected to lead to a strong contribution at the center of the isotropic hyperfine pattern. A hyperfine anisotropy of this type has been determined by Knight *et al.* for neutral scandium trimers in an argon matrix [177] and is put forward by Kato *et al.* to explain the Sc₃@C₈₂ spectrum at low temperatures [192]. However, Kato *et al.* have not proven their suggestion by a simulation, thus a simulation has been performed in the framework of this thesis. Model and simulation are discussed in the following.

Simulations for a Hyperfine Anisotropy with $A_{\perp} = 0$

The model suggested by Kato *et al.* [192] assumes that the coupling of the electron spin to each scandium nucleus *i* can be described by an axial symmetric hyperfine tensor \mathbf{A}_i . The second rank tensor is characterized by the principal perpendicular component A_{\perp} and the parallel component A_{\parallel} . At low temperatures, hyperfine anisotropies are not averaged and lead to an anisotropic powder lineshape. In order to have a high signal intensity at the center of the hyperfine pattern, the model proposes the particular tensor values $A_{\perp} = 0$ and $A_{\parallel} = 3A_{iso}$. The Hamiltonian for this situation has the following form:

$$\mathcal{H} = g_{\rm iso}\,\mu_{\rm B}\,\boldsymbol{B}\cdot\boldsymbol{S} + \sum_{i=1}^{3}\boldsymbol{S}\cdot\mathbf{A}_{i}\cdot\boldsymbol{I}_{i} - \sum_{i=1}^{3}g_{\rm n}\,\mu_{\rm n}\,\boldsymbol{B}\cdot\boldsymbol{I}_{i}\,.$$
(9.4)

The three terms represent the electron Zeeman, the hyperfine (hf), and the nuclear Zeeman interaction, respectively. When summing over the hf terms, the respective orientations of the tensors have to be taken into account. Fig. 9.5 displays a view of $Sc_3@C_{82}$ including the axis of rotation and the mirror planes which result from the C_{3v} symmetry. If the C_{3v} symmetry is to be retained, the unique tensor axes A_{\perp} have to lie in the mirror planes or be perpendicular to them. Since the model does not assume an interaction between the scandium nuclei and furthermore a powder average over all orientations is intended, one finds that the perpendicular orientation is equivalent to the in-plane orientation along the intersection of each mirror plane with the plane spanned by the scandium trimer. Thus only the configurations with the tensor axes lying in the mirror planes have to be considered. Symmetry then determines, that extremal hyperfine interactions appear when the unique tensor axis is either oriented parallel to the C_{3v} axis of the molecule or perpendicular to it. Therefore only these two limiting cases have to be considered. The other symmetry-allowed orientations yield hf interactions in-between those of the two extremal configurations.



Figure 9.5: View of $Sc_3@C_{82}$ with the mirror planes and the axis of rotation representing the C_{3v} symmetry.

The top row of Fig. 9.6 schematically illustrates the two extremal configurations by representing the axial hf tensors by ellipsoids of revolution at the positions of the scandium nuclei. The left column of Fig. 9.6 treats the case with the rotational symmetry axes of all tensors arranged in a parallel manner, perpendicular to the plane spanned by the three scandium atoms. The right column deals with the configuration where the axes are in plane, pointing toward the center of the trimer.

In order to get a signal contribution at the center of the hyperfine pattern, the model by Kato *et al.* proposes a perpendicular hf splitting of $A_{\perp} = 0$ G. This means that the usual approximation that the hyperfine field at the site of the nucleus is much larger than the external field is not valid and the total Hamiltonian of Eqn. 9.4 including the nuclear Zeeman term has to be diagonalized. Thus for the generation of a powder pattern, a 1024 × 1024 Hamiltonian matrix $((2S + 1)(2I + 1)^3 = 1024)$ has to be diagonalized for a large number of orientations. However, the symmetry of the problem allows analytic simplifications, so that a spectrum can be simulated on a standard PC (450 MHz) in a reasonable amount of time (< 2 h).

Parallel Orientation

The left part of Fig. 9.6 shows the simulation for parallel alignment of the hyperfine tensors and compares it to the measured spectrum. At the center of the simulated signal, the powder distribution (middle row, step-like function) for this case is flat. This means that the PP distance of the derivative line is determined by the steps of this function, which are separated by $A_{\parallel} = 3A_{\rm iso} = 18.75$ G. The comparison with the ESR spectrum at 140 K shows that the measured PP linewidth is significantly smaller. Furthermore, since the PP width of the modelled spectrum is determined by the hyperfine interaction, one can assume that it is rather independent of temperature. This is in contrast to the strongly temperature-dependent PP linewidth found from the fits to the measurements, as shown in Fig. 9.4.

Thus for parallel orientation of the hyperfine tensors, the model cannot explain the low-temperature spectrum.

In-Plane Orientation

For the orientation of the tensor symmetry axes in the plane of the scandium ions, the generated powder pattern has indeed a peak at the center, which is still retained after convolution with a Lorentzian function. The powder distribution and the convolved function are shown in the right plot at the center row of Fig. 9.6. However, as the comparison of the derivative model function with the spectrum shows, the wings of the simulated signal have too much weight to match the spectrum.

Conclusion

In conclusion, an anisotropic broadening of the hyperfine line components as put forward by Kato *et al.* cannot explain the single narrow Lorentzian line which is observed in the ESR at low temperatures. Therefore, a major reduction of the isotropic hyperfine coupling is needed to account for the low-temperature signal. This implies a substantial change in the electronic system and possibly also in the position of the scandium trimer inside the molecule. This change may be related to the chemical pressure exerted by the frozen solvent onto the fullerenes. However, as mentioned above, it is not related to the freezing of the solvent.



Figure 9.6: Simulations and comparison with the 140 K ESR spectrum for parallel (left) and in-plane (right) alignment of the ⁴⁵Sc hf tensors ($A_{\perp} = 0$ G, $A_{\parallel} = 18.75$ G). The top row schematically indicates the configurations by representing the hf tensors by ellipsoids at the positions of the scandium atoms (the picture regions correspond to a zoom into Fig. 9.5). The middle row diagrams show the generated powder pattern (step-like functions) and their convolution with a Lorentzian line of half linewidth $\Delta B_{\rm HWHM} = 6$ G. The Hamiltonian has been evaluated for $4 \cdot 10^4$ randomly generated sets of angles in order to arrive at a powder pattern. The bottom row diagrams compare the derivative of the simulations (red) with the spectra. While the simulation for parallel alignment of the tensors yields a too large PP linewidth, the result for the in-plane orientation puts too much weight on the wings of the spectrum.

9.2.3 X-Band Measurements After Sample Transfer

In order to get rid of the background signal produced by the glass ESR tube, the $Sc_3@C_{82}$ sample was transferred into a quartz X-band and W-band tube, respectively. Although $Sc_3@C_{82}$ is stable in air, this procedure was performed under a continuous argon gas flow. In order to check the sample after the transfer procedure, an X-band room-temperature spectrum was recorded, which is identical to the spectrum observed before. However, upon cooling of the sample one finds changes in the envelope function of the hyperfine pattern as well as in the width of the appearing center line.

The spectra together with the model functions derived from the fit are displayed in Fig. 9.7. The fit to the data reveals that a center line clearly exists, but it is broader



Figure 9.7: Left: Sc₃@C₈₂ X-band spectrum upon cooling (after sample transfer). The low-temperature signal is broader than before. The narrow contribution is due to an impurity. Right: Fit function using the 22-line pattern plus one Lorentzian line at the center position. The diamond shape of the hyperfine pattern at 240 K hints at a dependence of the linewidth on M_I^2 . Inclusion of M_I^2 terms thus improves the fit.

than before and thus not as eye-catching. The width of the center line before and after the sample transfer is plotted versus temperature in the left part of Fig. 9.8. Furthermore, upon cooling, the envelope function of the line pattern changes from a Gaussian to a diamond-like shape. This behavior occurs if the linewidth of the hyperfine satellites depends on M_I^2 . Assuming a linewidth of the type $\Delta B = \Delta B_0 + k M_I^2$, the temperature-dependent broadening can be extracted. The plot in Fig. 9.8 displays the temperature dependence of k. The fact that M_I^2 terms occur in the linewidth



Figure 9.8: Left: The linewidth of the center line is considerably larger than before the sample transfer. Right: Temperature dependence of the linewidth parameter kwhich measures the dependence of the width of the hyperfine components on M_I^2 : $\Delta B = \Delta B_0 + k M_I^2$.

hints at an incomplete motional averaging of the hyperfine anisotropy, as discussed in section 9.2. This was not observed before the sample transfer. Obviously, despite performing the transfer under a continuous argon flow, the sample had air contact. It is known that oxygen in solution affects the dynamics and the relaxation behavior of solved fullerenes. This has to be kept in mind when the W-band measurements are discussed.

9.2.4 Temperature-dependent W-Band Measurements

W-band measurements of $Sc_3@C_{82}$ were performed at various temperatures. As discussed in the previous section, the sample had air contact during the transfer from the X-band glass tube to the W-band tube. Unfortunately, due to the small inner radius of the W-band sample tube of only 0.4 mm, it is impossible to degas the solution in the tubes without losing most of the material. Therefore, it has not been attempted to degas the sample.

Fig. 9.9 gives an overview of the temperature dependence of the W-band signal of $Sc_3@C_{82}$. The room-temperature spectrum has changed only slightly compared to X band, fitting parameters are $\Delta B_{\rm FWHM} = 2.1$ G and a hf splitting of $A_{\rm iso} = 6.24$ G.



Figure 9.9: Temperature-dependence of the W-band spectrum of $Sc_3@C_{82}$ upon heating the sample.

The linewidth is marginally increased and the individual lines exhibit a small asymmetry which might indicate a partially resolved g anisotropy. In the transition regime, however, the hyperfine pattern develops a strong anisotropy which has not been observed at X band. The signal below the transition, at 160 K, is again quite similar to

the X-band signal, with a dominating center line with a width of $\Delta B_{\rm FWHM} = 14.32$ G. Thus one can infer that g anisotropy contributes only marginally to the linewidth. The asymmetry of the line pattern in the transitional regime is not observed at X band and therefore has to be related to g anisotropy. The unusual shape of several lines at 240 K and 220 K hints at an overlap of signals with slightly different positions. One can easily envisage that in the temperature range around 200 K the system passes through transitional states with slightly different g values. On the other hand, since the X-band signal changed after sample transfer, the W-band signal must also be influenced by the air contamination of the sample. Thereby the g anisotropy as well as molecular dynamics can change under the influence of oxygen and thus in combination lead to the observed signal anisotropy.

9.3 ¹³C Enriched $Sc_3@C_{82}$

The group of H. Dorn at Virginia Tech, USA, provided a $Sc_3@C_{82}$ sample with a ¹³C enrichment of about 10 %. The material is solved in Decalin. It has been investigated using X- and W-band ESR as well as SQUID measurements.

9.3.1 X-Band ESR at Room Temperature

Comparing the ESR spectra of the non-enriched materials $Sc@C_{82}$ (Fig. 8.2) and $Sc_3@C_{82}$ (Fig. 9.1), one finds that the ¹³C satellites which are clearly visible in the narrow-line spectrum of $Sc@C_{82}$ are absent for $Sc_3@C_{82}$. ¹³C satellite lines arise from the hyperfine coupling to ¹³C nuclei, which have a nuclear spin of I=1/2 with a natural abundance of 1.1 %. The absence of satellites in the case of $Sc_3@C_{82}$ implies that ¹³C couplings that have statistical relevance are so weak that they are hidden within the $Sc_3@C_{82}$ lines, whereas couplings larger than the linewidth are statistically irrelevant so that they cannot be discerned in the spectrum of non-enriched $Sc_3@C_{82}$.

This situation changes significantly when the material is enriched with 13 C to about 10 %. The spectrum then exhibits satellite lines for each of the scandium-hyperfine components, as displayed in Fig. 9.10. The right part of Fig. 9.10 shows that the spectrum is matched very well under the assumption that each of the 22 main lines has a symmetric pair of satellites.

However, the fit does not explain how this spectrum comes about. In order to reveal the origin of the spectrum, the following facts have to be considered:

• The probability p of finding a C_n cage which incorporates $m^{-13}C$ atoms depends



Figure 9.10: Left: X-band spectrum of the 10 % ¹³C enriched Sc₃@C₈₂ sample, measured at 220 K. Right: Comparison between fit function and data. The fit is based on the 22 scandium hyperfine components with an additional pair of ¹³C satellites for each component. For simplicity, center line and satellites are assumed to have the same linewidth. Fit parameters are amplitude, linewidth ($\Delta B_{\rm FWHM} = 1.45$ G), g factor (g = 1.9983), and satellite splitting ($A_{\rm C} = 4.23$ G) as well as scandium hyperfine splitting ($A_{\rm Sc} = 6.25$ G).



Figure 9.11: Probability distributions for the number of ${}^{13}C$ atoms on a C₈₂ cage in the case of natural abundance (dots) and 10 % ${}^{13}C$ enrichment (circles).

on the enrichment fraction f in the following way:

$$p(n,m,f) = \binom{n}{m} f^m (1-f)^{n-m} \,. \tag{9.5}$$

The probability is normalized: $\sum_{m=0}^{n} p = 1$. Fig. 9.11 displays the probability of finding a certain number of ¹³C atoms on a C₈₂ cage for the case of natural ¹³C abundance (f = 1.108 %) and for 10 % ¹³C enrichment (f = 10 %). While in the non-enriched case it is most probable to have no or one ¹³C atom on a cage, the probability maximum for 10 % enrichment is around eight ¹³C atoms per molecule. Thus one expects hyperfine multiplets, which arise from the coupling to more than one ¹³C atom. The multiplicity of the hyperfine splitting for m ¹³C atoms on the cage is given by M = 2mI + 1 = m + 1, since I=1/2 for ¹³C. Of these m + 1 lines, the *l*th line has a weight given by $\frac{1}{2^m} {m \choose l}$, $l \in [0, m]$. Using the Lorentzian line function introduced in section 9.2.1, one can write the multiplet arising from m ¹³C atoms as

$$\mathcal{M}(B; m, \Delta B, B_0, A_{\rm C}) = \frac{1}{2^m} \sum_{l=0}^m \binom{m}{l} \mathcal{L}(\Delta B, B - B_0 - \frac{A_{\rm C}}{2}(m-2l)). \quad (9.6)$$

 $A_{\rm C}$ hereby denotes the isotropic ¹³C hyperfine coupling. Fig. 9.12 shows simulated multiplets for different numbers of ¹³C atoms.

• As the number of ¹³C atoms is statistically distributed over the fullerene cages in the sample, all the multiplets add. They have to be weighted with their respective probability p(m), shown in Fig. 9.11, so that the total spectrum is given by

$$\mathcal{S}(B; \Delta B, B_0, A_{\rm C}) = \sum_{m=0}^{82} p(m) \,\mathcal{M}(B; m, \Delta B, B_0, A_{\rm C}) \,. \tag{9.7}$$

This situation is simulated in Fig. 9.13 for the cases of 10 % $^{13}{\rm C}$ enrichment and natural $^{13}{\rm C}$ abundance.

• Furthermore one has to consider different hf coupling strengths for different ¹³C positions on the cage. The simulation of ¹³C satellites lines shown in Fig. 8.2 revealed more than 7 different couplings for the case of the C₈₂ monometallo-fullerenes. The higher symmetry in the case of Sc₃@C₈₂ might reduce this number, but still more than one coupling strength is expected.



Figure 9.12: Multiplets arising from the coupling of the electron spin to an increasing number of ¹³C atoms. ¹³C hf coupling strength is $A_{\rm C} = 4.2$ G, half linewidth is $\Delta B_{\rm HWHM} = 1$ G.

The 'Strong Coupling Sites' Model

The ESR spectrum shown in Fig. 9.10 exhibits only two ¹³C satellite lines per ⁴⁵Sc hf component, whereas the simulation displayed in the left part of Fig. 9.13 shows that for one coupling strength, either a multiplet or a broad line for each ⁴⁵Sc hf component is expected. In order to resolve this contradiction, a simple model is introduced.

The model assume that the carbon positions on the C_{82} cage, which presumably have different hf coupling strengths, can be divided into two groups.



Figure 9.13: Simulated spectra of a paramagnetic C_{82} cage arising from the sum over all ¹³C hf multiplets weighted with their respective probability. For illustration, an identical ¹³C hf coupling of $A_{\rm C} = 4.2$ G for all carbon positions on the cage is assumed. Left: 10 % ¹³C enrichment for 3 different intrinsic linewidths. Right: C_{82} with ¹³C in natural abundance.

Members of the first group experience a strong hyperfine coupling which gives rise to resolved satellite lines. The coupling strength is supposed to be the same for all nuclei of this group and to be equal to the splitting of the two satellites observed for each ⁴⁵Sc hf line in the spectrum. In the following, members of this group are called 'strong coupling sites'.

Members of the second group experience a hyperfine splitting that is small compared to the linewidth. Thus the splitting cannot be resolved and at the most increases the linewidth. For simplicity the coupling of this group of carbon positions on the cage is set to zero.

If there are k 'strong coupling sites' on a carbon cage, then the probability p of finding a ¹³C atom on one of these sites is given by:

$$p(k,m,f) = \binom{k}{m} f^m (1-f)^{k-m} \,. \tag{9.8}$$

The summation of multiplets now has to be done according to this modified probability function. Simulations for various numbers of strong coupling sites and for two linewidths which lie in a reasonable range are shown in Fig. 9.14.

A comparison with Fig. 9.10 shows that either two or three 'strong coupling sites' can be involved, otherwise the satellites are over- or underpronounced. A simulation for three 'strong coupling sites' and a linewidth of $\Delta B_{\rm FHWM} = 1.45$ G is compared to the spectrum in Fig. 9.15. It is obvious that for three strong coupling sites the model slightly overestimates the satellite intensity. In fact, for two strong coupling sites the model fits data better. However, the C_{3v} symmetry of the molecule requires either



Figure 9.14: Simulated ¹³C splittings for different numbers of 'strong coupling sites'. A ¹³C hf constant of $A_{\rm C} = 4.2$ G has been applied. The spectra on the left side result from a convolution with a Lorentzian line of half width $\Delta B_{\rm HWHM} = 0.5$ G, for the spectra on the right side $\Delta B_{\rm HWHM} = 1$ G has been used.

one, three, or six strong coupling sites, as shown in Fig 9.16. Thus the deviation for the three site simulation is attributed to a 13 C enrichment lower than 10 %.

As a check of the result for 3 strong coupling sites, the equivalent spectrum for nonenriched $Sc_3@C_{82}$ is simulated. Fig. 9.17 shows that in this case the satellites are not visible, because the occupation of one of the three strong coupling sites is statistically irrelevant. This result confirms the validity of the assumption of only three carbon positions with strong hf coupling.

In conclusion, the model has shown that only few carbon sites have a coupling strong enough to produce satellites outside the main lines. From the intensity of the satellites, one can infer that the number of these strong coupling sites is between two and three per cage. Due to the threefold symmetry, only the cases of three sites and for illustration that of one site are considered. The site that only occurs once is



Figure 9.15: Left: X-band spectrum of the ¹³C enriched Sc₃@C₈₂ sample, recorded at 220 K. Right: Comparison between data and a simulation based on the 'strong coupling sites' model for 3 sites. In contrast to the fit shown in Fig. 9.10, the relative amplitudes now come out of the model. For the remaining parameters the fit values from above have been used ($\Delta B_{\rm FWHM} = 1.45$ G, g = 1.9983, $A_{\rm C} = 4.23$ G, $A_{\rm Sc} =$ 6.25 G).



Figure 9.16: Different sites on $Sc_3@C_{82}$. The top carbon atom sits on the C_3 symmetry axis and thus occurs only once. Nine atoms are located on the C_{3v} mirror planes, thus they form three groups of three equivalent atoms (white). All other carbons form 12 groups of six equivalent atoms each. The two groups which are closest to the scandium trimer are colored in black.



Figure 9.17: Left: X-band spectrum of the non-enriched Sc₃@C₈₂ sample, taken at 220 K. Right: Comparison between data and a simulation based on the 'strong coupling sites' model for 3 sites. The good agreement validates the model for the both the enriched and non-enriched sample ($\Delta B_{\rm FWHM} = 1.78$ G, g = 1.9987, $A_{\rm C} = 4.23$ G, $A_{\rm Sc} = 6.27$ G).

located on the rotational symmetry axis at the point where it passes through the upper hemisphere of the cage, as shown in Fig. 9.16. The sites that belong to groups of three equivalent positions occur only on the upper hemisphere.¹ Therefore, in order to account for the observed spectrum, the conclusion has to be drawn that in either case the spin density on the upper hemisphere is increased.

The magnitude of the resolved hyperfine splitting is $A_{\rm C}$ =4.2 G. This is more than a factor of two larger than the largest splitting observed for the monoendohedral materials presented in chapter 8. This indicates a more inhomogeneous charge distribution on the cage of the Sc₃@C₈₂ molecule. The unresolved hyperfine components are hidden within the linewidth of $\Delta B_{\rm FWHM}$ =1.45 G. Consequently the linewidth can be taken as the upper limit of the hyperfine splitting of the weakly coupling carbon positions.

¹This only holds for the isomer displayed in Fig. 9.16. In principle the second C_{3v} isomer could also be realized. However, synchrotron measurements identified the isomer used above [181]. Furthermore preliminary results from DFT calculations also favor this isomer [186].

9.3.2 Temperature-dependent X-Band ESR

Aside from the investigation of ${}^{13}C$ satellites, it has to be verified whether the electronic transition which manifests itself in a single narrow low-temperature signal for $Sc_3@C_{82}$ in TCB is also present in the enriched material solved in Decalin. Fig. 9.18 displays the temperature-dependent X-band spectra together with the corresponding fits.



Figure 9.18: Left: ¹³C enriched $Sc_3@C_{82}$ X-band spectrum upon cooling. Right: Fit function using the 22-line pattern with ¹³C satellites plus one Lorentzian line at the center position.

Around 220 K the hyperfine pattern disappears abruptly, while a narrow line at the center appears. Visual inspection of the sample during cooling showed that the specific cis/trans mixture of Decalin freezes at this temperature, hence in Decalin the transformation seems to be related to the freezing of the solvent. As in the case of non-enriched $Sc_3@C_{82}$, the narrow linewidth excludes a simple anisotropic broadening of the high-temperature signal. Only a change in the electronic structure can account for the strongly decreased hyperfine interaction.

In fact, upon freezing, Decalin contracts substantially, with a volume change of more

than 10 %. Thus one can expect a strong chemical pressure to be exerted on the molecules, which in turn can trigger the transformation to a different electronic state.



Figure 9.19: Temperature dependence of the ⁴⁵Sc hyperfine coupling (left) and the ¹³C coupling (right). Both increase roughly linearly with decreasing temperature. Dots are extracted from spectra upon heating, circles upon cooling.

In the temperature range above 220 K, the fits to the spectra allow the extraction of the ⁴⁵Sc and ¹³C hyperfine splittings. The plots in Fig. 9.19 show that both increase roughly linearly with decreasing temperature. This is probably related to a contraction of the molecules as the solvent is cooled.

The plot of the ESR susceptibilities shown in Fig. 9.20 demonstrates that upon cooling, the center line rises in intensity while the pattern loses intensity. This is the behavior already observed for the non-enriched $Sc_3@C_{82}$ material. The plot of the inverse susceptibility shows straight lines, which indicate Curie behavior, but also a jump in the susceptibility at around 220 K. Obviously the jump is related to the freezing of the solvent at this temperature. Since the spectrum at 220 K already shows an increased susceptibility compared to higher temperatures, but still displays an unchanged ESR signal, the change in susceptibility cannot be related to the transition in the electronic structure of the molecule. Furthermore, this effect has not been observed in the non-enriched $Sc_3@C_{82}$ material. Thus one can assume that the effect is an artefact which results from the high filling level of the ESR tube: the filling level was 25 mm. This is more than the height of the rectangular TE_{102} cavity (23 mm). When the solvent contracts upon freezing, more material is pulled into the cavity and thus a stronger signal results. Furthermore, the cavity mode is affected by the large sample and the quality factor improves when the solvent freezes, which also enhances the signal intensity.



Figure 9.20: Susceptibility upon cooling the sample. Left: Susceptibilities for the hf pattern, the center line, and the sum of both, as extracted from the fits to the data. Empty triangles represent the total susceptibility as obtained by a double integration of the ESR spectra. Right: The inverse plot of the total susceptibilities. A straight line through the origin indicates Curie behavior, which is observed here, except for the step between 210 and 220 K. As explained in the text, the step is an artefact which results from a too high filling level of the ESR tube.

Low-Temperature Behavior

Fig. 9.20 shows only a small discrepancy between the low-temperature susceptibility determined from the double integration of the spectra and the susceptibility determined from a Lorentzian fit to the center line. This means that the line-shape remains Lorentzian all the way down to 6 K. Fig. 9.21 plots the temperature-dependent linewidth in comparison with the width of the non-enriched $S_{c_3}@C_{s_2}$ material. Upon cooling, between 150 K and 100 K the linewidth increases substantially, but even at 6 K the line is narrower than the width of the room-temperature hyperfine pattern. No anisotropies are observed.

The increase in linewidth indicates that molecular motions slow down and thus anisotropies are no longer completely averaged at low temperatures. However, in contrast to monometallofullerenes, which show broad anisotropic spectra at low temperatures, the line broadening is still modest. This might be related to the abovementioned reduction in ⁴⁵Sc hyperfine coupling below about 200 K. The question whether the broadening is then related to g anisotropy will be addressed by W-band measurements presented in the next section.



Figure 9.21: Temperature dependence of the center line width of enriched $Sc_3@C_{82}$ (dots) compared with the non-enriched material (triangles). For the non-enriched sample in the glass tube, the signal could not be followed below 100 K due to the strong background signal. Furthermore the data above 240 K are not reliable, since the spectrum in this temperature range is dominated by the hyperfine pattern.

9.3.3 W-Band Measurements

W-band measurements of ¹³C enriched Sc₃@C₈₂ were performed at various temperatures. Fig. 9.22 gives an overview of the temperature dependence of the W-band signal of ¹³C enriched Sc₃@C₈₂. The room-temperature spectrum is practically identical to the X-band spectrum, with fit parameters $\Delta B_{\rm FWHM}$ =2.1 G, ⁴⁵Sc hf splitting $A_{\rm Sc}$ =6.24 G, and ¹³C splitting $A_{\rm C}$ =4.10 G. In comparison with the X-band roomtemperature parameters $\Delta B_{\rm FWHM}$ =1.95 G, $A_{\rm Sc}$ =6.17 G, and $A_{\rm C}$ =4.16 G, the deviations are within the error bars for the parameter determination.

At lower temperatures, the hyperfine pattern disappears and a narrow line appears close to the center. The spectrum at 255 K indicates that this line is not located exactly at the center of the hyperfine pattern. From a fit to the spectrum one finds a shift of 1.7 G towards higher fields. This relates to a g shift of $\Delta g = -0.00010$.

The comparison between the W-band and X-band linewidths plotted in Fig. 9.23 shows an increase in linewidth of almost a factor of two at W-band frequencies. This indicates that with the slowing down of internal motion in $Sc_3@C_{82}$, g anisotropy starts to contribute to the spectra.

In contrast to the W-band spectra obtained from the non-enriched sample (Fig. 9.9), no asymmetry of the hyperfine pattern is observed in the transition region. This



Figure 9.22: Temperature-dependence of the W-band spectrum of 13 C enriched Sc₃@C₈₂ upon heating.

confirms the assumption that the asymmetric line pattern found in the non-enriched material arises from the interaction with oxygen which intruded into the sample during transfer to the W-band tube.

Due to the high concentration of the ¹³C enriched $Sc_3@C_{82}$ solution, the W-band ESR signal is strong enough to enable the application of pulsed ESR techniques. A pulse-echo signal was obtained, which allowed the determination of relaxation rates. Thereby at 10 K at T_2 relaxation time of 16 µs was obtained, whereas the T_1 relaxation is about 15 ms. These relaxation times decrease rapidly at temperatures above 20 K



Figure 9.23: Temperature dependence of the center linewidth of ${}^{13}C$ enriched $Sc_3@C_{82}$ at X band (dots) compared with W band (circles).

until at 80 K no echo signal can be obtained anymore. The relaxation times obtained at 10 K are comparable to times found for monoendohedral fullerenes [193] and thus indicate that the scandium ions are probably attached to the cage walls and thus no relaxation-inducing motion remains. However, a complete analysis of the temperature dependence of the relaxation rates was not possible in the framework of this thesis, but nonetheless would be desirable since it might yield more information on potential low-temperature dynamics in $Sc_3@C_{82}$.

9.3.4 SQUID Measurements

The ESR sample of ¹³C enriched $Sc_3@C_{82}$ has also been investigated using a SQUID magnetometer.

The temperature-dependence of the static susceptibility (not displayed) follows the same Curie-behavior already found from the X-band ESR susceptibilities. At the freezing temperature of the solvent a small step in the susceptibility occurs. These findings are in tune with the ESR results.

At low temperatures the magnetization can be saturated by applying high fields. Fig. 9.24 shows saturation measurements between 2 K and 10 K. The sample magnetization does no longer increase linearly with the field, but shows a saturation behavior which can be described by the Brillouin function introduced in chapter 3. The decrease in magnetization at high fields results from the diamagnetic contribution of the solvent.



Figure 9.24: Left: Saturation of the paramagnetic magnetization at low temperatures. The fit function is the sum of a Brillouin function and a linear diamagnetic contribution. Fit parameters are listed in Tab. 9.1. Right: In order to assess the reliability of the fit, best fits for S=1/2, 3/2, and 5/2 are displayed. Corresponding parameters are listed in Tab. 9.2.

temperature (K)	number of spins	molecular spin S	$\chi_{\rm dia}~({\rm emu})$
2.0	$2.62\cdot 10^{17}$	2.47	$-1.17 \cdot 10^{-12}$
4.2	$2.53\cdot10^{17}$	2.65	$-1.25 \cdot 10^{-12}$
7.0	$2.35\cdot 10^{17}$	2.80	$-1.21 \cdot 10^{-12}$
10.0	$2.45\cdot10^{17}$	2.75	$-1.26 \cdot 10^{-12}$
average	$2.49\cdot 10^{17}$	2.67	$-1.22 \cdot 10^{-12}$

Table 9.1: Parameters extracted from the fits plotted in the left part of Fig. 9.24.

temperature (K)	number of spins	molecular spin S	$\chi_{\rm dia} \ ({\rm emu})$
2.0	$2.57\cdot 10^{18}$	1/2	$-3.75 \cdot 10^{-12}$
2.0	$5.25\cdot10^{17}$	3/2	$-1.78 \cdot 10^{-12}$
2.0	$2.58\cdot10^{17}$	5/2	$-1.16 \cdot 10^{-12}$

Table 9.2: Parameters resulting from the best fits to the saturation measurement at 2 K for a given spin S=1/2, 3/2, and 5/2. The corresponding functions are plotted in the right part of Fig. 9.24.

The solid lines plotted in the left part of Fig. 9.24 represent fit functions based on the Brillouin function plus a linear term which describes the constant diamagnetic susceptibility. Only three parameters determine the fit: the spin S per molecule, the number of spins n, and the diamagnetic susceptibility of the solvent. Fit parameters and their average are listed in Tab. 9.1. The average spin obtained from these fits is S = 2.67, the average number of spins $n = 2.49 \cdot 10^{17}$, and the average diamagnetic susceptibility $\chi_{\text{dia}} = -1.22 \cdot 10^{-12}$ emu. The right part of Fig. 9.24 displays best fits for different molecular spin states. Obviously only the function for a spin of S = 5/2matches the data appropriately.

Consequently the molecules have spin S = 5/2 at low temperatures. This unexpected spin configuration can only arise if the molecule has a symmetry lower than C_{3v} . One could imagine a situation where a triply charged cage has spin S = 3/2 and couples strongly to a spin S = 1 located on one of the scandium ions.

9.3.5 Summary

Temperature-dependent ESR investigations of a ${}^{13}C$ enriched and a non-enriched $Sc_3@C_{82}$ sample reveal the following:

• The ESR signal of both samples undergoes a transformation at temperatures around 200 K. This is observed at X-band as well as W-band frequencies. Thereby the isotropic room-temperature hyperfine pattern disappears and a narrow line component emerges at the center of the hyperfine pattern. Simulations show that the low-temperature signal cannot be understood in terms of anisotropic broadening of the room-temperature spectrum. The lowtemperature line indicates a different electronic state which is characterized by a reduction of the hyperfine coupling by almost a factor of ten. Such a strong modification of the electronic state is probably related to a structural change in the molecule. A possible scenario would be a deformation of the cage under the influence of chemical pressure exerted by the frozen solvent. This can force the scandium ions to occupy different positions, which results in a smaller overlap with the electronic wave function.

Susceptibility data from X-band ESR as well as SQUID measurements exhibits Curie-behavior for the low-temperature state. The ESR linewidth broadens, but the signal retains its Lorentzian shape. W-band ESR, however, indicates that g anisotropy contributes substantially to the low-temperature spectrum.

• Multiplicity and intensity of the ¹³C satellites in the room-temperature ESR

of the 10 % ¹³C enriched sample can only be understood if a small number (2 or 3) of sites with a strong hyperfine coupling of $A_{\rm C}$ =4.2 G exist. All other carbon positions on the cage must have a substantially smaller ¹³C hf splitting which is concealed by the linewidth of $\Delta B_{\rm FWHM}$ =1.45 G. From the molecular C_{3v} symmetry of the C₈₂ cage isomer it follows that these sites are located on the upper hemisphere of the C₈₂ cage. Since synchrotron measurement reveal a displacement of the scandium trimer from the cage center to the upper hemisphere [181], this result implies that the spin density close to the scandium trimer is increased. A reason for the increased spin density could thus be an electron density concentration induced by electrostatic attraction of the positively charged scandium ions.

• By comparing the ESR spectra of the non-enriched Sc₃@C₈₂ material before and after air contact, a strong influence of oxygen contamination on the signal has been found.

Summary

This thesis presents the characterization of paramagnetic states in fullerene materials, mainly by ESR at standard and high fields, i.e., at X-band (9.5 GHz) and W-band (95 GHz) frequencies. Furthermore, supplementary ¹³C and ¹H NMR, SQUID, x-ray, and Raman measurements were performed.

Investigated materials range from the alkali fullerides RbC_{60} and CsC_{60} , over bis(arene)chromium fullerides, mixed alkali/alkaline-earth fullerides, and fullerenium salts to the endohedral metallofullerene $Sc_3@C_{82}$. While in the fullerene salts the focus was put on solid state properties like metallicity and phase transitions, in endohedral $Sc_3@C_{82}$ molecular properties were studied in solution.

The following paragraphs present the conclusions which can be drawn from the experiments carried out in the framework of this thesis.

Metallic RbC_{60} and CsC_{60}

High-field ESR investigations of RbC₆₀ crystal samples for the first time allowed the resolution of g anisotropies in the orthorhombic polymer phase. The determination of the principal g-tensor values $g_{xx} = 2.0014$, $g_{yy} = 2.0012$, and $g_{zz} = 2.0019$ reveals that the anisotropy is small and non-axial. It reflects the orthorhombic crystal structure and gives no indication of a highly anisotropic electronic system. This finding contradicts the idea of a quasi-one-dimensional conductivity along the polymer chains which has been put forward by several groups.

Furthermore, the analysis of temperature-dependent ESR linewidths of RbC_{60} and CsC_{60} powder samples at standard and high fields permitted the evaluation of conduction electron scattering rates using the Elliott theory. Scattering rates were found to be in the same order of magnitude as rates in classical metals. Suppression of scattering in consequence of a reduced dimensionality of the electronic system was thus not observed.

These results underline that due to the spherical structure of the fullerene molecules, orbital overlap along all three crystal axes occurs in RbC_{60} and CsC_{60} and that there-

fore these alkali fullerides are not comparable to quasi-one-dimensional organic conductors like $(TMTSF)_2PF_6$ and similar Bechgaard salts.

Bis(Arene)Chromium Fullerides

Bis(toluene)chromium fulleride, i.e., $Cr(C_7H_8)_2C_{60}$, and bis(mesitylene)chromium fulleride, $Cr(C_9H_{12})_2C_{60}$, are two members of the small group of stable and well-defined transition metal fullerides. The chromium atom incorporated in the organometallic complex renders these materials interesting candidates for molecular magnets. In fact, SQUID, ESR, and NMR investigations reveal that a one-fold electron transfer from the chromium complex to the fullerene molecule leads to paramagnetic roomtemperature phases, which are characterized by the exchange interaction between the respective spin species of the bis(arene)chromium cations and the fullerene anions. However, both materials avoid a magnetically ordered ground state by forming spinsinglet $(C_{60})_2^{2-}$ dimers at low temperatures. These act as diamagnetic spacers between the paramagnetic bis(arene)chromium ions and thus reduce the exchange interaction strong enough to prevent the formation of magnetic order. The transition to the lowtemperature state differs for the two materials: While bis(toluene)chromium fulleride at 250 K undergoes a clear first order phase transition from a cubic high-temperature phase to a triclinic dimer phase, in bis(mesitylene)chromium fulleride the transformation extends over the broad temperature range from 180 K to 15 K. This smooth transformation can be explained by the thermal excitation of triplet states on the fullerene dimers at high temperatures. A fit of this triplet-excitation model to the magnetization data yields an intradimer exchange coupling of J/k = -74.5 K.

Mixed Alkali/Alkaline-Earth Fullerides

The two mixed alkali/alkaline-earth fullerides $CsBaC_{60}$ and $KCsBaC_{60}$ have been prepared from the azides of the respective metal elements, a method which enables the synthesis of fullerides with multiple dopant elements.

CsBaC₆₀ has been investigated with the aim of clarifying whether the expected threefold electron transfer in this material leads to superconductivity in analogy with alkali fullerides of the type A_3C_{60} , or whether a phase separation as observed in the A_2C_{60} occurs. While x-ray investigations establish an fcc structure with good crystallinity, Raman measurements reveal a disproportionation into C_{60}^- and C_{60}^{5-} anions, i.e., formal stoichiometries of CsC₆₀ and CsBa₂C₆₀. ESR investigations indicate metallic behavior, but find no signs of superconductivity. Thus one can conclude that the
unbalanced ratio of only two dopant ions versus the three interstitial sites per C_{60} in the fcc lattice of $CsBaC_{60}$ results in a charge disproportionation.

 KCsBaC_{60} is an fcc fulleride with a charge transfer of four electrons to C_{60} . This particular combination of structure and charge can only be achieved by doping with a mixture of alkali and alkaline-earth atoms. Unfortunately the samples available for this work were multiphase materials. By Raman measurements and ESR, beside a phase with the expected stoichiometry KCsBaC_{60} , a superconducting phase $\text{K}_2\text{CsC}_{60}$ with critical temperature $T_c = 22$ K and a paramagnetic phase with C_{60} monoanions were identified. The coexistence of different phases rendered an unambiguous assignment of observations to the KCsBaC_{60} stoichiometry impossible.

Fullerenium Salts

Fullerenium salts with stoichiometry $(AsF_6^-)_n C_{60}^{n+}$ have been investigated using x-ray diffraction and ESR. X-ray investigations do not allow a structure assignment to the diffractograms, so that one can infer that the materials are not single phase. X-band ESR finds an isotropic g value of 2.0024, which is characteristic for C_{60}^+ cations. This proves an electron transfer of at least n = 1 away from C_{60} , but probably a mixture of phases with n = 1-2 exists. The temperature dependence of ESR linewidths indicates metallic behavior. High-field ESR allows the resolution of g anisotropies in the order of $\Delta g = 0.0026$, which result from the non-cubic environment of the fullerenium ions.

Sc₃@C₈₂

ESR investigations of the endohedral trimetallofullerene $Sc_3@C_{82}$ in solution focussed on two topics: the clarification of a transformation observed in the ESR spectra and the investigation of ¹³C couplings in order to map out the spin-density distribution on the cage.

At about 200 K, the 22-line hyperfine pattern observed at room temperature vanishes and a single line appears in its place. Simulations show that this transformation results from a reduction of the hyperfine coupling by almost a factor of ten. Such a strong variation must go along with structural changes. The finding of a molecular spin of S = 5/2 at low temperatures furthermore suggests that the C_{3v} symmetry observed at room temperature is not retained during the transformation.

Analysis of the ¹³C hyperfine satellite lines of a 10 % ¹³C enriched Sc₃@C₈₂ sample reveals a rather inhomogeneous spin-density distribution on the C₈₂ cage. Simulations confirm that only three carbon positions on the cage are subject to a hyperfine coupling strong enough to produce hyperfine satellites. All other positions couple so weakly that their splitting is hidden within the ESR linewidth. From the cage structure one can infer that the three positions with increased coupling strength are located on the upper cage hemisphere. This may be related to the fact that according to synchrotron results the positively charged scandium trimer is also shifted towards the upper hemisphere and thus might induce an increased electron density in its vicinity.

Zusammenfassung

Die Aufklärung der kugelförmigen Struktur des Fullerenmoleküls C_{60} Mitte der 1980er Jahre durch Kroto, Smalley und Curl war der Ausgangspunkt für die Entdeckung einer ganzen Reihe hochinteressanter Materialien.

Auf molekularer Ebene erstaunte neben der Vielfalt von stabilen Käfigmolekülen verschiedener Größe und Form vor allem die Entdeckung von "gefüllten" Käfigen, so genannten "endohedralen Fullerenen". Bei diesen Materialien sind ein oder auch mehrere Atome in einem Käfig eingeschlossen, der meist durch einen Ladungsübertrag stabilisiert wird.

Zudem zeigte sich bald die Möglichkeit, C_{60} mit Alkaliatomen zu kombinieren, was zur Bildung von kristallinen Festkörpersystemen führte, so genannten Fulleriden. Diese Ladungstransfersalze zeigen je nach Größe des Elektronentransfers auf C_{60} isolierende, halbleitende oder metallische Eigenschaften. In kubischen Fulleriden mit dreifachem Ladungsübertrag wurde sogar Supraleitung mit Sprungtemperaturen bis zu 40 K beobachtet. Darüber hinaus treten in einigen Fulleriden interessante strukturelle Phasenübergänge auf, bei denen sich reversibel $(C_{60})_2$ -Dimere oder $(C_{60})_n$ -Polymerketten bilden.

Die vorliegende Arbeit befasst sich sowohl mit der Untersuchung von Festkörpereigenschaften verschiedener Fullerensalze als auch mit der Aufklärung molekularer Eigenschaften von endohedralem $Sc_3@C_{82}$ in Lösung. Die zentrale Untersuchungsmethode ist dabei die Elektronenspinresonanz (ESR). Neben der Standard-ESR bei 9,5 GHz (X-Band) kommt der Hochfeld-ESR bei 95 GHz (W-Band) eine wichtige Rolle zu. Diese bietet den Vorteil höherer Empfindlichkeit und einer um den Faktor 10 erhöhten Auflösung bezüglich des elektronischen *g*-Faktors. Ergänzende Untersuchungen wurden mit Kernspinresonanz (NMR), magnetischen Suszeptibilitätsmessungen, Röntgendiffraktometrie und Raman-Spektroskopie durchgeführt.

Bei den untersuchten Fullerensalzen sind Fulleride, also Materialien bei denen C_{60} als Elektronenakzeptor fungiert, und Fullereniumsalze mit C_{60} in der Rolle des Donators zu unterscheiden. Fulleride mit Alkaligegenionen (RbC₆₀ und CsC₆₀), organometallischen Komplexionen (Bis(aren)chrom-Fulleride) und gemischten Alkali/Erdalkali-Ionen (CsBaC₆₀ und KCsBaC₆₀) wurden in diesem Zusammenhang untersucht. Mit Fullereniumhexafluoroarsenat (AsF₆)_nC₆₀ stand eines der wenigen bisher synthetisierten Fullereniumsalze zur Verfügung.

Neben den Untersuchungen an Festkörpersystemen nimmt auch die temperaturabhängige ESR-Analyse von $Sc_3@C_{82}$ in Lösung breiten Raum in dieser Arbeit ein. Dabei wurde eine ESR-Probe von $Sc_3@C_{82}$ in Trichlorbenzol und eine Probe von 13 C-angereichertem $Sc_3@C_{82}$ in Dekalin (Dekahydronaphtalin) mit Standard- und Hochfeld-ESR untersucht.

Metallisches RbC_{60} und CsC_{60}

Die Alkalifulleride RbC₆₀ und CsC₆₀ sind interessante Festkörpersysteme, die eine Vielzahl strukturell verschiedener Phasen ausbilden. Eine der ungewöhnlichsten Strukturen besitzt die orthorhombische Raumtemperaturphase: hier sind alle Fullerenmoleküle in parallele $(C_{60})_n$ -Polymerketten eingebunden. Diese Phase bildet sich reversibel bei Abkühlung aus der kubischen Monomerphase, die oberhalb von 350 K stabil ist. Die Polymerphase ist metallisch und hat aufgrund der Polymerbindung zu Spekulationen über eine quasi-eindimensionale Leitfähigkeit Anlass gegeben. Quasi-eindimensionale Systeme können eine Instabilität gegenüber der Bildung von Ladungsdichte- oder Spindichtewellen aufweisen. Einige Arbeitsgruppen haben die Existenz eines isolierenden magnetischen Grundzustandes unterhalb von 50 K in RbC₆₀ und CsC₆₀ mit der Bildung einer Spindichtewelle zu erklären versucht. Dabei sind sie in den Widerspruch zu ¹³C-NMR-Messungen geraten, die nicht leitende sp^3 -hybridisierte Polymerbindungsatome ausmachen. Zudem zeigen Bandstrukturberechnungen ein eher isotropes elektronisches System.

Dieser Fragestellung der Dimensionalität der Leitfähigkeit wurde in der vorliegenden Arbeit mit Hilfe von ESR-Messungen bei X- und W-Band-Frequenzen nachgegangen. Weil dabei direkt die Leitungselektronen detektiert werden (CESR: conduction electron spin resonance), können über die Bestimmung des elektronischen *g*-Tensors Rückschlüsse auf die elektronische Struktur gezogen werden. Zudem kann man aus der Analyse der temperaturabhängigen Linienbreiten auch Informationen über die Streudynamik der Leitungselektronen gewinnen.

Die hohe Empfindlichkeit des W-Band-ESR-Spektrometers erlaubte die Untersuchung von RbC_{60} -Einkristallen, deren Abmessungen nur Bruchteile von Millimetern betragen. Die Untersuchungen zeigen eine Orientierungsabhängigkeit des ESR- Signals, aus der unter Berücksichtigung der Domänenstruktur der Kristalle die g-Tensorhauptwerte bestimmt werden konnten. Diese betragen $g_{xx} = 2,0014$, $g_{yy} = 2,0012$ und $g_{zz} = 2,0019$. Der g-Tensor lässt also keine ausgeprägte Axialität erkennen, wie man sie im Falle eines niederdimensionalen Systems erwarten würde.

Durch den Vergleich von CESR-Linienbreiten in X- und W-Band hat man auch bei nicht-aufgelösten Anisotropien in Pulversignalen die Möglichkeit, die *g*-Anisotropie abzuschätzen. Damit wird der dynamische Anteil der Linienbreite zugänglich, der die Spinrelaxation durch die Streuung der Leitungselektronen widerspiegelt. Mit Hilfe des von Elliott formulierten Zusammenhangs zwischen CESR-Linienbreite und Streuraten konnten phononische Raumtemperaturstreuraten von 3, 29 $\cdot 10^{13}$ s⁻¹ für RbC₆₀-Pulverproben und 7, 54 $\cdot 10^{13}$ s⁻¹ für CsC₆₀-Pulver ermittelt werden. Diese Raten liegen in einem Bereich, der für klassische Metalle typisch ist. Auch hier findet man also keinen Hinweis auf eine reduzierte Dimensionalität des elektronischen Zustandes, da eine solche sich durch verringerte Streuraten bemerkbar machen müsste.

Fazit dieser Untersuchungen ist also, dass die Monoalkalifulleride nicht mit niederdimensionalen organischen Leitern wie dem Bechgaardsalz (TMTSF)₂PF₆ zu vergleichen sind, sondern aufgrund der Kugelform der Fullerenmoleküle eher zur Ausbildung dreidimensionaler Bandstrukturen neigen.

Bis(aren)chrom-Fulleride

Die Bis(aren)chrom-Fulleride sind aus der Bestrebung entstanden, Fullerene mit Übergangsmetallen zu kombinieren, um auf diese Weise neue Materialien mit magnetischen Ordnungszuständen zu synthetisieren. Es zeigt sich jedoch, dass eine direkte Kombination von Übergangsmetallionen mit C₆₀ nicht zu stöchiometrischen Festkörpern führt und in der Regel auch kein Ladungsübertrag auf das Fulleren stattfindet. Diese Probleme lassen sich umgehen, indem man Übergangsmetallatome in Form von Organometallkomplexen mit C₆₀ kombiniert. Dies wurde zuerst durch Broderick *et al.* gezeigt, die Chrom in Form der Aren-Komplexe Bis(benzol)chrom (Cr(C₆H₆)₂), Bis(toluol)chrom (Cr(C₇H₈)₂) und Bis(mesitylen)chrom (Cr(C₉H₁₂)₂) verwendeten, um Bis(aren)chrom-Fulleride darzustellen. Dabei tritt ein einfacher Ladungstransfer pro Formeleinheit auf, so dass ausgehend von den diamagnetischen Edukten paramagnetische Gegenionen entstehen, was prinzipiell eine gute Basis für die Bildung magnetischer Ordnungszustände darstellt.

Diese drei Materialsysteme wurden im Rahmen der vorliegenden Arbeit in Zusammenarbeit mit der Gruppe von Prof. Jansen am MPI für Festkörperforschung in Stuttgart untersucht. Die Kristallstrukturen wurden mittels Röntgendiffraktometrie bestimmt. Zur Aufklärung der elektronischen Eigenschaften kamen magnetische Suszeptibilitätsmessungen, ¹³C-NMR und ESR unter Standard- (9,5 GHz, X-Band) und Hochfeld-Bedingungen (95 GHz, W-Band) zum Einsatz.

Es zeigt sich, dass das Bis(toluol)chrom-Fullerid die beste Kristallinität aufweist und bei 250 K einen Phasenübergang erster Ordnung durchläuft. Ein Schwerpunkt der folgenden Ausführungen liegt daher in der Aufklärung dieses Übergangs. Auch beim Bis(mesitylen)chrom-Fullerid tritt eine Umformung auf, die sich jedoch über den breiten Temperaturbereich von 180 K bis 15 K erstreckt. Die Versuche, diesen Übergang zu modellieren, sind ebenfalls im Folgenden dargestellt. Die Fulleride auf Basis des Bis(benzol)chrom-Komplexes weisen hingegen eine sehr schlechte Kristallinität auf, die durch den Einbau von Lösungsmittelmolekülen in das Kristallgitter hervorgerufen wird. Die Untersuchungen an diesen Systemen lassen daher nur wenige klare Aussagen zu und werden demgemäß in dieser Zusammenfassung nicht präsentiert.

Bis(toluol)chrom-Fullerid

Röntgendiffraktionsexperimente zeigen, dass $Cr(C_7H_8)_2C_{60}$ bei Raumtemperatur eine einfach kubische Cäsiumchloridstruktur aufweist, die bei 250 K in ein triklines Tieftemperaturgitter übergeht. Im Gegensatz zu den Alkaliatomen in den Alkalifulleriden sitzt der Chromkomplex aufgrund seiner Größe nicht auf den Zwischengitterplätzen des flächenzentrierten C_{60} -Kristalls, sondern erzwingt die geräumigere einfach kubische Struktur. Die Gitterkonstante der kubischen Einheitszelle beträgt a = 9,984 Å. Synchrotronuntersuchungen finden für die trikline Tieftemperaturphase die Gitterparameter a = 13,641 Å, b = 13,834 Å, c = 13,855 Å, $\alpha = 91,83^{\circ}$, $\beta = 116,78^{\circ}$, $\gamma = 119,33^{\circ}$ und ein Zellvolumen von V = 1924,8 Å³, was einer Verdopplung der Einheitszelle entspricht.

Magnetische Suszeptibilitätsmessungen zeigen, dass der Phasenübergang mit einer Änderung der Suszeptibilität des Materials verbunden ist. In der kubischen Phase findet man ein magnetisches Moment, das dem Curie-Verhalten zweier Spins S = 1/2pro Elementarzelle entspricht. Bei tiefen Temperaturen beobachtet man hingegen nur einen Spin S = 1/2 pro Formeleinheit. Die Raumtemperaturkonfiguration lässt sich durch den einfachen Elektronenübertrag vom diamagnetischen Bis(toluol)chrom-Komplex auf das ebenfalls diamagnetische C₆₀ verstehen, so dass zwei paramagnetische Gegenionen mit S = 1/2 entstehen. Das Verschwinden einer der beiden Spinsorten bei tiefen Temperaturen erschließt sich jedoch nicht auf den ersten Blick und wurde daher mit Hilfe der ESR weiter untersucht. X-Band-ESR zeigt bei im gesamten Temperaturbereich von 6 K bis 300 K ein einzelnes lorentzförmiges Signal. Beim Phasenübergang ändert sich der *g*-Faktor vom Hochtemperaturwert $g_{iso} = 1,9915$ auf $g_{iso} = 1,9870$ in der Tieftemperaturphase. Der Vergleich mit einer Referenzsubstanz ergibt, dass der Tieftemperaturwert dem Chromkomplex entspricht. Die Fullerenspins verschwinden also unterhalb des Phasenübergangs.

W-Band-ESR kann in der Tieftemperaturphase wegen des zehnmal höheren Magnetfeldes eine Anisotropie des g-Faktors auflösen, die durch die trikline Umgebung des Spins auf dem Chromkomplex zustande kommt. Die Hauptwerte des g-Tensors lauten $g_{xx} = 1,9910, g_{yy} = 1,9907$ und $g_{zz} = 1,9793$. Bei Raumtemperatur findet sich jedoch weiterhin ein isotropes lorentzförmiges Signal. Da man aufgrund der SQUID-Ergebnisse von der Existenz zweier Spinsorten ausgehen kann und zudem der g-Wert des isotropen ESR-Signals zwischen dem Chromkomplexwert und den für C₆₀-Ionen typischen Werten liegt, muss es sich bei dem beobachteten Spektrum um ein gemitteltes Signal der Spins der beiden Gegenionen handeln. Die direkte Nachbarschaft der Spins im Festkörper lässt eine starke Austauschwechselwirkung erwarten, die den Mechanismus zur Mittelung der ESR-Signale liefert.

Die Frage, auf welche Weise die Spins der Fullerenmoleküle verschwinden, lässt sich mit Hilfe der ¹³C-NMR klären. Die kubische Phase zeigt ein Fullerensignal, das aufgrund seiner großen Verschiebung von 43 ppm gegenüber neutralem C₆₀ einem paramagnetischen Käfig, in diesem Fall also C₆₀, entsprechen muss. Diese paramagnetische Verschiebung verschwindet bei tiefen Temperaturen und es entsteht ein Signal, das nur noch um 2 ppm gegenüber neutralem C₆₀ bei 143 ppm verschoben ist. Dieses Verhalten kennt man von der Dimerphase des RbC₆₀. Die kleine Verschiebung stellt dabei den Ladungseffekt dar, der auf den diamagnetischen (C₆₀)²⁻₂-Dimeren im Vergleich zum neutralen C₆₀ auftritt.

Der beobachtete Phasenübergang kann also schlüssig im Sinne einer $(C_{60})_2^{2-}$ -Dimerbildung erklärt werden. Daraus ergibt sich auch zwanglos das Auftreten einer verdoppelten Einheitszelle in der triklinen Struktur der Dimerphase von $Cr(C_7H_8)_2C_{60}$.

Bis(mesitylen)chrom-Fullerid

 $Cr(C_9H_{12})_2C_{60}$ besitzt eine rhomboedrische Kristallstruktur, die mit einer Gitterkonstante von a = 10, 124 Å und einem Winkel von $\alpha = 92, 44^{\circ}$ eng mit der kubischen Struktur von $Cr(C_7H_8)_2C_{60}$ verwandt ist. Untersuchungen der Suszeptibilität finden bei Raumtemperatur zwei Spins S = 1/2 pro Elementarzelle, die dem Chromkomplex und dem Fullerenion zugeordnet werden können. Allerdings beobachtet man in diesem Fullerid keinen abrupten Phasenübergang, sondern eine langsame Verkleinerung der paramagnetischen Suszeptibilität beim Abkühlen zwischen 180 K und 15 K. Unterhalb von 15 K liegt nur noch eine Spinsorte vor, die mit Hilfe von ESR-Messungen aufgrund ihres niedrigen g-Werte von circa $g_{iso} = 1.989$ wiederum dem Chromkomplex zugeordnet werden kann. Die Bildung von Dimeren analog zum Bis(toluol)chromfullerid liegt also nahe. Schwierigkeiten macht jedoch die Interpretation des breiten Temperaturbereichs, in dem der Übergang stattfindet.

Zwei Modelle wurden entwickelt, um den Temperaturverlauf der Suszeptibilität, d.h. der Magnetisierung bei der SQUID-Messung, anzupassen. Das "Dimerbildungsmodell" geht davon aus, dass die $(C_{60})_2^2$ -Dimere beim Erwärmen thermisch aktiviert aufbrechen und damit je zwei paramagnetische C_{60}^{-} -Monomere entstehen. Die Anpassung liefert dafür eine Aktivierungsenergie von E/k = 62,5 K. Das alternative "Singulett-Triplett-Modell" nimmt hingegen an, dass die Dimerisierung der Fullerene beim Erwärmen nicht aufgehoben wird, sondern dass eine thermische Anregung des Singulettzustandes in einen Triplettzustand auftritt. Die Anpassung dieses Modells liefert eine Austauschkopplung der Spins auf einem Dimer von J/k = -74,5 K. Da keine hochaufgelösten Strukturdaten zu dieser Substanz vorliegen, ist die Existenz einer leichten Dimerisierung bei Raumtemperatur nicht auszuschließen. Somit ist eine Modellierung der Daten mit beiden Ansätzen möglich. Allerdings kann das Dimerbildungsmodell nicht erklären, warum die Dimerbildung nicht zu einem Phasenübergang erster Ordnung wie im Falle des Bis(toluol)chromfullerids führt. Daher scheint das Singulett-Triplett-Modell eher geeignet, den Festkörperbedingungen Rechnung zu tragen.

Gemischte Alkali/Erdalkali-Fulleride

Ersetzt man in Alkalifulleriden die Alkaliatome durch Erdalkalielemente, so kann man bei gleicher Stöchiometrie den doppelten Elektronenübertrag auf C_{60} erzielen. Die Synthese von gemischten Alkali/Erdalkali-Fulleriden erlaubt es also, Ladungsübertrag und Stöchiometrie, die ja letztlich die Struktur bestimmt, getrennt voneinander zu verändern. In Zusammenarbeit mit F. Rachdi von der Université de Montpellier, Frankreich, wurden die kubischen Fulleride CsBaC₆₀ und KCsBaC₆₀ hergestellt und im Rahmen dieser Arbeit untersucht.

An CsBaC₆₀ interessierte die Frage, ob das Material durch den zu erwartenden dreifachen Ladungsübertrag wie die Alkalifulleride des Typs A_3C_{60} supraleitend wird, oder ob diese Stöchiometrie instabil ist und wie im Falle der A_2C_{60} zu einer Phasensepa-

ration führt. Das Fullerid wurde aus C₆₀-Pulver und den Aziden der Metallelemente hergestellt und mehrere Tage bei über 400°C getempert. Eine Röntgenstrukturuntersuchung fand die für Alkalifulleride typische kubisch-flächenzentrierte Struktur mit einer Gitterkonstante von a = 14, 18 Å und guter Kristallinität. Zur Kontrolle des Ladungsübertrags wurde eine Ramanmessung durchgeführt. Mit Hilfe einer empirischen linearen Beziehung zwischen der Frequenzverschiebung der Fühlecksmode $A_g(2)$ des Käfigs und der Ladung auf C₆₀ kann aus dem Ramanspektrum der Ladungszustand der Fullerene abgeleitet werden. Im Falle des CsBaC₆₀ findet man aus der Aufspaltung der $A_q(2)$ -Mode, dass die Ladungszustände C_{60}^- und C_{60}^{5-} zu gleichen Teilen in der Probe auftreten. Es muss also eine Disproportionierung in Bereiche der formalen Stöchiometrien CsC_{60} und $CsBa_2C_{60}$ stattgefunden haben. In der ESR findet man hingegen nur ein einziges isotropes Signal, das in Suszeptibilität und Temperaturabhängigkeit der Linienbreite die charakteristischen Verhaltensweisen eines Metalls zeigt. Die Tatsache, dass die beiden unterschiedlichen Fullerenionen nur ein ESR-Signal aufweisen, kann neben der vergleichbaren elektronischen Situation (C_{60}^- besitzt ein Elektron im HOMO, C_{60}^{5-} hingegen ein Loch) auch die Mittelung der Signale durch die Beweglichkeit der Leitungselektronen zur Ursache haben. Abschließend lässt sich also sagen, dass das Ungleichgewicht von drei verfügbaren Zwischengitterplätzen pro C_{60} in der kubischen Struktur im Vergleich zu nur zwei Gegenionen zu einer Disproportionierung oder auch Phasenseparation auf lokaler Ebene führt.

Von $KCsBaC_{60}$ wurden zwei Proben untersucht, die ebenfalls mit Hilfe der Azide hergestellt wurden. Ramanuntersuchungen zeigen jedoch, dass beide Proben aus mehreren Unterphasen bestehen. Röntgenuntersuchungen liefern eine kubisch-flächenzentrierte Struktur mit einer mittleren Gitterkonstante von a = 14, 29 A. ESR zeigt zwei Signale, die sich in ihrer Breite unterscheiden und wahrscheinlich zwei paramagnetischen Unterphasen mit einfach und dreifach geladenem C_{60} entsprechen. Die Phase mit dreifachem Ladungsübertrag zeigt Supraleitung, die mittels SQUID-Messungen und nichtresonanter Mikrowellenabsorption in der ESR nachgewiesen werden konnte. Die Sprungtemperatur von etwa 22 K ist der typische Wert für Alkalifulleride mit obiger Gitterkonstante. Demgemäß handelt es sich bei der supraleitenden Unterphase höchstwahrscheinlich um K₂CsC₆₀. Metallischer Charakter und Supraleitung finden sich auch in der Knight-Verschiebung der ¹³³Cs-NMR wieder und deuten darauf hin, dass alle Cäsiumkerne von dem supraleitenden Zustand beeinflusst werden. Das Material scheint also nicht in klar abgegrenzte Unterphasen zu zerfallen, sondern eine Phasenmischung auf lokaler Ebene auszubilden. Alles in allem muss jedoch klargestellt werden, dass die gewünschte Zusammensetzung $KCsBaC_{60}$ nicht in Reinform hergestellt werden konnte und daher auch die Zuordnung der Untersuchungsergebnisse zu einer bestimmten Stöchiometrie mehrdeutig ist. Hier wären demnach Untersuchungen zur Optimierung des Herstellungsprozesses von gemischten Alkali/Erdalkali-Fulleriden vonnöten.

Fullerenium-Salze

Fullerenium-Salze sind Materialien, in denen dem C₆₀-Molekül mit Hilfe eines starken Oxidationsmittels Elektronen entzogen worden sind. Aufgrund des elektrophilen Charakters der Fullerene ist die Herstellung der Fullerenium-Salze ungleich schwieriger als die der Fulleride, und es gibt bisher nur wenige Materialien dieses Typs. Nichtsdestotrotz besteht ein großes Interesse daran festzustellen, ob die Vielzahl der Festkörperphänomene, die man bei den Fulleriden gefunden hat, auch bei den Fullereniumsalzen auftritt. Zu diesem Zweck wurde in Zusammenarbeit mit der Gruppe von Prof. Jansen am MPI für Festkörperforschung in Stuttgart eine Reihe von Substanzen der Zusammensetzung $(AsF_6^-)_n C_{60}^{n+}$ synthetisiert. Röntgenstrukturuntersuchungen zeigen, dass sich dabei keine klare Kristallstruktur herausgebildet hat. Vermutlich liegen mehrere verschiedene Unterphasen vor, die einen Ladungsübertrag von n = 1-2 aufweisen.

Einen klaren Beweis für das Auftreten eines Ladungsübertrags liefert die Existenz eines ESR-Signals, zu dem nach Abschätzungen ein Großteil der Probe beiträgt. Der isotrope g-Wert von $g_{iso} = 2,0024$ liegt im für C₆₀-Kationen typischen Bereich und beweist damit die Existenz von C⁺₆₀-Ionen in (AsF₆)_nC₆₀. Damit handelt es bei dem Material in der Tat um ein Fullerenium-Salz des Typs Fullereniumhexafluoroarsenat.

Der Temperaturverlauf der dynamischen ESR-Linienbreiten deutet auf metall-artiges Verhalten hin. Die ESR-Suszeptibilität hingegen folgt nicht dem für Metalle typischen Pauli-Gesetz, sondern zeigt das Verhalten eines korrelierten Systems. Hochfeld-ESR bei W-Band-Frequenzen erlaubt es, die g-Anisotropie von $\Delta g = 0,0026$ aufzulösen, die jedoch nicht mittels eines einzelnen g-Tensors beschrieben werden kann. Dieses Ergebnis bestätigt die Aussage der Röntgendiffraktometrie, dass die Substanz aus mehreren verschiedenen Unterphasen besteht. Der Vergleich verschiedener $(AsF_6^-)_n C_{60}^{n+}$ -Ansätze zeigt demgemäß Unterschiede in der genauen Ausprägung der g-Anisotropie, wobei jedoch die Größenordnung der Anisotropie für alle Proben vergleichbar ist.

ESR-Untersuchungen an endohedralem $Sc_3@C_{82}$

Obwohl $Sc_3@C_{82}$ zu den ersten endohedralen Fullerenen gehört, die entdeckt wurden, sind weder die temperaturabhängige Dynamik der Scandiumionen im Käfig noch die Elektronendichte und die Spinkonfiguration stimmig geklärt. Aus diesem Grund wurden ESR-Untersuchung bei X- und W-Bandfrequenzen an zwei Proben von $Sc_3@C_{82}$ in Lösung durchgeführt. Dabei stand zum einen in Trichlorbenzol (TCB) gelöstes $Sc_3@C_{82}$ von der Gruppe Dunsch vom IFW Dresden zur Verfügung, zum anderen eine zu 10 % mit ¹³C angereicherte $Sc_3@C_{82}$ -Probe in Dekalin, die von der Gruppe um H. Dorn an der Virginia Tech, USA, stammt.

Scandium ist das erste Nebengruppenelement und hat die Elektronenkonfiguration $4s^23d^1$. Es ist leicht oxidierbar und man geht davon aus, dass in Sc₃@C₈₂ ein Elektron pro Scandium auf den Käfig übergeht. Der Käfig ist also paramagnetisch und somit der ESR zugänglich. Beide Sc₃@C₈₂-Proben zeigen in der ESR das typische 22-Linienspektrum, das durch die Hyperfeinkopplung des Elektronenspins an drei äquivalente Kerne mit dem jeweiligen Spin I = 7/2 entsteht. Aufgrund der Mittelung von Anisotropien in der flüssigen Lösung sind die Signale isotrop. Die Hyperfeinaufspaltung beträgt $A_{iso} = 6, 27$ G.

Beim Abkühlen der Sc₃@C₈₂-Lösungen verschwindet bei etwa 200 K das Hyperfeinspektrum, und eine einzelne Lorentzlinie entsteht an dessen Stelle. Die Breite dieser Linie ist mit etwa 6 G deutlich geringer als die Breite der Einhüllenden des 22-Linienspektrums. Diese Zentrallinie resultiert also nicht einfach im Zuge des Einfrieren des Lösungsmittels aus einer anisotropen Verbreiterung des hyperfeinaufgespaltenen Signals. Ein Szenario, wonach es sich hier um den Spezialfall einer Hyperfeinanisotropie mit senkrechter Komponente Null $(A_{\perp} = 0, A_{\parallel} = 3A_{iso})$ handelt, konnte durch die Simulation eines solchen Pulverspektrums als unzutreffend widerlegt werden. Die einzelne isotrope Lorentzlinie kann daher nur durch einen neuen elektronischen Zustand mit reduzierter Hyperfeinkopplung erklärt werden, der sich unterhalb von einer Temperatur von 200 K einstellt. Damit die Hyperfeinaufspaltung in der Linienbreite der Zentrallinie verschwinden kann, muss die Kopplungsstärke beim Übergang um fast eine Größenordnung reduziert werden. Eine derart starke Veränderung der elektronischen Struktur geht höchstwahrscheinlich mit einer strukturellen Veränderung einher. Eine Deformation des Käfigs unter dem Einfluss des chemischen Drucks des erkaltenden Lösungsmittels könnte eine Umordnung der Scandiumatome im Innern des Käfigs und damit auch die reduzierte Hyperfeinkopplung zur Folge haben.

Neben der Aufklärung des Tieftemperaturzustands wurde versucht, mit Hilfe der ¹³C-angereicherten Probe Informationen über die Spindichteverteilung auf dem Käfig

zu gewinnen. Ausgangspunkt der Untersuchungen war die Feststellung, dass bei der $Sc_3@C_{82}$ -Probe mit ¹³C in der natürlichen Häufigkeit von 1,1 % keine ¹³C-Satelliten zu beobachten sind, obwohl im Falle des monoendohedralen $Sc@C_{82}$ mehrere Satelliten sichtbar sind, die die Identifikation von mehr als sieben unterschiedlichen Kohlenstoffpositionen erlauben. Eine Erklärung hierfür ist die deutlich größere Linienbreite in $Sc_3@C_{82}$, die die ¹³C-Hyperfeinsatelliten überdeckt. Diese Situation sollte sich bei zehnprozentiger ¹³C-Anreicherung jedoch deutlich ändern. Da nun im Mittel acht ¹³C-Atome pro Käfig vorliegen, sollte ein beträchtlicher Teil der ESR-Intensität in den Satellitenlinien auftauchen. In der Tat findet man im Falle der ¹³C-angereicherten Probe ein Satellitenpaar zu jeder der 22 Scandiumhyperfeinkomponenten. Die Satellitenintensität ist jedoch auffallend klein. Simulationen zeigen, dass das gemessene Spektrum nur unter der Annahme verstanden werden kann, dass von den 82 Kohlenstoffpositionen nur drei eine Hyperfeinkopplung aufweisen, die so stark ist, dass auflösbare Satellitenlinien entstehen. Die Kopplungen aller anderen Positionen sind so klein, dass sie in der Linienbreite untergehen. Aufgrund der C_{3v} -Symmetrie des Moleküls kann man aus der Anordnung von dreifach entarteten Kohlenstoffpositionen auf dem Käfig die Schlussfolgerung ziehen, dass die erhöhte Hyperfeinkopplung in der oberen Hemisphäre des Moleküls auftritt. Damit kann man auch von einer erhöhten Elektronendichte in diesem Bereich ausgehen. Gemäß einer Synchrotronuntersuchung befindet sich auch das Scandiumtrimer in dieser Hemisphäre des Moleküls, so dass elektrostatische Anziehung der Grund für die Konzentration der Elektronendichte in dieser Käfigregion sein könnte.

Bibliography

- P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Grüner, and J. D. Thompson, Science 253, 301 (1991).
- [2] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, Science of Fullerenes and Carbon Nanotubes (Academic Press, San Diego, 1996).
- [3] Fullerenes: Chemistry, Physics and Technology, edited by K. M. Kadish and R. S. Ruoff (Wiley Interscience, New York, 2000).
- [4] H. Kroto, Science **242**, 1139 (1988).
- [5] H. W. Kroto, J. R. Health, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature 318, 162 (1985).
- [6] R. F. Curl and R. E. Smalley, Science **242**, 1017 (1988).
- [7] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature 347, 354 (1990).
- [8] R. D. Johnson, G. Meijer, and D. S. Bethune, Journal of the American Chemical Society 112, 8983 (1990).
- [9] T. M. Duncan, A Compilation of Chemical Shift Anisotropies (The Farragut Press, Madison, Wisconsin, 1990).
- [10] C. S. Yannoni, P. P. Bernier, D. S. Bethune, G. Meijer, and J. R. Salem, Journal of the American Chemical Society 113, 3190 (1991).
- [11] M. Ozaki and A. Takahashi, Chemical Physics Letters 127, 242 (1986).
- [12] S. Saito and A. Oshiyama, Physical Review Letters 66, 2637 (1991).
- [13] R. C. Haddon, L. E. Brus, and K. Raghavachari, Chemical Physics Letters 125, 459 (1986).

- [14] D. L. Lichtenberger, K. W. Nebesny, C. D. Ray, D. R. Huffman, and L. D. Lamb, Chemical Physics Letters 176, 203 (1991).
- [15] J. de Vries, H. Steger, B. Kamke, C. Menzel, B. Weisser, W. Kamke, and I. V. Hertel, Chemical Physics Letters 188, 159 (1992).
- [16] H. Steger, J. de Vries, B. Kamke, W. Kamke, and T. Drewello, Chemical Physics Letters 194, 452 (1992).
- [17] L.-S. Wang, J. Conceicao, C. Jin, and R. E. Smalley, Chemical Physics Letters 182, 5 (1991).
- [18] P. W. Fowler and D. E. Manolopoulos, An Atlas of Fullerenes (Clarendon Press, Oxford, 1995).
- [19] R. Ettl, I. Chao, F. N. Diederich, and R. L. Whetten, Nature **353**, 149 (1991).
- [20] F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao, and M. M. Alvarez, Science 254, 1768 (1991).
- [21] M. Kappes, F. H. Hennrich, R. H. Michel, A. Fischer, S. Richard-Schneider, S. Gilb, D. Fuchs, M. Buerk, K. Kobayashi, and S. Nagase, Angewandte Chemie (International Edition in English) 35, 1732 (1996).
- [22] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature 357, 142 (1992).
- [23] F. Diederich, R. Ettl, Y. Rubin, R. L. Whetten, R. Beck, M. Alvarez, S. Anz, D. Sensharma, F. Wudl, K. C. Khemani, and A. Koch, Science 252, 548 (1991).
- [24] Z. Slanina, X. Zhao, P. Deota, and E. Osawa, in *Fullerenes: Chemistry, Physics and Technology*, edited by K. M. Kadish and R. S. Ruoff (Wiley Interscience, New York, 2000), p. 283. See Ref. [3].
- [25] J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto, F. K. Tittel, and R. E. Smalley, Journal of the American Chemical Society 107, 7779 (1985).
- [26] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, and R. E. Smalley, Journal of Physical Chemistry 95, 7563 (1991).
- [27] E. Nishibori, M. Takata, M. Sakata, H. Tanaka, M. Hasegawa, and H. Shinohara, Chemical Physics Letters 330, 497 (2000).

- [28] R. D. Johnson, M. S. de Vries, J. Salem, D. S. Bethune, and C. S. Yannoni, Nature 355, 239 (1992).
- [29] E. G. Gillan, C. Yeretzian, K. S. Min, M. M. Alvarez, R. L. Whetten, and R. B. Kaner, Journal of Physical Chemistry 96, 6869 (1992).
- [30] T. J. S. Dennis and H. Shinohara, Chemical Physics Letters 278, 107 (1997).
- [31] T. S. M. Wan and H.-W. Zhang, Journal of the American Chemical Society 120, 6806 (1998).
- [32] R. Tellgmann, N. Krawez, S.-H. Lin, I. V. Hertel, and E. E. B. Campbell, Nature 382, 407 (1996).
- [33] M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi, and A. Khong, Science 271, 1693 (1996).
- [34] T. Almeida Murphy, T. Pawlik, A. Weidinger, M. Höhne, R. Alcala, and J.-M. Spaeth, Physical Review Letters 77, 1075 (1996).
- [35] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, and H. C. Dorn, Nature 401, 55 (1999).
- [36] S. Stevenson, P. W. Fowler, T. Heine, J. C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, and H. C. Dorn, Nature 408, 427 (2000).
- [37] L. Dunsch, presentation on the GKMR workshop in Rügheim, 2002.
- [38] L. J. Wilson, The Electrochemical Society Interface Winter 99, 24 (1999).
- [39] P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, Jr., A. B. Smith, III., and D. E. Cox, Physical Review Letters 66, 2911 (1991).
- [40] P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S. M. Huang, R. Kaner, F. Diederich, and K. Holczer, Nature 351, 632 (1991).
- [41] R. D. Johnson, C. S. Yannoni, H. C. Dorn, J. R. Salem, and D. S. Bethune, Science 255, 1235 (1992).
- [42] H. Kuzmany, M. Matus, B. Burger, and J. Winter, Advanced Materials 6, 731 (1994).

- [43] W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and D. R. M. Walton, Nature 353, 147 (1991).
- [44] C. Meingast and F. Gugenberger, Modern Physics Letters B 7, 1703 (1993).
- [45] J. P. Lu, X.-P. Li, and R. M. Martin, Physical Review Letters 68, 1551 (1992).
- [46] C. Wen, J. Li, K. Kitazawa, T. Aida, I. Honma, H. Komiyama, and K. Yamada, Applied Physics Letters 61, 2162 (1992).
- [47] Y. Iwasa, T. Arima, R. M. Fleming, T. Siegrist, O. Zhou, R. C. Haddon, L. J. Rothber, K. B. Lyons, H. L. Carter, A. F. Hebard, R. Tycko, G. Dabbagh, J. J. Krajewski, G. A. Thomas, and T. Yagi, Science 264, 1570 (1994).
- [48] A. M. Rao, P. Zhou, K. A. Wang, G. T. Hager, J. M. Holden, Y. Wang, W. T. Lee, X. X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, Science 259, 955 (1993).
- [49] T. Yildirim, O. Zhou, J. E. Fischer, N. Bykovetz, R. A. Strongin, M. A. Cichy, A. B. Smith, III., C. L. Lin, and R. Jelinek, Nature 360, 568 (1992).
- [50] P. W. Stephens, L. Mihaly, J. B. Wiley, S.-M. Huang, R. B. Kaner, F. Diederich, R. L. Whetten, and K. Holczer, Physical Review B 45, 543 (1992).
- [51] D. M. Poirier, D. W. Owens, and J. H. Weaver, Physical Review B 51, 1830 (1995).
- [52] F. Stepniak, P. J. Benning, D. M. Poirier, and J. H. Weaver, Physical Review B 48, 1899 (1993).
- [53] Q. Zhu, O. Zhou, J. E. Fischer, A. R. McGhie, W. J. Romanow, R. M. Strongin, M. A. Cichy, and A. B. S. III, Physical Review B 47, 13948 (1993).
- [54] R. Tycko, G. Dabbagh, D. W. Murphy, Q. Zhu, and J. E. Fischer, Physical Review B 48, 9097 (1993).
- [55] M. C. Martin, D. Koller, X. Du, P. W. Stephens, and L. Mihaly, Physical Review B 49, 10818 (1994).
- [56] P. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Jánossy, S. Pekker, G. Oszlányi, and L. Forró, Nature **370**, 636 (1994).

- [57] B. Verberck, K. H. Michel, and A. V. Nikolaev, Journal of Chemical Physics 116, 10462 (2002).
- [58] O. Chauvet, G. Oszlányi, L. Forró, P. W. Stephens, M. Tegze, G. Faigel, and A. Jánossy, Physical Review Letters 72, 2721 (1994).
- [59] F. Bommeli, L. Degiorgi, P. Wachter, H. Legeza, A. Jánossy, G. Oszlanyi, O. Chauvet, and L. Forró, Physical Review B 51, 14794 (1995).
- [60] Y. J. Uemura, K. Kojima, G. M. Luke, W. D. Wu, G. Oszlanyi, O. Chauvet, and L. Forró, Physical Review B 52, R6991 (1995).
- [61] W. A. MacFarlane, R. F. Kiefl, S. Dunsiger, J. E. Sonier, and J. E. Fischer, Physical Review B 52, R6995 (1995).
- [62] W. Plank, T. Pichler, and H. Kuzmany, Synthetic Metals **121**, 1107 (2001).
- [63] P. Launois, R. Moret, J. Hone, and A. Zettl, Physical Review Letters 81, 4420 (1998).
- [64] K. H. Michel and A. V. Nikolaev, Physical Review Letters 85, 3197 (2000).
- [65] K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Communications 33, 1119 (1980).
- [66] K. Mortensen, Y. Tomkiewicz, T. D. Schultz, and E. M. Engler, Physical Review Letters 46, 1234 (1981).
- [67] H. Alloul, V. Brouet, E. Lafontaine, L. Malier, and L. Forró, Physical Review Letters 76, 2922 (1996).
- [68] V. Brouet, H. Alloul, Y. Yoshinari, and L. Forró, Physical Review Letters 76, 3638 (1996).
- [69] A. Jánossy, N. Nemes, T. Fehér, G. Oszlányi, G. Baumgartner, and L. Forró, Physical Review Letters 79, 2718 (1997).
- [70] T. Saito, Y. Akita, and K. Tanaka, Physical Review B **61**, 16091 (2000).
- [71] K.-F. Thier, G. Zimmer, M. Mehring, and F. Rachdi, Physical Review B 53, R496 (1996).
- [72] P. Auban-Senzier, D. Jérome, F. Rachdi, G. Baumgartner, and L. Forró, Journal de Physique I 6, 2181 (1996).

- [73] V. A. Atsarkin, V. V. Demidov, and G. A. Vasneva, Physical Review B 56, 9448 (1997).
- [74] T. M. de Swiet, J. L. Yarger, T. Wagberg, J. Hone, B. J. Gross, M. Tomaselli, J. J. Titman, A. Zettl, and M. Mehring, Physical Review Letters 84, 717 (2000).
- [75] H. Sakamoto, S. Kobayashi, K. Mizoguchi, M. Kosaka, and K. Tanigaki, Physical Review B 62, R7691 (2000).
- [76] S. C. Erwin, G. V. Krishna, and E. J. Mele, Physical Review B 51, R7345 (1995).
- [77] E. J. Mele, G. V. Krishna, and S. C. Erwin, Physical Review B 52, 12493 (1995).
- [78] T. Ogitsu, T. M. Briere, K. Kusakabe, S. Tsuneyuki, and Y. Tateyama, Physical Review B 58, 13925 (1998).
- [79] M. Kosaka, K. Tanigaki, T. Tanaka, T. Atake, A. Lappas, and K. Prassides, Physical Review B 51, 12018 (1995).
- [80] M. C. Martin, D. Koller, A. Rosenberg, C. Kendziora, and L. Mihaly, Physical Review B 51, 3210 (1995).
- [81] G. Oszlányi, G. Bortel, G. Faigel, M. Tegze, L. Gránásy, S. Pekker, P. W. Stephens, G. Bendele, R. Dinnebier, G. Mihály, A. Jánossy, O. Chauvet, and L. Forró, Physical Review B 51, 12228 (1995).
- [82] G. Oszlányi, G. Bortel, G. Faigel, L. Gránásy, G. M. Bendele, P. W. Stephens, and L. Forró, Physical Review B 54, 11849 (1996).
- [83] C. Goze, F. Rachdi, M. Apostol, J. E. Fischer, and M. Mehring, Synthetic Metals 77, 115 (1996).
- [84] K.-F. Thier, M. Mehring, and F. Rachdi, Physical Review B 55, 124 (1997).
- [85] B. Simovic, D. Jérome, F. Rachdi, G. Baumgartner, and L. Forró, Physical Review Letters 82, 2298 (1999).
- [86] V. Brouet, H. Alloul, and L. Forró, Physical Review B 66, 155123 (2002).
- [87] C. Coulon, A. Pénicaud, R. Clérac, R. Moret, P. Launois, and J. Hone, Physical Review Letters 86, 4346 (2001).

- [88] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Nature 350, 600 (1991).
- [89] R. M. Fleming, A. P. Ramirez, M. J. Rosseinsky, D. W. Murphy, R. C. Haddon, S. M. Zahurak, and A. V. Makhija, Nature 352, 787 (1991).
- [90] J. H. Schön, C. Kloc, and B. Batlogg, Nature 408, 549 (2000).
- [91] J. H. Schön, C. Kloc, and B. Batlogg, Science **293**, 2432 (2001).
- [92] M. R. Beasley, S. Datta, H. Kogelnik, H. Kroemer, and D. Monroe, Report of the Investigation Committee on the Possibility of Scientific Misconduct in the Work of Hendrik Schön and Coauthors, 2002.
- [93] T. T. M. Palstra, O. Zhou, Y. Iwasa, P. E. Sulewski, R. M. Fleming, and B. R. Zegarski, Solid State Communications 93, 327 (1995).
- [94] T. Yildirim, L. Barbedette, J. E. Fischer, C. L. Lin, J. Robert, P. Petit, and T. T. M. Palstra, Physical Review Letters 77, 167 (1996).
- [95] A. R. Kortan, N. Kopylov, S. H. Glarum, E. M. Gyorgy, A. P. Ramirez, R. M. Fleming, F. A. Thiel, and R. C. Haddon, Nature 355, 529 (1992).
- [96] A. R. Kortan, N. Kopylov, S. Glarum, E. M. Gyorgy, A. P. Ramirez, R. M. Fleming, O. Zhou, F. A. Thiel, P. L. Trevor, and R. C. Haddon, Nature 360, 566 (1992).
- [97] A. R. Kortan, N. Kopylov, E. Ozdas, A. P. Ramirez, R. M. Fleming, and R. C. Haddon, Chemical Physics Letters 223, 501 (1994).
- [98] Y. Iwasa, H. Hayashi, T. Furudate, and T. Mitani, Physical Review B 54, 14960 (1996).
- [99] K. Ishii, A. Fujiwara, H. Suematsu, and Y. Kubozono, Physical Review B 65, 134431 (2002).
- [100] Y. Wang, X. Cao, H. U. Han, and G. Lan, Journal of Physics and Chemistry of Solids 63, 2053 (2002).
- [101] V. Venegas, J. Ortiz-López, G. Rueda-Morales, and F. Caleyo, Chemical Physics Letters 318, 655 (2000).

- [102] L. Qian, L. Norin, J.-H. Guo, C. Såthe, and A. Agui, Physical Review B 59, 12667 (1999).
- [103] H. Tanaka, K. Marumoto, S. Kuroda, T. Ishii, R. Kanehama, N. Aizawa, H. Matsuzaka, K. Sugiura, H. Miyasaka, T. Kodama, K. Kikuchi, I. Ikemoto, and M. Yamashita, Journal of Physics: Condensed Matter 14, 3993 (2002).
- [104] W. E. Broderick, K. W. Choi, and W. C. Wan, in *Electrochemical Society Proceedings Volume 14*, edited by K. M. Kadish and R. S. Ruoff (Electrochemical Society, Pennington, New Jersey, USA, 1997), p. 1102.
- [105] W. R. Datars, T. R. Chien, R. K. Nkum, and P. K. Ummat, Physical Review B 50, 4937 (1994).
- [106] A. M. Panich, P. K. Ummat, and W. R. Datars, Solid State Communications 121, 367 (2002).
- [107] J. A. Weil, J. R. Bolton, and J. E. Wertz, *Electron Paramagnetic Resonance* (John Wiley and Sons, New York, 1994).
- [108] J. C. P. Poole, *Electron Spin Resonance* (Dover Publications, Inc., Mineola, New York, 1983).
- [109] C. P. Slichter, Principles of Magnetic Resonance (Springer-Verlag, Berlin, Heidelberg, New York, 1989).
- [110] R. J. Elliott, Physical Review **96**, 266 (1954).
- [111] Y. Yafet, Solid State Physics 14, 1 (1963).
- [112] S. S. Eaton and G. R. Eaton, Applied Magnetic Resonance 11, 155 (1996).
- [113] C. A. Reed and R. D. Bolskar, Chemical Reviews 100, 1075 (2000).
- [114] J. Reichenbach, F. Rachdi, I. Luk'yanchuk, M. Ribet, G. Zimmer, and M. Mehring, Journal of Chemical Physics 101, 4585 (1994).
- [115] M. Bennati, R. G. Griffin, S. Knorr, A. Grupp, and M. Mehring, Physical Review B 58, 15603 (1998).
- [116] J. Hone, M. S. Fuhrer, K. Khazeni, and A. Zettl, Physical Review B 52, R8700 (1995).

- [117] W. Y. Zhou, S. S. Xie, L. Lu, E. S. Liu, and Z. Peng, Journal of Physics and Chemistry of Solids 61, 1159 (2000).
- [118] A. Stesmans and G. V. Gorp, Review of Scientific Instruments 60, 2949 (1989).
- [119] S. A. Smith, T. O. Levante, B. H. Meier, and R. R. Ernst, Journal of Magnetic Resonance 106a, 75 (1994).
- [120] M. Mehring, K. F. Thier, F. Rachdi, and T. de Swiet, Carbon 38, 1625 (2000).
- [121] K.-F. Thier, Ph.D. thesis, Universität Stuttgart, 2000.
- [122] J. Rahmer, A. Grupp, M. Mehring, J. Hone, and A. Zettl, Physical Review B 63, R081108 (2001).
- [123] K. Kopitzki, *Festkörperphysik* (Teubner, Stuttgart, 1993).
- [124] G. G. Maresch, M. Mehring, J. U. von Schütz, and H. C. Wolf, Chemical Physics 85, 333 (1984).
- [125] H. J. Pedersen, J. C. Scott, and K. Bechgaard, Solid State Communications 35, 207 (1980).
- [126] J. Rahmer, Master's thesis, Universität Stuttgart, 1998.
- [127] J. Rahmer, S. Knorr, A. Grupp, M. Mehring, J. Hone, and A. Zettl, in *Electronic Properties of Novel Materials Science and Technology of Molecular Nanostructures, XIII International Winterschool, Kirchberg, Austria*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (American Institute of Physics, Melville, New York, 1999), p. 32.
- [128] B. Renker, H. Schober, and M. Braden, Solid State Communications 109, 423 (1999).
- [129] S. Foner, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press, New York, 1963), p. 383.
- [130] J. Rahmer, S. Knorr, A. Grupp, M. Mehring, and B. Renker, Applied Magnetic Resonance 19/3-4, 525 (2000).
- [131] A. Hönnerscheid, L. van Wüllen, M. Jansen, J. Rahmer, and M. Mehring, Journal of Chemical Physics 115, 7161 (2001).

- [132] J. Rahmer, M. Mehring, A. Hönnerscheid, L. van Wüllen, and M. Jansen, in Electronic Properties of Molecular Nanostructures, XV International Winterschool, Kirchberg, Austria, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (American Institute of Physics, Melville, New York, 2001), p. 157.
- [133] V. Graves and J. J. Lagowski, Inorganic Chemistry 15, 577 (1976).
- [134] C. Elschenbroich and A. Salzer, Organometallchemie (Teubner, Stuttgart, 1993).
- [135] E. O. Fischer and J. Seeholzer, Zeitschrift f
 ür anorganische und allgemeine Chemie 312, 244 (1961).
- [136] A. Hönnerscheid, R. Dinnebier, and M. Jansen, Acta Crystallographica Section B 58, 482 (2002).
- [137] V. M. Orera, R. Alcalá, and P. J. Alonso, Journal of Physics C 19, 607 (1986).
- [138] Q. Zhu, D. E. Cox, and J. E. Fischer, Physical Review B 51, 3966 (1995).
- [139] P. K. Kahol and M. Mehring, Synthetic Metals 16, 257 (1986).
- [140] M. Mehring, personal communication, 2003.
- [141] A. Hönnerscheid, Ph.D. thesis, Max-Planck-Institut für Festkörperforschung, Stuttgart, 2003.
- [142] T. Yildirim, L. Barbedette, J. E. Fischer, G. M. Bendele, P. W. Stephens, C. L. Lin, C. Goze, F. Rachdi, J. Robert, P. Petit, and T. T. M. Palstra, Physical Review B 54, 11981 (1996).
- [143] J. Winter and H. Kuzmany, Physical Review B 52, 7115 (95).
- [144] H. Thurn, personal communication, 2002.
- [145] A. Rezzouk, Y. Errammach, F. Rachdi, D. Maurin, J. L. Sauvajol, and S. Sayouri, in *Proceedings to the Microwave Symposium 2000* (IEEE–MS2000, Tetuan, Morocco, May 10-12, 2001).
- [146] Y. Errammach, A. Rezzouk, F. Rachdi, and J. L. Sauvajol, Synthetic Metals 129, 147 (2002).
- [147] A. Dulčić, B. Rakvin, and M. Požek, Europhysics Letters 10, 593 (1989).

- [148] M. Požek, A. Dulčić, and B. Rakvin, Physica C 169, 95 (1990).
- [149] C. Kessler, Ph.D. thesis, Universität Stuttgart, 1996.
- [150] W. R. Datars and P. K. Ummat, Solid State Communications 94, 649 (1995).
- [151] A. Reich, personal communication, 2003.
- [152] CRC Handbook of Chemistry and Physics, 76 ed., edited by D. R. Lide (CRC Press, Boca Raton, 1995).
- [153] S. Bandow, H. Kitagawa, T. Mitani, H. Inokuchi, Y. Saito, H. Yamaguchi, N. Hayashi, H. Sato, and H. Shinohara, Journal of Physical Chemistry 96, 9609 (1992).
- [154] H. Shinohara, in Fullerenes: Chemistry, Physics, and Technology, edited by K. M. Kadish and R. S. Ruoff (Wiley Interscience, New York, 2000), p. 357. See Ref. [3].
- [155] G. Seifert, A. Bartl, L. Dunsch, A. Ayuela, and A. Rockenbauer, Applied Physics A 66, 265 (1998).
- [156] H. Bill and O. Pilla, Journal of Physics C 17, 3263 (1984).
- [157] J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, J. Conceicao, L. P. F. Chibante, A. Jain, G. Palmer, and R. E. Smalley, Chemical Physics Letters **190**, 460 (1992).
- [158] D. M. Poirier, M. Knupfer, J. H. Weaver, W. Andreoni, K. Laasonen, M. Parrinello, D. S. Bethune, K. Kikuchi, and Y. Achiba, Physical Review B 49, 17403 (1994).
- [159] S. Nagase, K. Kobayashi, T. Kato, and Y. Achiba, Chemical Physics Letters 201, 475 (1993).
- [160] T. Akasaka, W. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, S. Okubo, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, R. Nagahata, X. Gao, E. van Caemelbecke, and K. M. Kadish, Journal of the American Chemical Society **122**, 9316 (2000).
- [161] T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, X. Gao,

E. van Caemelbecke, and K. M. Kadish, Journal of Physical Chemistry B **105**, 2971 (2001).

- [162] M. Takata, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, and H. Shinohara, Nature 377, 46 (1995).
- [163] J. Lu, X. Zhang, X. Zhao, S. Nagase, and K. Kobayashi, Chemical Physics Letters 332, 219 (2000).
- [164] A. Gruß, M. C. Böhm, J. Schulte, and K. P. Dinse, Zeitschrift für Naturforschung 53 a, 801 (1998).
- [165] E. Nishibori, M. Takata, M. Sakata, M. Inakuma, and H. Shinohara, Chemical Physics Letters 298, 79 (1998).
- [166] M. Hoinkis, C. S. Yannoni, D. S. Bethune, J. R. Salem, R. D. Johnson, M. S. Crowder, and M. S. de Vries, Chemical Physics Letters 198, 461 (1992).
- [167] S. Suzuki, S. Kawata, H. Shiromaru, K. Yamauchi, K. Kikuchi, T. Kato, and Y. Achiba, Journal of Physical Chemistry 96, 7159 (1992).
- [168] M. Inakuma and H. Shinohara, Journal of Physical Chemistry B 104, 7595 (2000).
- [169] H. Shinohara, H. Sato, Y. Saito, M. Ohkohchi, and Y. Ando, Journal of Physical Chemistry 96, 3571 (1992).
- [170] C. S. Yannoni, M. Hoinkis, M. S. de Vries, D. S. Bethune, J. R. Salem, M. S. Crowder, and R. D. Johnson, Science 256, 1191 (1992).
- [171] H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, and Y. Saito, Nature 357, 52 (1992).
- [172] U. T. Höchli and T. L. Estle, Physical Review Letters 18, 128 (1967).
- [173] M. Rübsam, P. Schweitzer, and K.-P. Dinse, Chemical Physics Letters 263, 540 (1996).
- [174] H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, and Y. Saito, Journal of Physical Chemistry 97, 4259 (1993).
- [175] Y. Miyake, S. Suzuki, Y. Kojima, K. Kikuchi, K. Kobayashi, S. Nagase, M. Kainosho, Y. Achiba, Y. Maniwa, and K. Fisher, Journal of Physical Chemistry 100, 9579 (1996).

- [176] M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, and H. Shinohara, Physical Review Letters 78, 3330 (1997).
- [177] L. B. Knight, Jr., R. W. Woodward, R. J. V. Zee, and W. Weltner, Jr., Journal of Chemical Physics 79, 5820 (1983).
- [178] H. Shinohara, M. Inakuma, N. Hayashi, H. Sato, Y. Saito, T. Kato, and S. Bandow, Journal of Physical Chemistry 98, 8597 (1994).
- [179] P. H. M. van Loosdrecht, R. D. Johnson, M. S. de Vries, C.-H. Kiang, D. S. Bethune, H. C. Dorn, P. Burbank, and S. Stevenson, Physical Review Letters 73, 3415 (1994).
- [180] T. Kato, S. Suzuki, K. Kikuchi, and Y. Achiba, Journal of Physical Chemistry 97, 13425 (1993).
- [181] M. Takata, E. Nishibori, M. Sakata, M. Inakuma, E. Yamamoto, and H. Shinohara, Physical Review Letters 83, 2214 (1999).
- [182] S. P. Walch and C. W. Bauschlicher, Jr., Journal of Chemical Physics 83, 5735 (1985).
- [183] K. Kobayashi and S. Nagase, Chemical Physics Letters **313**, 45 (1999).
- [184] J. R. Ungerer and T. Hughbanks, Journal of the American Chemical Society 115, 2054 (1993).
- [185] M. R. Anderson, H. C. Dorn, S. Stevenson, P. M. Burbank, and J. R. Gibson, Journal of the American Chemical Society 119, 437 (1997).
- [186] M. Straka and M. Kaupp, personal communication, 2003.
- [187] S. Suzuki, Y. Kojima, Y. Nakao, T. Wakabayashi, S. Kawata, K. Kikuchi, Y. Achiba, and T. Kato, Chemical Physics Letters 229, 512 (1994).
- [188] D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries, and C. S. Yannoni, Nature 366, 123 (1993).
- [189] L. Dunsch, personal communication, 2000.
- [190] T. Kato, S. Bandou, M. Inakuma, and H. Shinohara, Journal of Physical Chemistry 99, 856 (1995).

- [191] A. Bartl and L. Dunsch, Synthetic Metals 121, 1147 (2001).
- [192] T. Kato, S. Okubo, M. Inakuma, and H. Shinohara, Physics of the Solid State 44, 410 (2002).
- [193] S. Knorr, Ph.D. thesis, Universität Stuttgart, 2002.

Lebenslauf

Name:	Jürgen Rahmer
Geburtsdatum:	07.02.1972
Geburtsort:	Böblingen
Eltern:	Erwin Rahmer und Marianne Rahmer, geb. Höhne
Familienstand:	ledig

Schulausbildung:

1978 - 1982	Eduard-Mörike-Grundschule, Böblingen
1982 - 1991	Otto-Hahn-Gymnasium, Böblingen
Juni 1991	Abitur

Zivildienst:

1991 – 1992 – Pflegedienst im städtischen Krankenhaus Sindelfingen

Wissenschaftliche Ausbildung:

1992 - 1998	Physikstudium an der Universität Stuttgart
1995 - 1996	Studienaufenthalt an der Oregon State University, USA
1997 - 1998	Studienabschluss, Diplomarbeit "Elektronenspin resonanz und Kern-Elektron-Doppelresonanz an AC_{60} (A=Rb,Cs)"
seit 1999	wissenschaftl. Mitarbeiter am 2. Physikalischen Institut
2001 - 2002	Stipendiat des Graduiertenkollegs "Modern Methods of Magnetic Resonance in Materials Science"
	Magnetic resonance in Materials Science

Dank

Ich danke allen, die im Großen und Kleinen am Zustandekommen meiner Arbeit beteiligt waren. Insbesondere gilt mein Dank ...

- ... Herrn Prof. Dr. M. Mehring für die Aufnahme an das 2. Physikalische Institut, die interessante Themenstellung sowie das stete Interesse und die vielen Ideen mit denen er meine Arbeit begleitet und gefördert hat.
- ... Herrn Prof. Dr. D. Schweitzer für die Übernahme des Mitberichts.
- ... Herrn Prof. Dr. M. Jansen am MPI für Festkörperforschung, dessen Gruppe ich viele interessante Fullerenmaterialien verdanke. Vor allem sei Andreas Hönnerscheid für die produktive Zusammenarbeit, Andreas Reich, Oliver Haufe, Dr. Martin Panthöfer und Holger Brumm für ESR-Proben und nette Stunden in Kirchberg, sowie Michail Sofin für verschiedene Erdalkalifulleride gedankt.
- ... Herrn Prof. Dr. E. Roduner und dem Kreis der Gruppenleiter für die Aufnahme in das Graduiertenkolleg "Moderne Methoden der magnetischen Resonanz in der Materialforschung", das meine Promotionszeit sehr bereichert hat. Vielen Dank auch an alle Mitkollegiaten für die gute Zeit!
- ... Dr. Ferid Rachdi für den Einstieg in die Erdalkalifulleride sowie für die freundliche Aufnahme und Betreuung in Montpellier.
- ... Prof. Dr. Liviu Giurgiu für interessante ESR-Proben und die freundschaftliche Zusammenarbeit.
- ... Dr. L. Dunsch, Prof. Dr. H. Dorn sowie Dr. J. Hone für spannende Fullerenmaterialien.
- ... der Deutschen Forschungsgemeinschaft für die Finanzierung im Schwerpunkt "Hochfeld-ESR in Biologie, Chemie und Physik" sowie im Graduiertenkolleg "Moderne Methoden der magnetischen Resonanz in der Materialforschung".
- ... den Laborkollegen für die gute Zeit, namentlich Andreas Heidebrecht für die Einführung in die Geheimnisse der Unix-Welt, die Schümli-Runden und vieles mehr, Dr. Stefan Knorr für die Einweisung in die W-Band-Kunst und für

Korrekturlesungen diverser Werke, Dr. Arthur Grupp für Rat und Tat bei vielerlei Problemen und für gute Zimmergenossenschaft in Kirchberg, Dr. Steffen Krämer, der mich an seinem umfangreichen NMR- und SQUID-Wissen teilhaben ließ, meinem Musik- und Promotionsgefährten Wolfgang Bronner, dem rasenden Reporter und Social-Event-Manager Mikey Schmid, Mit-Basser Martin Hecht, Werner Scherer, Dr. Carlo Thier für den Einstieg in die Alchemie der Alkalifulleride, Bernd Nebendahl, der mich auf den besten aller Editoren (Vi) gebracht hat, Dr. Andreas Mayer, Dragosch Peligrad und schließlich Dr. Christoph Kessler, durch den ich meine erste Berührung mit der Magnetresonanzbildgebung hatte.

- ... den "Denningers", nämlich Markus Schulte für die vielen musikalischen Koproduktionen und lustigen Abende auf den GK-Arbeitswochenenden, Hans-Jürgen Kümmerer für die Unterstützung in W-Band-Fragen und unterhaltsame Runden bei Tee und Keksen, Dr. Christian Weinzierl für die folgenschwere Einweisung in den X-Band-Durchflusskryostaten, Dr. Daniel Reiser, der mir den Weg ins ferne Q-Band gezeigt hat, Marcus Vidal, Dr. Thomas Rais und Herrn Prof. Dr. G. Denninger, von dem immer wieder viel Wissenswertes zu lernen war.
- $\label{eq:constraint} ... Ulrike Offenbeck für die ansteckend gute Laune und Hilfsbereitschaft sowie die Fernvermittlungen Rahmer@Hamburg \leftrightarrow Mehring@Stuttgart.$
- ... Dr. Gerhard Wäckerle, Herrn Prof. Dr. J. Paus sowie den Pausis Hermann Neumann und Robert Schumann, die für unterhaltsame Frühstücksrunden sorgten und immer hilfsbereit mit Rat und Tat zur Seite standen.
- ... den Werkstätten, vor allem den Herren Titz, Schobel & Schobel, Maurer und August.
- ... meinen Eltern für die ausdauernde Unterstützung während meiner über 10-jährigen Uni-Karriere.
- ... meiner Katrin.