

Far-infrared spectroscopy of lanthanide-based molecular magnetic materials

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

Vorgelegt von
Sabrina Haas
aus Detmold

Hauptberichter:	Prof. Dr. Martin Dressel
Mitberichter:	Prof. Dr. Joris van Slageren
Tag der mündlichen Prüfung:	13.05.2015

1. Physikalisches Institut der Universität Stuttgart
2015

Abstract

Due to their in many cases large magnetic moments and large magnetic anisotropies, lanthanides play an important role in magnetism. These special magnetic properties can be traced back to their inner, unclosed 4f-shell [1]. Since the early stages of research in single-molecular magnetism, these properties made them appealing building blocks for single-molecular magnets but their application was hampered by their weak exchange interactions. The key feature of single-molecular magnets is their slow relaxation of the magnetization of purely molecular origin [2]. Therefore, a breakthrough of lanthanides in the field of single-molecular magnetism was the observation of slow relaxation of the magnetization in a mononuclear terbium complex by Ishikawa *et al.* in 2003 [3], the first single-ion magnet. This discovery has boosted the efforts put into the research of lanthanide-based single-molecular magnetic materials.

For the study of lanthanides in single-molecular magnetic materials, various theoretical models like the crystal-field Hamiltonian needed to be adopted from prior research areas in lanthanides [4]. On the experimental side, the most utilized measurement techniques are magnetometry, susceptometry, and electron paramagnetic resonance (EPR). If applied to single crystals, these techniques can give detailed information about the kind of anisotropy [5]. However, for the interpretation of the relaxation process the energy-levels of the crystal-field split ground multiplet are of special importance. Due to the fact, that the thermally activated relaxation regime in lanthanide based single-ion magnets is attributed to an Orbach process via excited states inside the crystal-field split ground multiplet [6, 7]. The energy-levels can be extracted by the former mentioned techniques, but only by an indirect technique. Therefore, the measured data are fitted to the crystal-field Hamiltonian and with the acquired parameters the energy-levels can be reproduced. This technique can be applied for complexes with high-symmetry crystal fields, but as soon as the symmetry is low, the amount of crystal-field parameters increases, and the method gets inapplicable. Therefore, other techniques need to be employed to obtain additional information like luminescence or inelastic neutron scattering (INS) measurements [8, 9]. However, the most direct technique offers far-infrared spectroscopy, which was widely applied for the determination of the energy-level structure of lanthanide ions in the 60s and 70s of the last century [10, 11, 12, 13]. As the crystal-field splitting is in the range of a few hundred wavenumbers, transitions between the energy-levels can be directly observed by absorption lines in the spectrum bearing in mind the selection rules.

The aim of this thesis is to adopt the technique of transmission-far-infrared spectroscopy to the study of lanthanide-based single-molecular magnetic materials. Our second aim is to gain deeper insight into the relaxation dynamics of the studied materials. Our applied experimental setups are: A quasi-optical setup using backward wave oscillators (BWOs) that covers the frequency range from 4 cm^{-1} to 43 cm^{-1} . And, a far-infrared setup using a Bruker IFS 113v Fourier transform infrared spectrometer that covers the range from 20 cm^{-1} to 100 cm^{-1} . Both setups are used inside a variable magnetic field generated in a Spectromag 4000 (Oxford Instruments). The mylar windows of the Spectromag prevent measurements to frequencies higher than 100 cm^{-1} . The accessible frequency range limits our studies to the low-lying energy-levels. Fortunately, the low lying energy-levels are the most important ones in the relaxation process of single-molecular materials.

For our studies, we have chosen three complexes which cover different fields of lanthanide-based single-molecular magnetism. All of them were previously explored by static and dynamic magnetization measurements. The first complex, known as DyPhOPh, belongs to the class of single-chain magnets [14]. The second one, known as DyDOTA, acts as a single-ion magnet [15]. And the third one, DyPhOPh₂, is a building block of DyPhOPh and consists of a lanthanide ion and two nitronyl nitroxide radicals which are exchange coupled to each other [5]. In all of the complexes the lanthanide ion is surrounded by a crystal-field of low symmetry, hampering the determination of the energy-level structure by other techniques. For comparison, also isostructural compounds were studied in which the dysprosium ion was substituted by another lanthanide ion. For DyPhOPh the terbium complex TbPhOPh, for DyDOTA the terbium complex TbDOTA, and for DyPhOPh₂ HoPhOPh₂, TbPhOPh₂ and DyPhOEt₂, where in the latter one the nitronyl nitroxide radical was modified.

For the single-chain magnet DyPhOPh a coherent picture of the dynamic magnetic behavior was lacking. A crossover at a temperature of 3.8 K between two different regimes of the relaxation time - observed in temperature dependent AC-susceptibility measurement - was attributed to the switching between the finite- and the infinite-size regime of the Glauber model [14]. However, the difference of the relaxation barrier at the crossover deviates from the predicted value given by the Glauber model. Our results of the energy-level structure obtained by far-infrared spectroscopy suggest that the crossover in the relaxation process is rather governed by a switching between two relaxation pathways of the dysprosium ion than by a transition between the infinite- and finite-size regime of the Glauber dynamics. The switching between two relaxation pathways of a lanthanide ion was observed for single-ion magnets before [16]. The relaxation process was attributed to an Orbach process and the switching to a change of the relaxation pathway via which the Orbach process takes place. An experimental determination of the energy-levels was missing. Therefore, it was not possible to definitely attribute the switching to the change between two relaxation pathways via different excited states.

Therefore, we not only propose an alternative interpretation of the relaxation process

for the lanthanide-based single-chain magnet DyPhOPh that differs from transition metal based single-chain magnets but also confirm the switching of the Orbach relaxation pathway between two different excited levels in a lanthanide ion by experimental evidence.

The aim of our study of DyDOTA was to identify the relaxation process responsible for the thermally activated relaxation regime observed in AC-susceptibility measurements [15]. Our measurements revealed two close lying energy levels at 44 cm^{-1} and 55 cm^{-1} . The observed energy of the first excited states (Kramers doublet) (44 cm^{-1}) is nearly equal to the thermally activated relaxation barrier (42 cm^{-1}). The resemblance suggests that the underlying relaxation process can be described by an Orbach process via the first excited state. In the Orbach process the relaxation process takes place via a real excited state with the energy-barrier given by the energy difference between the ground state and the excited state [6]. Furthermore, the behavior of the observed absorption lines at 44 cm^{-1} (under the influence of an applied magnetic field) led us to an explanation for the crossover observed in AC-susceptibility measurements between the direct process and the Orbach process when a magnetic field is applied. As the field increases, our measurements suggest that the matrix element of the magnetic moment along the easy-axis increases. The matrix element of the magnetic moment is thought to be connected to the spin-phonon transition matrix element [17]. Therefore, this observation indicates that with increasing field the efficiency of the Orbach process via the first excited level increases leading to the observed crossover.

With the study of the complex DyPhOPh₂, we aimed to shed light onto the exchange interactions between the lanthanide ion and the nitronyl-nitroxide radicals [5]. We were able to identify several energy-levels of the compound by far-infrared spectroscopy. However, due the complexity and the interplay of the interactions in the compound, we were not able to find an appropriate model for the interpretation of the energy-level structure. Therefore, a reliable determination of the exchange coupling constant and the crystal field splitting was not possible. However, the obtained results offer the possibility for the comparison with more sophisticated theoretical models in the future.

Besides the summarized results of the studied compounds, the thesis presents new methods for the analysis of far-infrared spectra of lanthanide-based single-molecular materials. The developed methods solve various issues with which we were faced, during the study of the complexes by far-infrared spectroscopy. The presented methods are:

- **Issue** In addition to electronic absorption lines, in the frequency range from 4 cm^{-1} to 100 cm^{-1} also phononic and intramolecular vibrational absorption lines occur [18, 19]. A theoretical prediction of the phononic and intramolecular vibrational lines is hampered by the complex crystal structures of single-molecular magnetic materials. Therefore, the distinction has to be made by experimental

evidence.

Method Far-infrared spectra are acquired at different magnetic fields. Only the electronic absorption lines are influenced by the magnetic field due to the Zeeman term. The change of the lines in a magnetic field allows for the unambiguous identification of the electronic absorption lines. This method was adopted from earlier infrared studies of lanthanides in the 60s and 70s of the last century [13].

- **Issue** The electronic absorption lines are often masked by intense phononic and intramolecular vibrational absorption lines. Instead of an individual line, they are only recognizable as slight changes of the spectra at different fields. This issue raises the question how to extract characteristic parameters of specifically the electronic absorption lines.

Method To resolve this issue, the transmission spectra are converted to the absorption cross section of one lanthanide ion. To eliminate the contribution of the phononic and intramolecular vibrational absorption lines the spectra with and without field are subtracted. In addition, the cross section is divided by prefactors and the frequency. This newly derived quantity (the normalized absorption cross section) is then directly proportional to the change of the spectral weight in units of the transition matrix element. Therefore, this procedure allows for direct conclusions of the transition matrix element of the observed transitions.

- **Issue** Our samples consisted of randomly oriented microcrystalline powders of the complexes pressed to pellets. The strong magnetic anisotropy of the complexes leads to strong anisotropic spectroscopic g-factors. Instead of an overall Zeeman-shift of the lines in a magnetic field, the change of the lines with magnetic field can have various, a priori unknown shapes. Detailed far-infrared investigations of microcrystalline powders of lanthanide-based materials have not been previously reported in literature.

Method To qualitatively describe the effect of a magnetic field of varying intensity on the electronic absorption lines, a program was written which simulates the difference of the normalized absorption cross section for microcrystalline powder samples. The program is based on the crystal-field Hamiltonian. The input parameters are the crystal-field parameters of the lanthanide ion. The numerical integration over the different directions of the microcrystallites was implemented by the use of a Lebedev-Laikov grid [20].

The expected magnetic field changes of the electronic absorption lines were calculated for a variety of different parameter sets. The simulations yielded background information for the identification of the electronic absorption lines in the studied compounds. As the crystal field of the lanthanide ions in the studied compounds are of low symmetry, the crystal-field parameter space is huge and prevented the simulation of the acquired spectra with the crystal-field Hamiltonian.

The presented methods give a scheme for the general analysis of far-infrared spectra of lanthanide-based materials.

In addition, the thesis includes a review of the magnetic relaxation processes in lanthanide ions. The understanding of the relaxation process enabled us to relate the far-infrared measurements to previous relaxation measurements.

In conclusion, we have shown the applicability of far-infrared spectroscopy for the study of lanthanide-based single-molecular magnetic materials. The far-infrared studies of three different kinds of single-molecular materials, a single-ion magnet, a single-chain magnet and an exchange coupled cluster, yielded a deeper understanding of the complexes. In particular, we were able to gain insight into the relaxation processes of the compounds.

Zusammenfassung

Wegen ihrer, in vielen Fällen, großen magnetischen Momente und starken magnetischen Anisotropie spielen Lanthanoide eine wichtige Rolle in magnetischen Materialien. Diese speziellen magnetischen Eigenschaften können auf ihre innere, nicht voll besetzte 4f-Schale zurückgeführt werden [1]. Seit den Anfängen der Forschung im Bereich des Einzelmolekülmagnetismus machen diese Eigenschaften sie zu interessanten Kandidaten für Einzelmolekülmagnete. Allerdings wurde ihre Anwendung durch ihre schwache Austauschwechselwirkung erschwert. Die charakteristische Eigenschaft von Einzelmolekülmagneten ist die langsame Relaxation der Magnetisierung von rein molekularem Ursprung [2]. Bahnbrechend für die Nutzung von Lanthanoiden in Einzelmolekülmagneten war die Beobachtung der langsamen Relaxation der Magnetisierung in einem mononuklearen Terbium-Komplex von Ishikawa *et al.* im Jahr 2003 [3]. Diese Entdeckung verstärkte die Anstrengungen in die Erforschung von lanthanoid-basierten Einzelmolekülmagnetmaterialien.

Für die Untersuchung von lanthanoid-basierten Einzelmolekülmaterialien mussten verschiedene theoretische Modelle, wie der Kristallfeld-Hamiltonian, von anderen Forschungsgebieten, in denen Lanthanoide schon lange untersucht werden, übernommen werden [4]. Auf der experimentellen Seite sind die meist benutzten Messtechniken Magnetometrie, Suszeptometrie und Elektronenspinresonanz (EPR). Werden diese Techniken bei Einzelkristallen eingesetzt, können sie zu detaillierten Aussagen über die Art der Anisotropie führen [5]. Für die Interpretation des Relaxationsprozesses ist allerdings die Energieaufspaltung des Grundmultipletts von spezieller Bedeutung, da das thermisch aktivierte Relaxationsregime in Einzelionenmagneten einem Orbach-Prozess, der die angeregten Energieniveaus nutzt, zugeschrieben wird [6, 7]. Die Energieaufspaltung kann aus den genannten Messtechniken bestimmt werden, allerdings nur in indirekter Weise. Um dies zu erreichen, werden die gemessenen Daten mit einem entsprechenden Kristallfeld-Hamiltonian angefügt. Mit den dabei bestimmten Kristallfeld-Parameter können dann die Energieniveaus berechnet werden. Diese indirekte Methode funktioniert - einigermaßen - für Kristallfelder mit einer hohen Symmetrie, aber sobald die Symmetrie niedriger wird, steigt die Anzahl der Kristallfeld-Parameter und die Methode wird unbrauchbar. Daraus resultiert, dass andere Messtechniken angewandt werden müssen, wie z. B. Messungen der Lumineszenz oder der inelastischen Neutronenstreuung (INS) [8, 9]. Die direkteste Methode bietet jedoch Ferninfrarotspektroskopie, diese wurde in den 1970er und 1980er Jahren oft für die Bestimmung der Energieniveaus in Lanthanoidionen angewendet [10, 11, 12, 13]. Da die Energieaufspaltung normalerweise einige hundert Wellenzahlen beträgt, können

Übergänge zwischen den Energieniveaus unter Berücksichtigung der Auswahlregeln direkt durch Absorptionslinien im Spektrum beobachtet werden.

Das Ziel dieser Arbeit ist es, die Methode der Transmissions-Ferninfrarotspektroskopie auf lanthanoid-basierte Einzelmolekülmaterialien anzuwenden. Zusätzlich wollen wir, durch die dadurch bestimmten Energieniveaus, ein tieferes Verständnis des Relaxationsprozess in den untersuchten Materialien erreichen. Unsere angewandten experimentellen Aufbauten sind: Ein quasi-optischer Aufbau mit Backward-Wave Oszillatoren deckt den Frequenzbereich von 4 cm^{-1} bis 43 cm^{-1} ab. Und ein Ferninfrarotsetup mit einem Bruker IFS 113v Fourier-Transform-Infrarot Spektrometer den Bereich von 20 cm^{-1} bis 100 cm^{-1} . Beide Setups werden mit einem variablen magnetischen Feld benutzt, das in einem Spectromag 4000 (Oxford Instruments) erzeugt wird. Der zugängliche Frequenzbereich in dem Fourier-Transform-Infrarot Spektrometer ist durch die Mylar-Fenster des Spectromags auf Messungen niedriger als 100 cm^{-1} beschränkt. Der zugängliche Frequenzbereich grenzt unsere Messungen auf die unteren Energieniveaus ein. Glücklicherweise sind die unteren Energieniveaus die wichtigsten für den Relaxationsprozess.

Für unsere Untersuchungen habe wir drei Komplexe, die verschiedene Felder von Einzelmolekülmaterialien abdecken, ausgewählt. Alle Materialien wurden schon vorher in statischen und dynamischen Magnetisierungsmessungen untersucht. Der erste Komplex, DyPhOPh genannt, gehört zur Klasse der Einzelkettenmagnete [14]. Der zweite Komplex, DyDOTA genannt, ist ein Einzelionenmagnet [15]. Der dritte Komplex, DyPhOPh₂, ist ein Bestandteil von DyPhOPh und besteht aus einem Lanthanoidion und zwei Nitronyl-Nitroxid Radikalen, die durch Austauschwechselwirkungen miteinander gekoppelt sind [5]. In allen Komplexen ist das Lanthanoidion umgeben von einem Kristallfeld von niedriger Symmetrie, das die Bestimmung der Energielevel bei magnetischen Messungen erschwert. Zum Vergleich wurden jeweils auch noch isostrukturelle Komplexe mit anderen Lanthanoidionen untersucht; für DyPhOPh der Terbium-Komplex TbPhOPh, für DyDOTA der Terbium-Komplex TbDOTA und für DyPhOPh₂ HoPhOPh₂, TbPhOPh₂ und DyPhOEt₂, bei dem Letzteren wurde das Nitronyl-Nitroxide Radikal modifiziert.

Für den Einzelkettenmagneten DyPhOPh fehlte eine eindeutige Erklärung für das Verhalten in einem dynamischen Magnetfeld. Ein Wechsel zwischen zwei Regimen der Relaxationszeit bei einer Temperatur von 3.8 K - beobachtet in AC-Suszeptibilitäts-Messungen - wurde dem Übergang von einem endlichen zu einem unendlichen Größenregime in der Glauber Dynamik zugeschrieben [14]. Allerdings weicht der Unterschied der Relaxationsbarriere an dem Wechsellpunkt von dem erwarteten theoretischen Wert ab. Die Ergebnisse unserer Ferninfrarotmessungen legen nahe, dass der Wechsel zwischen den beiden Relaxationsregimen eher einem Wechsel des Relaxationsmechanismus innerhalb des Dysprosiumions als einem Wechsel zwischen den Größenregimen in der

Glauber Dynamik zuzuschreiben ist. Der Wechsel zwischen zwei Relaxationsmechanismen wurde schon vorher in Einzelionenmagneten beobachtet [16]. Der Relaxationsprozess wurde dort einem Orbach Prozess zugeschrieben und der Übergang einem Wechsel des angeregten Zustands, über den der Orbach Prozess stattfindet. Eine experimentelle Bestimmung der Energieniveaus wurde dort allerdings nicht gemacht. Dadurch war es nicht möglich den Übergang definitiv dem Wechsel zwischen den zwei Relaxationswegen zuzuschreiben.

Deshalb zeigen wir nicht nur eine andere Interpretation für den lanthanoidbasierten Einzelkettenmagneten DyPhOPh, die sich von den übergangsmetallbasierten Einzelkettenmagneten unterscheidet, sondern bestätigen auch den Wechsel des Relaxationsweges zwischen zwei verschiedenen angeregten Zuständen in einem Dysprosiumion.

Das Ziel der Untersuchung von DyDOTA war die Bestimmung der Art des Relaxationsprozesses, der für den thermisch aktivierten Relaxationsbereich, der in AC-Suszeptibilitätsmessungen beobachtet wurde, verantwortlich ist [15]. Unsere Infrarotmessungen zeigten zwei eng-beieinanderliegende Energielevel bei 44 cm^{-1} und 55 cm^{-1} . Die beobachtete Energie (44 cm^{-1}) des ersten angeregten Zustands (Kramers Duplet) ist quasi gleich zu der Relaxationsbarriere des thermisch aktivierten Regimes (42 cm^{-1}). Die Ähnlichkeit legt nahe, dass der Relaxationsprozess durch einen Orbach-Prozess via dem ersten angeregten Zustand beschrieben werden kann. Bei einem Orbach-Prozess findet der Relaxationsprozess via einem angeregten Energieniveau statt. Die Energiebarriere der Relaxation ist dabei durch die Energiedifferenz zwischen dem Grundzustand und dem angeregten Zustand gegeben [6]. Außerdem gab uns das Verhalten der Absorptionslinie bei 44 cm^{-1} in einem Magnetfeld Hinweise für den Übergang zwischen dem direkten Prozess zum Orbach Prozess, der beim Anlegen eines Magnetfelds in AC-Suszeptibilitätsmessungen beobachtet wurde. Und zwar legen unsere Messungen nahe, dass in einem Magnetfeld das Übergangsmatrixelement des magnetischen Moments des Übergangs parallel zu der Easy-Axis zu. Es wird angenommen, dass das Übergangsmatrixelement des magnetischen Moments mit dem Spin-Phonon Übergangsmatrixelement eng in Verbindung steht [17]. Diese Beobachtung legt daher nahe, dass mit ansteigendem Magnetfeld die Effizienz des Orbach Prozesses via des ersten angeregten Zustand zunimmt und damit zu dem Übergang zum Orbach Prozess führt.

Die Untersuchung des Komplexes DyPhOPh₂ hatte als Ziel neue Erkenntnisse über die Austauschwechselwirkungen zwischen dem Lanthanoidion und den Nitronyl Nitroxide Radikalen zu gewinnen. Es war uns möglich mehrere Energielevel in dem Komplex durch Ferninfrarotspektroskopie zu bestimmen. Allerdings war es uns durch die Komplexität und das Zusammenspiel der Wechselwirkungen nicht möglich, ein geeignetes theoretisches Modell für die Interpretation der Ergebnisse zu finden. Dadurch konnten wir die Größe der Austauschwechselwirkungen und die Kristallfeldaufspaltung nicht bestimmen. Jedoch geben die Ergebnisse die Möglichkeit für den Vergleich mit komplizierteren theoretischen Modellen in der Zukunft.

Neben - den soeben zusammengefassten Resultaten für die untersuchten Verbindungen - präsentieren wir in dieser Arbeit neue Methoden für die Analyse von Ferninfrarotspektren von lantanoidbasierten Einzelmolekülmagnetmaterialien. Die erarbeiteten Methoden bieten die Möglichkeit für die Bewältigung von verschiedenen Problemen, mit denen wir bei der Untersuchung der Verbindungen konfrontiert wurden. Die präsentierten Methoden sind:

- **Problem:** Zusätzlich zu den elektronischen Absorptionslinien treten in dem untersuchten Frequenzbereich von 4 cm^{-1} bis 100 cm^{-1} auch phononische und intramolekulare vibronische Absorptionslinien auf [18, 19]. Eine theoretische Vorhersage dieser Linien ist durch die komplexe Kristallstruktur in Einzelmolekülmagnetmaterialien erschwert und nicht ohne weiteres möglich. Dadurch muss die Unterscheidung experimentell erfolgen.

Methode: Die Ferninfrarotspektren werden bei verschiedenen Magnetfeldern aufgenommen. Durch das Magnetfeld werden nur die elektronischen Absorptionslinien durch den Zeeman-Effekt beeinflusst. Die Änderung im Magnetfeld ist deshalb ein eindeutiger Hinweis für die Identifikation der elektronischen Absorptionslinien. Diese Methode wurde aus früheren Studien an Lanthanoidionen übernommen [13].

- **Problem:** Die elektronischen Absorptionslinien sind oft von starken phononischen und intramolekularen vibronischen Absorptionslinien überlagert. Anstatt als individuelle Linie sind sie deshalb nur als leichte Änderung im Transmissionsspektrum bei einer Magnetfeldänderung sichtbar. Deshalb stellte sich die Frage, wie man Zugang zu den charakteristischen Parametern von nur den elektronischen Absorptionslinie bekommen kann.

Methode: Um das Problem zu lösen, rechnen wir die Transmissionsspektren in den Absorptionswirkungsquerschnitt pro Lanthanoidion um. Um die Anteile der phononischen und intramolekularen vibronischen Absorptionslinien zu beseitigen, werden von den Spektren im Feld die Spektren ohne Feld abgezogen. Zusätzlich wird der Absorptionswirkungsquerschnitt durch Vorfaktoren und durch die Frequenz geteilt. Die dadurch neu erhaltene Größe (der normalisierte Absorptionsquerschnitt) ist dann direkt proportional zu der Änderung des spektralen Gewichts in Einheiten des Übergangsmatrixelements.

- **Problem:** Die untersuchten Proben bestanden anstatt aus Einzelkristallen aus mikrokristallinem Pulver der Verbindungen, das zu Pellets gepresst wurde. Die starke magnetische Anisotropie der Verbindungen führt zu stark anisotropen spektroskopischen g-Faktoren. Anstatt einer Zeemannverschiebung der ganzen Linie in einem Magnetfeld, führt dies zu einer - a priori - nicht vorhersehbaren Veränderung der Linie. Detaillierte Ferninfrarotmessungen von Proben aus Pulver für lantanoidbasierte Materialien wurden bis jetzt in der Literatur noch nicht betrachtet.

Methode: Um qualitativ den Effekt des Magnetfeldes auf die elektronischen

Absorptionslinien zu beschreiben, wurde ein Simulationsprogramm geschrieben, das die Differenz des normalisierten Absorptionswirkungsquerschnitts zwischen verschiedenen Magnetfeldern für Pellets aus mikrokristallinem Pulver beschreibt. Die Input-Parameter des Programms sind die Kristallfeldparameter des entsprechenden Lanthanoids. Die numerische Integration über die verschiedenen Richtungen der Mikrokristallite in dem Pellet wurde durch ein Lebedev-Laikov Gitter implementiert.

Die erwarteten Magnetfeldänderungen der elektronischen Absorptionslinien wurden für verschiedene Parametersets berechnet. Die Simulationen geben Auskunft darüber, was für verschiedene Änderungen möglich sind, und helfen dadurch bei der Identifikation der elektronischen Absorptionslinien in den verschiedenen Proben. Da die Kristallfelder in den untersuchten Lanthanoidionen von niedriger Symmetrie sind, ist der Kristallfeld-Parameterraum groß und verhinderte die Simulation der aufgenommenen Spektren mit dem Kristallfeld-Hamiltonian.

Die, in dieser Arbeit präsentierten Methoden, bieten ein Schema, das allgemein für die Analyse von Ferninfrarotspektren von lanthanoidbasierten Materialien angewendet werden kann.

Zusätzlich enthält die Arbeit einen Überblick über die magnetischen Relaxationsmechanismen, die in Lanthanoidionen beobachtet werden können. Das Verständnis der Relaxationsprozesses erlaubte es uns, die Ergebnisse unserer Ferninfrarotmessungen mit vorherigen magnetischen Relaxationsmessungen in Verbindung zu bringen.

Zusammenfassend haben wir die Anwendbarkeit der Ferninfrarotspektroskopie für die Untersuchung von lanthanoidbasierten Einzelmolekülmagnetmaterialien gezeigt. Die Ferninfrarotstudien von drei verschiedenartigen Einzelmolekülmagnetmaterialien, einem Einzelionenmagnet, einem Einzelkettenmagnet und eines austauschgekoppelten Clusters, führten uns zu einem tieferen Verständnis der jeweiligen Komplexe. Insbesondere erhielten wir einen tieferen Einblick in die jeweiligen Relaxationsprozesse.

Contents

Abstract	3
Zusammenfassung	9
1 Introduction	19
1.1 Single-molecule magnets, single-ion magnets and single-chain magnets .	19
1.2 Characteristics and applications of lanthanides/rare earths	25
1.3 Far-infrared spectroscopy of lanthanide ions	28
1.4 Motivation and outline of the thesis	30
2 Theoretical background of lanthanides in slowly relaxing molecular materials	33
2.1 Lanthanides in static crystal fields	33
2.1.1 The Hamiltonian of the 4f-electrons	34
2.1.2 Russell-Saunders coupling scheme	35
2.1.3 Crystal field parametrization and the Stevens operators	36
2.1.4 J -mixing, non-pure Russell-Saunders wave functions, and con- figuration interaction	41
2.1.5 Analysis of experimental data	42
2.1.6 Low symmetry crystal fields and ab-initio calculations	42
2.2 Magnetic relaxation	43
2.2.1 Measurement techniques	43
2.2.2 Magnetic relaxation in cluster SMMs	44
2.2.3 Master equation	45
2.2.4 Phonon bath	48
2.3 Magnetic relaxation of lanthanides in crystal fields	49
2.3.1 Detailed description of spin-lattice interactions	52
2.3.1.1 Direct process	54
2.3.1.2 Two-Phonon Orbach process	57
2.3.1.3 Raman process	58
2.3.1.4 Orbach and Raman process using optical phonons	59
2.3.2 Magnetic relaxation of lanthanides in molecular magnetism: Dis- cussion of literature	60
2.4 Magnetic relaxation in single-chain magnets	62
2.4.1 Static magnetic properties	62
2.4.2 Dynamic magnetic properties	63

3	Methods and Materials	67
3.1	Experimental setup	67
3.1.1	Terahertz-Spectroscopy using backward-wave-oscillators	67
3.1.2	Fourier-Transform-Infrared-Spectroscopy	68
3.2	Analysis of the data	69
3.2.1	Fresnel equations for a plane-parallel slab	69
3.2.2	Modeling of the dielectric permittivity and magnetic permeability	71
3.3	Investigated samples	73
4	New methods for the analysis of far-infrared spectra of lanthanide ions	75
4.1	Introduction	75
4.2	Analysis of the magnetic field-dependent spectra	77
4.3	Simulation program for far-infrared spectra of lanthanide ions	80
4.3.1	Single crystal and one polarization direction	80
4.3.2	Averaging over the different directions of a powder	82
4.4	Example simulations for different crystal field Hamiltonians	82
4.5	Evaluation by the use of the spectroscopic g-factors	87
4.6	Distinction between electric and magnetic dipole transitions	88
5	Dy(PhOPh): A lanthanide-based single-chain magnet	91
5.1	Introduction	91
5.2	Methods and materials	93
5.3	Results	94
5.4	Discussion: Relation to the relaxation dynamics	100
5.5	Conclusion	102
6	DyDOTA: A single-ion lanthanide compound showing slow relaxation of the magnetization	105
6.1	Introduction	105
6.1.1	Magnetic relaxation	106
6.1.2	Luminescence and CASSCF-calculations	107
6.1.3	Motivation of far-infrared spectroscopy	108
6.1.3.1	Crystal-field splitting	108
6.1.3.2	Terahertz vibrations in hydrogen bonded networks	109
6.2	Methods and materials	111
6.3	Results and Discussion	111
6.3.1	Dielectric and optical phonon properties	112
6.3.2	Electronic transition inside the crystal-field split ${}^6\text{H}_{15/2}$ ground multiplet of dysprosium in DyDOTA	118
6.3.3	Electronic transition inside the crystal-field split ${}^7\text{F}_6$ multiplet of terbium in TbDOTA	123
6.3.4	Discussion: Relation of the results to the relaxation behavior	124
6.4	Conclusion	125

7	Ln(NITPhOPh) ₂ : One lanthanide ion coupled to two NIT-radicals	127
7.1	Introduction	127
7.2	Motivation of far-infrared spectroscopy	129
7.3	Methods and materials	130
7.4	Results and discussion	131
7.4.1	Dy(NITPhOPh) ₂	131
7.4.2	Dy(NITeTPhOPh) ₂	135
7.4.3	Tb(NITPhOPh) ₂	135
7.4.4	Ho(NITPhOPh) ₂	139
7.4.5	Comparison of the different compounds	139
7.5	Conclusion	141
8	Summary and Outlook	143
A	Appendix	147
A.1	Limits of the Beer-Lambert law for bulk samples	147
A.2	DyDOTA: additional measurements	149
A.3	Dy(PhOPh) ₂ : additional measurements	151
A.4	Dy(PhOPh) ₂ : theoretical considerations	153
	Bibliography	157
	Acknowledgements	167

1 Introduction

1.1 Single-molecule magnets, single-ion magnets and single-chain magnets

The fascinating discovery of slow relaxation of the magnetization and hysteresis in the molecular material $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4$ (abbreviated: Mn_{12}Ac) started the field of molecular magnetism in 1993 [21]. Hysteresis and slow relaxation of the magnetization is a well known feature of bulk ferromagnets. It was astonishing to observe these characteristics in a material, which shows no evidence of 3-dimensional ordering. Instead it consists out of twelve-ion manganese clusters coupled by superexchange through oxygen bridges. The four inner and eight outer spins which point in opposite directions lead to an effective giant-spin of $S=10$ at low temperatures (see Figure 1.1).

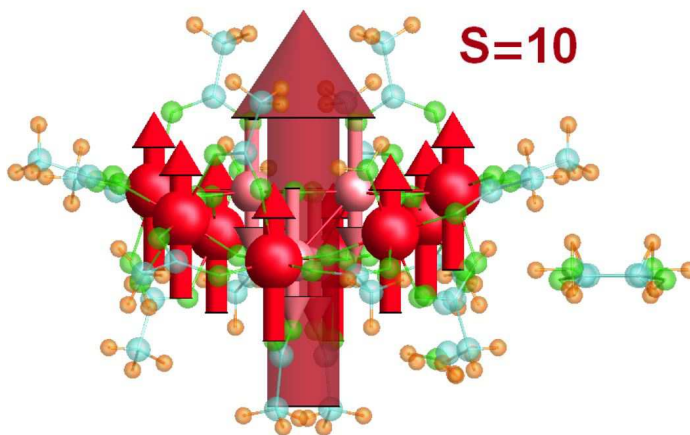


Fig. 1.1: View of $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4$. The four inner Mn^{3+} ions, each have a spin of $S=3/2$ and are pointing down (light pink). The eight outer Mn^{4+} ions, each have a spin $S=2$ and are pointing up (red). The spins of the cluster couple together to the giant spin $S=10$ (dark red) pointing in the direction of the Mn^{4+} ions.

The effective spin has a strong negative-magnetic anisotropy yielding an energy barrier of $U \sim 43 \text{ cm}^{-1}$ [21]. Each cluster is surrounded by acetate ligands suppressing interactions to the neighboring clusters. Therefore, the magnetic behavior originates

from an ensemble of identical manganese clusters, which are (in a good approximation) not interacting with each other. The observed hysteresis and slow relaxation can be attributed to the single molecules of the manganese clusters. As the molecules act as tiny magnets at low temperatures, this class of materials was termed single-molecule magnets (SMMs).

For technical applications they raised expectations to be able to store information on the molecular level. From a fundamental physical point of view, they offer the great possibility to observe quantum phenomena, i.e., quantum tunneling of the magnetization and Berry-phase interference [22]. Nowadays, attempts are made to attach SMMs to surfaces [23] and to use them as molecular devices [24, 25].

Superparamagnets and SMMs

If a ferromagnetic material gets smaller and smaller, at a certain volume (critical size) it exists solely out of one domain below a certain temperature. Instead of showing a phase transition, these small ferromagnetic particles show slow relaxation of the magnetization following a thermally activated mechanism at sufficiently low temperatures. These nanoparticles - normally of a size of a few nanometers (1000-10 000 atoms) - are usually called superparamagnets. Many superparamagnets possess an anisotropy axis leading to an easy-axis for the magnetization. the magnetization tends to align preferably parallel to the easy-axis. The anisotropy can stem from different origins, like shape-, magneto-crystalline-, or magneto-elastic anisotropie [26]¹. The affinity between superparamagnets and SMMs lies in the slow relaxation of the magnetization, being a key feature of SMMs. Superparamagnets represent the "top-down" and the SMMs the "bottom-up" approach to nanoscale magnetism. SMMs only consist of a few coupled metal ions surrounded by ligands. The ligands hinder a bulk magnetic order, keeping them to what is often called "zero-dimensional". The size ranges from one metal ion to the largest single-molecular cluster made of 84 manganese ions [27]. SMMs composed of only one metal ion represent a special subclass - they are often called single-ion magnets (SIMs).

Wide variety of SMMs

A wide variety of SMMs has been synthesized after the discovery of slow relaxation of the magnetization in Mn_{12}Ac with partially aesthetically appealing structures. In the beginning, they were primarily based on 3d-transition metal ions like manganese, cobalt, iron, vanadium or copper. For an elaborate review on the wide range and characteristics of 3d-transition metal ions, see Aromí *et al.* [28]. The best studied family

¹ The relaxation rate follows an Arrhenius law $\tau = \tau_0 \cdot \exp(KV/k_B T)$ with k_B the Boltzmann factor, in which the anisotropy barrier KV is proportional to the volume V . The magnitude of the parameters are around $\tau_0 = 10^{-9}$ s and $K = 1.5$ K/nm³ (for iron oxide).

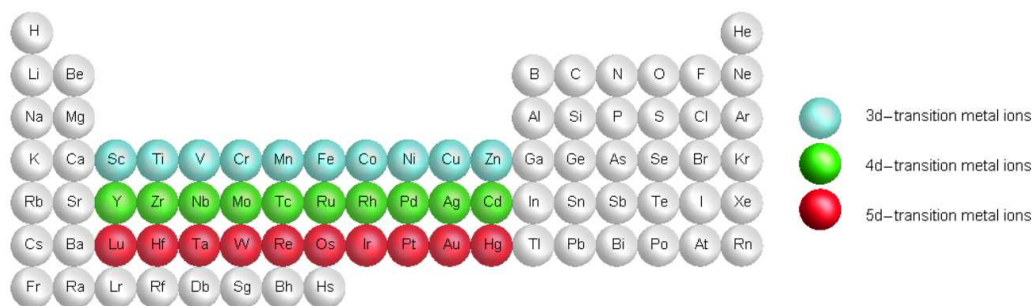


Fig. 1.2: Periodic table of elements: 3d-, 4d-, 5d- transition metal ions.

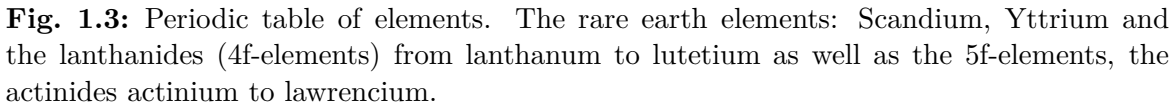
of SMMs are the manganese clusters, with a wide range of constituent manganese ions, ranging from 2 to 84 manganese ions, and embedded in different organic ligand shells [29]. In Mn_{12}Ac the anisotropy is established by a vectorial addition of the single ion anisotropies of the Jahn-Teller distorted octahedral coordination of the $\text{Mn}(\text{III})$ ions. The crystal field yields together with the spin-orbit coupling a zero-field anisotropy [30]. Besides the archetypal SMM Mn_{12}Ac , the SMM $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\text{Br}_8$ [31] was thoroughly investigated, because of its suitability for studies of the quantum tunneling of the magnetization. A different road was taken by using heavier transition metal ions (4d- and 5d- elements, see Figure 1.2) characterized by more radially extended valence orbitals, stronger spin-orbit coupling, a variety of oxidation states, and stronger exchange interactions [32].

In 2003 lanthanides (4f-elements, see Figure 1.3) received growing interest in the field of molecular magnetism, because of the observation of slow relaxation in a single-ion lanthanide compound, the lanthanide double-decker complex $[\text{Pc}_2\text{Tb}]^-\text{TBA}^+$ [3]. This discovery led to an extensive research of lanthanide and actinide based SMMs and SIMs [7, 33]. The special magnetic properties of lanthanides (and actinides) lies in their inner, unclosed 4f-shell (5f-shell). The shielding of the 4f-shell leads to small crystal field perturbations and strong spin-orbit couplings. Lanthanide-based magnetic materials are the subject of this thesis and will be further discussed in Chapter 2. In addition to pure clusters of 3d-, 4d-, 5d-, 4f- and 5f-elements, clusters were explored, in which elements of different periods were mixed together into heterometallic SMMs [34].

Features

The key feature of a SMM is the slow relaxation of the magnetization. A "good" SMM shows slow relaxation preferably at high temperatures. This property, which describes somehow the quality of a SMM, can be described in different ways. The most widely used characteristic quantities are the blocking temperature T_b and the anisotropy barrier U [2]. The blocking temperature can be defined as the highest temperature, at which a hysteresis in the magnetization can be observed. A drawback in this definition lies in the dependence of the blocking temperature on the sweeping

The aim in the years after the discovery of Mn_{12}Ac was to achieve long relaxation of the magnetization at preferably high temperatures. The route taken was to increase the size of the clusters. The idea was to increase the total spin of exchange coupled clusters, as the anisotropy barrier scales approximately with $S^2|D|$, with S the total spin and D the axial zero field splitting parameter. Unfortunately, as the total spin increases it became apparent that the anisotropy of the clusters decreased (for the reasons see [2, 7, 35, 36]). Besides all the efforts to increase the anisotropy barrier, up to date the highest anisotropy barrier (for clusters) is claimed as $U_{eff} = 60 \text{ cm}^{-1}$ (with $T_b = 4.5 \text{ K}$) for $\text{Mn}_6\text{O}_2(\text{Et} - \text{sao})_6(\text{O}_2\text{CPh}(\text{Me})_2)_2(\text{EtOH})_6$ [37].



The advent of single-molecule magnets on the single ion level

In 2003, Ishikawa *et al.* [3] observed slow relaxation in a single lanthanide ion, the lanthanide double-decker complex $[\text{Pc}_2\text{Tb}]^-\text{TBA}^+$ [3]. The discovery not only promoted the research in lanthanide ions, it also was the starting point for the upcoming approach to search for SMMs on the single-ion level. Instead of trying to resemble normal 3-dimensional ferromagnets by the use of a cluster with a 3-dimensional arrangement, it was realized that also single ions on its own can possess an energy-barrier for the reversal of magnetization, which leads to slow relaxation of the magnetization. The crystal field together with the spin-orbit coupling plays the crucial role for the existence of the energy-barrier. Nowadays, most known single-ion based SMMs - often called single-ion magnets (SIMs) - are based on lanthanide ions. But also transition metal based SIMs were discovered, based on e.g., cobalt or iron [38, 39, 40, 41, 42]. The special suitability of lanthanide ions for SIMs lies in their unclosed and well shielded 4f-shell. Thus, the interaction with the crystal field is reduced compared to 3d-transition metal ions and the angular momentum is not quenched. The spin-orbit coupling has to be considered before the crystal field interaction. Therefore, the total angular momentum J results as a good quantum number. Furthermore, the crystal field only splits the ground J - manifold, resulting in energy splittings of around a few hundred wavenumbers. Counterintuitively, the crystal-field perturbation results in a higher magnetic anisotropy for lanthanide ions than for 3d-transition metal ions. The smaller anisotropy of 3d-transition metal ions arises due to the quenching of the orbital momentum, the spin-orbit interaction is zero in first order for most transition metal ions [43]. Because of its high orbital momentum, especially dysprosium containing materials are preferably investigated [44].

The anisotropy barriers of single lanthanide ions often lie in the range of a few hundred wavenumbers (with a record anisotropy of $U_{eff} = 652 \text{ cm}^{-1}$ in a heteroleptic bisphthalocyanine complex [7, 45]). In comparison, up to date the highest anisotropy barrier for transition metal ions is claimed for the cobalt complex $[\text{Co}(\text{hfpip})_2\text{D2py}_2(\text{TBA})]_2$ with an anisotropy barrier of 67 cm^{-1} [46] (and in a series of iron complexes with an anisotropy barrier of $104\text{-}181 \text{ cm}^{-1}$ [7, 39]. The relaxation process of "cluster" SMMs and SIMs differ in a fundamental way. In lanthanide-based SIMs the relaxation barrier, in the thermally activated regime, is considered to be an Orbach process in most circumstances [3, 7, 16, 17, 47]. Without a magnetic field, in Kramers ions the ground manifold is split into at least twofold degenerate crystal field-levels. At most $(2J+1)/2$ different energy levels can be established. When a magnetic field is applied, the crystal field split levels lose their twofold degeneracy. A scheme of the Orbach process [6] via the first excited Kramers doublet in lanthanides is depicted in Figure 1.4 (b). The Orbach process can in general also take place via other excited states. The Orbach process operates via the exchange of energy with the phonon bath. The energy barrier of the Arrhenius process is determined by the energy difference of the ground and

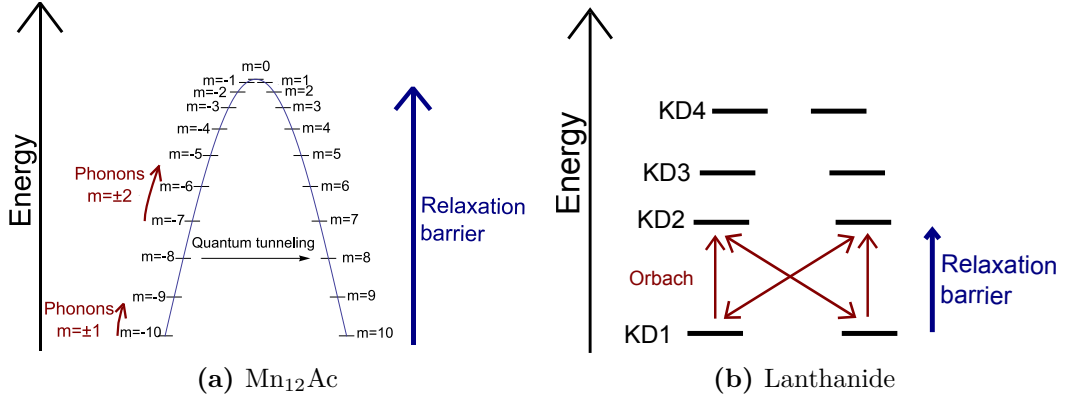


Fig. 1.4: (a) Sketch of the relaxation process and the relaxation barrier in the cluster SMM Mn_{12}Ac in zero magnetic field. (b) Sketch of the Orbach process and the relaxation barrier in lanthanide ions in zero magnetic field for Kramers ions like dysprosium. For Kramers ions every energy-value is two times degenerate leading to Kramers doublets (KD). The Orbach process depicted in (b) for lanthanides can also take place via the other excited levels.

the excited crystal field state via which the relaxation takes place. In difference, for "cluster" SMMs the energy barrier is determined by the height of the total anisotropy barrier $S^2|D|$ depicted in Figure 1.4 (a).

Some important SMMs together with their characteristic properties are shown in Table 1.1.

Single-chain magnets

Another growing field in molecular magnetism focuses on single-chain magnets (SCMs). The first explored SCM was the cobalt derivative $\text{Co}(\text{hfac})_2(\text{NITPhOMe})$ [48]. In contrast to SMMs (zero-dimensional) the cobalt ions build an 1-dimensional arrangement, but still without 3-dimensional ordering. The underlying mechanism for the slow relaxation of the magnetization in SCMs is given by the Glauber dynamics, suggested by Glauber in 1963 for the 1-dimensional Ising model [49]. The prerequisites for Glauber dynamics are a strong Ising anisotropy of the building blocks, a strong intrachain interaction with respect to the interchain interaction, and a ferro- or antiferromagnetic coupling between the building blocks along the chain. The original Glauber model treats the individual spins with a constant spin-flip attempt rate, which is temperature-independent. The origin of the slow relaxation lies only in the exchange coupling, which stabilizes ordered states. The Glauber model relies on statistical and mathematical considerations, and not on a physical equation of motion. The physical equilibrium is introduced by the Boltzmann population of states.

The Glauber approach was extended to additionally take into account the intrinsic anisotropy barrier of the constituents, leading to a temperature dependent spin-

	τ_0 (s)	U_{eff} (cm ⁻¹)	T_B (K)
Mn ₁₂ O ₁₂ (CH ₃ COO) ₁₆ (H ₂ O) ₄ [21]	$2.1 \cdot 10^{-7}$	43	3
Mn ₆ O ₂ (Et – sao) ₆ (O ₂ CPh(Me) ₂) ₂ (EtOH) ₆ [37]	$2 \cdot 10^{-10}$	60	4.5
[Fe ₈ O ₂ (OH) ₁₂ (tacn) ₆]Br ₈ [31]	$2 \cdot 10^{-7}$	16	3
[Co(hfpip) ₂ D2py ₂ (TBA)] ₂ [46]	$1.4 \cdot 10^{-9}$	67	5
Co(hfac) ₂ (NITPhOMe)[48]	$3 \cdot 10^{-11}$	108	6
[Pc ₂ Tb] ⁻ TBA ⁺ [3]	$6 \cdot 10^{-8}$	230	
[Pc ₂ Dy] ⁻ TBA ⁺ [3]	$6 \cdot 10^{-6}$	28	

Tab. 1.1: Some important SMMs together with their characteristic properties: The spin-flip attempt rate τ_0 (s), the effective anisotropy barrier U_{eff} (cm⁻¹), and the blocking temperature T_B (K).

flip attempt rate for the constituents on its own [50]. A relaxation time of $\tau = \tau_0 \cdot \exp((4J + \Delta)/k_B T)$ (with coupling constant J and the energy barrier Δ) was proposed for the infinite size regime and $\tau = \tau_0^* \cdot \exp((2J + \Delta)/k_B T)$ for the finite-size regime [50]. In the finite size regime the correlation length ξ exceeds the chain length L ($\xi \gg L$), the relaxation process starts with the nucleation of a domain wall at the chain end, with an energy cost of $2J$ due to the exchange interaction of the one residual neighbor. In the infinite-size regime the chain length is longer than the correlation length ($L \gg \xi$) and the relaxation process takes place primarily via a thermally activated random walk of the domain walls. The chain length L is determined by limiting geometrical factors or the occurrence of impurities. The model was verified for several single-chain magnets based on transition metal ions [50, 51].

For the use as anisotropic building blocks lanthanide ions are well suited. The first lanthanide-based SCM Dy(hfac)₃{NIT(C₆H₄OPh)} [14] will be studied by far-infrared spectroscopy in this thesis.

1.2 Characteristics and applications of lanthanides/rare earths

This thesis deals with the application of lanthanides in the field of molecular magnetism. In this chapter, we will recall general characteristics and applications of lanthanides outside of this field. The research in molecular magnetic materials not only yields the opportunity of tuning the molecular magnetic properties, but also reveals properties of lanthanides on the fundamental level, e.g., crystal field and exchange interactions. The research in molecular magnetism, therefore, makes a contribution

to the basic research in lanthanides which is also important for other fields, in which lanthanides are used. Especially the opportunity to observe lanthanide behavior on the molecular or single ion level in a well described environment is a special advantage of SMMs, SIMs and SCMs. Therefore, this chapter describes the general properties and technical applications of lanthanides.

Definition of rare earths and lanthanides

The terms rare earths elements (REE) and lanthanides are often used synonymously in the field of molecular magnetism. Following the International Union of Pure and Applied Chemistry (IUPAC) definition, the rare earth elements include the lanthanides as well as scandium and yttrium (see Figure 1.3). All the rare earth elements share similar chemical properties and can be found in the same ore deposits. The lanthanides are the f-block elements of the periodic table from Lanthanum to Lutetium, in which the 4f-shell is filled with electrons. Strictly speaking Lutetium and Lanthanum are d-block elements as isolated atoms. In the 3+ oxidation state (most common) the lanthanide reveal their character of filling the 4f-shell from lanthanum to lutetium. For lanthanum and cerium, the two 6s-electrons and the one d-electron, and for the other lanthanides the two 6s-electrons and one of the 4f-electrons are given away. The electronic configuration is then given by the Xenon core plus the 4f-shell ranging from lanthanum with an empty 4f-shell ($[\text{Xe}]f^0$) to lutetium with a filled 4f-shell ($[\text{Xe}]f^{14}$). In the field of molecular magnetism the use of the term lanthanide seems more likely as scandium and yttrium are not used, and additionally, the interesting magnetic properties arise from the electrons in the 4f-shell.

Production

China is the market leader of rare earths production holding 96% of the overall market. In order to escape the dependency from China, other countries especially the USA expand their abilities of obtaining REE resources. The problem of obtaining rare earths lies in its low concentration in minerals seldom exceeding 8-10% and the difficulty in the separation of the chemically similar rare earth elements. Therefore, the process of obtaining separated rare earth elements is lengthy, costly and more over it contains strong risks of environmental pollution and for the health of the workers. Rare earths containing minerals for example are bastnasite and monazite [52, 53].

Applications

The main applications - containing over 90% of the produced rare earths - are: 1. Catalysts (mainly fluid cracking catalysts), 2. Alloys, 3. Neodymium magnets, 4. Polishing powder for screens, lenses, and windows, 5. Optical glasses for lenses and lasers, and 6. Light converting phosphors for fluorescent lamps, LEDs, and displays

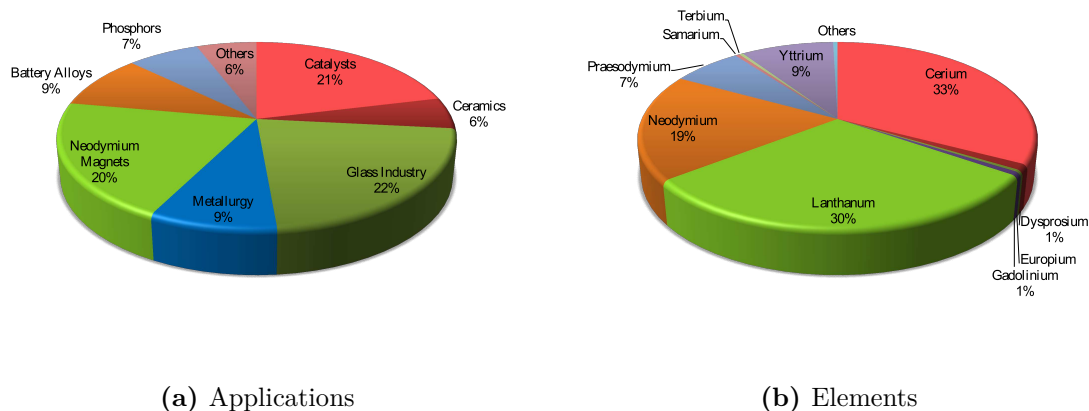


Fig. 1.5: Distribution of rare earth oxide consumption by market sector in 2008 [52, 53]. The data is based on estimates from the Lynas Corporation LTD and the Industrial Minerals Company of Australia Pty L.

[52, 54]. The most important chemical and physical properties making rare earths unique for applications are:

- for fluid catalytic cracking used in petroleum refineries $\Leftrightarrow$ the oxygen storage and release. (Lanthanum)
- for data storage and hard magnets (e.g., for wind turbines and electric motors) $\Leftrightarrow$ high coercivity, high magnetic anisotropy and large magnetic moment. (Neodymium, praseodymium, dysprosium, terbium)
- for LCD and plasma screens and compact fluorescent light bulbs $\Leftrightarrow$ the high fluorescence. (Yttrium, cerium, lanthanum, europium, dysprosium, gadolinium)
- for metallurgical applications $\Leftrightarrow$ the efficient hydrogen storage in rare earth alloys. (Cerium, yttrium, lanthanum, neodymium, praseodymium)
- and others.

An overview of the annual rare-earth consumption is given in Figure 1.5. For example an iPhone (Apple Inc.) uses eight rare earth elements, namely yttrium, lanthanum, praseodymium, neodymium, europium, gadolinium, terbium, and dysprosium for the color screen, phone circuitry, speakers, and the vibration unit². Therefore, modern technology is cannot be imagined without rare earths. Many applications of rare-earths consist of doping only low concentrations into a host material changing the chemical and physical properties of the host material in an intended fashion, e.g. silica optical fibers are doped with Er_2O_3 [54].

² Adapted from <http://www.rareelementresources.com/>

1.3 Far-infrared spectroscopy of lanthanide ions

Importance of energy-level structure for the relaxation process

The energy-level structure of molecular materials like SMMs, SIMs, and SCMs plays a crucial role for the relaxation process. In lanthanide-based single-ion magnets (SIMs) several relaxation pathways were found. For the first lanthanide-based SIM $[\text{Pc}_2\text{Tb}]^-\text{TBA}^+$ three major relaxation mechanisms were observed [47]: the direct process, the Raman process and the Orbach process. For all three processes the determination of the crystal-field perturbation is important. Especially for the Orbach process, a thermally activated process, where the energy barrier for the reversal of the magnetization is determined by the splitting between the crystal-field split states. It was found that the determined energy separation of the crystal field split states is slightly higher than the energy-barrier [9, 16, 47]. The discrepancy is attributed to under-barrier relaxation mechanisms. But still the role of the crystal field is not completely clear. In lanthanide-based single-chain magnets the situation is much more complicated and unknown. Both the anisotropy of single lanthanide ions and the 1-dimensional ordering have to be considered. This collective behavior which is already difficult to describe in the static case gets very ambitious to understand for the dynamic case. The 1-dimensional ordering in SCMs leads to Glauber dynamics [49, 51, 55], with an additional dynamic contribution from the very anisotropic building blocks (the lanthanide ions). Therefore the Glauber dynamics approach was extended to take into account also the anisotropy of the building blocks [50, 51]. The model works well for transition metal ions [50, 51], but a verification for lanthanide-based compounds remained unclear, because an explicit determination of the energy-level structure is still missing.

Measurement techniques for lanthanide-based SIMs

Considering all these issues, the importance of the energy-level structure for the development of compounds with longer relaxation times has been pointed out [2, 7]. The theoretical modeling has to face issues of strong spin-orbit coupling and often low-symmetry crystal fields [17, 43]. Recently, achievements on this issue have been made. First, by modeling the electrostatic crystal field leading to the crystal field parameters [56] and second by advanced ab-initio CASSCF (complete active space self-consistent field) calculations [17, 57]. In order to verify and to enhance the quality of the theoretical models, experimental data is necessary. To get access to the crystal field parameters and therefore the energy-level splitting, magnetic susceptibility measurements, or more precisely angular dependent susceptibility measurements and EPR-measurements (Electron Paramagnetic Resonance) can be used. An appropriate crystal field Hamiltonian is assumed and the crystal field parameters are varied to fit the susceptibility data. However, the parameters are not definite and unique, many

different sets of parameters fit the data. Different experimental data are fitted simultaneously to enhance the quality of the crystal field parameter, e.g., the combined use of NMR-shifts and magnetic susceptibility measurements [47]. Especially for lanthanides at low-symmetry sites, with which we deal mostly in this thesis, these approaches are not feasible due to the huge set of crystal field parameters. More direct techniques are optical absorption spectroscopy, luminescence [15, 58], or magnetic circular dichroism measurements (MCD). But these techniques are not suitable for all compounds, for example for $[\text{Pc}_2\text{Tb}]^-\text{TBA}^+$ these spectroscopic techniques are not accessible due to the strong optical absorption of the ligands. In luminescence measurements "hot" transitions can complicate the interpretation of the data. Recently, to solve this issue, inelastic neutron scattering (INS) measurements were established [9, 59].

Far-infrared spectroscopy for lanthanides

More directly the crystal field splitting (sometimes called Stark splitting) can be observed by means of far-infrared spectroscopy. The crystal field splittings of the ground manifold are typically between $0\text{-}600\text{ cm}^{-1}$ and directly observable in the far infrared region [13]. The frequency, at which a transition can be observed as an absorption line in the far-infrared spectrum, is directly proportional to the energy difference of the two participating states. The first work to determine the crystal field parameters in this way has been performed for the rare-earth iron garnets by Sievers *et al.* in 1963 [10], followed by further research on rare earth ethyl sulphates [11], anhydrous halides like LaCl_3 [12]. Moreover in a review article by Bloor and Copland [13] results from other compounds are discussed. In general, in far infrared spectra of magnetic materials several absorption mechanisms can appear [60]: exchange resonance (in ordered magnetic materials), electronic absorption lines and phonons (the terminology phonons is used in the following also for inter- and intramolecular excitations). To distinguish between the different mechanisms and to identify the electronic absorption lines, which are of crucial interest for this work, several methods can be applied. The first and most direct method is, to apply a magnetic field and to observe the Zeeman shift of the electronic absorption lines. For single crystals and Kramers ions the electronic absorption should split and shift in frequency giving also the opportunity to determine the spectroscopic g-value of the electronic state. This method is more complicated for powders of anisotropic materials, because the easy-axis of the lanthanide ion is pointing in different directions with respect to the magnetic field. Therefore, in a magnetic field the absorption line consists of contributions from all the different directions, leading to a broadening of the absorption line together with a shift. Because of the different contributions, the shift can be different for different directions. The behavior depends strongly on the states participating in the transition. These transitions are allowed by magnetic dipole selection rules, but can also include some parts of normally forbidden electric dipole transitions. For the identification of the phonon lines one can make use of the fact that the rare earths form isomorphous

compounds. The rare earth ions differ only slightly in their weight and this shift is nearly compensated by the contraction of the ion altering the force constantly (lanthanide contraction rule). By acquiring spectra of different rare-earth ions in the same compound the phonon lines should lie nearly at the same frequency. Often lanthanum is taken as reference because electronic absorption lines are not present here, leading to a clear identification of the phonons. The exchange resonance (namely antiferromagnetic and ferromagnetic) should only appear in ordered magnetic materials and can be identified by its temperature dependence.

1.4 Motivation and outline of the thesis

Despite the suitability to obtain the energy-level structure by far-infrared spectroscopy, the technique was not applied to lanthanide-based SIMs and SCMs until now. Parallel to this work also the first lanthanide-based SIM family $[\text{Pc}_2\text{Ln}]^-\text{TBA}^+$ was studied by far-infrared spectroscopy and yielded strong hints that the relaxation process takes place in the thermally activated regime via the first excited crystal field level [9]. In the field of molecular magnetism a comparable technique (named frequency domain magnetic resonance (FDMRS)) was established for the energy spectra of transition based single-molecule magnets [61, 62, 63].

The aim of this thesis is to show and test the applicability of far-infrared spectroscopy for lanthanide-based SIMs and SCMs. Furthermore we want to gain insight into the relaxation process of the studied compounds:

1. The single-chain magnet DyPhOPh ($\text{Dy}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}$) and the isostructural terbium compound TbPhOPh [14],
2. The single-ion magnet DyDOTA ($\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})]_4 \cdot \text{H}_2\text{O}$) and the isostructural terbium compound TbDOTA [15, 58],
3. The molecular magnet $\text{Ln}(\text{PhOPh})_2$ ($\text{Ln}(\text{hfac})_3(\text{NIT} - \text{C}_6\text{H}_4\text{OPh})_2$) ($\text{Ln}=\text{Dy}, \text{Tb}$, and Ho) and $\text{Dy}(\text{hfac})_3(\text{NIT} - \text{C}_6\text{H}_4\text{OEt})_2$ ($\text{Dy}(\text{PhOEt})_2$) [5, 64].

All of the compounds were previously explored by static and dynamic magnetization measurements and LnDOTA also by luminescence measurements [5, 8, 14, 15, 64]. The emphasis of the studies will lie for all compounds on the dysprosium derivative. The three compounds cover various issues of lanthanides in slowly relaxing molecular materials.

The first compound $\text{Dy}(\text{PhOPh})$ and its isostructural terbium analogue show single-chain-magnetic behavior. The relaxation dynamics of lanthanide-based SCMs is still under debate and the role of the anisotropic lanthanide building blocks in the Glauber dynamics approach is not clear.

The second compound DyDOTA belongs to the class of single-ion magnets. The

isostructural terbium analogue TbDOTA shows no slow relaxation of the magnetization and is studied for comparison. Studies on the energy-level structure can reveal the origin of the relaxation dynamics, which follows an Arrhenius behavior in an applied field (for DyDOTA), and is normally attributed to an Orbach relaxation mechanism [15].

The last two compounds $\text{Ln}(\text{PhOPh})_2$ and $\text{Ln}(\text{PhOEt})_2$ consist of a lanthanide ion coupled to two organic nitronyl nitroxide radicals. The two compounds differ only in the nitronyl-nitroxide radical. From a theoretical point of view, one is faced with the orbitally degenerate ground state of the lanthanide ion, the exchange interactions between the orbitally degenerate lanthanide ion and the radicals, and the exchange interaction between the radicals. Such compounds (one lanthanide ion coupled to two nitronyl nitroxides) were widely studied twenty years ago [65] and received new interest in the field of molecular magnetism.

For the interpretation of the far-infrared spectra of these compounds, new tools needed to be developed, because the electronic absorption lines, where strongly overlapped with phononic or intramolecular vibrational excitations. In addition, all our samples were pellets pressed out of microcrystalline powder. We present a general scheme for the analysis of far-infrared data, which includes the calculation of the normalized absorption cross section. This approach gives direct access to the transition matrix element of the magnetic dipole transition. In this thesis, therefore, a simulation program for the simulation of the magnetic field dependence of the electronic absorption lines is presented (based on MATLAB). The program calculates out of the crystal field parameters the difference of the normalized absorption cross section between in-field and zero-field spectra, which can be extracted out of the far-infrared transmission spectra. To take into account the random orientation of the microcrystallites, a Lebedev-Laikov grid was implemented.

The thesis is divided as follows: First, the fundamental static and dynamic properties of lanthanides faced to a crystal field are reviewed in Chapter 2. Second, the measurement techniques and an approach for the analysis of the data by the dielectric and magnetic permeabilities are presented in Chapter 3. In Chapter 4 a different approach for the analysis of the far-infrared data which uses the normalized absorption cross section is introduced. In addition, the simulation program - developed in this thesis - for the magnetic field dependence of the electronic absorption lines of lanthanide ions is described. The results of the studied compounds are presented in Chapter 5 for $\text{Ln}(\text{PhOPh})_\infty$, in Chapter 6 for LnDOTA, and in Chapter 7 for $\text{Ln}(\text{PhOPh})_2$ and $\text{Ln}(\text{PhOEt})_2$.

2 Theoretical background of lanthanides in slowly relaxing molecular materials

The structure of this section is as follows: First, the static (magnetic) properties of lanthanides in crystal fields are described. This is essential as the focus of this thesis lies on the determination of the crystal-field splitting by far-infrared spectroscopy. As the second aim of this thesis is the better understanding of the relaxation process in lanthanide-based single-molecular magnetic materials. In this thesis, previous results of the dynamic magnetic properties of the compounds by AC-magnetic susceptibility measurements are used. Therefore, the second part describes the basic relaxation mechanisms observed in AC-magnetic susceptibility measurements and its relation to the energy-level structure. The magnetic relaxation mechanisms of lanthanides in a crystal field are reviewed, especially the work done by Orbach [6]. Subsequently, the similarities and differences in the description of lanthanides and cluster SMMs are outlined. Finally, for the study of the single-chain magnet family $\text{Ln}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}$ [14] ($\text{Ln}=\text{Dy}$, Tb , and Ho) a short review of the theoretical description of the static and magnetic properties of single-chain magnets will be given.

2.1 Lanthanides in static crystal fields

In the lanthanide series the 4f-shell is partly filled with electrons. The predominant valence state of the lanthanides in crystals is the trivalent one. A few exceptions are made by the divalent and tetravalent valence state. In this thesis, we will only deal with the trivalent valence state which has then the electronic configuration $4f^N 5s^2 5p^6$. The series starts with lanthanum (empty 4f-shell) and ends with lutetium (completely filled 4f-shell). The 4f-shell is well shielded from the environment by the 5s- and 5p-electrons. A sketch of the electron density of the different shells with respect to the distance to the nucleus is shown in Figure 2.1 with the Bohr radius a_0 .

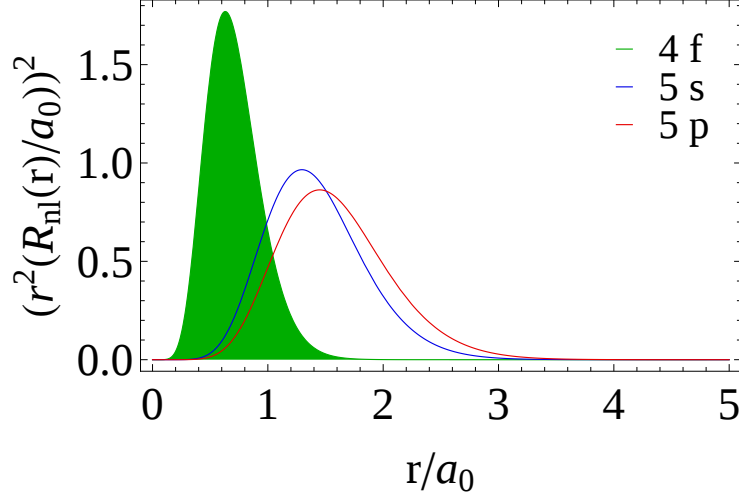


Fig. 2.1: Radial electron density distribution calculated as an approximation with Slater-type-orbitals and approximated orbital exponents [66] for Dysprosium (the Hartree-Fock method can also be applied [67])

2.1.1 The Hamiltonian of the 4f-electrons

As a good approximation the energy levels of isolated, trivalent lanthanide are determined only by the interactions between the electrons of the 4f-shell themselves. All other electronic shells are spherically symmetric (the inner ones and the outer ones). The Hamiltonian for the electrons in the 4f-shell can then be written as follows [68]:

$$\widehat{H} = \underbrace{-\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i}_{\widehat{H}_{kin4f}} - \underbrace{\sum_{i=1}^N \frac{Z^* e^2}{r_i}}_{\widehat{H}_{C_n}} + \underbrace{\sum_{i < j}^N \frac{e^2}{r_{ij}}}_{\widehat{H}_{C_{4f}}} + \underbrace{\sum_{i=1}^N \zeta(r_i) \mathbf{s}_i \cdot \mathbf{l}_i}_{\widehat{H}_{SO}}, \quad (2.1)$$

with $N=1, \dots, 14$ the number of electrons in the 4f-shell, $Z^* e$ the screened charge of the nucleus (screened by the electrons in the closed spherical, inner shells) and $\zeta(r_i)$ the spin-orbit coupling function. The first term $\widehat{H}_{kin4f}$ describes the kinetic energy of the 4f-electrons. The second term $\widehat{H}_{C_n}$ describes the Coulomb interaction with the nucleus, where the real charge of the nucleus is replaced by a screened charge, because the closed inner shells modify only the magnitude of the interaction, but not its symmetry. The first two terms are spherically symmetric and do not remove any of the degeneracies of the 4f-shell.

The third term $\widehat{H}_{C_{4f}}$ represents the Coulomb interaction between the 4f-electrons and the fourth $\widehat{H}_{SO}$ their spin-orbit interaction. The energy-level structure of the 4f-electrons results from the interplay of the spin-orbit and Coulomb interaction. In

lanthanides this two terms are of the same order of magnitude leading to an intermediate coupling scheme, where neither the pure Russell-Saunders coupling scheme (see Section 2.1.2) nor the j-j coupling scheme can be applied [68]. Therefore, the Hamiltonian of both interactions together needs to be diagonalized.

For lanthanide ions in a crystal an additional contribution in the Hamiltonian stems from the electric field created by the other crystal constituents. Therefore, an additional term $\widehat{H}_{CF*}$ has to be added to the Hamiltonian. The energy of the crystal field is much smaller than the other contributions and can, therefore, be treated as a perturbation for the lowest multiplet yielded by the other interactions (see next Section 2.1.2). As the crystal field splitting of special interest in this thesis a detailed discussion is given in Section 2.1.3.

2.1.2 Russell-Saunders coupling scheme

If the Coulomb interaction is much stronger than the spin-orbit interaction and the crystal field, the Russell-Saunders coupling scheme with the multiplet terms ^{2S+1}L [69, 70] can be applied. In the Russell-Saunders coupling scheme the spin and the angular momentum of all electrons couple first separately. This results in a total spin quantum number S and the total angular momentum number L of the electrons. S and L couple then to the total angular momentum J . The Russell-Saunders coupling scheme can be taken as a first approximation for the lanthanides, but they are better described by an intermediate coupling scheme resulting in non-pure Russell-Saunders wave functions (in which states with the same J but different L and S are mixed) but rather in a linear combination of them. However, the ground multiplets are typically 95% pure Russell-Saunders states. The mixing depends strongly on the energy difference between the ground multiplet and the first excited multiplet. The results for the intermediate coupling scheme can be found in the textbook of Dieke [71]. The energy levels are still labeled within the Russell-Saunders scheme denoting the wave-functions with the strongest influence. Using this scheme and taking into account the spin-orbit interaction the multiplets split into the levels labelled by $^{2S+1}L_J$. This leaves only J as a good quantum number.

The ground state of the Russell-Saunders coupling scheme is given by Hund's rule: The total spin angular momentum takes the maximum possible value, if there are different possibilities, the total angular momentum is maximized and for less than half filled shells $J=|L-S|$ and for more than half filled shells $J=|L+S|$.

2.1.3 Crystal field parametrization and the Stevens operators

The charge distribution of the surrounding crystal creates an electric field, which acts on the electrons of the aspheric 4f-shell. The crystal field breaks the degeneracy of the J-manifolds given by Hund's rule for different compositions of the magnetic quantum numbers M_J . The number of sublevels in which the manifold splits depends on the symmetry of the crystal field [72]. The following description of the crystal field with the derivation of the Stevens operators follows References [1, 73, 74, 75].

Parametrization of the Crystal-Field

The charges of the surrounding crystal create an electrostatic potential at the place of the 4f-electrons:

$$V_{CF} = \int \frac{\rho(\vec{R})}{|\vec{R} - \vec{r}|} d\tau_{\vec{R}}. \quad (2.2)$$

At first we only deal with one electron of the 4f-configuration. The potential energy for a certain charge distribution of the crystal $\rho(\vec{R})$ is given by:

$$\widehat{H}_{CF} = -e \int \frac{\rho(\vec{R})}{|\vec{R} - \vec{r}|} d\tau_{\vec{R}}, \quad (2.3)$$

where $\vec{R}$ is the position of the charge density and $\vec{r}$ the position of the 4f-electron. The origin of the coordinate system is located at the core of the lanthanide ion. We can develop $\frac{1}{|\vec{R} - \vec{r}|}$ into:

$$\widehat{H}_{CF} = -e \int \frac{\rho(\vec{R})}{R \sqrt{1 + (r/R)^2 - 2(r/R) \cos \omega}} d\tau_{\vec{R}} = \sum_{k=0}^{\infty} \left(\frac{r_{<}^k}{r_{>}^{k+1}} \right) P_k(\cos(\omega)) \quad (2.4)$$

with ω the angle between $\vec{R}$ and $\vec{r}$, $P_k(\cos(\omega))$ the Legendre polynomials, $r_{<}$ the smaller value of $\vec{R}$ and $\vec{r}$ and $r_{>}$ the larger value. The Legendre polynomials can be written as a sum of spherical harmonics:

$$P_k(\cos(\omega)) = \sum_{q=-k}^{+k} (-1)^q C_{-q}^k(\Theta, \Phi) \cdot C_q^k(\theta, \phi), \quad (2.5)$$

where Θ, Φ are the spherical coordinates of the charge distribution and θ, ϕ the spherical coordinates of the 4f-electron. The spherical harmonics $Y_q^k(\theta, \phi)$ appear in the C coefficients (Racah Tensors) $C_q^k(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}} Y_q^k(\theta, \phi)$. The crystal field Hamiltonian reads then:

$$\widehat{H}_{CF} = \sum_{k=0}^{\infty} \sum_{q=-k}^{+k} C_q^k(\theta, \phi) (-e) (-1)^q \int \rho(\vec{R}) C_{-q}^k(\Theta, \Phi) \frac{r_{<}^k}{r_{>}^{k+1}} d\tau_{\vec{R}}, \quad (2.6)$$

where the last part only consists of parameters of the charge distribution and can be evaluated for a certain charge distribution and written in the parameter form $(-e) (-1)^q \int \rho(\vec{R}) C_{-q}^k(\Theta, \Phi) \frac{r_{<}^k}{r_{>}^{k+1}} d\tau_{\vec{R}} = B_k^q$. The parameter k runs for an electron with a quantum number l from 2 over even integers up to 2l+1 and q runs from -k to k. For the f-electrons l=3 and k=2,4,6 and q=-6,-5....+6. With this parameters we can write the crystal field Hamiltonian in the Wybourne formalism as:

$$\widehat{H}_{CF} = \sum_{k=0}^{\infty} \sum_{q=-k}^{+k} B_k^q C_q^k(\theta, \phi). \quad (2.7)$$

There are also some different notations, for example, if one starts from a point charge model assuming that the charge distribution of the crystal does not enter the one of the 4f-electrons, one gets:

$$(B_k^q)^* = \sum_i \langle r^k \rangle \frac{Z_i e^2}{R_i^{k+1}} (-1)^q C_{-q}^k(\Theta, \Phi), \quad (2.8)$$

with charges i located at a distance R_i with a charge $Z_i e$. This formalism will be used in the next section. In this formalism the expectation value of $\langle r^k \rangle$ is independent of the point charges and one can also write $(B_k^q)^* = \langle r^k \rangle \bar{B}_k^q$ and use $(B_k^q)^*$ as the crystal field parameter. This notation is useful as in experiments only the $(B_k^q)^*$ can be determined. In literature all of the described different notations are used. They are connected by some prefactors which are given in tables, for example in References [1, 73, 75].

To obtain the crystal field parameters the first step is to apply symmetry arguments, which give the non-zero crystal field parameters (see Table 2.3). The determination of the magnitude of the crystal field parameters is a much more difficult task. Initially, the point charge model was used (Equation 2.8), which assumes that the neighboring atoms or ions act like point charges, creating the potential at the lanthanide ion. But

the calculated parameters did not reflect the magnitude correctly [73]. The reason is that the crystal in reality consists out of spatially extended cloud charges, which can penetrate each other as described by the model in the beginning of this chapter. To make this model more applicable, the charge density of different ions in the crystal are summed up, leading to the superposition model [70]. The results obtained from the superposition model yield reasonable results [76]. It is important to note that the crystal field parameters above can also be taken independent from any model and one can use them to compare different experimental results with each another.

Stevens formalism

In molecular magnetism the Stevens formalism [77] is widely used. The Stevens operator equivalents use the fact that the spherical harmonics $Y_q^k(\theta, \phi)$ transform under rotation like an irreducible presentation of the rotation group. To get the Stevens equivalents the crystal field potential is first expressed in cartesian coordinates. To expand the potential in cartesian coordinates, first the spherical harmonics (used here instead of the Racah-Tensors $C_q^k(\theta, \phi) = \sqrt{\frac{4\pi}{2k+1}}Y_q^k(\theta, \phi)$) expansion has to be changed into a tesseral harmonics expansion, because only these ones give real functions. The tesseral harmonics are defined as:

$$Z_0^k = \frac{1}{\sqrt{2}}Y_0^k \quad Z_q^k = \frac{1}{\sqrt{2}}(Y_{-q}^k + (-1)^q Y_q^k) \quad Z_{|q|}^k = \frac{i}{\sqrt{2}}(Y_q^k - (-1)^q Y_{-q}^k). \quad (2.9)$$

That yields for example for $k=2$ and $q=0$ without some prefactors:

$$V_{CF}(r, \theta, \phi) \sim (1 + \cos 3\theta) \rightarrow V_{CF}(x, y, z) \sim (3z^2 - r^2). \quad (2.10)$$

And for $k=2$ and $q=2$:

$$V_{CF}(r, \theta, \phi) \sim \sin^2 \theta \sin 2\phi \rightarrow V_{CF}(x, y, z) \sim \frac{xy}{r^2}. \quad (2.11)$$

For the lanthanides the interesting magnetic properties arise from the 4f-electron system subspace of the $(2J+1)$ -dimensional total angular momentum J eigenspace given by Hund's Rule. For the J -eigenspace the potential operator Z_k^q is equivalent to an angular momentum operator when replacing x, y, z by J_x, J_y, J_z and symmetrizing the J operators. For the equivalence, the equivalent operators must transform under symmetry operations in exactly the same way. The J operators have to be symmetrized, because for example x and y commute but J_x and J_y do not. The symmetrization

yields for $xy \rightarrow \text{sym}(J_x J_y) = (J_x J_y + J_y J_x)$. With the use of Equation 2.10 with $k=2$ and $q=0$, we obtain:

$$(3z^2 - r^2) \rightarrow \alpha_2(3J_z^2 - J(J+1)) = \alpha_2 \langle r^2 \rangle O_2^0. \quad (2.12)$$

and for 2.11 with $k=2$ and $q=2$:

$$\frac{xy}{r^2} \rightarrow \alpha_2(J_x J_y + J_y J_x) = \alpha_2 \langle r^2 \rangle O_2^2. \quad (2.13)$$

The Stevens operator is introduced as O_k^q . The factor α_k is the operator equivalent factor, which is different for different k and J values. The procedure is the same for the other k 's and q 's. Note that the Hamiltonian using the Stevens operators acts on the states of one manifold, for example on the ground manifold derived by Hund's rule. A basis set is given by $|4f^n : \text{LSJ}, M_J\rangle$ with L , S , and J of the manifold and the magnetic total angular momentum quantum number M_J . The crystal field Hamiltonian in the Stevens formalism reads:

$$\widehat{H}_{CF} = \sum_{k=2,4,6} \alpha_k \sum_{q=-k}^k A_k^q \langle r^k \rangle O_k^q(\hat{J}). \quad (2.14)$$

With $A_k^q \langle r^k \rangle$ the crystal field parameter, which also takes into account the radial integrals $\langle r^k \rangle$. The Stevens operators for $k=2, 4$ and 6 are depicted in Table 2.2.

Important to note is that the Stevens operators are also valid for more than one electron states: For the lanthanides they can be used for the J ground state given by Hund's rule. The multiplying factor α_k depends not only on the total angular momentum. The multiplying factor α_k is attributed to the charge density distribution of the electrons in the $4f$ -shell. If α_2 is negative the shape is oblate, if it is positive it is prolate [78]. The multiplying factors for the different lanthanides can be found in Table 2.1.

The Stevens operator crystal field parameter are related to the previously obtained Wybourne-parameters by some multiplying factors. We refer to the tables in References [1, 73, 75].

Often the crystal field parameter $A_k^q \langle r^k \rangle$ and the operator equivalent factor α_k are combined to one parameter B_k^q , which is also called Stevens crystal field parameter. The crystal field Hamiltonian is then simplified to:

$$\widehat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q(\hat{J}). \quad (2.15)$$

	Tb ³⁺	Dy ³⁺	Ho ³⁺	Er ³⁺
g_j	$\frac{3}{2}$	$\frac{4}{3}$	$\frac{5}{4}$	$\frac{6}{5}$
α_2	$\frac{-1}{3^2 \cdot 11}$	$\frac{-2}{3^2 \cdot 5 \cdot 7}$	$\frac{-1}{2 \cdot 3^2 \cdot 5^2}$	$\frac{2^2}{3^2 \cdot 5^2 \cdot 7}$
α_4	$\frac{2}{3^3 \cdot 5 \cdot 11^2}$	$\frac{-2^3}{3^3 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$	$\frac{-1}{2 \cdot 3 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$	$\frac{2}{3^2 \cdot 5 \cdot 7 \cdot 11 \cdot 13}$
α_6	$\frac{-1}{3^4 \cdot 7 \cdot 11^2 \cdot 13}$	$\frac{2^2}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$	$\frac{-5}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$	$\frac{2^3}{3^3 \cdot 7 \cdot 11^2 \cdot 13^2}$

Tab. 2.1: Ground state constants α_k used in the Stevens crystal field operator equivalent notation described in equation 2.14 [68].

k=2	$\hat{O}_2^0 = 3\hat{J}_z^2 - J(J+1)$ $\hat{O}_2^2 = \frac{1}{2}(\hat{J}_+^2 + \hat{J}_-^2)$
k=4	$\hat{O}_4^0 = 35\hat{J}_z^4 - 30J(J+1)\hat{J}_z^2 + 25\hat{J}_z^2 - 6J(J+1) + 3J^2(J+1)^2$ $\hat{O}_4^2 = \frac{1}{2}\{(7\hat{J}_z^2 - J(J+1) - 5)(\hat{J}_+^2 + \hat{J}_-^2)\}_S$ $\hat{O}_4^4 = \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4)$
k=6	$\hat{O}_6^0 = 231\hat{J}_z^6 - 315J(J+1)\hat{J}_z^4 + 105J^2(J+1)^2\hat{J}_z^2 - 525J(J+1)\hat{J}_z^2$ $+ 294\hat{J}_z^2 - 5J^3(J+1)^3 + 40J^2(J+1)^2 - 60J(J+1)$ $\hat{O}_6^4 = \frac{1}{2}\{(11\hat{J}_z^2 - J(J+1) - 38)(\hat{J}_+^4 + \hat{J}_-^4)\}$ $\hat{O}_6^6 = \frac{1}{2}(\hat{J}_+^6 + \hat{J}_-^6)$
$\{\hat{A}, \hat{B}\}_S$ is the shorthand notation for $\frac{1}{2}(\hat{A}\hat{B} + \hat{B}\hat{A})$	

Tab. 2.2: Stevens equivalent operators for $k = 2, 4$ and 6 and q even [1].

Unfortunately B_k^q is also used - in literature and in the beginning of this section - for the crystal field parameters of the Wybourne approach. Both are not identical. Therefore, care has to be taken, if the crystal field parameter B_k^q appears in the context of the Wybourne or Stevens formalism.

Symmetry considerations

In a crystal field of a certain symmetry, some of the crystal field parameters are zero. Therefore, any symmetry simplifies the crystal field Hamiltonian considerably. In Table 2.3 the crystal field parameters, which have to be considered, are presented for different crystal field symmetries.

k	$ q $	D_{2h}	D_{3h}	D_{4h}	$D_{\infty h}$	D_{2d}	D_{4d}	C_{2v}	C_{3v}	C_{4v}	$C_{\infty v}$	C_{2h}	C_{3h}	C_{4h}	C_2	S_4	C_1
2	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2	1																$\pm$
2	2	+						+				$\pm$			$\pm$		$\pm$
4	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4	1																$\pm$
4	2	+						+				$\pm$			$\pm$		$\pm$
4	3								+								$\pm$
4	4	+		+		+		+		+		$\pm$		$\pm$	$\pm$	$\pm$	$\pm$
6	0	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
6	1																$\pm$
6	2	+						+				$\pm$			$\pm$		$\pm$
6	3								+								$\pm$
6	4	+		+		+		+		+		$\pm$		$\pm$	$\pm$	$\pm$	$\pm$
6	5																$\pm$
6	6	+	+					+	+			$\pm$	$\pm$		$\pm$		$\pm$

Tab. 2.3: Scheme of crystal field parameters for different crystal field symmetries [79].

2.1.4 J -mixing, non-pure Russell-Saunders wave functions, and configuration interaction

In the above treatment, several effects namely the J -mixing, non-pure Russell-Saunders wave functions, and configuration interaction were neglected. They can be described in terms of higher order perturbations to the above treatment. In the following, the effects and their origin are shortly described for a deeper understanding, it is then referred to the literature.

Non-pure Russell-Saunders wave functions

The issue of non-pure Russell-Saunders wave functions was mentioned in Section 2.1.2 and is a result of the intermediate coupling scheme. The spin-orbit interaction mixes states with the same J but different L and S quantum numbers [68]. As described above, the ground multiplets are typically 95% pure Russell-Saunders state [11]. The mixing does not affect the Stevens operator equivalents, but changes the operator equivalent factors α_k . Therefore, it can be considered by a rescaling of the crystal parameters B_k^q [11].

J -mixing

J -mixing describes that, in lanthanides, multiplets with different J can be admixed by the crystal field Hamiltonian. Therefore, the J -mixing removes J and J_z as good quantum number. For this case J_z can be replaced by a weaker quantum number, the crystal quantum number, which corresponds to the irreducible representation of the symmetry group of the crystal field [69]. However, in many cases, especially when the energy differences between multiplets with different J are considerable, the J -mixing can be neglected. But, e.g., for the case of dysprosium ethyl sulphate the consideration of the J -mixing leads to a change of the energy-levels in the ground multiplet of around 2.5 cm^{-1} [11].

Configuration interaction

Configuration interaction describes the interaction between the $4f^n$ electron configuration to other configurations, e.g. closed 4d-shell or unfilled 5d-shell. The configuration interaction is caused by Coulomb interaction [68]. Again, the effect is small and primarily leads (in one multiplet) to a pure scaling of the crystal field parameters [80].

2.1.5 Analysis of experimental data

Working with the Stevens operators for the analysis of experimental data requires three preliminary steps:

- the determination of the total angular momentum J of the manifold in question. For most experimental data like magnetization measurements and far infrared measurements at low temperatures, the total angular momentum of the ground manifold is given by Hund's rule as described previously.
- the derivation of the symmetry of the surrounding crystal field. Due to symmetry considerations often many of the crystal field parameters can be set to zero [72].
- the Hamiltonian matrix can be set up.

After these steps the crystal field parameters can be fitted and compared to theoretically determined parameters or parameters derived from other experiments.

2.1.6 Low symmetry crystal fields and ab-initio calculations

In all compounds studied in this thesis the crystal field is of low symmetry. In a low symmetry environment the described crystal field model is difficult to use. For a certain crystal environment it can not be assumed that any of the crystal field parameters are zero. This leads for comparison with experimental data to a large overparametrization of the system. Another way of obtaining the splitting of the energy-levels is given by ab-initio calculations. The ab-initio technique used for lanthanides in low symmetry environments in the last years is the CASSCF/RASSI-SO (Complete Active Space Self Consistent Field) technique. The large spin-orbit coupling and the large number of electrons in the systems makes this technique very time-consuming and complicated [4].

For molecular magnetism, it was shown that many dysprosium compounds embedded in a low symmetry environment show single-molecule magnetic behavior, namely slow relaxation of the magnetization. Ab-initio calculations showed a strong Ising-like anisotropy of the ground Kramers-doublet with the maximum projection of nearly $|M_J| = 15/2$ [5, 17, 57, 81].

2.2 Magnetic relaxation

Magnetic relaxation lies at the heart of single-molecular magnetic materials. In the field of lanthanide-based single-molecular magnetic materials there are many open issues, e.g. different relaxation mechanisms often coexist in one material at the same temperature and complicate the interpretation. For the compounds studied in this thesis, we will discuss different possible relaxation mechanisms. Therefore, this section presents a general introduction into magnetic relaxation, the master-equation approach and the properties of the phonon bath, which takes part in the relaxation process. In addition, we will give a short summary, how the magnetic relaxation time is measured. After that, we will summarize in Section 2.3 and 2.4 the possible relaxation processes, which can occur in lanthanides and single-chain magnets.

Relaxation includes a coupling between the relaxing system and the environment. Therefore, it is not sufficient to set up only a Hamiltonian for the system itself, but in addition, to describe also the coupling to the environment. In single-molecular magnetic materials the relaxation of the magnetization takes place mainly by the interaction with the crystal lattice by the exchange of phonons. The process of relaxation describes that, if a system is in a non-equilibrium state, it will relax into its equilibrium with the relaxation time τ . In molecular magnetism the crystal under study is thought to consist out of individual non-interacting magnetic molecules. The return to equilibrium can be described by an exponential function $M(t) = M_0 + (M_0 - M_{eq}) \cdot \exp(t/\tau)$ with the relaxation time τ , the equilibrium magnetization M_{eq} , and the starting non-equilibrium magnetization M_0 . For real systems the process is sometimes slowed down due to correlation like dipolar coupling between the individual molecules. Furthermore, different relaxation times can occur [2]. In single-ion lanthanide compounds two or more different relaxation times can be observed (even at the same temperature).

2.2.1 Measurement techniques

There are three different measurement techniques used to determine the relaxation time. First the most obvious technique: The crystal of the magnetic material is magnetized inside a magnetic field, the magnetic field is then switched off, and the magnetic moment of the sample is monitored over time. The resulting magnetization curve can then be fitted with the exponential function and the relaxation time is derived.

Because this procedure can be time consuming for slow relaxing materials, the second technique, called AC-susceptibility, is more widely used. A small (few Oersted) oscillating magnetic field is applied and the in- and out-of phase magnetic signal of the sample is measured. In simple terms the relaxation time can be determined by the maximum of the out-of phase signal viewed over frequency with the formula $\nu_{max} = 1/\tau$ [2]. The relaxation time can also be determined by EPR-measurements. In

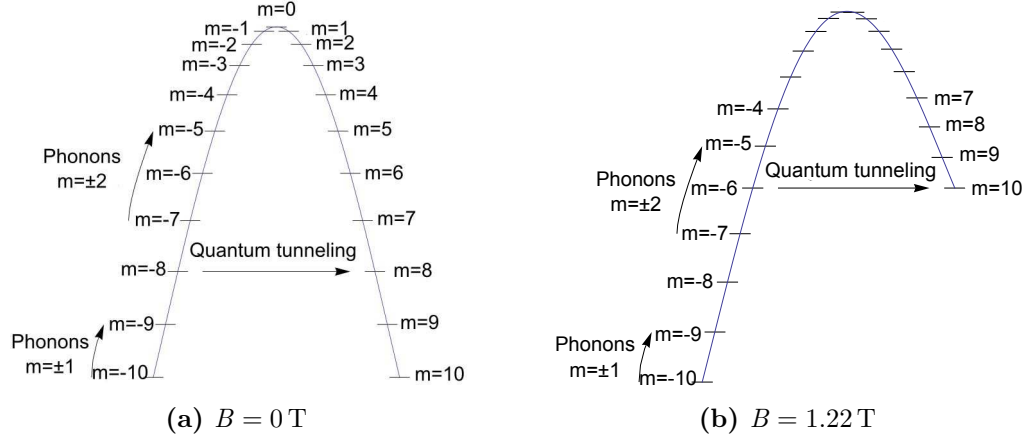


Fig. 2.2: Scheme of the relaxation process in Mn_{12}Ac for two different magnetic fields on the left $B = 0 \text{ T}$ and on the right $B = 1.22 \text{ T}$.

EPR-measurements a static magnetic field is applied and the transition between the two lowest states (for Kramers ions the ground doublet split by the magnetic field) is monitored and the relaxation time T_1 (spin-lattice) and T_2 (spin-spin) can be determined. In general, the spin-lattice relaxation time T_1 can be different from the relaxation time of the magnetization determined by AC-susceptibility measurements [2].

2.2.2 Magnetic relaxation in cluster SMMs

As an example of the relaxation process of single-molecular magnetic materials, Mn_{12}Ac is discussed in this chapter. The processes leading to magnetic relaxation in cluster SMMs are well explored, especially for Mn_{12}Ac [2, 82, 83]. At low temperatures, the spins of the manganese-ions couple together to form an effective spin with $S=10$, which is rigid at low temperatures. The system can then be described by a giant-spin Hamiltonian, which reads due to the tetragonal symmetry of the molecule:

$$\begin{aligned} \hat{H} &= -D\hat{S}_z^2 - A\hat{S}_z^4 + \hat{H}' + \hat{H}_{s-ph} \\ \hat{H}' &= E(\hat{S}_x^2 + \hat{S}_y^2) + g\mu_B\hat{\vec{S}}\hat{\vec{B}} \end{aligned} \quad (2.16)$$

where the D-term describes the axial anisotropy, the A-term the next higher order longitudinal term, the E-term the second order transverse anisotropy and the last term the Zeeman-energy due to an applied magnetic field. The terms differ strongly in their weight with $D \gg A \gg E$. $\hat{H}_{s-ph}$ describes the coupling to the phonon bath. The axial anisotropy splits the states of the $S = 10$ ground state into $(2S+1)/2$ twofold degenerate states with $m_S = \pm 10, 9, \dots, 1$ only the $m_S = 0$ is non-degenerate, leading

to an energy barrier structure. The degenerate pairs can only be split by a magnetic field. At low temperatures, only the two ground states $m_S = \pm 10$ are noteworthy populated. If the system is forced into a non equilibrium state by the application of an applied magnetic field, the relaxation of the magnetization consists mainly out of restoring the equilibrium population of the $m_S = \pm 10$ states after the field is switched off. The giant-spin Hamiltonian without the disturbing $\hat{H}'$ commutes with the $\hat{S}_z$ operator. Therefore, the magnetization in z-direction is a conserved quantity and the $m_S = \pm 10, 9, \dots, 1$ sublevels are eigenstates of the Hamiltonian. Without additional terms the magnetization can not relax. First we will discuss the spin-phonon term. The spin-phonon coupling can induce transitions between m-states differing in $m = \pm 1$ and $m = \pm 2$. This results in the observed behavior that the relaxation time follows an Arrhenius law with an activation barrier of $\Delta = DS^2$. To relax from $m_S = -10$ to $m_S = +10$ the spin has to climb up the barrier by the absorption of phonons because states on different sides of the barrier are not connected. The term $\hat{H}'$ does not commute with $\hat{S}_z$ can give rise to tunneling, if two states of different sides of the energy barrier have the same energy. For example, the E-term allows quantum tunneling between the ground states. However, E is small and connects $m_S = -10$ and $m_S = +10$ only by higher orders in perturbation. At low temperatures, where the relaxation by spin-phonon interaction is negligible, a constant relaxation time is observed which can be attributed to the quantum tunneling between the two ground states. If a magnetic field is applied, states at different sides of the barrier can coincide in energy, and quantum tunneling can be observed due to an abrupt decrease in the relaxation time (see Figure 2.2). This thermally activated tunneling process includes both the spin-phonon coupling to climb up to the state, in which tunneling can occur, and then tunneling to the other side of the barrier. The second order transverse anisotropy term $E(\hat{S}_x^2 + \hat{S}_y^2)$ only connects states differing in its m value by $m = \pm 4k$ with $k = 0, 1, 2, \dots$. Therefore, tunneling should only be observed if states of the same energy also differ by $m = \pm 4k$. In contrast experimental data revealed that quantum tunneling can be observed between all states with nearly the same amplitude, if they are of same energy. This was explained by isomer disorder of Mn_{12}Ac . The different relaxation pathways are summarized in Figure 2.2.

2.2.3 Master equation

For the description of the relaxation of the magnetization in single-molecular magnetic materials, it is useful, to introduce some general equations of non-equilibrium statistical mechanics, to describe how a system reaches its equilibrium state. The results will then be used in Section 2.3.1 for the derivation of the relaxation of the magnetization in lanthanides. The description follows in most parts Reference [84] and makes use of the master-equation approach. The master equation can be derived from the von-Neumann equation for the whole system (system + bath) by tracing over the degrees of freedom of the bath. Additionally, it is assumed that: first, system and bath

are uncorrelated at a time $t = 0$, second, system and bath are weakly coupled (Born approximation), third, the time-evolution at a time t only depends on the system state at the time t (Markov approximation).

In a non-equilibrium state the population numbers are changed, by e.g. an external force, from their equilibrium population. In general the system will then relax to its equilibrium state by transitions between the states. The following considerations are not limited to magnetic systems. They are in general applicable to non-equilibrium problems. Our system should consist out of n different states, which have a population according to p_j for the j th state. In statistical quantum mechanics the population of states is given by the diagonal elements of the density matrix. The time evolution of the system can be described by a phenomenological set of first-order differential equations, which can be set up in a so-called master equation:

$$\begin{aligned}\frac{d}{dt}p(\vec{t}) &= \mathbf{W}p(\vec{t}) \\ &= \sum_j w_{ij}p_j(t).\end{aligned}\tag{2.17}$$

The vector $p(\vec{t})$ contains the populations of the states p_j . The entries of the matrix $\mathbf{W}$ are the transition probabilities w_{ij} for the transition from the j th to the i th state. The diagonal elements are $w_{ii} = -\sum_{j \neq i} w_{ji}$. Thereby, it is ensured that the total population number is constant. We assume that the probabilities w_{ij} itself are time independent. In general also off-diagonal elements of the density matrix have to be taken into account, and more complex quantum master equations need to be used [82]. As for example, the here introduced master equation does not describe quantum tunneling of the magnetization.

In thermal equilibrium the population p_j of the states is given by the Boltzmann distribution

$$p_j^{equi} = \frac{e^{-E_j/k_B T}}{\sum_j e^{-E_j/k_B T}},\tag{2.18}$$

with the energy of the state E_j and the temperature T . In addition, the system should obey the detailed balance condition:

$$w_{ij}p_i^{equi} = w_{ji}p_j^{equi}.\tag{2.19}$$

Therefore,

$$\mathbf{W}\vec{p}^{equi} = 0. \quad (2.20)$$

Decomposition of the master equation into its eigenvectors and eigenvalues, yields the relaxation times together with the different relaxing modes given by the eigenvectors $\vec{p}_n$. The relaxation times τ_n for the different modes (eigenvectors) are:

$$\tau_n = -\frac{1}{\lambda_n}, \quad (2.21)$$

with λ_n the eigenvalue of the i th eigenvector.

With this considerations the solution of Equation 2.17 is by using the spectral decomposition [85] $\mathbf{W} = \sum_n \vec{p}_n \vec{p}_n^T$:

$$\begin{aligned} \vec{p}(t) &= \sum_n \vec{p}_n e^{\lambda_n t} (\vec{p}_n^T \cdot \vec{p}^0), \\ &= \vec{p}^{equi} + \sum_{n \neq n_0} \vec{p}_n e^{\lambda_n t} (\vec{p}_n^T \cdot \vec{p}^0). \end{aligned} \quad (2.22)$$

with $\vec{p}^0$ the population at the time $t = 0$ and by using normalized vectors $\vec{p}(t) \forall t$. $\vec{p}_n^T$ denotes the left eigenvector of $\mathbf{W}$ which is defined by $\mathbf{W}^T \vec{p}_n^T = \lambda_n \vec{p}_n^T$. The eigenvector $\vec{p}^{equi}$ of the equilibrium population corresponds to an eigenvalue $\lambda_{n_0} = 0$. The non-relaxing equilibrium mode leads to the above simplifications.

Finally, we are interested in the decay of the magnetization over time. Therefore, the next step is to relate the population of the states to the magnetization. In statistical quantum mechanics the magnetization (in z-direction) is given by $M = Tr\{\hat{\rho} \hat{S}_z\}$. We get $M_z(t) = \vec{m} \cdot \vec{p}(t)$, where $\vec{m}$ contains the magnetization (m-quantum numbers) of the different states. Therefore, the magnetization is given by:

$$\begin{aligned} M(t) &= \sum_n \vec{m} \cdot \vec{p}_n e^{\lambda_n t} (\vec{p}_n^T \cdot \vec{p}^0), \\ &= \vec{m} \cdot \vec{p}^{equi} + \sum_{n \neq n_0} \vec{m} \cdot \vec{p}_n e^{\lambda_n t} (\vec{p}_n^T \cdot \vec{p}^0). \end{aligned} \quad (2.23)$$

Depending on the starting configuration, the system can be divided into n different modes given by the eigenvectors with the weighting factor $\vec{p}_n^T \cdot \vec{p}^0$. Each of this modes reaches equilibrium independent from each other with a relaxation time $\tau_n = -1/\lambda_n$,

whereas the mode with λ_n corresponds to the equilibrium configuration, which does not decay. To every mode also belongs a part of the total magnetization difference $\Delta M_n = M_{0n} - M_{equi} = (\vec{m} \cdot \vec{p}_n) \cdot (\vec{p}_n^T \cdot \vec{p}^0) - \vec{m} \cdot \vec{p}^{equi}$ which decays with $\tau_n = -1/\lambda_n$. In the following we are often faced with two-level system, because only the two lowest states are of importance at low temperatures. Following the introduced approach, the master equation is given by a two-by-two matrix:

$$\frac{d}{dt} \begin{pmatrix} p_1(t) \\ p_2(t) \end{pmatrix} = \begin{pmatrix} -w_{21} & w_{12} \\ w_{21} & -w_{12} \end{pmatrix} \begin{pmatrix} p_1(t) \\ p_2(t) \end{pmatrix}. \quad (2.24)$$

The first eigenvalue of this equation is zero and belongs to the equilibrium configuration. The second eigenvalue represents the relaxation time of the system:

$$\tau_1 = -\frac{1}{\lambda_1} = \frac{1}{w_{12} + w_{21}}. \quad (2.25)$$

2.2.4 Phonon bath

For the considerations of the magnetic relaxation in lanthanides in Section 2.3.1, the properties of the phonon bath are of crucial importance. The density of states of a phonon bath of temperature T is given by for the wave-vector range $k + dk$ and the frequency range $\omega + d\omega$:

$$\begin{aligned} \rho_{ph,k} dk &= \frac{4\pi V}{(2\pi)^3} 3k^2 dk = \frac{4\pi M}{\varrho(2\pi)^3} 3k^2 dk \\ \rho_{ph,\omega} d\omega &= \frac{1}{2\pi^2 v^3} 3\omega^2 d\omega, \end{aligned} \quad (2.26)$$

where we have used the volume V , the mass M , the mass density ϱ , and the velocity of sound v of the crystal, the factor 3 arises from the three polarisation directions (two transversal and one longitudinal) which are assumed to have the same velocity. The two equations are connected by $k = \omega/v$. The Debye-model introduces a cutoff-frequency ω_D (cutoff-wavenumber k_D that there are no phonons above a certain frequency).

The Bose-Einstein statistics yields for the statistical average of the occupation of one mode:

$$\langle n_\omega \rangle = \frac{1}{e^{\hbar\omega/kT} - 1}. \quad (2.27)$$

Combining the two Equations 2.26 and 2.27 yields the energy density:

$$\rho_{ED,w}d\omega = \frac{3\hbar}{2\pi^2v^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} d\omega. \quad (2.28)$$

In second quantization creation and annihilation operators can be used to create and annihilate phonons acting on an abstract Hilbert space. The elements n_k of the Hilbert space represent the occupation number of a state with the wave vector $\vec{k}$. It can be shown that:

$$\begin{aligned} |n_k - 1\rangle &= \frac{1}{\sqrt{n_k}} \hat{a}^\dagger |n_k\rangle \\ |n_k + 1\rangle &= \frac{1}{\sqrt{n_k + 1}} \hat{a} |n_k\rangle. \end{aligned} \quad (2.29)$$

The above considerations are used in the next Section 2.3 for the description of the relaxation mechanisms in lanthanides.

2.3 Magnetic relaxation of lanthanides in crystal fields

For slowly relaxing magnetic materials (SMMs, SIMs, SCMs) the relaxation properties are of vital importance. From a theoretical point of view the description of the magnetic relaxation is much more challenging than the static magnetic properties. For lanthanide based single-ion magnets, primarily the description of the relaxation process is based on works done on lanthanides on other materials in the 1950s and 1960s of the last century [6]. The relaxation mechanisms observed for lanthanide ions are:

1. the direct process (one phonon process),
2. the Orbach process using acoustical phonons (two phonon process),
3. the Raman process (two phonon process),
4. the Orbach and Raman process using optical phonons,

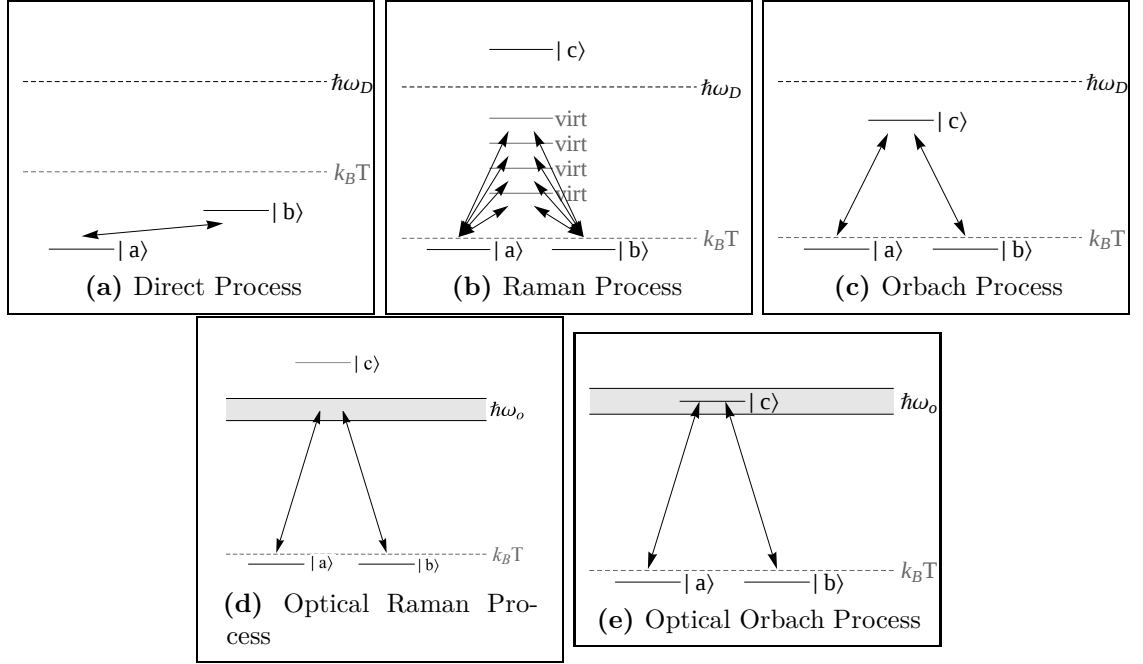


Fig. 2.3: Level Scheme for spin-lattice relaxation of non-Kramers ions with the Debye frequency ω_D and the optical phonon frequency ω_0 .

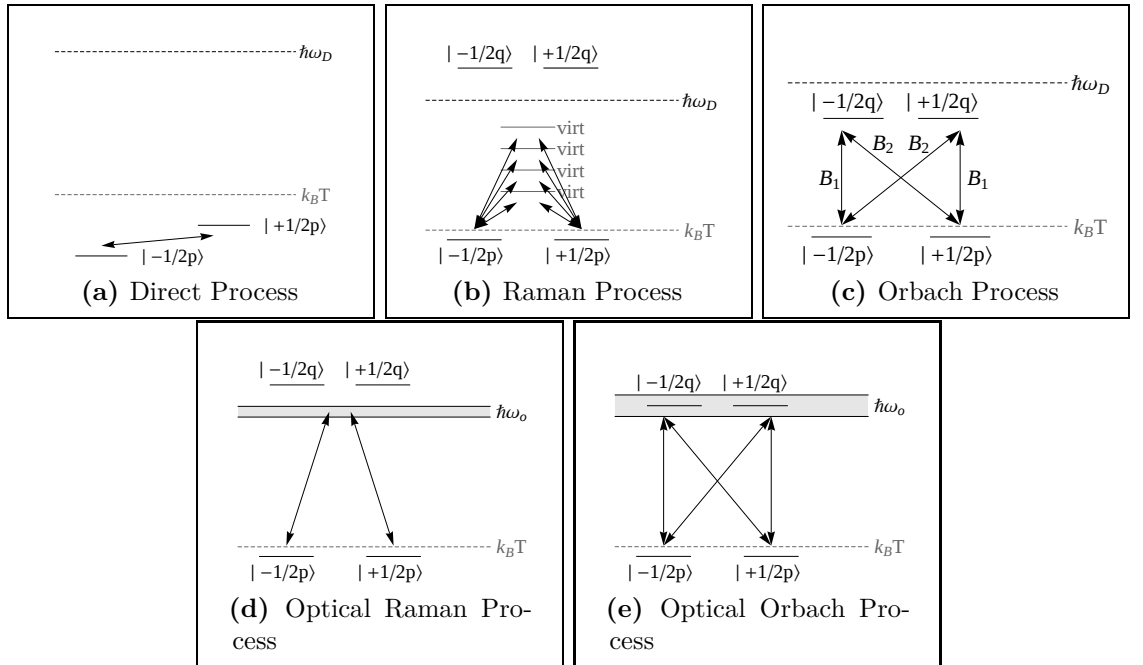


Fig. 2.4: Level Scheme for spin-lattice relaxation of Kramers ions with the Debye frequency ω_D and the optical phonon frequency ω_0 .

The processes take place by interactions with lattice vibrations (see Figure 2.3 and Figure 2.4 for a scheme of the processes). In addition to this processes also quantum tunneling e.g. between the ground states can take place which can alter the relaxation properties especially in zero magnetic field. A priori, it is difficult to judge, which of the above relaxation processes dominates in a certain compound. In addition, the direct calculation of the magnitudes of the above processes is complex or even impracticable - even when the static properties of the compound are known. Therefore, the relaxation process is determined by experimental evidences. As the different relaxation mechanisms follow different magnetic field- and temperature dependencies, the relaxation mechanism can be identified by best-fit methods. For Kramers-ions the relaxation time can be summarized as [6, 16, 86, 87, 88]

$$\begin{aligned}\tau_{exp}^{-1} &= \tau_{direct}^{-1} + \tau_{Orbach}^{-1} + \tau_{Raman}^{-1} + \tau_{optical}^{-1} + \tau_{QTM}^{-1} + \tau_{TA-QTM}^{-1} \\ \tau_{exp}^{-1}(T, B) &= AH^4T + Be^{-\Delta_c/kT} + CT^9(H^2T^7) + De^{-\Delta_{\hbar\omega_0}/kT} + \text{const}_{QTM}\end{aligned}\quad (2.30)$$

with Δ_c the energy difference to the excited doublet via which the Orbach process operates and Δ_{ω_0} the energy of the optical phonon mode active in the relaxation process. A, B, C, D, and E give the contribution of the different relaxation processes. And for non-Kramers-ions the relaxation time can be written as:

$$\begin{aligned}\tau_{exp}^{-1} &= \tau_{direct}^{-1} + \tau_{Orbach}^{-1} + \tau_{Raman}^{-1} + \tau_{optical}^{-1} + \tau_{QTM}^{-1} + \tau_{TA-QTM}^{-1} \\ \tau_{exp}^{-1}(T, B) &= AH^2T + Be^{-\Delta_c/kT} + CT^7 + De^{-\Delta_{\hbar\omega_0}/kT} + \text{const}_{QTM}.\end{aligned}\quad (2.31)$$

For the direct process and the optical phonon process, the relaxation time follows a temperature dependence including a thermal activation. The exponential dependence on temperature can be described by an Arrhenius law, where the energy barrier is given for the Orbach process by the energy of the excited doublet Δ_c and for the optical phonon process by the energy of the optical phonon $\hbar\omega_0$. To avoid confusion, it should be mentioned that the Raman process and the direct process, also include the thermal properties of the lattice, but normally the splitting of the ground doublet is lower in energy than the thermal energy kT . Therefore, the different dependencies on temperature are a consequence of the usually measured temperature range. At lower temperatures, also the direct process could lead to an exponential temperature dependence. Depending on the energy-level structure the Raman process for Kramers-ion can scale as T^9 or H^2T^7 [6]. It has to be mentioned that in general also other terms can be found caused by the spin-phonon interaction, which can be found for example in the work of Shrivastava [86]. A detailed description of the relaxation processes and a derivation of the different relaxation times is presented in the following Sections.

2.3.1 Detailed description of spin-lattice interactions

A fundamental issue is the type of interaction, which couples the "spin" (total angular momentum) to the thermal bath (the lattice). First attempts¹ were made by Waller (1932) [89] to model the coupling by modulation of the spin-spin interaction caused by the phonons. In this picture, the spins on one side are subject to an alternating magnetic field by spins on other sides, which fluctuate under the action of the lattice vibrations. But, the results were in striking contrast with experimental data. The obtained relaxation times were orders of magnitude higher than the experimental ones. Works done by Heitler and Teller (1936) [90], Kronig (1939) [91] and Van Vleck (1940) [92] considered the modulation of the crystal field as the driving causes for the relaxation process. Their results are of the correct order of magnitude. In our days this process is considered to be the most important one [3, 7]. A detailed overview is given by Orbach "Spin-lattice relaxation in rare-earth salts" [6] published 1961. This description often leads to the right temperature and magnetic field dependence. But, only seldom (and up to date not at all in molecular magnetism) quantitative results are obtained due to the difficulty of expanding the crystal field parameters in the dynamic case.

In the following, we will describe in detail the relaxation process caused by the modulation of the crystal field. The spin-lattice interaction is caused by the dynamic crystalline field effect: Deformations - due to phonons - of the equilibrium configuration of the surrounding ions change the crystalline electric field of the lanthanide ion. The approach follows the framework which Stevens [77] used to explain the static crystal field effects. Therefore, the orbit-lattice interaction is expanded in powers of the strain $\epsilon_{nm}(\vec{r}_j)$. In first order it reads:

$$\begin{aligned} V_{ol}(j) &= \sum_{n,m} V_n^m(\vec{r}_j) \epsilon_{nm}(\vec{r}_j) \\ &= \sum_{n,m} A_n^m \langle r^n \rangle \langle J || x_n || J \rangle O_n^m(j) \epsilon_{nm}(\vec{r}_j), \end{aligned} \quad (2.32)$$

where A_n^m is a constant as in the Stevens approach, $\vec{r}_j$ the radius vector to the j th lanthanide ion, $O_n^m(j)$ the Stevens operators, and $\langle J || x_n || J \rangle = \alpha, \beta$ or γ according as $n = 2, 4$ or 6 , respectively. The strain tensor components $\epsilon_{nm}(\vec{r}_j)$ transform according to an irreducible representation of the lattice. The rotation vectors are linear in the phonon annihilation and creation operators. In the following an averaged strain ϵ_{nm} will be used neglecting all directional properties.

A more intuitive expansion of the crystal field is given by, e.g., Shrivastava [86]. There,

¹ The historical survey follows the textbook of Abragam and Bleaney [1].

the spin lattice interaction is expanded by the normal coordinates into a Taylor series:

$$V_{ol,alternative} = \sum_i V_1 \frac{1}{R_i} \delta R_i \quad (2.33)$$

where

$$V_1 = \sum_i R_i \sum_{n,m} \frac{\partial}{\partial R_i} V_n^m \quad (2.34)$$

are the derivatives of the crystal potential, the coordinates of the i th neighbor of displacement δR_i , which is given by:

$$\delta R_i = \left(\frac{\hbar}{2M\omega} \right) \frac{1}{2} (\hat{a}_k^\dagger + \hat{a}_k) e^{i\vec{k}\vec{R}_i} \quad (2.35)$$

with the wave-vector $\vec{k}$ and the frequency ω of the lattice wave. If there is a center of symmetry, the exponential function reduces to the sine-function $\sin(\vec{k}\vec{R}_i)$. At low temperatures, the long-wave length approximation $\vec{k}\vec{R}_i \ll 1$ can be applied. The sine-function then reduces to $\sin(\vec{k}\vec{R}_i) \sim \vec{k}\vec{R}_i$. In general, the long-wave length approximation is not necessary and the anisotropy of the lattice waves can be taken into account by using Bessel-functions. A description of this procedure is given by Shrivastava [86]. Inserting Equation 2.35 into Equation 2.33 the spin lattice interaction Hamiltonian can be derived:

$$\hat{V}_{ol1} = \sum_k V_1 R^{-1} \left(\frac{\hbar}{2M\omega_k} \right)^{1/2} (\hat{a}_k^\dagger + \hat{a}_k) \sin(\vec{k}\vec{R}), \quad (2.36)$$

here we restricted ourselves to the first order of the Taylor expansion for acoustical phonons. Both expansions of the expansions - the first with respect to the strain ϵ_{nm} used by Orbach [6] and the second with respect to the normal coordinates used by Shrivastava [86] - are equivalent and lead to the same results.

The relaxation process caused by the described interactions can lead to different mechanisms which can be more or less pronounced depending on the host crystal, the temperature, and the magnetic field. The direct process is of first order in perturbation theory, the spin-lattice interaction operator V_{ol} acts once. The Raman- and Orbach process are of second order in perturbation theory, the spin-lattice interaction

operator V_{ol} acts twice. In difference to the Raman process, the Orbach process is a resonant process, like the direct process. In general it has to be mentioned that there can also be additional contributions by higher orders of perturbation. For example a two phonon process is also possible in first order of perturbation, if the spin-lattice interaction is expanded up to second order in the Taylor expansion. Here, we will only discuss one of the additional processes: the Orbach processes using optical phonons. In general, all of the previously discussed mechanisms can also be driven by optical phonons. Later on, another relaxation process will be discussed belonging to the quantum tunneling of the magnetization which is not directly influenced by the phonon bath.

2.3.1.1 Direct process

In the direct process a transition between the two lowest states $|a\rangle$ and $|b\rangle$ takes place by the absorption or emission of one phonon. The derivation assumes that the external magnetic field is much larger than the dipolar field between the spins. An extension for smaller fields is given by Orbach [93]. If a perturbation acts on a system, the probability per unit time to make a transition between two states is given by first-order time dependent perturbation theory as (using the notation by Shrivastava [86]):

$$P(b, n_k - 1 \leftarrow a, n_k) = \frac{2\pi}{\hbar} |\langle b, n_k - 1 | V_{ol1} | a, n_k \rangle|^2 \rho(E) \quad (2.37)$$

where $\rho(E)$ is the density of final states and $|a, n_k, n_k1, \dots, n_k D\rangle$ the Born-Oppenheimer products of the spin states. Inserting the spin-lattice interaction (Equation 2.36), the matrix element for the annihilation of an phonon $|\langle n_k - 1 | \hat{a}^\dagger | n_k \rangle|^2 = n_k$ (see Equation 2.29), the density of phonon states (see Equation 2.26), using the long-wavelength approximation, and integrating over the k-space results in:

$$P(b \leftarrow a) = \frac{2\pi}{\hbar} \int_0^{k_d} |\langle b | V_{ol1} | a \rangle|^2 \frac{\hbar}{2M\omega_k} k^2 n_k \delta(\Delta_{ab} - \hbar\omega_k) \frac{4\pi V}{(2\pi)^3} 3k^2 dk \quad (2.38)$$

where the Dirac δ -function ensures the conservation of energy, the notation $E_a - E_b = \Delta_{ab}$ is used, and the integration runs from zero to the Debye cut-off wave-vector k_D .

Using that $k = \omega/v$ ($dk = d\omega/v$) with v the velocity of sound and $\rho = M/V$, the equation becomes:

$$\begin{aligned} P(b \leftarrow a) &= \frac{2\pi}{\hbar} \int_0^{\omega_d} |\langle b|V_{ol1}|a\rangle|^2 \frac{4\pi\hbar}{2\rho(2\pi)^3} 3 \frac{\omega_k^3}{v^4} n_\omega \delta(\Delta_{ab} - \hbar\omega_k) \frac{1}{v} d\omega \\ &= \frac{3|\langle b|V_{ol1}|a\rangle|^2}{2\pi\hbar\rho v^5} \left(\frac{\Delta_{ab}}{\hbar}\right)^3 n(\delta_{ab}), \end{aligned} \quad (2.39)$$

where we have used in the last step that $\int f(a)\delta(a-x)dx = f(a)$, if a is part of the integration. This is the case because Δ_{ab} is small and, therefore, $\omega = \Delta_{ab}/\hbar$ lies between zero and the Debye cut-off frequency ω_D .

The probability for the inverse process - going from state $|b\rangle$ to state $|a\rangle$ - is equivalent to the former. In this process a phonon is created and the matrix element changes from $|\langle n_k - 1|\hat{a}^\dagger|n_k\rangle|^2 = n_k$ to $|\langle n_k + 1|\hat{a}|n_k\rangle|^2 = n_k + 1$. Therefore, we derive:

$$P(a \leftarrow b) = \frac{3|\langle b|V_{ol1}|a\rangle|^2}{2\pi\hbar\rho v^5} \left(\frac{\Delta_{ab}}{\hbar}\right)^3 (n(\Delta_{ab}) + 1), \quad (2.40)$$

with the transition matrix element $|\langle b|V_{ol1}|a\rangle|^2 = |\langle a|V_{ol1}|b\rangle|^2$. Using the master equation approach of Section 2.2.3, the relaxation time of the two-level system is given by Equation 1:

$$1/\tau_1 = P(a \leftarrow b) + P(b \leftarrow a) = \frac{3|\langle b|V_{ol1}|a\rangle|^2}{2\pi\hbar\rho v^5} \left(\frac{\Delta_{ab}}{\hbar}\right)^3 (2n(\Delta_{ab}) + 1). \quad (2.41)$$

The occupation of one mode $n(\delta_{ab})$ is given by the Bose-Einstein statistics (Equation 2.27). Using the definition of the cotangens hyperbolicus $\coth(x) = 1 + \frac{2}{e^{2x}-1}$, the last parentheses simplifies to $2n(\Delta_{ab}) + 1 = \coth(\hbar\omega/2kT)$.

Non-Kramers ions

For non-Kramers ions Equation 2.41 can directly be applied because the electric field of the spin-lattice interaction can connect states $|a\rangle$ and $|b\rangle$:

$$1/\tau_1 = \frac{3|\langle b|V_{ol1}|a\rangle|^2}{2\pi\hbar\rho v^5} \left(\frac{\Delta_{ab}}{\hbar}\right)^3 \coth(\hbar\omega/2kT). \quad (2.42)$$

To obtain a simple temperature and magnetic field dependence, the result can be further simplified: 1. Under the assumption that the two levels are degenerate at zero magnetic field, we obtain for the energy difference $\Delta_{ab} = \hbar\omega = g\mu_B H$. 2. If furthermore the applied magnetic field is small, so that $\hbar\omega \ll 2kT$, the cotangens hyperbolicus can be approximated by $\coth(\hbar\omega/2kT) \sim \frac{2kT}{\hbar\omega}$, which results in:

$$\begin{aligned} 1/\tau_1 &= \frac{3|\langle b|V_{ol1}|a\rangle|^2}{\pi\hbar^4\rho v^5}(g\mu_B H)^2 kT \\ &\sim H^2 T. \end{aligned} \quad (2.43)$$

Kramers ions

For Kramers ions the calculation is complicated by the fact that $|\langle b|V_{ol1}|a\rangle|^2 = 0$, if $|a\rangle$ and $|b\rangle$ are the time conjugated states of the lowest Kramers doublet. The direct process is only possible if a magnetic field is present that mixes excited states into the ground doublet. Instead of an external magnetic field, the hyperfine field or the dipolar field can produce the mixing [1]. A rather lengthy calculation (see Reference [6]) yields (using the notation $\pm\frac{1}{2}p$ for the ground Kramers doublet, $\pm\frac{1}{2}q$ for the first excited Kramers doublet, and Δ_q for the energy difference between the ground and first excited Kramers doublet):

$$1/\tau_1 = \frac{12\mu_B^4 g^2 \Lambda^2 H^4 kT}{\pi\hbar^4 \rho v^5 \Delta_q^2} |\vec{h} \cdot \langle -\frac{1}{2}q|\vec{J}| -\frac{1}{2}p\rangle|^2 |\langle -\frac{1}{2}p|V_{ol1}|\frac{1}{2}q\rangle|^2 \quad (2.44)$$

where $\Delta_{ab} = g\mu_B H$ with $g^2 = g_{\parallel}^2 \cos^2 \Phi + g_{\perp}^2 \sin^2 \Phi$ and Φ the angle between the z-axis (crystallographic symmetry axis) and the unit vector of the magnetic field $\vec{h}$. Further the Landé g-factor $\Lambda = \langle J||\Lambda||J\rangle$ was introduced. As a result we obtain the temperature and magnetic field dependence for the direct process:

$$1/\tau_1 \sim H^4 T. \quad (2.45)$$

The relaxation has a strong anisotropy with respect to the direction of the applied magnetic field. Here, we have only treated the interaction with the first excited doublet. In general, the treatment is the same, if higher excited doublets are considered.

2.3.1.2 Two-Phonon Orbach process

The two-phonon Orbach process between the two lowest states operates via an third real excited state $|c\rangle$. Therefore, one phonon is absorbed and another one is emitted. The easiest way is to treat this process as a two step direct process. Using the results obtained for the direct process (Equation 2.40), the first step includes the absorption of a phonon to go from $|b\rangle$ to $|c\rangle$:

$$\begin{aligned} P(c \leftarrow b) &= \frac{3|\langle b|V_{ol1}|c\rangle|^2}{2\pi\hbar\rho v^5} \left(\frac{\Delta_{ab}}{\hbar}\right)^3 (n(\Delta_{bc})) \\ &= B_1(n(\Delta_{bc})), \end{aligned} \quad (2.46)$$

where B_1 is introduced as a prefactor. Second a phonon needs to be emitted to go from $|c\rangle$ to $|b\rangle$:

$$\begin{aligned} P(a \leftarrow c) &= \frac{3|\langle b|V_{ol1}|c\rangle|^2}{2\pi\hbar\rho v^5} \left(\frac{\Delta_{ab}}{\hbar}\right)^3 (n(\Delta_{bc}) + 1) \\ &= B_2(n(\Delta_{bc})), \end{aligned} \quad (2.47)$$

where B_2 is introduced as another prefactor. The reverse process to go from $|a\rangle$ to $|b\rangle$ via $|c\rangle$ is equivalent. If we assume that $|a\rangle$ and $|b\rangle$ have approximately the same energy (low magnetic field), it follows that $\Delta_{ac} \sim \Delta_{bc} = \Delta_c$. If $\Delta_c \gg 2kT$ the population of the phonon modes can be approximated by $n(\Delta_c) = e^{-\Delta_c/kT}$. Solving the resulting system of differential equations with the assumption that the population of state $|c\rangle$ does not change in first order, we get [94, 95]:

$$1/\tau_1 \sim \frac{2B_1B_2}{B_1 + B_2} e^{-\Delta_c/kT}. \quad (2.48)$$

In the limit that $B_1 = B_2 = B$, it reduces to $1/\tau_1 \sim Be^{-\Delta_c/kT}$. In the limit that one of the transition matrix elements is considerably smaller than the other $B_1 \ll B_2$, $1/\tau_1 \sim B_1e^{-\Delta_c/kT}$, so that the smaller transition probability governs the relaxation process.

Kramers ions

For Kramers ions, it is more appropriate to assume that a relaxation process takes place via the two levels of the excited Kramers level. Due to the Kramers theorem,

there are only two different transition probabilities $|\langle b|V_{ol1}|c\rangle|^2 = |\langle a|V_{ol1}|d\rangle|^2 \sim B_1$ and $|\langle b|V_{ol1}|d\rangle|^2 = |\langle a|V_{ol1}|c\rangle|^2 \sim B_2$, which lead to [94, 95]:

$$1/\tau_1 \sim \frac{4B_1B_2}{B_1 + B_2} e^{-\Delta_c/kT}. \quad (2.49)$$

This reduces in the two extremal cases again to: for $B_1 = B_2 = B$ to $1/\tau_1 \sim 2Be^{-\Delta_c/kT}$ and for $B_1 \ll B_2$ to $1/\tau_1 \sim 2B_1e^{-\Delta_c/kT}$.

Throughout the discussion about the Orbach process, we have assumed that the energies of the excited levels $|c\rangle$ and $|d\rangle$ are lower than the Debye cut off frequency ω_D . If the energy of $|c\rangle$ and $|d\rangle$ is higher than ω_D , the Orbach process using accoustical phonons is not possible.

2.3.1.3 Raman process

The Raman process arises due to a non-resonant, two-phonon process and operates via a virtual excited state. The energy difference of the absorbed and the emitted photon corresponds to the level-separation of the two ground states $|a\rangle$ to $|b\rangle$. We will not discuss the derivation of the Raman-process in detail. The derivation can be found in Orbach[6] for the case that the spin lattice interaction expanded to first order in the Taylor expansion acts twice. The derivation for the case that the spin lattice interaction is expanded up to the second order in the Taylor expansion and acts once, can be found in Shrivastava[86]. The last case is only possible for non-Kramers ions. Both processes yield the same temperature dependence without a magnetic field dependence and are additive.

Non-Kramers ions

For non-Kramers ions the temperature dependence reads:

$$1/\tau_1 \sim T^7. \quad (2.50)$$

Kramers ions

And for Kramers ions it reads:

$$1/\tau_1 \sim T^9. \quad (2.51)$$

In the presence of an applied field the time conjugation of the Kramers ions can be lifted due to the admixture with excited levels. If the energy splitting between the first two excited doublets is small, the relaxation time can change to [6]:

$$1/\tau_1 \sim H^2 T^7. \quad (2.52)$$

2.3.1.4 Orbach and Raman process using optical phonons

Huang [87] introduced a spin-lattice relaxation process for Kramers ions, which uses optical phonons instead of acoustical phonons. He shows that, if the optical phonon energy is low, the bandwidth of the optical phonon is narrow, and the lattice vibration is even, the optical phonon process can dominate over the acoustical phonon process. Interestingly, for the case of optical phonons the temperature-dependence of the relaxation time of the Raman- and the Orbach process are equal. The thermal activation energy is given by the frequency of the optical phonon:

$$1/\tau_1 \sim e^{-\Delta_{\hbar\omega_0}/kT}, \quad (2.53)$$

with the phonon frequency ω_0 .

2.3.2 Magnetic relaxation of lanthanides in molecular magnetism: Discussion of literature

Most of the above discussed different relaxation times were observed experimentally. Here, we want to review² the observed relaxation processes of three well studied compounds: the lanthanide double decker compound $[\text{Pc}_2\text{Tb}]^-\text{TBA}^+$ [3], the polymetallic lanthanide alkoxide complex Dy_4K_2 [16], and the DyDOTA compound [15]:

1. Ishikawa *et al.* [47] observed in the two lanthanide double-decker complexes $[\text{Pc}_2\text{Tb}]^-\text{TBA}^+$ and $[\text{Pc}_2\text{Dy}]^-\text{TBA}^+$ contributions due to the direct process, the Raman-process and the Orbach-process, where the Orbach process is dominant above 25 K. Later on they studied the terbium compound in the low temperature range in detail up to 20 K in different magnetic fields and in a diluted sample. Contributions from both the direct process and ground state quantum tunneling were claimed to be observed. They point out that often the direct process and the quantum tunneling are mixed up in literature, and only detailed investigations can distinguish between them. In this temperature range contributions of the Raman process thought to be absent. A detailed hysteresis-study [96] of the two compounds shed light on the mechanism leading to ground state tunneling. It was shown that the coupling of the electron and nuclear spin system leads to coherent quantum tunneling. For terbium the nuclear spin $I = 3/2$ has a natural abundance of 100 %, the hysteresis loops show a staircase structure, the steps occur at magnetic fields, at which the avoided level crossings of the entangled $J_z I_z$ are expected. Hysteresis measurements for the dysprosium compound were more difficult to interpret. Dysprosium occurs in different isotopes with different nuclear spins, 44 % have a nuclear spin of $I = 5/2$ and the others $I = 0$. No clear staircase structure of the hysteresis loops were observed which could be attributed to two reasons: first, that only the dysprosium ions with $I = 5/2$ contribute to the staircase structure and second that the tunnel splittings are smaller than in the terbium compound. The only clear "step" is observed at $B = 0$, where the dysprosium ions with $I = 5/2$ are allowed to quantum tunnel, but the dysprosium ions with $I = 0$ are not because of the Kramers theorem. It is unclear, why the step observed at $B = 0$ is larger than expected, assuming that only dysprosium ions with non-zero nuclear spins contribute. It can be summarized the quantum tunneling in lanthanides occurs between the coupled electron and nuclear spin system.

2. The key feature of the relaxation study by Blagg *et al.* [16] of the polymetallic lanthanide alkoxide complex Dy_4K_2 is the preferential relaxation via the second excited Kramers doublet by a thermally activated relaxation process. The two observed relaxation barriers have an energy of $\Delta_{eff} = 316 \text{ K}$, which is associated with a relaxation process via the first excited doublet, and $\Delta_{eff} = 692 \text{ K}$, which is associated with a relaxation process via the second excited doublet. Interestingly, the relaxation barriers lie above the Debye cut-off frequency for acoustical phonons. Therefore, they propose

² We only summarize the results and interpretations made by the authors.

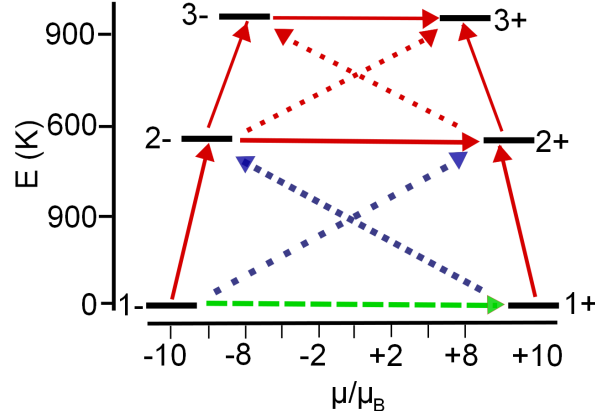


Fig. 2.5: Lowest three Kramers doublets of Dy_4K_2 and possible relaxation paths. The green dashed lines belongs to ground state quantum tunneling and the solid red lines to thermally activated quantum tunneling. Dashed red and blue lines show possible Orbach processes. The Figure is adopted from Ref. [16].

a process taking place via optical phonons.

The thermally activated relaxation process observed is referred to as an thermally assisted quantum tunneling process, which means that first the spin is excited by a phonon to the excited state, then tunnels to the other side of the barrier, and then relaxes to the ground state of that side of the barrier. A scheme of the proposed processes is depicted in Figure 2.5.

3. Relaxation studies of the compound DyDOTA in a wide temperature and magnetic field range revealed the competition between two relaxation pathways [15]: the direct and the Orbach process. As a consequence of magnetic dilution, the direct process is slowed down, whereas the barrier of the Orbach-process is not affected. The effective energy barrier of the thermally activated regime was determined as $\Delta_{eff} = 42 \text{ cm}^{-1}$. The energy of the first excited doublet was found as $\Delta_{eff} = 53 \text{ cm}^{-1}$ from luminescence spectra [8]. For more details of the relaxation process see Section 6.1.1. DyDOTA is also one of the complexes studied in this thesis by far-infrared spectroscopy (Chapter 6).

2.4 Magnetic relaxation in single-chain magnets

Theoretically, single-chain magnets are treated as isolated one-dimensional magnetic systems. For real systems, this implies that the magnetic coupling between constituents of the chains are much larger than the coupling to neighboring chains ($J_{intra} \gg J_{inter}$). Experimentally of course, the coupling between neighboring chains (e.g. due to dipolar coupling) cannot be entirely suppressed. However, if the coupling is small enough, effects should only be expected at low temperatures where $J \approx k_b T$.

Here, we will discuss only SCMs which can be treated in the Ising-limit. This is justified by the reason, that we are dealing with lanthanide ions with strong anisotropies. Our following description of the static and dynamic properties of the Ising-model follows the works of Clerac *et al.* [51], Miyasaka *et al.* [97], and a review article written by Vindigni [50].

2.4.1 Static magnetic properties

In the Ising-model the spin S of the system is assumed to point parallel or anti-parallel to a certain direction. The two directions are represented by σ ($\sigma = +1$ parallel and $\sigma = -1$ anti-parallel). As an example for an anisotropic dysprosium total angular momentum with a value of $J=15/2$ with a low lying Kramers doublet of $m_J=\pm 15/2$. The Kramers doublet can be described to be oriented parallel or anti-parallel to the anisotropy axis (z-axis) with $\sigma = \pm 1$.

The Ising chain consists out of Ising spins in an one-dimensional arrangement. Only the nearest-neighbor coupling is nonzero with a coupling constant J ; for $J > 0$ the coupling is ferromagnetic and for $J < 0$ antiferromagnetic. At $J = 0$ the system behaves like a system consisting of individual paramagnetic ions. The Ising-Hamiltonian reads (see also Figure 2.6):

$$H = -2J \sum_i S_{i,z} S_{i+1,z} = -2JS^2 \sum_i \sigma_i \sigma_{i+1}. \quad (2.54)$$

In general, for a one dimensional system the magnetic susceptibility is strongly connected with the correlation length. The correlation length is given by: $\langle s(i)s(j) \rangle = e^{|i-j|/\eta}$, and describes, how fast the correlation function of two spins at sites i and j decreases in dependence of the distance between them. The magnetic susceptibility in terms of the correlation length is:

$$\frac{\chi^T}{C} \cong 2\eta, \quad (2.55)$$

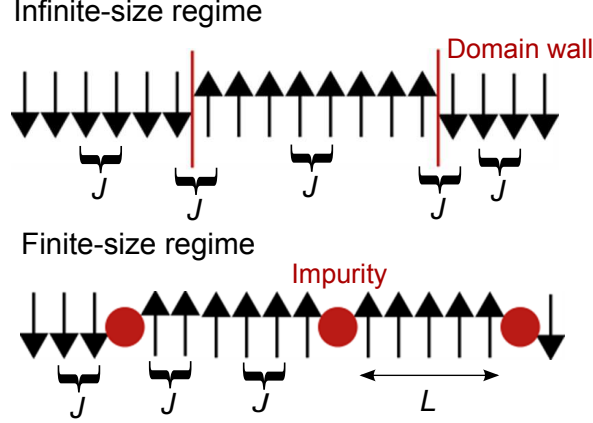


Fig. 2.6: Scheme of the one-dimensional Ising chain in the infinite- and finite-size regime. The nearest neighbor coupling is given by J and the finite-chain length in the finite-size regime by L . The domain walls are marked as red lines and the impurities as red circles.

with $C = g^2 \mu_B^2 S(S+1)/(3k_B)$ the Curie temperature of the chain. The correlation length is given by: $\eta = -\frac{1}{\ln(\exp(2\beta J))}$ with $\beta = k_B T$. For low T , η can be approximated by:

$$\eta = \frac{1}{2} \exp(4\beta J), \quad (2.56)$$

hence the correlation length diverges exponentially at low temperatures.

2.4.2 Dynamic magnetic properties

Glauber model

In the 1960s Glauber [49] introduced a stochastic extension of the Ising model to describe the dynamic properties of the Ising chain. The Glauber dynamics approach is widely applied for SCMs [50, 51, 55]. Glauber introduced probabilities for the single-spin flips of spin i , which depend only on the state of the first neighbor $i+1$. The spins are represented by stochastic functions $\sigma_i(t)$. The probability for a spin flip per unit time is given by:

$$W_i(\sigma_i) = \frac{1}{2\tau_0} \left(1 - \frac{\gamma}{2} \sigma_i(\sigma_i + \sigma_{i+1}) \right), \quad (2.57)$$

where τ_0 is the intrinsic probability for a spin flip in absence of interaction and γ is determined by the detailed balance condition to be $\gamma = \tanh(2J/kT)$. The choice of the transition probability fulfills the detailed balance criterium defined in Equation 2.19. The relaxation time for the Glauber model yields:

$$\tau = \frac{\tau_0}{1 - \tanh(4JS^2/k_BT)}. \quad (2.58)$$

At low temperatures, $4JS^2 \gg k_BT$ and the hyperbolic tangens can be approximated by $\tanh(4JS^2/k_BT) = 1 - \frac{2}{\exp(2 \times 4JS^2/k_BT) + 1} \approx 1 - 2 \exp(-8JS^2/k_BT)$. This gives:

$$\tau = \frac{\tau_0}{2} \exp(-8JS^2/k_BT). \quad (2.59)$$

Comparing Equation 2.59 for the relaxation time with the correlation length of the Ising model Equation 2.56, we can also write $\tau = 2\tau_0\eta^2$. Therefore, the relaxation times τ scales as η^2 at low temperatures. The Ising-chain consists out of domains of average size η separated by domain walls. At low temperatures, the relaxation occurs primarily by random motion of the domain walls, similar to the random walk in statistical physics. The time to travel a distance η is proportional to η^2 for a random walk. The prefactor τ_0 gives the time scale of the problem. In general also collective spin-flips can occur. For details see, e.g., Clerac *et al.*[51] and references therein.

Extended Glauber model

As described in Section 2.2 and 2.3 the building blocks of SCMs show thermally activated temperature dependencies. In the Glauber model, the time scale of the constituent chain units are included in the prefactor τ_0 . Therefore, for real materials the prefactor τ_0 in itself becomes temperature dependent. For lanthanide based SCMs, the constituents are lanthanide ions, which can in itself follow different relaxation mechanisms described in Section 2.3, like the Orbach process or the direct process. Since most of the work done on SCMs deals with building blocks, which show a thermally activated relaxation mechanism, the time scale for a single-spin flip in absence of coupling is introduced by taking $\tau_0 \sim \exp(\Delta_A/(k_BT))$ with Δ_A the energy barrier for relaxation. Introducing this in Equation 2.59:

$$\tau = \frac{\tau_{0,ext}}{2} \exp(-\Delta_A/k_BT) \exp(-8JS^2/k_BT). \quad (2.60)$$

The relaxation process has two distinguishable contributions, the last part coming from the random walk process at low temperatures, whereas the first part changes the spin flip attempt rate for every step in this random walk.

Finite-size regime

In the following, we will focus on the results obtained for the finite size regime; details of the derivation can be found in the review article by Clerac *et al.* [51]. In real compounds, the chain length is limited by the geometry and/or defects, leading to a finite chain length L in the compound (see also Figure 2.6). To study the finite size behavior, it is often desired to introduce a certain controllable amount of defects. Therefore, the compound is often doped with diamagnetic impurities. In lanthanide based SCMs for example, the magnetic lanthanide ions are substituted by the diamagnetic lanthanide ion Yttrium. As the correlation length grows exponentially by lowering the temperatures, the correlation length can exceed the chain length at low temperatures. Below a certain temperature (crossover) the finite chains behave as independent magnetic units with a spin of nS (with n the number of spins and S the value of the spin quantum number of each spin). This crossover is often called the superparamagnetic limit. The simplest approach assumes that all chains have the same finite chain length (monodisperse approximation). Below the crossover temperature, the finite chains behave independently of each other as superparamagnetic units. At sufficiently low temperatures, the magnetic susceptibility can be approximated as:

$$\frac{\chi_n T}{C} = \exp(4k_B T J S^2) \left(1 - \frac{1 - \exp(-2n \exp(-4k_B T J S^2))}{2n \exp(-4k_B T J S^2)} \right). \quad (2.61)$$

The crossover occurs when $2n \exp(-4k_B T J S^2) \approx 1$. Using the expression of the correlation length for the infinite size regime (Equation 2.59) this leads to $n \approx \eta/a$. Below the crossover the the susceptibility behaves as $\chi_n T/C \approx n$.

In the finite size regime, also the relaxation time changes. If $\eta \gg L$ the relaxation time can be approximated as:

$$\tau = \frac{\tau_0 L}{2a} \exp(4k_B T J S^2). \quad (2.62)$$

The relaxation time still shows an exponential behavior at low temperatures. Taking into account that defects or induced defects occur randomly in the compound, the description has to be extended to a stochastic model with a distribution of chain

lengths, called polydisperse approximation. The susceptibility in this case can be approximated by:

$$\frac{\langle\chi\rangle T}{C} \approx \frac{2}{c + 2 \exp(-4k_B T J S^2)}, \quad (2.63)$$

with c the probability of finding a defect and $\langle\chi\rangle$ the average magnetic susceptibility per site. The crossover is now smeared out and can be found when $\langle\chi\rangle T/C \approx \langle n \rangle$. At the crossover the relaxation time still follows approximately Equation 2.62, only by changing the chain length L to the average chain length $\langle n \rangle$. But, the discussion of the relaxation time is hampered by the fact, that the relaxation loses its exponential behavior. Instead the relaxation of the magnetization $m(t)$ is now given by:

$$m(t) = -t/\tau_\infty - 2\sqrt{t/\tau}. \quad (2.64)$$

3 Methods and Materials

3.1 Experimental setup

In this thesis, two different experimental techniques are used to record transmission spectra: Fourier-Transform-Infrared-Spectroscopy (FTIR) and a quasioptical setup using Backward-Wave-Oscillators (BWO). In contrast to Electron Paramagnetic Resonance (EPR), in both techniques the frequency is swept instead of the magnetic field to achieve the resonance condition between the electronic states and the incident light [62, 98, 99].

In both techniques the sample is placed in a cryostat with a split-coil superconducting magnet (Oxford Instruments Spectromag 4000). In this manner, we are able to monitor the change of the spectra with temperature (down to 2 K) and with magnetic fields (up to 7 T). In all measurements presented in this thesis the magnetic field is applied in Voigt geometry (magnetic field is perpendicular to the wave vector of the radiation).

Each spectrum was normalized by a reference spectrum taken through an empty aperture with a size equal to the sample.

3.1.1 Terahertz-Spectroscopy using backward-wave-oscillators

For the frequency range from $1\text{-}48\text{ cm}^{-1}$ backward wave oscillators (BWO) are used as radiation sources [100]. BWOs are vacuum electron tubes, which are placed in a magnetic field and are supplied with a high voltage. The frequency can be swept by changing the high voltage. The generated light is highly monochromatic, polarized and coherent. In our experiments, the magnetic field vector of the radiation is perpendicular to the static magnetic field. The quasi-optical setup is depicted in Figure 3.1. The generated electromagnetic wave leaves the BWO and is first collimated by lens 1, then focused by lens 2 to the sample, and then again collimated by lens 3 and focused to the detector by lens 4 to acquire the signal. For low frequencies $1\text{-}30\text{ cm}^{-1}$, a Golay-cell is used to detect the signal and for higher frequencies $30\text{-}48\text{ cm}^{-1}$ a pumped liquid helium bolometer (Infrared Laboratories HDL5). The lenses are made of fused-silica or teflon. For the general use of backward-wave-oscillators for spectroscopic measurements in the submillimeter range, we refer to Volkov et al. [101]. For the application

of this technique for single-molecule magnets see the PhD-thesis of Vongtragool [102] and References [61, 63].

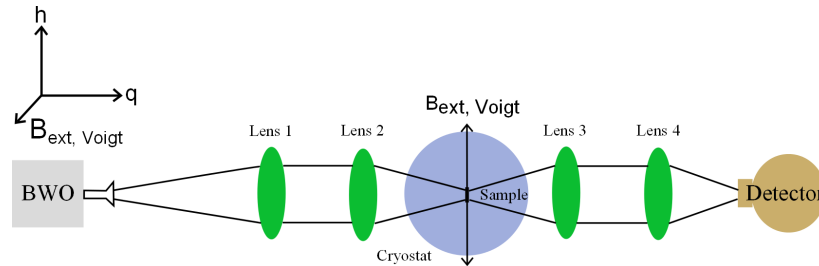


Fig. 3.1: Scheme of the beam path of the quasi-optical setup using BWOs. Upper left: Orientation of the external magnetic field $\mathbf{B}_{\text{ext}}$ in Voigt geometry, the polarization vector of the submillimeter light $\mathbf{h}$, and the vector of propagation of light $\mathbf{q}$

3.1.2 Fourier-Transform-Infrared-Spectroscopy

To record a wider spectral range a Fourier-Transform-Infrared-Spectrometer (Bruker IFS 113v) is used. The Bruker IFS 113v in general covers the spectral range from $10\text{-}10000\text{ cm}^{-1}$. However, the current Mylar windows of the Oxford Instruments Spectromag 4000 only allow measurements from $10\text{-}100\text{ cm}^{-1}$. The light source for this far infrared range is a mercury (Hg)-arc lamp, and the detector, a pumped liquid helium bolometer (Infrared Laboratories HDL5). A scheme of the beam path in the Bruker IFS 113v spectrometer connected to the Spectromag 4000 is depicted in Figure 3.2.

For the application and general considerations of the Fourier-Transform-Infrared spectroscopy exists a large number of literature; we refer here to the textbook of Griffith and de Haseth [103].

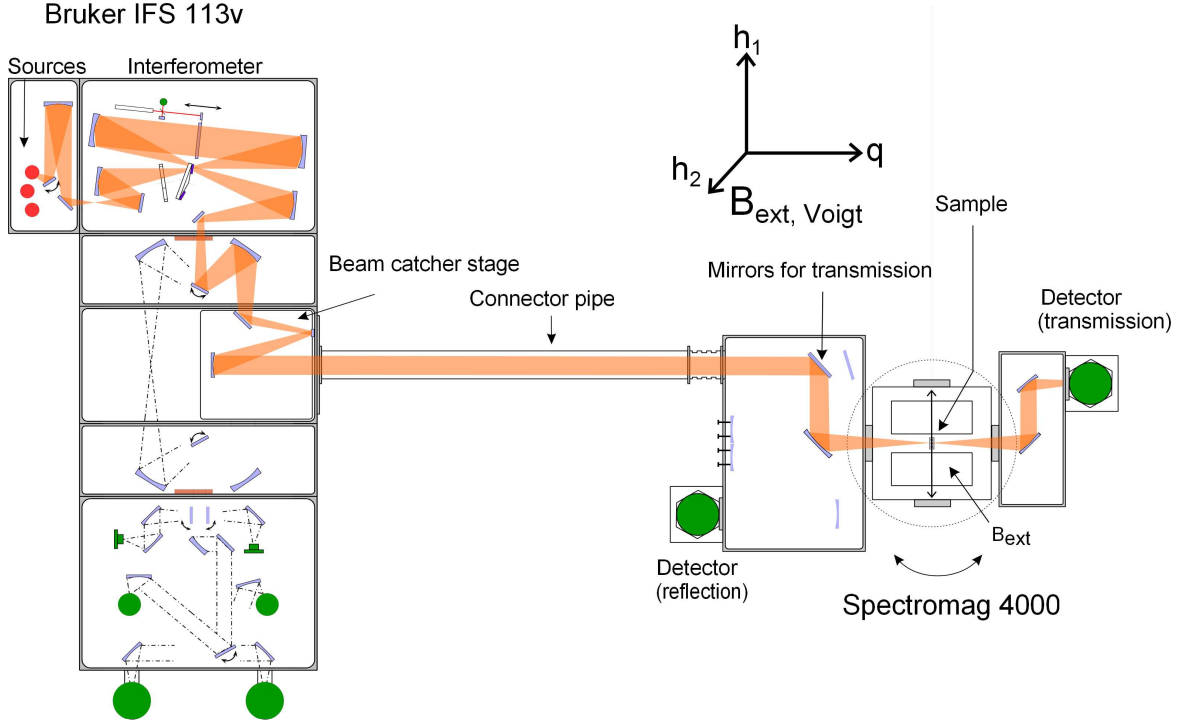


Fig. 3.2: Scheme of the beam path in the Bruker IFS 113v connected to the Spectromag 4000. Upper left: Orientation of the external magnetic field B_{ext} in Voigt geometry, the polarization vectors of the light h_1 and h_2 , and the vector of propagation of light q ¹.

3.2 Analysis of the data

3.2.1 Fresnel equations for a plane-parallel slab

The optical properties of a sample are described by their complex dielectric permittivity ($\hat{\epsilon} = \epsilon_1 + i\epsilon_2$) and the complex magnetic permeability ($\hat{\mu} = \mu_1 + i\mu_2$). The Fresnel equations lead to the following equations for the transmission through a plane-parallel slab at normal incidence [98, 99, 102]:

$$Tr(\omega) = E \frac{(1 - R)^2 + 4R \sin^2 \Psi}{(1 - RE)^2 + 4RE \sin^2(Q + \Psi)} \quad (3.1)$$

Q and E are obtained by the real part of the refractive index n , the imaginary part of the refractive index k , the frequency ω and thickness of the plane-parallel slab d :

¹ Figure based on drawings by Conrad Clauß [104] and David Neubauer.

$$E = \exp(-2k\omega d) \quad (3.2)$$

$$Q = n\omega d \quad (3.3)$$

with

$$n = \frac{\Theta_2}{2} \quad (3.4)$$

$$k = \sqrt{\frac{-\Theta_1 + \sqrt{\Theta_1^2 + \Theta_2^2}}{2}} \quad (3.5)$$

$$\Theta_1 = \epsilon_1\mu_1 - \epsilon_2\mu_2 \quad (3.6)$$

$$\Theta_2 = \epsilon_1\mu_2 - \epsilon_2\mu_1 \quad (3.7)$$

R and Ψ can also be obtained from the material parameter $\hat{\epsilon}$ and $\hat{\mu}$:

$$R = \frac{(a-1)^2 + b^2}{(a+1)^2 + b^2} \quad (3.8)$$

$$a = \sqrt{\frac{\alpha_1 + \sqrt{\alpha_1^2 + \alpha_2^2}}{2}} \quad (3.9)$$

$$b = \frac{\alpha_2}{2a} \quad (3.10)$$

$$\alpha_1 = \frac{\mu_1\epsilon_2 + \mu_2\epsilon_1}{\epsilon_1^2 + \epsilon_2^2} \quad (3.11)$$

$$\alpha_2 = \frac{\mu_2\epsilon_1 - \mu_1\epsilon_2}{\epsilon_1^2 + \epsilon_2^2} \quad (3.12)$$

$$\Psi = \arctan \frac{2b}{a^2 + b^2 - 1} \quad (3.13)$$

With this equations the transmission of light through a plane-parallel slab can be calculated for arbitrary dielectric permittivities and magnetic permeabilities. In Figure 3.3 the transmission spectrum of a plane-parallel pellet with a constant and real dielectric permittivity without magnetic contributions is shown. The oscillating pattern observed is created by the interference of transmitted beams (Figure 3.3). The phase-shift of the transmitted beams depends on the number of reflections inside of the sample, before the beams are transmitted. The sample resembles a Fabry-Pérot interferometer. The Fabry-Pérot like pattern provides information about the real and imaginary part of the refractive index function. The position of the maxima are related to the real part of the refractive index function and the height of the oscillations to the imaginary part.

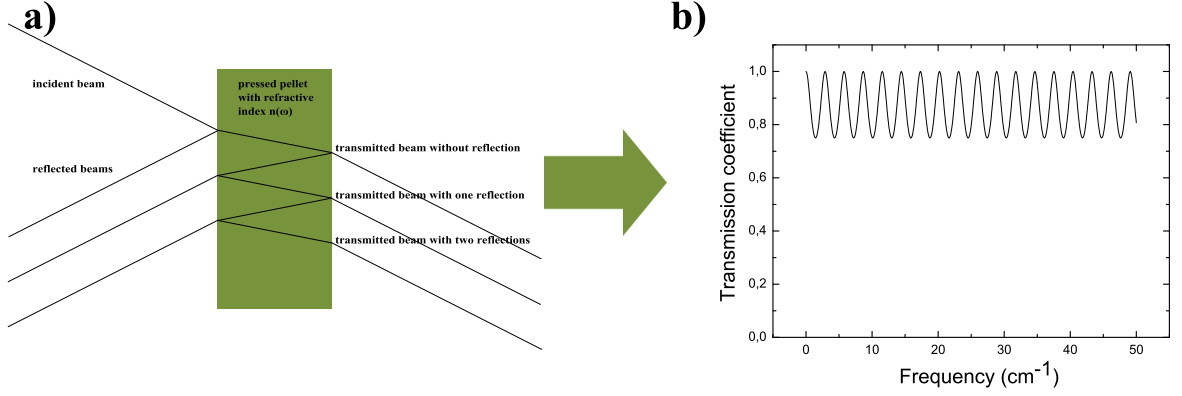


Fig. 3.3: a) Scheme of the Fabry-Pérot like resonances in a plane-parallel slab. b) Resulting oscillating pattern for a dielectric medium with $\epsilon = 3$ and $\mu = 1$ (resulting refractive index of $n=1.73$) and thickness 1 mm

3.2.2 Modeling of the dielectric permittivity and magnetic permeability

For non-conducting and magnetic materials, the transmission spectra (in the frequency range from 4-100 cm^{-1}) are normally governed by the appearance of several electric and magnetic absorption lines. Therefore, the dielectric permittivity and magnetic permeability functions can be reproduced by the introduction of several electric and magnetic oscillators:

$$\epsilon^*(\nu) = \epsilon_1(\nu) + i\epsilon_2(\nu) = \epsilon_0 + \sum_j \Delta\epsilon_{i,j} R(\omega), \quad (3.14)$$

$$\mu^*(\nu) = \mu_1(\nu) + i\mu_2(\nu) = 1 + \sum_j \Delta\mu_{i,j} R(\omega), \quad (3.15)$$

with $\Delta\mu$ the strength of the magnetic oscillators, $\Delta\epsilon$ the strength of the electric oscillators, and $R(\omega)$ the lineshape function, which can either be of Lorentzian or Gaussian type. ϵ_0 represents the electric permittivity at the lowest measured frequency. Most of the electric oscillators originate from phononic or vibrational excitations, and the lineshape function can be best described by a Lorentzian lineshape. The electric permittivity is, therefore, given by:

$$\epsilon^*(\nu) = \epsilon_1(\nu) + i\epsilon_2(\nu) = \epsilon_0 + \sum_j \Delta\epsilon_{i,j} \frac{\nu_{i,j}^2}{\nu_{i,j}^2 - \nu^2 + i\nu\gamma_{i,j}}, \quad (3.16)$$

with the resonance frequency $\nu_{i,j}$ and the damping factor $\gamma_{i,j}$. For the magnetic oscillators both Gaussian and Lorentzian lineshapes can appear. For a Gaussian lineshape, the magnetic permeability reads:

$$\begin{aligned}\mu_1(\omega) &= 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \mu_2(\omega)}{\omega'^2 - \omega^2} d\omega' \\ \mu_2(\omega) &= \omega \sqrt{\frac{\pi}{8}} \sum_{if} \frac{\Delta\mu_{if}}{\sigma_{if}} \left(\exp\left(\frac{-(\nu - \nu_L)^2}{2\sigma_L^2}\right) + \exp\left(\frac{-(\nu + \nu_L)^2}{2\sigma_L^2}\right) \right),\end{aligned}\tag{3.17}$$

and for the Lorentzian lineshape:

$$\mu(\omega) = 1 + \sum_{if} \Delta\mu_{if} \frac{\omega_{if}^2}{\omega_{if} - \omega^2 + i\omega\Delta\omega_{if}}.\tag{3.18}$$

Magnetic permeability of molecular magnets

For molecular magnets, the quantity of interest is the magnetic permeability. The electric permittivity is treated as a background. The electric oscillators (caused by phononic and vibronational excitations) are treated by free fitting parameters, to reproduce the spectrum outside of the magnetic oscillators.

The contribution of the magnetic permeability to the transmission spectrum can then be fitted with several magnetic oscillators. The interesting quantities in the fitting process are the center frequency of the resonance lines and the strengths of the magnetic resonance lines. In molecular magnets, the origin of the magnetic oscillators are allowed transitions between different electronic energy-levels. Therefore, they contain information about the underlying spin-Hamiltonian. For a given spin-Hamiltonian, the magnetic oscillators can be derived by theoretical arguments. The resonance frequency is given by the energy difference between the initial and final state of the transition. The strength of the transition (contribution of the transition to the static magnetic permeability) can be obtained by time-dependent perturbation theory as described in Kirchner *et al.* [62]. The strength depends on the the population difference of the two states determined by the Boltzmann distribution, the transition matrix element obtained by Fermi's golden rule, the number density of molecules in the sample and the g-factor. In addition for a powder pellet the random orientation of the crystals in the sample has to be taken into account. Then the contribution to the static magnetic permeability reads:

$$\Delta\mu_{if} = \frac{8\pi}{3} N_0 g^2 \mu_B^2 \frac{\sum_{\alpha=x,y,z} |\langle f | \hat{S}_\alpha | i \rangle|^2}{\hbar\omega_{i,f}} \frac{(\exp(-\frac{E_f}{k_B T}) - \exp(-\frac{E_i}{k_B T}))}{Z}\tag{3.19}$$

with N_0 density of magnetic molecules, μ_B the Bohr magneton, $\hbar$ the Planck constant, k_B the Boltzmann constant, $E_{f,i}$ the energy of the initial or final state, $\omega_{i,f}$ the transition frequency, and Z the partition function.

This modeling method was applied to molecular magnets, e.g. Mn_{12}Ac [61, 98, 105]. For the molecular magnets studied by this model, the magnetic resonance lines, were well separated from phononic lines. Therefore, the electric permittivity was fitted outside of the magnetic resonance lines, and kept constant, for the fitting of the magnetic resonance line.

3.3 Investigated samples

All samples investigated by far-infrared spectroscopy in this thesis are pressed pellets out of microcrystalline powder with a diameter of 1 cm. The thickness of the samples ranges from 0.5 mm to 4 mm.

The investigated samples are:

1. The single-chain magnet DyPhOPh ($\text{Dy}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}$) and the isostructural terbium compound TbPhOPh [14] (synthesized by Lapo Bogani (University of Stuttgart)),
2. The single-ion magnet DyDOTA ($\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})]_4 \cdot \text{H}_2\text{O}$) and the isostructural terbium compound TbDOTA [15, 58] (synthesized in the group of R. Sessoli (University of Florence)),
3. The molecular magnet $\text{Ln}(\text{PhOPh})_2$ ($\text{Ln}(\text{hfac})_3(\text{NIT} - \text{C}_6\text{H}_4\text{OPh})_2$) ($\text{Ln}=\text{Dy, Tb, and Ho}$) and $\text{Dy}(\text{hfac})_3(\text{NIT} - \text{C}_6\text{H}_4\text{OEt})_2$ ($\text{Dy}(\text{PhOEt})_2$) [5, 64] (synthesized by Lapo Bogani and Alexa Paretzki (University of Stuttgart)).

Details of the sample properties are given in the respective Chapters.

4 New methods for the analysis of far-infrared spectra of lanthanide ions

4.1 Introduction

The method for the analysis of the far-infrared spectra described in the previous Chapter requires that the distinction between electronic and phononic or intramolecular vibrational absorption lines is definite, either by theoretical calculations or through experimental evidence. Especially at low frequencies, below around 20 cm^{-1} , phonon and intramolecular vibrational lines are rare in most compounds. If, in this case, at low temperatures an absorption line appears in the spectrum, it can be assigned to an electronic transition. This assignment can be validated by the application of a magnetic field. For these cases the formerly described (Section 3.2) modeling method was widely used [61, 63, 99].

Unfortunately, when working with lanthanide containing compounds this distinction evolves into a complex task. Transitions between crystal field split energy-levels of the lowest Russel-Saunders multiplet lie in the frequency range up to a few hundred wavenumbers [10, 11, 13, 60, 106]. This primarily magnetic dipole active¹ absorption lines are embedded and overlapped in many compounds with infrared active phonons and intramolecular vibrons and a distinction can not be easily achieved. This issue is well known from far-infrared measurements which were conducted on lanthanide based materials in the 60s and 70s of the last century [10, 11, 12, 13]. To resolve this issue there are in general two possibilities, to identify the phononic and intramolecular-vibrational absorption lines or to identify the electronic absorption lines. For the compounds studied in this thesis a combination of both approaches is applied.

¹ The electronic transitions can also contain electric dipole contributions. Electric dipole transitions are normally forbidden inside the multiplet by the parity selection rule. However, in the case of low symmetry, the Dy^{3+} ion can be shifted from the center of symmetry, leading to a mixing with excited $4f^{n-1}5d^1$ states into the $4f$ configuration. As both are of opposite parity, this allows electric dipole transitions [107],[108] (see also Section 4.6).

Identification of the phononic and intramolecular vibrational absorption lines

Because of their definite valence state, lanthanides often form isomorphous compounds throughout the series. The phonon spectra of compounds with different lanthanides are similar. Since the mass change throughout the series is small, and nearly compensated by the ion contraction (lanthanide contraction law), which alters the force constant [13], the resonance frequency changes only slightly by the substitution of the lanthanide ion. Normally, it is favorable, to use for the comparison, a lanthanide without any electronic resonances in the far-infrared region; then all resonance lines can be directly identified to be of phononic or vibrational origin. Lanthanum, lutetium, and yttrium are well suited for this task because no electronic transitions are expected in the measured frequency range.

Identification of the electronic absorption lines

Definite identification of the electronic absorption lines can be achieved by the observation of the Zeeman effect. In a magnetic field $\vec{B}$, the Zeeman effect shifts the energy levels according to the Zeeman term in the Hamiltonian $\hat{H} = g\mu_B\hat{\mathbf{J}}\vec{B}$ with the g -factor g , μ_B the Bohr magneton and $\hat{\mathbf{J}}$ the total angular momentum operator. The manifestation of the Zeeman splitting in powder samples - like the ones used in this thesis - is more complex, because the direction of the magnetic field vector is pointing in a different direction for every crystallite and only a few studies of powder samples can be found in literature, e.g. References [60, 106]. Especially at low symmetry sites, the spectroscopic g -factor is different for all directions that leads to a broadening of the lines instead of an overall shift. If the electronic absorption lines are in addition of low intensity compared with the phononic and vibrational lines they are only recognizable as slight changes of the spectra at different fields. Under these circumstances, the easiest way to identify electronic absorption lines is to calculate the ratio of the spectra in field and without field. Small changes of the spectra get visible and the lines can be identified. The disadvantage of this approach lies in the fact that the ratio spectra are dependent on the sample parameters, used for a specific experiment, like the thickness and weight. Instead, a quantity is preferable, which only depends on material parameters.

Therefore, we will use in many cases a different and new approach for the analysis of the data, than the approach presented in Section 3.2. The new approach includes the following steps (see below for a detailed description):

- the absorption cross section is extracted from the transmission spectra,

- the phononic background is "removed" by subtracting the absorption cross section in zero-field from the one in an applied field.
- the absorption cross section is converted to a quantity directly proportional to the transition matrix element.

4.2 Analysis of the magnetic field-dependent spectra

Extraction of the absorption cross section from the transmission measurements

The absorption cross section can be calculated by using the Beer-Lambert law, which connects the transmission to the absorption coefficient α and to the absorption cross section σ :

$$T(\tilde{\nu}) = \frac{I(\tilde{\nu})}{I_0(\tilde{\nu})} = \exp^{-\alpha(\tilde{\nu})d} = \exp^{-\sigma(\tilde{\nu})Nd}, \quad (4.1)$$

with the frequency $\tilde{\nu}$ and the distance d which the light travels through the material (path length). We then gain for the absorption cross section:

$$\sigma(\tilde{\nu}) = -\ln(T(\tilde{\nu}))/(\tilde{\nu} N), \quad (4.2)$$

with the number density N . The limits of the Beer-Lambert law for bulk samples are discussed in Section A.1.

"Removing" the phononic background

In the absorption spectra, the phononic and the electronic part of the spectrum are additive. To eliminate the phononic background, spectra at different magnetic fields are acquired. In a magnetic field, the phononic background does not change². By subtracting the absorption cross section in zero-field from the one in an applied field, the phononic background is canceled out:

$$\Delta\sigma_{B-0}(\tilde{\nu}) = \sigma_B(\tilde{\nu}) - \sigma_0(\tilde{\nu}). \quad (4.3)$$

² For a strong spin-phonon coupling, also the phonon lines can change in a magnetic field. We assume here that this is not the case.

Unfortunately, in this step, information about the electronic spectrum is lost, too. Only the difference of the electronic spectra, caused by the Zeeman-term, are left. $\Delta\sigma_{B=0}(\tilde{\nu})$ only contains information about the electronic spectrum.

Absorption cross section for magnetic dipole transitions

The integrated absorption cross section for a magnetic dipole transition is given by [109]:

$$\left(\int \sigma(\tilde{\nu})d\tilde{\nu}\right) = \frac{8\pi^2\nu\eta}{hc} |\langle \Psi_f | \mu_B g_L \hat{J}_\kappa | \Psi_i \rangle|^2 \Delta N_{i,f}(T), \quad (4.4)$$

with η the refractive index of the crystal, κ the polarization direction of the incident light, $\Delta N_{i,f}(T)$ the population difference between the initial and final state calculated by the Boltzmann distribution, ν the resonance frequency in $[\text{cm}^{-1}]$, g_L the Lande g-factor of the multiplet, $|\langle \Psi_f | \mu_B g_L \hat{J}_\kappa | \Psi_i \rangle|^2$ the magnetic dipole transition matrix element, α the absorption coefficient, $d\tilde{\nu}$ the variable of integration given in wavenumbers. The physical constants are in CGS-units. It is often convenient, to factor out the Bohr magneton in the transition matrix element, which leads to:

$$\left(\int \sigma d\tilde{\nu}\right) = \frac{\pi e^2 h \nu \eta}{2m^2 c^3} |\langle \Psi_f | g_L \hat{J}_\kappa | \Psi_i \rangle|^2 \Delta N_{i,f}(T). \quad (4.5)$$

The new transition matrix element $|\langle \Psi_f | g_L \hat{J}_\kappa | \Psi_i \rangle|^2$ is then, for allowed magnetic dipole transitions, of the order of unity, in units of $\hbar$. Absorption lines in spectra can either be of Lorentzian or Gaussian (or more complex) shape. Therefore, we can express the absorption cross section for one magnetic dipole transition as:

$$\sigma(\tilde{\nu}) = \frac{\pi e^2 h \tilde{\nu} \eta}{2m^2 c^3} |\langle \Psi_f | g_L \hat{J}_\kappa | \Psi_i \rangle|^2 \Delta N_{i,f}(T) g_{\nu,\gamma}(\tilde{\nu}), \quad (4.6)$$

with $g(\tilde{\nu})$ the lineshape function. For a normalized Lorentzian lineshape $g_{\nu,\gamma}(\tilde{\nu})$ reads:

$$g_{\nu,\gamma}(\tilde{\nu}) = \frac{1}{2\pi} \frac{\gamma}{(\tilde{\nu} - \nu)^2 + \left(\frac{\gamma}{2}\right)^2}, \quad (4.7)$$

with ν the resonance frequency and γ the linewidth, and for the normalized Gaussian lineshape:

$$g_{\nu,\gamma}(\tilde{\nu}) = \frac{1}{\gamma\sqrt{2\pi}} \exp^{-\frac{1}{2}\left(\frac{\tilde{\nu}-\nu}{\gamma}\right)^2}, \quad (4.8)$$

with γ^2 the variance.

The terms of Equation 4.6 can be arranged in the following way:

$$\underbrace{|\langle \Psi_f | \hat{J}_\kappa | \Psi_i \rangle|^2 \Delta N_{i,f}(T) g_{\nu_{i,f}, \gamma_{i,f}}(\tilde{\nu})}_{\sigma^*(\tilde{\nu})} = \sigma(\tilde{\nu}) \frac{2m^2 c^3}{\pi e^2 h \tilde{\nu} \eta}. \quad (4.9)$$

The left side of the equation, only contains characteristic elements of the transition, and defines the new quantity $\sigma^*(\tilde{\nu})$, which we call normalized absorption cross section. The right side, contains quantities derived by the experiment ($\sigma(\tilde{\nu})$), physical constants, and the frequency $\tilde{\nu}$. In general, the absorption cross section can contain transitions between all of the crystal field split states. Therefore, a sum has to be taken over all the possible transitions inside the multiplet:

$$\sigma^*(\tilde{\nu}) = \sum_{i,f} |\langle \Psi_f | \hat{J}_\kappa | \Psi_i \rangle|^2 \Delta N_{i,f}(T) g_{\nu_{i,f}, \gamma_{i,f}}(\tilde{\nu}). \quad (4.10)$$

The normalized absorption cross section can be calculated by the crystal field Hamiltonian of the lanthanide ion with the use of Equation 4.15. This will be done in Section 4.3. As stated above due to the phononic background, experimentally we have only access to the difference of the normalized absorption cross section between in-field and zero-field measurements.

In summary, to obtain the difference of the normalized absorption cross section out of the transmission spectra measured in-field $T_B(\tilde{\nu})$ and zero-field $T_0(\tilde{\nu})$, the following equation can be applied:

$$\Delta \sigma_{B-0}^*(\tilde{\nu}) = \frac{-\ln(T_B(\tilde{\nu})) + \ln(T_0(\tilde{\nu}))}{Nd} \frac{2m^2 c^3}{\pi e^2 h \eta \tilde{\nu}}. \quad (4.11)$$

Apart from of the refractive index η , the equation only contains sample parameters (the number density N of lanthanide ions and the thickness d), which can be calculated from the formula weight of the sample and the sample dimensions, and physical constants given in CGS-units. The refractive index can not be determined by simple arguments for a certain compound. As an approximation of the refractive index, we use a fit of the far-infrared transmission spectra with multiple electric oscillators (as described in Section 3.2.2), and calculate out of the electric permittivity the refractive index of the material. As the refractive index depends on frequency, we take the average value of the refractive index over the measured frequency interval.

Advantages of evaluating the normalized absorption cross section

To present the measured spectra in terms of the difference of the normalized absorption cross section has several advantages:

- the normalized absorption cross section is independent of the sample properties, like weight and thickness. Therefore different measurements are directly comparable.
- a direct estimate of the transition matrix element of the observed magnetic dipole transition can be made. In a magnetic field of 6 T the spectral weight of an absorption line has partially moved away from the zero-field position and a peak is visible at the position of the zero-field line in the difference of the normalized absorption cross section. The peak area can be estimated by multiplying the height of the peak by the FWHM (and by multiplying it for a Lorentzian lineshape with the factor $\frac{1}{2\pi}$ and for a Gaussian lineshape with the factor $\frac{\sqrt{\pi}}{2\sqrt{\ln 2}}$).

4.3 Simulation program for far-infrared spectra of lanthanide ions

During the course of this thesis, a simulation program was written for the evaluation of far-infrared spectra of lanthanides by using Matlab. As described in the previous Section 4.2 the experimentally accessible quantity is the difference of the normalized absorption cross section between spectra in-field and zero-field (see Equation 4.11).

The aim of the simulation is to calculate the difference of the normalized absorption cross section out of the crystal field parameters of a certain lanthanide ion. The input parameters of our simulation program are, therefore, the crystal field parameters, the total angular momentum J and the Landé factor g of the ground manifold of the lanthanide ion. For the simulation of the experimental situation, also the temperature and the magnetic field have to be introduced. The output is given in form of the normalized absorption cross section. The experimentally accessible quantity $\Delta\sigma_{B-0}^*(\tilde{\nu})$ can be easily calculated by taking the difference between $\sigma_B^*(\tilde{\nu})$ in-field and $\sigma_B^*(\tilde{\nu})$ zero-field.

4.3.1 Single crystal and one polarization direction

First we will describe the simulation process for a single crystal, where the external magnetic field direction, and the polarization direction κ are given in the molecular reference frame. Our simulation program consists of the following steps:

- The matrix of the crystal field Hamiltonian³ is set up. For the crystal field Hamiltonian of the ground manifold the Stevens operator equivalent method is used here. With a magnetic field, the Hamiltonian reads (compare Equation 2.15):

$$\widehat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q(J) + g\mu_B \hat{\mathbf{J}}\mathbf{B}. \quad (4.12)$$

with B_k^q the crystal field parameters, g the Landé factor of the ground multiplet, and $O_k^q(J)$ the Stevens operators listed in Table 2.2.

- The eigenvectors and eigenvalues of the Hamiltonian are calculated:

$$\widehat{H}_{CF} |\text{CF}_i\rangle = E_i |\text{CF}_i\rangle. \quad (4.13)$$

- For all transitions between eigenstates $|\text{CF}_i\rangle$ and $|\text{CF}_f\rangle$ the resonance frequency, the magnetic dipole transition matrix element $|\langle \text{CF}_f | g\hat{J}_\kappa | \text{CF}_i \rangle|^2$, and the population difference between the two states is calculated.
- For the simulation of the absorption cross section, the resulting absorption line is calculated by

$$\sigma^*(\tilde{\nu}) = |\langle \text{CF}_f | g\hat{J}_\kappa | \text{CF}_i \rangle|^2 \Delta N_{i,f}(T) g_{\nu_{i,f}, \gamma_{i,f}}(\tilde{\nu}), \quad (4.14)$$

with the appropriate lineshape function $g_{\nu_{i,f}, \gamma_{i,f}}(\tilde{\nu})$ being either of Lorentzian or Gaussian type. The width $\gamma_{i,f}$ is estimated from the experimental data and also the lineshape (Lorentzian or Gaussian) is decided by experimental evidence.

- The absorption lines from all transitions are summed up:

$$\sigma^*(\tilde{\nu}) = \sum_{i,f} |\langle \Psi_f | g\hat{J}_\kappa | \Psi_i \rangle|^2 \Delta N_{i,f}(T) g_{\nu_{i,f}, \gamma_{i,f}}(\tilde{\nu}), \quad (4.15)$$

- The result is the normalized absorption cross section caused by the electronic transitions inside the crystal field split ground multiplet for one polarization direction.

³ In addition also the spin Hamiltonian presented in Section A.4 Equation A.5 was implemented.

4.3.2 Averaging over the different directions of a powder

In this thesis, all the samples were pressed pellets, which consist out of small crystallites. To mimic the experimental situation by a simulation, it has to be summed over the different crystallite directions with respect to the laboratory reference frame. The laboratory reference frame for the far-infrared setup, consists out of the direction of the applied magnetic field and the polarization direction. For the far-infrared measurements unpolarized light was used. In this situation, the polarization directions of the light are parallel and perpendicular to the applied field (in Voigt geometry). The laboratory reference frame is shown in Figure 3.2. In the laboratory frame, the molecular reference frame points in different directions and can be expressed in terms of the Euler angles α , β and γ . For the powder averaging process in our simulations, the laboratory reference frame is rotated instead of the molecular reference frame. Since the problem is a relative one, this is legitimate.

There are different schemes for obtaining orientational average sets. Here we will use a Gaussian Spherical quadrature scheme derived by Lebedev and Laikov [20]. The orientations and weights are taken from a list⁴ of M. Eden with an extension for the third Euler angle γ ; the procedure for obtaining these schemes are given in Ref. [110, 111]. A numerical approximation of the averaging process is necessary, because an analytical calculation is not possible. Therefore, to mimic the experimental situation, a weighted sum of the absorption cross section over the Euler angles has to be taken. As the absorption cross section for one crystallite $\sigma_{\alpha',\beta',\gamma',\kappa}^*(\tilde{\nu})$ in one laboratory reference frame, can be simulated by the scheme given in 4.3.1; the sum reads:

$$\sigma_{powder}^*(\tilde{\nu}) = \sum_{j=1,2} \frac{1}{2} \left(\sum_{i=1}^{N^S} w_i^S \sigma_{\alpha'_i^S, \beta'_i^S, \gamma'_i^S, \kappa_{i,j}^S}^*(\tilde{\nu}) \right) \quad (4.16)$$

where j labels the two different polarization directions, and the Lebedev set is given by $S = \{w_i^S, \alpha'_i^S, \beta'_i^S, \gamma'_i^S\}$ of N^S different orientations with the respective weight.

4.4 Example simulations for different crystal field Hamiltonians

The difference of the normalized absorption cross section can take on many different patterns depending on the crystal field Hamiltonian. To get an idea of the expected patterns, we calculated the difference of the normalized absorption cross section for

⁴ The lists were downloaded from <http://www.mmk.su.se/~mattias/OrientalionalAveraging/>

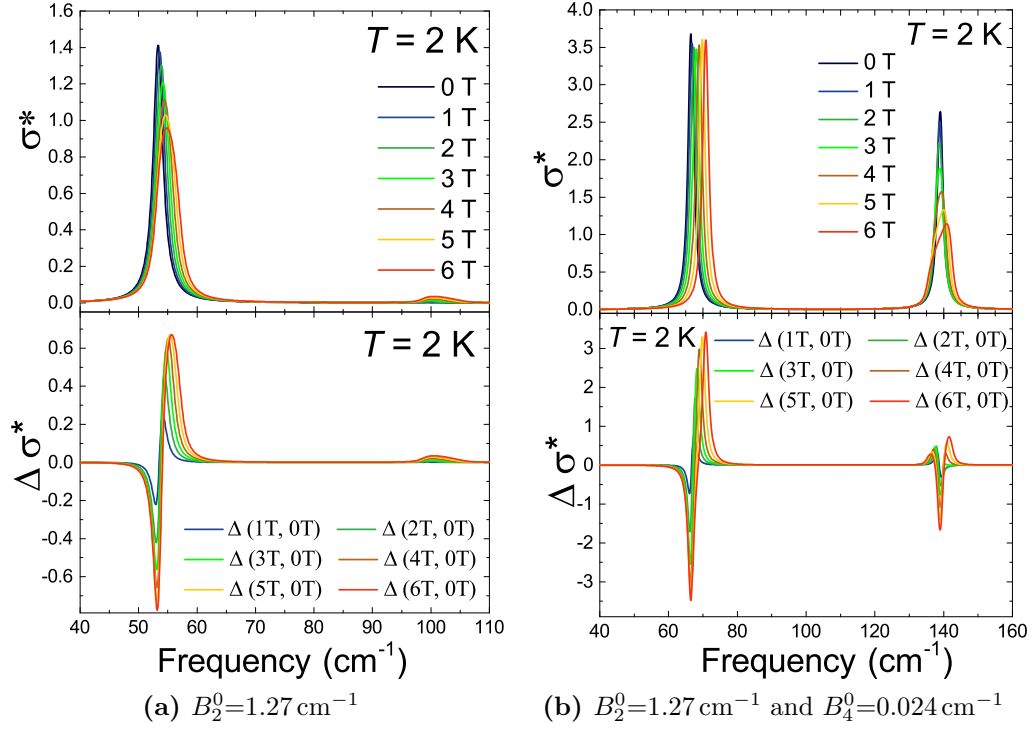


Fig. 4.1: Simulated normalized absorption cross section and the difference of the normalized absorption cross section between in-field and zero-field at $T=2 \text{ K}$.

different crystal field parameters. The simulations were conducted for samples of microcrystalline powder (see Section 4.3.2).

For every simulation a Lorentzian lineshape with a linewidth of $\gamma = 2 \text{ cm}^{-1}$ and a Lebedev grid with $N^S = 95964$ different sets of Euler angles were used. The lanthanide ion is in all simulations dysprosium with the ground multiplet $J = 15/2$ and the Landé factor $g = 4/3$.

Magnetic field dependence at $T=2 \text{ K}$

As a first example, we have assumed a crystal field Hamiltonian with axial symmetry, where the only non-zero crystal field parameter is B_2^0 and has the value $B_2^0 = 200 \text{ cm}^{-1}$. The results of the simulation for magnetic fields from 0-6 T at a temperature of 2 K are shown in Figure 4.1 (a). The crystal-field Hamiltonian splits the $J = 15/2$ multiplet into Kramers doublets, leaving only the Kramers degeneracy. The first absorption line at 53 cm^{-1} originates from the transition between the ground Kramers doublet $|\pm 15/2\rangle$ and the first excited Kramers doublet $|\pm 13/2\rangle$. The second transition at 100 cm^{-1} can be attributed to the transition between the ground Kramers doublet $|\pm 15/2\rangle$ and the second excited Kramers doublet $|\pm 11/2\rangle$. Whereas the first transition is allowed in

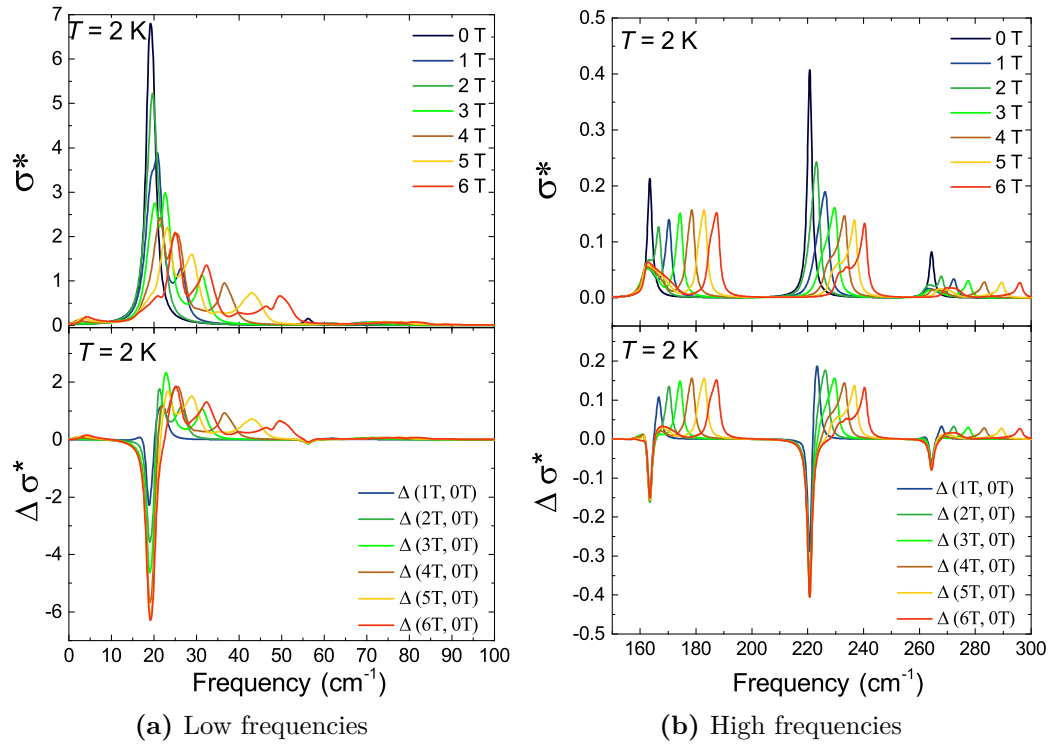


Fig. 4.2: Simulated normalized absorption cross section and the difference of the normalized absorption cross section between in-field and zero-field for dysprosium ethyl sulphate at $T=2\text{ K}$.

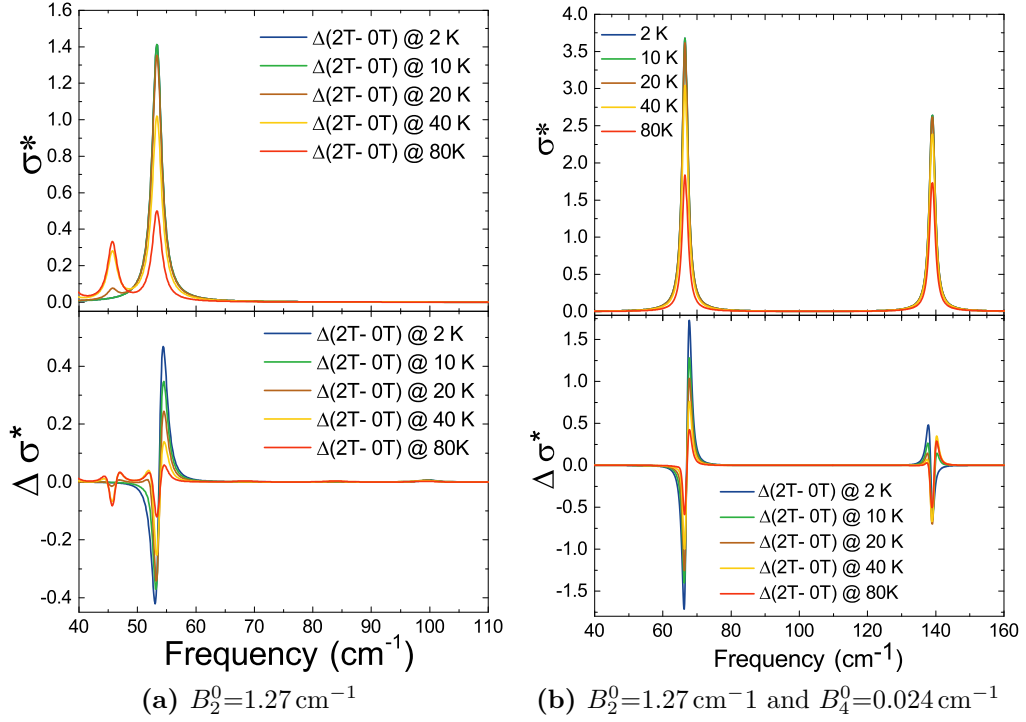


Fig. 4.3: Simulated temperature dependence of the normalized absorption cross section and the difference of the normalized absorption cross section between $B=2$ T and zero-field.

zero-field and shifts by the application of a magnetic field to higher frequencies, the second transition is forbidden in zero-field and gains intensity with increasing field. The second example assumes a crystal field Hamiltonian with the parameters $B_2^0 = 200 \text{ cm}^{-1}$ and $B_4^0 = -400 \text{ cm}^{-1}$, all other other parameters are zero. The result of the simulation for magnetic fields from 0-6 T at a temperature of 2 K are shown in Figure 4.1 (b). The first absorption line at 66 cm^{-1} can be attributed to the transition between the ground Kramers doublet $|\pm 11/2\rangle$ and the first excited Kramers doublet $|\pm 9/2\rangle$, the second at 140 cm^{-1} to the transition between the ground Kramers doublet $|\pm 11/2\rangle$ and the second excited Kramers doublet $|\pm 13/2\rangle$. Whereas, the first absorption lines moves to higher frequencies with increasing field, the second splits and moves to both lower and higher frequencies.

The third example uses the crystal-field Hamiltonian derived for dysprosium ethyl sulphate by Hill *et al.* [11] by the use of far-infrared spectroscopy on single crystals. The low frequency part is shown in Figure 4.2 (a) and the high frequency part in 4.2 (b).

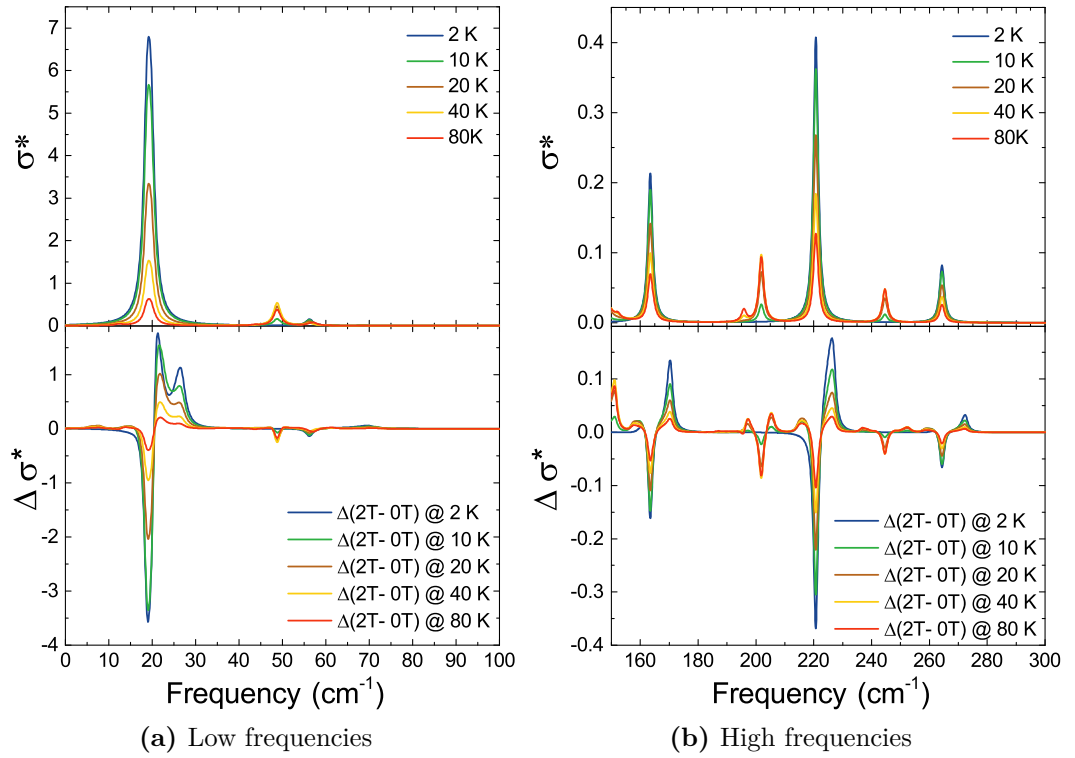


Fig. 4.4: Simulated temperature dependence of the normalized absorption cross section and the difference of the normalized absorption cross section between $B=2$ T and zero-field of dysprosium ethyl sulphate.

Temperature dependence

In addition, in Figure 4.3 and 4.4 the simulated temperature dependence of the normalized absorption cross section is shown for the three examples. It can be observed that the absorption lines caused by transitions from the ground state, the only ones observable at a temperature of 2 K, lose intensity with increasing temperature, according to the Boltzmann population of the states.

4.5 Evaluation by the use of the spectroscopic g-factors

If a simulation of the spectra is hampered by, e.g. too many crystal field parameters, the normalized absorption cross section can also be used to extract the spectroscopic g-factor of the transition. In powder samples, the spectroscopic g-factor g^{if} of the transition between the states i and f is different for all directions of the magnetic field and the observed absorption line is the sum over all directions. We will describe the spectroscopic g-factor in the laboratory reference frame (frame of the magnetic field $\vec{B}$) with x, y, z axes. The spectroscopic g-factor has to be determined for every direction (index j) of the magnetic field relative to the molecular frame on its own. Experimentally the spectroscopic g-factor is defined for a transition between the states i and f as [68]:

$$g_j^{if} = \frac{dW_j^{if}}{\mu_B dB_j}, \quad (4.17)$$

where dW_z^{if} is the splitting energy (measured by the resonance frequency) in a magnetic field $\vec{B} = (0, 0, B_z)$. Theoretically the spectroscopic g-factor for a transition between eigenstates i and f of the crystal field Hamiltonian is given by:

$$g_z^{if} = \frac{g_J \mu_B \hat{S}_z |\Psi_f(B_z)\rangle (B_z + \Delta B_z) - g_J \mu_B \hat{S}_z |\Psi_i(B_z)\rangle (B_z)}{\mu_B dB_z}, \quad (4.18)$$

where the eigenstates of the transition $|\Psi_f(B_x)\rangle$ need to be derived in the laboratory reference frame (frame of the magnetic field $\vec{B}$). Therefore, the crystal field Hamiltonian needs to be transformed into the laboratory reference frame by a tensorial transformation, leading to the crystal field Hamiltonian in the formulation $\hat{H}_{CF} = \sum_{k=2,4,6} \sum_{q=-k}^k B_k^{q*} O_k^{q*}(\hat{J})$. The intensity of the transition i and f depends on the transition matrix element of the polarization direction. As the measurements are performed with unpolarized light, the polarization direction of the light is parallel, as well as perpendicular, to the applied field. The laboratory reference frame is

shown in Figure 3.2. For the perpendicular polarized light, the intensity of the line is determined by the transition matrix element $\langle \Psi_i(B_z) | S_{x,y} | \Psi_f(B_z) \rangle$ multiplied by the population difference between the two states $N_{i,f}(T)$; and for parallel polarized light by the transition matrix element $\langle \Psi_i(B_z) | S_z | \Psi_f(B_z) \rangle$.

The spectroscopic g-factor g^{if} depends on the composition of the magnetic quantum numbers M_J of the eigenstates involved in the observed transition. Therefore, it yields additional information about the crystal-field Hamiltonian.

4.6 Distinction between electric and magnetic dipole transitions

Both modeling methods described in Sections 3.2.1 and 4.2 assume that the transitions inside the ground multiplet of lanthanides are caused by magnetic dipole transition. In the standard treatment electric dipole transitions are forbidden due to the parity selection rule, which states that the electric dipole operator can not connect states of the same parity. However, in non-centrosymmetric ligand fields mixing (of the $4f^{n-1}d^1$ -configuration with opposite parity into the $4f^n$ -configuration of the ground state) can take place [11, 112]. In addition, to odd-parity terms can be mixed into the ground state by coupling with odd-parity phonons or vibrons [11]. The origin of transitions in the ground manifold is strongly related to the "puzzle of rare earth spectra" which was raised in the beginning of the last century by Van Vleck and others [113], referring to the appearance of normally forbidden transitions between inter-manifold states. The puzzle was solved by the Judd-Ofelt theory in the 1960s [107]. It was also there, that the occurrence of normally forbidden transitions was attributed to the mixing with excited odd-parity states [107].

Experimental evidence that electric dipole transitions are also possible between states of the same manifold were found, e.g., for the rare-earth garnets $\text{Dy}_3\text{Fe}_5\text{O}_{12}$ by Rogers *et al.* [114], in the multiferroic compound HoMn_2O_5 by Sirenko *et al.* [115], and also mentioned by Komandin *et al.* [112] for DyScO_3 . But, up to date they are not mentioned in the field of lanthanide based SMMs. Instead it is often implicitly assumed that only magnetic dipole transitions are possible, e.g., Ungur *et al.* [17] and Blagg *et al.* [16].

In the following, we will discuss how it is possible to distinguish experimentally by means of far-infrared spectroscopy between electric and magnetic dipole transitions. Revisiting the Fresnel-equations for a plane-parallel slab in Section 3.2.1, we notice that the transmission depends on a quantity $\sqrt{\hat{\epsilon}(\omega) \times \hat{\mu}(\omega)}$ and the reflectivity on $\sqrt{\hat{\epsilon}(\omega)/\hat{\mu}(\omega)}$. It follows that in reflectivity measurements the shape of the resonance (for example Lorentz) is inverted for magnetic resonances compared with electric resonances, as can be seen in Figure 4.5.

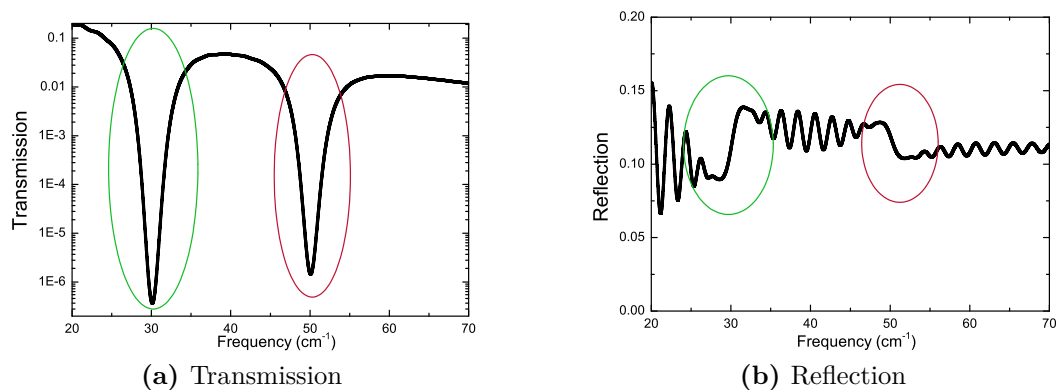


Fig. 4.5: Transmission and reflectivity spectra of a slab with a thickness of 1 mm and $\epsilon_{\infty} = 4$. The red circle marks an electric dipole transitions and the green one a magnetic dipole transition.

In general a transition can be of both electric and magnetic dipole character, leading to a hybrid mode. In transmission both contributions add up and a stronger absorption is observed. On the other hand, in reflectivity spectra the line intensities of electric and magnetic dipole transitions are subtractive and can lead to a complete canceling of the feature [114].

We can summarize that both reflectivity and transmission spectra are necessary for an experimental distinction between electric and magnetic dipole transitions.

Reflectivity measurements are difficult to conduct with powdered samples because a inhomogeneous interface distorts the spectrum considerably. Therefore, no reflectivity measurements were conducted in this thesis due to the absence of single crystals. In addition, for the compounds studied in this thesis, the reflectivity is small in the order of 3-7% hampering reflectivity measurements.

5 Dy(PhOPh): A lanthanide-based single-chain magnet

5.1 Introduction

Some results of this Chapter have been already published in Reference [116]. A key issue for the investigation of the magnetic relaxation process in molecular materials is the determination of their energy levels. In single-ion lanthanide magnets the relaxation process is proposed to take place by a thermally assisted mechanism via an excited real state with additional contributions due to under barrier processes (compare Section 2.3). For the Orbach relaxation process, the effective energy barrier is comparable to the energy of the excited state lowered by the contribution of under barrier mechanisms.

For single-chain magnets with anisotropic building blocks, the Glauber dynamics approach was extended to additionally take into account the intrinsic anisotropy barrier of the constituents (compare Section 2.4). A relaxation time of $\tau = \tau_0 \cdot \exp((4|J|S^2 + \Delta)/k_B T)$ (with coupling constant J and the energy barrier Δ) was proposed for the infinite-size regime and $\tau = \tau_0^* \cdot \exp((2|J|S^2 + \Delta)/k_B T)$ for the finite-size regime [50]. In the finite size regime the correlation length ξ exceeds the chain length L ($\xi \gg L$). The relaxation process starts with a spin flip at the chain end, with an energy cost of $2J$ due to the exchange interaction of the one residual neighbor. In the infinite size regime the chain length is longer than the correlation length ($L \gg \xi$) and the relaxation process takes place via a thermally activated random walk of the domain walls. The chain length L is determined by limiting geometrical factors or the presence of impurities. The model was verified for several single-chain magnets based on transition metal ions [50, 51].

In this study we will focus on two members (the terbium and dysprosium derivatives) of the lanthanide based isostructural single-chain-magnet family $[\text{Ln}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}]$ (LnPhOPh with $\text{Ln}=\text{Dy, Tb}$) in which the Ln^{3+} ions are coupled by nitronyl-nitroxide radicals leading to a polymeric one dimensional arrangement [14, 117]. The crystal structure is shown in Figure 5.1. The main emphasis will lie on the dysprosium derivative. The static magnetic behavior of DyPhOPh was explored by angle-dependent susceptibility measurements, and was modeled by using theoretical results (CASSCF-calculations) for the anisotropy of the Dy^{3+} spins and a classical Hamiltonian for the coupling between the spins [117]. In contrast to the static

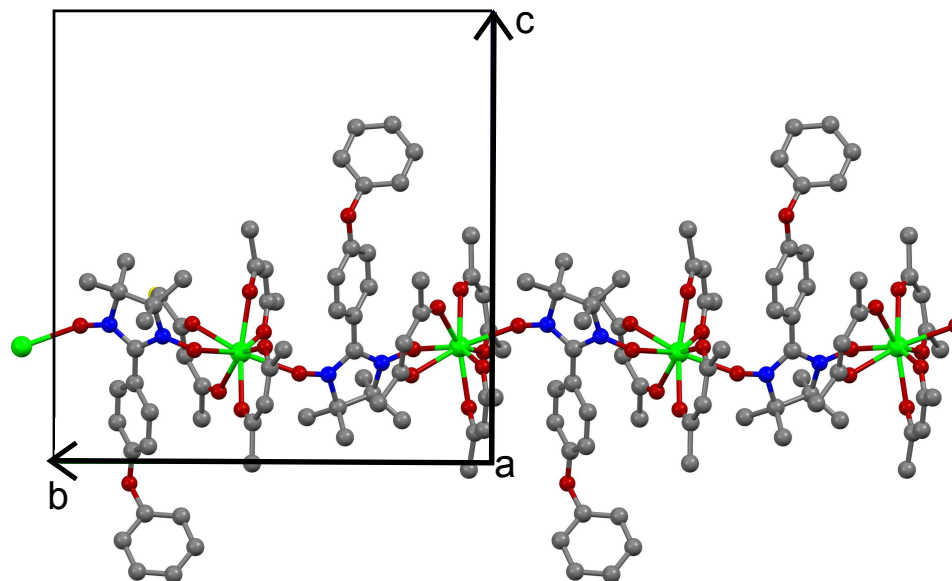


Fig. 5.1: View of the Crystal structure of Dy(NITPhOPh) [14] along the a -axis, showing the chain structure together with the unit cell. Color Scheme: Dy→green, O→red, C→gray, N→blue.

case, a coherent picture of the dynamic behavior is still lacking. Slow relaxation of the magnetization was observed in these compounds by alternating current susceptibility measurements. In DyPhOPh a crossover between two different relaxation regimes was observed, which was assigned to the crossover between an infinite-size regime and a finite-size regime [14]. The difference of the relaxation barrier at the crossover deviates from the predicted value given by the extended Glauber model, if the parameters extracted from the static magnetic susceptibility are used. This discrepancy was related to the neglected contribution of the radicals, which can contribute to the dynamic behavior, even if they are negligible for the static properties [57]. To shed light onto the relaxation dynamics, the aim of this study is to determine the energy level structure of the Dy^{3+} ion which plays a crucial role in the relaxation process. Our results suggest that the crossover in the relaxation process is rather governed by a switching between two relaxation pathways of the lanthanide ion than by Glauber dynamics.

In a low-symmetry environment, like in the compound LnPhOPh studied here, the experimental determination of the crystal-field split energy levels is complicated because none of the parameters in the crystal field Hamiltonian can be neglected a priori by the use of symmetry arguments [4, 43]. This makes techniques like the combined analysis of NMR-paramagnetic shifts and magnetic susceptibility data [47] difficult or inapplicable. Recently, the theoretical determination of the crystal field split lanthanide states by complete active space self-consistent field (CASSCF) calculations was provided, and applied to Ln^{3+} ions in LnPhOPh but an experimental verification

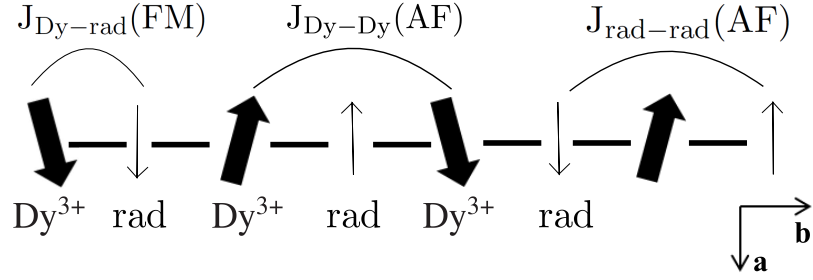


Fig. 5.2: Sketch of the spin alignment in DyPhOPh in the ab -plane determined in Bernot *et al.* [57] with bold arrows Dy^{3+} spins and thin arrows the radical spins. The magnetic interactions are labeled with FM=ferromagnetic and AFM=antiferromagnetic coupling.

is still missing [43, 81, 118].

Here we will use far-infrared spectroscopy to study the low lying energy levels of Dy^{3+} and Tb^{3+} in the single-chain-magnet LnPhOPh.

The lanthanide-based single-chain magnet DyPhOPh has been already well characterized by AC and DC magnetic susceptibility measurements [14, 57, 117]. The single-chain magnet consists of alternating Dy^{3+} ions and the organic nitronyl nitroxide radicals. Along the alternating units, ferromagnetic nearest-neighbor couplings were found between the radicals and the Dy^{3+} spins, antiferromagnetic next-nearest-neighbor coupling between the Dy^{3+} spins, and antiferromagnetic next-nearest-neighbor couplings between the radicals (see Figure 5.2). The DC magnetic behavior could be satisfactorily modeled at low temperatures by neglecting the radical contribution to the magnetization and taking into account only the Dy^{3+} spins. Angle-dependent magnetic measurements revealed that the Dy^{3+} spins act at low temperatures as Ising spins. The local easy axis is tilted 75° from the crystallographic b -axis (along the chain), leading to weak ferromagnetism along the b -axis. At 9 K, an inversion of the anisotropy axis was found which was explained by a change of the Dy^{3+} magnetism. Above 9 K the Dy^{3+} spin only acts as paramagnetic spin center along the local easy axis (tilted 75° from the crystallographic b -axis). Below 9 K, the antiferromagnetic coupling between the Dy^{3+} spins starts to play a significant role, leading to an uncompensated moment along the b -axes. The next nearest neighbor coupling constant was determined as $J=24$ K with Dy^{3+} taken as $S_{\text{eff}}=1/2$ with the classical Hamiltonian $\mathcal{H} = -\sum_i \{ J \mathbf{S}(i) \cdot \mathbf{S}(i+1) + D[S'_{z_i}(i)]^2 + \mu_0 \sum_{\alpha,\beta} H_\alpha g_{\alpha,\beta} S_\beta(i) \}$.

5.2 Methods and materials

The transmission spectra were acquired with a Bruker IFS 113 v Fourier Transform spectrometer connected to a Oxford Spectromag 4000 Split-Coil Magnet with Mylar

windows in the frequency range from 20-80 cm⁻¹ with a resolution of 0.5 cm⁻¹ using unpolarized light. For a detailed description of the setup (see Section 3.1.2). For lower frequencies the quasi-optical setup with BWO was used (see Section 3.1.1). Magnetic fields were applied up to 6 T in Voigt geometry. Each spectrum was normalized by a reference spectrum taken through an empty aperture with a size equal to the sample. The sample itself is a pressed pellet out of microcrystalline powder. The DyPhOPh pellet used for the far-infrared measurements has a weight of 51.3 mg and a thickness of 0.54 mm, for the BWO measurements 300 mg and 1.98 mm. The TbPhOPh pellet has a weight of 52.6 mg and a thickness of 0.40 mm. The compounds DyPhOPh and TbPhOPh were synthesized according to the procedure presented in Bogani *et al.* [14] at the University of Stuttgart by Lapo Bogani.

The acquired transmission spectra were fitted using the fresnel formulas for a plane parallel layer [62] presented in Section 3.2.1.

The vibrational and phononic absorption lines, which show no change with magnetic field are modeled with the electric oscillator model. The electronic transitions inside the ⁶H_{15/2} multiplet are modeled by the magnetic oscillator model, in which the contribution to the static magnetic permeability is given by $\Delta\mu_{i,j}$ [62, 98]:

$$\Delta\mu_{if} = \frac{8\pi}{3} N_0 \frac{\sum_{\alpha=x,y,z} g_{\alpha} \mu_B \alpha |\langle f | \hat{S}_{\alpha} | i \rangle|^2}{\hbar\omega_{i,f}} \times \frac{\exp(-\frac{E_f}{k_B T}) - \exp(-\frac{E_i}{k_B T})}{Z} \quad (5.1)$$

with the matrix element of the magnetic moment between the two participating states averaged over the three polarizations of light $\sum_{\alpha=x,y,z} g_{\alpha} \mu_B |\langle f | \hat{S}_{\alpha} | i \rangle|^2 / 3$, the population difference between the two states $\frac{\exp(-\frac{E_f}{k_B T}) - \exp(-\frac{E_i}{k_B T})}{Z}$, and the number density N_0 of (Ln³⁺) ions.

5.3 Results

Spectra in zero field: Overview

To identify the electronic absorption lines, the most appropriate way is to first exclude the phonon absorption lines. In Figure 5.3 b), a comparison between the transmission spectra of the DyPhOPh and the TbPhOPh compound is shown.

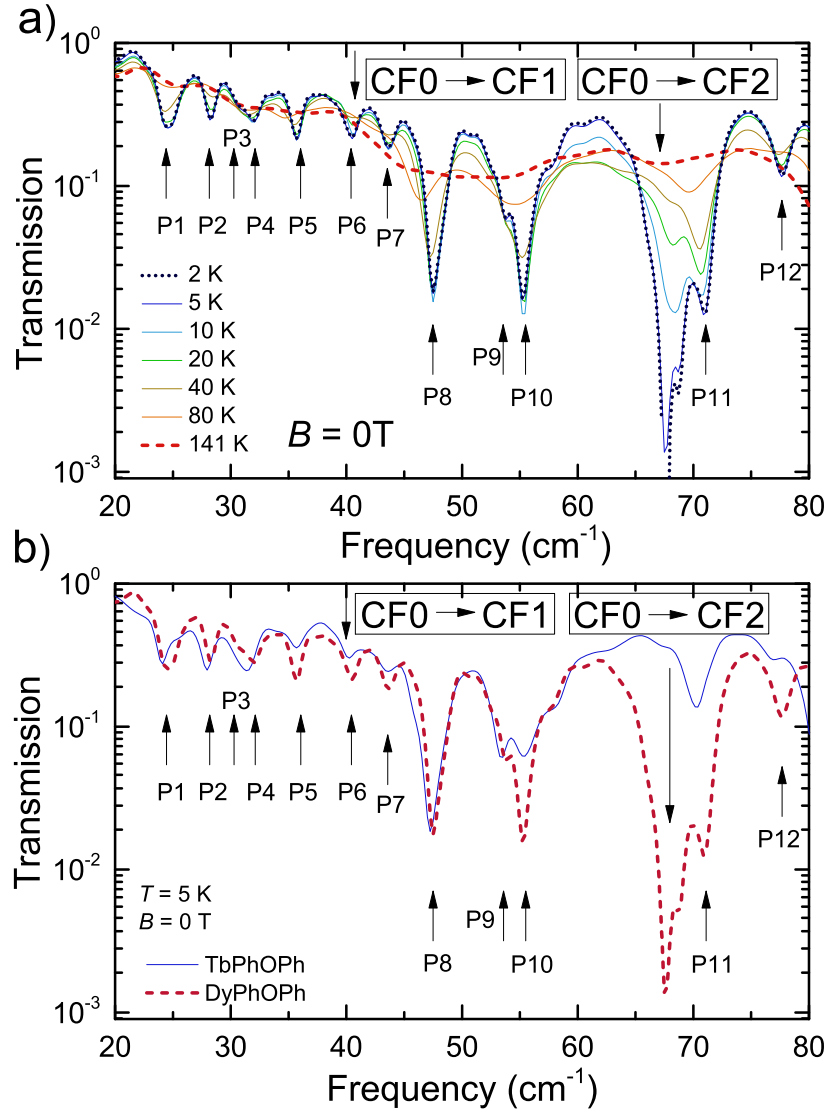


Fig. 5.3: a) Transmission spectra acquired for a powder pellet of DyPhOPh (thickness 0.54 mm) in the temperature range from 2 K–141 K without magnetic field. The phonon lines are labelled with P1–P12 and the electronic absorption lines with the CF0→CF1 and CF0→CF2 for the corresponding transitions inside the dysprosium $^6\text{H}_{15/2}$ multiplet. b) Comparison between the transmission spectra of DyPhOPh (thickness 0.54 mm) and TbPhOPh (thickness 0.40 mm) at $T=5 \text{ K}$ and $B=0 \text{ T}$.

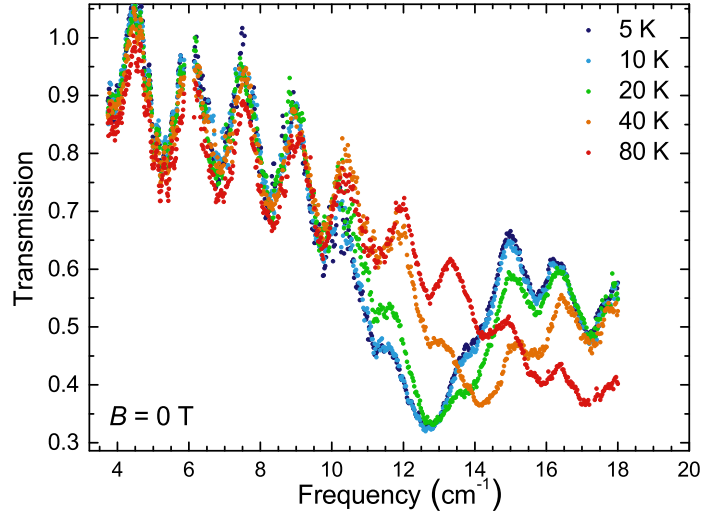


Fig. 5.4: Transmission spectra of DyPhOPh (thickness 1.98 mm) at 5 K measured with the BWO quasi-optical setup.

Both spectra reveal absorption lines at essentially the same frequencies (labeled P1-P12) (with partially different intensities). This behavior is characteristic for isostructural lanthanide compounds where one lanthanide ion is substituted by another lanthanide ion (like Dy^{3+} by Tb^{3+}). In this case, the substitution influences the far-infrared phonon spectrum only slightly, because both ions have nearly the same mass and, in addition, the mass change is compensated by a change in the ionic radius [13]. The temperature dependence shown in Figure 5.3 a) of the absorption lines confirms that they belong to phononic or vibrational excitations: They shift to slightly lower frequencies with increasing temperature due to the thermal expansion of the lattice. In addition, the damping factor increases with temperature, leading to a broadening of the lines.

The transmission spectra at lower frequencies were acquired with the BWO quasi-optical setup (see Section 3.1.1) and are shown in Figure 5.4. One additional absorption line can be identified at 12.5 cm^{-1} . The line shows a blue-shift with increasing temperature which is pretty uncommon for phononic or vibronic excitation. The origin of this line is unclear.

Identification of electronic absorption lines

DyPhOPh: The free Dy^{3+} ion ground state $^6H_{15/2}$ has half integral angular momentum. The low-symmetry crystal field will raise the degeneracy of the half integral J multiplet except for the Kramers degeneracy resulting in $(J+1/2)=8$ doublets [1]. In the 1-dimensional chain short-ranged correlations appear upon cooling, having a considerable influence below 10 K with no phase transition. At these temperatures the

chain will be split into several short segments, in which the Dy^{3+} spins are antiferromagnetically aligned, which can be schemetically depicted by $\uparrow\downarrow\uparrow$. By measuring the far-infrared spectra the obtained energy-levels of the Dy^{3+} also resemble the antiferromagnetic arrangement, and are in general different to the energy levels in the paramagnetic state at higher temperatures.

The magnetic field dependence of the transmission spectra at 2 K is shown in Figure 5.5 a). Normalizing the transmission spectra in zero field to the spectra in field (Figure 5.5 b)) reveals two absorption lines at $(40 \pm 2) \text{ cm}^{-1}$ and $(68 \pm 2) \text{ cm}^{-1}$, which can be assigned to electronic transitions experiencing a Zeeman-splitting in the applied magnetic field.

The features at 45 and 55 cm^{-1} coincide with the resonance frequency of two phonon lines (P8 and P10) and are artefacts of the magnetic field change of the strong electronic absorption line at 68 cm^{-1} .

At low temperatures, only the lowest Kramers doublet will have an appreciable population. Thus transitions in the far-infrared spectrum are only expected from the ground doublet. The first absorption line at $(40 \pm 2) \text{ cm}^{-1}$ is therefore identified as a transition from the ground Kramers doublet CF0 to the first excited doublet CF1. The inset of Figure 5.5 c) shows the temperature dependence of the ratio spectra with and without field, as the temperature increases, the field dependence becomes very weak and vanishes completely at 20 K. This behavior results from the Boltzmann population of the states. The zero-field spectrum was fitted with the method presented in Section 5.2, yielding at 5 K a contribution to the static magnetic permeability $\Delta\mu_{01} = 0.0005 \pm 0.0004$. Using equation 5.1, this results in an averaged matrix element of the magnetic moment of $(\sum_{\alpha=x,y,z} g_{\alpha} |\langle f | \hat{S}_{\alpha} | i \rangle|^2) / 3 = (3 \pm 2) \mu_B^2$.

The second absorption line lies at $(68 \pm 2) \text{ cm}^{-1}$ and is more pronounced. Even in the zero-field spectra (see Figure 5.3) it is clearly visible in DyPhOPh, but not in TbPhOPh. The identification as an electronic absorption line is verified by its magnetic field dependence (see Figure 5.5 a) and b)) and is assigned to the transition from CF0 to the second excited doublet CF2. This absorption reveals a splitting into two lines at 67.5 and 68.5 cm^{-1} , which can not be explained by the crystal field splitting (this conserves the Kramers degeneracy of the two doublets). The splitting is a direct evidence for an anisotropic exchange coupling acting on the Dy^{3+} spins, which can raise the Kramers degeneracy [13]. At 5 K, the contributions to the static magnetic permeability was determined for the two parts of the splitted absorption line as $\Delta\mu'_{02} = 0.004 \pm 0.001$ and $\Delta\mu''_{02} = 0.0008 \pm 0.0005$ resulting in an averaged matrix element of the magnetic moment of $(\sum_{\alpha=x,y,z} g_{\alpha} |\langle f | \hat{S}_{\alpha} | i \rangle|^2) / 3 = (47 \pm 14) \mu_B^2$ (both parts are added).

At 20 K, the appearance of a third absorption line at $(60 \pm 2) \text{ cm}^{-1}$ can be observed. We assign this absorption also to a transition from the CF0 to the second excited doublet CF2. But, in difference to the absorption line at 68 cm^{-1} the line originates from dysprosium ions in a paramagnetic arrangement ($\uparrow\uparrow\downarrow$) as the 1-dimensional chain short range correlations decrease with increasing temperature. For the first absorp-

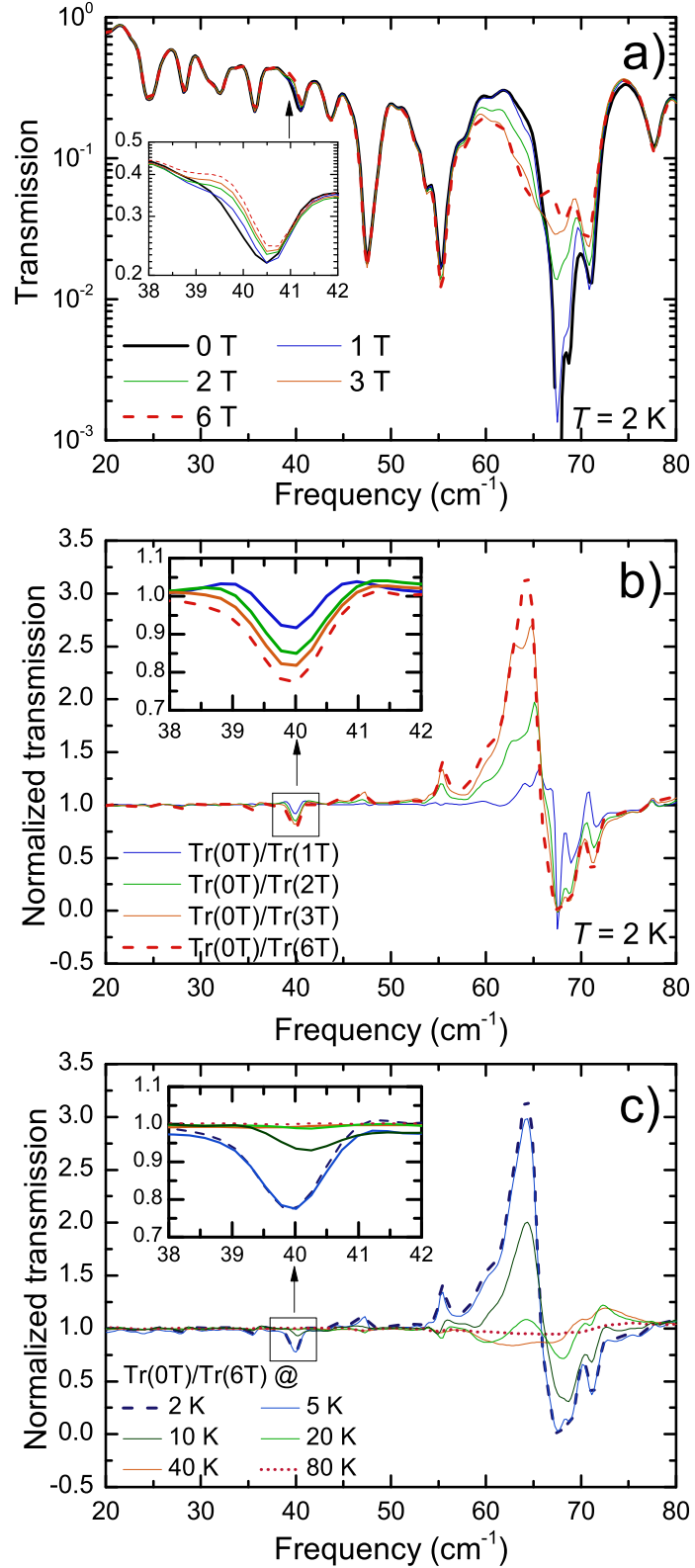


Fig. 5.5: a) Transmission spectra of DyPhOPh (thickness 0.54 mm) at 2 K b) Ratios of the transmission spectra of DyPhOPh at $B=0$ T normalized to spectra with an applied field ($B=1$ T-6 T) at 2 K. b) Ratios of the transmission spectra for DyPhOPh of the spectra at $B=0$ T normalized to spectra with an applied field of $B=6$ T at temperatures from 2 K-80 K.

tion line at $(40 \pm 2) \text{ cm}^{-1}$ the observation of the line associated to the paramagnetic arrangement is hampered by the small intensity of the line. The energy of the transition $\text{CF0} \rightarrow \text{CF2}$ in the paramagnetic arrangement of $(60 \pm 2) \text{ cm}^{-1}$ compares well with previously reported CASSCF-calculations for the crystal field splitting without any coupling, which resulted in energy levels at 40.5 and 58.8 cm^{-1} for the two lowest states [117]. The energy of the transition $\text{CF0} \rightarrow \text{CF1}$ found at low temperatures in the antiferromagnetically arrangement at $(40 \pm 2) \text{ cm}^{-1}$ can not be directly compared with the CASSCF-calculation for the pure dysprosium. In powder samples, the determination of the matrix element of the magnetic moment $\sum_{\alpha=x,y,z} g_{\alpha} \mu_B |\langle f | \hat{S}_{\alpha} | i \rangle|^2$ contains a strong inaccuracy, resulting from the scattering of the radiation inside the sample and can be strongly overestimated. However, the scattering should affect both lines equally. Therefore, we conclude that the transition matrix element of the transition $\text{CF0} \rightarrow \text{CF2}$ is sixteen times greater than that of the transition $\text{CF0} \rightarrow \text{CF1}$.

TbPhOPh: In contrast to Dy^{3+} , Tb^{3+} is a non Kramers ion with the ground multiplet 7F_6 with $J=6$. In principal, low-symmetry crystal fields can lift the degeneracy completely, leading to $(2J+1)=13$ crystal field levels. However, at low temperatures the Tb^{3+} ion is often modeled as a $S=1$ spin [117] with a non-Kramers ground state doublet. The spectra at 5 K with and without magnetic field are compared in Figure 5.6. The comparison reveals one electronic absorption line at $(45 \pm 2) \text{ cm}^{-1}$ at the low frequency shoulder of phonon P8, which shows eventually a splitting into a line at $(43 \pm 2) \text{ cm}^{-1}$ and $(46 \pm 2) \text{ cm}^{-1}$. The other features visible in the relative spectra (at $55 \pm 2 \text{ cm}^{-1}$ and $(70 \pm 2) \text{ cm}^{-1}$) can not be clearly identified as caused by an electronic transition, because they coincide with strong phonon absorption lines which can lead to artifacts.

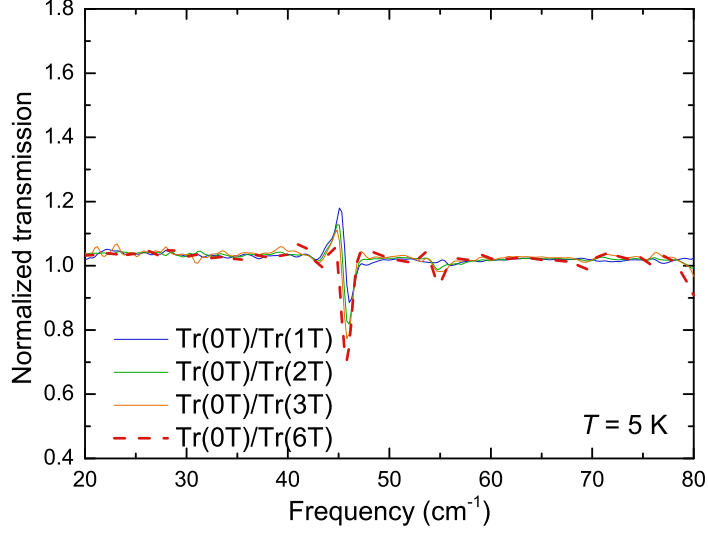


Fig. 5.6: Ratios of the transmission spectra of TbPhOPh (thickness 0.40 mm) at $B=0$ T normalized to spectra with an applied magnetic field ($B=1$ T-6 T) at $T=5$ K

5.4 Discussion: Relation to the relaxation dynamics

Previously reported results on the relaxation behavior studied by alternating current susceptibility revealed for DyPhOPh two distinguishable temperature regimes: At low temperatures, an Arrhenius behavior was found with a relaxation barrier of $\Delta' = (30 \pm 0.7) \text{ cm}^{-1}$. Above 3.8 K a crossover to an Arrhenius behavior with a relaxation barrier of $\Delta'' = (49 \pm 0.3) \text{ cm}^{-1}$ was observed [14]. The crossover was attributed to a transition from the finite-size regime to the infinite-size regime. In the following we will reassess this attribution and discuss, whether this relaxation behavior can be better explained by a switching between two relaxation pathways of the lanthanide ion or within the framework of the extended Glauber model for single-chain magnets with an additional anisotropy barrier.

For the extended Glauber model, the relaxation time is proposed to be $\tau = \tau_0 \cdot \exp((4|J|S^2 + \Delta)/k_B T)$ in the infinite size regime and $\tau = \tau_0^* \cdot \exp((2|J|S^2 + \Delta)/k_B T)$ for the finite size regime. For the crossover in the AC-susceptibility data, the difference for the relaxation barrier yields $\Delta'' - \Delta' = 2|J|S^2 = 19 \text{ cm}^{-1}$. Using the coupling constant $J = 24 \text{ K}$ given for the $\text{Dy}^{3+} - \text{Dy}^{3+}$ interaction [57] (with a tilting angle between the two local easy axes of $2\theta = 150^\circ$), the value of the extended Glauber model $2|J|S^2$ can be estimated as $2|J|'S^2 = 2S^2|J \cdot \cos(2\theta)| = 7.4 \text{ cm}^{-1}$ with an effective spin of $1/2$. The comparison of both results reveals a strong difference. The coupling is too weak to account for the measured value. This difference was attributed to the neglected contribution of the radical coupling to the model.

Our far-infrared results suggest a different reason for the crossover: the different re-

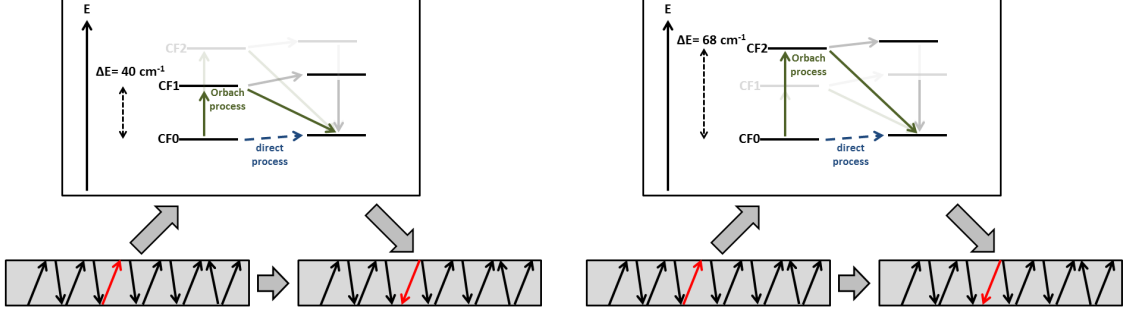


Fig. 5.7: Scheme of the proposed switching of the relaxation process in DyPhOPh. Only the arrangement of the dysprosium spins is shown, the radical spins are neglected. Left: Orbach process via the the first excited Kramers doublet CF1 proposed to be active at temperatures below the crossover at $T = 3.8$ K. Right: Orbach process via the the second excited Kramers doublet CF2 proposed to be active at temperatures above the crossover at $T = 3.8$ K. In addition, also the direct process is included which can lead to under-barrier relaxation.

laxation barriers are caused by different relaxation pathways - one via the first and one via the second excited Kramers doublet. The energy-level splitting of Dy^{3+} was determined at low temperatures as $(40 \pm 2) \text{ cm}^{-1}$ for the first, and $(68 \pm 2) \text{ cm}^{-1}$ for the second excited doublet. Assigning the low temperature relaxation barrier of $\Delta' = (30 \pm 0.7) \text{ cm}^{-1}$ to the first excited doublet and the high temperature barrier of $\Delta'' = (49 \pm 0.3) \text{ cm}^{-1}$ with the energy of the second excited doublet. The relaxation barrier and the corresponding value of the excited state differ by a factor of around 1.3-1.4. A factor of 1.3-1.4 agrees with relations found for the difference of the relaxation barrier to the energy of the excited doublet in other single-ion magnets caused by under barrier processes like the direct process [16, 47].

The proposed relaxation mechanism is different to the relaxation process described for transition-metal based single-chain magnets as presented in Section 2.4.2 and in Reference [50]. There the relaxation process takes place via the movement of the domain walls and the observed relaxation barrier is therefore given by $\tau = \tau_0 \cdot \exp((4|J|S^2 + \Delta)/k_B T)$ in the infinite-size regime. The relaxation barrier consists of the factor $\exp(\Delta/k_B T)$ coming from the single-ion anisotropy barrier at a spin next to a domain wall and the factor $\exp(4|J|S^2/k_B T)$ which considers the random walk, as the random walk needs a time of $\xi^2 = \tau_0 * \exp(4|J|S^2/k_B T)$ (with $\tau_0^* = \tau_0 \exp(\Delta/k_B T)$) to reverse one domain with the correlation length $\xi = \exp(2|J|S^2/k_B T)$. In contrast, we propose in our model that the relaxation in DyPhOPh takes place mainly by spin-flips inside of the domain walls, in the beginning of the relaxation process. The energy barrier to overcome is in this case the energy difference between the ground Kramers doublet and the excited doublet via which the Orbach relaxation process of the dysprosium can take place. This energy difference is directly measured by the far-infrared measure-

ment, as at low temperatures the spins are arranged in an antiferromagnetic alignment. A scheme of the proposed relaxation process for the two relaxation regimes is depicted in Figure 5.7.

The described picture of the switching of the relaxation process is also in agreement with unpublished AC-susceptibility measurements¹ conducted on samples of DyPhOPh where parts of the dysprosium ions were doped with diamagnetic yttrium ions in order to artificially reproduce the naturally occurring defects. Thereby, in the Glauber model approach, a transition to the finite-size regime is artificially reproduced which should lead to a decrease of the relaxation barrier Δ and an acceleration of the relaxation process [119]. However, the opposite trend was observed, the relaxation barrier Δ increased slightly in the yttrium-doped sample. As the doping with yttrium does not change the relaxation dynamics in the way proposed for the finite-size effect, this observation is an indication that the Glauber dynamics plays a subordinate role in the relaxation process as reflected in the above described more single-ion like picture. We want to stress that also in this picture the barrier of the relaxation of one of the dysprosium ions depends on the neighboring dysprosium spins. But, the relaxation barrier differs only slightly for the different spin arrangements. For the transition CF0→CF2 the transition frequencies can be determined for the antiferromagnetically arranged ($\uparrow\downarrow\uparrow$) at low temperatures (2 K) as $(68\pm2) \text{ cm}^{-1}$ and for the paramagnetic arrangement ($\uparrow\uparrow\downarrow$) at higher temperatures (20 K) as $(60\pm2) \text{ cm}^{-1}$.

In TbPhOPh the first excited energy level is located at $(45 \pm 2) \text{ cm}^{-1}$. The relaxation barrier was determined as $\Delta = (32.1 \pm 0.7) \text{ cm}^{-1}$ [117]) without any crossover between different relaxation regime. When comparing for TbDOTA, the first excited level with the relaxation barrier, we again find a factor of 1.4.

The single-ion relaxation mechanism presents a coherent picture for both LnPhOPh single chain magnets.

5.5 Conclusion

We have shown that far-infrared transmission spectroscopy can be used as an efficient tool to study the energy levels of low symmetry lanthanide ions inside single-chain magnets. For DyPhOPh at temperatures below 10 K, the energy of the lowest energy-levels was determined as $(40\pm2) \text{ cm}^{-1}$ and as $(68\pm2) \text{ cm}^{-1}$. These results give important information for the relaxation mechanism of lanthanide based single-chain magnets. The value of the energy-levels suggest that the relaxation of the magnetization takes place by an Orbach process via the first excited doublet (at low temperatures) and the second excited level (at higher temperatures) of the dysprosium ion with additional under barrier mechanisms. The crossover observed in the relaxation measurements is,

¹ Private communication with Roberta Sessoli (University of Florence) and the PhD-thesis of Kevin Bernot [64]

therefore, given by a switching of the relaxation pathway *inside* the dysprosium ion rather than by the change from the finite- to the infinite-size regime of the extended Glauber model.

6 DyDOTA: A single-ion lanthanide compound showing slow relaxation of the magnetization

6.1 Introduction

Lanthanides coordinated by the DOTA ligand ($\text{H}_4\text{DOTA} = 1,4,7,10$ -tetraazacyclododecane- $\text{N},\text{N}',\text{N}'',\text{N}'''$ -tetraacetic acid) are well known as functioning as contrast agents in magnetic resonance imaging [120]. The low temperature magnetic behavior of $\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ (DyDOTA) was studied by Car *et al.* [15] and revealed that it acts as a single-ion magnet, showing slow relaxation of the magnetization. In the following the lanthanide family $\text{Na}[\text{Ln}(\text{DOTA})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ with $\text{Ln}=\text{Dy}, \text{Tb}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}$ was investigated in depth by means of AC-susceptibility, angle-resolved susceptibility, and luminescence measurements [8, 15, 58]. The symmetry of the first coordination sphere of the Ln-ion is nearly tetragonal, but the tetragonal

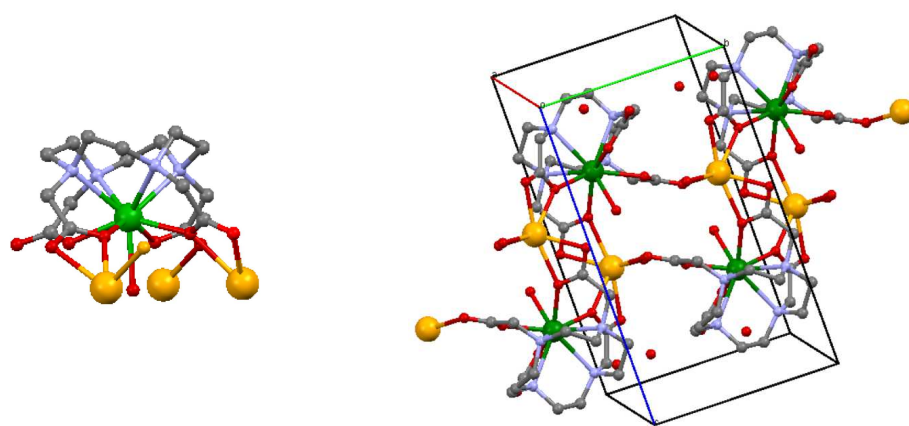


Fig. 6.1: Left: View of the quasi-tetragonal coordination sphere of DyDOTA [15]. Right: Crystal packing in the triclinic cell [15]. Color scheme: Dy→green, Na→yellow, O→red, C→gray, N→blue.

symmetry is absent when considering the wider coordination geometry (see Figure 6.1). The overall spacegroup of the crystal is triclinic (P-1). The crystal field at the dysprosium ion has a low symmetry and calculations with the crystal field Hamiltonian are hampered by the absence of symmetry. The theoretical treatment, therefore, included sophisticated ab-initio CASSCF calculations. In the following the previously obtained results will be summarized.

6.1.1 Magnetic relaxation

AC-susceptibility measurements revealed the presence of slow relaxation in the three Kramers-ion based compounds DyDOTA, ErDOTA, and YbDOTA (see for characteristic parameters Table 6.1) and an absence of slow relaxation in the non-Kramers ion compounds TbDOTA, HoDOTA, and TmDOTA [15]. Solely, for the Kramers ion DyDOTA slow relaxation was observed without a magnetic field. The absence of slow relaxation in the non-Kramers ions was related to the large tunneling splitting between the two lowest energy eigenstates. Neither the application of a static magnetic field, nor magnetic dilution with yttrium ion resulted in any observable slow relaxation. We will focus here on the relaxation process of DyDOTA. In detail, in DyDOTA two relaxation processes were observed: A fast process, which dominates in zero field, and a slower process, which was enhanced with respect to the faster process by the application of a static magnetic field (see Figure 6.2). The fast process was identified by its magnetic and temperature dependence to originate from the direct process (see Section 2.3.1.1). The slow relaxation process showed an Arrhenius behavior and was,

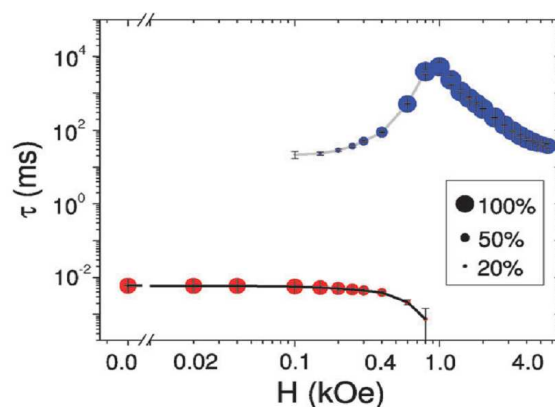


Fig. 6.2: Magnetic field dependence of the relaxation time extracted from AC-susceptibility measurements. Blue circles: fast process (direct process), Red circles: slow process (Orbach). The dimensions of the symbols represent the percentage of the isothermal susceptibility involved in the process. The grey line is a guide to the eye, while the black line represents the H^{-4} dependence expected for a direct process. Reproduced from Ref. [15] with permission from The Royal Society of Chemistry.

therefore, identified as an Orbach process (see Section 2.3.1.2). Magnetic dilution with Yttrium ions slowed down the fast process, but left the slow process unaffected. For ErDOTA and YbDOTA only the Orbach-process was observed. However, the Arrhenius behavior $\tau = \tau_0 \exp(\Delta E/k_B T)$ was only apparent in a small temperature window. Outside this range it deviated significantly from the Arrhenius law. Therefore, for a better estimation of the energy barrier of the Orbach-process a fit with an additional T^n contribution was conducted. The results of the energy barrier ΔE of the Arrhenius law for the three compounds are summarized in Table 6.1.

	$\Delta E(\text{cm}^{-1})$	$H_{DC}(\text{Oe})$	$\Delta(D2 - D1)(\text{cm}^{-1})$	$\Delta(D3 - D1)(\text{cm}^{-1})$
DyDOTA	42	900	64	112
ErDOTA	35	1000	20	63
YbDOTA	25	1000	197	379

Tab. 6.1: Characteristic values of the three LnDOTA compounds showing slow relaxation. The first value $\Delta E(\text{cm}^{-1})$ is the energy barrier of the Orbach process derived by AC-Susceptibility measurements with a static magnetic field $H_{DC}(\text{Oe})$. The last two rows: $\Delta(D2 - D1)(\text{cm}^{-1})$ and $\Delta(D3 - D1)(\text{cm}^{-1})$ show the energy difference between the ground and first excited energy state and the ground and second excited energy state derived by CASSCF-calculations [58].

6.1.2 Luminescence and CASSCF-calculations

The energy level structure of all of the compounds was obtained by CASSCF ab-initio calculations [8, 58]. Experimentally, the energy level structure was measured by luminescence for DyDOTA and TbDOTA. For DyDOTA a well resolved multiline emission spectrum was observed for transitions between the following multiplets with an excitation wavelength of 365 nm: $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$, and $^4F_{9/2} \rightarrow ^6H_{11/2}$. The experiments were conducted on powder samples at room temperature. In luminescence experiments the crystal field splitting of the multiplets leads to a multiline structure in the emission spectrum, caused by the different energy levels of the ground state. In general also "hot-bands" due to transitions starting from excited crystal-field states of the excited multiplet (here $^4F_{9/2}$) can be present. Analysis of the $^4F_{9/2} \rightarrow ^6H_{15/2}$ transitions revealed an overall-splitting of the ground multiplet by the crystal field comparable to the results obtained theoretically by the CASSCF-calculations. Also, the energy-level structure obtained by the luminescence spectra was well reproduced by the ab-initio calculations. For the relaxation process especially the difference between the ground and first excited crystal-field level of the ground multiplet is of interest, which was evaluated to be $53 \pm 8 \text{ cm}^{-1}$. For TbDOTA with an excitation wavelength of 380 nm well resolved multiline emission spectra were obtained for the transitions

$^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$. The overall crystal-field splitting of the 7F_6 ground multiplet was again well reproduced by the CASSCF calculations. The agreement of the individual energy-levels was not as good as for DyDOTA.

6.1.3 Motivation of far-infrared spectroscopy

6.1.3.1 Crystal-field splitting

In general, far-infrared spectroscopy in the study of lanthanide based SIMs has the same aim as luminescence spectroscopy. Both can give information on the crystal field splitting of the lowest multiplet. Therefore, the first aim of the far-infrared study is to provide an independent method to verify the energy levels structure revealed by the luminescence spectra.

In addition, it is assumed that the Orbach relaxation process operates via the first excited crystal-field doublet. Therefore, an accurate and precise determination of the energy-level structure is crucial to gain a deeper insight into the relaxation dynamics of lanthanides. Compared to luminescence spectroscopy, far-infrared spectroscopy has four main advantages. 1. The measurements can be performed with a higher spectral resolution and therefore a more precise determination of the energy-level structure is possible. 2. The determined energies at which absorption lines appear are directly connected to the energy-levels of the crystal-field split ground multiplet. 3. The issue of hot-bands, which hamper the interpretation of luminescence spectra is absent in far-infrared spectra. 4. By applying a magnetic field, the spectroscopic g-factors of the transitions can be determined.

For DyDOTA, the energy difference between the lowest two doublets obtained by the CASSCF-calculations and luminescence spectra is slightly higher than the energy-barrier for the reversal of the magnetization determined by the AC-susceptibility measurements. For DyDOTA the CASSCF-calculation revealed an energy-level at 64 cm^{-1} (measured by luminescence at $53 \pm 8\text{ cm}^{-1}$) and an energy-barrier for the reversal of the magnetization of 42 cm^{-1} . This observation is in agreement with previous results, where the energy-barrier for the reversal of the magnetization is lowered compared to the energy of the first excited crystal-field doublet [7]. The reason for this discrepancy is still under debate. In the field of molecular magnetism the difference is often attributed to under-barrier mechanisms like quantum tunneling or the direct process [16]. Whereas, in early studies of lanthanides the lowering of the energy-barrier was suggested to originate from a finite-level width of the first excited state. Young *et al.* [121] discussed the case that the linewidth originates from fluctuations in the local crystalline fields. In contrast, Lyo [122] related the linewidth to the natural linewidth due to the finite lifetime of the excited levels.

A special issue of the relaxation process of DyDOTA is the switching between the direct process and the Orbach process when the magnetic field is increased. To shed

light onto this issue, our aim of the far-infrared study is to determine the spectroscopic g-factor and the (magnetic field dependent) transition matrix element of the transition between the two lowest Kramers doublets. Especially, the transition matrix element is assumed to be relevant for the appearance of the Orbach process [16].

In addition to the magnetic properties of the ground multiplet, far-infrared spectroscopy offers the opportunity to study also the dielectric and optical phonon properties of the compound. In lanthanides based molecular magnets, optical phonons can take part in the relaxation process (see Section 2.3). A determination of the resonance frequencies is crucial to get a deeper understanding of the relaxation process. As optical phonons have a flat dispersion relation, they can only be active in a small energy window.

In addition, far-infrared spectroscopy offers the opportunity to study the frequency-dependent dielectric properties of the sample. With respect to the electronic transitions inside the ground multiplet, they are of crucial importance. As for magnetic dipole transitions the spectral weight $\int k_\sigma d\sigma$ (integrated over the absorption line) is proportional to the refractive index $\eta(\sigma)$ in that frequency range ($\int k_\sigma d\sigma \sim \eta(\sigma)$). A high refractive index enhances the absorption caused by a magnetic dipole transition. Therefore, for a quantitative analysis of the intensities of magnetic dipole transitions, the determination of the refractive index is necessary.

6.1.3.2 Terahertz vibrations in hydrogen bonded networks

Compounds that contain water are well known to exhibit a rich variety of resonances in the frequency range from 3 to 100 cm^{-1} [19]. The resonances are indications of the formation of weak intermolecular hydrogen bonds. The formation of hydrogen bonds is still an active field of research due its importance in many different fields e.g. biological systems and pharmacology (see Ref. [19] and references therein).

$\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ contains five water molecules which are situated at different lattice sites. A view along the b-axis of the crystal is shown in Figure 6.3 (a). $\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ forms a linear coordination polymeric structure along the b-axis. Hexameric, nearly planar water clusters (OW2, OW3, OW5) join these linear chains. The water hexamers are attached to the chain network by hydrogen bonds to the oxygen atoms.

The two residual water molecules are coordinated in the chain structure

$\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$: one to the dysprosium ion (OW1) and the other to the sodium ion. Both form hydrogen bonds with two nearby oxygens.

Therefore, $\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})] \cdot 4\text{H}_2\text{O}$ offers the opportunity to study the low-energy excitations of hydrogen-bonded water molecules.

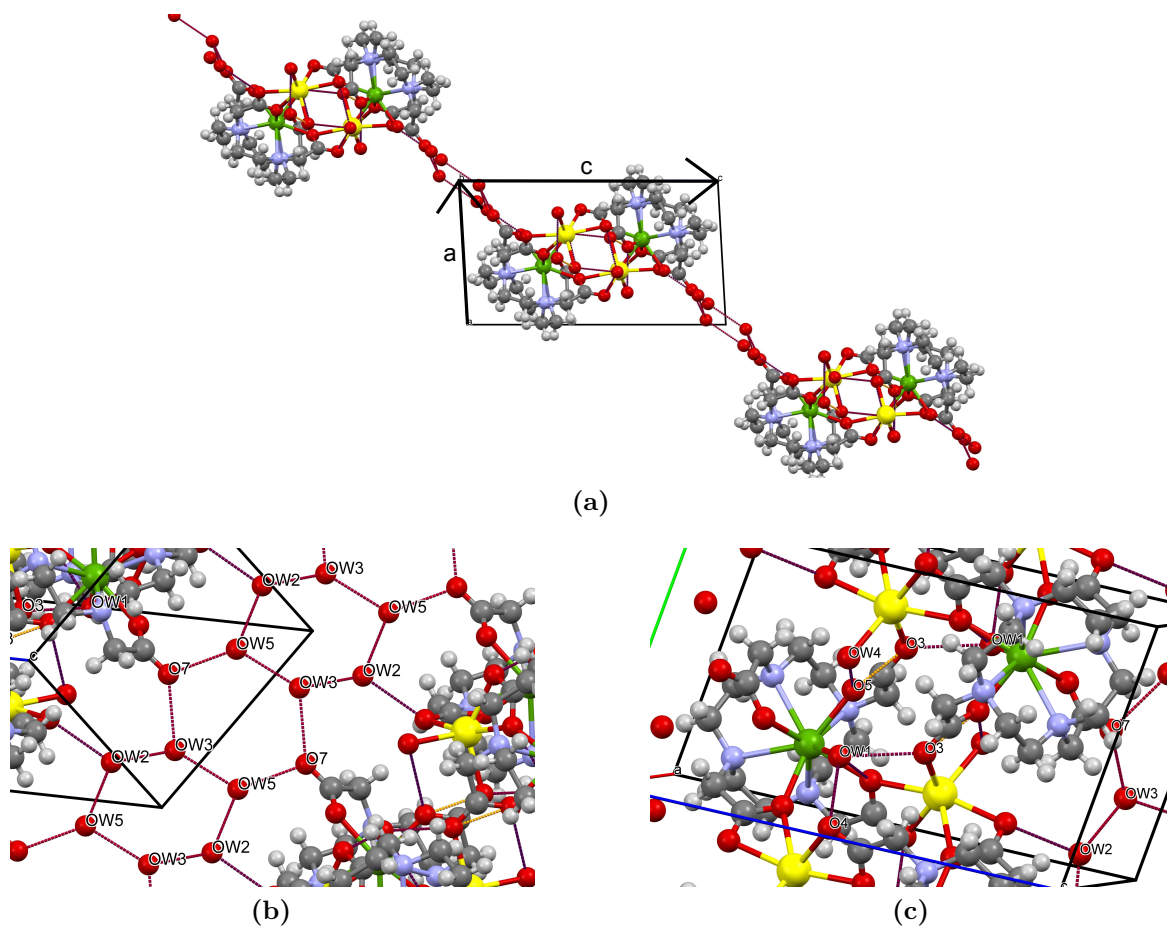


Fig. 6.3: (a) Crystal structure of DyDOTA [15] viewed along the b-axis. (b) Water molecules (OW2, OW3, OW5) connecting the molecular chains by forming hexamers. (c) Water molecules coordinated to the dysprosium ion (OW1) and the sodium ion (OW4)

6.2 Methods and materials

Transmission spectra of DyDOTA and TbDOTA were acquired with a Bruker IFS 113 v Fourier Transform spectrometer connected to an Oxford Spectromag 4000 Split-Coil Magnet with Mylar windows in the frequency range of 20-100 cm^{-1} with a resolution of 0.5 cm^{-1} . The experimental setup is presented in Section: 3.1.2. Magnetic fields were applied up to 6 T in Voigt geometry.

The samples $\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})]_4 \cdot \text{H}_2\text{O}$ and $\text{Na}[\text{Tb}(\text{DOTA})(\text{H}_2\text{O})]_4 \cdot \text{H}_2\text{O}$ were synthesized in the group of R. Sessoli (University of Florence). The synthesis procedure is described in the supplementary material of Car *et al.* [15]. For the far-infrared measurements microcrystalline $\text{Na}[\text{Ln}(\text{DOTA})(\text{H}_2\text{O})]_4 \cdot \text{H}_2\text{O}$ were pressed in a pellet. Due to strong phonon absorption of LnDOTA, dilution of the microcrystalline LnDOTA compound with eicosane was necessary. For the infrared properties of eicosane see Section: A.2.

The measurements were extended to the low frequency range (4-35 cm^{-1}) by the use of a coherent source THz spectrometer (compare Section: 3.1.1).

The sample compositions and characteristics are summarized in Table 6.2.

	Compound	Composition	Thickness	Formula weight	Number density
FTIR	DyDOTA1	7.0 mg DyDOTA + 65.5 mg eicosane	0.045 cm	676 g/mol	$1.8 \cdot 10^{20} \text{ 1/cm}^3$
	TbDOTA1	13.2 mg TbDOTA + 22.2 mg eicosane	0.030 cm	672 g/mol	$5.0 \cdot 10^{20} \text{ 1/cm}^3$
THz	DyDOTA2	46.8 mg DyDOTA	0.040 cm	676 g/mol	$1.3 \cdot 10^{21} \text{ 1/cm}^3$
	TbDOTA2	48.7 mg TbDOTA	0.036 cm	672 g/mol	$1.5 \cdot 10^{21} \text{ 1/cm}^3$
	DyDOTA3	1.7 mg DyDOTA	0.015 cm	676 g/mol	$1.4 \cdot 10^{21} \text{ 1/cm}^3$
	TbDOTA3	1.8 mg TbDOTA	0.016 cm	672 g/mol	$1.4 \cdot 10^{21} \text{ 1/cm}^3$

Tab. 6.2: Composition and characteristics of the samples used for the far-infrared and terahertz measurements of LnDOTA. The pellets of compounds LnDOTA1 and LnDOTA2 has a diameter of 1 cm, whereas LnDOTA3 only have a diameter of 0.3 cm

6.3 Results and Discussion

This section is divided into four parts: 1. The dielectric properties are determined and the optical phonon spectrum is discussed. 2. The far-infrared spectra of DyDOTA are analyzed with respect to electronic transitions inside the crystal-field split $^6\text{H}_{15/2}$

ground multiplet of the dysprosium ion. 3. The spectra of TbDOTA are analyzed with respect to electronic transitions inside the crystal-field split 7F_6 ground multiplet of the terbium ion. 4. The impact of the results for the interpretation of the magnetic relaxation process is discussed.

6.3.1 Dielectric and optical phonon properties

Optical phonons of DyDOTA and TbDOTA

The temperature dependence of the far-infrared spectrum of DyDOTA1 is shown in Figure 6.4 (a). For the identification of the lattice- and vibrational modes in Figure 6.4 (b) the spectra of TbDOTA1 and DyDOTA1 are compared. Both reveal absorption lines at nearly the same frequencies. As TbDOTA and DyDOTA are isostructural, all local and lattice vibrations of molecules or ions which do not include the lanthanide ion should stay the same. For vibrations, which include the motion of the lanthanide ion, the substitution of one lanthanide ion by another (here Dy-Tb) changes the lattice- and vibrational modes only slightly, because they have similar masses and, in addition, the mass change is compensated by a change in the ionic radius [123]. Therefore, all absorption lines in the far-infrared spectrum, which are labeled P1-P8, can be identified as lattice- and molecular vibrational modes. Further evidence for their phononic and vibrational character stems from the magnetic field dependence of the spectra. Figure 6.4 (c) shows the spectra of DyDOTA1 at 2 K in a magnetic field of 6 T and without a field. All lines show no change under the influence of a magnetic field, excluding them to stem from electronic transitions. The absorption line E1 can be attributed to a phonon mode of eicosane which was used as a diluent (compare Section: A.2).

In the following we will try to assign the different modes to certain vibrations of molecular units of ions in the crystal. For the complex crystal structure of DyDOTA this evolves into a complex task. As theoretical calculations are beyond the scope of this thesis, we will try to assign the phonons by their temperature dependence and by comparison with previous results obtained for similar molecular clusters.

In general FIR-spectra from $3\text{-}100\text{ cm}^{-1}$ contain vibrations which contain ions or molecular units of high mass, or low energy bonds. As the resonance frequency is proportional to $\nu_{\text{resonance}} \sim \sqrt{\frac{f}{m}}$.

The water molecules in LnDOTA are connected by hydrogen bonds to neighboring ions and the stretching and bending modes of the water molecules along the hydrogen bonds should occur in the measured frequency range [19]. In lanthanide containing compounds, also lattice phonon modes can be observed in the same frequency range due to the high mass of the lanthanide ions [123].

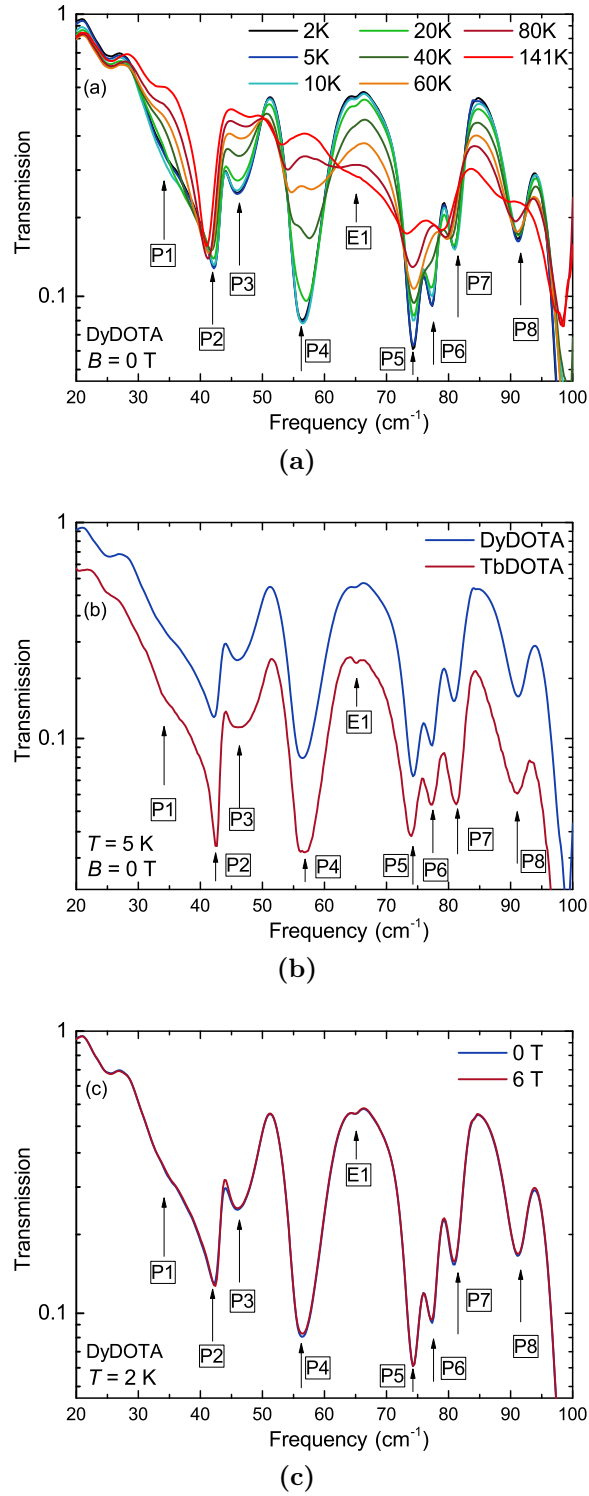


Fig. 6.4: (a) Far-infrared transmission spectra of DyDOTA1 in the temperature range from 2 K to 141 K at zero magnetic field. (b) Comparison of the transmission spectra of DyDOTA1 and TbDOTA1 at $T=5$ K and $B=0$ T. (c) Magnetic field dependence of the DyDOTA transmission spectra at $T=2$ K. The arrows indicate the phonon resonance frequencies. The phonons are labeled P1-P8.

	P1-1	P1-2	P2	P3-1	P3-2	P4-1	P4-2	P5	P6	P7	P8
ν_0 (cm ⁻¹)	35.6	39.5	42.2	45.7	47.7	56.2	58.3	74.2	77.4	81.0	91.1
f (cm ⁻²)	58	11.9	18.2	7.9	10.1	32.4	38.4	61.6	14.3	15.8	56.5
γ (cm ⁻¹)	10.2	3.7	2.8	2.4	3.0	3.5	6.3	5.5	2.4	2.2	6.4

Tab. 6.3: Parameters of the phononic absorption lines in DyDOTA1 obtained by fitting the transmission spectrum at 5 K and 0 T with the Fresnel equations introducing electric oscillators (compare Section 3.2.1). ν_0 - eigenfrequency, f - oscillator strength (intensity), and γ - damping. The labeling is according to Figure 6.3. For P1, P3, and P4 revealed a fine structure. The different contributions are labeled Px-1 and Px-2.

Characteristic of all of the absorption lines is the strong sharpening of the lines with decreasing temperature, except the width of the P2 phonon that changes only gradually (see Figure 6.4 (a)). The parameters (the eigenfrequency ν_0 , the oscillator strength f , and the damping γ) of a multiple dielectric oscillator fit of the lines using the Fresnel equations (compare Section 3.2.1) are presented in Table 6.3 for DyDOTA1 at 5 K and 0 T. The multiple oscillator fit of the transmission spectrum at 5 K showed the lines P1, P3, and P4 are best fitted by using two Lorentian-shaped electric oscillators (Table 6.3). Therefore, they either consist of two lines or out of one line which is highly asymmetric.

The temperature dependence of the resonance frequencies of the two different modes of P4 are depicted in Figure 6.5. The two lines show a different behavior, as the lower frequency line P4-1 undergoes a red-shift by increasing temperature, the higher frequency line P4-2 undergoes a blue-shift. The blue-shift is unusual for intermolecular vibration or bending modes.

The second line we want to discuss in more detail is the line P2 at 42 cm⁻¹. In contrast to the others lines, as the temperature is raised the linewidth stays nearly constant. As the change of the linewidth is related to the anharmonicity of the force field and the lifetime of the excited state, it follows that the force field is near to harmonic and that the phonon lifetime of the excited state is long. Furthermore, the resonance frequency of the mode only shows a small shift depicted in Figure 6.5. The shift occurs at 40 K where the first excited energy-level of the mode gets thermally populated according to the Boltzmann population of states for a state of 42 cm⁻¹. As the nature and physical extent of the interatomic forces decides the symmetry of the potential function, the low anharmonicity of the force field of P4 indicates that the modes have a different origin than the other modes. Figure 6.6 shows a comparison between the mode in DyDOTA and TbDOTA. The spectra were acquired with the BWO-THz setup with high resolution. The resonance frequency of the mode changes from 42.2 cm⁻¹ for

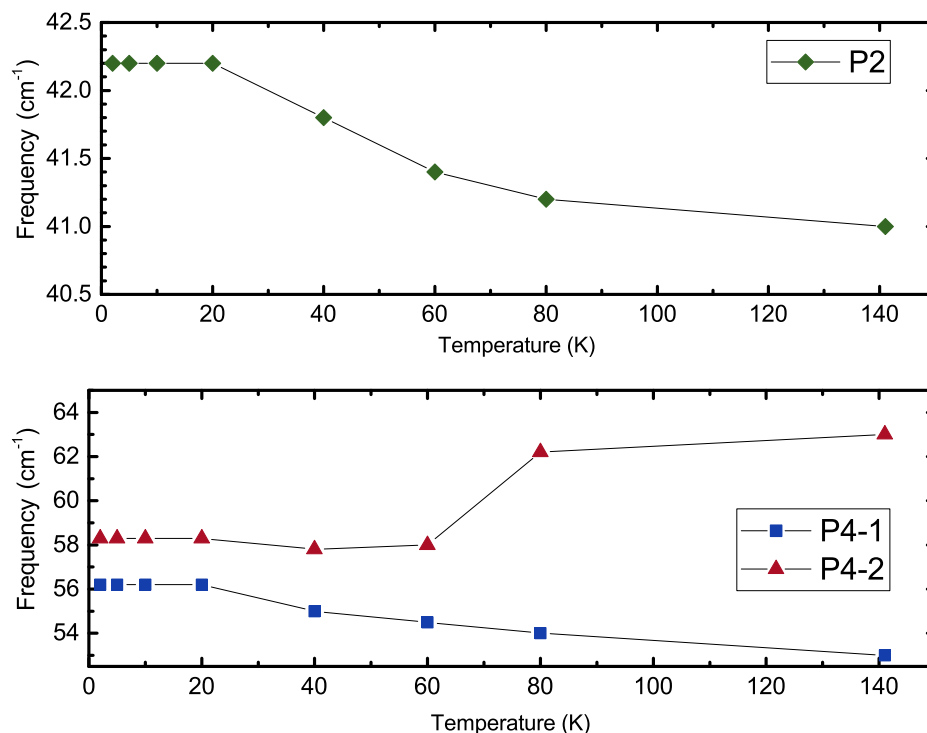


Fig. 6.5: Temperature dependence of the resonance frequencies of the phonons P2 and P4.

DyDOTA to 42.7 cm^{-1} for TbDOTA. The shift indicates that the lanthanide ion takes part in the motion underlying the P4-mode.

Without detailed theoretical calculations or a modified experiment, e.g. deuteration or removing the water molecules by heating, a definite assignment of the lines is not possible. However, there are hints that some of the lines can be caused by bending or stretching modes of the water molecules (OW1, OW2, OW3, OW4, OW5) inside the crystal structure: First, the strong sharpening of the lines except P2 with decreasing temperature. The sharpening of the lines for modes of water molecules are connected to anharmonic force fields [19]. Whereas, intramolecular lines sharpen also, the effect is often not as pronounced, as the stronger bonds inside of molecules are less anharmonic and less influenced by temperature changes.

Second, the intensities (taking into account the dilution of DyDOTA1 with eicosane) of the lines are high. Absorption lines caused by lattice vibrations without water in lanthanide ions are often less intense [9, 11, 124, 125]. Whereas, the intensities are comparable to the ones observed in water molecules bond to beryl, where the water molecule is hosted within i.e. cages of inorganic mineral that form one-dimensional hollow cylinders [126].

Third, a line at 53 cm^{-1} in far-infrared measurements and at 60 cm^{-1} in Raman measurements was observed in liquid water [19, 127, 128, 129]. It was attributed to a torsional vibration mode originating from the bending motion of the intermolecular

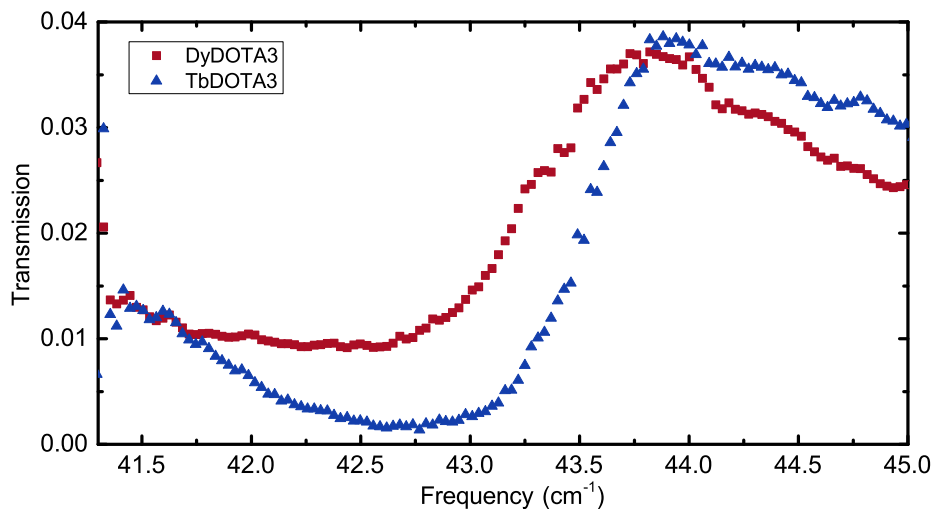


Fig. 6.6: BWO-THz-Transmission of DyDOTA3 and TbDOTA3 at 2 K and 0 T. Comparison of the P4 phonon in DyDOTA and TbDOTA.

hydrogen bond [127], but the attribution is still under debate [130]. Recently a resonance frequency around 50 cm^{-1} was also observed for water molecules bond to beryl [126]. It is possible that the resonance line P4 in DyDOTA has the same origin as the previously discussed ones. The blue-shift (observed for the mode P4-2) was also observed for an intermolecular vibration mode of sucrose along a hydrogen bond in the far-infrared by Walther *et al.* [131]. They attributed the blue-shift to a scenario where weak noncovalent forces such as van der Waals forces weaken the hydrogen bond modes. However, also there no definite explanation was possible.

Dielectric properties of DyDOTA and TbDOTA

For the determination of the low frequency dielectric properties, the Fabry-Perot resonances of the transmission spectrum were fitted using the Fresnel equations for a planparallel pellet. The fits are shown in Figure 6.7. The real part of the refractive index was determined to be around 3.9 for DyDOTA2, 4.0 for TbDOTA2, and 2.5 for DyDOTA1. The difference of the refractive index of DyDOTA1 and DyDOTA2 is attributed to the dilution of DyDOTA with eicosane in the sample DyDOTA1. In the following section for the calculation of the normalized absorption cross section of the electronic absorption lines in DyDOTA the refractive index of DyDOTA1 2.5 is used. As the refractive index does not change noticeably with temperature and magnetic field it is considered constant for all fields and temperatures. The same value is also taken for TbDOTA, because the real part of the refractive index is only slightly influenced by the substitution of the lanthanide ion.

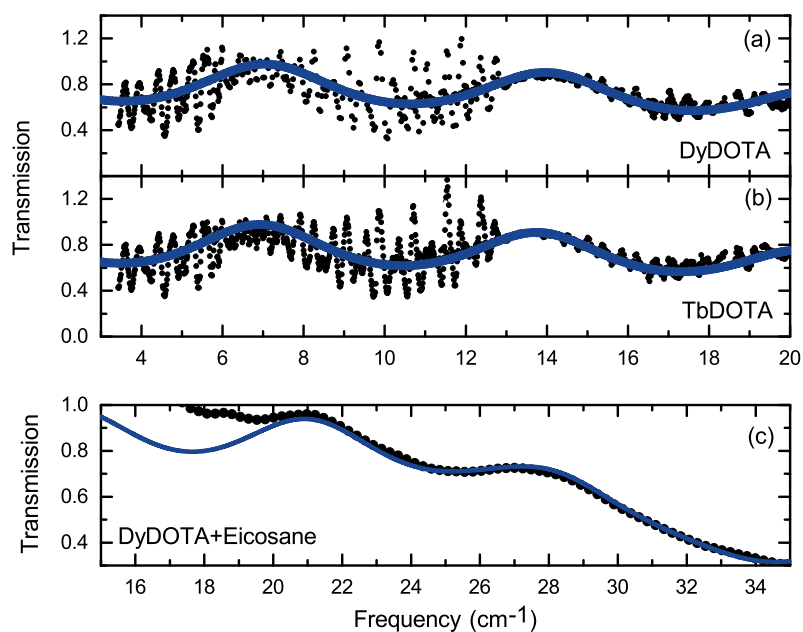


Fig. 6.7: Fit of the BWO-THz-Transmission spectrum of DyDOTA2 (a) and TbDOTA2 (b) at 2 K and 0 T. (c) Fit of the far-infrared transmission spectrum of DyDOTA1 at 2 K and 0 T.

6.3.2 Electronic transition inside the crystal-field split ${}^6\text{H}_{15/2}$ ground multiplet of dysprosium in DyDOTA

As described in the previous Section 6.3.1 none of the strong absorption lines in Tb-DOTA or DyDOTA are connected to an electronic absorption line. However, by applying a magnetic field the transmission spectra of DyDOTA show slight changes in the frequency range from 40 cm^{-1} to 65 cm^{-1} (see Figure 6.4 (c)). To resolve small changes, the difference of the normalized absorption cross section (definition see Chapter 4) between spectra in a magnetic field and without field is shown in Figure 6.8. We use the difference of the normalized absorption cross (defined in Section 4.2) to resolve small changes of the spectra when a magnetic field is applied. It allows direct conclusions about the strength of magnetic dipole transitions in terms of the transition matrix element $|\langle f|g\hat{J}|f\rangle|^2$. We can identify two features, one between 42 cm^{-1} and 55 cm^{-1} , and the second between 55 cm^{-1} and 60 cm^{-1} . The third feature at 85 cm^{-1} is attributed to an instability of the spectrometer at that frequency.

A dip observed in the difference of the absorption cross section appears when spectral weight is shifted away by the application of the magnetic field. Therefore, we identify

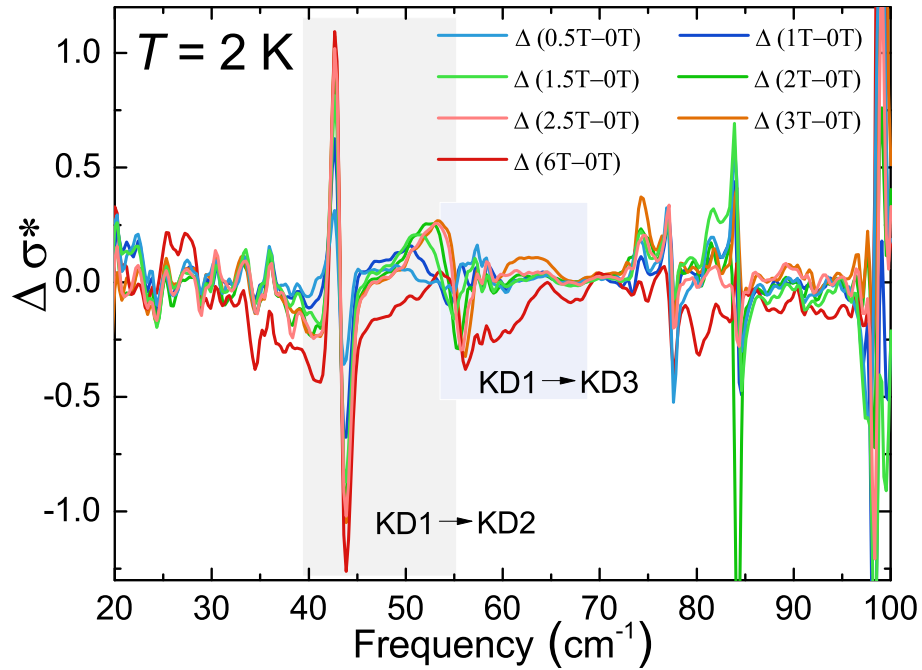


Fig. 6.8: Difference of the normalized absorption cross section of DyDOTA1 at 2 K between spectra in-field and without field ($\sigma^* = -\ln(\text{Tr}(\mathbf{xT})) + \ln(\text{Tr}(\mathbf{0T})) = \frac{8\pi^3\eta N\omega}{hc} \cdot \frac{1}{3} |\langle f|g\hat{J}|f\rangle|^2$). The feature assigned to the electronic absorption line from the ground Kramers doublet (KD1) to the first excited Kramers doublet (KD2) is marked with a grey background. The feature assigned to the line from the ground Kramers doublet (KD1) to the second excited Kramers doublet (KD3) is marked with a blue background.

the zero-field position of the first absorption line at 44 cm^{-1} . Through the application of the magnetic field, spectral weight is transferred to lower frequencies appearing as an upward peak in the difference spectra at 43 cm^{-1} . In addition, on the high-frequency shoulder of the dip, an upward peak appears which increases and shifts two higher frequencies with increasing magnetic field. The interpretation of this unusual shape is the following: As described in Section 4.5 the spectroscopic g-factor for a sample made of powder is different for every crystallite direction, as the magnetic field points for every crystallite in a different direction relative to the molecular frame. We propose that the direction of the magnetic field results for most crystallites into a small negative spectroscopic g-factor, leading to a shift to lower frequencies. The direction of the magnetic field results for other crystallites in a positive spectroscopic g-factor, but for these crystallites the transition matrix element is zero in zero-field, and the transition only gains intensity by the application of a magnetic field, leading to the feature on the left shoulder of the dip. We propose that crystallites with an easy axis parallel to the magnetic field are responsible for this shift to higher frequencies (see Figure 6.9 (a)). A zoom-in of the feature is depicted in Figure 6.9 (c). A possible energy-level diagram along the easy-axis direction is shown in Figure 6.9 (b). In Figure 6.9 (d), a fit to the normalized absorption cross section is shown. The fit was conducted by assuming an absorption line of Lorentzian shape at 44 cm^{-1} at zero-magnetic field; for the fit the absorption line was shifted to lower frequencies with increasing magnetic field with a spectroscopic g-factor of $g_{\text{spec}} = -0.5/\mu_B \frac{\text{cm}^{-1}}{\text{T}}$ (with μ_B the Bohr magneton in units of $\frac{\text{cm}^{-1}}{\text{T}}$). An additional absorption line of Lorentzian shape was introduced with a zero-field position at 44 cm^{-1} which shifts to higher frequencies in a magnetic field with a spectroscopic g-factor of $g_{\text{spec}} = 3/\mu_B \frac{\text{cm}^{-1}}{\text{T}}$ (for the projection of the magnetic field to the easy-axis a sine function was used), and gains intensity with increasing magnetic field. The feature which shifts with a spectroscopic g-factor of $g_{\text{spec}} = 3/\mu_B \frac{\text{cm}^{-1}}{\text{T}}$ (grey background in Figure 6.9 (d)) to higher frequencies is attributed to crystallites with an easy-axis parallel to the direction of the magnetic field.

The second feature between 55 cm^{-1} and 60 cm^{-1} reveals a dip at 55 cm^{-1} and the spectral weight shifts to higher frequencies when the magnetic field is increased. By the application of the magnetic field the dip is overlapped from the high frequency shoulder of the first transition.

Our assignment of the two electronic absorption lines is further confirmed by the temperature dependence of the normalized absorption cross section (see Figure 6.10): when the temperature increases, the features decrease at temperatures from 2 K to 40 K and then vanish at 60 K, as expected from the Boltzmann distribution for the population of states. The decrease with temperature indicates that both transitions originate from the ground state. Therefore, we assign the first absorption line at 44 cm^{-1} to the transition from the ground Kramers doublet to the first excited doublet in the dysprosium ground multiplet $^6\text{H}_{15/2}$ and the second absorption line to the transition from the ground Kramers doublet to the second excited Kramers doublet.

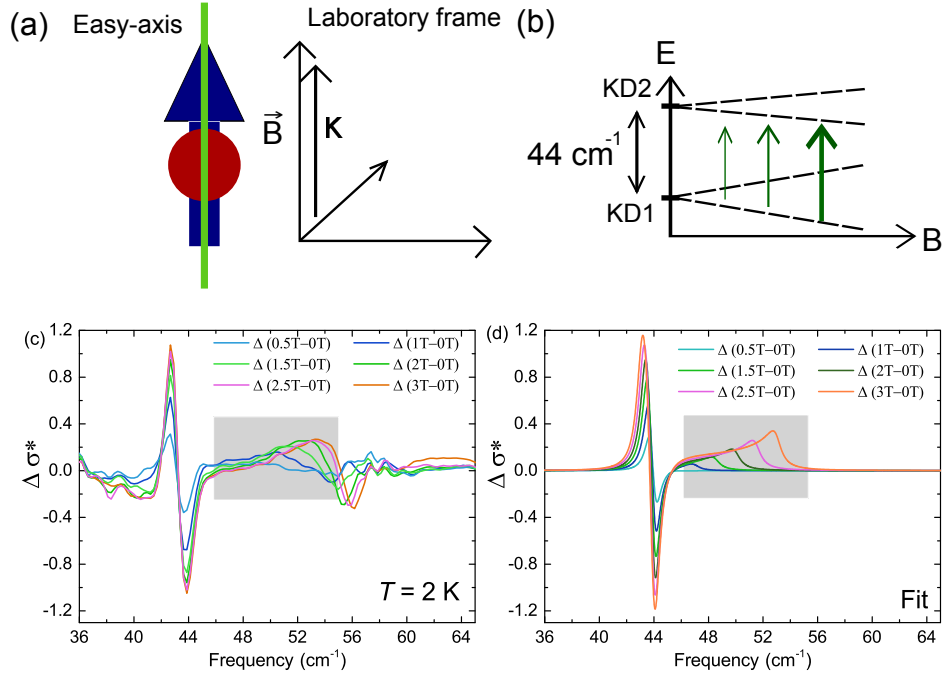


Fig. 6.9: (a) Relative direction of the easy-axis in the crystallites of DyDOTA in the laboratory reference frame ($\vec{B}$ magnetic field and κ the polarization direction) which we propose to be responsible for the feature (marked with a grey background) shown in (c). (b) Schematic view of a possible energy-level diagram for the magnetic field parallel to the easy-axis. The green arrows indicate the possible transitions induced by the oscillating magnetic field in the direction of the easy-axis. The thickness of the arrows indicate the magnitude of the transition matrix element. (c) Experimental normalized absorption cross section at 2 K of DyDOTA1. (d) Fit to the normalized absorption cross section. Details of the fit are described in the main text.

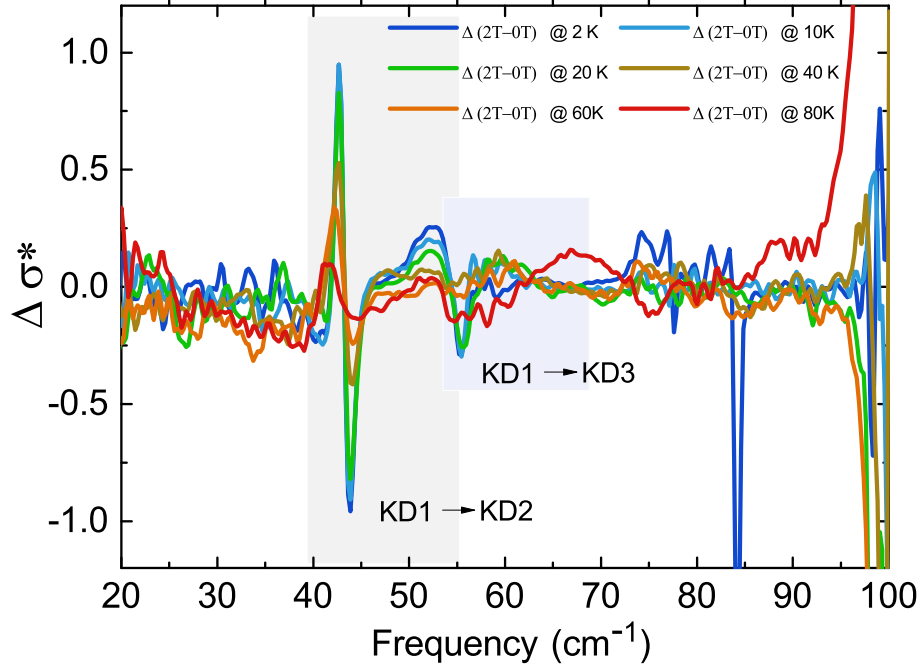


Fig. 6.10: Difference of the normalized absorption cross section of DyDOTA1 between spectra in a field of 2 T and without a field at different temperatures. The feature assigned to the electronic absorption line from the ground Kramers doublet (KD1) to the first excited Kramers doublet (KD2) is marked with a grey background. The feature assigned to the line from the ground Kramers doublet (KD1) to the second excited Kramers doublet (KD3) is marked with a blue background.

We were not able to find crystal field parameters which reflect the measured spectra using the simulation program presented in Section 4.3. As for DyDOTA no reduction of the crystal field parameters due to symmetry considerations is possible, there are 27 crystal field parameters.

The measurements were also extended to lower frequencies down to 4 cm^{-1} by the use of the coherent source THz spectrometer described in Section 3.1.1. The transmission spectra are shown in Figure 6.11 (a) without field and in an applied field of 6 T. No additional absorption line and no dependence on magnetic field is visible in the frequency range from $4\text{--}20\text{ cm}^{-1}$.

The experimentally determined energy levels at 42 cm^{-1} and 55 cm^{-1} do not compare well with the CASSCF-calculation [8], where the two lowest energy-levels were calculated at 64 cm^{-1} and 112 cm^{-1} . In addition, they are also not in agreement with previous luminescence measurements, where the two lowest doublets were determined to lie at 53 cm^{-1} and 110 cm^{-1} . A comparison of the results of the luminescence measurements [8], the CASSCF-calculations [8], and the far-infrared measurements are shown in Figure 6.12. However, reconsidering the raw luminescence data [8], the peak assigned to the energy of the first doublet at 53 cm^{-1} has a small fine-structure, which

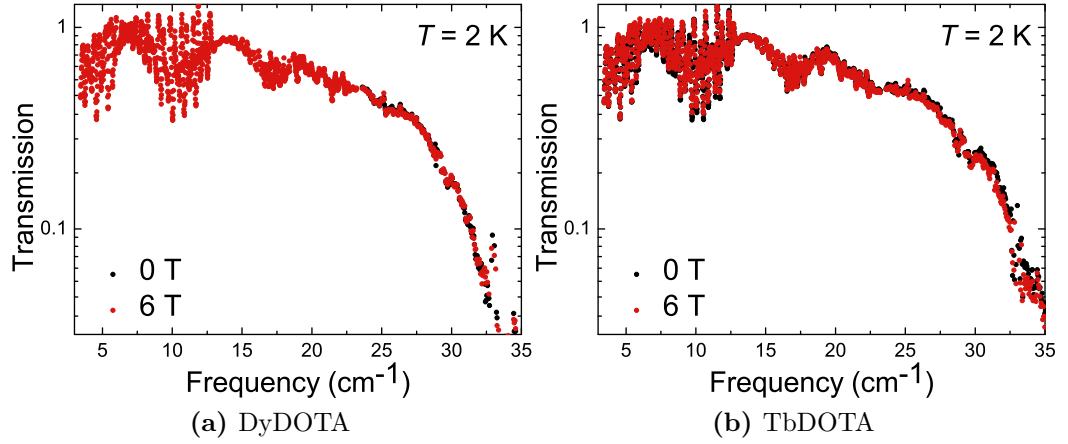


Fig. 6.11: THz-transmission spectra of DyDOTA (a) and TbDOTA (b) for $B=0$ T and $B=6$ T at $T=2$ K.

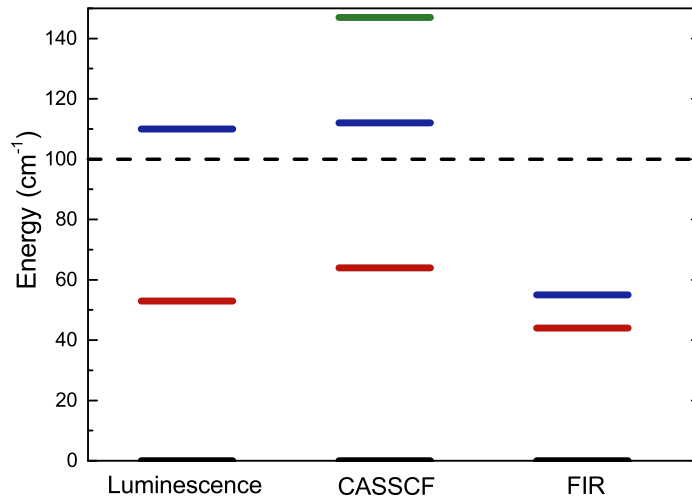


Fig. 6.12: Comparison of the results of energies of the low lying Kramers doublets of DyDOTA obtained by luminescence measurements [8], CASSCF-calculations [8], and far-infrared measurements. The dashed line indicates the limit of the accessible frequency range for the conducted far-infrared measurements.

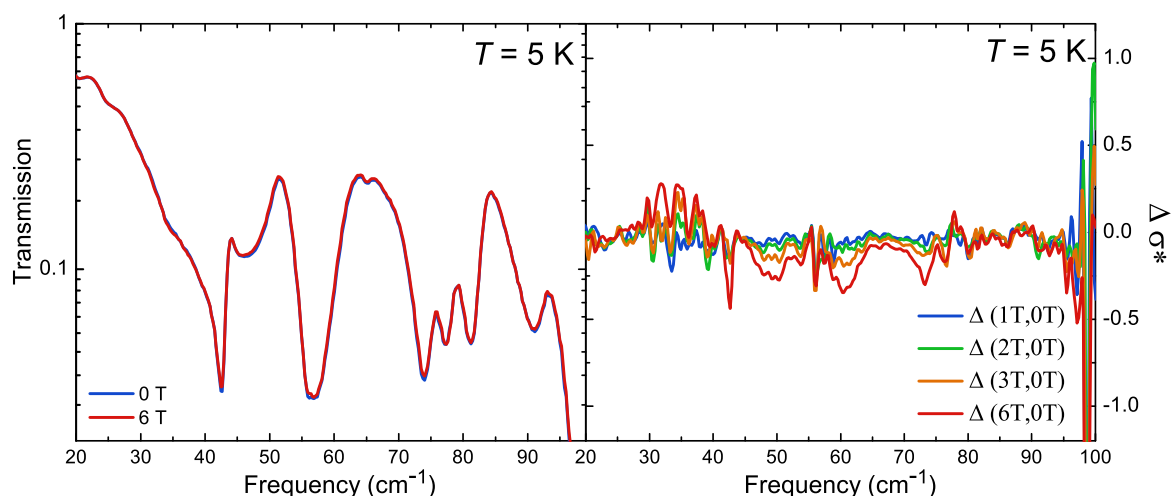


Fig. 6.13: Left: Transmission spectra of TbDOTA at $T=5$ K in magnetic fields of 0 T and 6 T. Right: Difference between the in-field and zero-field normalized absorption cross section at $T=5$ K.

can also be indicative of two close lying peaks. If the luminescence data are interpreted in this way, the two close lying peaks at 53 cm^{-1} are in agreement with our far-infrared results.

Far-infrared spectra acquired with the Bruker 113 are known to contain small, magnetic field-dependent changes of the spectra when a magnetic field is applied also with no sample in the beam path. The source of the induced systematic error is unknown. To check, if the results of the magnetic field-dependent changes observed in the DyDOTA compound are caused by the sample or by a systematic error we conducted additional experiments (compare Appendix A.2). We are confident that the results are not caused by a systematic error, but are instead a material property as discussed before. In addition, the far-infrared measurements were repeated several times with different sample thicknesses and the results stayed qualitatively the same.

6.3.3 Electronic transition inside the crystal-field split 7F_6 multiplet of terbium in TbDOTA

In Figure 6.13 (left) the far-infrared spectra of TbDOTA at $T=5$ K in zero magnetic field and in a field of 6 T are shown. We are not able to observe any absorption line associated to an electronic transition inside the 7F_6 multiplet of terbium. Also the difference in the normalized absorption cross section shows no feature which shifts in magnetic field. The small deviations of the difference of the normalized absorption cross section are of the same order of magnitude as for DyDOTA. However, the noise of the TbDOTA data is higher than for DyDOTA due to the use of a different sample

holder.

For terbium an electronic energy level inside the 7F_6 multiplet is proposed at 25 cm^{-1} and 30 cm^{-1} by CASSCF-calculations [58]. Note that for terbium a non-Kramers ion the degeneracy of the ground multiplet with $J=6$ can be lifted totally by the crystal field, leading to 13 crystal field levels. The proposed energy-levels at 25 cm^{-1} and 30 cm^{-1} are located at the low frequency border of our far-infrared spectrometer. Therefore, the measurements were extended to cover also lower frequencies down to 4 cm^{-1} by the use of a coherent source THz spectrometer described in Section 3.1.1. The transmission spectra are shown in Figure 6.11 (b) without field and for the highest applied field of 6 T. No additional absorption line and no dependence on magnetic field is visible in the frequency range of $4\text{--}20\text{ cm}^{-1}$. Therefore, we can conclude that for TbDOTA no electronic transition can be observed by the use of optical spectroscopy in the range of $4\text{--}100\text{ cm}^{-1}$.

6.3.4 Discussion: Relation of the results to the relaxation behavior

For DyDOTA, the electronic transition observed at 44 cm^{-1} from the ground state to the first excited state suggests, that the thermally activated relaxation mechanism in DyDOTA is caused by an Orbach-relaxation mechanism (see Section 2.3.1.2). The energy of the first excited Kramers doublet (44 cm^{-1}) agrees well with the measured relaxation barrier in AC-susceptibility measurements at 42 cm^{-1} [15]. In addition, the far-infrared results give a hint for the switching of the relaxation pathway in DyDOTA from the direct process to the Orbach process [15]: the switching can be caused by an increase of the transition matrix element between the states of the lowest Kramers doublet and the first excited Kramers doublet in a magnetic field (depicted in Figure 6.9). The matrix element of the magnetic moment¹ is an indicator of the relevance of the Orbach process via that state [17]. Therefore, the increase of the Orbach process with respect to the direct process with a magnetic field in DyDOTA can be caused by the magnetic field induced increase of the matrix element of the magnetic moment along the easy-axis. A definite answer to this problem can be obtained by single crystal measurements. In single-crystal measurement it can be tested if the shift to higher frequencies of the absorption line at 42 cm^{-1} is connected to the proposed effect along the easy-axis (compare Figure 6.9).

The second aim our far-infrared measurements was to study the optical phonon properties of DyDOTA and its possible influence on the relaxation mechanism. Unfortunately,

¹ In our definition the transition matrix element $|\langle f|g\hat{J}|f\rangle|^2$ is directly proportional to the matrix element of the magnetic moment $|\langle f|g\mu_B\hat{J}|f\rangle|^2$.

a definite assignment of the observed optical phonon modes was not possible. Therefore, we are not able to decide if the observed phonons play a role in the magnetic relaxation process.

6.4 Conclusion

In conclusion, we have studied the energy-level structure of DyDOTA and TbDOTA by means of far-infrared spectroscopy in the frequency range of 4-100 cm^{-1} .

A drawback of the study of LnDOTA by far-infrared spectroscopy was caused by the strong phonon absorption of LnDOTA. Presumably, the reason for the stronger phonon absorption is given by the water molecules in the crystal structure of LnDOTA. Studies of the far-infrared absorptions of water are in itself an active field of research, but are a drawback for the study of electronic absorption lines. As the electronic absorption lines are superimposed by phonon lines, the definite identification of the electronic lines was hampered. Therefore, we conclude that water containing single-molecular materials are not well suited for far-infrared spectroscopy.

However, for DyDOTA, the energy of the two lowest Kramers doublets were identified at 44 cm^{-1} and 55 cm^{-1} by their behavior in a magnetic field. The energy of the first excited Kramers doublet (44 cm^{-1}) suggests that the thermally activated relaxation mechanism with a relaxation barrier of 42 cm^{-1} observed in DyDOTA can be attributed to an Orbach relaxation mechanism. The splitting of the electronic absorption line in a magnetic field gives a possible explanation for the switching of the relaxation pathway in DyDOTA: The increase of the matrix element of the magnetic moment with increasing magnetic field can raise the probability of the Orbach process with respect to the direct process.

For TbDOTA, no electronic absorption line was visible in the far-infrared spectra.

7 $\text{Ln}(\text{NITPhOPh})_2$: One lanthanide ion coupled to two NIT-radicals

7.1 Introduction

The study of the compound $\text{Ln}(\text{NITPhOPh})_2$ faces different issues of lanthanide based single-molecular magnetic materials.

First, from a magnetic point of view, the complex consists of three interacting, magnetic centers: A lanthanide ion with strong spin-orbit coupling and two NIT-radicals with an isotropic spin. The exchange coupling between an ion with an orbitally degenerate ground state (like most of the lanthanides) to only spin carriers is complicated, because the spin Hamiltonian fails to describe the situation. In addition both the crystal field effect and the exchange interaction are relevant in the same temperature range that makes the disentanglement of both in magnetization measurements challenging. A sketch of the interactions (nearest and next nearest neighbor) is depicted in Figure 7.1 on the right side. Both nearest-neighbor coupling between the lanthanide spin and the radical spin, and next-nearest neighbor interaction transmitted by the lanthanide ion between the two radical spins are of the same order of magnitude [5].

The second reason to study the complex stems from the observation that $\text{Tb}(\text{NITPhOPh})_2$ and $\text{Dy}(\text{NITPhOPh})_2$ in its own show slow relaxation of the magnetization - $\text{Tb}(\text{NITPhOPh})_2$ without an applied magnetic field and $\text{Dy}(\text{NITPhOPh})_2$ in an applied field [5].

In addition $\text{Ln}(\text{NITPhOPh})_2$ can be viewed as a building block of the SCM $\text{Ln}(\text{NITPhOPh})$ and can, therefore, shed light on the complex relaxation dynamics of the single-chain magnets.

In the past, studies on several compounds using lanthanides bound to stable organic radicals like the nitronyl nitroxide were conducted [132, 133, 134]. The nitronyl nitroxide acts as a weak ligand and can only interact with relatively strong Lewis acids. Therefore, hexafluoroacetylacetonates (hfac) are used to bind the metal to the nitronyl nitroxide radicals. Through magnetic measurements of the studied compounds, anti-ferromagnetic interactions between the two radicals mediated by the lanthanide ion

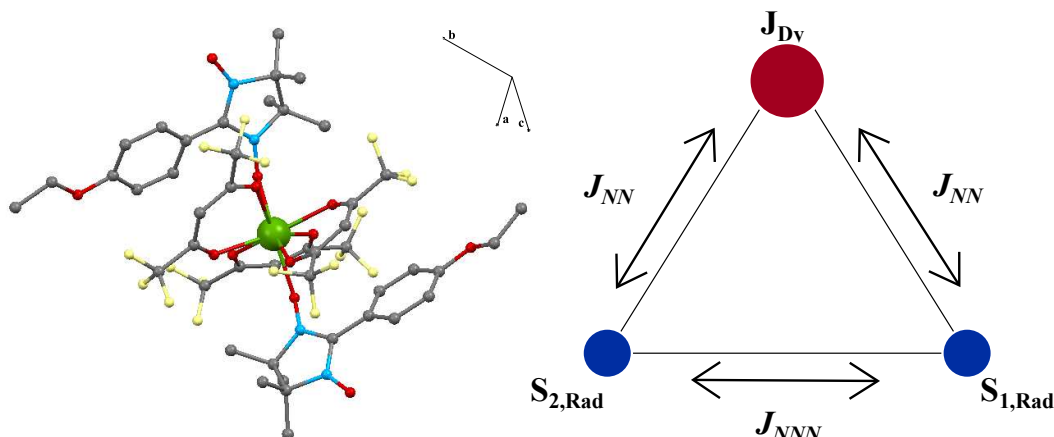


Fig. 7.1: Left: Crystal structure of $\text{Dy}(\text{NITPhOEt})_2$ [57]. Color Scheme: Dy→green, O→red, C→gray, N→blue, F→yellow. Right: Scheme of the magnetic coupling of $\text{Dy}(\text{NITPhOEt})_2$ and $\text{Ln}(\text{NITPhoPh})_2$.

were found. For the heavy lanthanides (namely Gd, Tb, Dy, Ho), a ferromagnetic interaction was found between the lanthanide and the radicals [65, 132]. The challenge is to disentangle contributions of the magnetization from the different crystal-field levels and the exchange interactions [65, 133]. Different approaches are used to gain useful insight into the magnetic interactions in these compounds.

- The contribution of the lanthanide ion itself (crystal-field effects) can be studied by substituting the nitronyl nitroxide radical by diamagnetic nitron, which should give the same crystal surrounding like the nitronyl nitroxide radical.
- The exchange interaction between the radicals mediated by the lanthanide can be obtained using a diamagnetic lanthanide ion like lanthanum or Yttrium.
- Gadolinium as an S-state ion is often used to circumvent the issues arising from the strong spin-orbit coupling of the lanthanide with an orbital momentum. For gadolinium a spin Hamiltonian approach can be used to fit the magnetization data and the exchange couplings can be extracted.

The mechanisms leading to the antiferromagnetic nature of the coupling between the radicals, and especially the ferromagnetic coupling between the radical and the lanthanide ion, are non-trivial and not predictable from theoretical considerations. It is proposed that the lanthanides are involved in the superexchange pathway between the two radicals [135]. It is assumed that a fraction of unpaired electrons is transferred from the radicals into the empty 5d- and 6s-orbitals of the lanthanide ion. The effect is proposed to be twofold [135]: First, the unpaired radical in the empty shell will polarize the electron of the other radical, leading to an antiferromagnetic coupling. Second, the 4f-electrons of the lanthanide ion will be kept parallel to the electron spin of the

radical by Hund's rule, now in the empty shell of the lanthanide ion. This mechanism results in a ferromagnetic coupling between the radical spin and the lanthanide spin [135].

In a previous work [5] the magnetization behavior of $\text{Dy}(\text{NITPhOEt})_2$ was studied. Due to the strong anisotropy of the lanthanide ions in a low-symmetry environment and the different exchange couplings, the magnetic modeling of the compound is difficult and strongly overparametrized for powder samples. $\text{Dy}(\text{NITPhOPh})_2$ crystallizes in a monoclinic space-group with the dysprosium ion in a general position, hampering the use of angle-resolved measurements. Therefore, the compound $\text{Dy}(\text{NITPhOEt})_2$ was synthesized, which crystallizes in a triclinic space-group, allowing for angle-resolved magnetic measurements, which then yield the anisotropy of Dy^{3+} . The crystal field effects and the exchange couplings are thought to be very similar in both compounds. Angle-resolved measurements were used to determine the easy-axis of Dy^{3+} , which compares well with CASSCF-calculations. Magnetic measurements along the easy-axis then allowed for the determination of the exchange interactions by fitting of the measurements with the spin-Hamiltonian:

$$\hat{H} = J_{NNN}\hat{\mathbf{S}}_{R1}\hat{\mathbf{S}}_{R2} + J_{NN}(\hat{S}_{R1z} + \hat{S}_{R2z})\sigma + g_{R1z}\hat{S}_{R1z}\mu_B H_z + g_{R2z}\hat{S}_{R2z}\mu_B H_z + g_{Dy}\sigma\mu_B H_z, \quad (7.1)$$

where Dy^{3+} is treated as an Ising-Spin with $\sigma = \pm 1$. In the fitting process J_{NNN} and J_{NN} are strongly dependent on each other. Therefore, J_{NNN} was determined by magnetization measurements of Y^{3+} in the same compound, which yielded $J_{NNN} = 15 \text{ cm}^{-1}$. Under the assumption that the exchange coupling of the radicals is equally transmitted by Dy^{3+} and Y^{3+} the best fit for Dysprosium-radical coupling yielded $J_{NN} = -13.5 \text{ cm}^{-1}$. The obtained values give an overall splitting of the Ising ground state of 22 cm^{-1} , where the ground state is given by the singlet state ($S=0$) of the two radicals, the first excited by the triplet state ($S=1$) with $m_S = 1$ parallel to the direction of the respective Ising ground state at an energy of 8 cm^{-1} , the second excited by the triplet state $m_S = 0$ state, and the third excited state by the triplet state $m_S = -1$ at 22 cm^{-1} .

7.2 Motivation of far-infrared spectroscopy

Due to the complicated interpretation of magnetization measurements, other measurement techniques like EPR-studies are desirable. But $\text{Dy}(\text{NITPhOPh})_2$ like most Dy^{3+} derivatives is EPR-silent, because of fast electronic relaxation that broadens the EPR signal [5].

Far-infrared spectroscopy could offer the possibility to close this gap. Especially, because it can yield precise determination of the energy-level structure which is difficult to extract from magnetization measurements. To our knowledge, we present the first far-infrared study on a compound containing lanthanides coupled to nitronyl nitroxide radicals.

7.3 Methods and materials

Transmission spectra of Dy(NITPhOPh)₂, Tb(NITPhOPh)₂, Ho(NITPhOPh)₂ and Dy(NITPhOEt)₂ were acquired with a Bruker IFS 113 v Fourier Transform spectrometer connected to a Oxford Spectromag 4000 Split-Coil Magnet with Mylar windows in the frequency range from 15-85 cm⁻¹ with a resolution of 0.5 cm⁻¹. The experimental setup is presented in Section 3.1.2. Magnetic fields were applied up to 6 T in Voigt geometry. The sample is a pellet pressed out of microcrystalline powder.

The measurements were extended to the low frequency range for Dy(NITPhOPh)₂ from 4-35 cm⁻¹ by the use of a coherent source THz spectrometer (compare Section: 3.1.1).

The sample compositions and characteristics are summarized in Table 7.1. The compounds were synthesized according to the procedure presented in the PhD-thesis of Kevin Bernot [117] at the University of Stuttgart by Lapo Bogani and Alexa Paretzki.

	Compound	Weight	Thickness	Formula weight	Number density
FTIR	Dy(NITPhOPh) ₂	108.6 mg	0.090 cm	1434 g/mol	$6.5 \cdot 10^{20}$ 1/cm ³
	Dy(NITPhOEt) ₂	65.0 mg	0.058 cm	1338 g/mol	$6.4 \cdot 10^{20}$ 1/cm ³
	Tb(NITPhOPh) ₂	145.6 mg	0.125 cm	1431 g/mol	$6.3 \cdot 10^{20}$ 1/cm ³
	Ho(NITPhOPh) ₂	156.3 mg	0.130 cm	1437 g/mol	$6.4 \cdot 10^{20}$ 1/cm ³
THz	Dy(NITPhOPh) ₂	300 mg	0.246 cm	1434 g/mol	$6.5 \cdot 10^{20}$ 1/cm ³

Tab. 7.1: Composition and characteristics of the samples used for the far-infrared and terahertz measurements of Ln(NITPhOPh)₂ and Dy(NITPhOEt)₂.

7.4 Results and discussion

7.4.1 Dy(NITPhOPh)₂

The results of the far infrared spectroscopy of Dy(NITPhOPh)₂ are shown in Figure 7.3. In the transmission spectra (top left) a change with magnetic field can be observed in nearly the entire frequency range at a temperature of 2 K (Figure 7.3 top left). The normalized absorption cross section between spectra in-field and without field (Figure 7.3 bottom left) reveals three magnetic field dependent features at 27 cm⁻¹, 42 cm⁻¹, and 70 cm⁻¹⁽¹⁾. The two latter features reveal a fine structure which can be an indication that the features consist of two resonance lines. To solve this issue, we compared the spectra with spectra obtained for a different sample of Dy(NITPhOPh)₂ with a different thickness (see Appendix A.3). The comparison leads us to the assumption that only one transition is observed in each of the three features.

The temperature dependence of the normalized absorption cross section (Figure 7.3 bottom right) shows that the three magnetic features decrease with increasing temperature. The observed temperature dependence implies that the transitions causing the absorption lines originate from the ground state due to the Boltzmann statistics.

The energy-level structure of Dy(NITPhOPh)₂ results of the interplay of the dysprosium crystal-field split ground multiplet ⁶H_{15/2} and the dysprosium-radical as well as the radical-radical exchange coupling (coupling scheme shown in Figure 7.1). In the following, we will try to assign if the transitions observed are primarily caused by transitions between the radical state or if they originate from transitions inside the dysprosium ground multiplet. To cut the upcoming story short, we will get to the conclusion that this aim is not possible. However, we will discuss in the following different models and which impact they have on the interpretation of the analysis of the far-infrared spectra.

As a first model, we will assume that the radical-radical J_{NNN} coupling is antiferromagnetic and isotropic and the coupling dy-radical J_{NN} is ferromagnetic, isotropic, and equal for the two radicals. The assumptions of the antiferro- and ferromagnetic nature of the coupling are based on the observations on other lanthanide-nitronyl nitroxide radical compounds [133, 134] and on the angle-resolved single crystal magnetization measurements conducted on Dy(NITPhOEt)₂ as presented in the introduction. About the kind of isotropy or anisotropy no detailed studies exist for lanthanides with a first order angular momentum.

In general, the modeling of lanthanides with a first order orbital momentum, which are exchanged coupled to other spin carriers, is severely complicated by the strong spin-orbit coupling of the lanthanide ion. Thus, the use of simple spin Hamiltonians

¹ The real part of the refractive index of $\eta = 1.6$ was determined by a fit to the low frequency measurements using the BWO quasi-optical setup. The data and the fit are shown in Appendix A.3

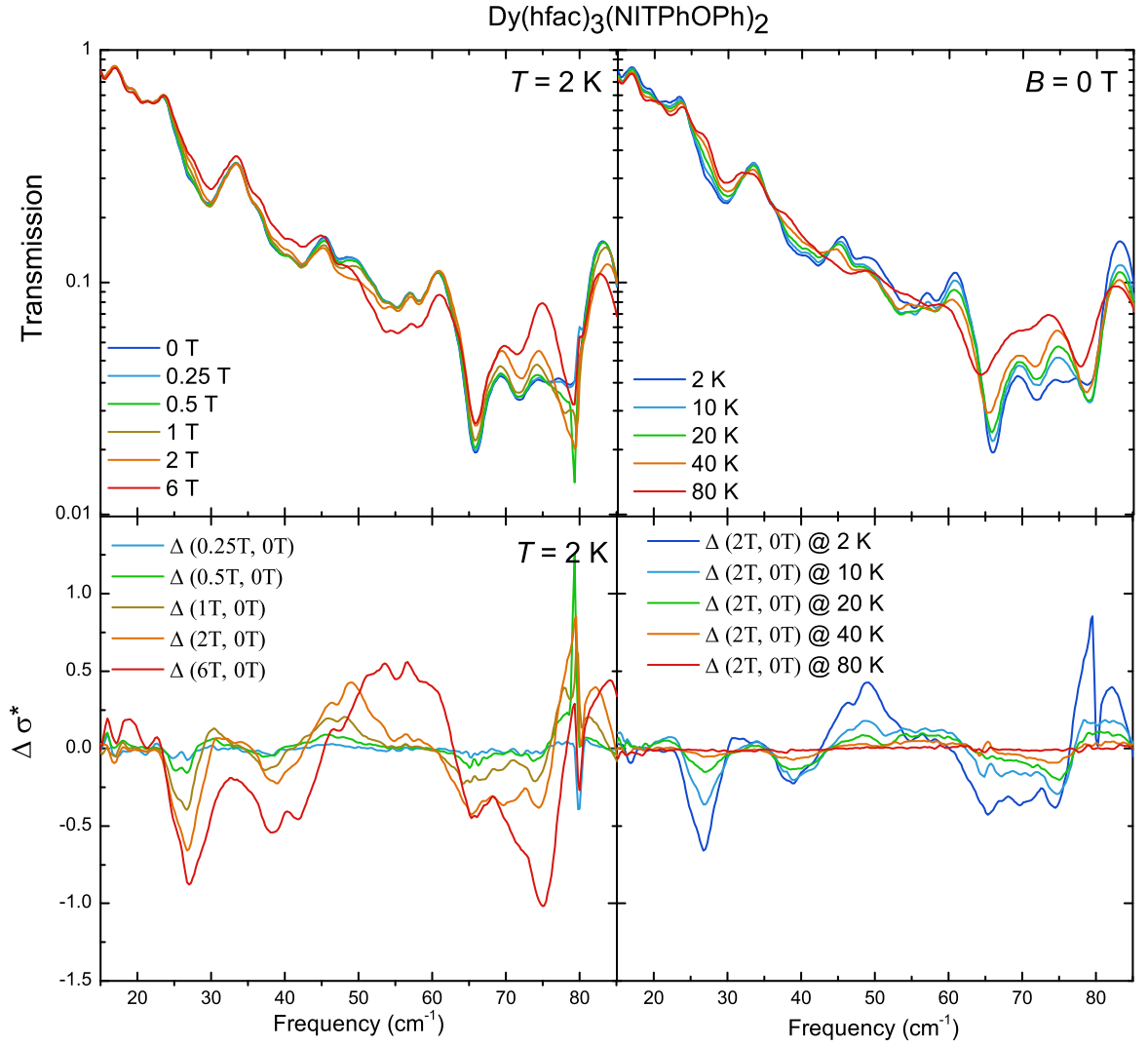


Fig. 7.2: Top left: Transmission spectra of $\text{Dy}(\text{NITPhOPh})_2$ at $T=2 \text{ K}$ in magnetic fields from 0 T-6 T. Top left: Transmission spectra at $B=0 \text{ K}$ at temperatures from 2 K-80 K. Bottom left: Difference between the in-field and zero-field normalized absorption cross section at $T=2 \text{ K}$. Bottom right: Difference between the $B=2 \text{ T}$ and zero-field normalized absorption cross section at temperatures from 2 K-80 K.

is hampered.

However, in our first model we will use a "simple" spin Hamiltonian for the interpretation of our data. Motivated by the Ising spin Hamiltonian used for the ground crystal field state of Dy(NITPhOEt)₂ (Equation 7.1), the following Hamiltonian will be used:

$$\begin{aligned}
 \hat{H} = & \underbrace{\sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q(\hat{\mathbf{J}})}_{\hat{H}_{crystal}} + \underbrace{J_{NNN} \hat{\mathbf{S}}_{R1} \hat{\mathbf{S}}_{R2}}_{\hat{H}_{spin-spin}} + \underbrace{J_{NN} (\hat{\mathbf{S}}_{R1} + \hat{\mathbf{S}}_{R2}) \hat{\mathbf{J}}_{Dy}}_{\hat{H}_{Dy-spin}} \\
 & + \underbrace{g_{R1z} \hat{\mathbf{S}}_{R1} \mu_B \mathbf{H}}_{\hat{H}_{Zeeman-rad1}} + \underbrace{g_{R2z} \hat{\mathbf{S}}_{R2} \mu_B \mathbf{H}}_{\hat{H}_{Zeeman-rad2}} + \underbrace{g_{Dy} \hat{\mathbf{J}}_{Dy} \mu_B \mathbf{H}}_{\hat{H}_{Zeeman-Dy}}.
 \end{aligned} \tag{7.2}$$

Here, the crystal field interaction is introduced by the first term, the radical-radical interaction by the second, the Dy-radical interaction by the third, and the Zeeman interaction with a magnetic field by the last three terms. A discussion of this Hamiltonian with the above assumption is given in Appendix A.4 and leads to the following results.

We obtain the result that for this model the observed absorption lines in the far-infrared measurements reveal the energy-level structure of the crystal field splitting inside the dysprosium ground multiplet and are independent of the coupling strength. The above considerations offer the opportunity to compare the experimental energy-level splitting of Dy³⁺ in Dy(NITPhOEt)₂ and Dy(NITPhOPh)₂ with results obtained by CASSCF-calculations for Dy³⁺ in the surrounding crystal field [5]². In Figure 7.3 the energy-level structures obtained by far-infrared spectroscopy on Dy(NITPhOPh)₂, by CASSCF-calculations of the energy-levels of the crystal field split ground multiplet ⁶H_{15/2} of dysprosium in Dy(NITPhOPh)₂, and the energy-level structure obtained by far-infrared spectroscopy on the single-chain magnet Dy(NITPhOPh) are shown. Two of the energy-levels (27 cm⁻¹ and 70 cm⁻¹) determined by far-infrared spectroscopy are also found in the CASSCF-calculations. The third energy-level at 42 cm⁻¹ has no counterpart in the CASSCF-calculations. According to the above described model, the CASSCF-results should be directly comparable to the far-infrared results. A discrepancy between energy-levels found by far-infrared spectroscopy and CASSCF calculations was also observed for the single-ion magnet (NBu₄)⁺[DyPc₂]⁻ · 2dmf [9]. There, the discrepancy was related to simplifications due to the reduction of the basis set, which were necessary in the CASSCF-calculations due to limited computational resources, and the fact that the structure of the molecule was determined at 100 K in difference to experimental data measured at 10 K. Details to the CASSCF-calculations

² CASSCF-calculations for Dy(NITPhOPh)₂ and Dy(NITPhOEt)₂ were performed by Javier Luzon (University of Florence). For details of the calculation compare Bernot *et al.* [5]. For the CASSCF-calculations the radicals were substituted with its closed shell analogues.

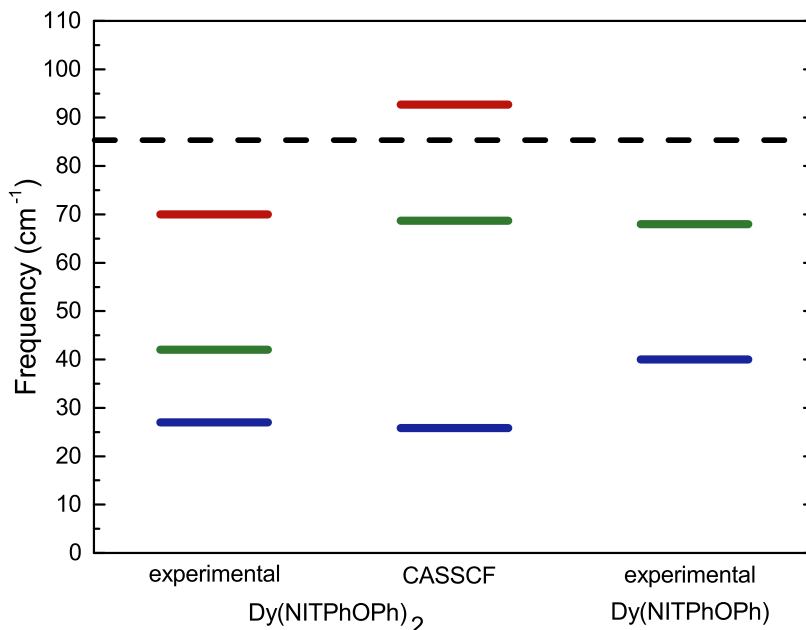


Fig. 7.3: Energy-level structure obtained by: (1) far-infrared spectroscopy on $\text{Dy}(\text{NITPhOPh})_2$, (2) CASSCF-calculations of the energy-levels of the crystal field split ground multiplet $^6\text{H}_{15/2}$ of dysprosium in $\text{Dy}(\text{NITPhOPh})_2$, and (3) the energy-level structure obtained by far-infrared spectroscopy on the single-chain magnet $\text{Dy}(\text{NITPhOPh})$.

for $\text{Dy}(\text{NITPhOPh})_2$ can be found in Bernot *et al.*[5]. The structure of the molecule used for the CASSCF-calculations was obtained at 150 K. Therefore, an analogue behavior might be encountered for the compound studied in this work.

In addition, the results of $\text{Dy}(\text{NITPhOPh})_2$ are compared with the energy-level obtained for the single-chain magnet $\text{Dy}(\text{NITPhOPh})$ in the previous section. The crystal fields surrounding the dysprosium ions are very similar to each other, and therefore a similar crystal field splitting is expected. Two of the energy-levels (42 cm^{-1} and 70 cm^{-1}) are comparable in energy. However, the third energy-level at 27 cm^{-1} is only found in $\text{Dy}(\text{NITPhOPh})_2$.

The above discussion of the spin-Hamiltonian relied on the isotropy of the exchange interaction (rad-rad) between the two radicals. This assumption is questionable. The exchange interaction is transmitted by the dysprosium ion which shows a strong magnetic anisotropy. However, if this assumption is not valid, the disentanglement of contributions stemming from the crystal-field splitting and the exchange coupling is not possible. Therefore, both contributions need to be modeled simultaneously, which leads to an overparametrization of the model. In addition as stated before the use of the spin-Hamiltonian is limited, and does not reproduce the behavior of a lanthanide ion with first order orbital momentum correctly. Furthermore, the analysis of the spectra combined with magnetization data does not solve this issue.

7.4.2 Dy(NITetOPh)₂

The far-infrared results of Dy(NITPhOEt)₂ are presented in Figure 7.4. In the transmission spectra a change with magnetic field can be observed in nearly the entire frequency range at a temperature of 2 K (Figure 7.4 top left). The difference of the normalized absorption cross section (Figure 7.4 bottom left) leads us to the identification of several lines: Three strong absorption features, changing with magnetic field, can be identified: the first one at 23 cm⁻¹, the second one at around 31 cm⁻¹, and the third one at around 60 cm⁻¹. For the latter two features a fine structure is observed, which can be a hint that they consist of more than one line.

All features decrease by increasing temperature from 2 K to 40 K and vanish at 80 K (Figure 7.4 bottom right). The observed temperature dependence implies that the transitions causing the absorption lines originate from the ground state due to the Boltzmann statistics.

Since Dy(NITPhOEt)₂ has a similar crystal structure as Dy(NITPhOPh)₂, both the crystal field splitting of the ground dysprosium multiplet ⁶H_{15/2} and the exchange interaction should be comparable. This is indeed observed, both compounds show a similar change with magnetic field. The observed features show only small frequency shifts. The absorption lines of Dy(NITPhOEt)₂ are sharper than the ones of Dy(NITPhOPh)₂. The smaller linewidth suggests that the spin-phonon coupling for Dy(NITPhOEt)₂ is smaller.

The interpretation of the far-infrared data is parallel to the one of Dy(NITPhOPh)₂ presented in Section 7.4.1.

7.4.3 Tb(NITPhOPh)₂

The results of the far-infrared measurements of Tb(NITPhOPh)₂ are depicted in Figure 7.5 on the left. The magnetic field dependent spectra of the terbium derivative show clear changes with the application of a magnetic field at 5 K (Figure 7.5). For the terbium derivative, the difference of the normalized absorption cross section between in-field and zero-field measurements reveals a well defined absorption line at 21 cm⁻¹. By the application of a magnetic field the line shifts to higher frequencies. The shift of the line was well reproduced by a fit to the data (Figure 7.6) assuming an absorption line of Lorentzian shape with a FWHM=7 cm⁻¹ that shifts with a spectroscopic g-factor of $g_{spec} = 1/\mu_B \frac{cm^{-1}}{T}$ (with μ_B the Bohr magneton in units of $\frac{cm^{-1}}{T}$) to higher frequencies. For the definition of the spectroscopic g-factor in this case see Section 4.5. The simulated absorption feature is shown together with the experimental normalized absorption cross section in Figure 7.6 a). The smaller change with magnetic field at 31 cm⁻¹ can be attributed to the overlapping of the shoulders of the absorption line at 21 cm⁻¹ with the phonon line located at 31 cm⁻¹.

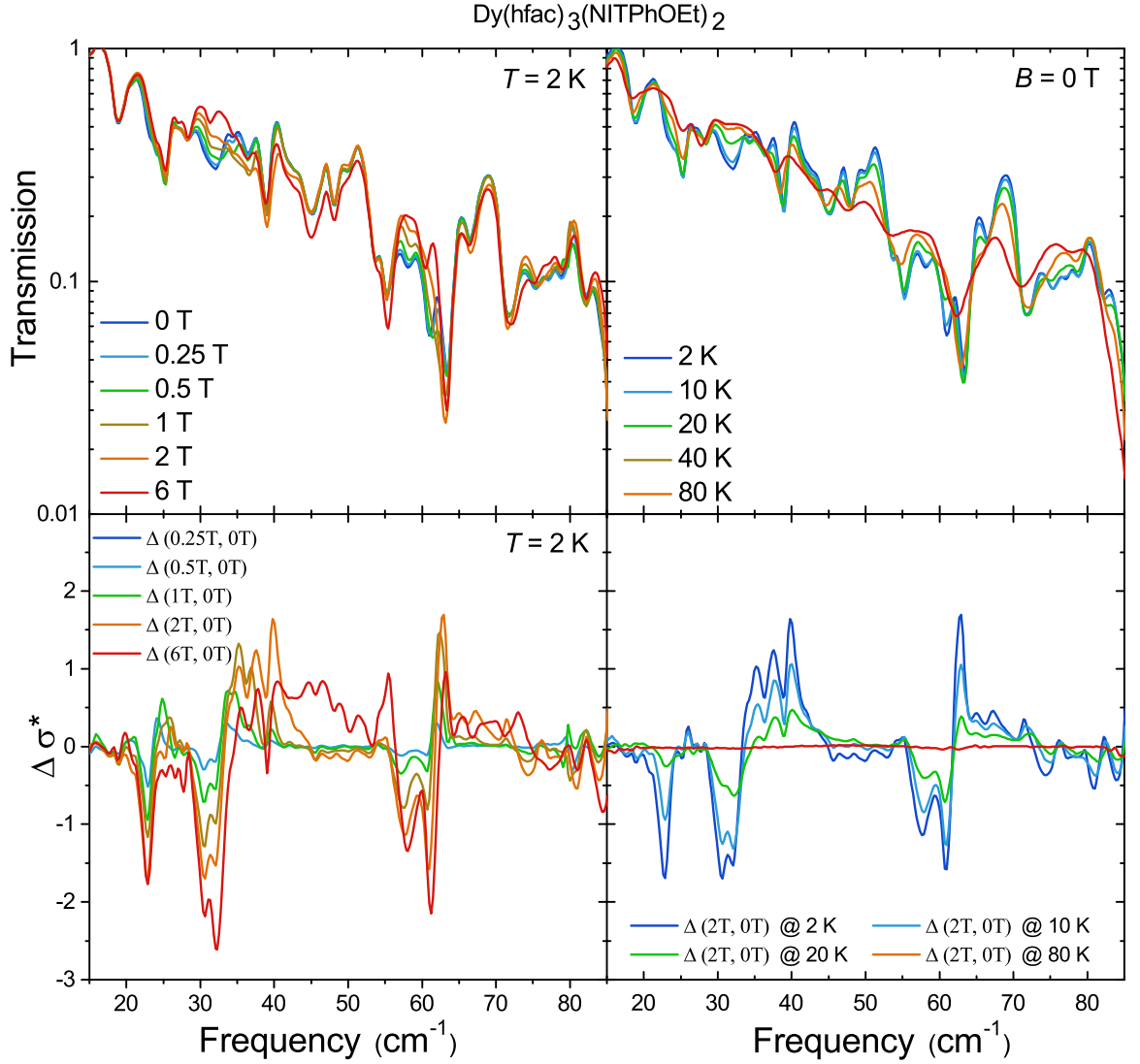


Fig. 7.4: Top left: Transmission spectra of $\text{Dy}(\text{NITPhOEt})_2$ at $T=2\text{K}$ in magnetic fields from 0 T-6 T. Top left: Transmission spectra at $B=0\text{K}$ at temperatures from 2 K-80 K. Bottom left: Difference between the in-field and zero-field normalized absorption cross section at $T=2\text{K}$. Bottom right: Difference between the $B=2\text{T}$ and zero-field normalized absorption cross section at temperatures from 2 K-80 K.

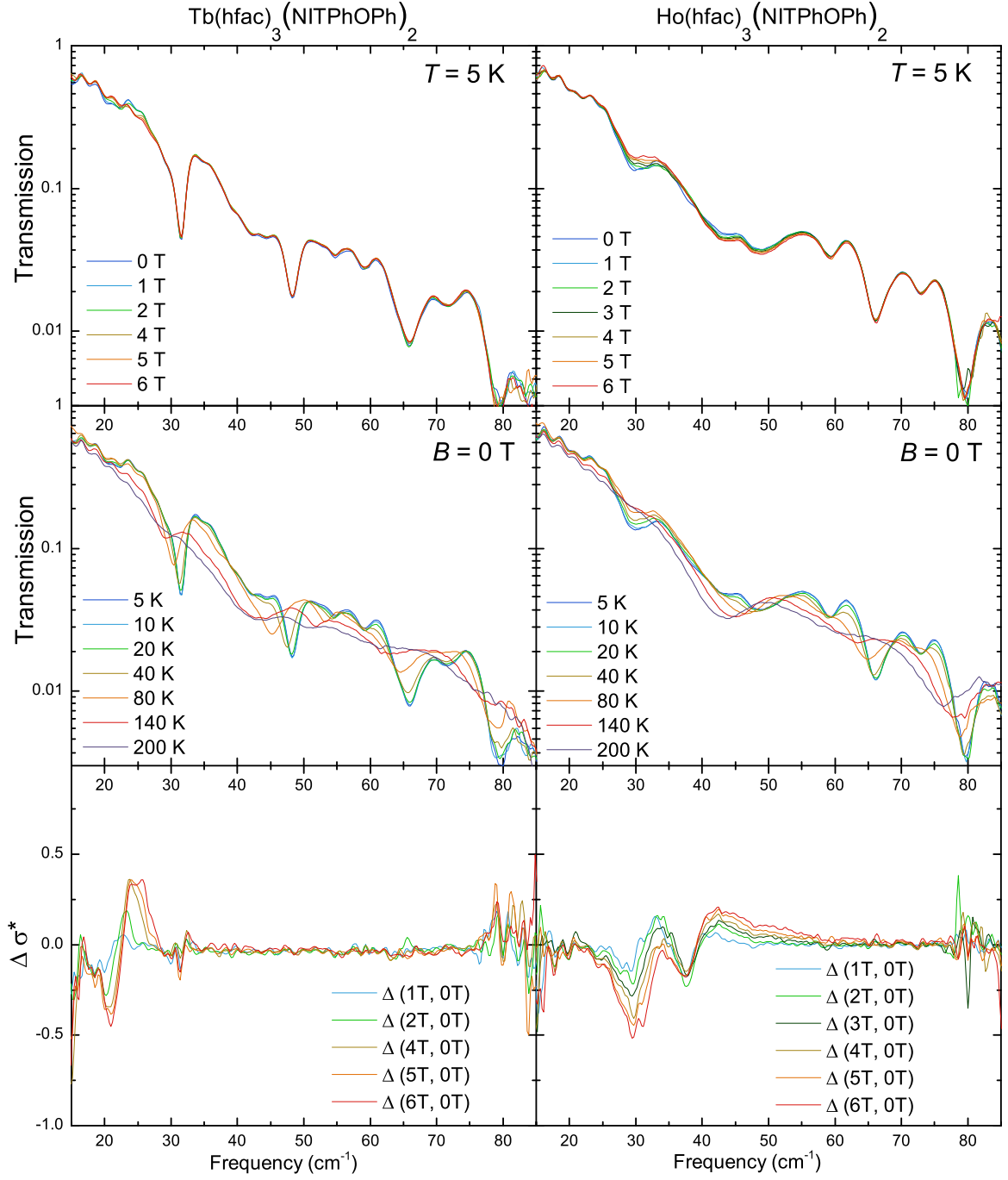


Fig. 7.5: Left column: Far-infrared measurements of $\text{Tb}(\text{NITPhOPh})_2$. Right column: Far-infrared measurements of $\text{Ho}(\text{NITPhOPh})_2$. First row: Transmission spectra at $T = 5 \text{ K}$ in magnetic fields from 0 T-6 T. Second row: Transmission spectra at $B = 0 \text{ T}$ at temperatures from 5 K-200 K. Third row: Difference between the in-field and zero-field normalized absorption cross section at $T = 5 \text{ K}$.

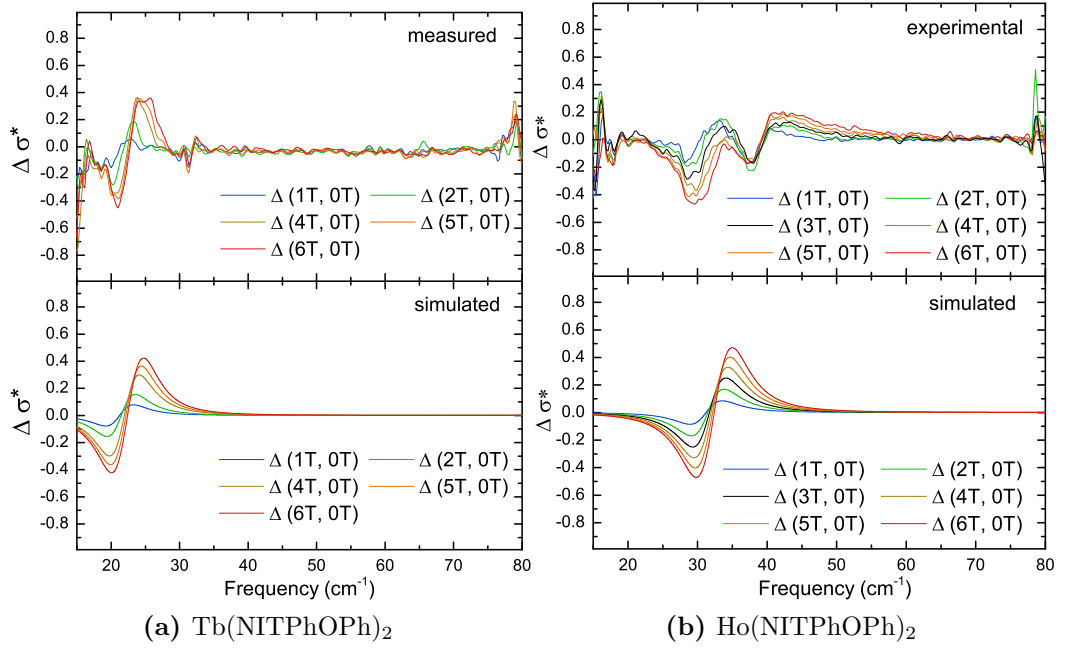


Fig. 7.6: Upper Row: Measured difference of the normalized absorption cross section at 5 K of $\text{Tb}(\text{NITPhOPh})_2$ and $\text{Ho}(\text{NITPhOPh})_2$. Lower Row: Simulated difference of the normalized absorption cross section. Parameters for the simulation: $\text{Tb}(\text{NITPhOPh})_2$: Lorentzian lineshape, $\text{FWHM}=7 \text{ cm}^{-1}$, spectroscopic g-factor $g_{\text{spec}} = 1$, zero field position at 22 cm^{-1} , integrated absorption cross section $\int k_{\sigma} d\sigma = 10$. $\text{Ho}(\text{NITPhOPh})_2$: Lorentzian lineshape, $\text{FWHM}=8 \text{ cm}^{-1}$, spectroscopic g-factor $g_{\text{spec}} = 1$, zero field position at 31 cm^{-1} , and integrated absorption cross section $\int k_{\sigma} d\sigma = 14$.

7.4.4 Ho(NITPhOPh)₂

For Ho(NITPhOPh)₂ an electronic absorption line can be identified at around 30 cm⁻¹, which shifts by the application of an applied field to higher frequencies. Inside the feature at 38 cm⁻¹ an additional dip is observed in the magnetic field dependent spectra, which we attribute to an artifact, resulting from non-suppressed Fabry-Perot resonances in the zero-field spectrum. The spectroscopic g-factor is extracted again by simulations using a Lorentzian absorption line. The position of the line moves to higher frequencies by the application of an applied field proportional to a spectroscopic g-factor of $g_{spec} = 1/\mu_B \frac{cm^{-1}}{T}$. The simulations are shown in Figure 7.6 b).

7.4.5 Comparison of the different compounds

In Figure 7.7 the identified energy-levels of the measured compounds are summarized. As stated previously in Section 7.4.1 an interpretation of the data by the use of a model Hamiltonian was not possible. However, a comparison of the results show that all of the compounds (Ln(NITPhOPh)₂) reveal an energy-level around 25 cm⁻¹: for the terbium derivative at 21 cm⁻¹, for the dysprosium derivative at 27 cm⁻¹, and for the holmium derivative at 30 cm⁻¹. Remarkably, the magnetic field dependence of the corresponding absorption lines is similar. For Tb(NITPhOPh)₂ and Ho(NITPhOPh)₂ a fitting of the results was possible when using for both cases a spectroscopic g-factor of $g_{spec} = 1/\mu_B \frac{cm^{-1}}{T}$. For Dy(NITPhOPh)₂ the extraction of the spectroscopic g-factor was hampered due to the overlapping of the feature with other absorption lines. However, also the magnetic field dependence of the dysprosium line is in accordance to a spectroscopic g-factor of $g_{spec} = 1/\mu_B \frac{cm^{-1}}{T}$. The similar spectroscopic g-factor can be an indication that the energy-level around 25 cm⁻¹ has the same origin in all of the compounds. Suitable for the explanation of the similar feature is the splitting of the energy-level due to the exchange interaction between the lanthanide ion and the radical (see Equation A.8).

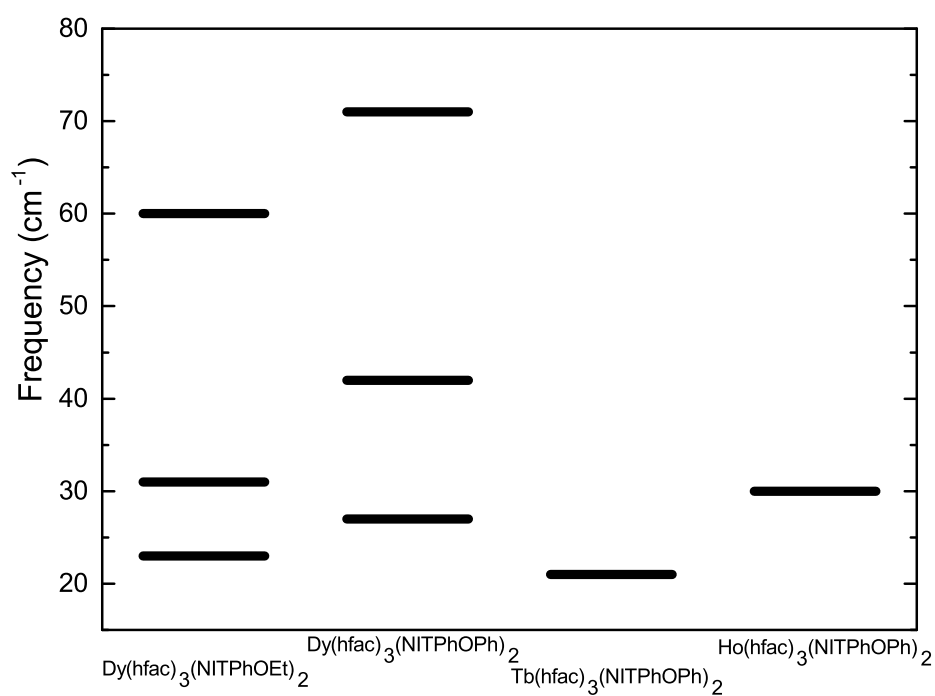


Fig. 7.7: Scheme and comparison of the energy-level structure of $\text{Dy}(\text{NITPhOPh})_2$, $\text{Tb}(\text{NITPhOPh})_2$, $\text{Ho}(\text{NITPhOPh})_2$, and $\text{Dy}(\text{NITPhOEt})_2$ obtained by far-infrared spectroscopy.

7.5 Conclusion

We were able to identify several energy-levels in the compounds $\text{Ln}(\text{NITPhOPh})_2$ (with $\text{Ln}=\text{Dy}$, Tb , and Ho) and $\text{Dy}(\text{NITPhOEt})_2$ by the use of magnetic field dependent far-infrared spectroscopy. These results were then compared with theoretical models. However, due to the complex nature of the interactions in these complexes, we were not able to find an unambiguous theoretical model for the description of our experimental data.

8 Summary and Outlook

One aim of this thesis was to shed light onto the relaxation process of lanthanide-based single-molecular magnetic materials showing slow relaxation of the magnetization. As the energy-level structure plays a crucial role in the relaxation process, an advantage of far-infrared spectroscopy was that it offers direct access to the energy-level structure without the use of a certain model Hamiltonian.

The single-molecular magnetic materials, studied by far-infrared spectroscopy in this thesis were:

1. The single-chain magnet DyPhOPh ($\text{Dy}(\text{hfac})_3\{\text{NIT}(\text{C}_6\text{H}_4\text{OPh})\}$) and the isostructural terbium compound TbPhOPh [14],
2. The single-ion magnet DyDOTA ($\text{Na}[\text{Dy}(\text{DOTA})(\text{H}_2\text{O})]_4 \cdot \text{H}_2\text{O}$) and the isostructural terbium compound TbDOTA [15, 58],
3. The molecular magnet $\text{Ln}(\text{PhOPh})_2$ ($\text{Ln}(\text{hfac})_3(\text{NIT} - \text{C}_6\text{H}_4\text{OPh})_2$) ($\text{Ln}=\text{Dy}$, Tb, and Ho) and $\text{Dy}(\text{hfac})_3(\text{NIT} - \text{C}_6\text{H}_4\text{OEt})_2$ ($\text{Dy}(\text{PhOEt})_2$) [5, 64].

They have in common that the lanthanide ion is situated in a crystal field of low symmetry. In a low-symmetry crystal field the use of the crystal field Hamiltonian is hampered by the overparametrization of the system. In addition, for compound 1. and 3. we had to deal not only with the overparametrized crystal-field Hamiltonians but also with the exchange couplings to the neighboring ions.

The first part of the thesis reviewed the theoretical treatment of lanthanides in crystal fields. Focus was put on the relaxation processes present in lanthanides.

As far-infrared spectroscopy was not used in the field of lanthanide-based single-molecular magnetic materials, before. We were faced with different issues: During the studies, it was realized that the far-infrared spectra of the compounds only give access to the change of the electronic absorption lines in a magnetic-field. In zero-field measurements, the distinction between electronic and phononic or intramolecular vibrational absorption lines was not possible. Therefore, new analysis tools were developed. We presented a quantity which we termed the normalized absorption cross section. It can be calculated easily out of the far-infrared data and gives direct access to the intensity of the transition in terms of the transition matrix element. This quantity can be directly calculated out of the Hamiltonian of the system. A program was

written to calculate the normalized absorption cross section out of the crystal field Hamiltonian for lanthanides. Within this software, a Lebedev-Laikov grid [20] was implemented for the simulation of powder samples to take into account the random orientations of the crystallites. Due to the low symmetry of the compounds studied in this thesis, we were not able to use the program for the simulation of our measured spectra. However, the program yields a tool for further studies on other systems and was used in this thesis to get an idea which shapes can be, in general, observed for electronic resonance lines in lanthanide compounds in powder samples, as nearly no measured data on powdered samples exist in literature.

In the second part of the thesis, the experimental results of the - by far-infrared spectroscopy - studied compounds are presented. The results yielded access to the energy-level structure of the compounds and offered, thereby, the possibility to get a deeper understanding into the relaxation process.

For the single-chain magnet DyPhOPh the far-infrared measurements revealed the energies of the two lowest Kramers doublet in the crystal-field split ${}^6H_{15/2}$ multiplet. The energies of the two doublets led us to a new interpretation of the relaxation mechanism. We propose that a switching between two relaxation pathways inside of the dysprosium ground multiplet is responsible for the observed crossover in the relaxation measurements rather than the prior attribution to the transition from the infinite- to the finite-size regime.

For the single-ion magnet DyDOTA, the two lowest energy-levels were determined. The energy of the lowest level at 44 cm^{-1} is consistent with an Orbach process being responsible for the thermally activated relaxation mechanism (with a relaxation barrier of 42 cm^{-1} [15]) observed in the compound in a magnetic field. In addition, the extracted spectroscopic g-factor of the transition gave a possible explanation for the switching of the relaxation process from the direct process to the Orbach process by the application of a magnetic field.

For $\text{Ln}(\text{PhOPh})_2$ ($\text{Ln}=\text{Dy}$, Tb , and Ho) and $\text{Dy}(\text{PhOEt})_2$, where a lanthanide ion is coupled to two nitronyl nitroxide radicals, several energy-level were determined. However, we were not able to interpret our results due to the complexity of the underlying crystal-field interactions and exchange interactions.

Although the results of this thesis allowed for a deeper understanding of the studied compounds, a drawback was imposed by the limited accessible frequency range from 4 cm^{-1} to 100 cm^{-1} . Therefore, only the low lying energy-levels of the crystal field split ground multiplet of the lanthanide ions could be determined. As the overall crystal field splitting is of the range of around 800 cm^{-1} the frequency range could be extended to broaden the scope of the applicability. The limitation of the accessible frequency range was caused mainly by the mylar windows of the cryostat. This issue can be solved by replacing the windows with polyethylene windows.

For future studies also single-crystal measurements are desirable, as they allow for the study of the orientational dependence of the spectroscopic g-factor and for polarization

dependent measurements. Polarization dependent measurements can give information about the kind of the electronic transitions whether they are either of electric dipole or magnetic dipole character. In addition, we have pointed out that also reflection measurements can resolve the nature of the transitions, as electric dipole transitions have an inverted shape compared to magnetic dipole transitions.

Despite the possible experimental improvements, the obtained energy-levels of the studied lanthanide-based molecular magnetic materials offer the possibility for the improvement of the applied theoretical models.

In conclusion we have shown that far-infrared spectroscopy is an efficient tool for the study of lanthanide-based single-molecular materials. Furthermore, the results offered the opportunity of a deeper understanding of the relaxation pathways in the the studied lanthanide-based single-molecular magnetic materials. The deeper understanding provides the possibility to further enhance the relaxation times, which is the key feature of single-molecular materials.

A Appendix

A.1 Limits of the Beer-Lambert law for bulk samples

The Beer-Lambert law connects the transmission of light to α , the absorption coefficient, or to σ , the absorption cross section (see also Equation 4.2):

$$T(\omega) = \frac{I(\omega)}{I_0(\omega)} = \exp^{-\alpha(\omega)d} = \exp^{-\sigma(\omega)Nd}, \quad (\text{A.1})$$

with d , the distance, the light travels through the material (path length). We then gain for the absorption coefficient:

$$\sigma(\omega) = -\ln(T(\omega))/(Nd). \quad (\text{A.2})$$

In the Beer-Lambert law, it is assumed that the transmission spectrum is only determined by the absorption of the material. Unfortunately, for bulk samples, in addition to the absorption, the transmission depends on the reflection. To disentangle the absorption from the reflection, the optical properties of the sample need to be derived. For the determination of the optical properties of a sample like the complex electric permittivity¹, two independent quantities like the transmitted intensity and the phase need to be measured. In general, when measuring only one optical property like the transmission or the reflectance in a finite frequency interval, the determination of the complex electric permittivity is not directly feasible. However, in order to fix this problem expedient models and assumptions are required. A general approach is given by Kuzmenko, which is used for the program package RefFIT [136]. To model the optical properties, a multiple oscillator fitting of the spectra is carried out. At every

¹ It is assumed that the magnetic permeability is 1 in the measured frequency range.

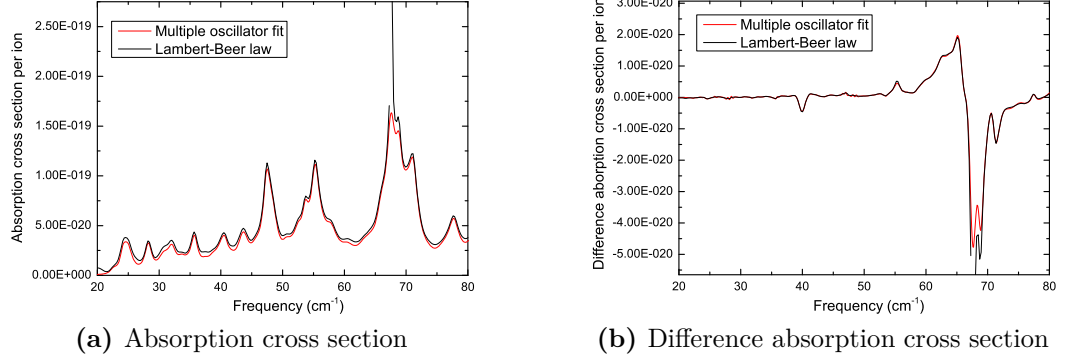


Fig. A.1: (a) Absorption cross section of DyPhOPh. (b) Difference of the absorption cross section in-field ($B=2T$) and zero-field. The red line shown was derived by the multiple oscillator model of Kuzmenko [136]. The black line was derived by the use of $\sigma_{ion} = -\ln(T(\omega))/(Nd)$

measured frequency point an electric oscillator is introduced, leading to a parametrization of the imaginary part of the permittivity ϵ_2 , ϵ_2 . The real part of the permittivity ϵ_1 in this approach is given by the Kramers-Kronig transformation:

$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega', \quad (\text{A.3})$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega'. \quad (\text{A.4})$$

Different lineshapes can be used for the oscillators. Kuzmenko [136] suggests a triangular lineshape, because it has no low and high frequency tails, instead it is located only at the respective frequency point.

In the following, we will only use this approach to check the error, which arises due to the use of the simple Equation A.2 for the absorption cross section by neglecting the reflectivity of the material. In Figure A.1 a comparison of the two different approaches for the compound DyPhOPh is shown: the absorption cross section shown in red was derived, by using the multiple oscillator fitting. The absorption cross section shown in black, was derived by the Beer-Lambert law (Equation A.2). Obviously the deviation of the two models is small for the absorption cross section. However, by taking the difference of the absorption cross section in-field and zero-field, the deviation nearly disappears (Figure A.1 b)). The strongest deviation is visible at around $66-69 \text{ cm}^{-1}$ and can be attributed to the reason that the transmission is zero at 66.5 cm^{-1} , which makes the $\ln(T)$ meaningless at this point and furthermore causes problems during fitting with the multiple oscillator model.

We can summarize that the Beer-Lambert law is a good approximation for this example. However, the use of the Beer-Lambert law is only justified, for compounds with a small refractive index, resulting in a low reflectance. All the compounds studied in this thesis have a refractive index between 1.4-1.7 inside the measured frequency range. As the reflectivity without internal reflections is given by $R = (\frac{n_1-1}{n_1+1})^2$, only 3-7 % of the incident light is reflected (outside of the Fabry-Pérot resonances). Therefore, we can use the Beer-Lambert law for the compounds studied in this thesis.

A.2 DyDOTA: additional measurements

Far-infrared measurements of pure eicosane were acquired to distinguish between absorption lines caused by DyDOTA and eicosane. The spectra of a pure eicosane pellet (thickness = 2.2 mm, weight = 184 mg) at temperatures of 5 K and 30 K are shown in Figure A.2. Three absorption lines are visible labeled E1-E3 with E1 being the most intense line. The whole spectra show no change by the application of a magnetic field of 6 T. The refractive index was determined by a fit of the Fabry-Pérot resonances as $\eta = 1.5$.

Additional experiments were conducted, to check, if the magnetic field dependent changes are caused by a systematic experimental error or by the sample.

The first electronic absorption was identified at 44 cm^{-1} . The first part of the absorption line from $41\text{-}46\text{ cm}^{-1}$ is also accessible by the coherent source THz spectrometer using BWOs described in Section 3.1.1. The spectra of DyDOTA $\mathbf{3}$ at 2 K and at 0 T and 6 T are shown in Figure A.3 (a). The change with magnetic field is the same as previously observed in the far-infrared measurements. We can, therefore, exclude that a magnetic field dependent change of the mercury (Hg)-arc lamp is responsible for the effect. In this frequency range, in BWO measurements the same detector (a pumped liquid helium bolometer) is used as in the far-infrared measurements. However, in measurements using BWO set-up the bolometer is placed around 0.5 m away from the Spectromag, and no magnetic field dependent changes were observed. Therefore, we can conclude that the magnetic field dependent effect in DyDOTA in this frequency range is not caused by a systematic measurements error but rather by the sample itself. It is also an indication that the small magnetic field dependent changes at other frequencies are caused by the sample itself. For a comparison the spectra of TbDOTA $\mathbf{3}$ with no magnetic field change are shown in Figure A.3 (b).

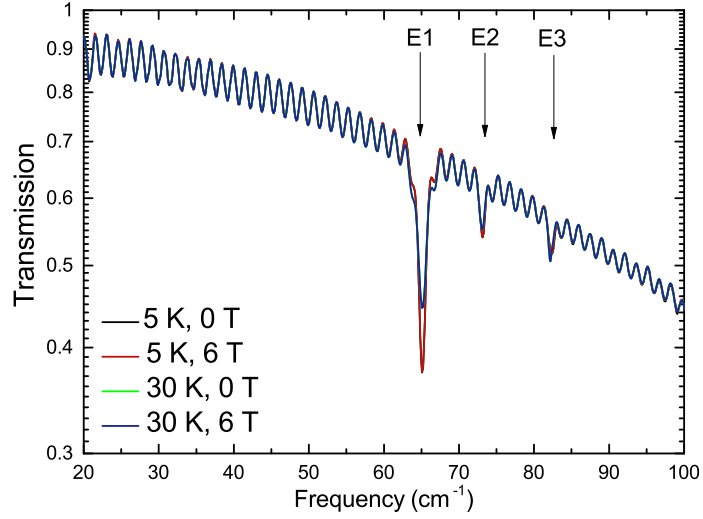


Fig. A.2: Far-infrared spectra of eicosane at temperatures of 5 K and 30 K. The phononic absorption lines are labeled with E1-E3. The spectra at different magnetic fields 0 T and 6 T show no changes in the whole frequency range.

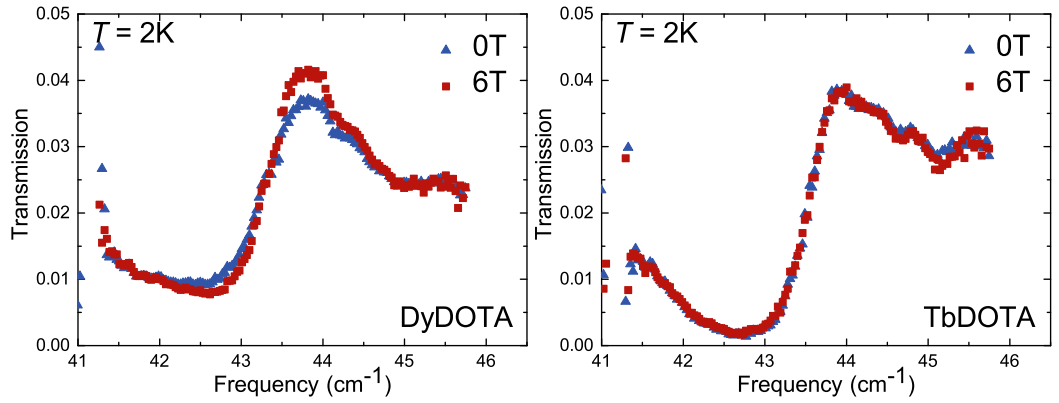


Fig. A.3: BWO-THz-Transmission of DyDOTA3 and TbDOTA3 at 2 K and in magnetic fields of 0 T and 6 T.

A.3 Dy(PhOPh)₂: additional measurements

In Figure A.4 the spectra of Dy(PhOPh)₂ acquired with the BWO quasi-optical setup (see Section 3.1.1) are shown. The spectrum at a temperature of 40 K was fitted using the Fresnel equations and yielded for the real part a refractive index value of $\eta = 1.6$. The refractive index of $\eta = 1.6$ was used for the calculation of the normalized absorption cross section in Section 7 for all temperatures and also for the samples Dy(PhOEt)₂, Tb(PhOPh)₂, and Ho(PhOPh)₂. The origin of the absorption feature between 10-17 cm⁻¹ is unclear.

In Figure A.5 the difference of the absorption between spectra in-field and without field of Dy(PhOPh)₂ are depicted. The sample had a thickness of 1.1 mm and a weight of 100.5 mg. Unfortunately, the sample was possibly contaminated with grease. Grease does not change the spectra qualitatively the spectra of Dy(PhOPh)₂. However, it permits the calculation of the normalized absorption cross section as the amount of Dy(PhOPh)₂ in the sample is unknown.

Comparison of the difference of the absorption of this sample with the one presented in Section (see Section 7) leads us to the assumption that the three features observed are caused by three resonances.

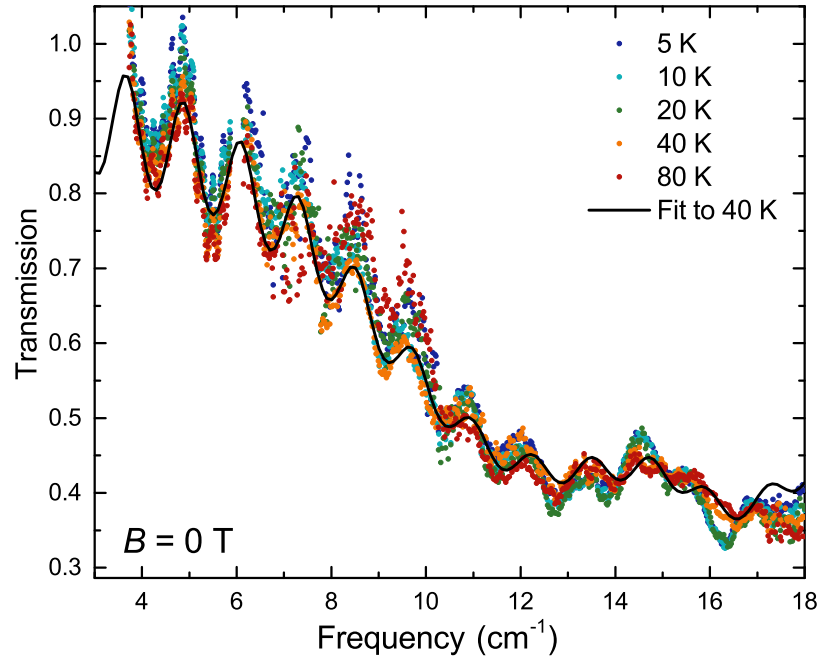


Fig. A.4: Spectra of $\text{Dy}(\text{PhOPh})_2$ acquired with the BWO quasi-optical setup at different temperatures without a magnetic field. The black line shows the fit obtained for the spectrum at 40 K.

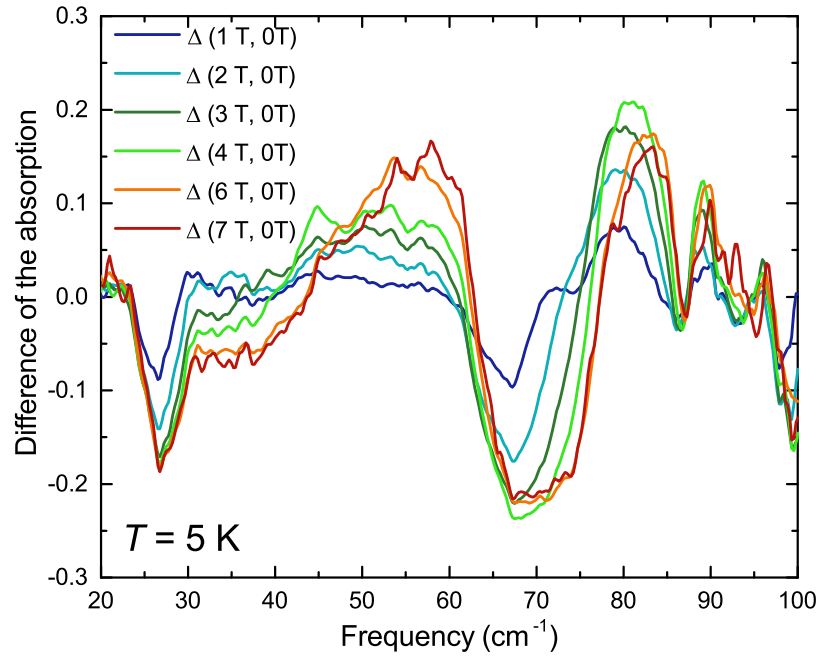


Fig. A.5: Difference of the absorption of the far-infrared spectra of $\text{Dy}(\text{PhOPh})_2$ between spectra in-field and without field at $T=5 \text{ K}$. For the sample composition see text.

A.4 Dy(PhOPh)₂: theoretical considerations

In the following we will give a detailed discussion of the spin-Hamiltonian presented in Section 7 and its impact on the nature of observed far-infrared resonances in Dy(PhOPh)₂:

$$\begin{aligned}
\hat{H} = & \underbrace{\sum_{k=2,4,6} \sum_{q=-k}^k B_k^q O_k^q(\hat{\mathbf{J}})}_{\hat{H}_{crystal}} + \underbrace{J_{NNN} \hat{\mathbf{S}}_{R1} \hat{\mathbf{S}}_{R2}}_{\hat{H}_{spin-spin}} + \underbrace{J_{NN} (\hat{\mathbf{S}}_{R1} + \hat{\mathbf{S}}_{R2}) \hat{\mathbf{J}}_{Dy}}_{\hat{H}_{Dy-spin}} \\
& + \underbrace{g_{R1z} \hat{\mathbf{S}}_{R1} \mu_B \mathbf{H}}_{\hat{H}_{Zeeman-rad1}} + \underbrace{g_{R2z} \hat{\mathbf{S}}_{R2} \mu_B \mathbf{H}}_{\hat{H}_{Zeeman-rad2}} + \underbrace{g_{Dy} \hat{\mathbf{J}}_{Dy} \mu_B \mathbf{H}}_{\hat{H}_{Zeeman-Dy}}.
\end{aligned} \tag{A.5}$$

Here, the crystal field interaction is introduced by the first term, the radical-radical interaction by the second, the Dy-radical interaction by third, and the Zeeman interaction with a magnetic field by the last three terms. Without additional knowledge about the crystal field interaction, the model Hamiltonian has an important property in zero field: The product state of every eigenfunction $|\Psi_i\rangle$ of the crystal field hamiltonian $\hat{H}_{crystal}$ only acting on the dysprosium angular momentum and the singlet state of the two radicals is an eigenstate of the model Hamiltonian with the eigenvalue E_i . Due to the Kramers theorem every eigenvalue is doubly degenerate. Namely if:

$$\hat{H}_{crystal} |\Psi_i\rangle = E_i |\Psi_i\rangle, \tag{A.6}$$

then

$$\hat{H} \{ |\Psi_i\rangle, \overbrace{\frac{1}{\sqrt{2}}(|\uparrow\rangle |\downarrow\rangle - |\downarrow\rangle |\uparrow\rangle)}^{spin\ singlet\ of\ radicals} \} = E_i \{ |\Psi_i\rangle, \overbrace{\frac{1}{\sqrt{2}}(|\uparrow\rangle |\downarrow\rangle - |\downarrow\rangle |\uparrow\rangle)}^{spin\ singlet\ of\ radicals} \} \tag{A.7}$$

To verify this, the product state $\{ |\Psi_i\rangle, \frac{1}{\sqrt{2}}(|\uparrow\rangle |\downarrow\rangle - |\downarrow\rangle |\uparrow\rangle) \}$ can be inserted into the Hamiltonian. The first term $\hat{H}_{crystal}$ acts only on the dysprosium angular momentum and is by construction its eigenstate. The second term $\hat{H}_{spin-spin}$ acts only on the radical spins and the singlet state is an eigenstate of this term. The third term $\hat{H}_{spin-Dy}$ acts on both the dysprosium angular momentum and the radical spins. However, due to the symmetry of the interaction between the two radical spins and the dysprosium total angular momentum, every contribution of the first radical spin is canceled by the

second radical spin. In addition, the eigenvalue of the model Hamiltonian is equal to the eigenvalue of the solely crystal field Hamiltonian E_i . The above considerations are not true for the product states with the triplet wave functions of the radicals, because the interaction term $J_{NN}(\hat{\mathbf{S}}_{R1} + \hat{\mathbf{S}}_{R2})\hat{\mathbf{J}}_{Dy}$ can mix the triplet states with the dysprosium crystal field states.

Angular-dependent magnetization measurements revealed that the ground state of the coupled system belongs to the singlet state of the radicals separated by 8 cm^{-1} from the first singlet state of the radicals. The exchange coupling constants were derived as $J_{NNN} = 15\text{ cm}^{-1}$ (antiferromagnetic) and $J_{NN} = -13.5\text{ cm}^{-1}$ (ferromagnetic) for ground state Ising-Hamiltonian. For the model Hamiltonian to fit the results of the Ising-Hamiltonian (Equation 7.1) we adjusted the exchange coupling to $J_{NN} = J_{NN}^{Ising} \cdot \frac{m_J^{sing}}{m_J} = -13.5 \cdot \frac{1/2}{15/2}\text{ cm}^{-1} = -0.9\text{ cm}^{-1}$. Here, it was assumed that the ground multiplet has a m_J value close to $15/2$.

Therefore, the ground state of the coupled system belongs to the product states $||\Psi_1\rangle, \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)\rangle$ and $||\Psi_2\rangle, \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle)\rangle$, where $|\Psi_1\rangle$ and $|\Psi_2\rangle$ are the two states belonging to the lowest Kramers doublet of the crystal field split dysprosium ground multiplet. For the spectra acquired at 2 K, only the twofold degenerate ground state has an appreciable population. Therefore, all observed transition observed at 2 K originate from the two ground states. In addition, the selection rules for the singlet product states allow only transition to other singlet product states. Therefore, in this model the observed absorption lines summarized in Figure 7.7 reveal the energy-level structure of the crystal field splitting inside the dysprosium ground multiplet.

However, an error could arise due to the fact that the above assumptions are violated. We assumed that only transitions between the product states of the crystal-field dysprosium and singlet radical states are observable. In addition in this model, the crystal-field splitting of the dysprosium ground multiplet is not changed by the radical. A drawback of the used spin Hamiltonian (Equation A.5) is that it does not describe the exchange coupling of the orbitally degenerate ground state of the dysprosium ion and the radicals in an appropriate way. Therefore, we will discuss in the following more realistic, but also more complicated models for the coupling.

As Kahn *et al.* [137] pointed out, the exchange interaction only takes place between the spin of the lanthanide ion and the radicals and not as assumed in our previous model Hamiltonian (Equation A.5) between the total angular momentum and the radical spins. The Hamiltonian of the exchange interaction then changes to:

$$\hat{H}_{ex} = J_{NNN}\hat{\mathbf{S}}_{R1}\hat{\mathbf{S}}_{R2} + J_{NN}(\hat{\mathbf{S}}_{R1} + \hat{\mathbf{S}}_{R2})\hat{\mathbf{S}}_{Dy}. \quad (\text{A.8})$$

The Zeeman-interaction changes also [137], but as we will only discuss the zero-field case here, this is of minor importance. Kahn *et al.* [137] modeled first the ligand field effect on the lanthanide ion and obtained the crystal field splitting and the associated

eigenfunctions of the crystal-field split ground multiplet. And second, they computed the exchange interaction in the tensorial product state $\{|\Psi_{\text{Ln}}\rangle, |\text{S}_{\text{R1}}\rangle, |\text{S}_{\text{R2}}\rangle\}$. Although this different approach changes the exchange interaction for the different crystal field levels considerably, our assumptions made above for the simplified spin hamiltonian considering the product states of the crystal field states and the singlet radical states hold also for this more sophisticated model. Therefore, all the above statements for the measured spectra at low temperature, where only the ground state is considerably populated hold. In addition, also the above assumptions made for the selection rules should not change.

Another approach, uses irreducible tensor operators for the coupling between orbitally degenerate lanthanide ions and only spin carriers like the radicals [65]. The exchange coupling in this framework reads:

$$\hat{H}_{ex} = \sum_{k=0}^{2I} \sum_{q=-k}^k \alpha_k^q T_q^{[k]}(i) s(i) S(R_1, 2) \quad (\text{A.9})$$

where i indicates the i th electron of the lanthanide ion and $S(R_1, 2)$ the spin of the only spin carrier in our case radical 1 or radical 2. It follows that now there are $(2I+1)(I+1)$ different coupling constants, which complicate any theoretical modeling considerably. However, we think that also this treatment does not query our above considerations due to the symmetry of the radical coupling.

To summarize the above theoretical considerations: If we assume that the radical-radical J_{NN} coupling is antiferromagnetic and isotropic and the coupling dy-radical J_{NN} is ferromagnetic, isotropic, and equal for the two radicals, the result is that for this model the observed absorption lines in far-infrared measurements reveal the energy-level structure of the crystal field splitting inside the dysprosium ground multiplet and are independent of the coupling strength.

Bibliography

- [1] A. Abragam and B. Bleaney. *Electron Paramagnetic resonance of transition ions*. Oxford University Press, 1986.
- [2] D. Gatteschi, R. Sessoli, and J. Villain. *Molecular Nanomagnets*. OUP Oxford, 2006.
- [3] N Ishikawa, M Sugita, T Ishikawa, S Koshihara, and Y Kaizu. *Lanthanide double-decker complexes functioning as magnets at the single-molecular level*, J. Am. Chem. Soc. **125** (2003), 8694–8695.
- [4] L. Sorace, C. Benelli, and D. Gatteschi. *Lanthanides in molecular magnetism: old tools in a new field*, Chem. Soc. Rev. **40** (2011), 3092–3104.
- [5] K. Bernot, J. Luzon, L. Bogani, M. Etienne, C. Sangregorio, M. Shanmugam, A. Caneschi, R. Sessoli, and D. Gatteschi. *Magnetic Anisotropy of Dysprosium in a Low-Symmetry Environment: A Theoretical and Experimental Investigation*, J. Am. Chem. Soc. **131**.15 (2009), 5573–5579.
- [6] R. Orbach. *Spin-Lattice Relaxation in Rare-Earth Salts*, Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences **264** (1961), 458–484.
- [7] D. N. Woodruff, R. E. P. Winpenny, and R. A. Layfield. *Lanthanide Single-Molecule Magnets*, Chem. Rev. **113** (2013), 5110–5148.
- [8] G. Cucinotta, M. Perfetti, J. Luzon, M. Etienne, P.-E. Car, A. Caneschi, G. Calvez, K. Bernot, and R. Sessoli. *Magnetic Anisotropy in a Dysprosium-DOTA Single-Molecule Magnet: Beyond Simple Magneto-Structural Correlations*, Angew. Chem., Int. Ed. **51** (2012), 1606–1610.
- [9] R. Marx, F. Moro, M. Dorfel, L. Ungur, M. Waters, S. D. Jiang, M. Orlita, J. Taylor, W. Frey, L. F. Chibotaru, and J. van Slageren. *Spectroscopic determination of crystal field splittings in lanthanide double deckers*, Chem. Sci. (2014).
- [10] A. J. Sievers and M. Tinkham. *Far Infrared Spectra of Rare-Earth Iron Garnets*, Phys. Rev. **129** (1963), 1995–2004.
- [11] J. C. Hill and R. G. Wheeler. *Far-Infrared Spectra of Erbium, Dysprosium, and Samarium Ethyl Sulphate*, Phys. Rev. **152** (1966), 482–494.
- [12] A. Hadni, G. Morlot, and P. Strimer. *Far-infrared electronic transitions in solids*, IEEE J. Quantum Electron. **3**.3 (1967), 111 –116.
- [13] D Bloor and G. Copland. *Far infrared spectra of magnetic ions in crystals*, Rep. Prog. Phys. **35** (1972), 1173.

- [14] L. Bogani, C. Sangregorio, R. Sessoli, and D. Gatteschi. *Molecular Engineering for Single-Chain-Magnet Behavior in a One-Dimensional Dysprosium-Nitronyl Nitroxide Compound*, Ang. Chem. Int. **117** (2005), 5967–5971.
- [15] P.-E. Car, M. Perfetti, M. Mannini, A. Favre, A. Caneschi, and R. Sessoli. *Giant field dependence of the low temperature relaxation of the magnetization in a dysprosium-DOTA complex*, Chem. Comm. **47** (2011), 3751–3753.
- [16] R. J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E. J. L. McInnes, L. F. Chibotaru, and R. E. P. Winpenny. *Magnetic relaxation pathways in lanthanide single-molecule magnets*, Nat. Chem. **5.8** (2013), 673–678.
- [17] L. Ungur and L. F. Chibotaru. *Magnetic anisotropy in the excited states of low symmetry lanthanide complexes*, Phys. Chem. Chem. Phys. **13** (2011), 20086–20090.
- [18] G. Chantry. *Submillimetre Spectroscopy*. Academic Press, London, 1971.
- [19] M. Takahashi. *Terahertz Vibrations and Hydrogen-Bonded Networks in Crystals*, Crystals (2014).
- [20] V. Lebedev and D. Laikov. *A quadrature formula for the sphere of the 131st algebraic order of accuracy*, Doklady Mathematics **59.3** (1999), 447–481.
- [21] R. Sessoli, D. Gatteschi, A. Caneschi, and M. Novak. *Magnetic bistability in a metal-ion cluster*, Nature **365** (1993), 141–143.
- [22] D. Gatteschi and R. Sessoli. *Quantum Tunneling of Magnetization and Related Phenomena in Molecular Materials*, Angew. Chem., Int. Ed. **42** (2003), 268–297.
- [23] A. Cornia, M. Mannini, P. Sainctavit, and R. Sessoli. *Chemical strategies and characterization tools for the organization of single molecule magnets on surfaces*, Chem. Soc. Rev. **40** (2011), 3076–3091.
- [24] R. E. P. Winpenny. *Stretch for a moment*, Nature Nanotech. **8** (2013), 159–160.
- [25] W. Wernsdorfer. *Molecular nanomagnets: towards molecular spintronics*, Int. J. of Nanotechnology **7** (2010), 497–522.
- [26] O. Petravic. *Superparamagnetic nanoparticle ensembles*, Superlattices and Microstructures **47.5** (2010), 569–578.
- [27] A. J. Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A. Abboud, and G. Christou. *Giant Single-Molecule Magnets: A Mn₈₄ Torus and Its Supramolecular Nanotubes*, Angew. Chem., Int. Ed. **116.16** (2004), 2169–2173.
- [28] G. Aromí and E. K. Brechin. *Synthesis of 3d Metallic Single-Molecule Magnets*, Single-Molecule Magnets and Related Phenomena. Ed. by R. Winpenny. Vol. 122. Structure and Bonding. Springer Berlin Heidelberg, 2006, pp. 163–206.
- [29] G. Christou. *Single-molecule magnets: a molecular approach to nanoscale magnetic materials*, Polyhedron **24.16** (2005), 2065–2075.
- [30] D. Gatteschi. *Single molecule magnets: a new class of magnetic materials*, Journal of Alloys and Compounds **317** (2001), 8–12.
- [31] A. L. Barra, D. Gatteschi, and R. Sessoli. *High-Frequency EPR Spectra of Fe₈O₂(OH)₁₂(tacn)₆Br₈: A Critical Appraisal of the Barrier for the Reorienta-*

- tion of the Magnetization in Single-Molecule Magnets*, Chem. Eur. J. **6** (2000), 1608–1614.
- [32] X. Wang, C. Avendaño, and K. Dunbar. *Molecular magnetic materials based on 4d and 5d transition metals*, Chem. Soc. Rev. **40** (2011), 3213–3283.
- [33] R. A. Layfield. *Organometallic Single-Molecule Magnets*, Organometallics **33.5** (2014), 1084–1099.
- [34] G. P. Guedes, S. Soriano, L. A. Mercante, N. L. Speziali, M. A. Novak, M. Andruh, and M. G. F. Vaz. *New Synthetic Route toward Heterometallic 3d-3d and 3d-4f Single-Molecule Magnets. The First CoII-MnIII Heterometallic Complex*, Inorg. Chem. **52.15** (2013), 8309–8311.
- [35] O. Waldmann. *A Criterion for the Anisotropy Barrier in Single-Molecule Magnets*, Inorganic Chemistry **46.24** (2007), 10035–10037.
- [36] F. Neese and D. A. Pantazis. *What is not required to make a single molecule magnet*, Faraday Discussions **148** (2011), 229–238.
- [37] C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou, and E. K. Brechin. *A Record Anisotropy Barrier for a Single-Molecule Magnet*, J. Am. Chem. Soc. **129.10** (2007), 2754–2755.
- [38] S. Mossin, B. L. Tran, D. Adhikari, M. Pink, F. W. Heinemann, J. Sutter, R. K. Szilagyi, K. Meyer, and D. J. Mindiola. *A Mononuclear Fe(III) Single Molecule Magnet with a $3/2 \rightleftharpoons 5/2$ Spin Crossover*, J. Am. Chem. Soc. **134.33** (2012), 13651–13661.
- [39] J. M. Zadrozny, M. Atanasov, A. M. Bryan, C.-Y. Lin, B. D. Rekker, P. P. Power, F. Neese, and J. R. Long. *Slow magnetization dynamics in a series of two-coordinate iron(II) complexes*, Chem. Sci. **4** (2013), 125–138.
- [40] J. M. Zadrozny and J. R. Long. *Slow Magnetic Relaxation at Zero Field in the Tetrahedral Complex $\text{Co}(\text{SPh})_4^2-$* , J. Am. Chem. Soc. **133.51** (2011), 20732–20734.
- [41] D. E. Freedman, W. H. Harman, T. D. Harris, G. J. Long, C. J. Chang, and J. R. Long. *Slow Magnetic Relaxation in a High-Spin Iron(II) Complex*, J. Am. Chem. Soc. **132.4** (2010), 1224–1225.
- [42] Y.-Y. Zhu, C. Cui, Y.-Q. Zhang, J.-H. Jia, X. Guo, C. Gao, K. Qian, S.-D. Jiang, B.-W. Wang, Z.-M. Wang, and S. Gao. *Zero-field slow magnetic relaxation from single Co(II) ion: a transition metal single-molecule magnet with high anisotropy barrier*, Chem. Sci. **4** (4 2013), 1802–1806.
- [43] R. Sessoli and A. K. Powell. *Strategies towards single molecule magnets based on lanthanide ions*, J. Coord. Chem. **253** (2009), 2328–2341.
- [44] D. Gatteschi. *Anisotropic dysprosium*, Nat. Chem. **3.10** (2011), 830.
- [45] C. R. Ganivet, B. Ballesteros, G. de la Torre, J. M. Clemente-Juan, E. Coronado, and T. Torres. *Influence of Peripheral Substitution on the Magnetic Behavior of Single-Ion Magnets Based on Homo- and Heteroleptic Tb(III) Bis(phthalocyaninate)*, Chem. Eur. J. **19.4** (2013), 1457–1465.
- [46] D. Yoshihara, S. Karasawa, and N. Koga. *Cyclic Single-Molecule Magnet in Heterospin System*, J. Am. Chem. Soc. **130.32** (2008), 10460–10461.

- [47] N Ishikawa, M Sugita, T Ishikawa, S Koshihara, and Y Kaizu. *Mononuclear lanthanide complexes with a long magnetization relaxation time at high temperatures: A new category of magnets at the single-molecular level*, J. Phys. Chem. B **108**.31 (2004), 11265–11271.
- [48] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, and M. A. Novak. *Cobalt(II)-Nitronyl Nitroxide Chains as Molecular Magnetic Nanowires*, Angew. Chem., Int. Ed. **40**.9 (2001), 1760–1763.
- [49] R. J. Glauber. *Time-Dependent Statistics of the Ising Model*, J. Math. Phys. **4**.2 (1963), 294–307.
- [50] A. Vindigni. *Statistics and game theory in single-chain magnet relaxation*, Inorg. Chim. Acta **361** (2008), 3731–3739.
- [51] C. Coulon, H. Miyasaka, and R. Clérac. *Single-Chain Magnets: Theoretical Approach and Experimental Systems*, Single-Molecule Magnets and Related Phenomena. Ed. by R. Winpenny. Vol. 122. Structure and Bonding. Springer Berlin Heidelberg, 2006, pp. 163–206.
- [52] T. Goonan. *Rare earth elements - End use and recyclability: U.S. Geological Survey Scientific Investigations Report 2011-5094*, 15 p. available only at <http://pubs.usgs.gov/sir/2011/5094/> (2011).
- [53] R. Bade. *Rare earths review - Is the hype justified?: Libertas Corporate Finance Limited*, (2010).
- [54] S. V. Eliseeva and J.-C. G. Bunzli. *Rare earths: jewels for functional materials of the future*, New J. Chem. **35** (6 2011), 1165–1176.
- [55] L. Bogani, A. Vindigni, R. Sessoli, and D. Gatteschi. *Single chain magnets: where to from here?*, J. Mater. Chem. **18** (2008), 4750–4758.
- [56] N. F. Chilton, D. Collison, E. J. L. McInnes, R. E. P. Winpenny, and A. Soncini. *An electrostatic model for the determination of magnetic anisotropy in dysprosium complexes*, Nat. Comm. **4** (2013), 2551.
- [57] K. Bernot, J. Luzon, A. Caneschi, D. Gatteschi, R. Sessoli, L. Bogani, A. Vindigni, A. Rettori, and M. G. Pini. *Spin canting in a Dy-based single chain magnet with dominant next-nearest-neighbour antiferromagnetic interactions*, Phys. Rev. B **79** (2009), 134419.
- [58] M.-E. Boulon, G. Cucinotta, J. Luzon, C. Degl’Innocenti, M. Perfetti, K. Bernot, G. Calvez, A. Caneschi, and R. Sessoli. *Magnetic Anisotropy and Spin-Parity Effect Along the Series of Lanthanide Complexes with DOTA*, Angew. Chem., Int. Ed. **125**.1 (2013), 368–372.
- [59] K. S. Pedersen, L. Ungur, M. Sigrist, A. Sundt, M. Schau-Magnussen, V. Vieru, H. Mutka, S. Rols, H. Weihe, O. Waldmann, L. F. Chibotaru, J. Bendix, and J. Dreiser. *Modifying the properties of 4f single-ion magnets by peripheral ligand functionalisation*, Chem. Sci. **5** (4 2014), 1650–1660.
- [60] J. Yamamoto, B. T. Smith, and E. E. Bell. *Far-infrared spectra of dysprosium and terbium iron garnet*, J. Opt. Soc. Am. **64**.6 (1974), 880–883.

-
- [61] J. van Slageren, S. Vongtragool, B. Gorshunov, A. A. Mukhin, N. Karl, J. Krzystek, J. Telser, A. Muller, C. Sangregorio, D. Gatteschi, and M. Dressel. *Frequency-domain magnetic resonance spectroscopy of molecular magnetic materials*, Phys. Chem. Chem. Phys. **5** (2003), 3837–3843.
- [62] N. Kirchner, J. van Slageren, and M. Dressel. *Simulation of frequency domain magnetic resonance spectra of molecular magnets*, Inorg. Chim. Acta **360** (2007), 3813–3819.
- [63] J. Slageren. *New Directions in Electron Paramagnetic Resonance Spectroscopy on Molecular Nanomagnets*, EPR Spectroscopy. Ed. by M. Dresscher and G. Jeschke. Vol. 321. Topics in Current Chemistry. Springer Berlin Heidelberg, 2012, pp. 199–234.
- [64] K. Bernot. *Lanthanides in molecular magnetism: from mononuclear single molecule magnets to single chain magnets*. PhD thesis. l Institut National des Sciences, 2007.
- [65] C. Benelli and D. Gatteschi. *Magnetism of Lanthanides in Molecular Materials with Transition-Metal Ions and Organic Radicals*, Chem. Rev. **102.6** (2002), 2369–2388.
- [66] E. Clementi and W. P. Raimondi D. L. and. Reinhardt. *Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons*, J. Chem. Phys **47** (1967), 1300.
- [67] A. Freeman and R. Watson. *Theoretical Investigation of some magnetic and spectroscopic properties of Rare-Earth Ions*, Phys. Rev. **127** (1962), 6.
- [68] S. Huefner. *Optical spectra of Transparent Rare Earth compounds*. Academic Press, 1978.
- [69] G. Ofelt. *Intensities of Crystal Spectra of Rare Earth ions*, J. Chem. Phys. **37** (1962), 511.
- [70] D. Newman. *Theory of lanthanide crystal fields*, Adv.Phys. **20** (1971), 197–256.
- [71] G. H. Dieke. *Spectra and energy levels of rare earth ions in crystals*. New York : Interscience Publ., 1968.
- [72] H. Bethe. *Termaufspaltung in Kristallen*, Ann. Phys. **5** (1929), Band 3, Heft 2.
- [73] S. Huefner and H. Schmidt. *Spectroscopic Investigation of Some Rare Earth Ion Garnets*, Phys. kond. Mat. **4** (1965), 262–274.
- [74] A. Kiss. *Multipolar ordering in f-electron systems*. PhD thesis. Budapest University of Technology and Economics, 2004.
- [75] H. Lueken. *Magnetochemie*. Teubner Stuttgart, 1999.
- [76] D Newman and G. Stedman. *Interpretation of crystal-field parameters in rare-earth-substituted garnets*, J. Chem. Phys **51** (1969), 3013.
- [77] K. Stevens. *Matrix Elements and Operator Equivalents connected with the magnetic Properties of Rare Earth Ions*, Proc. Phys. Soc. **65** (1952), 209.
- [78] R. Skomski and D. J. Sellmeyer. *Anisotropy of rare-earth magnets*, J. Rare Earth **27** (2009), 675.
- [79] C. G rller-Walrand and K. Binnemans. *Handbook on the Physics and Chemistry of Rare Earths*. Elsevier Science B.V., 1998.

- [80] K. Rajnak and B. G. Wybourne. *Configuration Interaction in Crystal Field Theory*, The Journal of Chemical Physics **41.2** (1964), 565–569.
- [81] L. Ungur, W. Van den Heuvel, and L. F. Chibotaru. *Ab initio investigation of the non-collinear magnetic structure and the lowest magnetic excitations in dysprosium triangles*, New J. Chem. **33** (2009), 1224–1230.
- [82] M. N. Leuenberger and D. Loss. *Spin tunneling and phonon-assisted relaxation in Mn₁₂-acetate*, Phys. Rev. B **61** (2000), 1286–1302.
- [83] T Pohjola and H Schoeller. *Spin dynamics of Mn-12-acetate in the thermally activated tunneling regime: ac susceptibility and magnetization relaxation*, Phys. Rev. B **62** (2000), 15026–15041.
- [84] R. Kubo, M. Toda, and N. Hashitsume. *Statistical Physics 2*. 1991.
- [85] T. F. Jordan. *Linear operators for quantum mechanics*. John Wiley & Sons, New York, 1969.
- [86] K. N. Shrivastava. *Theory of Spin-Lattice Relaxation*, physica status solidi (b) **117.2** (1983), 437–458.
- [87] C.-Y. Huang. *Optical Phonons in Electron Spin Relaxation*, Phys. Rev. **154** (1967), 215–219.
- [88] J. Dreiser, K. S. Pedersen, A. Schnegg, K. Holldack, J. Nehrkorn, M. Sigrist, P. Tregenna-Piggott, H. Mutka, H. Weihe, V. S. Mironov, J. Bendix, and O. Waldmann. *Three-Axis Anisotropic Exchange Coupling in the Single-Molecule Magnets $NEt_4[MnIII_2(5-Brsalen)_2(MeOH)_2MIII(CN)_6]$ ($M=Ru, Os$)*, Chem. Eur. J. **19.11** (2013), 3693–3701.
- [89] I. Waller. *Über die Magnetisierung von paramagnetischen Kristallen in Wechselfeldern*. German, Zeitschrift für Physik **79.5-6** (1932), 370–388.
- [90] W. Heitler and E. Teller. *Time Effects in the Magnetic Cooling Method. I*, Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences **155.886** (1936), 629–639.
- [91] R. de L. Kronig. *On the mechanism of paramagnetic relaxation*, Physica **6.1** (1939), 33–43.
- [92] J. H. Van Vleck. *Paramagnetic Relaxation Times for Titanium and Chrome Alum*, Phys. Rev. **57** (1940), 426–447.
- [93] R. Orbach. *Spin-Lattice Relaxation in Rare-Earth Salts: Field Dependence of the Two-Phonon Process*, Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences **264** (1962), 485–495.
- [94] S. Geschwind, G. E. Devlin, R. L. Cohen, and S. R. Chinn. *Orbach Relaxation and Hyperfine Structure in the Excited $\bar{E}(^2E)$ State of Cr^{3+} in Al_2O_3* , Phys. Rev. **137** (1965), A1087–A1100.
- [95] E. A. Harris and K. S. Yngvesson. *Spin-lattice relaxation in some iridium salts I. Relaxation of the isolated ($IrCl_6$)²⁻ complex*, Journal of Physics C: Solid State Physics **1.4** (1968), 990.
- [96] N. Ishikawa, M. Sugita, and W. Wernsdorfer. *Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets: Bis(phthalocyaninato)terbium and*

- Bis(phthalocyaninato)dysprosium Anions*, Angewandte Chemie International Edition **44.19** (2005), 2931–2935.
- [97] H. Miyasaka, M. Julve, M. Yamashita, and R. Clerac. *Slow Dynamics of the Magnetization in One-Dimensional Coordination Polymers: Single-Chain Magnets*, Inorganic Chemistry **48.8** (2009), 3420–3437.
- [98] A. A. Mukhin, V. D. Travkin, A. K. Zvezdin, S. P. Lebedev, A. Caneschi, and D. Gatteschi. *Submillimeter spectroscopy of Mn₁₂ – Ac magnetic clusters*, Europhys. Lett. **44** (1998), 778.
- [99] A. Mukhin, B. Gorshunov, M. Dressel, C. Sangregorio, and D. Gatteschi. *Optical spectroscopy of crystal-field transitions in the molecular magnet Fe₈*, Phys. Rev. B **63** (2001), 214411.
- [100] G. Kozlov and A. Volkov. *Millimeter and Submillimeter Wave Spectroscopy*. Springer, Berlin, 1998.
- [101] A. Volkov, Y. Goncharov, G. Kozlov, S. Lebedev, and A. Prokhorov. *Dielectric measurements in the submillimeter wavelength region*, Infrared Phys. **25** (1985), 369–373.
- [102] S. Vongtragool. *Frequency-Domain Magnetic Resonance Spectroscopy on the Mn₁₂acetate Single-Molecule Magnet*. PhD thesis. University Stuttgart, 2004.
- [103] P. Griffiths and J. de Haseth. *Fourier Transform Infrared Spectrometry*. John Wiley & Sons, New York, Chichester, Brisbane, 1986.
- [104] C. Clauß. *Optische Untersuchung zur Ladungsordnung zwei-dimensionaler Leiter*. PhD thesis. University of Stuttgart, 2008.
- [105] J. van Slageren, S. Vongtragool, B. Gorshunov, A. Mukhin, and M. Dressel. *Frequency-domain magnetic resonance spectroscopy*, J. Magn. Magn. Mater. **272-276** (2004), E765–E767.
- [106] D. Bloor and J. R. Dean. *Spectroscopy of rare earth oxides systems. 1. Far infrared spectra of the rare earth sesquioxides, cerium dioxide and nonstoichiometric praseodymium and terbium oxides*, J. Phys. C **5** (1972), 1237.
- [107] B. J. Judd. *Optical Absorption Intensities of Rare-Earth Ions*, Phys. Rev. **127** (1962), 750–761.
- [108] T. D. Kang, E. Standard, K. H. Ahn, A. A. Sirenko, G. L. Carr, S. Park, Y. J. Choi, M. Ramazanoglu, V. Kiryukhin, and S.-W. Cheong. *Coupling between magnon and ligand-field excitations in magnetoelectric Tb₃Fe₅O₁₂ garnet*, Phys. Rev. B **82** (2010), 014414.
- [109] R. MacFarlane. *Perturbation Methods in the Calculation of Zeeman Interactions and Magnetic Dipole Line Strengths for d³-Trigonal-Crystal Spectra*, Phys. Rev. B **1** (1970), 3.
- [110] M. Eden. *Solid State NMR of Multiple-Spin Systems*. PhD thesis. Physical Chemistry Division, Stockholm University, 1999.
- [111] M. Eden and H. Levitt. *Computation of orientational averages in solid state NMR by gaussian spherical quadratures*, J. Magn. Reson. **132** (1998), 220–239.
- [112] G. A. Komandin, E. S. Zhukova, V. I. Torgashev, A. V. Boris, A. A. Boris, E. A. Motovilova, A. S. Prokhorov, L. S. Kadyrov, B. P. Gorshunov, and M. Dressel.

- Terahertz-infrared spectra of the rare-earth scandate DyScO₃ single crystal*, J. Appl. Phys. **114**.2 (2013), 024102.
- [113] J. Van Vleck. *The puzzle of Rare-Earth spectra in solids*, 1938.
- [114] P. D. Rogers, Y. J. Choi, E. C. Standard, T. D. Kang, K. H. Ahn, A. Dubroka, P. Marsik, C. Wang, C. Bernhard, S. Park, S.-W. Cheong, M. Kotlyanskii, and A. A. Sirenko. *Adjusted oscillator strength matching for hybrid magnetic and electric excitations in Dy₃Fe₅O₁₂ garnet*, Phys. Rev. B **83** (2011), 174407.
- [115] A. A. Sirenko, S. M. O'Malley, K. H. Ahn, S. Park, G. L. Carr, and S.-W. Cheong. *Infrared-active excitations related to Ho³⁺ ligand-field splitting at the commensurate-incommensurate magnetic phase transition in HoMn₂O₅*, Phys. Rev. B **78** (2008), 174405.
- [116] S. Haas, E. Heintze, S. Zapf, B. Gorshunov, M. Dressel, and L. Bogani. *Direct observation of the discrete energy spectrum of two lanthanide-based single-chain magnets by far-infrared spectroscopy*, Phys. Rev. B **89** (17 2014), 174409.
- [117] K. Bernot, L. Bogani, A. Caneschi, D. Gatteschi, and R. Sessoli. *A Family of Rare-Earth-Based Single Chain Magnets: Playing with Anisotropy*, J. Am. Chem. Soc. **128**.24 (2006), 7947–7956.
- [118] L. F. Chibotaru, L. Ungur, and A. Soncini. *The Origin of Nonmagnetic Kramers Doublets in the Ground State of Dysprosium Triangles: Evidence for a Toroidal Magnetic Moment*, Angew. Chem., Int. Ed. **47**.22 (2008), 4126–4129.
- [119] L. Bogani, R. Sessoli, M. G. Pini, A. Rettori, M. A. Novak, P. Rosa, M. Massi, M. E. Fedi, L. Giuntini, A. Caneschi, and D. Gatteschi. *Finite-size effects on the static properties of a single-chain magnet*, Phys. Rev. B **72** (6 2005), 064406.
- [120] M. Bottrill, L. Kwok, and N. J. Long. *Lanthanides in magnetic resonance imaging*, Chem. Soc. Rev. **35** (6 2006), 557–571.
- [121] B. Young and H. Stapleton. *Apparent lowering of energy levels as measured by Orbach relaxation rates*, Physics Letters **21**.5 (1966), 498–501.
- [122] S. K. Lyo. *Interference and Intermediate-Level-Width Corrections to the Orbach Relaxation Rate*, Phys. Rev. B **5** (3 1972), 795–802.
- [123] D. Bloor and J. Campbell. *FarInfrared Spectra and Zeeman Effect of RareEarth Double Nitrates*, Chem. Phys. **54** (1971), 3268.
- [124] T. D. Kang, E. C. Standard, P. D. Rogers, K. H. Ahn, A. A. Sirenko, A. Dubroka, C. Bernhard, S. Park, Y. J. Choi, and S. W. Cheong. *Far-infrared spectra of the magnetic exchange resonances and optical phonons and their connection to magnetic and dielectric properties of Dy₃Fe₅O₁₂ garnet*, Phys. Rev. B **86**.14 (2012).
- [125] D. Talbayev, A. D. LaForge, S. A. Trugman, N. Hur, A. J. Taylor, R. D. Averitt, and D. N. Basov. *Magnetic Exchange Interaction between Rare-Earth and Mn Ions in Multiferroic Hexagonal Manganites*, Phys. Rev. Lett. **101**.24 (2008).
- [126] E. S. Zhukova, V. I. Torgashev, B. P. Gorshunov, V. V. Lebedev, G. S. Shakurov, R. K. Kremer, E. V. Pestriakov, V. G. Thomas, D. A. Fursenko, A. S. Prokhorov, and M. Dressel. *Vibrational states of a water molecule in a nano-cavity of beryl crystal lattice*, The Journal of Chemical Physics **140**.22, 224317 (2014), –.

-
- [127] B. L. Yu, Y. Yang, F. Zeng, X. Xin, and R. R. Alfano. *Reorientation of the H₂O cage studied by terahertz time-domain spectroscopy*, Applied Physics Letters **86**.6, 061912 (2005).
- [128] G. E. Walrafen. *Raman Spectral Studies of Water Structure*, The Journal of Chemical Physics **40**.11 (1964), 3249–3256.
- [129] J. Hasted, S. Husain, F. Frescura, and J. Birch. *Far-infrared absorption in liquid water*, Chemical Physics Letters **118**.6 (1985), 622–625.
- [130] J. A. Padró and J. Martí. *An interpretation of the low-frequency spectrum of liquid water*, The Journal of Chemical Physics **118**.1 (2003), 452–453.
- [131] M. Walther, B. M. Fischer, and P. U. Jepsen. *Noncovalent intermolecular forces in polycrystalline and amorphous saccharides in the far infrared*, Chemical Physics (2003).
- [132] J.-P. Sutter, M. L. Kahn, S. Golhen, L. Ouahab, and O. Kahn. *Synthesis and Magnetic Behavior of Rare-Earth Complexes with N,O-Chelating Nitronyl Nitroxide Triazole Ligands: Example of a [GdIII Organic Radical]₂ Compound with an S=9/2 Ground State*, Chemistry - A European Journal **4**.4 (1998), 571–576.
- [133] M. L. Kahn, J.-P. Sutter, S. Golhen, P. Guionneau, L. Ouahab, O. Kahn, and D. Chasseau. *Systematic Investigation of the Nature of The Coupling between a Ln(III) Ion (Ln = Ce(III) to Dy(III)) and Its Aminoxyl Radical Ligands. Structural and Magnetic Characteristics of a Series of Ln(organic radical)₂ Compounds and the Related Ln(Nitrone)₂ Derivatives*, Journal of the American Chemical Society **122**.14 (2000), 3413–3421.
- [134] C. Benelli, A. Caneschi, D. Gatteschi, L. Pardi, P. Rey, D. P. Shum, and R. L. Carlin. *Magnetic properties of lanthanide complexes with nitronyl nitroxides*, Inorg. Chem. **28**.2 (1989), 272–275.
- [135] C. Benelli, A. Caneschi, D. Gatteschi, and R. Sessoli. *Magnetic properties and phase transitions in molecular based materials containing rare earth ions and organic radicals (invited)*, Journal of Applied Physics **73**.10 (1993), 5333–5337.
- [136] A. B. Kuzmenko. *Kramers-Kronig constrained variational analysis of optical spectra*, Review of Scientific Instruments **76** (2005).
- [137] M. L. Kahn, R. Ballou, P. Porcher, O. Kahn, and J.-P. Sutter. *Analytical Determination of the Ln-Aminoxyl Radical Exchange Interaction Taking into Account Both the Ligand-Field Effect and the Spin-Orbit Coupling of the Lanthanide Ion (Ln=DyIII and HoIII)*, Chemistry - A European Journal **8**.2 (2002), 525–531.

Acknowledgements

I would like to acknowledge here my gratitude for many people who contributed either directly or indirectly to this work.

First, I would like to thank my supervisor Prof. Martin Dressel who gave me the opportunity to perform my PhD work at the 1. Physikalische Instituts of the University of Stuttgart. Moreover, I thank him for the supervision of the project, for always having an open door, and the proofreading of the thesis.

I am sincerely grateful to Prof. Joris van Slageren not only because he kindly accepted to co-referee my thesis. Much more, I would like to thank him for fruitful discussions about my work, correction of my thesis, and his knowledge-sharing of the study of lanthanides by far-infrared spectroscopy.

Many thanks to Dr. Lapo Bogani without whom I would not have started to study the interesting compounds presented in this thesis. Moreover, I would like to thank him for the synthesis of most of the compounds.

Most of the work done in this Thesis was based on previous studies done by the group of Prof. Roberta Sessoli at the University of Florence. They also provided me with the LnDOTA samples. I would like to thank Roberta Sessoli for her scientific advice and many insightful discussions and suggestions for my project. I really enjoyed my stay in Florence and it was a great source of encouragement and new ideas for me.

Alexa Paretzki, I would like to thank for the synthesise of some of the compounds studied in this thesis and for discussions about chemistry-related issues.

My deepest gratitude goes to Dr. Conrad Clauß. He taught me nearly everything I know about lab work and problem solving. Many lab sessions would have failed without his help; he always offered help when needed, irrespective of the time of day and even if it was weekend or New Year's Eve. More important, I would like to thank you for always having an open ear for me, uncountable after work activities, ... in short for being a friend.

Special thanks to Dr. Sina Zapf for introducing me to the infrared lab and proofreading of my manuscripts. She encouraged me when things went wrong and shared my good and bad times in the lab and at the institute with me.

Thanks also to the whole infrared team; especially, to Rebecca Beyer, Tobias Peterseim, and Dr. Dan Wu who always offered a helping hand and broadened my horizon in

Acknowledgements

many discussions. I know that I could always ask them for advice and opinions on lab related issues.

I also would like to thank the molecular magnetism team, especially Eric Heintze, Dr. ShangDa Jiang, Christian Cervetti, Michael Slota, and Dr. Ralph Hübner.

Raphael Marx and Maria Dörfel for the lively exchange about lanthanide spectroscopy and their collaboration.

It was great pleasure for me to work with Prof. Boris Gorshunov who shared his knowledge about THz-spectroscopy with me. I would like to thank him for his kindness and great sense of humor.

Dr. Mark Scheffler, I would like to thank for the nice collaboration when I worked as a teaching assistant of his "Licht und Materie" lecture.

Thanks to Gabi Untereiner who worked next door to me in the beginning of my thesis. I enjoyed the time we spent together. She always was a help for technical and experimental issues.

Agnieszka Cienkowska-Schmidt, I would like to thank for her great efforts in handling the administrative issues.

In regards of solving theoretical issues, I thank Dr. Jörg Ummethum and Prof. Jürgen Schnack for fruitful discussions.

I also want to thank the members of the low temperature department for their kindness, every time I was there to pick up a can of Helium.

Thanks to all other past and current members of the 1. Physikalische Institut for the nice working atmosphere. Especially, I would like to thank: Eva Rose, Dr. Bruno Gompf, Uwe Pracht, Julia Ostertag, Dr. Tomislav Ivek, Christoph Schlegel, Dr. Helga Kumric, Stefano de Zuani, and David Neubauer.

Finally, I would like to thank my parents, my grandfather, and my brother for their support and constant encouragement over the years. Jens, thank you for your patience and support, and for the proofreading of the thesis.

Declaration of originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references.