Solid State Communications, Vol. 67, No. 10, pp. 981-984, 1988.
Printed in Great Britain.
0038-1098/88 $3.00 + .00
Pergamon Press plc

STATIC AND ESR SUSCEPTIBILITIES OF THE AMBIENT PRESSURE SUPERCONDUCTORS β- AND α_t-$(BEDT\text{-}TTF)_2I_3$ AND $(BEDT\text{-}TTF)_2Cu(SCN)_2$

S. Klotz and J.S. Schilling

Sektion Physik, University of Munich, Schellingstr. 4, D–8000 Munich 40, W. Germany
and
Walther–Meissner–Institut für Tieftemperaturforschung, D–8046 Garching, W. Germany

S. Gärtner and D. Schweitzer

Abteilung für Molekulare Physik, Max–Planck–Institut für Medizinische Forschung,
D–6900 Heidelberg, W. Germany

(Received July 10, 1988 by M. Cardona)

Whereas the static spin–susceptibility $\chi_s(T)$ of β- and α_t-$(BEDT\text{-}TTF)_2I_3$ at 5.7 tesla increases in a slow monotonic manner with temperature, $\chi_s(T)$ for the organic superconductor $(BEDT\text{-}TTF)_2Cu(SCN)_2$ displays a markedly structured temperature dependence. This gives evidence for two or more phase transitions in the metallic phase at temperatures near 100 K and 50 K, in addition to the onset of superconductivity at 5.7 tesla below ~ 8 K. Good agreement is found between the absolute magnitudes of static and ESR susceptibility results, thus confirming that orbital susceptibility contributions are of negligible importance here. Cooling in low magnetic fields reveals that superconductivity in $(BEDT\text{-}TTF)_2Cu(SCN)_2$ sets in at a temperature near 8.5 K, with a 7.6% Meissner effect in 14 G field.

1. Introduction

The discovery[1] in 1981 of superconductivity near 1 K in $(TMTSF)_2PF_6$ under pressure has been followed by the synthesis of approximately fifty further organic superconductors, a number of which are superconducting at ambient pressure. The highest values of the superconducting transition temperature T_c have involved radical salts obtained from the organic donor BEDT–TTF (bisethylenedithiolotetrathiafulvalene). Subjecting the 1 K – superconductor β-(BEDT–TTF)$_2$I$_3$ to a particular pressure/temperature cycle[2] results in a compound with a slightly altered structure which is superconducting at 8 K; unfortunately, this altered structure is only stable for temperatures below 125 K. The discovery[3, 4] and confirmation of ambient–pressure superconductivity at 8 K in α_t-(BEDT–TTF)$_2$I$_3$ is thus of considerable importance because the α_t–phase remains stable for all temperatures below 350 K. The α_t–phase is obtained directly from nonsuperconducting α–(BEDT–TTF)$_2$I$_3$ by annealing at 70°C for approximately four days. The crystal structures of the β- and α_t–phases are quite similar, although the precise relative atomic positions in the α_t–phase are not yet established. The close similarity of the β- and α_t–structures is also supported by ^{13}C–NMR, ESR–linewidth, and Raman measurements.[4]

The existence of a new ambient pressure BEDT–TTF superconductor with the counter anion $Cu(SCN)_2$ has recently been reported by Urayama et al.[5] and confirmed by Gärtner et al.[6] The resistive midpoint of the superconducting transition occurs at approximately 10.4 K, the highest T_c–value reported to date for an organic superconductor. Although x-ray diffraction results[7] reveal that no change in phase occurs in this compound between 300 K and 104 K, recent thermopower studies[6] point to possible phase transitions at temperatures near 90 K and 50 K. Whereas the electrical resistivity passes through a clear maximum at ~90 K[5, 6] and the static magnetic susceptibility data χ_s appear to falloff somewhat below 90 K,[5] the ESR susceptibility data are not sufficiently accurate to resolve any structure in $\chi_s(T)$.[6] Some questions still remain unclarified concerning the precise atomic coordinates in this compound at low temperatures.

Measurements of the Pauli spin–susceptibility χ_s provide information on the density of electron states at the Fermi energy $N(E_f)$ as well as on the importance of electron–electron interactions. Whereas the temperature and pressure dependences of the spin–susceptibility of the Bechgaard salts[8, 9] (eg. $(TMTSF)_2PF_6$), TTF–TCNQ,[10, 11] and other organic metals[11] are often highly anomalous, χ_s for α– or β-(BEDT–TTF)$_2$I$_3$ is found to change relatively little with temperature or pressure.[9, 12] In the present paper we present precision measurements of $\chi_s(T)$ for α_t-(BEDT–TTF)$_2$I$_3$ and (BEDT–TTF)$_2$Cu(SCN)$_2$. The magnetic susceptibility was measured using both static Faraday and standard ESR techniques. Experimental preparation and measurement techniques have been given in previous papers.[4, 6, 12]

2. Results on α_t-(BEDT–TTF)$_2$I$_3$

The static spin–susceptibility $\chi_s(T)$ at 5.7 tesla of a 96 mg sample of randomly oriented crystals of α_t–(BEDT–TTF)$_2$I$_3$ is plotted in Fig. 1 as a function of temperature. $\chi(T)$ for the β–phase of the same compound is also shown. Since in the virgin α–phase $\chi_s(T)$ drops sharply due to the metal–insulator transition as

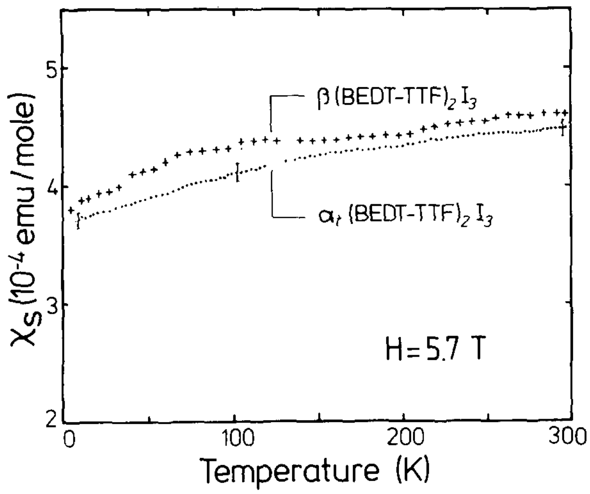

Fig. 1 Static spin-susceptibility of β- and α_t-(BEDT-TTF)$_2$I$_3$ as a function of temperature in a magnetic field of 5.7 tesla. Data for β-phase are taken from Ref. 12. Vertical lines give error in χ_s for the α_t-phase assuming the temperature independent value $\chi_{core} = -5.2\text{x}10^{-4}$ emu/mole. Similar error bars apply for the β-phase.

the temperature passes through T $\simeq$ 135 K,[12] the absence of any observable anomaly at 135 K for the α_t-phase allows the estimate that this phase is free of any residual α-phase component to better than 0.2%. The complete absence of a low-temperature Curie dependence bears witness to the magnetic purity of the samples studied. As discussed in a previous paper,[12] the appropriate value of the temperature independent core diamagnetism is $\chi_{core} \simeq -5.2\text{x}10^{-4}$ emu/mole (1 mole = 1149 g) which should be essentially the same for α-, α_t-, and β-phases. The spin-susceptibility is then given by $\chi_s(T) = \chi(T) - \chi_{core}$, where χ is the total measured susceptibility. In Fig. 1 $\chi_s(T)$ for the α_t-phase is seen to differ little from that of the β-phase, underscoring the similarity of the two phases. With decreasing temperature $\chi_s(T)$ falls for both phases at a slow monotonic rate which increases distinctly for temperatures below ~100 K for the β-phase and ~150 K for the α_t-phase. At least part of this temperature dependence can be attributed to thermal contraction effects, as emphasized by Klotz et al.[10] for the β-phase. The more severe decrease in $\chi_s(T)$ below 100 K for the β-phase may be due to the distortion of the linear I_3-anion chains below 125 K in this $T_c \simeq$ 1 K superconductor. At room temperature, $\chi_s \simeq +(6.8 \pm 0.07)\text{x}10^{-4}$, $+(4.6 \pm 0.1)\text{x}10^{-4}$, and $+(4.5 \pm 0.07)\text{x}10^{-4}$ emu/mole for the α-, β-, and α_t-phases, respectively (since χ_{core} is the same for all three phases, the above error limits do not include the uncertainty in χ_{core}); using the simple formula $\chi_s = 2\mu_b N(E_f)$, we derive, respectively, the values $N(E_f)$ = 10.5, 7.1, and 6.9 states/(eV-spin-f.u.).

The relative temperature dependence of the spin-susceptibility χ_s for crystals of α_t-(BEDT-TTF)$_2$I$_3$ was previously investigated by standard ESR methods in the temperature range from 5 - 300 K.[4] We have recently determined the absolute value of χ_s for this compound in the following way: first, we measured the ESR signal of a single crystal of α-(BEDT-TTF)$_2$I$_3$ and calculated $\chi_s(\alpha)$ in the usual way from the linewidth and the intensity of the signal in arbitrary units.[12] The same single crystal was then annealed for several days at 70°C in order to obtain the α_t-phase.[4] After this procedure the ESR signal of this α_t-(BEDT-TTF)$_2$I$_3$ crystal was measured and $\chi(\alpha_t)$ was calculated again. Fig. 2 shows the ESR signal of the conduction electrons at 300 K for both phases. For the α-crystal the sensitivity of the ESR receiver was eight times higher than for the transformed α_t-crystal. The ratio of the two susceptibilities obtained was $\chi_s(\alpha_t)/\chi_s(\alpha) = 0.686 \pm 0.02$ at room temperature. Taking the value of $\chi_s(\alpha) = +6.8\text{x}10^{-4}$ emu/mole from Ref. 12 we thus obtain $\chi_s(\alpha_t) = +(4.6 \pm 0.14)\text{x}10^{-4}$ emu/mole, a value which agrees well with the above value from the present static susceptibility measurement.

3. Results for (BEDT-TTF)$_2$Cu(SCN)$_2$

In Fig. 3 the spin-susceptibility $\chi_s(T)$ of a 74 mg sample of the new organic superconductor (BEDT-TTF)$_2$Cu(SCN)$_2$ is compared to that of the α_t-phase (the value of the core diamagnetism for this compound

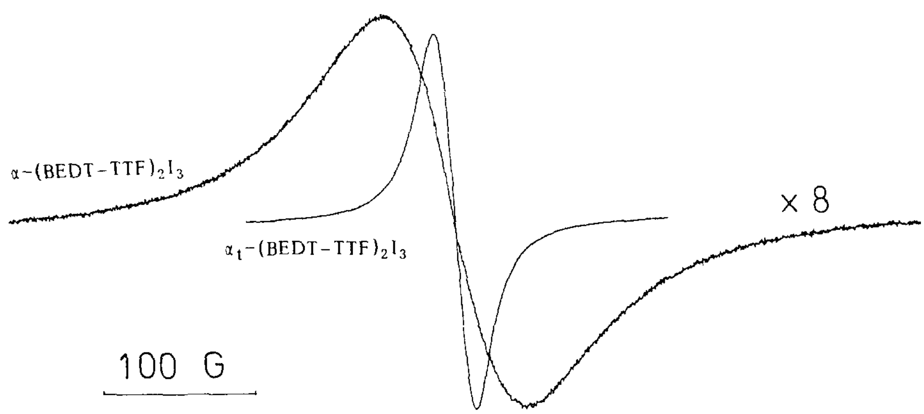

Fig. 2 ESR signal of a single crystal of α-(BEDT-TTF)$_2$I$_3$ before and after the heat treatment which transforms it into the a_t-phase. The ESR curve for the α-phase has been magnified eightfold; it is seen to be broader than for the α_t-phase which has a width similar to that for the β-phase(Ref. 4,12).

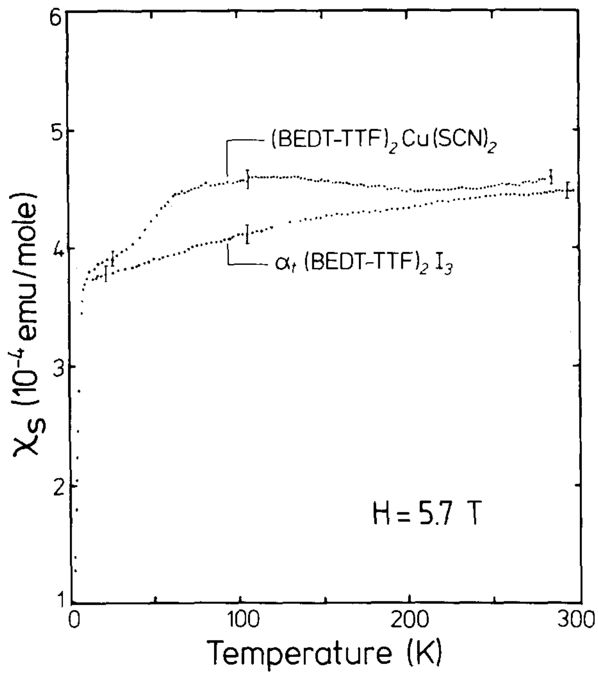

Fig. 3 Static spin-susceptibility of (BEDT–TTF)$_2$Cu(SCN)$_2$ and α_t–(BEDT–TTF)$_2$I$_3$ as a function of temperature in a magnetic field of 5.7 tesla. The nonmonotonic temperature dependence for the former compound indicates the occurrence of phase transitions; the drop in $\chi_s(T)$ below 10 K arises from the superconducting transition (Meissner effect). Vertical lines give error estimate of χ_s assuming the temperature independent value $\chi_{core} = -4.74\text{x}10^{-4}$ emu/mole.

is given[5] by $\chi_{core} = -4.74\text{x}10^{-4}$ emu/mole). The temperature dependence of $\chi_s(T)$ for the former compound reveals prominant structure which was not clearly resolved in previous work.[5, 6] The susceptibility passes through a shallow minimum at 220 K and a broad maximum at 100 K followed by a more pronounced falloff below 60 K (the sharp drop for temperatures below 10 K arises from the superconducting transition (Meissner effect)). The markedly structured temperature dependence of χ_s for (BEDT–TTF)$_2$Cu(SCN)$_2$ thus indicates the possibility of two or more phase transitions near 100 K and 50 K, thus supporting the thermopower results[6] discussed above. Structural studies to liquid helium temperatures would be useful to help clarify the nature of these transitions. It is interesting to note that the resistivity[5, 6] of this compound also passes through minimal and maximal values at roughly the same temperatures as $\chi_s(T)$. This parallelism could perhaps arise from the anomalous increase in the separation of the highly conducting planes in this compound upon cooling which would lead to increased electron localization in the bc–plane, i.e. a decrease in the three dimensionality of the system. Increased localization would be expected to lead to an increase in both the bulk resistivity and the susceptibility due to electron–electron correlation effects. As was pointed out by Urayama et al.,[5] the fact that the spin-susceptibility is only weakly temperature dependent would appear to rule out the possibility that the negative resistivity slope between 300 K and 100 K is due to a decrease in carrier charge density as a gap opens up; such a carrier charge decrease would lead to a decrease in χ_s as found for α–(BEDT–TTF)$_2$I$_3$.[12] The value of the spin-susceptibility of (BEDT–TTF)$_2$Cu(SCN)$_2$ at 280 K (χ_s(280 K) = +(4.6 ± 0.08)x10^{-4} emu/mole) allows the estimate N(E$_f$) = 7.1 states/(eV–spin–f.u.), in good agreement with the work of Nozawa et al.[13] who argue that this value appears to be strongly enhanced.

We have recently determined directly in an ESR experiment that χ_s(300 K) = +(4.4 ± 0.4)x10^{-4} emu/mole for (BEDT–TTF)$_2$Cu(SCN)$_2$. This value compares well with that from the above static Faraday measurements. The relatively large error in the ESR value originates from inaccuracies in weighing the tiny crystal (530 ± 50 μg). The good agreement between the magnitude of the spin-susceptibility as derived from both static susceptibility and ESR work indicates that orbital contributions to the static susceptibility are relatively unimportant.

The low-field static susceptibility of (BEDT–TTF)$_2$Cu(SCN)$_2$ was measured upon cooling (Meissner effect), as shown in Fig. 4. No attempt was made to correct the measured data for demagnetization factor effects as the sample consisted of 74 mg of finely subdivided crystals with random orientation. From these data and the known volume per mole (508.4 cm^3/mole), the percentage of the full Meissner effect ($\chi = -1/4\pi$ emu/cm^3) at low temperatures (2 K) is estimated to be 7.6% at 14 G, 3.9% at 40 G, 2.6% at 60 G, 2.0% at 80 G, 1.5% at 106 G, and 0.00074% at 5.7 tesla (from Fig. 3). In an ac susceptibility measurement at 0.3 G an effect of at least 70% was observed.[6] At low fields the onset of superconductivity is seen to occur at temperatures near 8.5 K. Urayama et al.[5] find a similar onset temperature with ~5% Meissner signal for 100 G applied field. In contrast to the results of Nozawa et al.,[13] we observe no increase in the low-field susceptibility curves

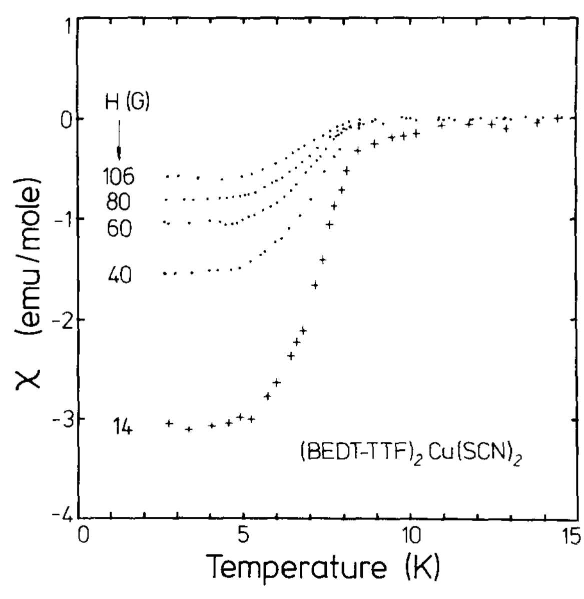

Fig. 4 Measured static magnetic susceptibility of (BEDT–TTF)$_2$Cu(SCN)$_2$ at low magnetic fields as a function of temperature upon cooling (Meissner curves). The size of the Meissner signal is seen to decrease rapidly at higher fields.

as the sample is cooled below 6 K, underscoring the relative freedom of our samples from paramagnetic impurities. The fact that a clear transition toward diamagnetism is still observed near 8 K for an applied field of 5.7 tesla (Fig. 3) speaks for an unusually high value of H_{c2}. Oshima et al.[14] have estimated that for $H \| c$, $H_{c2}(7\ K) \simeq 10$ tesla and $\partial H_{c2}/\partial T \simeq -4$ tesla/K.

Acknowledgements - The authors would like to thank M. Weger for useful discussions. The generous support of this research by the Deutsche Forschungsgemeinschaft is acknowledged. Two of the authors (S.K. and J.S.S.) are grateful to members of the Walther-Meissner-Institute in Garching for discussions and cooperation in the course of this research.

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