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Magnetic susceptibility of α and β phases of di[bis(ethylenediothiolo)tetrathiafulvalene] tri-iodide [(BEDT-TTF)$_2$I$_3$] under pressure

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We report static magnetic susceptibility data, $\chi(T)$, for the α and β phases of the organic conductor di[bis(ethylenediothiolo)tetrathiafulvalene] tri-iodide [(BEDT-TTF)$_2$I$_3$] both at ambient pressure and under applied pressures of up to 10 kbar. Ambient pressure ESR data for both phases below 300 K are also presented. The temperature dependence of the spin susceptibility $\chi_s^\beta(T)$ for the superconductor β-(BEDT-TTF)$_2$I$_3$ is unusually small for organic conductors; the pressure derivative $\partial \ln\chi_s^\beta/\partial P$ is found to be only moderate in magnitude (-3.3% per kbar) and independent of temperature below 300 K. For the α phase, $\partial\ln\chi_s^\alpha/\partial P \simeq -2.0\%$/kbar at ambient temperature.

I. INTRODUCTION

During the last six years, two families of organic crystals have been found to exhibit metallic conductivity down to liquid-helium temperatures and, depending on their chemical composition and the applied pressure, even to become superconducting. These families are the isostructural Bechgaard salts[1] (TMTSF)$_2X$, where TMTSF is tetramethyltetraselenafulvalene and X is a monovalent anion, and the (BEDT-TTF)$_nX_m$ salts where BEDT-TTF is bis(ethylenedithiolo)tetrathiafulvalene, X is a monovalent anion or iodine complex, and n and m are integers. The latter salts have a variety of crystal structures and stoichiometries[2] even for the same electron acceptor X. Studies on organic compounds under hydrostatic pressure have proved to be invaluable not only in providing the initial evidence for superconductivity,[3-6] but also because there are other low-temperature states associated with spin-density waves (SDW's), charge-density waves (CDW's), anion ordering, etc., so that the phase diagrams are unexpectedly rich.[1,7] Although there have been a number of investigations of transport properties under pressure,[1] less is known about the effect of pressure on the magnetic properties, for example, on the spin susceptibility χ_s. One motivation for such studies is that in organic metals the resistivity,[1] spin susceptibility,[8-10] NMR relaxation rates,[11] and superconducting transition temperature T_c (Refs. 5, 6, and 12) appear to depend sensitively on pressure; another motivation is that at room temperature the spin susceptibility χ_s of most organic conductors is enhanced by a factor of 2–5 over the Pauli paramagnetism expected for noninteracting electrons using a reasonable value for the tight-binding bandwidth $4t_{\parallel}$, such as that corresponding to band-structure calculations or derived from optical measurements of the plasma frequency.[13] In addition, χ_s is usually strongly temperature dependent in organic metals, typically falling by a factor of 2 from 300 to 100 K.[1,14] One possible explanation of these features is that χ_s is enhanced by electron-electron interactions. Because of the quasi-one-dimensional electronic structure, these give rise to $\log_{10}T$ terms in the susceptibility-enhancement factor,[15] which would be responsible for the unusual temperature dependence. In a completely different approach, the behavior of χ_s has been attributed[16] to a type of polaron effect, namely, band narrowing arising from quadratic electron-phonon coupling. In this case χ_s is enhanced if the mean free path along the chains is of the order of one lattice constant, and there should then be a close relationship between the pressure or temperature dependence of χ_s and that of the electrical conductivity σ. For organic conductors the increase of σ with pressure is large (typically $\partial\ln\sigma/\partial P \simeq +20$–$30\%$/kbar at room temperature[1]). For one of the materials studied here, β-(BEDT-TTF)$_2$I$_3$, which, incidentally, has by far the highest T_c value found until now (8 K at 1.5 kbar),[5,6] one finds at room temperature the enormous pressure derivative $\partial\ln\sigma/\partial P \simeq +70\%$/kbar.[5,6,17] Since the compressibility of this substance takes on the value $K \simeq \partial\ln V/\partial P \simeq -1.03\%$/kbar at room temperature,[18] this gives $\partial\ln\sigma/\partial\ln V \simeq K^{-1}\partial\ln\sigma/\partial P \simeq -68$. This value should be compared with that for a normal metal, such as Pb, where $\partial\ln\sigma/\partial\ln V \simeq -6$ at 300 K.[19]

In an attempt to test some of these ideas experimentally, we have started to measure the magnetic susceptibility of a series of TMTSF and BEDT-TTF compounds under pressure using a Faraday balance and a miniature binary Cu-Be pressure clamp, extending previous work on TMTSF-DMTCNQ,[20] where DMTCNQ is dimethyltetracyanoquinodimethane, and (perylene)$_2$(AsF$_6$)$_{0.75}$(PF$_6$)$_{0.35}$-0.85CH$_2$Cl$_2$.[10] Here we report studies of the static magnetic susceptibility and electron-spin resonance[21] at ambient pressure and the static susceptibility under high pressure for two crystallographic modifications of the (BEDT-TTF)$_2$I$_3$ salts: (i) the α phase, where the metal-semiconductor transition[22] at

135 K is suppressed by pressure at the rate of -11 K/kbar,[23,24] and (ii) the superconducting β phase, which is currently of great interest because the application of only 1.5 kbar raises T_c from 1.2 to 8 K;[5,6] after pressure is released there is still evidence for a superconducting transition at 8 K.[5,6,17] Although we have not yet searched for superconductivity in the β phase by magnetic-susceptibility measurements under pressure, resistivity measurements made by Creuzet *et al.*,[17] on crystals prepared in Heidelberg at the same time as those for the present studies do give evidence for high-T_c superconductivity under pressure. In this connection we would like to mention that resistivity studies[25] at ambient pressure on one of the crystals which had been previously exposed to 10 kbar pressure during the course of the present $\chi(T,P)$ measurements showed a sharp drop starting at 11 K; we tentatively ascribe this drop to the onset of superconductivity, but probably only in small regions of the sample.

The crystal structure of the α and β phases of (BEDT-TTF)$_2$I$_3$ has been studied by three independent groups.[26–29] In the α phase there are two parallel BEDT-TTF stacks whose molecules are inclined at approximately 70° to each other. In the β phase there is only one type of stack and the intrastack overlap is stronger. For both α and β phases there are several short S-S contacts between the stacks, so electronically they are much more two dimensional than most organic metals.[26–29] The metal-semiconductor transition at 135 K in the α phase is rapidly suppressed by pressure, and above 12 kbar the material may be semimetallic at low T.[23] For the β phase there is evidence in x-ray studies for a structural phase transition starting at 200 K;[30] however, the thermoelectric power exhibits an anomaly at 120 K.[31]

ESR studies[31,32] on the β phase show that, within the experimental accuracy of $\sim 10\%$, χ_s is temperature independent from 5 to 50 K,[32] or 5–300 K,[31] with a value of $+8.5\times10^{-7}$ emu/cm^3, which corresponds to $+4.36\times10^{-4}$ emu/mole of (BEDT-TTF)$_2$I$_3$. The room-temperature ESR linewidth is 20–25 G which is a factor of 3–4 narrower than that of the α phase.[31]

II. EXPERIMENT

The samples of (BEDT-TTF)$_2$I$_3$ were prepared by electrocrystallization as described previously.[26] The small canted rhombohedral crystals of the β phase were removed by hand under a microscope from the majority α-phase platelets. In these experiments the samples were not pressed into pellets, but measurements were carried out on a large number of crystalline samples. The ambient pressure measurements were carried out using a pure Cu crucible with 5 g mass and the total sample mass was approximately 130 and 50 mg for the α and β phases, respectively. In the high-pressure clamp the sample mass was normally near 45 mg.

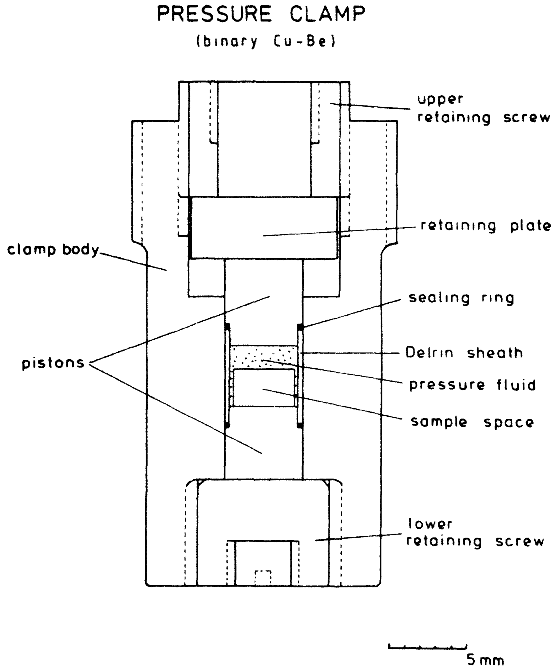

FIG. 1. Binary Cu-Be pressure clamp with 46 g mass suitable for high-pressure static magnetic susceptibility studies to 10 kbar on very weakly magnetic substances.

Measurements of the static magnetic susceptibility at ambient and high pressure were carried out using a standard Faraday balance system employing a superconducting magnet with main (5.7 T) and gradient (0.064 T/cm) coils and a Cahn R-100 microbalance. The present pressure clamp shown in Fig. 1 is of standard design[33] and is a scaled-down 46-g version of the one used in previous studies by Moritz *et al.*[10] Other changes made are that the binary Cu-Be alloy used contained even fewer magnetic impurities (the Curie term at low temperatures corresponded to less than 0.3 ppm of $S=\frac{5}{2}$ free spins), binary Cu-Be pistons of 5 mm diameter were employed instead of alumina, and magnetic compensation[33] was provided by molybdenum, which is superconducting below $T_c=0.92$ K, rather than by tantalum, where $T_c=4.48$ K. Due to the small magnitude of the change in the magnetic susceptibility of the organic samples under pressure, the pressure dependences of the susceptibility of both the Delrin pressure cell and the pressure fluid represent potentially important corrections. To minimize these corrections, the pressure cell shown in Fig. 1 was designed to reduce as much as possible the volume of the highly compressible cell parts (pressure fluid and Delrin sheath).[34] The pressure cell consists of a 0.4-mm-thick sheath of Delrin sealed at either end by a ring of unhardened binary Cu-Be on a hardened binary Cu-Be piston. A less volatile pressure fluid than the standard n-pentane-isopentane, namely, a 50 vol %–50 vol % mixture of n-hexane–n-heptane was used. Nominal hydrostatic pressures of up to 11 kbar were generated at room temperature; in a separate experiment, the pressure calibration was checked using a Manganin gauge. The pressure remaining at low temperature was determined by measuring the superconducting transition temperature of Pb.[19] The pressure in a piston-cylinder cell as used here decreases upon cooling due to the large thermal contraction of the pressure fluid. This pressure decrease in the present experiments is approximately 4—5 kbar, a relatively large value. That most of this pressure decrease occurs between 300 and 50 K is indicated by previous electrical resistivity studies[19] in a piston-cylinder cell. As we will discuss later, the apparent temperature dependence of the diamagnetism of the pressure fluid between 300 and 50 K is, in fact, due to pressure losses.

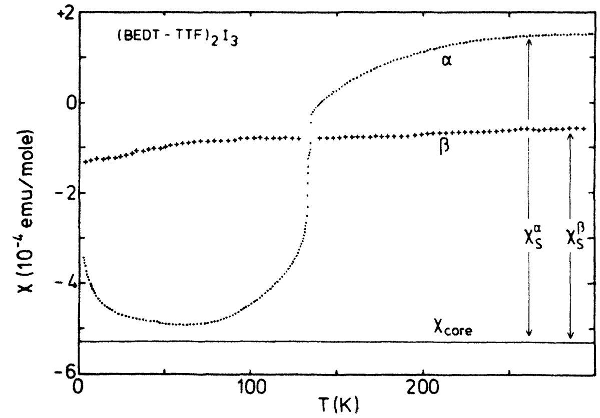

FIG. 2. Data points give total measured static magnetic susceptibility of α- and β-(BEDT-TTF)$_2$I$_3$ versus temperature in magnetic field H of 5.7 T. For the α phase H is parallel to the c^* direction (see text); β-phase crystallites are randomly oriented. χ_{core} gives diamagnetic contribution from core electrons (see text). Paramagnetic spin susceptibility χ_s is given by difference $\chi - \chi_{\text{core}}$.

The magnetic susceptibility was normally measured in a field of 5.7 T; however, the linearity of the magnetization-versus-field curves at room temperature was always checked after changing the pressure to ensure that no ferromagnetic contamination had been introduced. In a separate experiment the magnitudes of the diamagnetism of the heptane-hexane fluid at room temperature (-0.89×10^{-6} emu/g) and Delrin (-3.0×10^{-7} emu/g) were found to decrease under pressure at the rate of $-(0.78\pm0.1)$%/kbar and less than 0.2%/kbar, respectively.

At certain fixed temperatures the force on the sample-clamp assembly arising from the inhomogeneous magnetic field could be measured reproducibly to ±10 μg, even if the clamp had been removed from the sample tube between measurements. This corresponds to a susceptibility error of $\pm0.05\times10^{-4}$ emu/mole, or only approximately 1% of the spin susceptibility of a typical organic conductor with 50 mg mass. However, as discussed in the following section, the pressure dependence of the spin paramagnetism $\chi_s(T)$ of the organic sample is not known to this accuracy because of uncertainties in the changes in the core diamagnetism of the sample, and, at low temperatures, due to errors in correcting the measured data for the magnetism of the pressure clamp.

ESR experiments were performed in a rectangular microwave cavity at 9.3 GHz in the temperature range from 300 to 4.2 K. For the α phase thin crystalline platelets about 2—3mm across and 50—100 μm thick were used; the ESR line shape was purely Lorentzian. The β-phase crystals investigated had the shape of canted rhombohedrons with sidelengths of 0.1—0.2 mm; the ESR line shape was Dysonian[35] at all temperatures.

III. RESULTS AND DISCUSSION

A. Static magnetic susceptibility at ambient pressure

The ambient pressure static susceptibility data for α- and β-(BEDT-TTF)$_2$I$_3$ are shown in Fig. 2. The measured susceptibility χ is the sum of a diamagnetic contribution χ_{core} from the core electrons and a paramagnetic contribution χ_s from the conduction electrons, the Pauli spin susceptibility. The value of the core diamagnetism $\chi_{\text{core}}=-5.2\times10^{-4}$ emu/mole was determined by measuring the susceptibility of insulating BEDT-TTF, χ_{ET}, at room temperature and adding to it the Pascal constants[36] for the I$_2$ molecule plus the I$^-$ ion, i.e.,

$$\begin{aligned}\chi_{\text{core}}&=2\chi_{\text{ET}}+\chi_{\text{I}_2}+\chi_{\text{I}^-}\\&=2(-1.96\times10^{-4})+(-0.89\times10^{-4})\\&\quad+(-0.51\times10^{-4})\ \text{emu/mole}\end{aligned}$$

equals -5.2×10^{-4} emu/mole of (BEDT-TTF)$_2$I$_3$. The measured value of $\chi_{\text{ET}}=-1.96\times10^{-4}$ emu/mole is in good agreement both with that (-1.88×10^{-4} emu/mole) calculated from the Pascal's constants[36] for the BEDT-TTF molecule as well as with the results of parallel experiments by Gross.[37] In our experiments the orientation of the BEDT-TTF crystals was essentially random with respect to the direction of the applied magnetic field. Below room temperature χ_{ET} shows a small temperature dependence which was analyzed as the room-temperature value plus a small Curie tail; the value of the Curie constant corresponds to an $S=\frac{1}{2}$ defect on one BEDT-TTF molecule out of every 500, or a defect concentration of 0.2%. The Curie tail seen in Fig. 2 for the α phase corresponds to a 0.27% defect concentration. No evidence for a Curie tail is seen in the β phase, underscoring the high purity of the samples used.

The spin susceptibility of both α- and β-(BEDT-TTF)$_2$I$_3$ is given by the difference $\chi_s=\chi-\chi_{\text{core}}$, where χ is the measured susceptibility. At room temperature the absolute value of the spin susceptibility of the α phase is $\chi_s^\alpha=(+6.8\pm0.3)\times10^{-4}$ emu/mole of (BEDT-TTF)$_2$I$_3$. As seen in Fig. 2, χ_s is only weakly temperature dependent in the metallic region for both phases; this is very unusual in organic conductors and may perhaps be due to the strong bonding between chains.

B. Spin susceptibility for the α phase

The measured susceptibility at room temperature for the α phase with the magnetic field (5.7 T) oriented parallel to the c^* direction [perpendicular to the (a,b) plane] takes on the value $\chi^\alpha=+1.45\times10^{-4}$ emu/mole, as seen in Fig. 2. Orienting the magnetic field perpendicular to the c^* direction shifts the χ curve in Fig. 2 downward by the constant amount 0.42×10^{-4} emu/mole over the entire temperature range 3—300 K; thus for H$\perp$c*, χ^{α}(300 K)$=+1.03\times10^{-4}$ emu/mole. This anisotropy in χ^{α} with magnetic field direction was first observed by Gross;[37] his results are in good agreement with ours. Within our experimental accuracy of about 2% of χ_s, the spin susceptibility of the α phase is thus isotropic; ESR g-factor studies on β-(BEDT-TTF)$_2$I$_3$ indicate that the anisotropy in χ_s is only about 0.3%.[38] The anisotropy in the room-temperature value of the measured susceptibility χ^{α} reported above would thus appear to originate from the core-diamagnetism contribution χ_{core}; the magnitude of this anisotropy parallel and perpendicular to c^* is 0.42×10^{-4} emu/mole, which is 8% of the value of χ_{core}.

The gradual falloff in χ_s with temperatue below 200 K could possibly be a precursor of the metal-insulator transition at 135 K. This possibility should, however, be checked by structural studies, especially since, as discussed below, this fall-off does not appear to change with pressure. At temperatures below the phase transition, the α phase becomes completely diamagnetic ($\chi_s^{\alpha}\rightarrow0$), showing that, unlike some of the Bechgaard salts,[1] the transition is not to a SDW (spin-density-wave) ground state. This conclusion is consistent with the fact that over the entire temperature range the spin susceptibility χ_s has an identical temperature dependence whether the magnetic field is oriented parallel or perpendicular to c^*.

The measured susceptibility for the α phase in the temperature region near the metal-insulator transition at 135 K is shown in Fig. 3 on an expanded temperature scale. In this figure the phase transition is clearly seen to exhibit a steplike structure which may correspond either to two separate phase transitions or to two crystallographic modifications with slightly different transition temperatures T_p. As there are two types of BEDT-TTF stacks in the α phase, the former hypothesis is attractive. The transition was studied upon cooling and warming; within 2 K no temperature hysteresis was observed in the susceptibility.

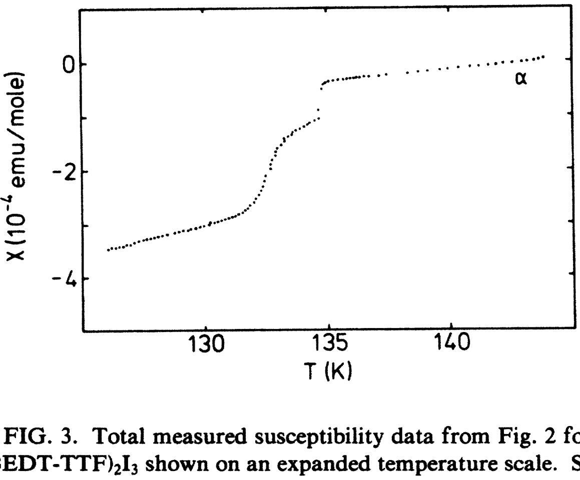

FIG. 3. Total measured susceptibility data from Fig. 2 for α-(BEDT-TTF)$_2$I$_3$ shown on an expanded temperature scale. Steplike structure at the metal-insulator transition at 135 K is clearly visible.

ESR measurements on the α phase are in good agreement with the above static susceptibility results. Figure 4 shows the ESR peak-to-peak linewidth (LW) at 9.3 GHz and the derived spin susceptibility χ_s^{α} versus temperature for an α-(BEDT-TTF)$_2$I$_3$ crystal, measured with the static magnetic field H both parallel and perpendicular to the c^* direction. The spin susceptibility for H$\|$c* is nearly constant above 200 K, while between 135 and 200 K it decreases by about 45%. At 135 K, χ_s^{α} drops abruptly by about a factor of 3—4 before decreasing monotonically at lower temperatures.

C. Spin susceptibility for the β phase

As seen in Fig. 2, the absolute value of the spin susceptibility of the β phase at room temperature is $\chi_s^{\beta}=(+4.6\pm0.3)\times10^{-4}$ emu/mole; the main source of uncertainty lies in the estimate of the value of χ_{core}. This value of χ_s^{β} is a factor of 1.5 smaller than for the α phase, which is probably due to the lower density of states arising from the improved molecular overlap in the β phase.[26–29] We have no explanation for the slight fall in

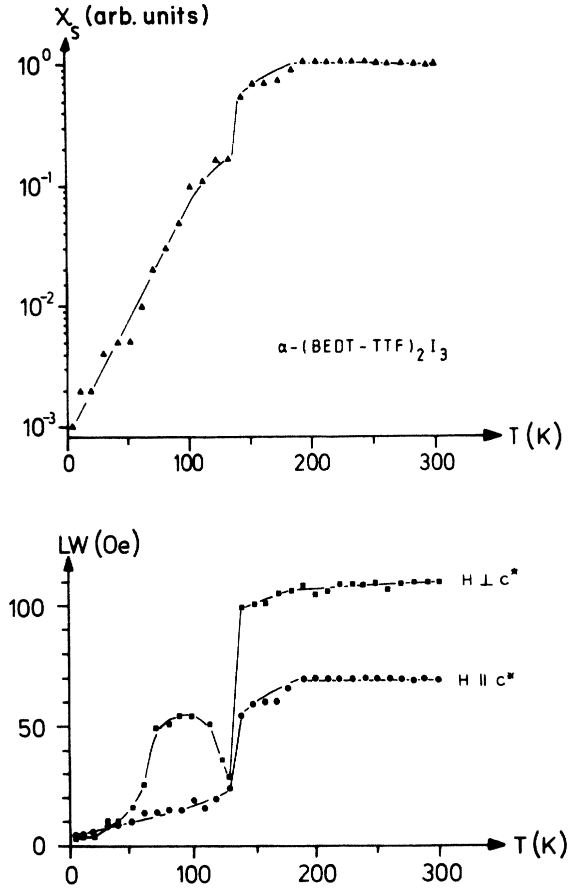

FIG. 4. Spin susceptibility χ_s^{α} and linewidth (LW) versus temperature from ESR studies at 9.3 GHz on a crystal of α-(BEDT-TTF)$_2$I$_3$. χ_s is given in arbitrary units on a logarithmic scale.

$\chi^{\beta}(T)$ which occurs at temperatures below about 80 K,[39] but it might have the same origin as the anomalous pressure dependence of T_c for the β phase, namely, as discussed earlier, there may be a metal-metal phase transition in this temperature region.

Figure 5 shows the ESR results obtained for a β-(BEDT-TTF)$_2$I$_3$ crystal. The ESR spin susceptibility is nearly temperature independent over the entire temperature range. The spin susceptibility has been corrected at all temperatures for the reduced penetration by the microwave magnetic field (skin effect) using a thin-slab calculation and is, within the error bars, consistent with the weak temperature dependence observed in the above static susceptibility measurements, but is in contrast to values reported by Venturini *et al.*[38] The ESR peak-to-peak linewidth changes by nearly a factor of 10 between 300 and 4.2 K. A comparison of the ESR linewidths in Figs. 4 and 5 shows that the room-temperature linewidth of the α phase is about 5 times larger than that of the β phase. Therefore, as pointed out earlier,[31] the ESR linewidth at room temperature can be used as a convenient method to discriminate between the α and β phases.

As stated above, for β-(BEDT-TTF)$_2$I$_3$ the room-temperature value of the spin susceptibility is $\chi_s^{\beta}=(+4.6\pm0.3)\times10^{-4}$ emu/mole. In a tight-binding one-dimensional (1D) model with an open Fermi surface and a quarter-filled hole band, this corresponds to a bandwidth $4t_{\parallel}$ of 0.25 ± 0.02 eV, where $t_{\parallel}$ is the overlap integral in the stack direction. It is interesting to compare this value with the bandwidth determined from optical studies[40–42] or band-structure calculations[43,44] in order to obtain the susceptibility-enhancement factor. However, there are several uncertainties in such a procedure. Firstly, different analyses of very similar optical data[40–42] within a 1D model lead to $4t_{\parallel}$ values ranging from 0.66 (Ref. 42) to 0.9 eV (Refs. 40 and 41). Secondly, it has been recently claimed[45] that there is substantial optical absorption from interband processes which were not taken into account in the above estimates of $4t_{\parallel}$.

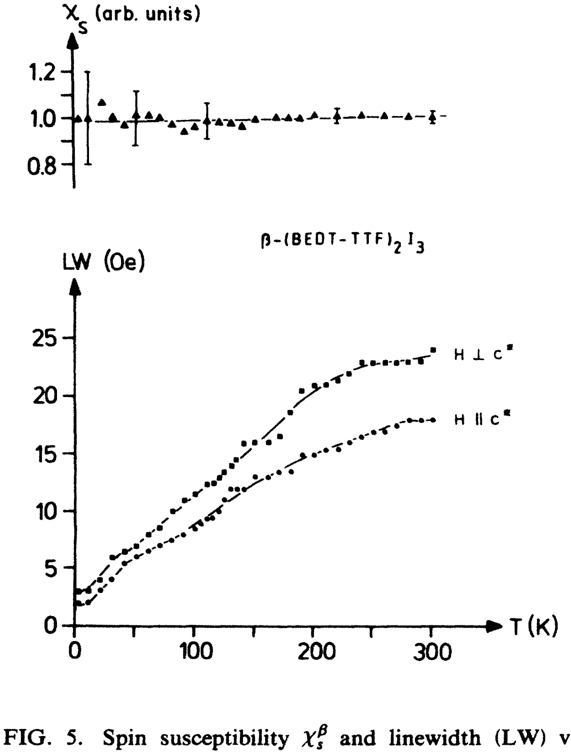

FIG. 5. Spin susceptibility χ_s^{β} and linewidth (LW) versus temperature from ESR studies at 9.3 GHz on a crystal of β-(BEDT-TTF)$_2$I$_3$. χ_s is in arbitrary units.

Because recent band-structure calculations[27,43] indicate that the Fermi surface is closed in the highly conducting (a,b) plane, we should also consider a 2D model here. For a cylindrical (2D) Fermi surface we calculate that the above value of χ_s^{β} corresponds to an effective mass $m^*=5.4m_e$, where m_e is the free-electron mass and the Fermi energy $E_F=0.072$ eV. This value is substantially smaller than the value $E_F=0.23$ eV determined recently from optical data [see Fig. 3(c) of Ref. 44]. The latter value corresponds to a closed Fermi surface of the type calculated in Ref. 27, but the band-structure parameters have been adjusted slightly to give a better fit to the optical data,[44] and interband effects were taken into account. Thus within either the 1D or the 2D model the susceptibility of the β phase appears to be enhanced by a factor of 3 ± 0.5 over the value corresponding to the bare bandwidth. However, this enhancement factor must be treated with caution because for the 1D model there are uncertainties in $4t_{\parallel}$, as discussed above. For the isotropic 2D model there may be deviations from the law $E=\hbar^2k^2/2m$ near E_F due to the complicated band structure [see Fig. 3(c) of Ref. 44]. Thus, while the value of m^* may well be correct, these effects could lead to an overestimation of the enhancement factor. In addition, there is a good degree of dimerization along the b axis (stack axis).[27] This dimerization creates gaps in the Fermi surface. However, the effect of these gaps on the electronic density of states, and on the spin susceptibility, would not be expected to be large.

D. Effect of pressure on the spin susceptibility

The effect of hydrostatic pressure on the measured room-temperature susceptibility χ of the α and β phases is shown in Figs. 6(a) and 6(b). From 2 to nearly 11 kbar the susceptibility of both phases is seen to decrease in an essentially linear fashion with pressure, within experimental error. The data in Fig. 6 have been corrected for the pressure dependence of the pressure fluid and Delrin sheath, as discussed above. In view of the superconductivity of the β phase, it is important to establish the variation in χ^{β} from 1 bar to 2 kbar, the latter being the lowest pressure at which we could seal the clamp at room temperature. The absolute values of χ^{β} at 2 kbar are within $\pm2\%$ of the ambient-pressure values, so we conclude that no significant changes in χ^{β} occur in the low-pressure region of 1 bar to 2 kbar at room temperature.

In order to obtain precise values for $\partial\ln\chi_s/\partial P$ from the measured values $\partial\ln\chi/\partial P$, one needs to know how the core diamagnetism of the sample, χ_{core}, changes with pressure. We estimate this derivative by studying the pressure dependence of the diamagnetism of insulating BEDT-

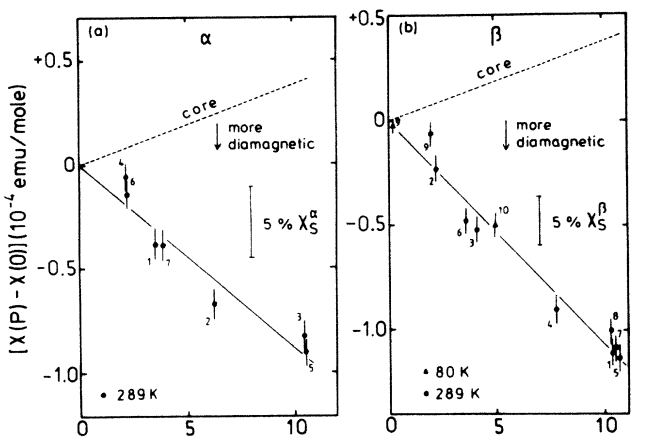

FIG. 6. Data points give change under pressure of the total measured static susceptibility at ambient temperature for (a) α-(BEDT-TTF)$_2$I$_3$ and (b) β-(BEDT-TTF)$_2$I$_3$. Numbers give order of measurement. Dashed line gives estimated change under pressure of the core diamagnetism χ_{core} (see text). In (b) two data points at 80 K are shown.

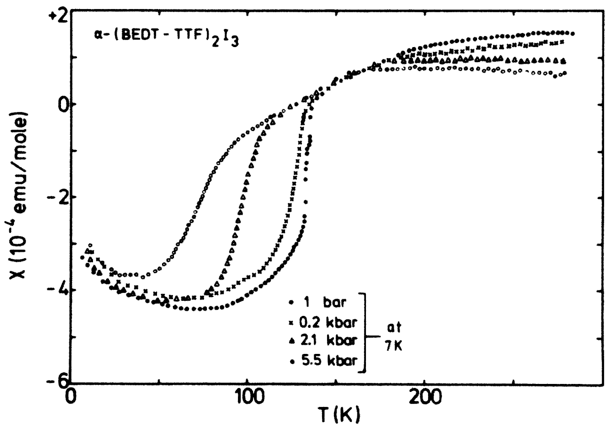

FIG. 7. Temperature dependence of the total measured static susceptibility of α-(BEDT-TTF)$_2$I$_3$ at four different pressures: the pressures at 290 K (1 bar; 1.3, 5.7, and 10.4 kbar) reduce to 1 bar; 0.2, 2.1, and 5.5 kbar, respectively, at low temperatures (7 K).

TTF; we assume that both the diamagnetism of BEDT-TTF and that of (BEDT-TTF)$_2$I$_3$ experience the same *relative* change under pressure, i.e., $(-0.76\pm0.2)\%$/kbar, as shown by the dashed line in Figs. 6(a) and 6(b). This fractional change under pressure is thus, within experimental error, identical to that for the organic pressure fluid. Thus from Fig. 6 we find that the logarithmic derivatives of the spin susceptibility for the α and β phases are $\partial\ln\chi_s/\partial P=(-2.0\pm0.1)\%$/kbar and $\partial\ln\chi_s/\partial P=(-3.3\pm0.15)\%$/kbar. These values would change to -1.3%/kbar and -2.4%/kbar, respectively, if we were to totally neglect the pressure dependence of χ_{core}. We also measured $\chi^\beta(T)$ for the β phase in two runs where the pressures at low temperature were 0.2 and 5 kbar. For this phase the relative change of the spin susceptibility is found to be $\partial\ln\chi_s/\partial P=(-3.3\pm0.5)\%$/kbar, independent of temperature for $T\leq300$ K.

The temperature dependence of the measured susceptibility of the α phase is shown in Fig. 7 for four different pressures.[45] In the metallic region χ_s is seen to be only weakly pressure dependent. The temperature of the metal-insulator transition T_p is strongly suppressed under pressure, in agreement with the conductivity studies.[23] However, the falloff in χ_s^α above T_p is not pressure dependent; this would support the point of view that this falloff is probably *not* a precursor effect but rather an intrinsic property of the spin susceptibility.

Below the temperature of the metal-semiconductor transition T_p, we obtain a temperature-dependent energy gap $2\Delta(T)$ by fitting χ_s^α to the formula[46]

$$\chi_s^\alpha=2\chi_0^\alpha/[\exp(\Delta/T)+1]\ . \tag{1}$$

χ_0 was taken to be $\chi_s(T_p)$, which forces Δ to zero at T_p. The results of such an analysis are shown in Fig. 8 and compared with the BCS curve expected for a mean-field Peierls transition. From Fig. 8 one can see that the Δ values are small, about twice the BCS values at ambient pressure. Etemad[47] found a similar ratio, twice the BCS value, for conductivity energy gaps of several derivatives of TTF-TCNQ (tetrathiofulvalene-tetracyanoquinodimethane). Conductivity measurements on the α phase[25] at ambient pressure also give small values for the energy gap 2Δ (850 K between 35 and 70 K, compared with 800 K at 80 K from the susceptibility). The small value of Δ indicates that in the α phase the structure of the BEDT-TTF stacks is only slightly altered by the phase transition. The phase transition is less sharp under pressure and at 5 kbar seems closer to the mean-field BCS-like behavior.

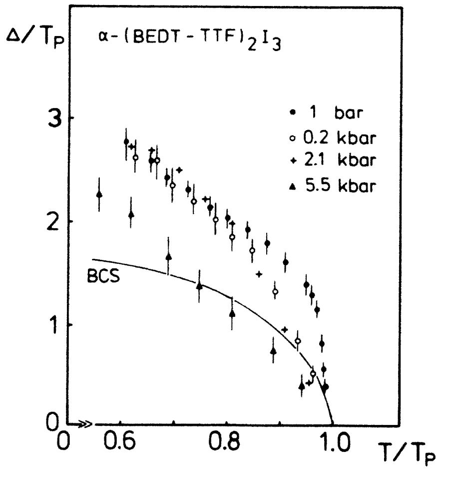

FIG. 8. Relative energy gap versus relative temperature derived from fit of data in Fig. 7 using Eq. (1). T_p is temperature of the metal-insulator transition which decreases with pressure. Solid line is the BCS curve.

IV. CONCLUSION

The main result of this work is that the pressure dependence of the spin susceptibility is surprisingly small for both the α and β phases of (BEDT-TTF)$_2$I$_3$; the most probable values of $\partial \ln \chi_s/\partial P$ are -2.0%/kbar and -3.3%/kbar, respectively. The uncertainty in the value of the bare band density of states at the Fermi energy $N(E_F)$ amounts to about a factor of 2 for the various organic metals. Since the exchange-enhancement factor of the susceptibility lies between 2 and 5, the large uncertainty in $N(E_F)$ poses a serious difficulty to an interpretation of the data. However, since both β-(BEDT-TTF)$_2$I$_3$ (Ref. 18) and TTF-TCNQ (Ref. 48) have comparable values of the compressibility ($K=1.04\%$/kbar and 1.06%/kbar, respectively), it would be reasonable to assume that the pressure dependence of the bare bandwidth $4t_{\parallel}$ for β-(BEDT-TTF)$_2$I$_3$ is comparable to that for TTF-TCNQ, i.e., $+2\%$/kbar to $+3\%$/kbar,[13,48] as determined from optical reflectivity under pressure or from band-structure calculations combined with compressibility data. It would thus appear that the modest pressure dependence $\partial \ln \chi_s/\partial P$ observed in the present experiments for the α and β phases could be a simple band-broadening effect, i.e., $\chi_s \propto t_{\parallel}^{-1}$. This result is in marked contrast to that for TTF-TCNQ, where the change of χ_s under pressure in an ESR experiment is much larger, $(-9\pm1)\%$/kbar,[8,9] than that of $t_{\parallel}$.

As mentioned above, other properties of the α and β phases show much larger pressure dependences; the room-temperature conductivity changes by $+22\%$/kbar (Ref. 37) and $+70\%$/kbar (Ref. 5), respectively, $\partial \ln T_p/\partial P$ for the α phase is -8%/kbar,[23] while for the high-T_c superconducting β phase, which is stable above 1.3 kbar, the initial slope $\partial \ln T_c/\partial P$ is -15%/kbar.[5,6]

Within the conventional BCS theory of superconductivity, T_c is a function of the electron-phonon coupling constant λ, where[49]

$$\lambda=\frac{\langle I^2\rangle N(E_F)}{M\omega^2}\,, \tag{2}$$

where I is the electron-phonon matrix element and M the atomic mass. λ depends on pressure due to the pressure dependence of $N(E_F)$, I, and ω. As discussed above, the pressure dependence of $N(E_F)$ should be approximately -3%/kbar. When the tight-binding approximation applies, the pressure dependence of I is like that of the bandwidth, and thus of $1/N(E_F)$, i.e., $+3\%$/kbar. This leaves a pressure dependence of $+3\%$/kbar in $\eta \equiv \langle I^2\rangle N(E_F)$. In "ordinary" superconductors like Pb, Sn, Al, etc. the tight-binding approximation is not valid, and $\langle I^2\rangle$ does not increase with pressure and, therefore, η actually decreases with pressure.

The phonon frequency ω changes with pressure in organic materials like naphthaline and anthracene by approximately $+6\%$/kbar.[50] This yields a contribution of -12%/kbar to λ, which considerably exceeds that of η. In neutral TTF, the pressure dependence of ω is somewhat smaller, namely about $+4\%$/kbar.[51] Similar values are observed in P$_4$S$_3$[52] and values around $+3\%$/kbar are observed in S$_4$N$_4$ and As$_4$S$_4$.[53] For these lower values, the electronic contribution cannot be neglected; unfortunately, we do not even know the sign of $\partial \ln\eta/\partial P$ yet, i.e., whether η increases or decreases with pressure. Thus, as a rough approximation, we assume that the pressure dependence of λ to be due to that of ω. Then it follows that

$$\frac{\partial \ln T_c}{\partial \ln V}=\left[\frac{\partial \ln T_c}{\partial \ln\lambda}\right]\left[\frac{\partial \ln\lambda}{\partial \ln\omega}\right]\left[\frac{\partial \ln\omega}{\partial \ln V}\right]=2\gamma\left[\frac{\partial \ln T_c}{\partial \ln\lambda}\right], \tag{3}$$

where γ is the Grüneisen constant.

T_c for 1D organic metals was calculated within the conventional BCS theory by Horovitz.[54] From his results, assuming equal forward and backward electron-phonon coupling, we can use the McMillan equation[49]

$$T_c=\frac{\Theta}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right]. \tag{4}$$

If we neglect μ^* in a first approximation, $T_c \simeq (\Theta/1.45)\exp[-(1+\lambda)/\lambda]$ and, consequently, $\partial \ln T_c/\partial \ln\lambda = 1/\lambda$. It thus follows that $\partial \ln T_c/\partial \ln V \simeq \gamma(2/\lambda-1)$. If we ignore the Θ prefactor in Eq. (4), then $\partial \ln T_c/\partial \ln V \simeq 2\gamma/\lambda$. This approximation is fair when λ is small (up to 0.5, roughly). For larger values of λ, μ^* cannot be neglected, and also the variation of the prefactor, $\partial \ln\Theta/\partial \ln\lambda = -\frac{1}{2}$, must be taken into account.

The value of the Grüneisen constant for naphthalene and anthracene ranges from about 4 for the higher-frequency external modes to about 6 for the low-frequency ones.[50] The value for TTF-TCNQ is similar, as can be inferred from the work of Debray *et al.*[48] and is approximately 3 for similar organic materials.[51] Moreover, the pressure dependence of the conductivity of TFF-TCNQ and TSF-TCNQ is very well accounted for by a Grüneisen constant of 3.5.[55] We may assume a similar value for the Grüneisen constants of (BEDT-TTF)$_2$I$_3$, namely, $\gamma=4$—6 for the low-frequency modes, which probably contribute most to the value of T_c. For a value of $T_c \simeq 8$ K, λ is probably in the range 0.5—1, like that of Pb. Thus we see that if γ is relatively high (4—6) and λ is small (0.5—0.6), then $\partial \ln T_c/\partial \ln V \simeq 13$—24, while the experimental value is 15. Thus, good agreement with experiment is obtained. If λ is large ($\lambda \simeq 1$) and $\mu^* \simeq 0.25$, we obtain a value of 12—18, which is also in good accord with experiment. However, if γ is relatively small (3—4), and λ is very large ($\lambda \simeq 1.5$), or $\lambda \simeq 1$, and $\mu^* \simeq 0.1$, then there is a large discrepancy. The discrepancy is particularly large if the matrix element $\langle I^2\rangle$ increases significantly with pressure.

In the small-λ case, where the McMillan theory applies, we are still far away from the maximum T_c value for this series of compounds, which should be 12—13 K; in any case, the large derivative $\partial T_c/\partial P$ seems to indicate that we are not yet close to the maximum T_c for this series of compounds. It is tempting to speculate that there is some softening of the $2k_F$ phonon because of the closeness of the Peierls transition,[56] which is possibly observed in the α phase. Such a softening could, of course, increase the value of γ. Reliable values of γ and λ should be obtained before more definite statements can be made.

In summary, the present work indicates that for both α and β phases of (BEDT-TTF)$_2$I$_3$ the temperature and pressure dependences of the susceptibility, unlike the other properties, are not anomalously large. For the β phase, at least, the change in the spin susceptibility χ_s under pressure would seem consistent with what one would expect from estimated changes in the bare bandwidth. The evidence presently available indicates that χ_s is enhanced by about a factor of 3 at ambient temperature and pressure. However, this estimate is critically dependent on the interpretation of the optical properties and must be taken with caution because of the complicated band structure. We feel that more reliable band-structure calculations are required for a definitive understanding of the susceptibility, and its pressure dependence. We propose to discuss these questions in more detail in a subsequent publication reporting the results of similar measurements on the Bechgaard salts.

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