Magnetic susceptibility and ESR of the organic conductor bis(ethylenedithiolo) tetrathiafulvalene perchlorate [$(BEDT\text{-}TTF)_3(ClO_4)_2$]: Evidence for a Peierls transition

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$(BEDT\text{-}TTF)_3(ClO_4)_2$ is a typical member of a large group of isostructural compounds formed by the bis(ethylenedithiolo) tetrathiafulvalene (BEDT-TTF) molecule. This subclass of BEDT-TTF compounds generally displays a metal-insulator phase transition when cooled below room temperature. The origin of these phase transitions is not known in these compounds. We present static magnetic susceptibility and ESR data for single crystals of $(BEDT\text{-}TTF)_3(ClO_4)_2$ which suggests that the phase transition is a mean-field-like Peierls transition. The large size of the spin susceptibility indicates that it is considerably enhanced by Coulomb interactions over the corresponding Pauli susceptibility for noninteracting electrons. We estimate a value for the on-site Coulomb interaction U of about 3—4 eV, compared to an estimated bandwidth $4t$ of $\simeq 0.75$ eV.

INTRODUCTION

Following the discovery of superconductivity in the sulphur-based organic conductor, $(BEDT\text{-}TTF)_2ReO_4$ [where BEDT-TTF is bis(ethylene-dithiolo) tetrathiafulvalene],[1] and the subsequent finding of superconducting ground states at ambient pressure in a number of ET (where we use the designation ET for BEDT-TTF) salts of the anions, I_3^- (Refs. 2—9) and simple derivatives of this anion (Refs. 10—12), much of the work on this class of compounds has concentrated on the low-temperature properties of the conducting state. However, the large majority of ET salts have an insulating ground state at ambient pressure. Moreover, unlike the selenium-based Bechgaard salts,[13] the ET salts have a wide range of stoichiometry and crystal structures.[14,15] It is possible that a systematic study of the magnetic and other physical properties of the ET compounds might give some insight into the conditions necessary for superconductivity in organic conductors. A comparison of the physical properties of the ET compounds with those of the Bechgaard family may also prove useful. One important continuing area of ambiguity in the Bechgaard salts concerns the interpretation of properties where electron-electron interactions are important. Few studies, as far as we are aware, have yet been made to address this question in the ET family. Of particular relevance are magnetic susceptibility studies.

In this short paper, we report measurements of static magnetic susceptibility and ESR properties of $ET_3(ClO_4)_2$ crystals at ambient pressure, down to liquid-helium temperatures. The perchlorate salt is a typical member of a series of isostructural ET salts formed with many of the smaller anions such as Br^-, FSO_3^-, BF_4^-, and IO_4^- (Ref. 14). At atmospheric pressure, these compounds are metallic with electrical conductivities of $\simeq 100\ (\Omega\,\mathrm{cm})^{-1}$ at room temperature, but they undergo metal-insulator transitions at lower temperatures.

EXPERIMENTAL

Single crystals of $ET_3(ClO_4)_2$ were grown by the usual electrochemical methods as described in Ref. 16. Only one phase was found for the ClO_4^- anion even though various growth rates and solvents were employed, which shows that the formation of this compound is insensitive to growth conditions. The crystals had the form of thin platelets of size approximately $1\times1\times0.1$ mm^3. Static susceptibility measurements made on two batches of randomly oriented crystals using the Faraday-balance technique,[17] at fields up to 0.94 T, gave essentially the same results. In one case, large corrections had to be made for some unidentified ferromagnetic contamination, thus only results for the uncontaminated batch are reported here. ESR measurements were made with a standard 9-GHz spectrometer with the static field along the crystallographic a axis and the rf magnetic field along the crystallographic b axis.

RESULTS AND DISCUSSION

Static magnetic susceptibility data (χ_{meas}) for 3.29 mg of randomly oriented single crystals are shown in Fig. 1. The temperature-independent core diamagnetism calculated from Pascal's constants is shown by the dashed line in Fig. 1. There is a sharp drop in susceptibility from the ambient value at 171 K (T_c) which corresponds to the metal-insulator transition observed in conductivity studies. At low temperatures, apart from a small Curie contribution associated with localized spins, the measured susceptibility is not significantly different from the expected core diamagnetism. This therefore rules out the

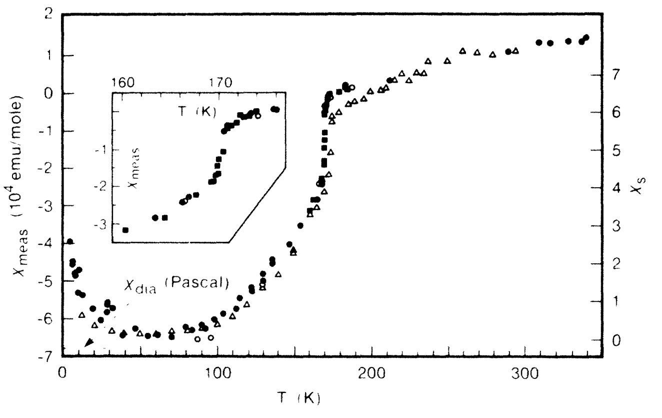

FIG. 1. Static susceptibility data for randomly oriented crystals of $ET_3(ClO_4)_2$ as a function of temperature. The left-hand scale shows measured values, χ_{meas}, and the right-hand scale shows these values corrected for core diamagnetism to obtain the spin susceptibility, χ_s. Data taken on warming and cooling at standard rates are shown as ● and ■, and those on warming after rapid cooling by ○ (see text). The open triangles show spin susceptibility data obtained from ESR, normalized to the same value of χ_s at 295 K. The inset shows χ_{meas} near the phase transition.

possibility of a spin-density ground state which has been observed in various Bechgaard salts.[13] Within the experimental uncertainty of ±0.5 K, there was no evidence for superheating or supercooling even though—as shown in the inset to Fig. 1—the transition is so sharp that it could have some first-order character, namely a discontinuity in the order parameter at T_c.

In some of the Bechgaard salts, the metal-insulator transitions arising from anion ordering are strongly affected by the cooling rates employed. Therefore, we made an experiment in which the sample was warmed up after rapidly cooling through T_c (295—130 K in 100 sec). This gave the same susceptibility curve as for normal cooling and warming rates (295—77 K in 30 min and 77—295 K in about 4 h, respectively).

Analysis of the low-temperature data shows that it fits a law of the form $B+C/T$ from 4.2 to 70 K. The Curie constant C corresponds to 0.37% $S=\frac{1}{2}$ spins per mole of $ET_3(ClO_4)_2$ while $B=-(6.55\pm0.1)\times10^{-4}$ emu/mole, which, as mentioned above, is not significantly different from the value, -6.8×10^{-4} emu/mole, calculated using Pascal's constants. The spin-susceptibility, χ_s, scale shown on the right-hand side of Fig. 1, is obtained using the former value. The magnitude of the room-temperature spin susceptibility, $\chi_s=7.5\times10^{-4}$ emu/mole, indicates important Coulomb interactions from the following self-consistent reasoning. First, if we calculate the Pauli paramagnetism expected for noninteracting electrons with a tight-binding bandwidth, $4t_{\parallel}=0.75$ eV, and band filling of $\frac{2}{3}$, we find that the measured spin susceptibility is enhanced by a factor of almost 4 compared to the Pauli susceptibility. We have estimated[18] the bandwidth within a simple one-dimensional tight-binding band model neglecting Coulomb interactions from the plasma frequency, $\omega_p/2\pi c\simeq10\,500$ cm^{-1}, determined for $ET_3(ClO_4)_2$ by Kuroda *et al.*[19] The estimate depends upon the molecular repeat distance along the stacks: we used a value of 4.2 Å which we obtained from the measured crystal structure.[14,20] If the bandwidth were in fact somewhat smaller, the enhancement would of course be correspondingly reduced. Although generally for organic conductors, such an enhancement is attributed to the influence of electron-electron Coulomb interactions,[21] it has recently been suggested that it could arise from band narrowing caused by electron-phonon interactions.[22] However, we can estimate a value for the on-site Coulomb repulsion energy U from the room temperature susceptibility and the bandwidth using the formalism developed by Torrance[21] for the case $U\gg4t$. We find, for $4t=0.75$ eV, that $U\simeq4$ eV, but note that since $U\propto t^2$, small variations in t will considerably affect the value of U—for example, if $4t=0.55$ eV, then $U\simeq2$ eV. Thus U is indeed large compared to the bandwidth which is consistent with an enhanced spin susceptibility.

An ESR line was observed from room temperature down to 5 K with a peak-to-peak linewidth in the derivative signal (ΔH) varying from 57 to 0.6 G, as shown in Fig. 2. The spin susceptibility was also obtained from the intensity of the ESR signal (i.e., the product of the height and the square of the linewidth of the derivative signal). These data are shown as a semilog plot of effective number of spins (arbitrary units) versus temperature in Fig. 3. Below 50 K, a Curie law is obeyed within experimental error. In Fig. 1, the spin susceptibility obtained by ESR (χ_{ESR}) is compared with the static spin-susceptibility data, after normalizing χ_{ESR} to have the same value at 295 K. With this normalization procedure, the single crystal used for ESR had a lower Curie term, corresponding to 0.15% spins per mole. In the metallic region above T_c, χ_{ESR} shows slightly more temperature dependence, but this is probably within the experimental uncertainty of the ESR intensity. Apart from these two small differences, there is excellent agreement between the ESR and static susceptibility data in Fig. 1.

After subtracting the respective Curie components, we have analyzed the remaining spin susceptibility below T_c to obtain the energy gap, 2Δ, associated with the metal-

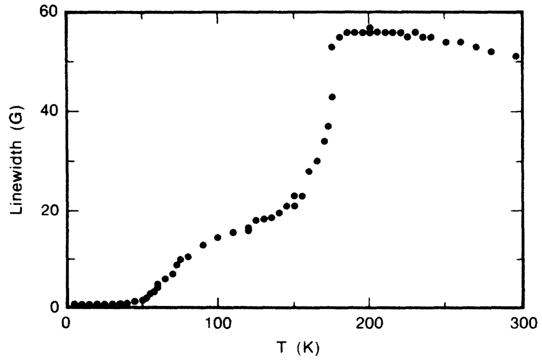

FIG. 2. ESR linewidth (peak to peak in first derivative of absorption line) versus temperature for a single crystal of $ET_3(ClO_4)_2$ with H_0 parallel to the a crystallographic axis.

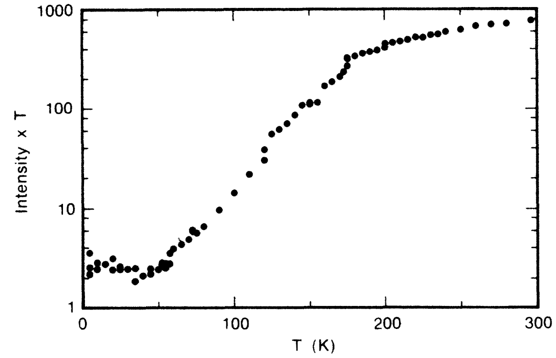

FIG. 3. ESR intensity multiplied by absolute temperature (i.e., effective number of spins) versus temperature on a semilogarithmic scale. Below 50 K, a Curie law is obeyed within experimental error. The same data is also shown on a linear scale in Fig. 1.

insulator transition. These results are shown in Fig. 4. We have obtained Δ using the formula,

$$\chi_s = 2\chi_0 \Big/ \left[\exp\frac{\Delta}{T} + 1 \right] , \quad (1)$$

and have (rather arbitrarily) taken χ_0 to be the spin susceptibility measured just above T_c (at 175 K). Equation (1) corresponds to a flat band of noninteracting electrons with a gap, $2\Delta(T)$, centered at the Fermi level (in this approximation, one neglects the narrow peaks in the density of states on either side of the gap). This is a more appropriate method[23] for obtaining Δ than the more usual $\ln(\chi T)$ versus $1/T$ plots when $\Delta \simeq T$, because it takes the temperature dependence of Δ into account. Nevertheless, the latter method, $\ln(\chi_{\text{ESR}} T)$ versus $1/T$, does give similar values for Δ below 100 K, as shown by the hatched area in Fig. 4. Note that χ_{ESR} gives more accurate values for the spin susceptibility in the region $T \ll \Delta$ where the static susceptibility is dominated by the core diamagnetism. Equation (1) is only approximate, and in particular, it is not clear how it should be modified in the presence of electron-electron interactions which are presumably responsible for the enhancement of χ_s.

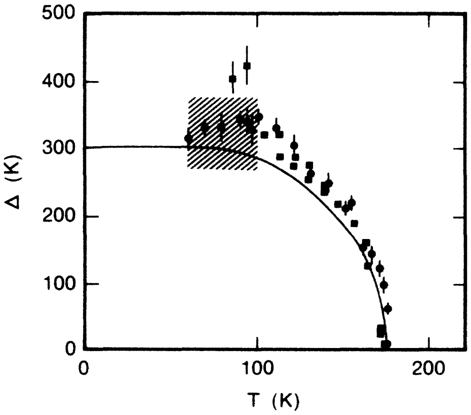

FIG. 4. Half-energy gap, Δ, versus temperature, (●) from ESR data, (■) from static susceptibility data, using Eq. (1). The shaded area corresponds to the possible range of (constant) Δ values obtained from the slope of $\ln(\chi_{\text{ESR}} T)$ versus $1/T$ below 100 K. The continuous solid line is the BCS mean field value with $\Delta(0) = 1.75 k_B T_c$.

From Fig. 4, one obtains a value of Δ extrapolated to $T=0$ of $\Delta(0) \simeq 330$ K. This value is very close to the Bardeen-Cooper-Schrieffer (BCS) value of $1.75 T_c$ and furthermore, the overall T dependence is quite similar to the mean-field BCS behavior, although the experimental values may fall more rapidly than BCS near T_c.

The activation energy for the conductivity, using a formula equivalent to Eq. (1), is 900 ± 100 K,[24] which is roughly 3 times larger than that from χ_s. In organic semiconductors, this is often considered to be a sign of important electron-electron interactions.[21] For example, in the limit of very strong interactions, the electrons are localized and the magnetic susceptibility then arises from triplet excitons, and in this case the two activation energies can differ by several orders of magnitude. For an intermediate case one can expect a smaller difference—perhaps as small as the factor of three, which we find for $ET_3(ClO_4)_2$.

The small value of the susceptibility gap and small T_c indicate that the phase transition is associated with a very small rearrangement of the ET or ClO_4 molecules. Indeed, it is tempting to ascribe it to a Peierls transition, which is mean-field-like because of the relatively strong interchain coupling in this class of compounds. Preliminary diffuse x-ray scattering studies give no evidence for a Peierls distortion in this material.[25] However, a displacive phase transition has recently been found in another compound containing the ET molecule, ET_2ReO_4, by x-ray techniques.[26]

The temperature dependence of the ESR linewidth, ΔH, in Fig. 2, shows three distinct regions. In the metallic region, it is temperature independent to within 10%, as is the electrical conductivity.[24] Below 50 K, there is a very narrow line, 0.5–2 G wide, associated with localized spins which are responsible for the Curie term in the susceptibility. At first sight, it might appear that the anomaly in linewidth near 80 K signals a second phase transition, but as shown in Fig. 3, this is not apparent in the ESR intensity. We propose that the anomaly in ΔH comes from the fact that at low temperatures the ESR intensity arises from localized spins, and at higher temperatures it is increasingly determined by the conduction-electron density. Thus as the temperature is raised from 5 K, the linewidth of the localized spins increases, perhaps as a result of interactions with the increasing number of phonons or conduction electrons. Then above about 80 K, the ESR intensity reflects the signal from the conduction electrons whose linewidth has a different temperature dependence.

After this article had been written, ESR data for $(BEDT\text{-}TTF)_3(ClO_4)_2$ similar to those we presented above were described in a paper by Enoki *et al.*[27] The conclusions reached by Enoki *et al.* are not substantially different from our own.

SUMMARY

Static and ESR studies on $(BEDT\text{-}TTF)_3(ClO_4)_2$ give consistent values for the temperature dependence of the spin susceptibility. In the metallic region χ_s is considerably enhanced, probably because of Coulomb interactions. The energy gap below T_c is small and may perhaps be caused by a mean-field-like Peierls transition. Since the susceptibility well below T_c is not significantly different from χ_{dia} estimated from Pascal's constants, the possibility of a magnetic ground state can be eliminated. It would be interesting to know the size of the spin susceptibility for other ET compounds, particularly for those with different structures and those which become superconducting, in order to better understand the significance of Coulomb interactions with respect to physical behavior.

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[1] S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, Phys. Rev. Lett. **50**, 270 (1983).

[2] E. B. Yagubskii, I. F. Shchegolev, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, A. V. Zvarykina, and L. I. Buravov, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 12 (1984) [JETP Lett. **39**, 12 (1984)].

[3] E. B. Yagubskii, I. F. Shchegolev, S. I. Pesotskii, V. N. Laukhin, P. A. Kononovich, M. V. Kartsovnik, and A. V. Zvarykina, Pis'ma Zh. Eksp. Teor. Fiz. **39**, 275 (1984) [JETP Lett. **39**, 328 (1984)].

[4] R. P. Shibaeva, V. F. Kaminskii, and E. B. Yagubskii, Mol. Cryst. Liq. Cryst. **119**, 361 (1985).

[5] V. N. Laukhin, E. E. Kostyuchenko, Yu. V. Sushko, I. F. Shchegolev, and E. B. Yagubskii, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 68 (1985) [JETP Lett. **41**, 81 (1985)].

[6] K. Murata, M. Tokumoto, H. Anzai, H. Bando, G. Saito, K. Kajimura, and T. Ishiguro, J. Phys. Soc. Jpn. **54**, 2084 (1985).

[7] M. Tokumoto, K. Murata, H. Bando, H. Anzai, G. Saito, K. Kajimura, and T. Ishiguro, Solid State Commun. **54**, 1031 (1985).

[8] V. B. Ginodman, A. V. Gudenko, and L. N. Zherikhina, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 41 (1985) [JETP Lett. **41**, 49 (1985)].

[9] H. Schwenk, C.-P. Heidemann, F. Gross, E. Hess, K. Andres, D. Schweitzer, and H. J. Keller, Phys. Rev. B **31**, 3138 (1985).

[10] J. M. Williams, H. H. Wang, M. A. Beno, T. J. Emge, L. M. Sowa, P. T. Copps, F. Behroozi, K. D. Carlson, and G. W. Crabtree, Inorg. Chem. **23**, 3839 (1984).

[11] H. H. Wang, M. A. Beno, U. Geiser, M. A. Firestone, K. S. Webb, L. Nunez, G. W. Crabtree, K. D. Carlson, J. M. Williams, L. J. Azevedo, J. F. Kwak, and J. E. Schirber, Inorg. Chem. **24**, 2465 (1985).

[12] H. Schwenk, S. S. P. Parkin, V. Y. Lee, and R. L. Greene (unpublished).

[13] For a review, see D. Jerome and H. J. Schulz, Adv. Phys. **31**, 299 (1982).

[14] S. S. P. Parkin, E. M. Engler, V. Y. Lee, and R. R. Schumaker, Mol. Cryst. Liq. Cryst. **119**, 375 (1985).

[15] G. Saito, T. Enoki, M. Kobayashi, K. Imaeda, N. Sato, and H. Inokuchi, Mol. Cryst. Liq. Cryst. **119**, 393 (1985).

[16] E. M. Engler, V. Y. Lee, R. R. Schumaker, S. S. P. Parkin, R. L. Greene, and J. C. Scott, Mol. Cryst. Liq. Cryst. **107**, 19 (1984).

[17] M. Miljak and J. R. Cooper, Fizika (Alma-Ata) **7**, 49 (1975).

[18] J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, and P. E. Seiden, Phys. Rev. B **19**, 730 (1979).

[19] H. Kuroda, K. Yakushi, H. Tajumi, and G. Saito, Mol. Cryst. Liq. Cryst. **125**, 135 (1985).

[20] S. S. P. Parkin and E. M. Engler (unpublished).

[21] J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, Phys. Rev. B **15**, 4738 (1977).

[22] H. Gutfreund, O. Entin-Wohlman, and M. Weger, Mol. Cryst. Liq. Cryst. **119**, 457 (1985).

[23] H. R. Zeller, Adv. Solid State Phys. **13**, 31 (1973).

[24] S. S. P. Parkin *et al.* (unpublished).

[25] R. Moret (private communication).

[26] S. Ravy, R. Moret, J. P. Pouget, R. Comes, and S. S. P. Parkin, Phys. Rev. B **33**, 2049 (1986).

[27] T. Enoki, K. Imaeda, M. Kobayashi, H. Inokuchi, and G. Saito, Phys. Rev. B **33**, 1553 (1986).