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Temperature-dependent Hall coefficient of the organic superconductor β-di[bis(ethylenedithiolo)tetrathiafulvalene]tri-iodide [β-(BEDT-TTF)$_2$I$_3$]

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We report Hall-effect data (R_H) for two single crystals of the organic superconductor β-(BEDT-TTF)$_2$I$_3$ in the low-T_c phase (β_L). An unexpected temperature dependence is obtained with a broad maximum in R_H near 40 K. A possible interpretation in terms of electron-electron scattering is discussed.

The organic superconductor β-di[bis(ethylenedithiolo) tetrathiafulvalene] tri-iodide [β-(BEDT-TTF)$_2$I$_3$], shows several fascinating properties:[1] It has a low (β_L) and high (β_H) T_c superconducting phases with $T_c = 1.2$ and 8 K, respectively, unusual structural phase transitions, and displays Shubnikov de Haas oscillations in high magnetic fields. For the β_H phase these oscillations are very large and they correspond to a Fermi surface (FS) which is closed in the a-b plane with very weak dispersion along the low-conductivity c axis.[2] However, the understanding of some basic properties is still incomplete. For example, it is very unusual for a material with a conductivity of only 25–35 $(\Omega\,\mathrm{cm})^{-1}$ at 300 K to show metallic behavior. The spin susceptibility is much less temperature dependent than in other organic conductors and there is almost no enhancement relative to the measured electronic specific heat. However, the enhancement relative to the calculated density of states has been estimated to be only 30% (Ref. 1) or as high as a factor of 3.[3] Furthermore, until now there were no measurements of one of the simplest and most important physical quantities, the Hall coefficient (R_H).

Hall measurements are less common for organic conductors because the crystals are small and fragile and there are difficulties in making proper noise-free contacts.

The common feature of the available data in quasi-one-dimensional conductors tetrathiafulvalene-7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ),[4] hexamethylenetetraselenafulvalene-7,7,8,8-tetracyanoquinodimethane (HMTSF-TCNQ),[5] and tetramethyltetraselenafulvalene-dimethyltetracyanoquinodimethane (TMTSF-DMTCNQ) (Ref. 6) is that R_H is temperature dependent, $d|R_H|/dT < 0$ in the metallic phase, much above the transitions to a Peierls semiconductor or to a semimetallic state. This behavior was attributed by Weger[4] to a dimensional crossover, i.e., to a diffusive-coherent transition between the chains. However, this early work referred to coherent motion at low temperatures between different types of chains namely holelike HMTSF and electronlike TCNQ chain.

It is not clear whether the coherent-diffusive transition will cause R_H to be T dependent in a single-chain system. Although β-(BEDT-TTF)$_2$I$_3$ is a single-chain system it is unusual in that it has less conductivity anisotropy, than the Bechgaard salts, and there is probably no diffusive-coherent transition in the a-b plane. Indeed Bulaevskii has convincingly argued that at all temperatures the conductivity is dominated by electron-electron umklapp scattering over a closed FS.[1]

The Hall data reported here do show considerable temperature dependence. As discussed below, this may be possibly ascribed to the strong relaxation time anisotropy associated with electron-electron scattering.

The Hall effect was measured on two single crystals of β-(BEDT-TTF)$_2$I$_3$. Contact areas were made by evaporating gold over the ends and on the sides of the crystal (see Fig. 1). Two voltage contacts were placed on each side of the crystal, so that if necessary the resistive voltage could be zeroed out for the Hall voltage measurements, and also the conductivity and magnetoresistance could be measured in the same run. Gold wires were attached to them with silver paint. The contact resistances were less than 25 Ω at room temperature.

Hall constant (R_H) measurements were carried out with direct current along the needle axis in a fixed magnetic field of 6 T along the low-conductivity c^* direction (Fig. 1). Instead of varying the magnetic field, it was effectively reversed by rotating the sample around the needle axis by 180°. At least three rotations were made at each temperature in order to obtain consistent values for

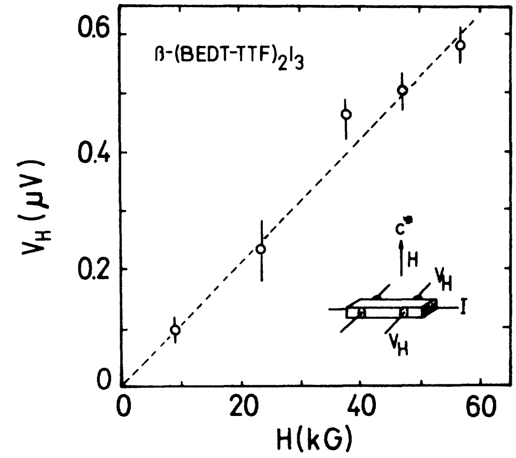

FIG. 1. Linear dependence of Hall voltage of a single-crystal β_L-(BEDT-TTF)$_2$I$_3$ at 4.2 K. Inset shows contact geometry, current in the highly conducting a-b plane, and field along the low-conductivity c^* axis.

the Hall voltage V_H. For currents of 2-5 mA the typical values of V_H (at 4.2 K) were 0.13-0.58 μV. The sign of R_H was determined by comparison with a standard *p*-type silicon sample measured in the same run.

The Hall voltage (V_H) was measured as a function of magnetic field up to 6 T at 4.2 K. In Fig. 1 it is shown that V_H is the linear function of the magnetic field H. R_H is thus given by the formula $R_H = V_H W/IH$, where W is the thickness of the sample in the direction parallel to H and I is the current through the sample.

In Fig. 2 we show resistivity versus temperature for one of the crystals used for Hall effect (sample 2) in the β_L state. This was the first cooling and it is evident from Fig. 2 that there is no anomaly below 8 K connected with a small fraction of the β_H phase as is usually observed in β-(BEDT-TTF)$_2$I$_3$ monocrystals.[1] For samples 1 and 2 the room-temperature values of the needle axis resistivity were 3.06×10^{-2} and 2.67×10^{-2} Ω cm, respectively, in good agreement with Ref. 1, as is the magnitude of the T^2 law below 40 K (3×10^{-7} Ω cm/K^2).

In Fig. 3 we show the Hall constant R_H as a function of temperature for the two crystals measured. The dashed line is to guide the eye. R_H is positive over the whole temperature interval (1.5-150 K). The positive value of R_H agrees with the sign of the high-temperature thermoelectric power.[7] R_H is seen to be temperature dependent, i.e., to increase with temperature to a maximum in the range 20-40 K. In the temperature interval 2-20 K, R_H rises by about 55%. Above 40 K R_H falls with further increase in temperature and at about 150 K it takes about the same value as at 4.2 K.

In Fig. 4 we show the Hall mobility $\mu_H = R_H/\rho$ over the whole temperature interval. μ_H rises to a value of 100 cm^2/V s at low T and tends to saturate below 10 K. At high temperatures μ_H is extremely small, 0.3 cm^2/V s. Usually such low values are an indication of a breakdown of a band picture and the onset of localization. However, this may not be so in the present unusual case where μ_H is dominated by electron-electron scattering.[1]

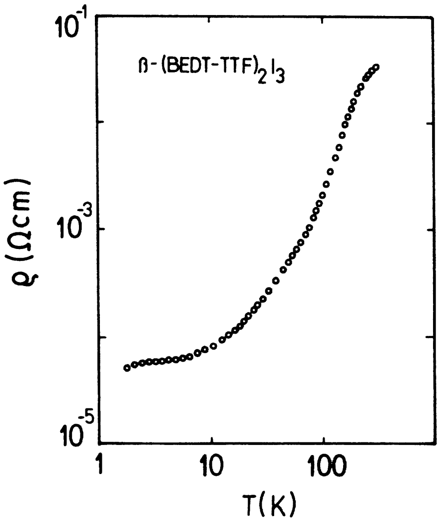

FIG. 2. Overall needle-axis-resistivity–temperature behavior for one pair of contacts on a single crystal used for Hall measurements (sample 1 in Fig. 3). At low T the resistivity obeys the law $\rho(T) = A + BT^2$, with $A = 3\times10^{-5}$ Ω cm and $B = 3\times10^{-7}$ Ω cm/K^2. According to Ref. 1, the deviations from a T^2 law above 100 K are due to thermal expansion, although there is a phase transition associated with the iodine sublattice near 180 K.

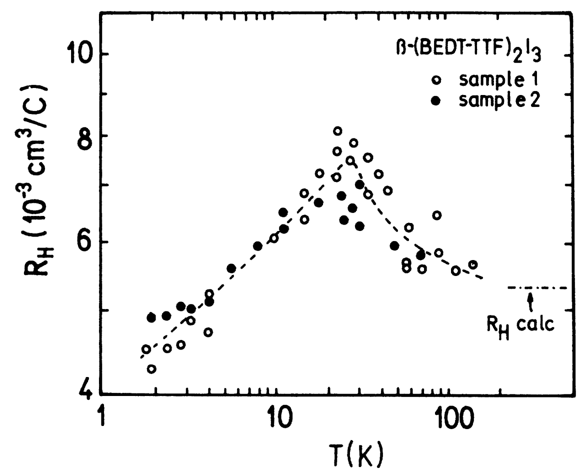

FIG. 3. Temperature dependence of the Hall coefficient for two single crystals from 2 to 150 K. The value of R_H calculated within a single-band model is indicated by a dash-dotted line.

In β-(BEDT-TTF)$_2$I$_3$ the I$_3^-$ anion takes one electron from two BEDT-TTF molecules, and there is nominally one hole per unit cell in the BEDT-TTF bands. This is in agreement with the sign of R_H found experimentally. For a single band the kinetic formula for the low-field Hall constant $R_H = 1/nec$ is usually valid for a constant relaxation time τ. Using the unit-cell volume of $V = 852.2$ Å^3 (Ref. 8) and one hole per unit cell, we find that $n = 1.17\times10^{21}$ carriers/cm^3 and $R_H = 1/ne = 0.532\times10^{-2}$

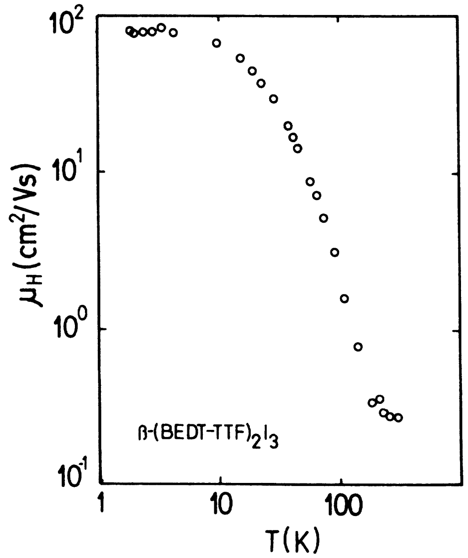

FIG. 4. Hall mobility obtained for sample 1 from the results in Figs. 2 and 3.

cm^3/C. This value of R_H is indicated by a dashed line in Fig. 3.

We can see that the high-temperature value is close to the calculated one and that at low temperatures the limiting value is (15–20)% lower. In principle a scattering time τ which varies over the FS can give rise to an enhanced Hall coefficient according to the formula:[9] $R=(1/nec)\langle\tau^2\rangle/\langle\tau\rangle^2$. In the present case one possible reason for the T dependence of R_H is the following. At low T, τ arises from electron-impurity (disorder) scattering and is reasonably constant over the FS so R_H is not enhanced. Then at intermediate temperatures τ arises from electron-electron Umklapp scattering as suggested by Bulaevskii.[1] Referring to Fig. 5 (Ref. 10), those electrons near the Brillouin zone boundary (P) have a significantly larger possibility of undergoing electron-electron Umklapp scattering than those further away from a zone boundary (Q). Thus when electron-electron scattering is dominant R_H is enhanced due to the anisotropy in τ.

The question arises as to why R_H falls again above about 40 K, even though electron-electron scattering is dominant up to room temperature.[1] At high enough temperatures [when 4 kT$\simeq E_F$ (the Fermi energy)] electron-electron scattering would certainly become isotropic because of thermal smearing and R_H would no longer be enhanced. However, in order to obtain a maximum in R_H at 40 K as observed experimentally, a characteristic energy much smaller than E_F must be important. Perhaps this could be the energy difference between electron states near P and those at the nearby Brillouin-zone face (Fig. 5). There are several possible reasons why R_H could change when 4 kT approaches this characteristic energy, but we think that the dominant mechanism can only be identified by detailed calculations. First, as mentioned by Friedel in the context of Ref. 2, a peak in the density of states arising from a two-dimensional Van Hove singularity is to be expected as the Brillouin-zone face is approached and this could make R_H temperature dependent. Second, near the Brillouin-zone boundary there is a transition from closed to open orbit electronic states. This could also affect R_H, since for an open Fermi surface R_H is given by a somewhat different formula.[4] Furthermore, for an open Fermi surface the geometrical restrictions on electron-electron scattering associated with k conservation are different. Note that all the above tendencies are enhanced by thermal expansion which causes the Brillouin zone to contract.

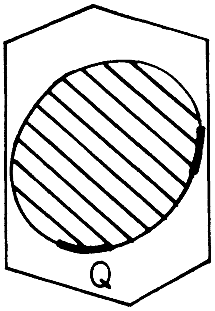

FIG. 5. Hole Fermi surface and Brillouin zone of (BEDT-TTF)$_2$I$_3$ after Ref. 10. Regions P and Q are discussed in the text.

Detailed calculations with a realistic band structure and density of states would be required to see whether thermal smearing could give a maximum in R_H as low as 40 K. Such calculations should also account for the observed T dependence of the susceptibility anisotropy which also shows a maximum near 40 K.[11]

One experimental prediction of the above picture is that for the high-T_c β_H phase or other similar BEDT-TTF salts with lower residual resistivities R_H should remain high to lower temperatures, since the isotropic (residual) scattering rate is much smaller.

In conclusion we have found evidence for a T-dependent Hall coefficient in the low-T_c phase of β-(BEDT-TTF)$_2$I$_3$. One possible explanation involves electron-electron scattering and the influence of the region of the Fermi surface near the Brillouin zone boundary. Alternatively, the unusual temperature dependence of R_H might be associated with the breakdown of the band picture at higher temperatures. But in this case it should occur for the majority of single chain organic conductors irrespective of whether they have open or closed Fermi surfaces. Similar measurements on both BEDT-TTF and Bechgaard salts are required in order to understand the origin of this effect.

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