Hall effect in the organic conductor $(ET)_2TlHg(SCN)_4$

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The Hall effect in the organic metal α-$(ET)_2TlHg(SCN)_4$ has been studied over the temperature range 1.8–20 K. The field was directed along various crystallographic axes in the conducting plane of the crystal. The Hall constant is positive over the entire temperature range. It increases sharply near 10 K. This behavior is interpreted as a metal–metal phase transition at 10 K.

The electron systems of essentially all known organic metals are systems of a reduced spatial dimensionality: either quasi-1D or quasi-2D. The former are characterized by an instability of the metallic state of the electron system and thus by a metal–insulator transition as the temperature is lowered.[1] The quasi-2D metals are stabler with respect to a transition to an insulating state. Many of them not only retain their metallic state but even become superconductors.[2]

Conductors synthesized on the basis of the ET molecule are typical members of the class of organic quasi-2D metals.[2–4] Among them, however, the family α-$(ET)_2MHg(SCN)_4$, where M=K, Tl, Rb, NH_4, stands out. These materials combine the properties of quasi-1D and quasi-2D metals.[5–7] The Fermi surface of these isostructural compounds consist of two sheets.[8] The first is a closed cylinder with axis along $\mathbf{K}_b$. The second consists of two slightly corrugated planes which are approximately perpendicular to $\mathbf{K}_a$ ($\mathbf{K}_a$, $\mathbf{K}_b$, and $\mathbf{K}_c$ are reciprocal-lattice vectors). The first sheet, which is characteristic of quasi-2D systems, is responsible for the Shubnikov–de Haas oscillations which are observed in the compounds[7,9] with M=K, NH_4, Tl. The second sheet, which is characteristic of quasi-1D metals, seems to be determined by a partial insulating transition at $T_p = 10$ K. Hints of such a transition are also seen[7,10,11] in the compounds with M=K, Tl, Rb. (This partial transition to an insulating state is not detected in the salt with M=NH_4, which is a superconductor with T_c=0.8–1.4 K; Refs. 5 and 12.) The antiferromagnetic order observed[13] below T_p in the salt with M=K suggests that a Peierls transition occurs in this family of conductors at $T = T_p$ and is accompanied by the formation of a spin density wave.

In this letter we are reporting the direct observation of such a transition, based on the temperature dependence of the Hall constant in the conductor α-$(ET)_2TlHg(SCN)_4$.

The test sample was a thin single-crystal platelet, nearly square in shape, with approximate dimensions of $1.2\times1.2\times0.015$ mm. An x-ray diffraction analysis of the sample revealed that the **a** and **c** crystallographic axes were directed along the diagonals of the square. A pair of platinum measurement leads was cemented with conducting paste to the ends of each diagonal. Any pair of the contacts formed in this

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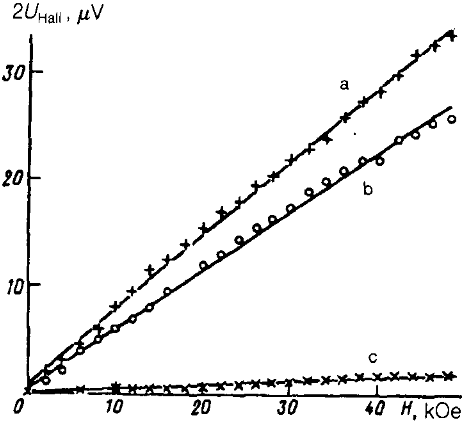

FIG. 1. Field dependence of the Hall voltage at various temperatures. a—$T=1.8$ K; b—6; c—20 K. $I=1$ mA.

manner could be used to pass a measurement current (i.e., they could be used as current contacts), while the other pair could be used to measure the transverse voltage (i.e., they served as potential contacts). In one series of measurements the current flowed approximately along the **a** direction, i.e., nearly perpendicular to the planes of the second sheet of the Fermi surface. In this case the Hall voltage was measured near the **c** direction. In a second series of measurements the current flowed along **c** . In all cases the magnetic field was directed perpendicular to the **ac** plane, i.e., perpendicular to the plane of the single crystal.

In general, the total voltage across the potential contacts was measured in these experiments. This total voltage includes, in addition to the transverse Hall component, a parasitic voltage which arises because of the imperfect geometry of the contacts. It is a simple matter to eliminate this parasitic voltage, by reversing the direction of the magnetic field with respect to the crystal. In our experiment we took the approach of reversing the field, rather than rotating the crystal through 180°. The field of 48 kOe was restored within a few tens of oersteds according to an independent Hall field pickup.

The temperature dependence of the Hall voltage was measured in the following way: A measurement current was passed along one of the diagonals of the crystal in a field of 50 kOe. The transverse voltage between the other pair of contacts (the potential contacts) was measured at certain temperatures. The field was then reversed, and the voltage was remeasured at the same temperatures. The difference between the measurements at each temperature was taken to be twice the Hall voltage. To verify that the results found correspond to the Hall voltage, we measured the field dependence of the voltage across the potential contacts in forward and reverse fields at some of the temperatures. The values of the difference between these results at temperatures of 1.8, 6, and 20 K are shown in Fig. 1. We see in Fig. 1 that the difference between the voltages in the forward and reverse fields can be described quite well by straight lines which pass through the origin. This situation is characteristic of specifically a Hall voltage. This check was made repeatedly. The actual voltages across the potential contacts varied from experiment to experiment, but the field dependence of their

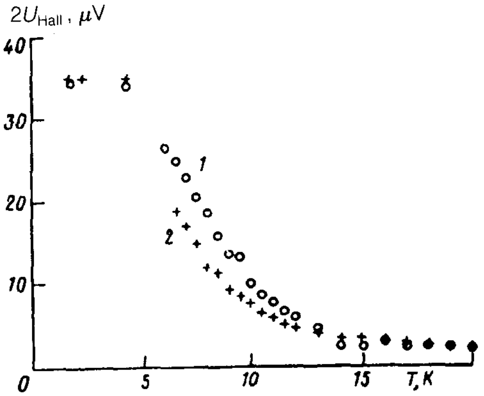

FIG. 2. Temperature dependence of the Hall voltage in a field $H=48$ kOe for two current directions: 1—$I \parallel$ **a**; 2—$I \parallel$ **c**.

difference (Fig. 1) was reproducible in all cases. The voltage measurements were carried out in an automatic procedure at a direct current of 1 mA. For each measurement, the temperature was stabilized within 0.01 K.

Figure 2 shows the results of measurements of the temperature dependence of the Hall constant over the temperature range 1.5–20 K in a field of 48 kOe for two, mutually perpendicular directions of the current. The results of these measurements for the different current directions are essentially identical. Analysis of the experimental conditions shows that the slight difference stems from heating of the crystal due to a difference in the quality of the pairs of contacts. It can be seen from Fig. 2 that the Hall coefficient is independent of the temperature in the interval 12–20 K. Beginning at about 12 K, the Hall constant increases sharply with decreasing temperature. Its value increases by a factor of about 20 at $T=4.2$ K, and then saturation sets in.

The sharp increase in the Hall coefficient with decreasing temperature is direct evidence of a metal–metal phase transition, associated with a decrease in the number of charge carriers in the crystal. At a qualitative level, this decrease in concentration can be understood easily as a phase transition of the Peierls type in a system of carriers associated with the "quasi-1D" sheet of the Fermi surface. Such a transition should be accompanied by a complete or partial nesting of Fermi quasiplanes and thus a transition of the quasi-1D system to an insulating state. Quantitatively, on the other hand, the increase in the Hall constant by a factor of nearly 20 is more difficult to understand. If the phase transition were accompanied by only a nesting of quasiplanes, and if the cylindrical sheet of the Fermi surface remained unchanged, as was suggested in Ref. 7, then the increase in the Hall constant due to the decrease in the number of carriers should not have exceeded a factor of 3 to 5. The reason is that, according to the calculations of Ref. 8, the cross-sectional area of the cylinder is 16% of the area of the corresponding cross section of the Brillouin zone. These results may thus be taken as evidence that there is a more radical restructuring of the Fermi surface in $(ET)_2TlHg(SCN)_4$ below 10 K, and that this restructuring affects the "quasi-2D" sheet of the Fermi surface. One possible version of such changes was studied in detail in Ref. 14.

The Hall coefficient exhibits no anisotropy. Significantly, there is a pronounced anisotropy in other properties, e.g., the conductivity and the thermal emf. In fact, the thermal emf implies different signs for the carriers along the **a** and **c** directions: Electrons for the first direction and holes for the second.[15] In our experiment, we observe only a positive sign of the Hall constant, for both voltages. This positive sign corresponds to holes over the entire temperature range. A simple quantitative estimate of the hole concentration at high temperatures yields 2×10^{21} cm^{-3}, which is in reasonable agreement with the stoichiometric value.

In this study we did not test the suggestion that the magnetic field might itself affect the extent to which the carriers go into an insulating state.[7] In this case the Hall voltage would depend on the field in a complicated, nonlinear way. That conclusion contradicts our experiment, at least in fields up to 50 kOe (Fig. 1).

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