Hall effect in the organic conductor α-(BEDT-TTF)$_2$KHg(SCN)$_4$, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene

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Hall-effect measurements below 20 K and up to 23 T on single crystals of the organic conductor α-(BEDT-TTF)$_2$KHg(SCN)$_4$ are reported. The sign of the Hall coefficient R_H is positive in the whole temperature range, indicating a hole carrier. R_H obtained from the H-linear dependence of the Hall resistance R_{xy} steeply increases below 10 K and saturates around 4 K. This increase in R_H coincides with anomalies observed in the static magnetic susceptibility and the electrical resistance at about 10 K. This finding suggests a reconstruction of the Fermi surface associated with the spin-density-wave (SDW) gap formation in this magnetic-phase transition. The high-field R_{xy} above about 10 T at 4.2 K deviates from the H-linear dependence, suggesting that the SDW formation might change with fields.

Charge-transfer salts consisting of the molecules TMTSF or BEDT-TTF, which denote tetramethyl-tetraselenafulvalene or bis(ethylenedithio)tetrathiafulvalene, have played leading roles in studying low-dimensional electronic properties associated with magnetism and/or superconductivity.[1] The former salt, (TMTSF)$_2$X, with various monovalent anions X, is characterized as a highly anisotropic, two-dimensional electronic system. This system has attracted much attention because of the variety of ground states, for example, the spin-density-wave (SDW) state. The SDW state is caused by the instability of the quasi-one-dimensional open Fermi surface of the system. The latter salt, (BEDT-TTF)$_2$X, possesses a layer structure which consists of the conducting BEDT-TTF and insulating anion sheets. The electronic properties are isotropic two dimensional, and the Fermi surfaces observed in many BEDT-TTF salts by the Shubnikov–de Haas (SdH) and de Haas–van Alphen (dHvA) effects are found to be cylindrical closed ones.[2] In comparison to (TMTSF)$_2$X, (BEDT-TTF)$_2$X can remain metallic even at low temperatures, probably because the Fermi-surface instability could be less significant than that of (TMTSF)$_2$X. As is well known, many BEDT-TTF salts exhibit superconductivity at ambient pressure.

The organic conductor α-(BEDT-TTF)$_2$KHg(SCN)$_4$ studied in the present paper was synthesized[3] as a modification of the superconducting κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, with a critical temperature T_c of about 10 K.[4] However, it was soon found to be metallic without the superconducting transition. The related salt α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$, with almost the same crystal structure, is clarified to be superconducting at 0.8 K.[5,6] Recently, α-(BEDT-TTF)$_2$KHg(SCN)$_4$ has been extensively studied as follows. Anisotropic behavior in the static magnetic susceptibility was observed below 10 K ($=T_A$), suggesting that an antiferromagnetic order might develop.[7] This phase transition is associated with shoulder-type anomaly in the zero-field electrical resistance.[8] The magnetoresistance below T_A shows charac-

teristic features[7-12] which have never been observed in other BEDT-TTF salts. The magnetoresistance rapidly increases with increasing fields and then takes a maximum at H_c (for example, 10 T at 0.5 K). With further increase of fields, it decreases continuously up to H_A ($=23$ T), where a kink structure appears and then the magnetoresistance increases again. The hysteretic behavior is clearly observed for increasing and decreasing fields between H_B ($=7$ T) and H_A. We have proposed the magnetic-phase diagram on the basis of these observations.[10]

The band-structure calculation[13] proves that two bands exist at the Fermi level; one forms the two-dimensional close orbit (cylinder), and the other the quasi-one-dimensional open one (a pair of corrugated sheets). The measurements of SdH (Refs. 7, 9, 11, 12, 14, and 15) and dHvA (Ref. 12) oscillations observed at low temperatures below 4 K reveal the existence of the cylindrical Fermi surface. A pair of the open Fermi surfaces expected from the calculation are likely to be nested against each other, leading to the SDW. The magnetic origin of this salt has been discussed in terms of this instability of the quasi-one-dimensional band.[7,11] This issue is still controversial.

The measurement of the Hall coefficient R_H gives us useful information on the carrier properties. To shed more light on the phase transition at T_A, and to study how the electronic properties might change at T_A, we have measured the Hall effect below 20 K and up to 23 T. The temperature and field dependence of R_H are presented and discussed with the magnetic-phase diagram.

The single crystals were grown by the usual electro-chemical oxidation method.[3] The typical shape of the as-grown crystals is thick rectangular. The size of the crystals used in the measurements is $1.07 \times 0.61 \times 0.02$ mm^3 (sample 1) and $1.60 \times 0.56 \times 0.03$ mm^3 (sample 2). The longest direction is almost parallel to the (c+a) axis. The axes x, y, and z used in this paper are parallel to the longest direction, perpendicular to the x axis in the plane and normal to the plane, respectively. The electronic terminals are made of the evaporated gold films and the gold

wires (10 μm diameter) are glued onto the gold films with silver paint. The Hall voltage V_{xy} is measured by the four-terminal method using dc currents I (100–300 μA) in the magnetic field H parallel to the z axis. The 15-T superconducting and 23-T hybrid magnets at the High-Field Laboratory for Superconducting Materials (HFLSM) are used. The transverse magnetoresistance R_{xx} is particularly large in our geometry. In order to remove the spurious voltage induced at the Hall terminals, V_{xy} is defined as half of the difference between the voltage measured with upward $(+z)$ and downward $(-z)$ magnetic fields by inverting the sample. In both cases the fields are swept at the same rate (0.25 T/min) at a fixed temperature. R_H is given by the formula $R_H = V_{xy}/(djH)$, where j is the current density and d is the distance between the Hall terminals.

Figure 1 shows the isothermal Hall resistance R_{xy} $(= V_{xy}/I)$ of sample 1 as a function of magnetic field. As seen in this figure, R_{xy} is almost proportional to the field. The slope of R_{xy} becomes large with decreasing temperature. The SdH oscillations superimpose the curve above 10 T at 2 K.[16]

R_H is obtained from the constant slope of R_{xy}. Figure 2 shows the temperature dependence of R_H for two samples, where both data are normalized at 2.0 K and the solid lines are to guide the eye for each sample. The sign is positive over the whole temperature range. In the temperature regime above 10 K, R_H increases slightly with decreasing temperature. Below $\sim$ 10 K, very close to T_A, there appears a rapid increase of R_H, followed by saturation below about 4 K. The value at 20 K is about one-tenth and one-fifth of saturated values for samples 1 and 2, respectively. This sample dependence might be due to the inhomogeneous current path and/or experimental error in measuring the sample size. Although the carrier density n is difficult to estimate for the present metal with both close and open bands, we could obtain $n = +2.8 \times 10^{25}$ and $+1.4 \times 10^{25}$ m^{-3} at 2 K for samples 1 and 2, using the simple relation $R_H = -1/ne$. The absolute value of n is not mentioned in more detail.

Figure 3 shows the Hall resistance R_{xy} and the magnetoresistance $\Delta R_{xx}/R_0 = [R_{xx}(H) - R_{xx}(0)]/R_{xx}(0)$ at
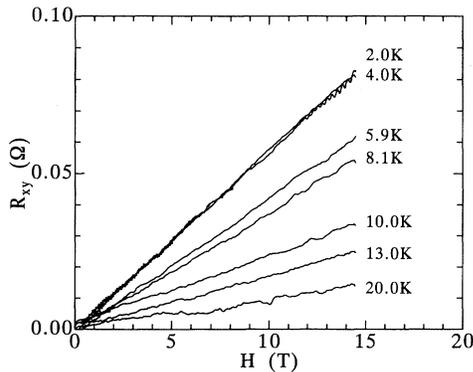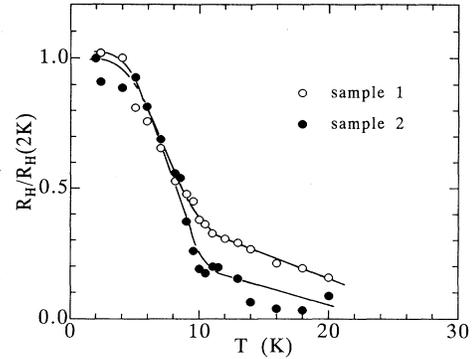

FIG. 2. The temperature dependence of the Hall coefficient normalized at 2 K. The open and filled circles denote the data of samples 1 and 2, respectively. The solid lines are guides for the eye in each sample.

4.2 K as a function of the magnetic field up to 23 T perpendicular to the xy plane for sample 1. The behavior of the magnetoresistance well reproduces our previous results.[10] However, the kink structure becomes blunt and the hysteresis is not observed at this temperature within experimental error. In the low-field regime ($H < 10$ T), R_{xy} is proportional to the field, as shown by the solid straight line in the figure. The deviation from the H-linear dependence starts at about 10 T, as indicated by the arrow. It is found that the slope becomes smaller and smaller with fields in this nonlinear regime. At the phase boundary H_A, where the kink structure appears in R_{xx}, no remarkable structure is observed in R_{xy}. The field dependence, however, becomes linear again at $H > 18.5$ T, as indicated by the arrow, very close to H_A, as shown by the broken line. It should be noted that this line does not converge to the origin ($H = 0$, $R_{xy} = 0$). The slope is about one-fifth of that at low fields.

The band-structure calculation using the tight-binding approximation[13] predicts two bands at the Fermi level, which are determined from two carriers in a unit cell due

FIG. 1. The magnetic-field dependence of the Hall resistance R_{xy} of sample 1 of α-(BEDT-TTF)$_2$KHg(SCN)$_4$.
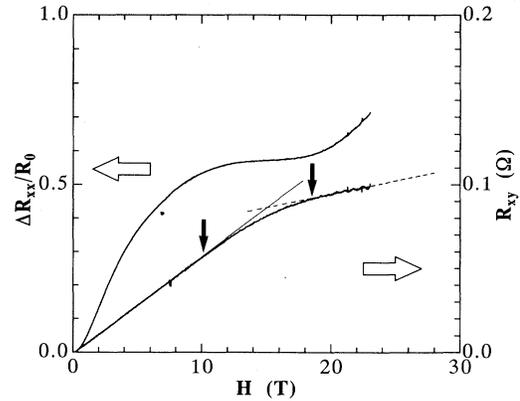

FIG. 3. The Hall resistance R_{xy} and magnetoresistance $\Delta R_{xx}/R_0$ of sample 1 at 4.2 K. The solid and broken lines show the H-linear dependence of R_{xy} in low and high fields.

to the charge transfer of one electron from two BEDT-TTF molecules to $KHg(SCN)_4$. The volume encompassed by the close orbit in the Brillouin zone corresponds to the carrier density of 0.38 holes in a unit cell at room temperature. This value is in good agreement with the value of 0.33 holes/unit cell obtained experimentally at about 1 K from the SdH effect.[14] Therefore we conclude that the phase transition at T_A should not be associated with a significant change in the volume of the closed Fermi surface, i.e., the corresponding carrier density.

The following qualitative model for the temperature dependence of the Hall coefficient is proposed on the basis of the experimental results. Above T_A, both bands exist and play each role in the metallic conduction. The small change of R_H can be understood by the two-carrier model[17] in terms of the different temperature dependence of the relaxation times. It is assumed that, at T_A, the SDW gap starts to open partially at the Fermi level due to the partial nesting of the sheetlike Fermi surface. The metallic conduction is carried mainly by carriers on the closed Fermi surface which is not affected by the SDW gap formation. The gap develops with decreasing temperature from T_A down to about 4 K, inducing large changes in R_H with temperature. Below about 4 K, the resultant reconstruction of the Fermi surface is completed, and then the Hall coefficient takes a constant value. According to this model, the conduction carrier density decreases below T_A, and the resistivity should show an enhancement. The very similar enhancement has already been observed in pure chromium. (See the recent review by Fawcett.[18]) Figure 4 shows the zero-field resistance plotted as a function of T^2, indicating that the relation $R = B + AT^2$ holds in $\sim 10 < T \lesssim 18$ K, where A and B are constant. The T^2 dependence has been seen in many other BEDT-TTF and TMTSF salts.[19] The resistance starts to deviate upward from the T^2 dependence at T_A. This feature is qualitatively consistent with the model mentioned above.

The similar phenomena of the Hall coefficient and the resistivity anomaly have been observed in a heavy fermion system URu_2Si_2.[20,21] The resistivity peak at 17 K is ascribed to the SDW formation. The Hall coefficient increases steeply below 17 K and becomes nearly constant around 2 K. The major part of the Fermi surface might disappear when the SDW gap(s) open(s), and the remaining carriers become superconducting below 1.5 K.

As shown in Fig. 3, the magnetic-field dependence of the Hall resistance at 4.2 K below T_A starts to deviate downward from the H-linear dependence above 10 T. The deviation means that the Hall coefficient becomes small with fields. At H_A, where the magnetoresistance shows the kink structure, the phase transition from the magnetic to normal-metal phases occurs. The nesting of the sheetlike Fermi surface might be removed at the boundary, according to the present SDW model and our phase diagram.[10] There appears to be a significant difference in R_{xy} between above T_A and above H_A, while the slope of R_{xy} above H_A is almost the same as that
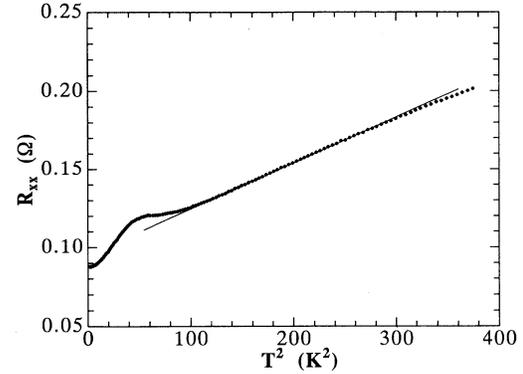

FIG. 4. The temperature dependence of the resistance in zero field, plotted as a function of T^2. The solid line shows the T^2 dependence.

above T_A. The reason for the different behavior in R_{xy} cannot be explained at present.

The magnetic-field regime between H_C ($\simeq 10$ T) and H_A ($\simeq 18.5$ T) is a nonlinear crossover regime between the low- and high-field ones. The linearity at low field below H_C indicates that any significant change does not occur in the band structure, while, in the nonlinear regime, the partial nesting of the sheetlike Fermi surface might be altered with fields. This change is expected to close the SDW gap in a manner due to the nesting. Thus the conduction carrier density would increase in this regime, leading to the negative slope of the magnetoresistance observed in the same field regime. In this way, the Hall resistance measurements could make clear the phase diagram determined by the magnetoresistance,[10] in order to understand how the Fermi surface relates to the phase transition.

In conclusion, the Hall resistance of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ is measured in both the magnetic and normal-metal phases. R_H increases steeply below the temperature of the phase boundary. In high fields above about 10 T, R_{xy} deviates from the linear behavior and shows the H-linear dependence again above H_A. The temperature and field dependence of the Hall coefficient and the shoulder-type anomaly of the resistance could lead us to a possible model for explaining the change of R_{xy} at the phase boundary, where the partial SDW gap(s) might open due to the nesting of the sheetlike Fermi surface, and the gap might alter with temperatures and fields. In order to discuss the Hall effect quantitatively, we need a comprehensive theory of the Hall resistance in a quasi-two-dimensional, two-band system.

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