Uniaxial Strain Effects on Transport Properties of a Supramolecular Organic Conductor $\theta$-(DIETS)$_2$[Au(CN)$_4$]

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(Received February 3, 2003)

Pressure-controlled switching between an insulating state and a superconducting state has been successfully realized on a supramolecular organic conductor $\theta$-(DIETS)$_2$[Au(CN)$_4$] [DIETS = diiodo(ethylenedithio)diselenadithiafulvalene]. Strong contact between iodine on the donor (DIETS) molecule and nitrogen on the anion [Au(CN)$_4$] generates characteristic uniaxial strain effects on transport properties. Under the ambient pressure, the present system undergoes a semiconductor–insulator transition at 226 K. The effect of strains parallel to the conduction plane (ab-plane) is very small. Even under uniaxial strains up to 20 kbar along the a- and b-axis directions, the transition is not suppressed. Surprisingly, however, the c-axis strain induces a superconducting state with $T_c$ of 8.6 K at 10 kbar. Band parameter calculation and the conductivity anisotropy ratio suggest that an increase in the bandwidth $W$ associated with a c-axis strain transforms the system to the metallic and superconducting states. In the metallic state under c-axis strain, the temperature ($T$) dependence of the Hall coefficient ($R_H$) and the Hall angle ($\theta_H$) is expressed as $R_H \propto T^{-1}$ and $\cot \theta_H \propto T^2$.

KEYWORDS: $\theta$-(DIETS)$_2$[Au(CN)$_4$], supramolecule, superconductor, uniaxial strain, resistivity, Hall effect

DOI: 10.1143/JPSJ.72.1014

Since organic materials are soft, they easily change their properties when subjected to pressure.1–3) The supramolecular organic conductor $\theta$-(DIETS)$_2$[Au(CN)$_4$] has a so-called $\theta$-type crystal structure (Fig. 1).4,5) The calculated band structure and Fermi surface are similar to those of other $\theta$-type salts. This material is characterized by the intermolecular interaction between the iodine atom on the donor molecule and the cyano group on the Au(CN)$_4$ anion. The I–N intermolecular distance (3.018 Å) is much shorter than the sum of van der Waals radii (3.53 Å). The I–N contacts form supramolecular chains 1 and 2 extending along the $2a = \pm b$ directions (Fig. 1). Under ambient pressure, this material is a semiconductor at high temperatures above 226 K, where a transition to an insulator occurs. This semiconductor–insulator transition is not suppressed under hydrostatic pressure. Only a shift of the critical temperature is observed from 226 K at ambient pressure to about 150 K at pressure $p = 18$ kbar.5)

However, conditions become different under uniaxial strain. In this work, we adopted a new experimental technique developed by Maesato et al.5,7) and examined the transport properties of $\theta$-(DIETS)$_2$[Au(CN)$_4$] under uniaxial strains along the a-, b- and c-crystal axes (refer to Fig. 1). We have found that the strong I–N contact causes unique pressure effects on the transport properties of this crystal.

Samples were immersed in an epoxy liquid (Stycast 1266/ A). Then the epoxy containing the samples was molded into a cylindrical shape and was placed in the cylinder of a clamp-type pressure cell. Uniaxial strain was induced by compressing it in one direction. This process is essentially the same as that described by Maesato et al.5,7) The relation between the pressure applied on the epoxy and the strain was checked using a strain gauge. In the experiment, we measured resistance and Hall voltage as functions of temperature and magnetic field. A conventional dc method with 6 probes was adopted. The current was applied along the a-axis and the magnetic field normal to the ab-plane.

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parallel to the conduction plane (ab-plane). Under ambient pressure, this material shows a semiconductor-insulator transition at 226 K. One can see that the transition temperature is lowered with increasing strains along both the a- and b-axes (Fig. 2). Even under the pressure of 20 kbar, the transition is not suppressed. The semiconducting temperature is only extended to about 150 K. The temperature dependence of the carrier density gives the energy gap $\varepsilon_g$ in the semiconducting state and the insulating state (inset of Fig. 2). The energy gap in the semiconducting state, for example, changes from about 100 meV under ambient pressure to about 60 meV at the b-axis strain of 10 kbar. In the insulating state, $\varepsilon_g$ decreases from about 1.3 eV to about 540 meV.

Under the c-axis strain, on the other hand, a qualitatively different transport phenomenon is observed. As shown in Fig. 3, the c-axis strain suppresses the transition. The system clearly exhibits a metallic behavior. Under the strain of about 5 kbar, for example, although we find a remnant of the insulator transition at about 220 K, the resistivity decreases by lowering the temperature from 300 K to 30 K. This suggests that there are two metallic states, M1 (above 220 K) and M2 (from 200 K to 30 K). The upturn of the resistivity is observed at 30 K.

The most important phenomenon we note in Fig. 3 is an abrupt drop in the resistance in the lowest temperature region under the strain above 6.5 kbar. The drop of the resistance below 2 K is recognized in the data at $p_c = 6.5$ kbar. In the sample under $p_c = 10$ kbar, the anomaly becomes apparent at a higher temperature ($T_c = 8.6$ K) and we can see the drop up to $p_c = 20$ kbar ($T_c < 2$ K). This anomaly is sensitive to the magnetic field, as demonstrated in the inset of Fig. 3. Based on these observations, we ascribe this drop of the resistance to the appearance of the superconducting state.

Let us consider the effects of uniaxial strain on this material. In the conventional $\theta$-type salts, the electronic state is governed by the dihedral angle between adjacent donor molecules interrelated by transfer integral $q$ in Fig. 1. This dihedral angle affects the transfer integral $q$ and thus the bandwidth. If the present salt were the conventional $\theta$-type, the a-axis strain would increase the dihedral angle and reduce the bandwidth, while the b-axis strain would work oppositely. The strong donor-$\cdots$anion linkage through the I-$\cdots$N contact, however, would not allow such changes of the dihedral angle in the present system (Fig. 1). Therefore, the uniaxial strain within the ab-plane is not effective (Fig. 2). Under the c-axis strain, the other hand, the supramolecular chains 1 and 2 formed by the I-$\cdots$N contact would slide into each other along c-axis. If there were no supramolecular chain, the c-axis strain would only reduce the distance between the conduction layer and the anion without causing significant structural changes within the conduction layer. In order to analyze the effect of the structural change on the conduction band, we have performed a calculation which simulates the variation of the transfer integral $q$ and bandwidth $W$ when the distance between chains 1 and 2 is decreased by $\Delta$. This calculation was performed for the 16 K structure. Figure 4 confirms that the transfer integral $q$ is enhanced under c-axis strain. When the $\Delta$ value is 0.5 Å, for example, about a 20% increment in the transfer integral $q$ is elicited. The bandwidth $W$ increases by about 7%.

We have roughly checked the increase in $q$ under c-axis strain, with the conductivity anisotropy ratio $\sigma_a/\sigma_b$, within the ab-plane at room temperature. Under the c-axis strain, the anisotropy ratio decreases monotonically from $\sigma_a/\sigma_b \sim 3.3$ under ambient pressure to $\sigma_a/\sigma_b \sim 1.8$ under strain $p_c = 10$ kbar. This suggests the enhancement of $q$. It is well known that the two-dimensional system with $q \gg p$ has the
isotropic conductivity ratio \( \sigma_d/\sigma_b = 1 \). In the systems with \( q \ll p \), on the other hand, the conductivity anisotropy ratio within the conduction plane is large. It should be added that both the \( a \)- and \( b \)-strains affect \( \sigma_d/\sigma_b \) weakly.

It is of interest to compare the above simulation with that for other \( \theta \)-type salts. In \( \theta-(\text{BEDT-TTF})_2[\text{RbCo(SCN)}_4] \), for example, the \( \Delta \)-dependence of \( q \) is small, as shown in Fig. 4. This means that the strain along the interlayer direction does not greatly affect the resistivity in conventional \( \theta \)-type salts. A comparison with conventional \( \theta \)-type salt suggests that the larger shift of the donor molecule along the long molecular axis in the pristine crystal structure of \( \theta-(\text{DIETS})_2[\text{Au(CN)}_4] \) (Fig. 4) causes a loss of the intermolecular overlap of HOMOs. The increase in \( \Delta \) effectively enhances overlap of \( S \) and \( Se \) atoms in the five-membered rings with large coefficients of the HOMO in \( \theta-(\text{DIETS})_2[\text{Au(CN)}_4] \).

Another issue that we must consider is an enhancement of the interlayer interaction. Although the interlayer interaction is enhanced by the \( c \)-axis strain, this material is still quite two-dimensional even under strain \( p_c = 10 \text{kbar} \). The conductivity anisotropy ratio \( \sigma_d/\sigma_a \) under strain \( p_c = 10 \text{kbar} \) is more than 1000 at low temperatures.

All these results lead us to the conclusion that the increase in the bandwidth \( W \) of the two-dimensional band under the \( c \)-axis strain gives rise to metallic and superconducting states. This indicates that we can intentionally control various transport properties of the supramolecular organic conductor \( \theta-(\text{DIETS})_2[\text{Au(CN)}_4] \) by the uniaxial strain method, as summarized in a tentative diagram in Fig. 5.

We mention here briefly the effects of hydrostatic pressure. Although the semiconductor–insulator transition is not suppressed under hydrostatic pressure up to 18 kbar, the behavior of the resistivity under the hydrostatic pressure of 18 kbar is similar to that under \( c \)-axis uniaxial strain of 2 kbar (Fig. 3).\(^4\) It is well known that the effects of strain in the hydrostatic pressure method are smaller than those in the uniaxial strain method. We expect the appearance of the metallic state “M2” and/or superconductivity under high hydrostatic pressure of more than 20 kbar.

Lastly, an anomalous Hall effect under the \( c \)-axis strain is described. To clarify the transport property under \( c \)-axis strain, we have investigated the temperature dependences of the Hall coefficient \( R_H \) and the Hall angle \( \theta_H \) which is defined as \( \cot \theta_H = \rho H/R_H \) mainly in the metallic state “M2” below 200 K. Under the magnetic field used in this experiment (1 T), the Hall coefficient in the M2 state is field-independent.

The results are given in Fig. 6. The Hall coefficient \( R_H \) is found to be positive below 200 K indicating the dominant carrier to be the hole. In the insulating (“I1”) state below 226 K under ambient pressure and the nonmetallic (“I2”) state below 30 K under the strain \( p_c = 5 \text{kbar} \), temperature dependence of the Hall coefficient is enhanced by the decreasing the carrier density with decreasing temperature. An important finding in this experiment is the strong temperature dependence of the Hall coefficient \( R_H \) in the metallic phase (“M2”). In a usual metal, the Hall coefficient is temperature-independent. Under strain \( p_c = 10 \text{kbar} \), however, for example, \( R_H \) increases by about one order of magnitude from about 0.02 cm\(^2\) s\(^{-1}\) at 200 K to about 0.3 cm\(^2\) s\(^{-1}\) at 8 K.

For a single carrier system with an isotropic energy band, the Hall coefficient gives the carrier density \( n = |e|en \). In this assumption, our result indicates that the carrier density in the M2 phase decreases by about one order of magnitude with decreasing temperature. At low temperature, the system is in a state with a low carrier density of about \( 2 \times 10^{19} \text{ cm}^{-3} \). However, it is difficult to expect that such a
low-carrier-density state exhibits superconductivity. Therefore, in the present system, the temperature dependence of the Hall coefficient $R_H$ would not be due to the change in the carrier density.

Notably, the Hall coefficients in the metallic states for the three c-axis strains ($p_c = 5, 6.5$ and $10$ kbar) are expressed as $R_H \propto T^{-1}$. The same relation ($R_H \propto T^{-1}$) is reported for the two-dimensional high-$T_c$ cuprates$^{10–12}$ and organic superconductor $\kappa$-type salts.$^{13,14}$ According to the theoretical works by Kontani et al., the behavior of the antiferromagnetic (AF) correlation length $\xi_{AF}$ exhibits the temperature dependence of the Hall coefficient ($R_H \propto \xi_{AF}^2 \propto T^{-1}$).$^{15,16}$ The Hall angle $\theta_H$ is described as $\cot \theta_H = \alpha T^2 + C$ (all data on the complicated behavior of both the resistivity and the Hall coefficient is expressed well by the Hall angle $\theta_H$).

Surprisingly, we found that the quadratic temperature dependence $\cot \theta_H = \alpha T^2 + C$ also holds for the present system. The data is plotted in the inset of Fig. 6 as a function of $T^2$.

However, we should emphasize that the present system is not in the AF state. The insulator transition at $226$ K under ambient pressure is probably due to charge disproportionation. In fact, many $\theta$-type crystals have been reported to exhibit a charge ordering state.$^{17,18}$ Some superconductivity mediated by the charge fluctuation is also reported.$^{19}$ If this material is such a material, the behavior shown in Fig. 6 ($R_H \propto T^{-1}$ and $\cot \theta_H \propto T^2$) is possibly a general characteristic of the transport property for a strongly correlated system. The strain dependences of the Hall coefficient and the slope of $\cot \theta_H$ may be explained to be due to the changes in the carrier density and the bandwidth. More elaborate experiments and theoretical studies are necessary to clarify the mechanism of this unusual transport property.

In conclusion, we have revealed the following unique strain effects on the transport properties of the supramolecular organic conductor $\theta$-(DIETS)$_2$[Au(CN)$_2$] with strong intermolecular $1\cdots N$ contact. (1) The strains parallel to the conduction plane ($p_c$ and $p_d$) do not significantly affect the semiconductor–insulator transition up to $20$ kbar, which is different from the case of the conventional $\theta$-type salts. Probably, the strong donor–anion linkage hinders the change of the dihedral angle between adjacent donor molecules and leads to this behavior. (2) The c-axis strain ($p_c$), perpendicular to the conduction plane, readily suppresses the semiconductor–insulator transition and induces the superconducting transition. The band parameter calculation and the conductivity anisotropy ratio suggest that the metallic and superconducting states induced by the c-axis strain are due to the increases in the bandwidth $W$. (3) The metallic (M2) state under the c-axis strain exhibits the transport property characterized by the relations $R_H \propto T^{-1}$ and $\cot \theta_H = \rho H/R_H \propto T^2$, which is similar to the case of the high-$T_c$ cuprates.

Further investigation will lead us to interesting phenomena derived from the strong correlation associated with the charge disproportionation. This work was partially supported by a Grant-in-Aid for Scientific Research (Nos. 14740223, 14740390 and 14204033) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. One of the authors (T.I.) also thanks the Forum on Iodine Utilization.

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