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LOW TEMPERATURE PHYSICAL PROPERTIES OF THE ORGANIC CONDUCTOR, (DIMET)$_2$I$_3$ AFTER THERMAL TREATMENT

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Abstract

The effect of thermal treatment on the electrical conductivity was studied for a quasi-one-dimensional organic conductor, (DIMET)$_2$I$_3$ (DIMET=dimethyl(ethylenedithio)tetrathiafulvalene). After heating the samples up to a temperature between 340 and 370 K, the electric resistivity was measured at low temperature down to 2 K and under pressure up to 1.6 Gpa. (DIMET)$_2$I$_3$ shows irreversible decrease in the electric resistivity between 350 and 356 K on heating. It was found that the heating above 350 K suppresses the spin-density-wave transition at 40 K and another metal-insulator transition appears at 18 K.

Keywords: electric resistivity, quasi-one-dimensional organic conductor, spin-density-wave, temperature-pressure phase diagram, TG-DTA

Introduction

It is well known that many varieties of molecular-based organic conductors show not only metallic physical properties but also superconductivity. The nature of free charge carriers (electrons and/or holes) is, however, very different in the organic conductors from that in conventional metals and superconductors. Remarkable features of the electronic system of the organic conductors are its low dimensionality and rather strong on-site Coulomb energy (U). (DIMET)$_2$I$_3$ is one of such unconventional metals. Molecules of an organic donor, DIMET (dimethyl(ethylenedithio)tetrathiafulvalene) stack along the b-axis of the crystal and a quasi-one-dimensional (Q1D) electronic system is formed by weak and anisotropic overlap of HOMO of DIMET molecules. The 2:1 stoichiometry of the donor and the anion gives the 3/4-filled conduction band. The

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dimerization of DIMET along the *b*-axis splits the band into the fully filled lower and half-filled upper ones. An electronic system is known to change from metallic state to Mott insulating one when U/W becomes large (>>1) in the half–filled system. Although the electric resistivity of $(DIMET)_2I_3$ is metallic below room temperature as is predicted by the tight-binding band calculation, we believe that W and U are comparable to each other in this system. Indeed an isostructural salt, $(DIMET)_2AuI_2$ is semiconducting below room temperature and considered to be in Mott insulating state. A half-filled band is realized in many organic conductors due to their chemical composition and the dimerization of the organic molecules. Since the band-filling is a crucial factor for electronic systems having a narrow bandwidth, it is interesting to investigate what occurs if the band-filling is changed in the organic conductors as in high-T_c superconductors.

Recently we found that the electric resistivity of the Q1D conductors including the DIMET salts show irreversible rapid decrease on increasing temperature around 350 K on heating [1]. Since the electrical conduction occurs in the donor column, the rapid decrease in the resistivity is not due to decomposition of the donor column. The TG-DTA measurement suggests that the serious decomposition of these organic conductors occurs between 400 and 450 K [1]. The slight decrease of the mass was, however, observed in the TG curves below 400 K. This suggests that occurrence of partial escape of the anions from the crystal and resulting change in the band-filling. Namely, for example, if $2I_3^-$ in $(DIMET)_2I_3$ escapes as $3I_2$ leaving $2e^-$ in the crystal, it is probable that the band-filling increases from 1/2 and low temperature physical properties also change drastically. In this study, we investigate the effect of thermal treatment and the possible change in the band-filling on the electronic state of $(DIMET)_2I_3$ at ambient pressure and under pressure.

Experimental

The method of sample preparation is described elsewhere [2]. The electric resistivity was measured by the DC four-probe method along the most resistive *c**-axis for better reproducibility. Annealed gold wires were attached as the electrodes on the opposing crystal surface (//*ab*) with carbon paste (XC-12, Fujikura-kasei Co.). The carbon paste itself survives well above 500 K as was checked by using chromel wire as a sample.

TG-DTA was carried out using a commercial system (TAS 100 with a TG unit (Thermoxflex TG8110), Rigaku Co.). Powdered sample (0.66 mg) was exposed in the flow of N_2 gas (50 mL min^{-1}) and temperature was changed with the rate of 5 K min^{-1}.

The thermal treatment was carried out by heating each single crystal with a heater in vacuum (<10^{-3} Pa) up to a target temperature by 20 K h^{-1} with measuring the resistivity. The heater power was turned off after the target temperature was achieved. Low temperature measurement of the resistivity was carried out both at ambient pressure and under hydrostatic pressure up to 1.63 GPa at low temperature. The pressure cell and the method to determine the pressure at low temperature are detailed in the literature [3].

Results and discussion

Thermal treatment

Figure 1 shows the temperature dependence of the normalized resistivity of $(DIMET)_2I_3$ on the thermal treatment between 340 and 370 K for five samples (#1–5). Heating up to 350 K does not seem to change the resistivity very much (#1 and #2). The resistivity decreases above 350 K as was observed for that measured along the *b*-axis (#3–5) [1]. A sharp minimum at 361 K and another maximum were also observed for the sample heated up to 370 K (#5). The room temperature resistivity after the thermal treatment is lower for the sample heated up to higher temperature.

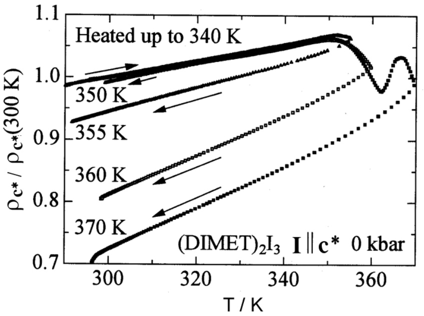

Fig. 1 The normalized electric resistivity of $(DIMET)_2I_3$ above room temperature up to 340 (#1), 350 (#2), 355 (#3), 360 (#4) and 370 (#5), respectively

The TG-DTA curves are shown in Fig. 2 [1]. A rapid decrease in the mass and a sharp exothermic peak are seen at about 460 K, respectively. Thus $(DIMET)_2I_3$ is considered to decompose completely above T_d=460 K, while the electric resistivity becomes unmeasurable above 370 K. This is probably due to the deterioration of the crystal surface because the shiny surface becomes rough by heating.

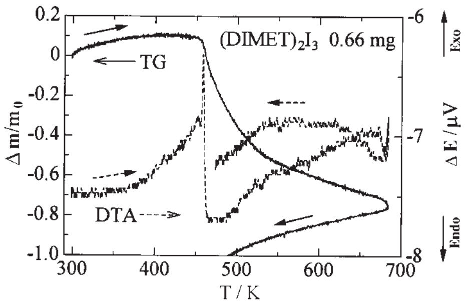

Fig. 2 TG-DTA curves for $(DIMET)_2I_3$

Irreversible decrease in the electric resistivity above 350 K

There are two possible explanations for the irreversible rapid decrease in the resistivity above 350 K. The first explanation directly takes into account the band-filling. Since I_3^- leaves the electron on its escape, the filling of the Q1D band will be increased by heating. When one assumes the following dispersion relation that is expected for the Q1D metals with dimerized donor stacks along the *a*-axis,

$$E=\pm\sqrt{t_{a1}^2+t_{a2}^2+2t_{a1}t_{a2}\cos(k_a a)}+2t_b\cos(k_b b) \qquad (1)$$

singularities of the density of states will appear as in the inset in Fig. 3. Here t_{a1} and t_{a2} are alternating transfer integrals along the most conducting *a*-axis and t_b is that along the second conducting *b*-axis; *a* and *b* are lattice constants; k_a and k_b are wave numbers. Note that the dispersion along the least conducting ***c***-axis is ignored and the relation between ***a*** and ***b*** are changed in $(DIMET)_2I_3$. One can calculate numerically the electric conductivity tensor, σ from Eq. (1) by solving the Boltzmann equation within the semiclassical relaxation time approximation [4].

$$\sigma_{xx}=-\frac{e^2\tau}{2\pi^2 c}\int v_x v_x\left(\frac{\partial f}{\partial E}\right)\mathrm{d}k_a\mathrm{d}k_b,\quad v_x=v_a+v_b\cos(\pi-\gamma) \qquad (2)$$

where τ is the relaxation time; *c* and γ are lattice constants; *f* is the Fermi distribution function; v_a and v_b are carrier velocity components calculated as $v_i=(1/h)(\partial E/\partial k_i)$. Figure 3 shows the inverse of the *xx*-component of the calculated conductivity as a function of the filling of the upper band, *n* at 10 and 400 K, respectively, by assuming realistic magnitude of the transfer integral as t_{a1}=176 meV, t_{a2}=144 meV and t_b=16 meV. The inverse conductivity increases when *n* increases from the half-filling *n*=0.5. An anomaly appears when *n* passes the singularity at about 0.7. The anomaly seems more distinct at higher temperature due to the broadening of $\partial f/\partial E$ but the present calculation does not reproduce the decrease in the resistivity.

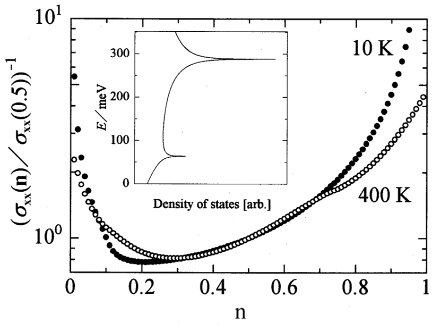

Fig. 3 The band-filling dependence of the *xx*-component of the calculated electric conductivity tensor a dimerized Q1D metal. The inset shows the density of states of the upper band

Another explanation is based on the chemical pressure effect by the anion escape. The gradual increase in ΔE above 350 K in Fig. 2 suggests the occurrence of a kind of chemical reaction that decreases the mass little. No structural data have not been obtained for the heated (DIMET)$_2$I$_3$. Almost the same but slightly smaller lattice parameters were, however, observed for an isostructural organic superconductor (DMET)$_2$I$_3$ (DMET = dimethyl(ethylenedithio)diselenadithiafulvalene) after heating up to 370 K as compared with the virgin sample [5]. Since (DMET)$_2$I$_3$ also shows the same kind of irreversible decrease in the electric resistivity as in (DIMET)$_2$I$_3$ at high temperature [1], such shrink of the crystal lattice is also expected for (DIMET)$_2$I$_3$. Then the packing of the donors will be densified and the resistivity will decrease as is often observed on applying pressure.

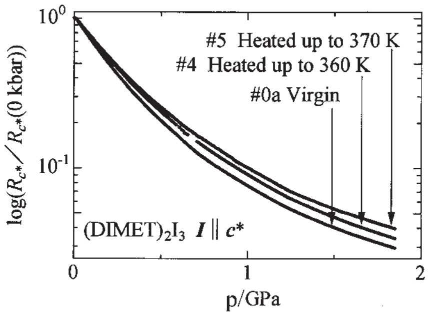

Fig. 4 Pressure dependence of the c^*-axis resistivity of (DIMET)$_2$I$_3$ at room temperature for the virgin sample (#0a) and those heated up to 360 (#4) and 370 K (#5), respectively

The pressure dependence of the resistivity shows that the heated crystals have already shrunk a little before pressurizing. The result at room temperature is shown in Fig. 4 for a virgin (#0a) and the samples heated up to 360 (#4) and 370 K (#5), respectively. The pressure was increased stepwise after measuring the temperature dependence of the resistivity. The absolute value of the resistivity was corrected to exclude the small influence of the difference in 'room temperature'. The pressure dependence is smaller for the sample heated up to higher temperature. This is just what expected when the anion escapes.

Electric resistivity below 300 K

The low temperature resistivity is shown for the five thermally treated samples (#1–5) and another virgin one (#0b) in Fig. 5. The rapid increase in the resistivity at T_{SDW}=40 K was observed for the virgin, 340 and 350 K-samples (#0b, #1 and #2) and this is due to the spin-density-wave (SDW) transition reported previously [2, 6]. It was found that the thermal treatment above 355 K seems to suppress the SDW transition but causes another metal-to-insulator (M–I) transition at $T_{\mathrm{M-I}}$=18 K (#3–5). This is the evidence that the thermal treatment changes not only the resistivity but also the

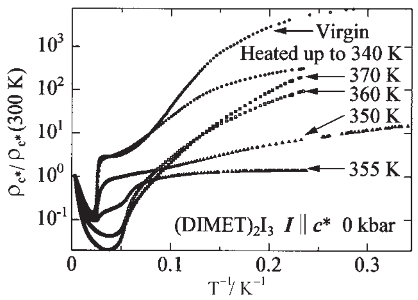

Fig. 5 Normalized electric resistivity of the virgin (#0b) and the heated samples (#1:340, #2:350, #3:355, #4:360, #5:370 K) of (DIMET)$_2$I$_3$

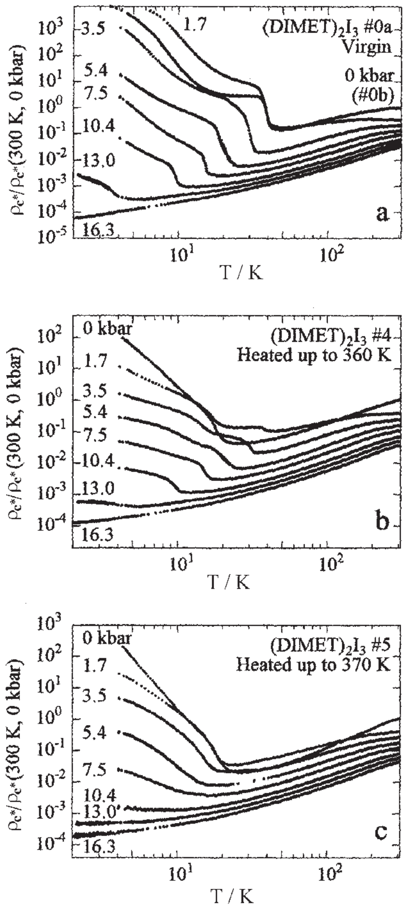

Fig. 6 Temperature dependence of the resistivity of (DIMET)$_2$I$_3$ at 0 GPa and under pressure for the virgin sample (a, #0a and #0b) and those heated up to 360 K (b, #4) and 370 K (c, #5), respectively

electronic state of $(DIMET)_2I_3$. It is important that there exists no intermediate state having the M-I transition temperature between 18 and 40 K. This probably discards the possibility of continuous change in the band-filling by the thermal treatment, at least, for $(DIMET)_2I_3$.

The measurement under hydrostatic pressure was carried out for two of the thermally treated samples (#4 and #5) with the virgin sample (#0a) simultaneously (Fig. 6). The magnitude of the pressure indicated in Fig. 6 is that at lowest temperature except for 0 GPa. The SDW transition, which is observed as the upturn of the resistivity, is suppressed between 1.30 and 1.63 GPa as was reported previously (#0a) [2]. The upturn of the resistivity of #4 and #5 is also suppressed by pressure.

It was found that the resistivity of #4 shows another anomaly around 40 K in addition to that at T_{M-I}=17 K at 0.17 GPa as in Fig. 6b. This stepwise increase in the resistivity on cooling was also observed at 0.35 and 0.54 GPa. The temperature of the new anomaly is very close to T_{SDW} of the virgin sample at each pressure in Fig. 6a. This implies that, in #4, there remains a kind of domain unchanged by the present thermal treatment up to 360 K. Since the temperature of the resistivity upturn is almost the same for #0b and #4 above 0.74 GPa, the upturn for #4 in this pressure range is due to the SDW transition that occurs in the unchanged domain. On the other hand, $(DIMET)_2I_3$ is considered to be almost fully changed by heating up to 370 K and the M–I transition is suppressed above 1.0 GPa as shown for #5 in Fig. 6c.

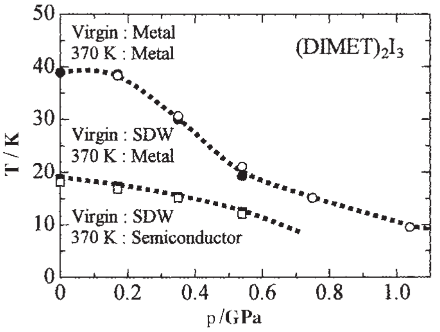

Fig. 7 Temperature-pressure phase diagram of $(DIMET)_2I_3$ before and after heat treatment. Open and close circles denote the SDW transition temperatures from #0a and #4, respectively. Open and closed squares denote the M-I transition temperatures from #5 and #4, respectively. The broken curves are guide to eye

The temperature-pressure phase diagram in Fig. 7 was made by determining T_{SDW} and T_{M-I} as temperature of peaks in the numerical derivative of the Arrhenius plot of the electric resistivity in Fig. 6. Closed circles (T_{SDW}) and closed squares (T_{M-I}) are from #0a and #5, respectively. Open circles and open squares are determined from #4 and coincide with the closed circles and the closed squares, respectively, as is expected from the assumption that the higher temperature anomalies of the resistivity in Fig. 6b at 0.17, 0.35 and 0.54 GPa are due to remaining domain unaffected by heating. It is unclear whether the new M–I transition is the same kind as the SDW transition that occurs in the virgin sample because the anion escape probably results in the change in the band-filling as well as the bandwidth by the shrink of the crystal, and furthermore the nesting condition of the Q1D Fermi surface.

Conclusions

We studied the effect of thermal treatment on the electronic state of $(DIMET)_2I_3$ by changing the heating temperature between 340 and 370 K. Rapid decrease in the resistivity was observed between 350 and 356 K and this is probably explained by the small shrink of the crystal lattice by the possible anion escape. The heating above 355 K suppresses the SDW transition at 40 K and a new M–I transition becomes to occur at 18 K. The new M–I transition in the heated sample is suppressed by pressure above 1.0 GPa, while the SDW transition of the virgin sample survives even above 1.6 GPa. The present study shows that the electronic state of $(DIMET)_2I_3$ is irreversibly controlled by the thermal treatment.

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5 The lattice parameters of $(DMET)_2I_3$ are a=6.703 Å, b=7.752 Å, c=16.254 Å, α =94.85°, β=105.92°, γ=78.25° and V=794.8 Å^3, respectively. (M. Z. Aldoshina, L. O. Atovmyan, L. M. Gol’denberg, O. N. Krasochka, R. N. Lyubovskaya, R. B. Lyubovskii and M. L. Khidekel’, Dokl. Akad. Nauk SSSR 289 (1986) 1140 (in Russian); Phys. Chem., 289 (1986) 689. (English translation)) We determined the lattice parameters after heating the sample up to 370 K as a=6.726 Å, b=7.750 Å, c=16.273 Å, α =95.55°, β=106.67°, γ=76.97° and V=791.7 Å^3, respectively.

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