Effect of Hydrostatic Pressure on Molecular Conductors, Pd(dmit)$_2$ Salts


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Abstract

A series of molecular conductors \( \beta^-\text{(cation)}[\text{Pd(dmit)}_2] \) (cation = Et$_2$Me$_2$P and Me$_2$P) exhibit various complicated pressure-induced phenomena. Resistivity measurements under high pressure up to 8 GPa have been carried out using a clamp-type piston-cylinder cell and cubic anvil type high pressure apparatus. The Et$_2$Me$_2$P salt shows non-metallic phases at low and high pressure regions, between which a metallic phase appears. The application of pressure suppresses the low-temperature resistivity of this salt. However, the non-metallic behavior still remains at low temperature under 8 GPa. For the Me$_2$P salt, the metal-to-non-metal transition temperature reaches a minimum at 0.83 GPa and turns to increase with increasing pressure up to 8 GPa, showing no metallic state at low temperature.

Keywords: Organic conductors based on radical anion salts, conductivity, Metal-Insulator transition

1. Introduction

The soft nature of organic materials makes the high-pressure experiments efficient in studying their physical properties. The organic conductors such as \((\text{TMTTF})_2X^\prime\) and \((\text{BEDT-TTF})_2X^\prime\) salts are known to exhibit various physical properties depending on the pressure [1]. Upon these compounds, strongly correlated electrons play an important role. In general, the pressure generally weakens the electron correlation by reducing the ratio of the on-site Coulomb energy to the bandwidth, localized electrons in a Mott insulator, originating from strong Coulomb repulsion between the conduction electrons, are expected to itinerate under high pressure. Substitution of anion \(X\) has an effect similar to the pressure. Sometimes this effect is called a chemical pressure effect.

A family of two-dimensional organic conductors, \( \beta^-\text{(cation)}[\text{Pd(dmit)}_2] \) (dmit = 1,3-dithiol-2-thione-4,5-dithiolate; cation = Me$_2Z^\prime$, Et$_2$Me$_2Z^\prime$; \( Z = P, As, Sb \)) have been synthesized and investigated for years because these salts show a wide variety of physical properties induced by pressure [2-6]. For instance, \( \beta^-\text{Et$_2$Me$_2$P[Pd(dmit)$_2$]}\) is an insulator with activation energy of 500 K at ambient pressure and is easily metallized by applying pressure of 0.6 GPa. When the metallic state is stabilized, \( *\text{Corresponding author. Tel.: +81-48-467-4504. E-mail address: yshiti@riken.jp} \) superconductivity appears below 4 K. Moreover, with further increase of pressure above 1.2 GPa, another non-metallic state (non-metal II) appears and this non-metal II phase is retained up to 2.0 GPa [5]. On the other hand, small cation salt, the Me$_2$P salt is insulating at low temperature under hydrostatic pressure up to 1.5 GPa [2]. These salts are considered to be Mott insulators at ambient pressure. However, the cation dependence cannot be explained by the simple chemical pressure effect. We have carried out resistivity measurement of both Et$_2$Me$_2$P and Me$_2$P salts under high-pressure up to 8.0 GPa. In these experiments, a cubic anvil type high pressure apparatus equipped with a cryostat was used [7]. This technique is the same as used in the recent discovery of the superconducting transition above 14 K in \( \beta^-\text{(BEDT-TTF)$_2$ICl$_2$} \) under 8 GPa by Taniguchi et al. [8].

2. Experimental

Single crystals of \( \beta^-\text{Et$_2$Me$_2$P[Pd(dmit)$_2$]}\) and \( \beta^-\text{Me$_2$P[Pd(dmit)$_2$]}\) were prepared by the air oxidation method as described elsewhere [3].

High-pressure resistivity measurements under the pressure range \( P < 1.5 \text{ GPa} \) were performed using a simple clamp-type piston-cylinder high-pressure cell [9]. Actual pressures at low temperatures were determined by
measuring the superconducting transition temperature of tin set in the pressure cell together with the sample. The pressure dependence of the superconducting transition temperature of tin is known to be highly accurate. Primary and secondary coils for ac susceptibility measurements were wound directly around the tin manometer. Resistivity measurements over the pressure range 1.5 < P < 8 GPa were carried out by means of the cubic anvil type high pressure apparatus combined with the liquid helium cryostat. In this pressure system, the pressure was kept constant during heat cycles. A schematic drawing of the cubic anvil type high pressure apparatus is shown in Fig. 1. A cubic-shaped pyrophylite case as a gasket was placed in the center of the anvils. In order to generate a homogeneous quasi-hydrostatic pressure at low temperature, Teflon cell in which the sample with a pressure transmitting fluid was used and was surrounded by the cubic-shaped gasket. A 1:1 mixture of Fluorinert FC-70 and FC-77 was used as the pressure transmitting fluid. The resistivity was measured by means of the standard dc four-probe technique with current parallel to the crystallographic b-axis. As the electrical leads, four Au wires of 15 μm diameter were attached to the sample with carbon paste.

3. Results and Discussions

3.1. \( \text{Li}_2\text{Me}_2\text{P} \) salt

Figure 2 shows the resistivity of \( \text{Li}_2\text{EHMe}_2\text{P}[\text{Pd(dmit)H}]_2 \) as a function of temperature at various pressures. The low temperature non-metallic behaviour was observed, showing resistivity gradually decreasing with increasing pressure. The metal-to-non-metal transition temperature \( T_{\text{MN}} \) is defined by the resistivity minimum also slightly decreased with increasing pressure. Figure 3 is a logarithmic plot of the resistivity versus the reciprocal temperature for \( \text{Li}_2\text{EHMe}_2\text{P}[\text{Pd(dmit)H}]_2 \) under various pressures. The simple thermal activation model cannot explain the results. The resistivity behaviour deviates from the activation type at low temperatures. To understand the general tendency of the pressure effect, we here estimate the energy gap by linear fitting for the plot of \( \ln R \) vs. \( 1/T \) at the range of \( 1/T_{\text{MN}} < 1/T < 0.02 \) (Fig. 3). The energy gap \( E_{\text{g}} \) obtained for the \( P = 2 \) GPa data. It decreases with increasing pressure to 2.96 K at \( P = 8 \) GPa at an average rate \( \Delta E_{\text{g}} / \Delta P = -1.8 \) K / GPa. From the linear extrapolation, we expect that \( E_{\text{g}} \) will vanish at 9.6 GPa.

The pressure-temperature phase diagram is shown in Fig. 5 (a). The phase boundary in the low pressure region is based on Ref. 5. As mentioned above, \( T_{\text{MN}} \) lowers only gradually with increasing pressure. Even above 2 GPa, \( T_{\text{MN}} \)
stays above 100 K and seems to approach a finite value. This is not expected for the usual suppression of the Mott insulating state in organic materials, as observed in the low-pressure region here.

3-2. Me₃P salt

Temperature dependence of resistivity of the β'-Me₃P[Pa6(dmit)₂] salt under various pressures up to 1.5 GPa is shown in Fig. 4 (a). At ambient pressure, temperature dependence of resistivity can be explained well with the activation model. Metallic behaviour was observed above 0.5 GPa. The metal-to-non-metal transition temperature T_mn decreased with applying pressure up to 0.8 GPa, followed by an up-turn around 1 GPa (Fig. 5 (b)). Figure 4 (b) shows the temperature dependence of the resistivity for the Me₃P salt obtained by the use of the cubic anvil apparatus. Up to 8.0 GPa, T_mn increased with increasing pressure, whereas the resistivities below T_mn were suppressed by the pressure. We have estimated the energy gap E_g of Me₃P salt; E_g/k_B = 746 K is obtained for the P = 2.5 GPa data. It decreases with pressure up to 8 GPa at an average rate d(E_g/k_B)/dP = -110 K / GPa.

3-3. Discussion

Fig. 4. Temperature dependence of resistivity of β'-Me₃P[Pa6(dmit)₂] at various pressure obtained by use of (a) the piston cylinder type apparatus, and (b) the cubic anvil type apparatus. The inset of (a) is a magnification around anomalies.

Fig. 5. Pressure-temperature phase diagram of β'-Et₂Me₃P[Pa6(dmit)₂] and β'-Me₃P[Pa6(dmit)₂]. Open circles are T_mn obtained by use of the cubic anvil. Closed circles are TMN obtained by use of the piston cylinder. The low-pressure data for β'-Et₂Me₃P[Pa6(dmit)₂] are based on Ref. 5.
According to the high pressure X-ray structure analyses for the Et$_3$Me$_2$P salt, a structural transition was recognized at low temperature under 2 GPa [10]. The low temperature structure is characterized by alternating arrangement of two non-equivalent layers of \([\text{Pd(dmit)}]_2\) layers. One of the layers is suggested to afford partial nesting of the Fermi surface, on the basis of tight-binding band calculations [10]. The non-metallic behaviour of the Et$_3$Me$_2$P salt above 1 GPa would be related to this change in the band structure.

The stability of the metallic state at low pressures (< 1 GPa) is ruled basically by the band width. It has been argued that the degree of magnetic frustration, arising from the quasi-triangular arrangement of the spin-1/2 dimers, \([\text{Pd(dmit)}]_2\), also affects the stability of the metallic state, because the paramagnetic insulating state is relatively destabilized by the frustration [11]. The Me$_2$P salt is less frustrated than the Et$_3$Me$_2$P salt. The difference in the phase boundary at the low pressures range between the two salts can be related to this structural character of the two salts, though the band width also increases by applying pressure.

Unlike the Et$_3$Me$_2$P salt, the low temperature metallic region separating the non-metal I and II is absent in the Me$_2$P salt. To explain this cation dependence of the electronic properties, the variation of the Fermi surface due to the broken symmetry at a high pressure should be taken account of, particularly for the non-metal II phase. The structural difference, referring to the lattice anisotropy, is significant at low pressures, which is related to the band width and frustration. It seems that the two non-metallic phases in the Et$_3$Me$_2$P salt merge into one in the Me$_2$P salt. However, as the slope of the resistivity at low temperatures (Fig. 4) suggests, the electronic state should be different in the low and high pressure regions even in the Me$_2$P salt. There should be competition between the two non-metallic state in the intermediate pressure region near the dip of $T_{\text{c}}$ in Fig. 5 (b). To understand this pressure-induced phenomenon more clearly, further experiments such as magnetic study are desired.

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