A NEW MOLECULAR SUPERCONDUCTOR $\beta'$-Et$_2$Me$_2$P[Pd(dmit)$_2]$$_2$

($dmit = 2$-thioxo-1,3-dithiole-4,5-dithiolate)

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The anion radical salt $\beta'$-Et$_2$Me$_2$P[Pd(dmit)$_2]$$_2$ is non-metallic at ambient pressure. An application of pressure induces a metallic behavior and the system exhibits a superconducting transition in the pressure region of 6.9-10.4 kbar with $T_c = 4.0-1.8$ K (onset). Under higher pressure, however, non-metallic behavior appears in the low-temperature region. The isostructural salt $\beta'$-Et$_2$Me$_2$Sb[Pd(dmit)$_2]$$_2$ also shows pressure-induced metallic behavior. However, not a superconducting transition above 1.6 K, nor a high-pressure non-metallic behavior is observed at pressures up to 16.4 kbar. These Pd(dmit)$_2$ salts can be characterized by an existence of two different types of bands near the Fermi level. The counter cation dependence of the electronic state under pressure suggests that dimensionality of the electronic structure plays an important role. © 1998 Elsevier Science Ltd

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1. INTRODUCTION

Intensive studies on the magnetic quantum oscillations in the molecular conductors have revealed that they often exhibit clear and simple electronic structures which can be well described by the simple tight-binding band calculation and are sensitive to the modification of the molecular arrangement in the crystal [1]. In most molecular metals, the conduction band originates from only one frontier molecular orbital of an organic molecule. In some molecular materials, however, there exist "two" bands with different characters near the Fermi level and interplay of these two bands provides unique physical properties. An application of pressure easily affects the interplay and changes the electronic state drastically.

The metal dithiolene complex Pd(dmit)$_2$ has provided various molecular conductors, including four high-pressure superconductors [2]. This molecule is considered to construct a unique two-band system associated with HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) bands [3]. We have investigated Se-substitution and cation effects on the high-pressure molecular superconductor $\beta$-Me$_4$N[Pd(dmit)$_2]$$_2$ ($\beta$-Me$_4$N salt; $T_c = 6.2$ K, at 6.5 kbar) [4] and pointed out an interrelation between the correlation effect and the dimensionality of the electronic structure [5]. The anion radical salt Et$_2$Me$_2$N[Pd(dmit)$_2]$$_2$ is another type of high-pressure superconductor ($T_c = 4$ K, at 2.4 kbar) whose crystal structure is different from that of the $\beta$-Me$_4$N salt [6]. We have found, however, that a series of isostructural anion radical salts Et$_2$Me$_2$Z[Pd(dmit)$_2]$$_2$ ($Z = P$, As, Sb) show crystal structure quite similar to that of the $\beta$-Me$_4$N salt except for the molecular arrangement around the cation sites [7]. We call this structural type the $\beta'$-type. We report here that $\beta'$-Et$_2$Me$_2$P[Pd(dmit)$_2]$$_2$ ($\beta'$-Et$_2$Me$_2$P salt) is a high-pressure superconductor while the isostructural $\beta'$-Et$_2$Me$_2$Sb[Pd(dmit)$_2]$$_2$ ($\beta'$-Et$_2$Me$_2$Sb salt) does not show a superconducting transition. The counter cation effect in these two-band systems is discussed.

2. EXPERIMENTAL

Preparation and crystal structure data of $\beta'$-Et$_2$Me$_2$P and $\beta'$-Et$_2$Me$_2$Sb salts were described in the previous report [7].

Electrical resistivity in the crystallographic ab plane was measured by the standard four-probe method. Gold
leads (15 µm diameter) were attached to the sample with carbon paste. The contacts remained ohmic through the measurement. Resistivity measurements under pressure were performed in a clamp cell with a 1:1 mixture of Fluorinert No. FC70 and FC77, as the pressure transmitting medium. The pressure was calibrated with the superconducting transition temperature of Pb. Resistance measurements under the magnetic field were carried out by standard a.c. techniques using the current of 10 µA. We applied the fields approximately parallel to the conducting ab-plane. Temperature dependence of the resistance was measured using an 8 T superconducting magnet (Cryogenic Consultants Limited). The temperature of samples under the magnetic field was determined by a Cernox sensor attached to the pressure cell. The static magnetic susceptibility was measured in the 1.8 < T < 300 K temperature range at 0.5 T for randomly oriented single crystals (26 mg) using a Quantum Design MPMS SQUID susceptometer. The linearity of magnetization up to 5.0 T was checked at 300, 50 and 20 K.

3. RESULTS AND DISCUSSION

Under ambient pressure, the room-temperature resistivity of the Et₂Me₂P salt is rather small (about 10⁻¹ Ω·cm⁻¹). The resistivity increases with decreasing temperature in the entire temperature region [Fig. 1(a)]. The static magnetic susceptibility (χ) is found to be paramagnetic and shows a broad maximum around 80 K followed by a slightly rapid decrease down to about 20 K (Fig. 2). Although a Curie component at low temperatures hindered the observation of a magnetic phase transition in the χ–T curve, the recent ESR study has clearly revealed an antiferromagnetic transition at 17–18 K [8]. Such magnetic properties are frequently observed in the β(β')-type Pd(dmit)₂ salts and indicates that a correlation effect plays an important role in the non-metallic state at the low-pressure region [5, 9]. The pressure dependence of the room-temperature resistivity shows a monotonous decrease with increasing pressure up to 14 kbar followed by almost pressure-independent behavior up to 19.4 kbar. A clearly metallic behavior is observed above 5 kbar. The temperature where the resistivity shows a minimum sharply decreases with increasing pressure. Under 6.9 kbar, the resistivity turns to increase at 34 K and the resistivity at about 4 K becomes 3–30 times as large as the room-temperature value. Below 4.0 kbar, the resistivity decreases sharply and becomes zero. The magnetic field dependence of the resistivity around this transition is shown in Fig. 3. With increasing the magnetic field strength, the transition temperature shifts to lower temperatures, which strongly suggests that this transition is attributed to a superconducting transition. This superconducting transition could not be observed when the current above 100 µA was applied. This suggests that the critical current is rather low. With increasing pressure, the resistivity minimum grows faint and the superconducting transition temperature (Tₙ) decreases down to 1.8 K at 10.4 kbar (dTₙ/dP ≈ −0.6 K kbar⁻¹). Under higher pressure, the system shows a gradual change to a non-metallic state which is enhanced by increasing pressure [Fig. 1(b)]. It should be noticed that the resistivity in this non-metallic state tends to saturate. Figure 4 shows a pressure–temperature phase diagram for the Et₂Me₂P salt. It should be noted that the superconducting phase is situated between two non-metallic states.

In the isostructural Et₂Me₂Sb salt, the effect of pressure is also the suppression of the non-metallic

![Fig. 1. Temperature dependence of the resistivity in the crystallographic ab plane at various pressure for the β'-Et₂Me₂P salt.](image-url)
behavior. However, neither a superconducting transition, nor a high-pressure non-metallic behavior occurs (Fig. 5). The Et$_2$Me$_2$Sb salt remains metallic up to the highest pressure (16.4 kbar).

The crystal structure of this $\beta'$-Pd(dmit)$_2$ system is based on the stack of strongly dimerized Pd(dmit)$_2$ anions. The conduction band is formed by the two-dimensional HOMO band [3]. This HOMO band is narrow and half-filled. Magnetic properties suggest that the present system at ambient pressure is close to the Mott insulator. The one-dimensional LUMO band is located immediately below the HOMO band. An application of pressure is considered to enhance band widths of HOMO and LUMO bands and lead to an overlap of these two bands. As a result of electron transfer from the LUMO band to the HOMO band, there should be a pressure region where the HOMO band is no longer half-filled. (Of course, our model does not explicitly include the on-site Coulomb energy and thus this electron transfer process should be more complicated.) In this pressure region, the system would exhibit metallic (and superconducting) behavior. At the same time, however, one-dimensional character of the Fermi surface associated with the LUMO band should be enhanced, which would explain the non-metallic behavior under higher pressure. It should be mentioned that there is a possibility that the LUMO band becomes half-filled. This also explains the high-pressure non-metallic behavior. In order to clarify this point, it should be quite important to reveal magnetic properties of the high-pressure non-metallic state. In any way, the electronic state under very high pressure would be governed by the one-dimensional LUMO band. If this “band overlap” were the only parameter, all the $\beta'$-Pd(dmit)$_2$ salts would behave in the same manner (non-metal $\rightarrow$ metal(superconductor) $\rightarrow$ non-metal) with increasing pressure. However, the pressure effect on the resistivity behavior is quite sensitive to the choice of the cation. We proposed that the second factor which governs the electronic state of the $\beta'$-Pd(dmit)$_2$ salts is the dimensionality of the electronic structure [5]. Calculations of intermolecular overlap integrals suggest that the high-pressure metallic phase appears more easily in the system with the higher dimensionality. This suggests that the enhanced dimensionality leads to a reduction of the effective Coulomb interaction. The counter cation affects intermolecular spacings and overlapping modes of Pd(dmit)$_2$ molecules and tunes intermolecular interactions. We roughly estimate two-dimensional character of the HOMO band by a ratio of
inter-dimer HOMO···HOMO interactions $r/B$ ($r$ is the largest transverse interaction and $B$ is the one along the stacking direction, see [5] and [7]). In the $\beta'$-type salts, the larger cation tends to allow the stronger two-dimensionality ($r/B$ values are 0.82 for the Et$_2$Me$_2$P salt and 0.96 for the Et$_2$Me$_2$Sb salt). The superconducting $\beta$-Me$_4$N salt also exhibits a two-dimensional character strongly ($r/B = 0.92$). On the other hand, the $\beta'$-Me$_4$I salt which does not show the high-pressure metallic phase exhibits lower dimensionality ($r/B = 0.61$) [5].

Let us now compare the Et$_2$Me$_2$I and Et$_2$Me$_2$Sb salts from the viewpoint of the superconductivity. The former shows the superconducting state accompanied by the high-pressure non-metallic state. On the other hand, the latter remains metallic under high pressure. The two-dimensional character of the latter system is slightly stronger than that of the former. The absence of the superconducting state and the high-pressure non-metallic state in the Et$_2$Me$_2$Sb salt suggests that an enhancement of the two-dimensionality leads to "good" metallic state, but is not favorable for the superconducting state.

In summary, the superconductivity under high pressure in the $\beta'$-Et$_2$Me$_2$P salt has been established. Comparison with the isostructural $\beta'$-Et$_2$Me$_2$Sb salt suggests an importance of the dimensionality for the superconductivity in this system. A series of $\beta'$-Pd(dmit)$_2$ salts which can accept a variety of chemical modifications are suitable for the systematic study of the two-band system. Further studies including low-temperature X-ray crystal structure analysis and measurements of magnetic properties (susceptibility and $^{13}$C-NMR) under high pressure are in progress.

REFERENCES


