Uniaxial Strain Effects in the Conducting Pd(dmit)$_2$ System
(dmit = 1,3-Dithiol-2-thione-4,5-dithiolate)

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Uniaxial strain effects in the two-dimensional strongly correlated electron system with the dimer structure, $\beta^-$-(cation)[Pd(dmit)$_2$]$_2$, (cation = Me$_2$Sb, Et$_2$Me$_2$P), are described. These salts are Mott insulators at ambient pressure. Under hydrostatic pressure, the insulating state is suppressed and the metallic state accompanied by the superconductivity appears. We have demonstrated that the uniaxial strain along the crystallographic $b$-axis induces the superconductivity more effectively than the hydrostatic pressure. When the Et$_2$Me$_2$P salt is compressed along the $b$-axis ($p_b$), the superconductivity appears at 6.1 K for $p_b = 4.5$ kbar. In the Me$_2$Sb salt, on the other hand, the superconductivity is observed at 8.4 K for $p_b = 4.5$ kbar. In each salt, the critical temperature is enhanced and the critical pressure is reduced, compared with those under hydrostatic pressure. The effect of the $b$-axis strain on interdimer interactions has been simulated by the extended Hückel method, which indicates that the $b$-axis strain effectively enhances the band width and reduces the correlation effect.

KEYWORDS: Pd(dmit)$_2$, uniaxial strain, electronic structure, superconductivity, strongly correlated electron system

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1. Introduction

The strongly correlated electron systems in both organic and inorganic materials have provided a variety of fascinating physical problems. Among them, we are investigating the electronic state of a series of molecular conductors based on the metal complex Pd(dmit)$_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) under hydrostatic pressure and uniaxial strain. The $\beta^-$-type anion radical salts of Pd(dmit)$_2$ with tetrahedral closed-shell cations, (cation)[Pd(dmit)$_2$]$_2$, are classified into the strongly correlated two-dimensional (2D) system associated with a narrow and half-filled conduction band. In crystals of these salts, the monoclinic unit cell with the space group $C2/c$ contains crystallographically equivalent two conduction layers (I and II) separated from each other by the insulating cation layer. Strongly dimerized Pd(dmit)$_2$ molecules stack along the $a + b$ direction in the layer I and along the $a$-$b$ direction in the layer II. Essential properties of the electronic structure near the Fermi level can be discussed using the dimer unit [Pd(dmit)$_2$]$_2$. The $\beta^-$-type Pd(dmit)$_2$ salts are Mott insulators at ambient pressure.\textsuperscript{1,2) An important point is that the dimer units [Pd(dmit)$_2$]$_2$ form a 2D quasi-triangular lattice and magnetic properties indicate that the spin frustration operates in the insulating state.\textsuperscript{3) Under hydrostatic pressure, these salts exhibit various electronic states depending on the counter cation. Cation dependence in the hydrostatic pressure effect classifies $\beta^-$-type Pd(dmit)$_2$ salts into three types. Type A salts (cation = Me$_2$P, Me$_2$As; Me = CH$_3$) remain non-metallic behavior up to about 17 kbar. Type B salts (cation = Me$_2$Sb, Et$_2$Me$_2$P; Et = C$_2$H$_5$) exhibit a metallic state accompanied by the superconductivity, and another non-metallic behavior is observed in the higher pressure region. X-ray crystal structure analysis for the Et$_2$Me$_2$P salt under high pressure and at low temperature indicated that this high pressure non-metallic state is relevant to the structural transition with a symmetry breaking.\textsuperscript{4)} This structural transition, where the space group is lowered from $C2/c$ to $P\bar{1}$, makes the two conduction layers (I and II) crystallographically non-equivalent. The non-equivalence of the two conduction layers provides an anisotropic Fermi surface which can undergo the (partial) nesting. Type C salt (cation = Et$_2$Me$_2$Sb) also turns metallic under hydrostatic pressure, but the superconductivity and the high-pressure non-metallic behavior are absent.\textsuperscript{5) Recently, we have revealed that an application of the uniaxial strain along the $b$-axis effectively induces a metallic state accompanied by the superconductivity in the Me$_4$As salt which belongs to the type A.\textsuperscript{6) On the other hand, the uniaxial strain along the $a$-axis enhances the insulating behavior in the low pressure region. These uniaxial strain effects indicate that the electronic state of this unique strongly correlated 2D electron system with the quasi-triangular structure is full of variety. We report here the uniaxial strain effects on the type B salts, the Me$_2$Sb and Et$_2$Me$_2$P salts. Under hydrostatic pressure, each of them shows a metallic state accompanied by the superconductivity. The maximum critical temperature $T_c$ values are 5.3 K at 9.0 kbar in the Me$_2$Sb salt and 4.0 K at 7.0 kbar in the Et$_2$Me$_2$P salt, respectively.\textsuperscript{7)
calculation, the extended Hückel molecular orbital calculations were performed.\(^1\) The transfer integral \(t\) was estimated from the overlap integral \(S\) by the approximation, \(t \approx \epsilon S\) (\(\epsilon\) is a constant with the order of the orbital energies of frontier orbitals).

3. Experimental Results

3.1 \(\text{Me}_2\text{Sb}\) salt

Uniaxial strain effects on the \(\text{Me}_2\text{Sb}\) salt are similar to those on the \(\text{Me}_2\text{As}\) salt (type A).

The \(a\)- and \(c^*\)-axis strains enhance the insulating behavior at the strain below 2 kbar. This is contrary to the hydrostatic pressure effect [Figs. 1(a) and 1(c)]. With increasing pressure, the insulating state tends to be suppressed in turn, but no metallic resistivity behavior is observed up to 15 kbar.

On the other hand, the \(b\)-axis strain suppresses the Mott insulating state. At \(p_b = 4\) kbar, the system shows a broad resistivity minimum around 150 K followed by a weak upturn, and an abrupt decrease of the resistivity is observed at 7.3 K. This abrupt resistivity drop can be observed up to 7 kbar. This anomaly is sensitive to the magnetic field, as demonstrated in the inset of Fig. 1(b)-1. Based on the recovery of the resistivity by the applied magnetic field, we ascribe this resistivity drop to an appearance of the superconductivity. The maximum \(T_c\) is 8.4 K at \(p_b = 4.5\) kbar [Fig. 1(b)-1]. To our knowledge, this is the highest \(T_c\) in the molecular superconductors based on the metal dithiolene complexes. It should be noticed that the maximum \(T_c\) is raised and the critical pressure \(P_c\) is lowered by the \(b\)-axis strain, compared with those under hydrostatic pressure. This suggests that the \(b\)-axis strain suppresses the Mott insulating state more effectively than the hydrostatic pressure. In the higher pressure region \((p_b > 10\) kbar), the resistivity upturn grows gradually and the superconductivity disappears [Fig. 1(b)-2].

Under the \(a\)-, \(b\)-, and \(c^*\)-strains examined in this work, the high-pressure non-metallic behavior reported in the hydrostatic pressure experiment was not observed clearly.

3.2 \(\text{Et}_2\text{Me}_2\text{P}\) salt

Uniaxial strain effects on the \(\text{Et}_2\text{Me}_2\text{P}\) salt are slightly different from those on other salts.

Temperature dependence of the resistivity for the \(\text{Et}_2\text{Me}_2\text{P}\) salt under the uniaxial strain along the \(a\)-axis \((p_a)\) is shown in Fig. 2(a). An application of the strain of 2 kbar increases the resistivity in the high temperature region. The further application of the \(a\)-axis strain steadily suppresses the insulating (semiconducting) behavior. At \(p_a = 15\) kbar, only one order of magnitude difference between the room temperature resistivity and that at 1.4 K is observed. The non-metallic state, however, remains even at 15 kbar.

On the other hand, an application of the \(c^*\)-axis strain of 2 kbar decreases the resistivity in the high temperature region [Fig. 2(c)]. The further application of the \(c^*\)-axis strain in turn increases the resistivity in the high temperature region, and suppresses the upturn of the resistivity in the low temperature region. The most prominent feature is the superconductivity observed at 2.6 K under 10 kbar. The pressure region where the superconductivity appears is very narrow. Under the strains of 8 and 12 kbar, no super-

![Fig. 1. Temperature dependence of the resistivity \(\rho\) for \(\text{Me}_2\text{Sb-}[\text{Pd(dmit)}_2]\) under the uniaxial strain (a) along the \(a\) direction, (b)-1 along the \(b\) direction in the intermediate pressure region (an inset shows an effect of magnetic field on the resistivity at 4.5 kbar), (b)-2 along the \(b\) direction in the higher pressure region, and (c) along the \(c^*\) direction.](image-url)
Temperature independent resistivity behavior appears. Conductivity can be observed. Above 12 kbar, almost temperature independent resistivity behavior appears. When the sample is compressed along the $b$-axis, the metallic behavior of resistivity is readily induced as shown in Fig. 2(b). Under the $b$-axis strain above 10 kbar, the insulating behavior is entirely suppressed and the resistivity decreases with lowering temperature in the overall temperature range. The most significant feature is an abrupt drop of the resistivity observed in the intermediate pressure region ($4 \leq p_b / \text{kbar} \leq 10$). In the sample under $p_b = 4.5 \text{kbar}$, the abrupt resistivity drop can be apparently observed at 6.1 K. Recovery of the resistivity by the applied magnetic field [inset of Fig. 2(b)] indicates that this is due to the superconductivity. With increasing the strain, the $T_c$ value shifts downward and the superconductivity disappears under the strain of 15 kbar. This superconductivity induced by the $b$-axis strain should be compared with that under the hydrostatic pressure. Under the hydrostatic pressure, the maximum $T_c = 4.0$ K at 7.0 kbar. As is the case of the Me$_2$Sb salt, therefore, the $b$-axis strain induces the superconductivity more effectively. It should be noticed that the resistivity at $P_c = 15$ kbar slightly increases, compared with that at $p_b = 10$ kbar. However, the high-pressure non-metallic behavior reported in the hydrostatic pressure experiment was not observed clearly under the $b$-strain as well as under the $a$-, and $c^*$-strains.

4. Discussion

In this Pd(dmit)$_2$ system, the conduction band originates from the HOMO (highest occupied molecular orbital) of the Pd(dmit)$_2$ molecule. The unit cell contains only one crystallographically independent Pd(dmit)$_2$ molecule and there are two conduction layers (I and II) in the unit cell. These two conduction layers are interrelated to each other by the glide plane symmetry. Since the Pd(dmit)$_2$ molecules are strongly dimerized, we can describe the band structure around the Fermi level based on the dimer unit. Table I displays intra- ($t_A$) and inter- ($t_B$, $t_s$, and $t_r$) dimer transfer integrals for the Me$_4$Sb and Et$_2$Me$_2$P salts. The interlayer transfer integrals are very small and are neglected in the

<table>
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<th>Cation</th>
<th>$t_A$ (meV)</th>
<th>$t_B$ (meV)</th>
<th>$t_s$ (meV)</th>
<th>$t_r$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et$_2$Me$_2$P</td>
<td>445.8</td>
<td>29.4</td>
<td>29.3</td>
<td>24.3</td>
</tr>
<tr>
<td>Me$_4$Sb</td>
<td>450.1</td>
<td>30.0</td>
<td>28.4</td>
<td>25.4</td>
</tr>
</tbody>
</table>

Fig. 2. Temperature dependence of the resistivity $\rho$ for Et$_2$Me$_2$P-[Pd(dmit)$_2$]; under the uniaxial strain (a) along the $a$ direction, (b) along the $b$ direction (an inset shows an effect of magnetic field on the resistivity at 4.5 kbar), and (c) along the $c^*$ direction (an inset shows an effect of magnetic field on the resistivity at 10 kbar).
following discussion. Based on the tight-binding approximation, two branches of the conduction HOMO band associated with the layer I and layer II can be approximately described as follows:

\[ \epsilon_1(k) = 2.0[ t_B \cos k(a_p - b_p) + t_s \cos k(\alpha_p - \beta_p) ] \]

\[ \epsilon_2(k) = 2.0[ t_B \cos k(a_p - b_p) + t_s \cos k(\alpha_p + \beta_p) ] \]

where the C-centered monoclinic cell is reduced to the primitive one as \( a_p = (a+b)/2 \), \( b_p = b \), \( \epsilon_p = c \). In the \( \beta \)-type salts, the transfer integrals exhibit a relation \( t_B \gg t_B \approx t_s \approx t_s \). The interdimer transfer integrals determine the dispersion of the conduction band, while the intradimer transfer integral is correlated to the effective on-site Coulomb energy on the dimer \( (U_{\text{eff}}) \). The band width \( (W) \) is determined mainly by two large inter-dimer transfer integral \( t_B \) and \( t_s \), and the smallest transfer integral \( t_s \) governs anisotropy of the band structure. Since essential effects of the uniaxial strain on the electronic structure can be described by anisotropic changes of these transfer integrals, we focus our attention on how each uniaxial strain changes the transfer integrals \( t_s \), \( t_B \), \( t_s \), and \( t_t \) within the conduction layer. In this discussion, we neglect the cation–anion interactions because they are primarily small.

Recently, X-ray crystal structure analysis under hydrostatic pressure was performed for the Et\(_2\)Me\(_2\)P salt. The tight-binding band calculations based on structural data indicate that the application of hydrostatic pressure enhances the interdimer transfer integrals, especially \( t_B \). The intradimer transfer integral \( t_s \), however, also increases simultaneously. Therefore, there occur enhancements of both \( W \) and \( U_{\text{eff}} \) under the hydrostatic pressure. In the Et\(_2\)Me\(_2\)P salt, the enhancement of \( W \) overcomes that of \( U_{\text{eff}} \) and reduces the electron correlation effect, which leads the system to the metallic state.

Unfortunately, there are not crystal data under the uniaxial strain for the present system, and crystal structure analysis under the uniaxial strain is difficult and limited to the low pressure region. In general, it is not easy to estimate the uniaxial effect on the electronic structure without structural data. If the molecular arrangement along the considering direction is simple, however, it is possible to simulate the uniaxial effect on the electronic structure. In the present system, the \( b \)-axis strain corresponds to such a good-natured case. The \( b \)-axis strain gives an equivalent effect on both conduction layers (I and II). Along the \( b \)-axis, it is enough just to consider the translation symmetry through the vector \( b \) for the calculation of the transfer integral. The Pd(dmit)\(_2 \) molecular plane is nearly perpendicular to the \( b \)-axis (the angles between the normal of the molecular plane and the \( b \)-axis are \( \pm 104.4^\circ \) for the Me\(_2\)Sb salt and \( \pm 104.5^\circ \) for the Et\(_2\)Me\(_2\)P salt, respectively), and the eclipsed configuration with the short Pd - Pd contact in the dimer is expected to be rigid against the external force parallel to the \( b \)-axis.

Therefore, the \( b \)-axis strain effect on the intradimer transfer \( t_s \) can be approximately negligible. In order to estimate the \( b \)-axis strain effect, we have adopted a simple distortion model for the quasi-triangular lattice (inset in Fig. 3), and calculated the interdimer transfer integrals \( t_B \), \( t_s \), \( t_t \), and the band width \( W \) for the Et\(_2\)Me\(_2\)P salt. As shown in Fig. 3, the \( b \)-axis strain effectively enhances the interdimer transfer integral \( t_s \), which results in an enhancement of \( W \). Under the \( b \)-axis strain, \( t_B \) and \( t_s \) increase more gradually than \( t_t \). Considering that the \( b \)-axis strain hardly affects the intradimer transfer integral \( t_s \), we can ascribe an essential role of the \( b \)-axis strain to more effective reduction of the electron correlation than the hydrostatic pressure. The situation is the same for the Me\(_2\)Sb salt.

On the other hand, it is easily expected that the \( a \)-axis strain largely affects the intradimer transfer integral \( t_A \), because normals of the Pd(dmit)\(_2 \) molecular planes are at rather small angles to the \( a \)-axis (\( \pm 22.9^\circ \) for the Me\(_2\)Sb salt and \( \pm 25.0^\circ \) for the Et\(_2\)Me\(_2\)P salt). The uniaxial strain along the \( a \)-axis also gives the equivalent effect on each conduction layer. Since the \( a \)-axis is orthogonal to the \( b \)-axis, the \( a \)-axis strain should have the smallest effect on \( t_s \). Therefore, the enhancement of the insulating behavior in the low pressure region observed in both salts would be associated with an effective enhancement of the electron correlation. As for the higher pressure region, it should be noticed that the \( a \)-axis strain can also affect the interdimer transfer integrals \( t_B \) and \( t_s \). Since the insulating behavior is suppressed with further increase of the strain, \( U_{\text{eff}} \) should be in competition with \( W \) which is enhanced by \( t_B \). Unfortunately, a quantitative analysis of the \( a \)-axis strain effect, which will explain the difference between the Me\(_2\)Sb and Et\(_2\)Me\(_2\)P salts, is difficult at present.

The \( c \)-axis strain effects for the present two salts appear differently. In the case of the Me\(_2\)Sb salt, the effect of the \( c \)-axis strain is similar to that of the \( a \)-axis strain. The \( c \)-axis strain enhances the insulating behavior in the low pressure region. This appears due to the worst strain configuration for the enhancement of the interdimer transfer integrals within the conduction layer and an inclination of the molecular plane out of the \( c \)-axis (the normal is at an angle of 65.4° to the \( c \)-axis) which leads to an enhancement of \( t_A \). With further increase of the strain, the insulating behavior is suppressed, but the insulating state remains up to 15 kbar. On the other hand, in the Et\(_2\)Me\(_2\)P salt, the \( c \)-axis strain gradually suppresses the non-metallic behavior and leads to the almost temperature-independent resistivity behavior at 15 kbar, though the angle between the normal of the
molecular plane and the $c^*$-axis is close to that in the Me$_2$Sb salt (64.3°). Furthermore, at the intermediate pressure of 10 kbar, the superconductivity appears at 2.6 K. This is the first example of the superconductivity induced by the strain along the inter-layer direction in the Pd(dmit)$_2$ salts. Such unique strain-induced superconductivity has been reported in an organic conductor $\alpha$-(BEDT-TTF)$_2$-KHg(SCN)$_4$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene$^{17,18}$) and a supramolecular conductor (DIETS)$_2$-[Au(CN)$_4$] (DIETS = diiodo(ethylenedithio)diselenadithiafulvalene$^{19}$). In the former case, the external force along the inter-layer direction can affect the band structure within the conduction plane, possibly leading to an increase in the Fermi surface warping. The strain-induced superconductivity in the latter compound can be explained by an enhancement of the band width through the supramolecular interaction.$^{16}$ In the Et$_2$Me$_2$P salt, since the molecular long axis of Pd(dmit)$_2$ is not parallel to the $c^*$-axis, it is likely that rotations of Pd(dmit)$_2$ molecules are caused by the $c^*$-axis strain and the band structure within the conduction layer is modified. For more quantitative discussion, further investigations including the X-ray diffraction are in progress.

Lastly, we mention briefly the high pressure non-metallic behavior observed under the hydrostatic pressure for the present two salts. Under the $a$-, $b$-, and $c^*$-strains, such a behavior was not observed clearly, except that the resistivity under the $b$-axis strain was slightly enhanced in the high pressure region for each salt. Considering that the high pressure non-metallic state is relevant to the structural transition does not clearly occur under the uniaxial strain conditions examined in this work.

5. Conclusion

In conclusion, we have demonstrated that molecular conductors $\beta'$-(cation)[Pd(dmit)$_2$]$_2$ (cation = Me$_2$Sb, Et$_2$Me$_2$P) exhibit various types of electronic states when compressed along the crystallographic $a$, $b$, and $c^*$ axes. Especially, the $b$-axis strain suppresses the Mott insulating state and induces the superconductivity more effectively than the hydrostatic pressure. This can be explained by the enhancement of the interdimer transfer integral $t_\alpha$ with little enhancement of the intradimer transfer integral $t_A$.

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5) Recently, we have found that newly synthesized Et$_2$Me$_2$Sb salt undergoes a unique charge separation transition which leads to a non-magnetic insulating state at about 70 K under ambient pressure. Notably, in the previous sample prepared in the presence of Et$_3$MeSb$^+$ ions as impurities, this charge separation transition is completely suppressed. Surprisingly, an ordinary X-ray crystal structure analysis indicated that there is no difference in the cation site between the previous and new crystals. In previous papers, $\beta'$-(Et$_3$Me$_2$As)-[Pd(dmit)$_2$]$_2$ was classified into the type C. Very recently, however, we have found that the sufficiently pure crystal of the Et$_2$Me$_2$As salt exhibits superconductivity at 5.5 K under 8 kbar. This new result suggests that the Et$_2$Me$_2$As salt would belong to the type B. Details will be reported elsewhere.