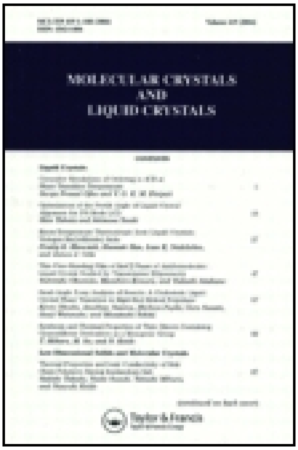

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Pressure-Temperature Phase Diagram of Molecular Conductors Related to the High-Pressure Superconductor, β-$Me_4N[Pd(dmit)_2]_2$

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To cite this article: Hiroshi Sawa , You-Liang Liu , Shuji Aonuma & Reizo Kato (1996): Novel Pressure-Temperature Phase Diagram of Molecular Conductors Related to the High-Pressure Superconductor, β-$Me_4N[Pd(dmit)_2]_2$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 131-136

To link to this article: http://dx.doi.org/10.1080/10587259608030790

Mol. Cryst. Liq. Cryst., 1996, Vol. 285, pp. 131–136
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NOVEL PRESSURE-TEMPERATURE PHASE DIAGRAM OF MOLECULAR CONDUCTORS RELATED TO THE HIGH-PRESSURE SUPERCONDUCTOR, β-$Me_4N[Pd(dmit)_2]_2$

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Abstract Dependence on cation size or terminal chalcogen atom X in the anion radical salts of $Pd(dmiX)_2$ (X=S(t), Se(se)) with the tetrahedral cation Me_4Z^+ (Z=N, P, As and Sb) was investigated by resistivity measurements under high-pressure, X-ray crystal structure analyses and band calculations. At ambient pressure, these systems are considered to be a two-dimensional Mott insulator. β-$Me_4N[Pd(dmit)_2]_2$ is a superconductor with T_C=6.2 K at 6.5 kbar. In spite of very similar dimerized column structures, other compounds show very different temperature dependences of resistivity under pressure. The stability of the high-pressure metallic state is influenced by the dimensionality of the electronic structure at ambient pressure, which links to the degree of the dimerization.

INTRODUCTION

The molecular conductors based on metallodithiolenes have been investigated vigorously. Many organic metals and superconductors have been discovered derived from metal complexes of 1,3-dithiol-2-thione-4,5-dithiolate (dmit) and related compounds.[1] Among them, $Pd(dmit)_2$ system is of special interest because of the following features : 1) The energy gap ΔE between HOMO and LUMO in the $Pd(dmit)_2$ molecule is small, 2) $Pd(dmit)_2$ molecules tend to dimerize strongly. As a result, near the Fermi level, we can expect a coexistence of two bands with have different characters, which provides very unique physical properties. In addition, the system could be finely tuned by the ligand and counter cation size. In this paper, we describe novel pressure effects in a series of molecular conductors $Me_4Z[Pd(dmiX)_2]_2$ (X=S(t), Se(se); Z=N, P, As, Sb).

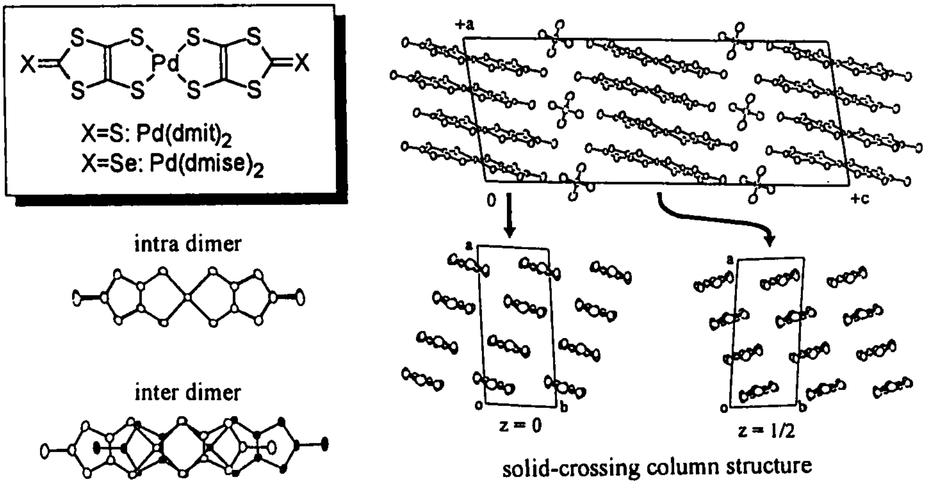

FIGURE 1 Crystal structure of $Me_4Z[Pd(dmiX)_2]_2$.

EXPERIMENTAL

Single crystals of $Me_4Z[Pd(dmiX)_2]_2$ were obtained as black plates by the electrochemical oxidation of a solution containing $(Me_4Z)_2[Pd(dmiX)_2]$ and $Me_4 \cdot ClO_4$ in acetone-acetonitrile (1:1) at 20°C under Ar or air oxidation of a solution containing $(Me_4Z)_2[Pd(dmiX)_2]$ in acetone and acetic acid. Electrical resistivity was measured by the standard d.c. four-probe method. Resistivity measurements under high-pressure were performed in a clamp cell. Crystal structure determinations were performed using 4-circle X-ray diffractometer at room temperature and warped imaging plate system with refrigerator at low temperature. Magnetic susceptibility was measured by the SQUID magnetometer.

RESULTS AND DISCUSSION

At ambient pressure

At ambient pressure, all the compounds show a semiconductive behavior. Magnetic susceptibility of $Me_4P[Pd(dmise)_2]_2$ system is almost constant (3.7×10^{-4} emu/mol) down to 100K. Below 100K, the susceptibility decreases gradually but the existence of the magnetic order is obscured by the Curie term due to impurities or defects (Fig.2).

$Me_4Z[Pd(dmiX)_2]_2$ salts have very similar crystal structure to that of β-$Me_4N[Pd(dmit)_2]_2$ (monoclinic, $C_{2/c}$) (Figure 1). The unit cell consists of two

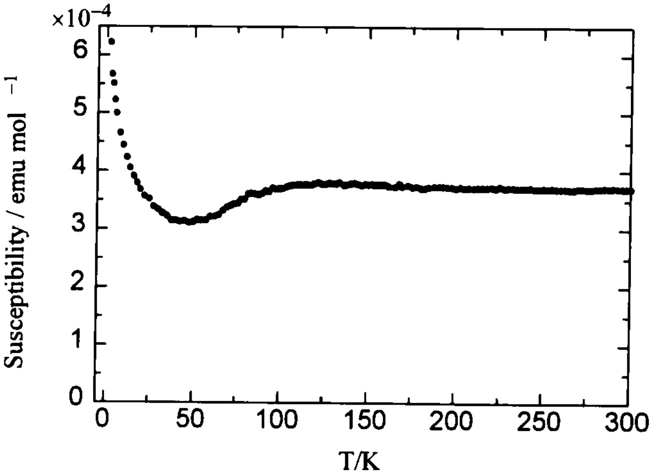

FIGURE 2 Temperature dependence of the magnetic susceptibility for $Me_4P[Pd(dmise)_2]_2$.

solid-crossing $Pd(dmiX)_2$ columns along the $a+b$ and $a-b$ directions. Each of them consists of strongly dimerized $Pd(dmit)_2$ molecules with an eclipsed configuration and very short Pd···Pd distance. These columns build layers parallel to the ab plane which are separated from each other by a cation sheet.

Below 230K, weak Bragg spots indicating $2a\times2b$ structure are observed in $Me_4P[Pd(dmit)_2]_2$ system. Such a super structure is also observed in the β-$Me_4N[Pd(dmit)_2]_2$ system.[3] When we take the dimer as a unit, this phenomenon indicates that the regular column in the room-temperature structure turns non-regular at low temperature. However, it does not influence other physical properties. At 8K, we could solve only the average crystal structure because the super spots are too weak to solve the whole structure. Changes in intermolecular spacings (from room temperature to 8K) are 3.72 → 3.67Å(inter-dimer) and 3.32 → 3.32Å(intra-dimer), respectively. This result indicates that the inter-dimer interaction associated with the loosely-packed part is more sensitive to the thermal contraction than the intra-dimer interaction.

Since the valence of $Pd(dmiX)_2$ is $-1/2$, each dimer has one electron. In these compounds, the energy gap created by the dimerization is larger than the energy gap between HOMO and LUMO. Due to the symmetry of each molecular orbital, intermolecular interactions among HOMO's are two-dimensional (2D), while

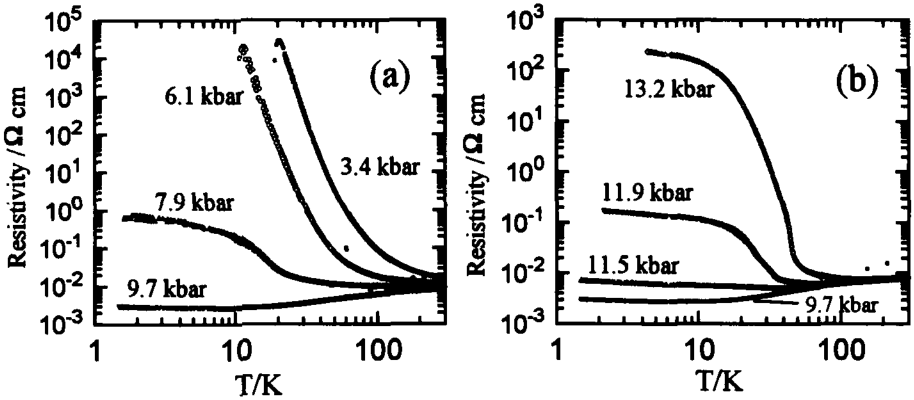

FIGURE 3 Temperature dependence of the resistivity for $Me_4Sb[Pd(dmit)_2]_2$ under pressure.

those among LUMO's are one-dimensional (1D). Therefore, the conduction band is half-filled 2D HOMO band (anti-bonding). The insulating state at ambient pressure is considered to come from the strong correlation. This would be the reason why the super structure does not affect the physical properties. It should be noted that the LUMO band (bonding) is located immediately below the conduction band.

Pressure effect

Among $Me_4Z[Pd(dmiX)_2]_2$ salts, only β-$Me_4N[Pd(dmit)_2]_2$ is a superconductor with T_C=6.2 K at 6.5 kbar.[4] In other $Pd(dmit)_2$ salts, the larger size of counter cation induces the metallic state under the lower pressure.[5] However, the critical pressure in $Me_4Sb[Pd(dmit)_2]_2$ is higher (*ca.* 10 kbar) than that of β-$Me_4N[Pd(dmit)_2]_2$ (Fig.3a). The $Pd(dmise)_2$ system exhibits lower critical pressure than the $Pd(dmit)_2$ system with the same counter cation, except for $Me_4N[Pd(dmise)_2]_2$.

The pressure-induced metallic state, however, does not show a superconducting transition down to 1.5K (Fig.3a). Furthermore, the metallic state turns unstable under higher pressure as shown in Fig.3b. In this pressure region, the pressure shifts the metal-insulator transition temperature upwards and makes the transition sharper.

Crystal and Electronic structure

What is the difference between β-$Me_4N[Pd(dmit)_2]_2$ and other salts? Compared with β-$Me_4N[Pd(dmit)_2]_2$, they show some obvious differences in interrelations between $Pd(dmit)_2$ dimers and cations. Therefore we call this structure β'-type.[5] The most

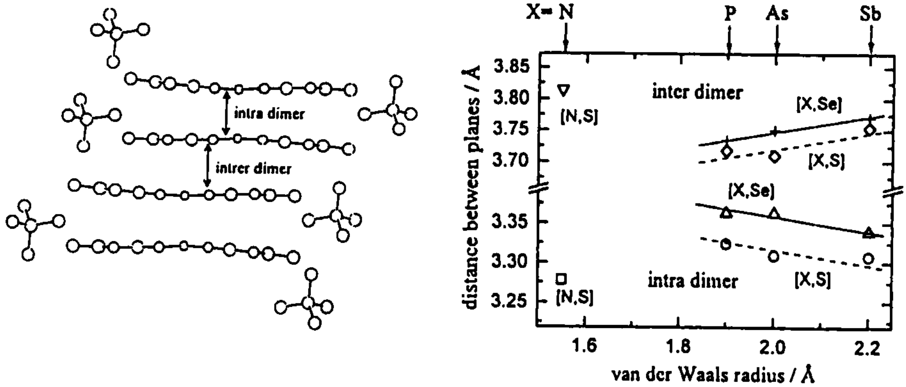

FIGURE 4 Size dependences of the intermolecular spacings. [Z,X] means $Me_4Z[Pd(dmiX)_2]_2$ (i.e. $[P,S] \equiv Me_4P[Pd(dmit)_2]_2$)

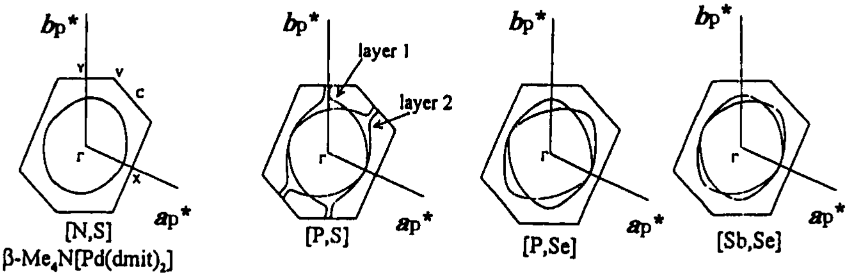

FIGURE 5 Calculated Fermi surface. The C-centered cell is reduced to the primitive one as $a_p=(a+b)/2$, $b_p=b$, $c_p=c$.

important difference in regard of the electronic state is intermolecular spacings and inter-dimer overlapping mode. Figure 4 shows the relation between the size of the central atom in the cation and intermolecular spacings. β-$Me_4N[Pd(dmit)_2]_2$ shows the largest inter-dimer spacing and smallest intra-dimer spacing. In the series of β'-type salts, the larger cation tends to enlarge the inter-dimer spacing and reduce the intra-dimer spacing. In order to understand the electronic structure, the tight-binding band structures have been calculated based on the crystal structure at ambient pressure. The resultant Fermi surfaces are shown in Fig.5. The shape of the Fermi surface associated with the HOMO band varies according to the interaction with the LUMO band and the anisotropy of the inter-dimer interactions. An enlargement of dimerization tends to enhance the dimerization gap. This dimerization gap governs the separation between LUMO and HOMO bands. Therefore, in the dmit

(X=S) salts, β-$Me_4N[Pd(dmit)_2]_2$ with the largest dimerization gap exhibits the most isotropic Fermi surface. On the other hand, The Se substitution (X=Se) gives wider band width and larger dimerization gap than the case of X=S. Consequently, in the $Pd(dmiX)_2$ system, the stronger dimerization enhances the two-dimensional character of the electronic structure.

The application of pressure would enhance dominantly inter-dimer interactions, which means reduction of the dimerization. This leads to an increase in band widths of both HOMO and LUMO bands and to an overlap of these two bands, which reduces the effective on-site Coulomb energy and stabilizes metallic state. At the higher pressure, however, the contribution of the LUMO band with 1D character increases at the Fermi level, which leads to the Peierls instability. This would be an origin of the high-pressure non-metallic state.

ACKNOWLEDGEMENT

We thank to Prof. M. Kinoshita and Dr. Y. Hosokoshi for the SQUID measurement. This work was partially supported by a Grant-in-Aid for scientific research on Priority Area "Novel Electronic States in Molecular Conductors" (Area No.253/06243105).

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