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Two Pressure-Induced Superconducting Anion Radical Salts Exhibiting Different Spin States at Ambient Pressure

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Pressure-induced superconducting behavior was found in two anion radical salts, $\mathrm{EtMe_3Z[Pd(dmit)_2]_2}$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate, Z = P, As), which are Mott insulators and exhibit different magnetic and structural transitions at ambient pressure.

Since the discovery of high-temperature superconducting cuprates, extensive studies of strongly correlated electron systems have been carried out from new experimental and theoretical viewpoints of materials science. In a system with a half-filled energy band, where each unit in the crystal has one conduction electron, strong on-site Coulomb energy (U) and narrow bandwidth (W) induce an insulating state. In this Mott insulating state, the spin degrees of freedom play a crucial role in determining the physical properties. In particular, the spin frustration effect in the presence of the strong correlation has attracted intense attention. For geometrically frustrated spin systems where long-range ordering of spins tends to be suppressed, the possibility of a unique quantum liquid state has been theoretically proposed.[1] The Mott insulating state of molecular conductors with a triangular lattice is of special interest because the systems can become superconducting under pressure, and a possible resonating valence bond theory of superconductivity, emphasizing the role of frustration, has been proposed.[2] A series of anion radical salts of the metal dithiolene complex $\mathrm{Pd(dmit)_2}$ with tetrahedral countercations $\mathrm{Et}_x\mathrm{Me}_{4-x}\mathrm{Z}^+$ ($x = 0, 2$; Z = P, As, Sb), β'-$\mathrm{Et}_x\mathrm{Me}_{4-x}\mathrm{Z[Pd(dmit)_2]_2}$, belong to the strongly correlated two-dimensional (2D) system and provide a variety of cases for the study of interplay among correlation (U/W), frustration, and HOMO−LUMO double bond formation.[3] In the crystals, the strongly dimerized $\mathrm{Pd(dmit)_2}$ units form a 2D quasi-triangular lattice. Due to the strong dimerization and the small energy difference between HOMO and LUMO, the conduction band originates from the HOMO of the $\mathrm{Pd(dmit)_2}$ molecule. At ambient pressure, all these salts are Mott insulators, where the spins are localized on each dimer unit $\mathrm{[Pd(dmit)_2]_2^-}$ and form a spin-1/2 Heisenberg spin system on the quasi-triangular lattice. They are frustrated paramagnets[4] that undergo antiferromagnetic transition or charge separation transition at low temperatures. The application of (hydrostatic or uniaxial) pressure can induce a metallic or superconducting state that strongly depends on the cation.[3a] Our attempt to tune the electronic state of $\mathrm{Pd(dmit)_2}$ salts with a series of countercations $\mathrm{EtMe_3Z^+}$ (Z = N, P, As, Sb) has led to new pressure-induced superconducting salts that exhibit different magnetic and structural transitions in the Mott insulating state.

Single crystals of $\mathrm{EtMe_3Z[Pd(dmit)_2]_2}$ (Z = P, As) were obtained as black plates by aerial oxidation of $\mathrm{(EtMe_3Z)_2[Pd(dmit)_2]}$ in acetone containing acetic acid at 5 °C. Their crystal structures were determined by the X-ray diffraction method. $\mathrm{EtMe_3P}$ salt **1** exhibits a new packing motif with the space group $P2_1/m$.[5] The unit cell contains two crystallographically equivalent anion layers (Figure 1). The anion arrangement within the conduction layer is similar to that in the previously reported β'-type salts. The dimers are stacked uniformly along the c axis within each layer, whereas the β'-type salts exhibit two different stacking directions. In the molecular conductors with strongly dimerized structures, the essence of the band structure near the Fermi level can be extracted by treating each dimer as an effective unit.[3a] Intra- and inter-dimer HOMO−HOMO overlap integrals indicate that the strongly dimerized $\mathrm{[Pd(dmit)_2]_2^-}$ units form an almost regular triangular lattice (Figure 1c).

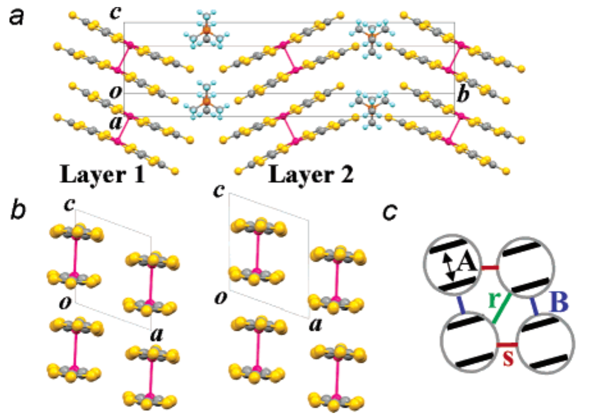

Figure 1. Crystal structure of **1** (a) viewed from the a^*-axis and (b) end-on projection of anion arrangements in layer 1 (left) and layer 2 (right). (c) Schematic quasi-triangular lattice of $\mathrm{Pd(dmit)_2}$ dimers and intra- and interdimer HOMO−HOMO overlap integrals ($\times 10^{-3}$): $A = -45.37$, $B = -2.80$, $s = -2.75$, $r = -2.91$.

The temperature dependence of static magnetic susceptibility for **1** measured by SQUID is well-described by high-temperature expansion calculations using the Padé approximants for the 2D spin-1/2 Heisenberg antiferromagnet on the triangular lattice ($J/k_B = 250$ K)[4] and exhibits a second-order transition to a nonmagnetic spin-gapped state at 25 K.[6] We have already reported that the β'-$\mathrm{Et_2Me_2Sb}$ salt undergoes a charge separation transition ($2\mathrm{[Pd(dmit)_2]_2}^{-1/2} \rightarrow \mathrm{[Pd(dmit)_2]_2}^- + \mathrm{[Pd(dmit)_2]_2}^0$) leading to a nonmagnetic state, which is driven by the HOMO−LUMO double bond formation in the neutral dimer.[7] Crystal structure analysis of **1** at 10 K, however, revealed another type of nonmagnetic state. The 10 K structure holds the space group $P2_1/m$, but the unit cell is doubled as $\boldsymbol{a} = \boldsymbol{a}_\mathbf{o}$, $\boldsymbol{b} = \boldsymbol{b}_\mathbf{o}$, $\boldsymbol{c} = 2\boldsymbol{c}_\mathbf{o} + \boldsymbol{a}_\mathbf{o}$, where $\boldsymbol{a}_\mathbf{o}$, $\boldsymbol{b}_\mathbf{o}$, and $\boldsymbol{c}_\mathbf{o}$ are the unit cell vectors at room temperature.[5] All the dimer units are crystallographically equivalent, which means that **1** exhibits no charge separation in contrast to the $\mathrm{Et_2Me_2Sb}$ salt. On the other hand, the stacking period of the dimers is doubled and alternation of the interdimer distances (3.762(9), 3.854(9) Å) indicates pairing of the dimers. Such a singlet state induced by lattice distortion in the 2D frustrated spin system is observed for the first time in the present compound.[6]

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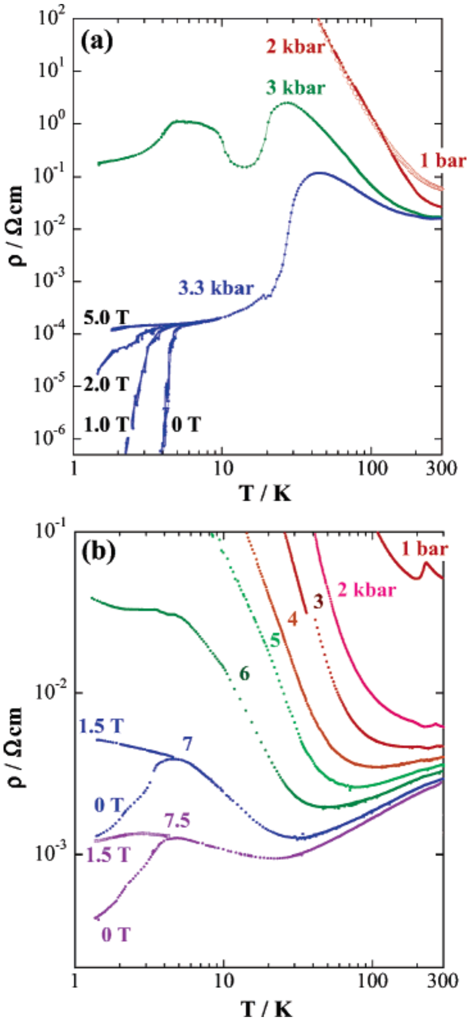

Figure 2. Electrical resistivity under various pressures for **1** (a) and **2** (b).

$EtMe_3As$ salt **2** belongs to the β′-type with the "solid crossing" column structure, where the unit cell contains two crystallographically equivalent $Pd(dmit)_2$ columns parallel to the $\boldsymbol{a} \pm \boldsymbol{b}$ directions.[8] The cation is disordered with two possible orientations. Intra- and interdimer HOMO−HOMO overlap integrals ($A = -44.57$, $B = -3.12$, $s = -3.08$, $r = -2.39$; the notations are the same as those given in Figure 1c) suggest a slightly anisotropic triangular interaction among the dimers. Compound **2** shows temperature-dependent magnetic susceptibility that is well-explained by the spin-1/2 Heisenberg triangular antiferromagnet model ($J/k_B = 260$ K) and undergoes an antiferromagnetic transition at 23 K. An easy axis is perpendicular to the conduction plane, as in the case of other β′-type $Pd(dmit)_2$ salts. In addition, the magnetic susceptibility shows a small anomaly around 230 K. Crystal structure analysis at 150 K indicates that this anomaly is associated with cation ordering.[8]

These two salts with different magnetic states, the nonmagnetic spin-gapped state (**1**) and the antiferromagnetic ordered state (**2**), became metallic and superconducting under hydrostatic pressure (Figure 2). Electrical resistivity parallel to the conduction layer was measured with the standard four-probe method using the clamp cell technique. Both salts are semiconducting at ambient pressure. The resistivity anomaly around 230 K observed in **2** is due to the cation ordering. The resistivity behavior of **1** changes drastically in the narrow pressure region, from semiconducting at 2 kbar to superconducting ($T_c = 5$ K) at 3.3 kbar (Figure 2a), suggesting that the superconducting phase is in the vicinity of the spin-gapped state. The anomalous resistivity peak below 10 K observed at 3 kbar is reproducible and suggests that the insulating phase cuts into the metallic phase in the low-temperature region of the pressure−temperature phase diagram. For **2**, the resistivity anomaly easily disappears, and the metallic region expands gradually with increasing pressure (Figure 2b). An abrupt decrease in resistivity appears at 4.3 K and 7 kbar. Magnetic field dependence confirmed that this is an indication of the superconductivity.

The β′-type $Pd(dmit)_2$ salts are characterized by the correlation parameter (U/W) and the anisotropy of the interdimer interactions (frustration parameter).[3a] In this scheme, **2** is situated between the Et_2Me_2As salt and the Me_4As salt, both of which show superconductivity under hydrostatic or uniaxial pressure.[3a] The present results indicate that the tuning of the electronic state with the choice of the cation works well in **2**, despite the existence of cation ordering transition. On the other hand, the $EtMe_3P$ cation has provided an unexpected new crystal structure. The dimer lattice in **1** is close to a regular triangular lattice where the spin frustration operates remarkably. The system releases the frustration through the unique transition to the spin-gapped nonmagnetic state accompanied by the lattice distortion, which has never been observed in the β′-type salts. This work demonstrates that the small chemical modification at the cation site provides quite different spin states at ambient pressure, both of which are situated in the vicinity of the superconductivity. NMR and high-magnetic-field studies of **1** and **2** are in progress.

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Supporting Information Available: X-ray crystallographic information, CIF data, and magnetic susceptibility data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) X-ray data for **1**: $C_{17}H_{14}PPd_2S_{20}$, $M = 1103.27$, $T = 297$ K, monoclinic, $a = 6.3962(3)$, $b = 36.6911(5)$, $c = 7.9290(3)$ Å, $\beta = 114.302(2)°$, $V = 1695.92(10)$ Å^3, space group $P2_1$/m (No. 11), $Z = 2$, $R(F^2)$ $(I > 2.00\sigma(I))$ = 0.0332, $wR(F_2) = 0.0909$ (all data), GOF = 1.047; T =10 K, monoclinic, $a = 6.3270(2)$, $b = 36.536(1)$, $c = 14.2620(5)$ Å, $\beta = 90.552(3)°$, $V = 3296.70(18)$ Å^3, space group $P2_1$/m (No. 11), $Z = 4$, $R(F^2)$ $(I > 2.00\sigma(I)) = 0.0630$, $wR(F_2) = 0.1890$ (all data), GOF = 1.051.
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(8) X-ray data for **2**: $C_{17}H_{14}AsPd_2S_{20}$, $M = 1147.22$, $T = 297$ K, monoclinic, $a = 14.470(3)$, $b = 6.3779(11)$, $c = 37.304(7)$ Å, $\beta = 97.011(2)°$, $V = 3417.1(11)$ Å^3, space group $C2$/c (No. 15), $Z = 4$, $R(F^2)$ $(I > 2.00\sigma(I))$ = 0.0317, $wR(F_2) = 0.0827$ (all data), GOF = 1.000; $T = 150$ K, triclinic, $a = 6.3330(3)$, $b = 7.7930(4)$, $c = 37.267(2)$ Å, $\alpha = 96.164(3)$, $\beta = 90.982(3)$, $\gamma = 113.079(3)°$, $V = 1678.72(15)$ Å^3, space group $P1$ (No. 2), $Z = 2$, $R(F^2)$ $(I > 2.00\sigma(I)) = 0.0653$, $wR(F_2) = 0.1723$ (all data), GOF = 1.046.

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