New Molecular Superconductor, $[Me_2Et_2N][Pd(dmit)_2]_2$

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$[Me_2Et_2N][Pd(dmit)_2]_2$ is a new molecular super-
conductor with T_c=4 K at 2.4 kbar. It is of interest that
the insulating phase emerges when superconducting state
is suppressed at high pressure. The crystal belongs to
triclinic system and has the dimeric columns of $Pd(dmit)_2$.

Recently, we have reported a new superconductor $\beta-[(CH_3)_4N]$
$[Pd(dmit)_2]_2$ (T_c = 6.2 K at 6.5 kbar) which is isomorphous to the high
pressure superconductor, $[(CH_3)_4N][Ni(dmit)_2]_2$ (dmit=4,5-dimercapto-1,3-
dithiole-2-thione).[1,2] The determination of the phase diagram has
revealed the existence of a "pre-superconducting region" where the
resistivity drops rapidly with decreasing temperature.[3] It is well-known
that in spite of the increasing number of the molecular superconductors,
there is no ambient pressure superconductor based on the planar π-acceptor
molecules.[4] For the purpose of the research for the first ambient-
pressure superconductor based on the planar π-acceptor molecules, we have
examined $[(CH_3)_2(C_2H_5)_2N][Pd(dmit)_2]_2$ (abreviated as $[Me_2Et_2N][Pd(dmit)_2]_2$
) because $\alpha-[Me_2Et_2N][Ni(dmit)_2]_2$ is an exceptional π-acceptor conductor
with stable metallic state at ambient pressure.[5] Although our aim could
not be realized perfectly, we have found a new molecular superconductor
above 2.3 kbar.

The black plates of $[Me_2Et_2N][Pd(dmit)_2]_2$ were obtained by the
oxidation of $[Me_2Et_2N]_2[Pd(dmit)_2]$. X-Ray examination has revealed that
$[Me_2Et_2N][Pd(dmit)_2]_2$ is not isomorphous to $\alpha-[Me_2Et_2N][Ni(dmit)_2]_2$ with
the characteristic mode of the molecular arrangement named "spanning

overlapping arrangement" of Ni(dmit)$_2$ [5] nor to β-[(CH$_3$)$_4$N][Pd(dmit)$_2$]$_2$ with "solid crossing columns" of Pd(dmit)$_2$.[2] Crystal data of [Me$_2$Et$_2$N] [Pd(dmit)$_2$]$_2$ is triclinic, space group P$\bar{1}$, a=8.218(4), b=18.422(10), c= 6.277(3) Å, α=96.76(5), β=115.70(3), γ=90.09(5)° , V=848.9(6)Å^3 , Z=1. Intensities were measured on a Rigaku automated four-circle diffractometer with Mo Kα radiation. Independent 3113 reflections (2θ < 55°, |Fo|>3σ(|Fo|)) were used for the structure analysis. The structure was solved by the direct method and refined to the conventional R-value of 0.048. The Pd(dmit)$_2$ anions form strongly dimerized stacks, along the [101] direction (Fig. 1). The interdimer separation is 3.764 Å. The Pd(dmit)$_2$ anions within the dimer pair are eclipsed with intradimer separation of 3.290 Å. The Pd...Pd distance and the shortest Pd...S distance within a dimer are 3.149 Å and 3.886 Å, respectively. The Pd atom is 0.074 Å deviated from the plane formed by four sulfur atoms. Two Pd(dmit)$_2$ molecules which form a dimer curve away from each other to lower the ligand-ligand repulsion between two monomers. The dimethyldiethyl-ammonium cations are not in an ordered state but have two conformations.

The resistivities along the direction parallel to (010) were measured by the four-probe method using the clamp-type pressure cell. The room-temperature conductivity was 10 - 80 S cm^{-1}. As shown in Fig. 2, the resistivity behavior at ambient pressure was different from sample to sample, which may be ascribed mainly to the anisotropy of the resistivity in (010). Every sample becomes non-metallic at low temperature but the resistivity increases rather slowly with decreasing temperature. Above 2.3 kbar, the resistivity drop indicating superconducting transition was observed. All the crystals (three crystals), whose resistivity
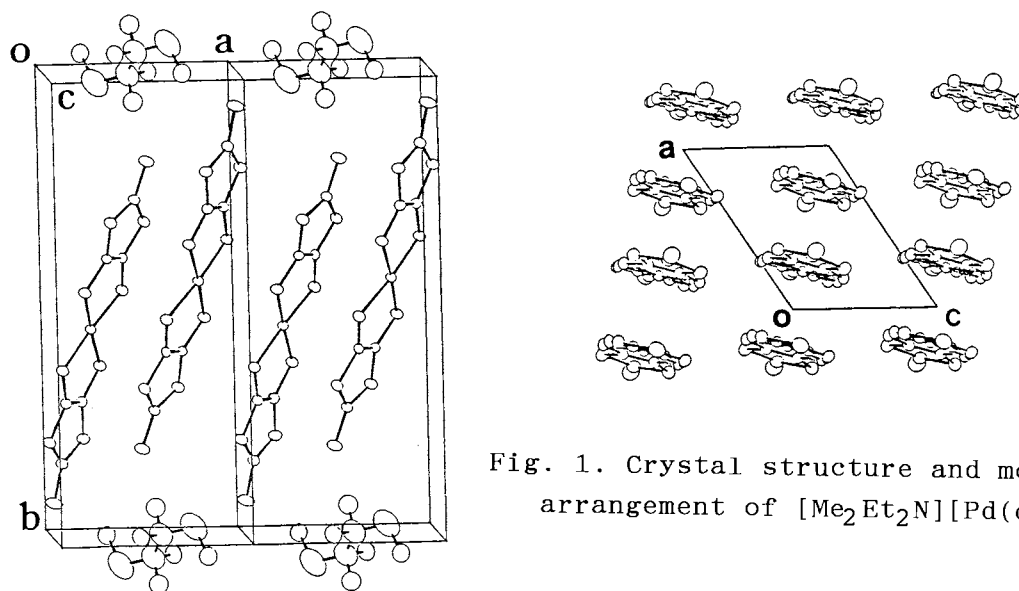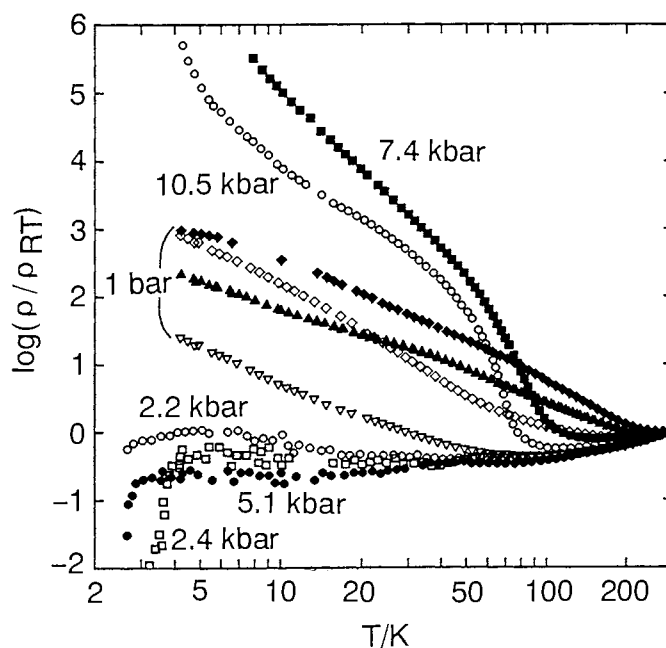

Fig. 1. Crystal structure and molecular arrangement of [Me$_2$Et$_2$N][Pd(dmit)$_2$]$_2$.

Fig. 2. Temperature dependences of resistivities of [Me$_2$Et$_2$N][Pd(dmit)$_2$]$_2$. High-pressure data presented were obtained from the same crystal.

measurements were made above 2.3 kbar, exhibited the same behavior.   To confirm the superconductivity, the magnetic field dependence of the resistivity was measured up to 1T.   The resistivity was recovered when the magnetic field is applied to the direction perpendicular to the crystal plane (//(010)) (Fig. 3).   Thus [Me$_2$Et$_2$N][Pd(dmit)$_2$]$_2$ is the sixth superconductor based on M(dmit)$_2$(M=Ni, Pd) molecules.[6]   Interestingly, in this system, an insulating state is stabilized   above 7 kbar.   Usually metallic state appears when superconducting phase disappears at high pressure, because metallic state tends to be stabilized by applying pressure.   However, in this system, there must be an insulating state
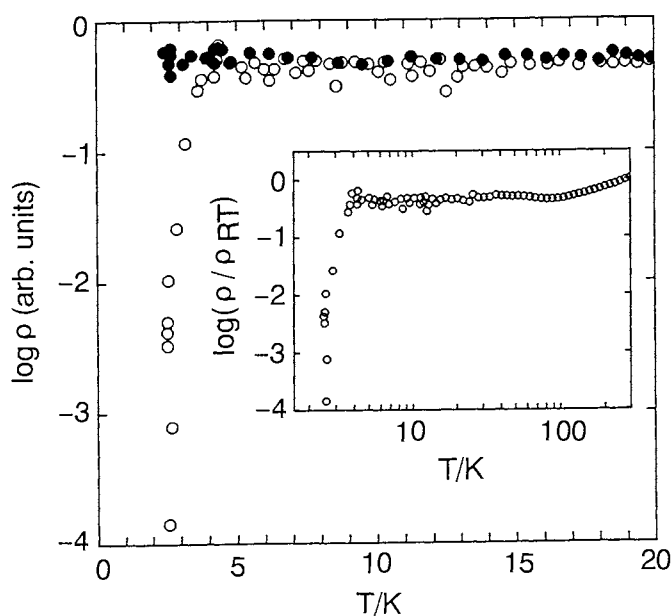

Fig. 3. Superconducting transition of [Me$_2$Et$_2$N][Pd(dmit)$_2$]$_2$ at 3.8 kbar (Tc=3.4 K). The open circles are resistivities without magnetic field and the closed circles are those under magnetic field (H= 1 T).
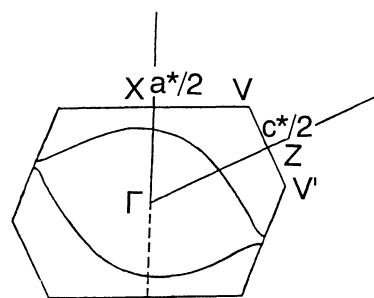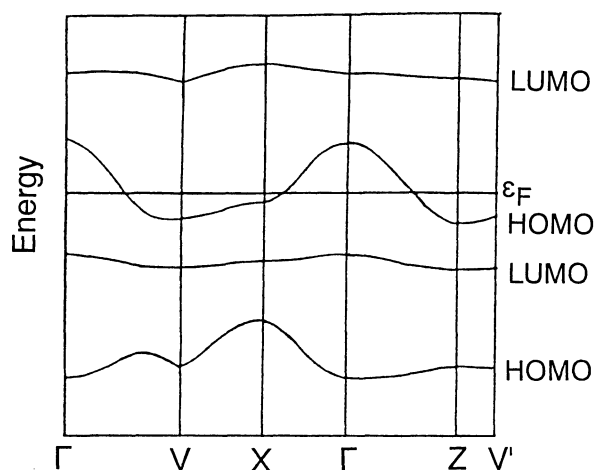
Fig. 4. Tight-binding band structure and Fermi surface of $[Me_2Et_2N][Pd(dmit)_2]_2$.

stabilized at high pressure.

Owing to the dimerization of $Pd(dmit)_2$, both the HOMO band and the LUMO band are split into two. The preliminary examination of the optical reflectivity showed that the upper energy band of HOMO is raised above the lower energy band of LUMO.[7] Thus, the conduction band is formed mainly from the HOMO. The intermolecular overlap integrals between the LUMO and the HOMO of $Pd(dmit)_2$ were calculated by the extended Huckel method using Slater-type orbitals and semi-empirical parameters. The energy difference of HOMO-LUMO is estimated as 0.5 eV. The barely closed 2D metallic Fermi surface was obtained (Fig. 4).

The authors are grateful to Dr. K. Murata for kindly lending us the high-pressure cell.

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