CHEMISTRY LETTERS, pp. 2163-2166, 1991.

New Molecular Superconductor, β-[$(CH_3)_4N$][$Pd(dmit)_2$]$_2$

Akiko KOBAYASHI, Hayao KOBAYASHI,*[†] Akihito MIYAMOTO,[†]
Reizo KATO,[††] R. A. CLARK,[†††] and A. E. UNDERHILL[†††]
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
[†]Department of Chemistry, Faculty of Science,
Toho University, Funabashi, Chiba 274
[††]Institute for Solid State Physics, The University of
Tokyo, Roppongi, Minato-ku, Tokyo 106
[†††]Department of Chemistry and Institute of Molecular and Biomolecular
Electronics, University of Wales, Bangor, Gwynedd LL57 2UW, U.K.

High-pressure resistivity studies on [$(CH_3)_4N$][Pd$(dmit)_2$]$_2$ have revealed the system to be a new molecular superconductor. The superconducting transition has been observed above 6kbar. The mid-point transition temperature T is 6.2 K at 6.5 kbar. The crystal has the structure almost isomorphous to the high-pressure superconductor, [$(CH_3)_4N$][$Ni(dmit)_2$]$_2$.

Up to now, three types of molecular superconductors based on the transition metal complexes have been reported.1) TTF[$Ni(dmit)_2$]$_2$ is the first one found by Cassoux et al.,2) who have also discovered the superconductivity of the Pd-analog, TTF[$Pd(dmit)_2$]$_2$.3) We have reported another type superconductor with closed-shell cations, [$(CH_3)_4N$][$Ni(dmit)_2$]$_2$, which exhibits a superconducting transition at 5 K and 7 kbar.4) In order to examine the possibility of superconductivity in the Pd-analog, we examined the pressure dependence of the electrical conductivity of α-[$(CH_3)_4N$][$Pd(dmit)_2$]$_2$ but no sign of a superconducting transition could be observed up to 12 kbar.5) Nevertheless, we have considered that there still remained a possibility of finding superconductivity in other modifications or at higher pressure. In fact, the reexamination of the high-pressure resistivity of [$(CH_3)_4N$][$Pd(dmit)_2$]$_2$ has revealed the existence of a new superconductor.

The black plates of [$(CH_3)_4N$][$Pd(dmit)_2$]$_2$ were obtained by the electrochemical method from the 1:1 mixed solution of acetonitrile and acetone containing [$(CH_3)_4N$]$_2$[$Pd(dmit)_2$] and [$(CH_3)_4N$]ClO_4.

The resistivities were measured by the four-probe method using the clamp-type pressure cell (Fig. 1). The room temperature conductivity was about 30 S cm^{-1}. In the low-pressure region (<4 kbar), no clear metallic behavior was observed at above 5 kbar, the system began to exhibit metallic conductivity. At 5-6 kbar, the system showed an anomaly around 50 K and transformed to an insulating state below 30 K. At higher pressure, the metal-insulator transition was suppressed and a resistivity drop indicating a superconducting transition was observed. All the crystals (four crystals), whose resistivity measurements were made up to 6 kbar, exhibited superconducting behavior (Fig. 2). To confirm the presence of the superconductivity, the magnetic field dependence of the resistivity was measured at 1.6 K up to 1T (Fig. 3). The resistivity was recovered when the magnetic field is applied to the direction perpendicular to the crystal plane (//(001)). The superconductivity was not broken when the magnetic field was parallel to the plane. This type of anisotropy is common in molecular superconductors and reflects the large anisotropies of the crystal structures and electronic structures of the system.

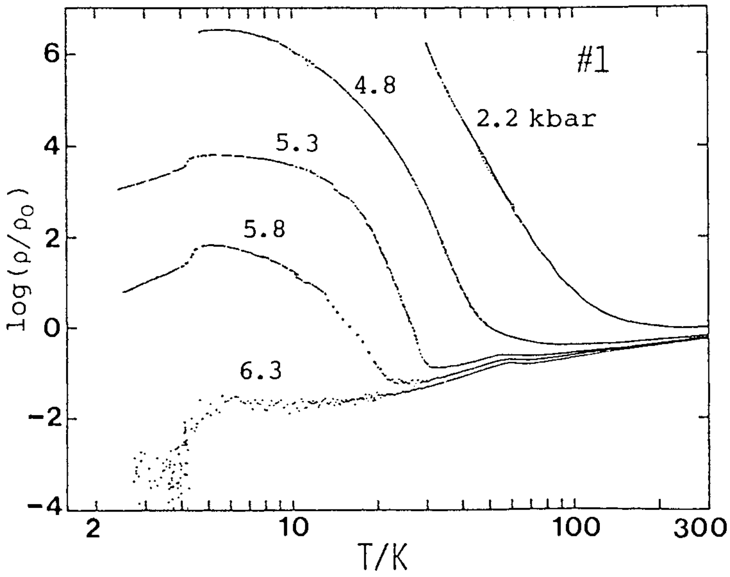

Fig. 1. Temperature dependences of resistivities of β-[$(CH_3)_4N$][$Pd(dmit)_2$]$_2$ at high pressure.

We have examined the X-ray diffraction patterns and made a crystal structure analysis of the crystal after the high-pressure resistivity measurements and whose resistivity behavior is presented in Fig. 1. The crystal was found to be twinned. The obtained crystal data are : monoclinic, C2/c, a=14.541(3) Å, b=6.329(2), c=35.136(5), β=90.98(1)° . V=3233.0(1.1) $Å^3$. The cell parameters are in perfect agreement with those of β-[$(CH_3)_4N$][$Pd(dmit)_2$]$_2$ (β-form (C2/c): a=14.523 Å, b=6.320, c=35.134, β=90.94° ; α-form (P$\bar{1}$): a=35.480 Å, b=7.807, c=6.320, α=112.10°,

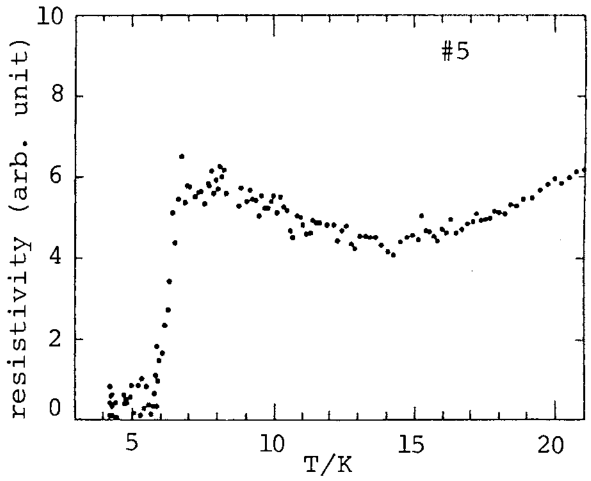

Fig. 2. Superconducting transition of β-$[(CH_3)_4N][Pd(dmit)_2]_2$ at 6.5 kbar. (T_c(mid point) = 6.2 K).

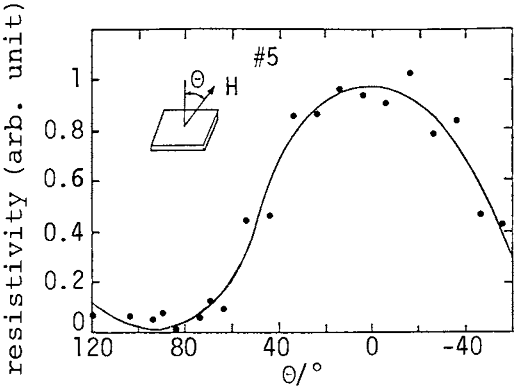

Fig. 3.

Resistivity of β-$[(CH_3)_4N][Pd(dmit)_2]_2$ under magnetic field (H= 1T) at 1.6 K. The angle θ denotes the direction of H.

β= 94.21, γ=92.70).[5] The crystal structure is isostructural to $[(CH_3)_4N][Ni(dmit)_2]_2$ (Fig. 4). But the electronic structure of the Pd (or Pt) system is believed to be different from that of the Ni system,[6] because of the strong dimeric nature of the $M(dmit)_2$ columns (M=Pd, Pt). Intermolecular interaction within the dimers (A-A′ (Fig. 4)) is much stronger than the inter-dimer interaction, and the conduction band is considered to be formed from the HOMO of $M(dmit)_2$ instead of the LUMO.[6] At high pressure, the dimeric nature of the column might be diminished and the LUMO might form the conduction band. Consequently, there may be some possibility of detecting an indication of such a change of the electronic structure in the pressure and temperature(T) dependences of the resistivities(ρ). This was one of the motivations of the present study and will characterize the electronic structure of this new molecular superconductor. There are at least three anomalies in the ρ vs. T curves (anomaly around 50 K, metal-insulator transition and superconducting transition). In order to clarify the nature of these anomalies, further works are required.

The details of the pressure dependence of T_c and the anisotropy of H_{c2} will be reported in near future.

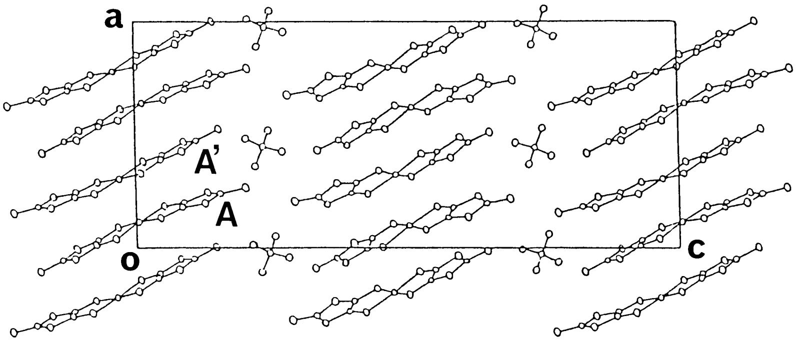

Fig. 4. Crystal structure of β-$[(CH_3)_4N][Pd(dmit)_2]_2$.

The authors thank to a Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture, Japan(A. K., R. K. and H. K.) and the SERC for the support(R. A. C. and A. E. U.). Thanks are also due to the collaborative research project support of the British Council.

References

1) P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, and A. E. Underhill, Coord. Chem. Rev., in press (1991).
2) L. Brossard, M. Ribault, L. Valade, and P. Cassoux, Physica B & C (Amsterdam), 143, 378 (1986); L. Brossard, M. Ribault, L. Valade, and P. Cassoux, Phys. Rev. B, 42, 3935 (1990).
3) L. Brossard, H. Hurdequint, M. Ribault, L. Valade, J. -P. Legros, and P. Cassoux, Synth. Met., 27, B157 (1988); L. Brossard, M. Ribault, L. Valade, and P. Cassoux, J. Phys. (Paris), 50, 1521 (1989).
4) A. Kobayashi, H. Kim, Y. Sasaki, R. Kato, H. Kobayashi, S. Moriyama, Y. Nishio, K. Kajita, and W. Sasaki, Chem. Lett., 1987, 1819; K. Kajita, Y. Nishio, S. Moriyama, R. Kato, H. Kobayashi, W. Sasaki, A. Kobayashi, H. Kim, and Y. Sasaki, Solid State Commun., 65, 361 (1988).
5) A. Kobayashi, H. Kim, Y. Sasaki, K. Murata, R. Kato, and H. Kobayashi, J. Chem. Soc., Faraday Trans., 86, 361 (1990).
6) A. E. Underhill, R. A. Clark, I. Marsden, M. Allan, R. H. Friend, H. Tajima, T. Naito, M. Tamura, H. Kuroda, A. Kobayashi, H. Kobayashi, S. Ravy, and J. P. Pouget, J. Phys. Condense. Matter 3, 933 (1991); E. Canadell, S. Ravy, J. P. Pouget, and L. Brossard, Solid State Commun., 75, 633 (1990); A. Kobayashi, A. Miyamoto, H. Kobayashi, A. C. Clark, and A. E. Underhill, J. Mater. Chem., in press, 1, (1991); H. Tajima, T. Naito, M. Tamura, A. Kobayashi, H. Kuroda, R. Kato, H. Kobayashi, R. A. Clark, and A. E. Underhill, Solid State Commun., 79, 337 (1991).

(Received August 29, 1991)