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# The First Molecular Superconductor Based on π-Acceptor Molecules and Closed-Shell Cations, $[(CH_3)_4N][Ni(dmit)_2]_2$, Low-Temperature X-Ray Studies and Superconducting Transition

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Low-temperature structural study of $[(CH_3)_4N][Ni(dmit)_2]_2$ suggested that the rotational freedom of methyl group seems to play an important role in the "metal-semimetal" transition. Superconducting transition was observed at 5 K (7 kbar).

Although many molecular superconductors have been reported since the discovery of the first organic superconductor, Bechgaard salt composed of π-donor molecules TMTSF and closed-shell anions ($ClO_4$,$PF_6$...), there is no superconductor based on π-acceptor molecules and closed-shell cations, that is, the reversed case of Bechgaard salt. In accordance with the recent molecular designing analysis,[1] we considered that $[(CH_3)_4N][Ni(dmit)_2]_2$ can be a possible candidate of the molecular superconductor composed of multi-sulfur π-acceptor molecules and tetrahedral closed-shell cations(dmit=isotrithionedithiolate). Recently, we have found that $[(CH_3)_4N][Ni(dmit)_2]_2$ undergoes a metal-semimetal transition with large hysteresis.[2] In order to make clear the origin of the metal-semimetal transition and the possibility of the superconductivity at high pressure, we performed low-temperature structural studies and resistivity measurements and found that $[(CH_3)_4N][Ni(dmit)_2]_2$ is a new type of molecular superconductor(Tc=5 K at 7 kbar).

As reported previously,[2] the room-temperature conductivity of $[(CH_3)_4N][Ni(dmit)_2]_2$ is about 50 S $cm^{-1}$ along the direction parallel to (001) and $10^{-2}$ S $cm^{-1}$ along the direction perpendicular to it. Figure 1 shows the change of the resistivity behavior during the cooling and heating cycles. In the cooling process, the system shows a transition around 100 K, where the resistivity shows a jump. This jump becomes smaller with increasing the cycles. In the heating process, the hysteresis loop is closed around 200-250 K. In the third cycle, the loop becomes flat and the temperature dependence of the resistivity becomes almost metallic over all the temperature range(65-300 K).

For the purpose of examining the possibility of the structural change at the metal-semimetal transition temperature, the X-ray oscillation photographs were taken using monochromated Mo Kα radiation at 92 K after the crystal was dipped into liquid $N_2$ (Fig. 2). Diffuse scattering due to the normal lattice vibrations was observed. However, any extra reflections indicating the development of the periodical lattice modulation wave could not be obtained, which indicates that the metal-semimetal transition is not accompanied by any changes of the periodicity of the crystal structure. Crystal data at 95 K are: $(C_4H_{12}N)[Ni(C_3S_5)_2]_2$, monoclinic, C2/c, a=13.675(4), b=6.476(2), c=36.048(10) Å, β=94.74(2)°, V=3181.5(1.7) Å$^3$, Z=8. The crystal structure at 95 K was refined based on 3418 reflections ($2\theta < 55°$(MoKα)). Final R-value was 6.7 %. The structure is essentially same to the room-temperature structure (Fig. 3). The possibility of the inclusion of solvent molecules (acetonitrile) was examined. But no indication was observed. The residual peaks were lower than those of hydrogen atoms.

The crystal is composed of the metal layer with 1D fourfold stacks of $[Ni(dmit)_2]$ and cation sheets arranged alternately along [001]. Owing to the glide plane parallel to [001], the metal layers with the $[Ni(dmit)_2]$ stacks along [110] and those along $[1\bar{1}0]$ appear alternately along [001]. As reported in Ref. 2, the system has a plane like Fermi surface approximately perpendicular to the stacking direction. But due to the alternation of two types of the metal layers the two Fermi surfaces with different orientation must be superposed(Fig. 4 ), indicating $[(CH_3)_4N][Ni(dmit)_2]_2$ to be a system with multi-Fermi surfaces. As pointed out by us, the multi-Fermi surface system is stable against the lattice-modulation wave,[1,3] which will be the reason why any X-ray satellite reflections or diffuse streaks were not observed.

The temperature dependence of the lattice constants are shown in Fig. 5. The thermal expansion coefficients (130 K $< T <$ 300 K) are: $\alpha_a = 7.7 \times 10^{-5}$/K, $\alpha_b = 3.2 \times 10^{-5}$, $\alpha_c = 2.5 \times 10^{-5}$. The fairly large discrepancy between the lattice constant c in the cooling process and that in the heating process seems to suggests some relation with the hysteresis phenomena.

There remains the problem as to the origin of the large hysteresis of the resistivity. One possible mechanism may be the transition originated from rotational motion of methyl groups of the cation. The positions of the hydrogen atoms of one of the two independent methyl groups could not be found on the difference Fourier maps of the room-temperature structure. This indicates that one of the two methyl groups is rotationally disordered at room temperature. The 95 K structure gave the positions of all the hydrogen atoms. So that the freedom of the rotational motion of methyl group is considered to be almost frozen at 95 K. The freezing and melting of the rotational freedom of methyl group will play an important role in the metal-semimetal transition with hysteresis. Considering that the methyl rotation does not produce a large structure change, the small change of the resistivity at the metal-semimetal transition seems to be natural. Intermolecular overlap integrals of LUMO(S) were calculated on the structure at 95 K. Overlap integrals along the 1D column are 50 % larger than those at room temperature. The simple tight-binding band structure is essentially same to that

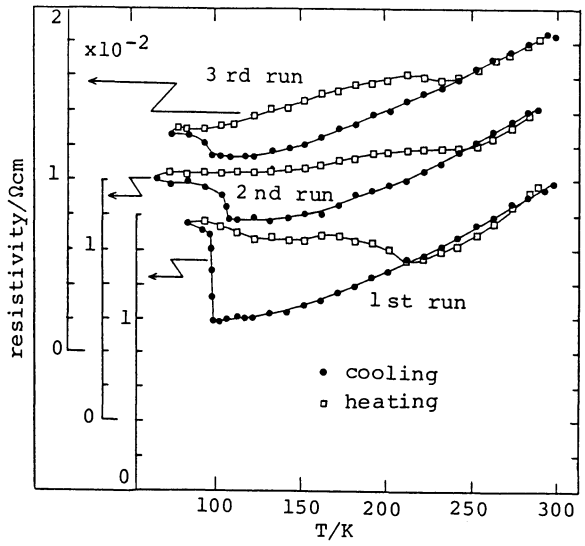


Fig. 1. Change of the resistivity of temperature cycles.

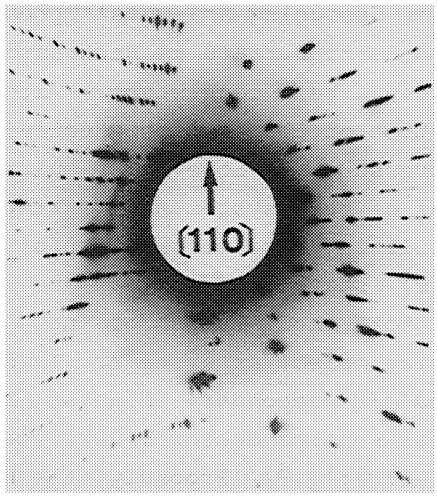


Fig. 2. Oscillation photograph at 92 K.

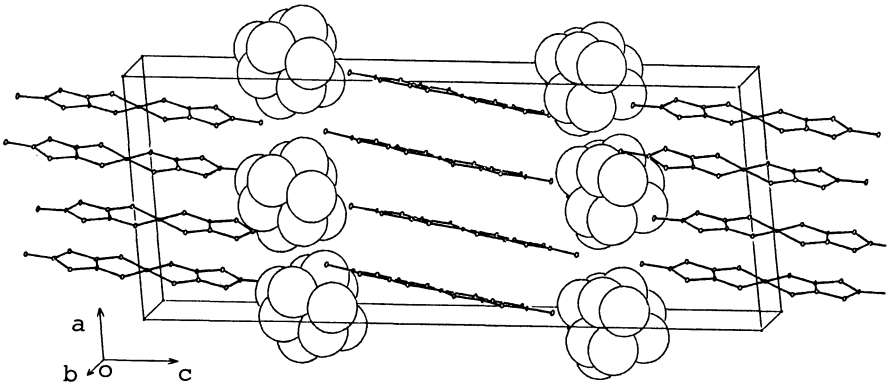


Fig. 3. Crystal structure at 95 K. Large circles indicate van der Waals radii of the hydrogen atoms.

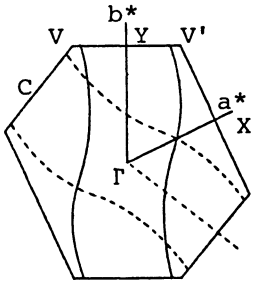


Fig. 4. Multi-Fermi surfaces(see Ref. 2).

of the room-temperature structure.

The pressure dependence of the resistivity was measured up to 7 kbar. The metal-semimetal transition was suppressed and superconducting transition behavior was observed above 3 kbar (Fig. 6). The superconducting transition temperature Tc is enhanced with increasing pressure. The transition temperature Tc is 5 K at 7 kbar. The positive pressure effect of Tc($dTc/dp>0$) is the same as the case of $(TTF)[Ni(dmit)_2]_2$[4] and reversal to the case of $TMTSF_2X(X=ClO_4,PF_6..)$[5] and $\beta$-$(BEDT\text{-}TTF)_2X$ ($X=I_3$, $IBr_2$).[6] These facts will give an important hint to enhance the transition temperature of the molecular superconductors. The magnetic field effect on the superconducting transition was measured and the anisotropy of $Hc_2$ and the coherence lengths were determined. The detail will be reported in the separate paper.[7]

We have found the molecular superconductor $[(CH_3)_4N][Ni(dmit)_2]_2$ composed of $\pi$-acceptor molecules and closed-shell cations. The close side-by-side contacts of $[Ni(dmit)_2]$ and the weak intermolecular transverse interaction expected from the

molecular designing analysis[1] produce a quasi-1D Fermi surface as Bechgaard salt, which may be consistent with the observation of the superconductivity at high pressure. However, multi-Fermi surfaces of this system may be important for realizing the metallic (or semi-metallic) state. This may be a new aspect for the design of new superconducting molecular systems. Tc of this compound is secondary highest in the molecular superconductors, next to 8 K of β-(BEDT-TTF)$_2$I$_3$.[6] Probably the super conducting transition temperature of this system will increase at the higher pressure, which is now being examined.

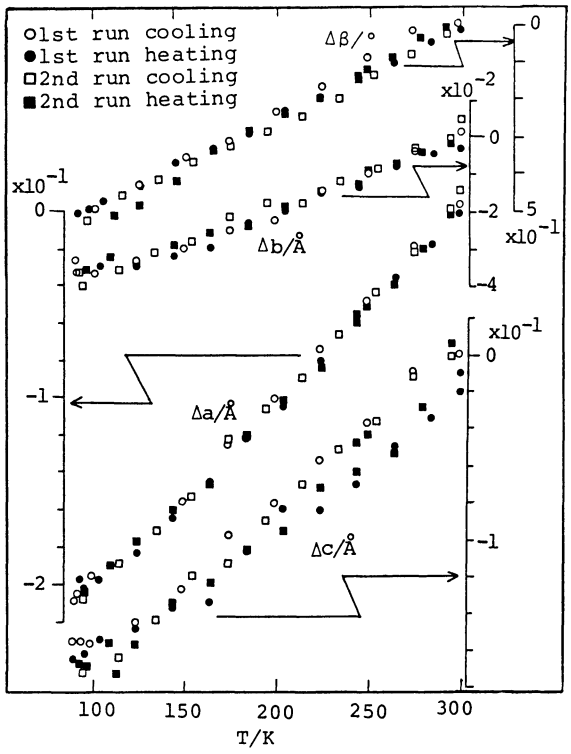


Fig. 5. Temperature dependence of lattice constants.

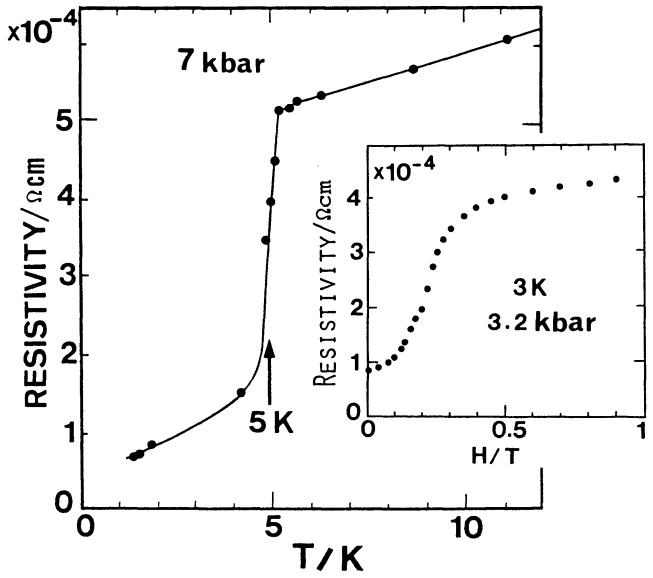


Fig. 6. Superconducting transition and it's magnetic field effect.

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