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THE CRYSTAL AND ELECTRONIC STRUCTURES OF A NEW MOLECULAR CONDUCTOR, (TMTSF)[Ni(dmit)$_2$]

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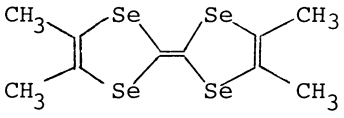
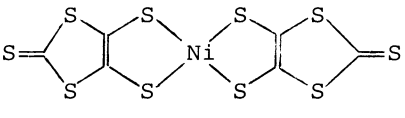
The crystal of (TMTSF)[Ni(dmit)$_2$] has a 9-fold superstructure. The amplitude of the transverse sinusoidal lattice modulation wave (≃1 Å) is extremely large compared with that of usual Peierls distortion wave. Despite of the high room-temperature conductivity (≃300 Scm^{-1}), this system is a semiconductor (E_a(R.T.)=0.034 eV). The fundamental structure is composed of segregated uniform stacks of TMTSF and Ni(dmit)$_2$.

The recent discoveries of organic superconductors have aroused a large interest in the field of molecular metals.[1] Unlike typical molecular metals such as KCP and TTF-TCNQ, the organic superconductors exhibit considerable two-dimensional(2-D) properties. The intermolecular interaction between multi-sulfur (selenium) π-donor and π-accpeptor molecules is essential to enhance the dimensionality of the molecular metals.

In this report, the crystal and electronic structures of a new molecular conductor, (TMTSF)[Ni(dmit)$_2$] will be reported (dmit=isotrithionedithiolate).



TMTSF



Ni(dmit)$_2$

The black lustrous crystals of (TMTSF)[Ni(dmit)$_2$] were obtained electrochemically from the 1,1,2-trichloroethane solution of TMTSF and (Bu_4N)[Ni(dmit)$_2$]. The Weissenberg and oscillation photographs show that the crystal lattice is modulated periodically by transverse sinusoidal wave (Fig. 1). The satellite reflections appear at the interval of **b***/9, indicating the 9-fold superstructure. Crystal data are: ($C_{10}H_{12}Se_4$)($C_6S_{10}Ni$), monoclinic , $P2_1/n$, a=15.227(4), b=34.559(5), c=25.455(6) Å, β=105.70(2)°, V=12895(5) Å^3, Z=18. The unit lattice vectors of the fundamental lattice ($\mathbf{a}_o$,$\mathbf{b}_o$,$\mathbf{c}_o$) are: $\mathbf{a}_o$=**a**, $\mathbf{b}_o$=**b**/9, and $\mathbf{c}_o$=**c**, where **a**, **b** and **c** are the lattice vectors of the modulated superstructure. In the analysis of the superstructure, the reflections (hk$l$) with the indices

[0,η,ζ]

Fig. 1. Weissenberg photograph of (TMTSF)[Ni(dmit)$_2$].

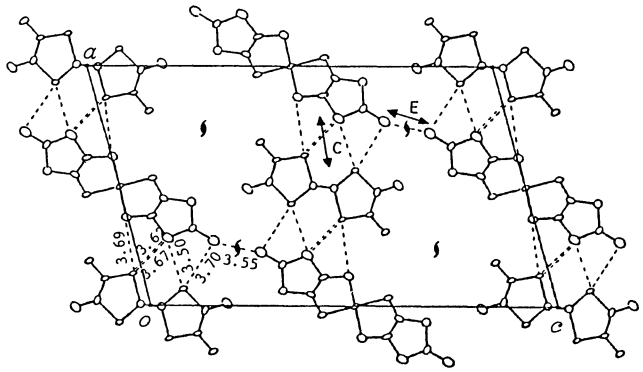


Fig. 2. Projection of Fundamental Structure along $\mathbf{b}_o$.

k≠9n, are regarded as satellite reflections. The intensities of the main(n=0) and satellite(n≠0) reflections from the crystal lattice modulated by transverse sinusoidal wave with the amplitude of |p**a**+q**c**|, are written as,[2)]

$$I(\xi,\eta,\zeta)=|F(\xi,\eta,\zeta)|^2 J_n^2(2\pi(p\xi+q\zeta)) \quad (1)$$

where ξ=h, η=k+n/9 and ζ=l, and J_n is the n-th Bessel function. The systematic change of the intensities of the main and satellite reflections permitted a rough estimation of the amplitude of the periodical lattice distortion (PLD) wave: pa=0.9, qc=0.5 Å. The fundamental structure was solved by the Patterson method. The block-diagonal least-squares refinement gave a final R-value of 0.13. Considering the large difficulties in the assignment of satellite reflection, this result is quite satisfactory. The obtained fundamental structure is shown in Fig. 2. The TMTSF and Ni(dmit)$_2$ molecules are stacked face-to-face to form segregated uniform columns with the small lattice spacing of 3.840 Å(=b/9). The mode of the intermolecular overlapping of TMTSFs is approximately that of the direct overlapping, with the short interplanar distance of 3.75 Å. However, the degree of intermolecular overlapping is small in the Ni(dmit)$_2$ column. The molecular plane of TMTSF is not parallel to that of Ni(dmit)$_2$. The dihedral angle between these two planes is 27°.

It is of interest that despite of the large room-temperature conductivity (300 S cm^{-1}), this system exhibits a semiconductive behavior (E_a(R.T.)=0.034 eV).

The anisotropy of the intermolecular overlap integrals(S) between the HOMOs of the donor molecules and/or LUMOs of the acceptor molecules plays the most important role to determine the electron conduction path. The transfer integral(t) is approximately proportional to S (t≃-ES, where E is a constant of the order of the energy of HOMO (∿10 eV[4)]). Owing to the close contacts and direct overlapping along the TMTSF stack, the corresponding band width will be larger than that of $(TMTSF)_2X$.[5)] On the other hand, the overlap integral along the Ni(dmit)$_2$ column is very small (Fig. 3). The simple tight-binding band structure can be easily obtained as,

$$E_{\pm}(\mathbf{k})=(t_A+t_B)\cos\mathbf{kb} + \varepsilon_o/2 + \sqrt{D} \quad (2)$$

$$D=((t_A-t_B)\cos\mathbf{kb} - \varepsilon_o/2)^2 + 4t_C^2\sin^2\mathbf{ka}/2 \quad (3)$$

where ε_o is the energy difference between the HOMO of TMTSF and the LUMO of

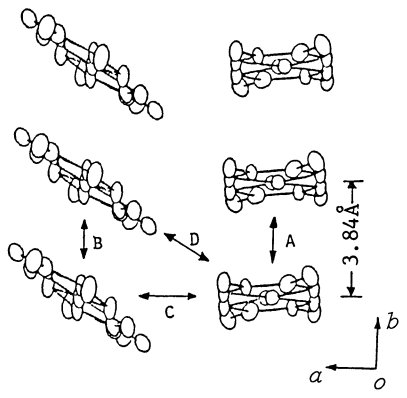
$Ni(dmit)_2$ and t_A, t_B and t_C are the transfer integrals between the molecules shown in Figs. 2 and 3. The other smaller interactions were neglected. $E_{\pm}(\mathbf{k})$ is independent of **kc**. The small dispersion of the $Ni(dmit)_2$ band makes it easy to estimate the approximate value of ε_o. Since the energy dispersion is extremely small along the a* direction, the system has plane-like Fermi surfaces perpendicular to the b axis. Contrary to the holes in the TMTSF columns, the electrons in the $Ni(dmit)_2$ columns will not be mobile because of the small transfer energy. As seen from Eqs. 2 and 3, the effect of the interchain interaction becomes zero when $\mathbf{ka}=0$ and the upper and lower bands contact at $\mathbf{k}=\mathbf{k}_o$ (see Fig. 4, where ε_o was determined by assuming that the wave number vector of PLD ($\mathbf{b}^*_o/9$) is equal to $2\mathbf{k}_o$ (see later discussion)). In the other positions ($\mathbf{k}\neq\mathbf{k}_o$), the energy bands are splitted into two bands. Since both the signs of t_A and t_B are plus, the Fermi wave number k_F is different from $\mathbf{k}_o$ (if $t_A > 0$ and $t_B < 0$, $\mathbf{k}_F=\mathbf{k}_o$).

The plane-like Fermi surface suggests that the system would be a 1-D metal if the structure were not modulated. Therefore, the semiconductive behavior must be originated from the existence of the PLD wave. There seems to be two characteristic PLDs which make the metallic state unstable: (1) Peierls distortion with the periodicity of $2k_F$; (2) the PLD with the periodicity of $2k_o$. Preliminary experimental evidences appear to prefer the second possibility:

(1) Rough estimation of the degree of charge transfer (ρ) based on the IR spectra ($\nu_{C=C}(Ni(dmit)_2) \simeq 1300\ cm^{-1}$) indicates that $\rho > 0.3e$. If the PLD were originated from Peierls instability of TMTSF columns, the wave length of PLD would be $(2/\rho)b_o$ ($<7b_o$), which is smaller than the observed wave length ($9b_o$).

(2) Considering the small amplitude of the Peierls distortion wave (<0.15 Å),[3] the obtained amplitude of PLD wave in (TMTSF)[$Ni(dmit)_2$] ($\simeq$1 Å) is too large to be attributed to the Peierls instability.

(3) Since the molecular plane of TMTSF is nearly perpendicular to the b axis, the



INTERACTION	S(x10^{-3})		
A	-40.59	D	0.24
B	-1.16	E(Fig.2)	-0.41
C	1.85		

Fig. 3 Molecular stackings and the intermolecular interactions.

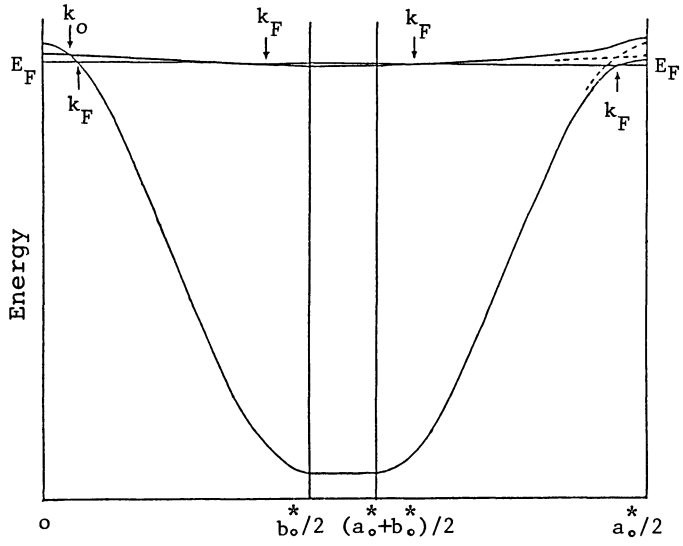


Fig. 4. Schematic drawing of energy band (fundamental structure).

intrachain overlap integral is weakly dependent on the transverse molecular displacement. Therefore, the transverse modulation is unfavorable for the formation of Peierls gap. The large PLD will produce a large increase of the elastic energy but the decrease of the electronic energy will be very small. Thus it is not plausible that PLD is originated from Peierls instability.

Besides the well-known Peierls instability, which is a single-chain property, another type lattice instability will appear in two-chain system with crossing band. The interchain interaction (t_C) will be modulated by the transverse PLD wave. Since $E_{\pm}(\mathbf{k}_o)=E_{\pm}(-\mathbf{k}_o)$ (see Eq. 2), the effect of the perturbation due to PLD will become largest when the periodicity of PLD is $2k_o$. The energy depression of the lower energy band at $\mathbf{k}_o$ is equal to the perturbation energy $\Delta V = |\int \Psi_{TMTSF} H' \Psi_{Ni(dmit)_2} dr|$, where H' is perturbation which produces a periodical modulation of the transfer integral, t_C. If ΔV is the same order of $|t_A - t_B - \varepsilon_o/2|$, $E_-(\mathbf{k})$ will be depressed to the energy level lower than Fermi energy(E_F), and system will become semiconductive. Thus the relatively large interchain interaction ($t_C > t_B$) and the large amplitude of the PLD wave will give a reasonable interpretation for the narrow-gap semiconductive behavior of (TMTSF)[Ni(dmit)$_2$]. The detailed analyses of the superstructure and electronic properties will be reported elsewhere.

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