INFRARED NEAR-ISOTROPY IN A MIXED STACK ORGANIC CONDUCTOR: OMTSF-Ni(DMIT)$_2$

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ABSTRACT

From transport measurements the mixed stack organic conductor OMTSF-Ni(DMIT)$_2$ (OMTSF: bis-tetramethylene-TSF, Ni(DMIT)$_2$: (4,5-dimercapto-1,3-dithiole-2-thione)nickel) is known to possess near isotropy in the crystallographic a-c plane, where there are indeed a large number of close interstack contacts in different directions. A study is presented of the polarized infrared reflectance spectra for various directions in the a-c plane. Only weak polarization dependence is found in the entire frequency range. The spectra display a broad, asymmetric CT band at 2,600 cm^{-1} as well as a number of distinct electron-molecular vibration features. One of the spectra is discussed within a simple model for the coupling between charge transfer processes and intramolecular vibrations.

INTRODUCTION

The immense research efforts in the area of organic linear chain charge transfer salts, which really began with the synthesis of the first real organic metal, TTF-TCNQ, in 1972 [1,2], grew to new heights, when organic superconductors based on the molecules TMTSF and BEDTTF were found [3,4]. A common feature of the organic superconductors appears to be that they in contrast to for example TTF-TCNQ, which must be characterized as a quasi-one-dimensional metal, have appreciable interchain contacts. Thus they have a significant two- or three-dimensional character (although they may still be quite anisotropic). These interstack contacts often result from closely positioned heteroatoms (e.g. S and Se) on different molecules. Thus popular molecules in the hunt for organic superconductors tend to have many heteroatoms on their periphery.

One such molecule is Ni(DMIT)$_2$ ((4,5-dimercapto-1,3-dithiole-2-thione)nickel) with 12 S-atoms along the periphery. Two Ni(DMIT)$_2$ complexes have been reported superconducting, the first being TTF-(Ni-(DMIT)$_2$)$_2$ [5]. We have investigated several semiconducting Ni(DMIT)$_2$- complexes [6,7], among them the 1:1 complex with OMTSF (bis-tetramethylene-TSF), i.e. a molecule similar to TMTSF, but with

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closed methylene rings on the ends. The triclinic crystal structure [8] shows parallel stacks (along the crystallographic a-axis) of alternating donor (D: OMTSF) and acceptor (A: $Ni(DMIT)_2$) molecules (mixed stacks). There are indeed many short contacts between Se and S both along the stacks and between neighbour stacks (along the c-axis). A side view of the structure is shown in Fig. 1. The room temperature conductivity, σ(300K) $\approx$ 10 S/cm, quite high for a mixed stack material. However, the conductivity is activated. Assuming simple semiconductor behaviour, the material has an energy gap for excitation of charge carriers of order 0.12 eV. Preliminary microwave loss measurements indicate considerable conductivity both along the a-and the c-axes.

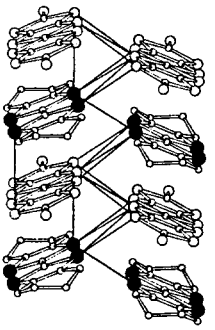

Fig. 1. Perspective view of the intermolecular contacts in OMTSF-$Ni(DMIT)_2$ [6,8]. The filled circles are the Se-atoms in OMTSF.

In the present work we present the room temperature polarized reflectance in the a-c -plane. Little anisotropy is observed in the infrared, where charge transfer excitations dominate. Thus the transport properties seems rather isotropic in the a-c -plane. We discuss one of the spectra in terms of a simplified model, which describes isolated DA-pairs with allowance for coupling of the oscillating charge to intramolecular vibrational modes.

EXPERIMENTAL

Shiny black platelets of OMTSF-$Ni(DMIT)_2$ were formed on an electrode by oxidation of a solution of OMTSF in the presence of n-BA-$Ni(DMIT)_2$. The typical size of the optically accessible faces are 1x0.3 mm^2. The faces are (010), i.e. contains the a- and c-axes. The a-axis has an angle of $\approx 40^{\circ}$ with the longest (needle) direction of the platelets [9].

Polarized reflectance spectra have been monitored in the range 100-27,000 cm^{-1}. The far and mid infrared part of the spectra (to $\approx$ 3,500 cm^{-1}) were measured with a Bruker IFS113V rapid scan Fourier transform spectrometer equipped with an A510 reflectance attachment and various wire grid polarizers. The near infrared and visible (from $\approx$ 3,000 cm^{-1}) was covered using a Perkin-Elmer 98 monochromator with interchangeable gratings and prisms. Here polarized radiation was obtained using a Glan-Thompson prism. Gold and aluminum mirrors were used as reference in the infrared and visible spectral regions respectively.

RESULTS

The polarized reflectance in the far to mid infrared was measured for 4 polarizations: Along the needle direction of the platelet (0°) and 45°, 90°, and 135° from this orientation. The data are presented in Fig.2. The remarkable feature is that there are only rather small differences between the polarizations. In

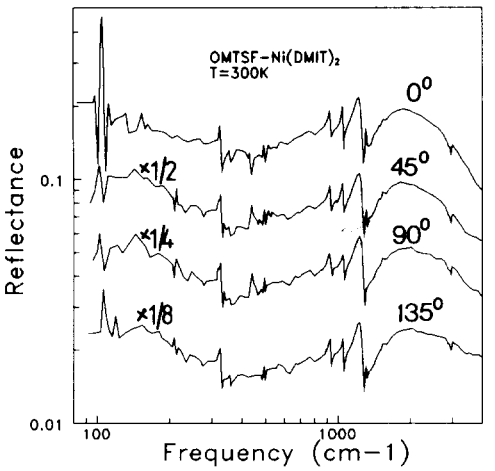

Fig. 2. Polarized reflectance spectra of OMTSF-Ni(DMIT)$_2$. The angles refer to the needle direction. Notice the logarithmic axes. The spectra are scaled to facilitate inspection.

spite of the obvious anisotropy of the crystal structure, the charge transfer excitations and the molecular vibration features are virtually the same for all orientations in the a-c -plane. Therefore we shall in the following concentrate on one spectrum (the 0^{O}) for further analysis.

However, looking into the details of the spectra, there are indeed changes with orientation. The most remarkable is the sharp structure near 100 cm^{-1}. The low frequency suggests that it is due to a mode where the molecule(s) or large parts of them move more or less rigidly (e.g. a librational mode). Such a mode is quite likely to have considerable polarization dependence.

The main vibronic features may tentatively be assigned as follows: The dip at 2,950 cm^{-1} can only be due to C-H stretching modes, thus originates from the OMTSF molecules. Independent studies of the vi-

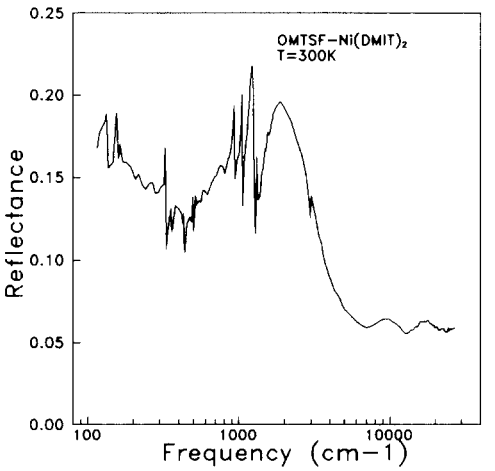

Fig. 3. Reflectance along needle axis of OMTSF-Ni(DMIT)$_2$ crystal. Notice the logarithmic axis.

bration spectrum of Ni(DMIT)$_2^-$ suggest that the modes at $\approx$ 1,060 cm^{-1} and $\approx$ 1,340 cm^{-1} can be assigned to this molecule. The intense feature with a minimum near 1,300 cm^{-1} may be associated with the central C=C mode in OMTSF, which always appears strongly in TTF-derived molecules [10].

In the following we focus on the 0^{O}-spectrum. The reflectance over a wider range is shown in Fig. 3. The spectrum indicates transitions at 10,000-12,000 cm^{-1} and at 17,000 cm^{-1} and above, which may be associated with intramolecular excitons. To further study the details in the interesting low frequency part of the spectral range we have performed a Kramers-Kronig transformation of the data assuming constant reflectivities in the ranges not covered. The accuracy of the result should be fairly good in the range 500-10,000 cm^{-1}. The frequency dependent conductivity, which quantitatively gives the distribution of

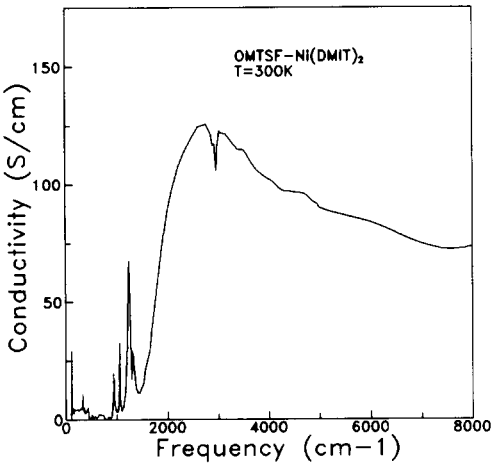

Fig. 4. Frequency dependent conductivity of OMTSF-Ni(DMIT)$_2$ along needle axis.

oscillator strength is shown in Fig. 4 in the range 100-8,000 cm^{-1}. In this plot the distinct charge transfer band is seen to peak at 2,600 cm^{-1}, with an onset at about half that frequency, consistent with the observed activation energy in DC-conductivity. We shall for simplicity assume that the whole band is associated with DA charge transfer processes.

DISCUSSION

With the assumption that the observed spectral features are mainly due to charge oscillations between D and A molecules, coupled to breathing (A_g) modes on the molecules, we may fit the following model dielectric function to the data:

$$\epsilon(\omega) = \epsilon_{core} + \frac{\omega_p^2}{\omega_{CT}^2(1-D(\omega)) - \omega^2 - i\omega\gamma_e}$$

In this expression, ϵ_{core} describes the background dielectric constant, ω_p^2 is a measure for the intensity of the CT-band, ω_{CT} is its position, while γ_e is its width. The effect of the intramolecular A_g-modes is taken into account by the function:

$$D(\omega) = \sum_{i=D,A} \sum_{n_i} \frac{\lambda_{n_i}\omega_{n_i}^2}{\omega_{n_i}^2 - \omega^2 - i\omega\gamma_{n_i}},$$

where i specifies donor and acceptor molecule respectively and n_i numbers the individual modes. ω_{ni} and

γ_{ni} are the natural frequencies and linewidths of the modes which couple to the oscillating electrons via dimensionless coupling constants, λ_{ni}. Fig. 5 presents a fit of this model to the data points in the interesting region from 800-3,200 cm^{-1}. The model, the details of which will be published elsewhere [11], is a generalization of the self-dimer model [12], and is one of a family of models describing the strongly enhanced vibronic features frequently observed in semiconducting CT-complexes [13]. In the present case

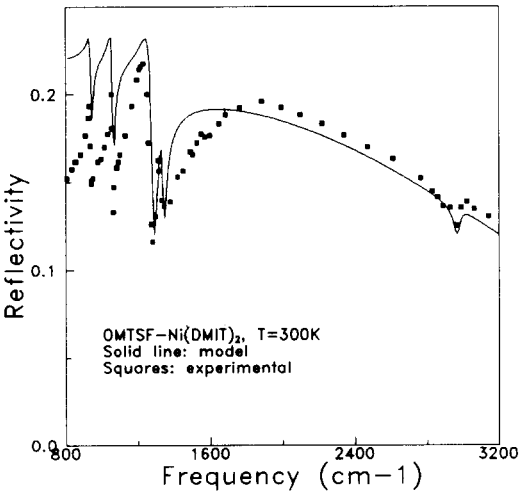

Fig. 5. Fit of DA-model to experimental reflectance points.

it builds on the simplest possible description of a DA-pair [14] with a ground state degree of charge transfer, ρ, between 0 and 1. To employ such a model we assume localized carriers and DA-pairing, assumptions which are clearly not strictly justifiable. However, with the limitations of the model in mind, the parameters may be linked to physical quantities through the following equations [11]:

$$\omega_p^2 = \frac{2e^2a^2N_d\omega_{CT}\rho(1-\rho)}{\hbar\epsilon_o},$$

$$\hbar\omega_{CT} = 2\Delta\sqrt{1+(t/\Delta)^2}, \quad \rho = 1-\frac{(t/\Delta)^2/2}{1+(t/\Delta)^2-\sqrt{1+(t/\Delta)^2}},$$

$$\lambda_{n_i}\omega_{n_i}\omega_{CT} = 4\rho(1-\rho)g_{n_i}^2.$$

In these equations t is the DA transfer integral, Δ is half the difference between the D and A orbital energies, and g_{ni} are the bare coupling energies (measured in units of frequency). N_d is the DA-pair density and a is the D to A center distance. The principally determined model parameter are: $\epsilon_{core} = 2.6$, ω_p = 5,600 cm^{-1}, ω_{CT} = 2,600 cm^{-1}, and γ_e = 4,000 cm^{-1}, which by the above equations, and N_d = $1.4 \cdot 10^{21}$ cm^{-3} and a = 5.0 Å [8], lead to a degree of charge transfer of ρ = 0.14 (bond length analysis seems to suggest near neutral molecules [9]), a transfer integral, t = 0.11 eV, and half the site energy difference, Δ = 0.12 eV. For the molecular vibration features this first analysis leads to the results given in the table below.

The g-values (which are intrinsic to the molecule and orbital) are close to what is found in related molecules [10]. This confirms the consistency of the approach, although the quality of the fit in Fig. 5 is not quite satisfactory. It is possible that more than one CT-process should be taken into account.

TABLE 1
Molecular vibration parameters for OMTSF-Ni(DMIT)$_2$.

ω_{Ai} (cm^{-1})	λ_{Ai}	g_{Ai} (cm^{-1})	ω_{Di} (cm^{-1})	λ_{Di}	g_{Di} (cm^{-1})
			941	0.005	160
1,062	0.008	220	1,290	0.03	460
1,343	0.014	320	2,970	0.003	220

CONCLUSIONS

We have demonstrated that OMTSF-Ni(DMIT)$_2$ is an example of an organic charge transfer complex which is almost isotropic in two dimensions. The Ni(DMIT)$_2$ molecule clearly enables transverse contacts in linear chain compounds. We have analyzed the infrared data within a simple DA-charge oscillation model, which takes into account the coupling to intramolecular vibrational modes. The results demonstrate how infrared and optical measurements can provide estimates for a number of physical parameters for such materials.

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