Temperature dependence of electronic optical absorption in $(NMe_4^+ \cdot TCNQ^{-\cdot})_2 TCNQ$

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Abstract

The temperature dependence of the linearly polarized optical absorption spectrum has been measured in single crystals of $(NMe_4^+ \cdot TCNQ^{-\cdot})_2 TCNQ$, where NMe_4 and TCNQ are tetramethylammonium and tetracyanoquinodimethane, respectively, in the temperature range between -100 and +150 °C. In addition to intense $TCNQ^{-\cdot}$ dimer bands, strongly temperature-dependent satellite bands appear at around 1.3 eV and 1.9 eV. The singular behavior of the intensity and peak position of the 1.3 eV band shows that a second order phase transition takes place at 126 °C. The origin of this band is discussed in relation to the mechanism of the phase transition.

1. Introduction

The substance, $(NMe_4^+ \cdot TCNQ^{-\cdot})_2 TCNQ$, is one of organic ferromagnets [1]. It exhibits a small magnetic moment with the coercive field of the order of 300 Oe at room temperature. So far several similar substances have been synthesized [2, 3]. They contain neutral and radical TCNQ or TCNQ-related molecules in a molar ratio of 1 : 2. Some of them remain ferromagnetic upon being heated up to 80 °C [2].

Here we report on the results of the first optical approach to the electronic properties of $(NMe_4^+ \cdot TCNQ^{-\cdot})_2 TCNQ$. To obtain information on the electronic structure of TCNQ molecules we measure the polarized absorption spectrum for single crystals in the near-infrared to visible region in a wide range of temperature.

2. Experiment

The as-grown crystals which are 1-2 μm thick and approximately 200×200 μm² wide are used as the samples. The wide surfaces are parallel to the *ab* plane of the monoclinic crystal structure [1]. The linearly polarized absorption spectrum is measured with the probe light incident normal to this plane using a microscope-spectrometer system equipped with a temperature-controllable optical cell (Linkam TH-600PM).

It emerges from this measurement that there are two types of crystals, which we classify as type-I and type-II. Their absorption spectra resemble one another well but differ quantitatively. Figures 1(a) and 1(b) show the absorbance spectra of a type-I sample for *E //a* and *E //b*, respectively, at several temperatures, where *E* is the electric field of light. The clear polarization dependence of the overall spectrum reflects the fact that all the TCNQ molecules
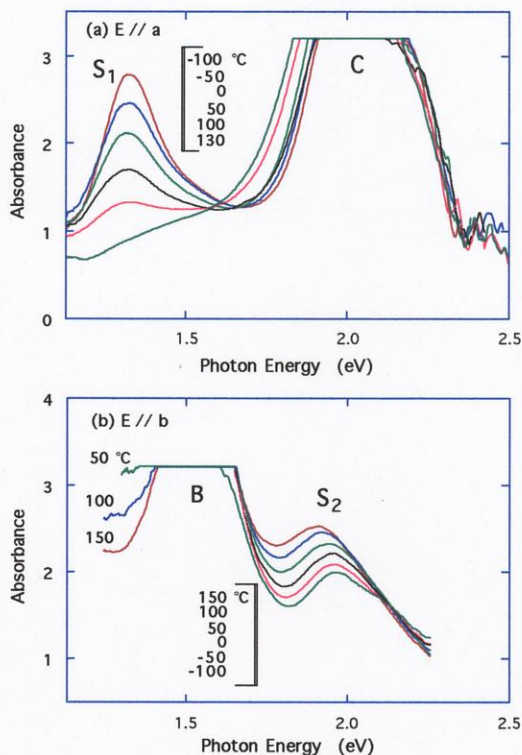

Fig. 1. Absorption spectra of a type-I sample for (a) *E //a* and (b) *E //b* at various temperatures.

are stacked with their molecular plane normal to the *b*-axis.

In the spectral range of the present experiment, there appear strong bands around 2.0 eV for *E //a* and around 1.5 eV for *E //b*,

corresponding to the bands C and B, respectively, which are inherent of dimers of TCNQ⁻ in complex salts [4, 5]. In addition, a comparatively weak band (S_1) is observed around 1.3 eV for $E \,/\!/\, a$ and a band (S_2) around 1.9 eV for $E \,/\!/\, b$. The band S_1 diminishes with increasing temperature to disappear into the background at 126 °C, whereas the band S_2 grows continuously until the crystal is decomposed at around 200 °C. Their intensities are plotted in Figs. 2(a) and 3, respectively. Both bands shift towards lower energies with increasing temperature, as shown in Figs. 2(b) and 3. The low energy tail of the C band also exhibits a continuous redshift as shown in Fig. 3. These temperature dependencies are reversible upon temperature cycling as long as the highest temperature does not exceed 150 °C.
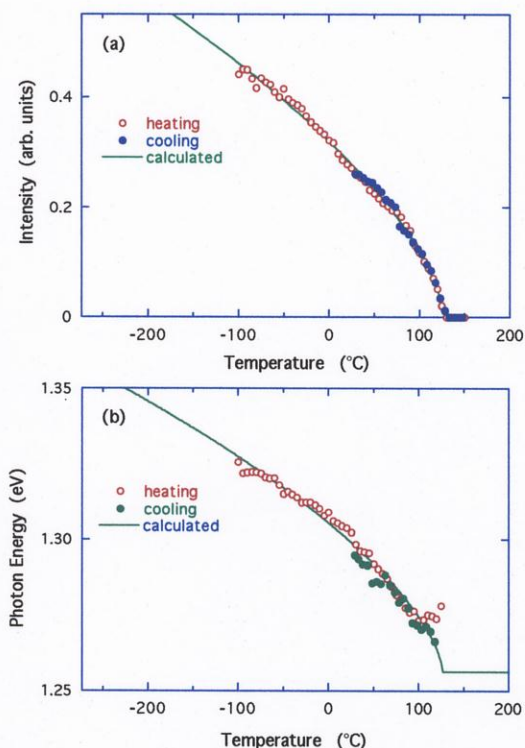

Fig. 2. Temperature dependence of (a) integrated intensity and (b) peak position of the S_1 band of a type-I sample. The solid lines are the fits of Eq.(1).

The variation of the integrated intensity and peak position of the S_1 band can be expressed well in terms of the power law

$$F(T) - F(T_c) = A(1 - \frac{T}{T_c})^{\beta} , \qquad (1)$$

where T is the absolute temperature, T_c is the critical temperature and A and β are numerical constants. The least-squares fit of Eq. (1) to the experimental data of the integrated intensity, for which $F(T_c)$ = 0, gives $T_c = 399$ K, $A = 0.66$ and $\beta = 0.63$. With the same values of T_c and β, we obtain $F(T_c) = 1.256$ eV and $A = 0.102$ eV for the peak position. Because of the poor accuracy of the experimen-

tal peak position just below T_c, there remain significant ambiguities in the values of the parameters for the peak position.

The type-II samples exhibit the S_1 band at about 0.05 eV above that of the type-I samples. Among several spectroscopic differences between the two types, the main difference lies in the fact that T_c lowers to 60 °C in the type-II samples.
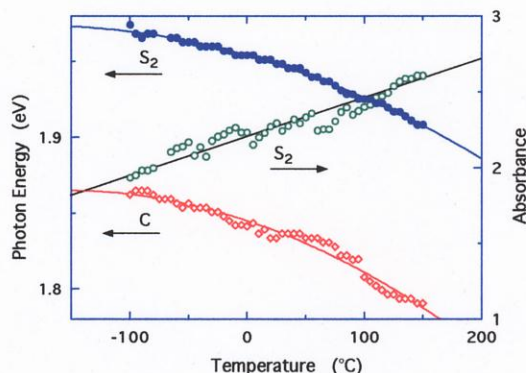

Fig. 3. Temperature dependencies of intensity and peak position of the S_2 band and the spectral position of the C band at absorbance of 2.0 of a type-I sample.

3. Discussion

The singular behavior of the temperature dependencies of the intensity and peak position of the S_1 band shows that a second order phase transition takes place at 126 and 60 °C in the type-I and type-II samples, respectively. The reason for this difference between two different crystal types is unknown at present.

An assignment of the S_1 band is the magnon sideband of a spin-forbidden transition. If the spins of the unpaired electrons of TCNQ⁻ radicals are ordered, they would have the spin wave excitations. The large dipole matrix element of the C band, as well as the electron-magnon coupling, might contribute to the large intensity of the S_1 band at low temperatures. An alternative assignment is the charge-transfer band peculiar to slipped TCNQ⁻ dimers [6]. In fact, in the present substance, TCNQ⁻ radicals form slipped dimers at room temperature [1]. In addition, a preliminary x-ray experiment suggests that the dimers are eclipsed at high temperatures [7]. In view of the behavior of the S_1 band, the observed phase transition might be related to the transformation of TCNQ⁻ dimers between the slipped and eclipsed forms.

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