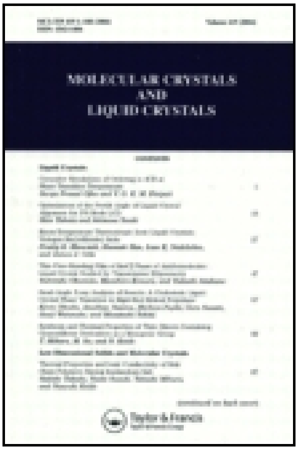

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Pressure Dependence of Electron Distribution along the TCNQ Columns in $(TEDA)_2$ $TCNQ_3$

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High-pressure infrared absorption has been measured in the single crystals of $(TEDA)_2TCNQ_3$ *at room temperature. An energy gap of a direct type with the size of approximately 0.23 eV is observed at ambient pressure. In the molecular-vibration region, the absorption peaks caused by the C=C stretching are observed at 1518 and 1504* cm^{-1}*, suggesting that the excess electrons are less localized in this substance as compared with other 2:3 TCNQ complexes. The behavior of these peaks suggests that a phase transition takes place at 1.0 GPa. In the high-pressure phase the excess electrons tend to be more localized instead of being delocalized, as indicated by the increasing of the energy spacing of those modes. The charge-transfer degrees of the TCNQ molecules are estimated to be 0.60 and 0.80 (low-pressure phase) and 0.56 and 0.88 (high-pressure phase).*

Keywords: electron localization; high pressure; infrared spectroscopy; TCNQ complexes

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INTRODUCTION

It is well known that the distribution of excess electrons over the TCNQ molecules determines the electric properties in the complexes comprising the segregated stack of TCNQ molecules and donor cations. This distribution is usually expressed in term of the charge-transfer degree ρ of individual TCNQ molecules. In most of the 2:3 TCNQ compounds, the excess electrons are localized on certain molecular sites so that the charge-transfer degree of the individual TCNQ molecules is either ~ 0 or ~ 1 for neutral and radical molecules, respectively. For this reason the electrical conductivity in these substance is only slightly higher than that of the insulating 1:1 TCNQ complexes.

The present work deals with $(TEDA)_2TCNQ_3$, where TEDA is triethylenediamine. This substance exhibits relatively high electrical conductivity at room temperature compared with the other substance of the same class, although it is still not comparable to metallic compounds [1,2]. This is because the excess electrons are less localized in this substance. The X-ray diffraction study has shown that the TCNQ molecular columns are constructed by the repetitive stack of A/B/B, where A and B are TCNQ molecules with $\rho = 0.8$ and 0.6, respectively. The columns are almost parallel to the a axis of the triclinic structure.

Several complexes of this class are expected to undergo a pressure-induced insulator-to-metal transition as the result of the wider overlapping in the electron wavefunctions. This overlapping will change the distribution of electrons along the columns, which is represented by the change in ρ of each TCNQ molecules. However, to the best of the authors' knowledge, none of these complexes has been reported to exhibit such a transition. In Cs_2TCNQ_3, for example, although excess electrons are significantly delocalized at around 3.6 GPa [3], which corresponds to significantly higher electrical conductivity compared with its value at ambient pressure [4], the semiconducting character remains up to 8 GPa [5]. Nevertheless, the change in the distribution of electrons along the TCNQ column that is induced by pressure is interesting.

Infrared, as well as Raman, spectroscopy has been widely used to study such change. It is very well known that the frequency of several molecular vibrations is very sensitive to the amount of charge of a molecule. Therefore, this frequency is often used to determine ρ of a molecule, including its change throughout a phase transition [3,6,7].

The purpose of this work is to explore the effect of pressure on the charge distribution on the TCNQ molecules in the system, which is less localized at ambient pressure. We have measured the pressure dependence of the infrared absorption caused by the molecular vibrations. We have paid particular attention on the pressure dependence of the C=C vibration modes, which have been widely used to determine ρ in several TCNQ complexes.

EXPERIMENTAL PROCEDURE

The substance is synthesized and crystallized using the previously reported method [1,2]. The as-grown single crystals, approximately $100 \times 150\,\mu m^2$ wide and $1\,\mu m$ thick, are used as the samples. The wide surfaces of the samples are parallel to the *ab* plane of the crystals, and the probe light incident is normal to these surfaces. The pressure is generated using a diamond anvil cell (DAC). Daphne oil is employed as the pressure-transmitting medium. The infrared absorption is measured using an FT-IR spectrometer equipped with a microscope. The ruby-florescence method is used for calibrating the pressure. We also measure the linearly polarized infrared absorption at ambient pressure to explore the anisotropy of this substance. However, only the unpolarized absorption is measured in the high-pressure experiment because the film polarizer suitable for measurement with DAC in the infrared region is not available.

RESULTS

Figure 1 shows the linearly polarized infrared-absorption spectra for E//a and E//b at ambient pressure and room temperature, where a and b are the crystal axes and E is the electric field of light. The spectra exhibit a strong anisotropy as usually found in the substances of this class. In both polarizations, at low energy the spectra are featured by several sharp absorption peaks caused by the molecular vibrations. In the E//a spectrum a broad absorption band is observed at higher energy. Such an absorption band is not observed in E//b polarization, except for a weak tail of an electronic absorption band that appears at higher energies [2]. Compared to the spectrum of other substances in this class, we can assign this band to the lowest-lying electronic transition, which is equivalent to the valence band–conduction band transition. The absorption edge suggests an energy gap of a direct type. However, it is quite difficult to determine the size of the gap because a strong and relatively broad molecular-vibration band appears near the edge and causes a problem in determining the actual edge. By extrapolating the absorption edge to the energy at zero absorption, with a little ambiguity, we can estimate the size of the energy gap of 0.23 eV.

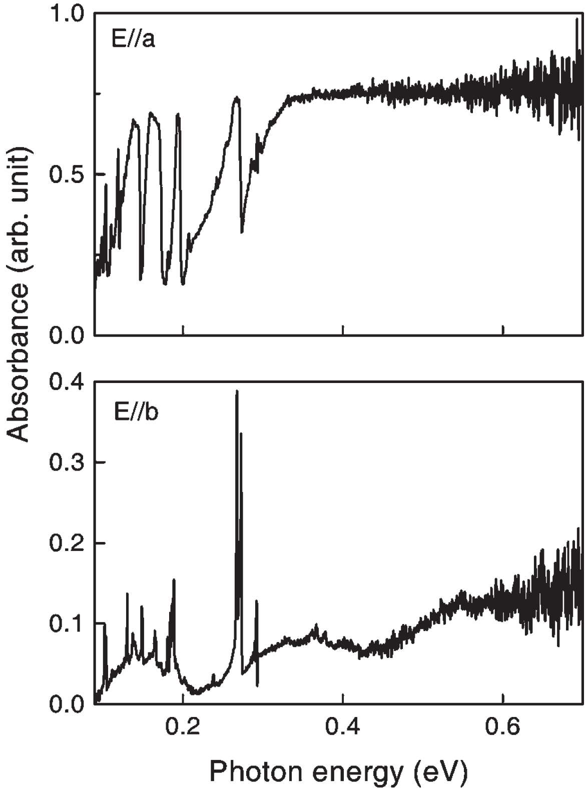

FIGURE 1 Linearly polarized infrared absorption spectra at room temperature and ambient pressure, for E//a (upper) and E//b (lower).

The unpolarized infrared-absorption spectrum is very similar to the E//b spectrum. This is because the actual quantity measured in the present experiment is the intensity of light transmitted through the sample. When the absorption is very strong, such as the case of E//apolarization, the transmission is very weak, and vice versa. In the measurement with the unpolarized light, we measure the average of the component from all polarization directions; therefore, the transmitted light will be dominated by the light from the direction where the absorption is weak, that is, E//b. Because of this problem, we failed to observe the pressure dependence of the absorption edge.

Viewed from the scale of the whole range of the present measurement, there is no significant change observed in the unpolarized spectra with the changing pressure. To have a more detail observation, we focus our attention on the behavior of the C=C stretching modes.

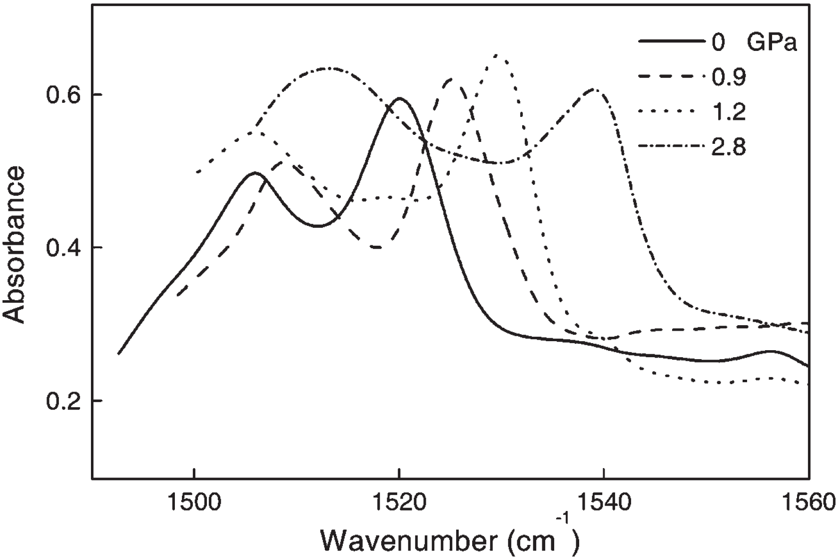

FIGURE 2 Infrared absorption spectra caused by the C=C vibrations at several pressures.

Figure 2 shows the unpolarized infrared absorption caused by the molecular vibration in the C=C stretching region at several pressures. The spectrum at ambient pressure is in good agreement in spectral position with the previous observation. The modes that correspond to the vibration of $TCNQ^0$ (1543 cm^{-1}) and $TCNQ^-$ (1506 cm^{-1}) appear at 1518 and 1504 cm^{-1}, respectively. As pressure increases, both modes shifts toward the higher-energy side while maintaining their energy spacing. At 1 GPa, however, both modes are displaced in a reverse direction to each other, resulting in an abrupt increase in their energy spacing. At higher pressures up to $\sim$3.3 GPa they keep shifting toward the higher-energy side while slightly increasing their energy spacing. The pressure dependence of their energy is shown in Figure 3a.

DISCUSSION

The value of the optical-energy gap obtained in the present experiment is smaller than previously reported value. Bandraux et al. [2] have observed an energy gap of 0.5 eV, about twice of the value of the activation energy estimated from the electrical-resistivity measurement. It should be noted, however, that this value is estimated from an unpolarized absorption spectrum measured in the

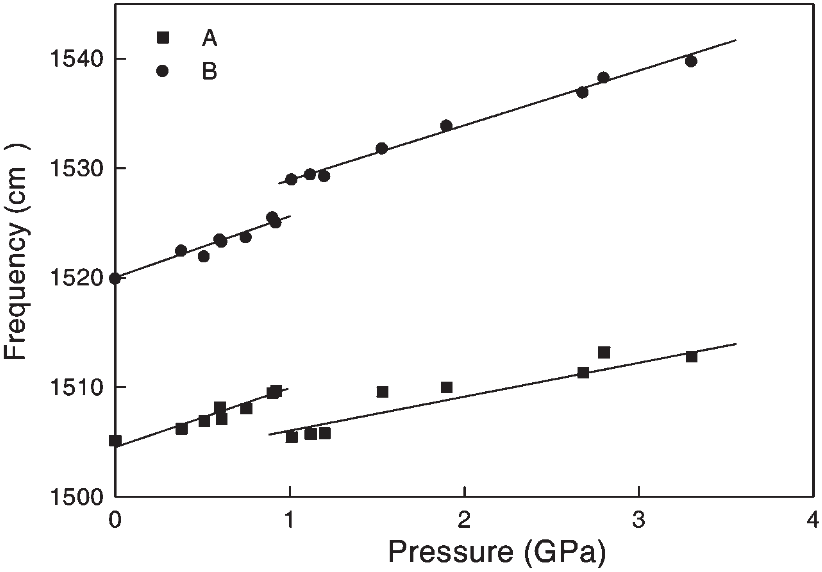

FIGURE 3 Pressure dependence of the frequency of the C=C stretching modes. The solid lines are the guides for the eyes.

powdered sample. Besides, the lowest energy of the spectral range of the measurement is only slightly lower than 0.5 eV. The previous authors, therefore, did not really see the absorption edge as clearly observed in our spectrum. We cannot argue any further on how the optical-energy gap is related to the conductivity-energy gap because this relation depends very much on the mechanism of the conductivity, which remains unclear to date.

We use the frequency of the C=C stretching mode to estimate ρ of each molecules. It is noteworthy that the linearity of the frequency of this mode with the amount of charge on the TCNQ molecules has been proven to be valid in Cs_2TCNQ_3 [8]. In fact, previous authors also used this mode to estimate the same quantity in the present substance [1]. Let the actual valence of A and B molecules be $-\rho^{\mathrm{A}}$ and $-\rho^{\mathrm{B}}$, respectively. Then, because the frequency difference $\Delta\nu$ of a given infrared mode between the radical-like and neutral-like molecules is known to vary nearly linearly to $\rho^{\mathrm{A}} - \rho^{\mathrm{B}}$ [5], the following relationship is expected to hold to a good approximation at a pressure P:

$$\frac{\Delta\nu(P)}{\Delta\nu(0)} = \frac{\rho^{A}(P) - \rho^{B}(P)}{\rho^{R}(0) - \rho^{N}(0)} \tag{1}$$

where ρ^{R} and ρ^{N} are the charge-transfer degree of fully radical (=1) and fully neutral (=0) molecules, respectively. Considering that the formal charge for every three molecules is 2e, we have

$$2\rho^{B}(P) + \rho^{A}(P) = 2 \tag{2}$$

These formulas provide $\rho^{A} = 0.8$ and $\rho^{B} = 0.6$ at ambient pressure and room temperature. It is noteworthy that these values are in good agreement with the results from the X-ray diffraction [2] but different from the infrared study [1]. The latter is not because of the difference in the vibration frequency but because of the different method of analysis. In the previous report, the value of ρ is determined based on only the frequency of C=C vibrations and neglects the amount of the formal charge.

The values of ρ tell us that the excess electrons are less localized in this substance. This results in a relatively small intersite Coulomb repulsion energy and consequently reduces the gap. It is well known that the size of the gap in TCNQ complexes depends very much on this

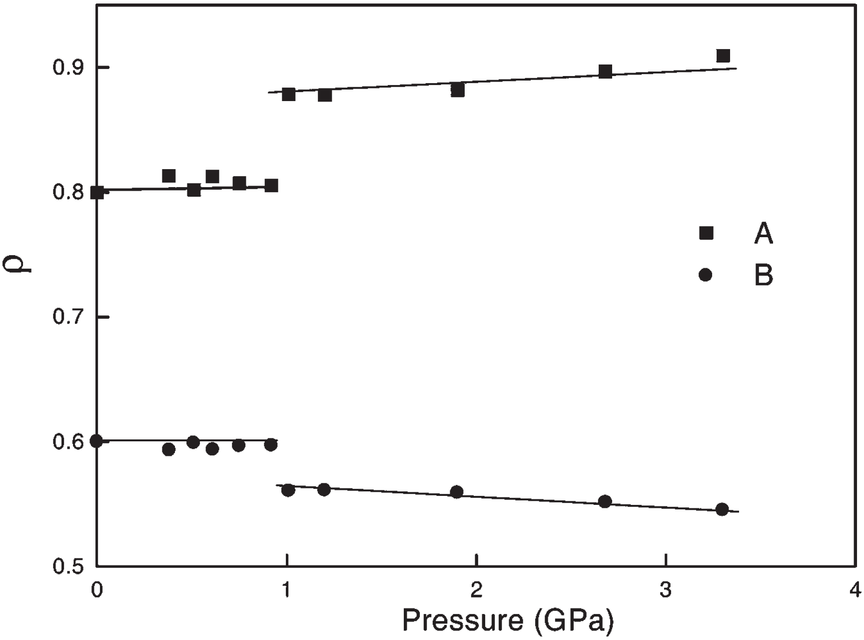

FIGURE 4 Pressure dependence of the charge-transfer degree *r* calculated from frequency of the C=C stretching modes shown in Figure 3. The solid lines are the guides for the eyes.

quantity. This explains why the size of the gap in this substance is significantly smaller than that of Cs_2TCNQ_3, in which excess electrons are more localized [9].

The results of the present experiment also suggest that a phase transition takes place at around 1.0 GPa, as indicated by the discontinuous change of the energy spacing of the C=C stretching modes. This can be considered to arise from the change in the values of ρ. To explore this change more carefully, we calculate ρ at each pressure and plot it as shown in Figure 4. It emerges from the figure that in the high-pressure phase the excess electrons tend to be more localized instead of being delocalized. The values of ρ at high pressures are approximately $\rho^A = 0.88$ and $\rho^B = 0.55$. Such effect is not unusual. In fact, several metals even turn into nonmetals when brought under certain pressure. If the pressure increases further, however, the metal state will be achieved again [10]. We can suggest that similar process takes place in this substance as well: it would turn into metal when the applied pressure is sufficient.

CONCLUSION

The size of the energy gap in $(TEDA)_2TCNQ_3$ at ambient pressure and room temperature is consistent with the charge-transfer degree of its molecules, which suggest that the excess electrons are less localized in this substance. Nevertheless, the excess electrons tend to be more localized at high pressure.

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