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Two-step neutral-ionic phase transition in organic charge-transfer compounds: Possible staging effect

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A two-step neutral-ionic transition has been discovered in a 1:1 mixed-stack charge-transfer crystal, (3,3′,5,5′) tetramethylbenzidine-(7,7,8,8) tetracyanoquinodimethane (TMB-TCNQ) under pressure. The fraction of ionized molecules changes discontinuously at two critical pressures, $P_1 \sim 6$ and $P_2 \sim 20$ kbar, demonstrating a characteristic feature of a staging phenomena. This result is interpreted in terms of a frustration effect of Coulomb interactions in the crystal, as predicted theoretically by Hubbard and Torrance.

A phase transformation in organic mixed-stack charge-transfer (CT) compounds, the so called neutral-ionic transition (NIT),[1] has received considerable attention in this decade from both experimental and theoretical viewpoints. Previous studies have been focused on tetrathiafulvalene-chloranil (TTF-CA) which undergoes a temperature-induced NIT (TINIT) at $T_c = 81$ K and a pressure-induced NIT (PINIT) at around 11 kbar at room temperature,[1,2] where the degree of charge transfer ρ from the donor (TTF) to the acceptor (CA) changes from 0.3 to 0.7.[2] Recently a new type of NIT has been discovered in (3,3′,5,5′)tetramethylbenzidine-(7,7,8,8)tetracyanoquinodimethane (TMB-TCNQ) revealing another aspect of this phenomenon.[3,4] Although the change in ρ in the latter crystal is fairly small (from 0.6 to 0.7), the infrared and ESR measurements clearly demonstrate that the first-order phase transition at $T_c \sim 200$ K is evidently a TINIT.[3] The high-temperature phase above T_c is diagrammatic, and can be classified as a "quasineutral" phase in the terminology of NIT, in spite of the fairly large value of $\rho \sim 0.6$. Here, we report on the PINIT in TMB-TCNQ in which a two-step transition has now been clearly observed.

As the first step of the study on TMB-TCNQ, we made an x-ray-diffraction measurement. Vapor-phase-grown powder samples of monoclinic TMB-TCNQ were loaded in a diamond anvil cell, and the Mo $K\alpha$ x-ray powder-diffraction patterns were photographed with a 1-day exposure. Four strong reflections (011), (040), (200), and $(\bar{1}13)$ were used to determine the monoclinic lattice parameters. All these reflections were single lines in the pressure range measured. The unit cell was assumed to remain in the same monoclinic structure as at ambient pressure. Pressure-dependent lattice parameters a,b,c are plotted in Fig. 1, with each parameter normalized to the ambient-pressure value. (The monoclinic angle β is 100.19° at $P = 0.$ and shows very little pressure dependence.) An abrupt decrease in the parameters is found to occur at around $P_1 \sim 5$ kbar. Combined with the optical data to be shown later, the observed reduction of lattice size can be attributed to the onset of PINIT. The contraction of the a parameter implies an increase in the Madelung energy in the one-dimensional stack, whose contribution is known to be the most important for the occurrence of the NIT.[5] Note that the lattice contraction at P_1 is considerably anisotropic in particular within

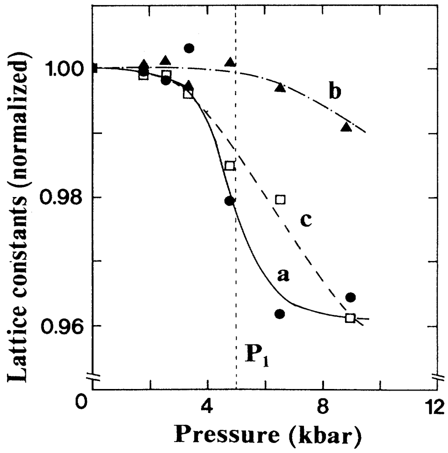

FIG. 1. Pressure dependence of lattice parameters a,b,c for TMB-TCNQ. Each quantity is normalized by that at the ambient pressure. The lattice parameters at ambient pressure are as follows: $a = 6.722$ Å, $b = 21.873$ Å, $c = 8.108$ Å, and $\beta = 100.19°$.

the *bc* plane: The change in the *b* parameter is fairly small, whereas the *c* parameter shows a significant reduction near P_1. Such anisotropic contraction has important implications in understanding the characteristic features of the PINIT in TMB-TCNQ.

For the experimental confirmation of the occurrence of the NIT, the most sensitive and useful means are measurements of the electronic and vibrational spectra. Optical reflection measurements were made on monoclinic TMB-TCNQ single crystals with the typical size being about $0.3 \times 0.3 \times 0.2$ mm^3, which have been grown by a cosublimation method.[3] The polarized reflection spectra were measured at room temperature on the as-grown (011) surface by applying hydrostatic pressure up to about 40 kbar in a diamond anvil cell. A polarizing microscope was used for the microspectroscopic reflection measurements under high pressures.

The reflection spectra for $E \perp a$ (stack axis) shown in Fig. 2 represent an intramolecular electronic excitation band in TCNQ at various pressures. In the low-pressure region, the reflection spectra show a single peak at 2.2 eV with a reflectivity of about 20%. This peak is shown to be sensitive to the degree of charge transfer (ρ) of TCNQ. The peak energy at low pressure indicates that $\rho \sim 0.6$.[3] This state is the quasineutral phase. When pressure is raised above 6 kbar, the spectra show a discontinuous change as seen in Fig. 2. This spectral change is obviously associated with the structural change shown in Fig. 1. Emergence of a red-shifted component in the reflection spectra is convincing evidence for the onset of PINIT. When the pressure is increased further, the spectra show another unexpected discontinuous change at $P_2 \sim 20$ kbar, indicating the onset of the second NIT at P_2. Such a two-step discontinuous phase transition can be seen as a successive color change of the crystal, from golden yellow to orange at P_1, and from orange to red at P_2.

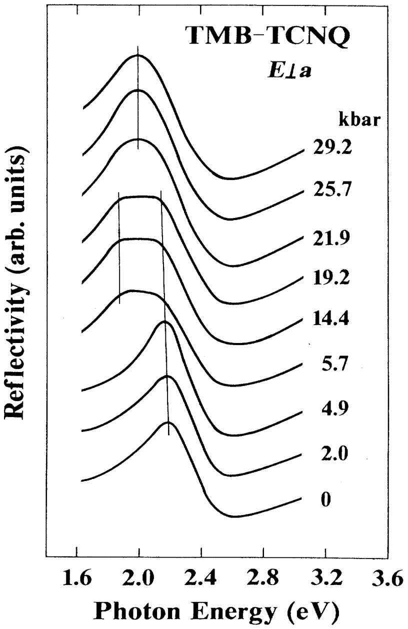

FIG. 2. Polarized reflection spectra of the TMB-TCNQ crystal at various pressures (at room temperature).

The phase transition at P_1 was reproducible in pressure cycles in all crystals investigated. By contrast, the phase transition at P_2 showed the following feature. When pressure was raised to P_2, the crystal surface often showed a striated pattern composed of orange or red colored domains elongated along the stacking axis. The typical domain size was 0.05 mm in width and 0.2 mm in length. When the pressure was increased, the red domains expanded in size until the whole crystal was eventually converted to the red phase. These observations indicate that the phase transition at P_2 has a stronger first-order character than that at P_1. When presure was released, the reflection spectra recover the same shape as that of the unpressed crystal, but after repeated applications of pressure, the spectral changes at P_1 and P_2 became less sharp. The sharp two-step transitions can be observed only on fresh single crystals.

The two discontinuous spectral changes as shown in Fig. 2 are regarded as unambiguous evidence for the double-stepped PINIT. Such a feature has not been observed in the previous PINIT in other kinds of mixed-stack CT crystals.[6,7] In order to investigate the unique features of this PINIT in TMB-TCNQ, we analyzed the spectra at each pressure in terms of the imaginary part ε_2 of the complex dielectric function by means of the Kramers-Kronig transformation of the reflection spectra.

Figure 3 shows that ε_2 spectra at three representative pressures; 4.9 kbar ($P_1 < 1$), 9.7 kbar ($P_1 < P < P_2$), and 27 kbar ($P > P_2$). Note that all the ε_2 spectra cross at the same point (within experimental error) located at 2.18 eV (the isosbestic point). This result indicates that the ε_2 spectra in the pressure range between P_1 and P_2 can be analyzed as a superposition of the low- and high-pressure components as expressed by the expression, $\varepsilon_2(P,\omega) = (1-F)\varepsilon_2(4.9\ \text{kbar},\omega) + F\varepsilon_2(27\ \text{kbar},\omega)$. Here, F represents the fraction of high-pressure component at each pressure. An example of the calculated spectra is shown in Fig. 3 for $P = 9.7$ kbar. Similar analysis was possible for the ε_2 spectra in the intermediate phase assuming appropriate values of $F = 0.5$–0.7. Note that not the reflection spectra but only the ε_2 spectra in the inter-

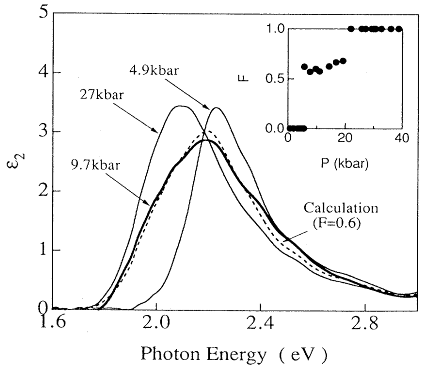

FIG. 3. Experimental ε_2 spectra at 4.9, 9.7, and 27 kbar. The dashed line shows a calculated spectrum, using the fraction $F=0.6$. The inset shows the pressure dependence of the F value.

mediate phase can be expressed by the superposition of those in the high- and low-pressure phase. This result implies that the coexistence of neutral and ionic species occurs on the microscopic scale less than the order of one wavelength.

The pressure dependence of the F values thus obtained is plotted in the inset of Fig. 3. The interpretation for this result is that TMB-TCNQ undergoes a sharp double-stepped transition; from the uniform neutral phase to the neutral-ionic coexisting phase with a nearly 1:1 mixture of quasineutral and quasi-ionic molecules at P_1, and finally to the high-pressure quasi-ionic phase at P_2.

Such a two-step change of the charge distribution in TMB-TCNQ reminds us of a theoretical prediction previously given by Hubbard and Torrance.[8] In the simplest approximation, only a sharp single-step NIT is expected to occur uniformly in the crystal.[5] However, as Hubbard and Torrance have discussed, if contributions from the repulsive and attractive interstack Coulomb interactions are taken into account, the NIT may occur in a multistepped manner through various intermediate phases. Later on, Bruinsma, Bak, and Torrance[9] and Bak[10] have theoretically argued that such a situation may even lead to an infinitely stepped sequence of the first-order transition known as a Devil's staircase. A stepwise change of electrical conductivity has been reported in TTF-CA near T_c leading to a suggestion that it might be an indication of the Devil's staircase.[11] However clear-cut evidence is still lacking.

To illustrate the physical picture of this phenomenon, we have drawn in Fig. 4 a schematic model of the lattice structure of TMB-TCNQ in the bc plane (perpendicular to the stack axis a).[3] The smallest molecular separation is the distance between TMB and TCNQ along the a axis ($a/2=3.361$ Å). The attractive intrastack Coulomb interaction works as a trigger of NIT.[5] On the other hand, the neighboring stacks contribute to the repulsive and attractive interstack Coulomb interactions in the $\langle 001\rangle$ and $\langle 0\bar{1}1\rangle$ directions, respectively. Note that the interstack distance c $(=8.108$ Å) along the $\langle 001\rangle$ direction is smaller than the distance d $(=11.664$ Å) along the $\langle 0\bar{1}1\rangle$ direction. Accordingly, the repulsive interaction in the $\langle 001\rangle$ direction surmounts the latter attractive interaction. Then, this dominantly repulsive interstack interaction will tend to prohibit a uniform quasi-ionic state above P_1. These arguments lead us to an interpretation that the first step of the PINIT is the transition to a neutral-ionic coexisting phase in which one half of molecules are converted to the quasi-ionic state. Considering the crystal structure of TMB-TCNQ, the most probable model of this phase is a superstructure composed of alternating neutral and ionic layers parallel to the (011) plane, as depicted by hatched and unhatched layers in Fig. 4. In this configuration, the intrastack interaction along the a axis and the interstack interaction in the (011) plane are both attractive, in favor of the uniform ionic state within the (011) layer. Such a configuration will be more stable than the uniform ionic state, since the repulsive interstack Coulomb interaction in the (001) plane is weakened by the intervening neutral layers. The fairly large anisotropy in the compressibility in the bc plane, shown in Fig. 1, seems to be responsible for the stabilization of the neutral-ionic coexisting phase in TMB-TCNQ.

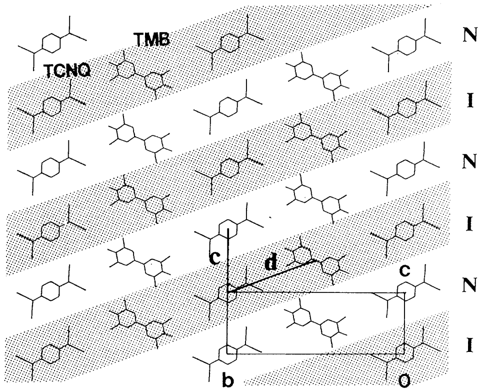

FIG. 4. Molecular arrangement in the monoclinic TMB-TCNQ crystal projected to the bc plane. Possible configuration of the neutral-ionic coexisting phase is shown by shaded quasi-ionic layers and unshaded quasineutral layers parallel to the (011) plane.

Similar discussion has been made by Hubbard and Torrance, anticipating a possible staging effect in the NIT for TTF-CA.[5] Although subsequent experimental results on TTF-CA could not verify their prediction, essentially the same model is applicable to TMB-TCNQ. This is quite reasonable if we consider the fact that the crystal structure and the anisotropic compressibility favor the staging effect in TMB-TCNQ more than in TTF-CA. In TMB-TCNQ, the lattice constant b is significantly larger than c, so that the repulsive Coulomb interaction along the $\langle 001\rangle$ direction will predominate over the attractive interaction along the $\langle 0\bar{1}1\rangle$ direction. In TTF-CA, on the other hand, the repulsive interstack interaction must be considerably smaller than the attractive one because of the smaller ratio of lattice constants [$c/b=1.912$ in TTF-CA,[12] in contrast to $b/c=2.698$ in TMB-TCNQ (Ref. 3)].

Finally we shall make an additional remark on the phase diagram in TMB-TCNQ. From the optical spectra at low temperature,[3] it has been concluded that the low-temperature phase is also the neutral-ionic coexisting phase. However, the fraction of quasi-ionic molecules in the low-temperature phase is different from that observed in the high pressure phase at room temperature. Such a complex phase diagram in the temperature-pressure plane is attributable to the dominant contribution of the frustration effect of Coulomb interaction as described above. To elucidate quantitatively the various aspects of the staging phenomena in TMB-TCNQ, we shall have to make an extended analysis by taking account of the transfer integral between adjacent molecules and the electron-lattice coupling together with the Coulomb interaction.

In conclusion, we have discovered a distinct double-stepped NIT in the TMB-TCNQ crystal under pressure. The fraction of ionized molecules changes discontinuously at the two critical pressures. A competitive effect of attractive and repulsive Coulomb interactions between donor and acceptor molecules has been suggested to be responsible for this anomalous phenomenon observed in organic CT crystals.

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