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Optical reflectivity spectra of the mixed-stack organic charge-transfer crystal tetrathiafulvalene-*p*-chloranil under hydrostatic pressure

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Optical reflectivity spectra and electric conductivity have been measured on single crystals of tetrathiafulvalene (TTF)-*p*-chloranil under hydrostatic pressure up to 11 kbar at room temperature. From their characteristic behavior under pressure, it is concluded that TTF-*p*-chloranil crystals undergo a gradual pressure-induced neutral-to-ionic (N-I) transition in an intermediate region from 0 to about 10 kbar, in contrast with a first-order temperature-induced N-I transition. In this pressure range, both quasineutral and quasi-ionic molecular domains coexist in the lattice, until a discontinuous transition to a dimerized ionic phase occurs at about 11 kbar. It is suggested that the dynamical behavior of N-I domain walls is responsible for a pressure-induced exponential increase of the electric conductivity.

I. INTRODUCTION

There exists a boundary between the nominally neutral and nominally ionic crystals among a number of 1:1 mixed-stack donor-acceptor (D-A) organic complexes. A simple picture for this so-called neutral-ionic (N-I) boundary has been presented by McConnell *et al.*[1] in terms of a competition between the effective ionization energy of a D-A pair and the long-range electrostatic (Madelung) energy gained by the ionized lattice. It has been predicted that application of hydrostatic pressure might cause a neutral-to-ionic (N-I) phase transition across the N-I boundary due to a decrease of intermolecular distances which leads to an increase of the electrostatic energy.[1] The predicted pressure-induced N-I transition (PINIT) has been discovered by Torrance *et al.* in several 1:1 mixed-stack D-A crystals located near the N-I boundary.[2] Subsequently, a temperature-induced N-I transition (TINIT) has been discovered in one of these crystals, tetrathiafulvalene (TTF)-*p*-chloranil (hereafter TTF-CA), at ambient pressure.[3] These findings have triggered intensive studies on the experimental and theoretical aspects of the N-I transition in TTF-CA crystal and related mixed-stack charge-transfer (CT) crystals.

In previous studies by Torrance *et al.*,[2,3] the PINIT in TTF-CA crystals was followed in the transmission spectra of thin sublimed films. The spectra observed at $P=0$ and 15 kbar (shown in Fig. 1 in Ref. 2) demonstrate clearly that the N-I transition takes place somewhere between these two pressure values. From a visual observation of the pressure-induced color change in the film from yellow to red, these authors concluded that TTF-CA undergoes the N-I transition at about 8 kbar at room temperature.[2] There has been no detailed single-crystal study as yet of the optical spectra of the TTF-CA crystal as a function of pressure.

On the other hand, there have been rather extensive studies on the TINIT in TTF-CA crystals. The visible and infrared reflectivity spectra of TTF-CA crystals[4,5] show that TINIT occurs sharply at $T_c = 81$ K indicating an Ehrenfest first-order transition. However, when even a small amount (several mol %) of a weak substitutional acceptor of trichloro-*p*-benzoquinone is introduced into the TTF-CA crystal, the TINIT occurs through a fairly wide temperature region where both quasineutral and quasi-ionic molecules are found to coexist.[6] It is important, therefore, to use well-characterized single crystals to avoid spurious effects of impurities, defects or strains, in any detailed study of the N-I transition in TTF-CA crystals.

In this paper we report on the visible reflectivity spectra of TTF-CA single crystals under hydrostatic pressure from $P=0$ to about 11 kbar at room temperature. The electric conductivity has also been measured under pressure to obtain additional information. It is shown from these studies that the PINIT occurs gradually in the pressure range from $P=0$ to about 8 kbar, in agreement with the results of recent infrared molecular vibration spectroscopy under pressure.[7,8] The pressure dependence of the electric conductivity is discussed in relation with the gradual N-I transition under pressure.

II. EXPERIMENTAL PROCEDURE

Single crystals of TTF-CA were grown by the plate-sublimation method[9] from purified polycrystalline powders of TTF and *p*-chloranil.[4] The high-pressure measurements were made by using a Polter-type high-pressure

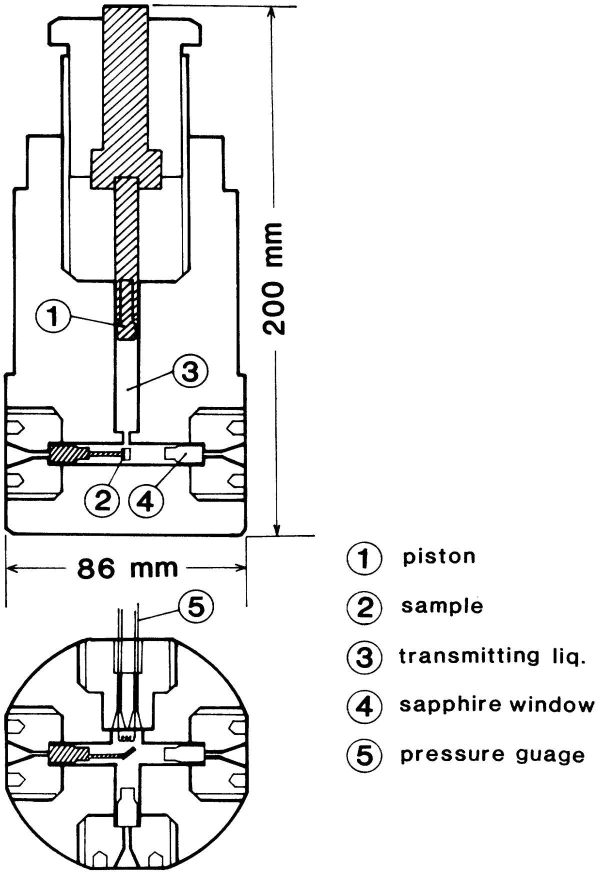

FIG. 1. High-pressure optical cell used in the study.

optical cell[10] which is schematically illustrated in Fig. 1. A single-crystal sample was mounted stress free on the top of a stainless-steel plug screwed into one of the window holes. Two sapphire windows were provided at right angles for the reflectivity measurements. Glycerin was used as the pressure transmitting liquid in the optical measurements, because it is chemically inert against TTF-CA crystals and does not solidify up to about 12 kbar. A Manganin-wire pressure gauge was used to monitor the pressure with an accuracy of about 0.1 kbar. The optical reflectivity spectra were measured on the (001) face using mostly unpolarized light, because the pressure-induced photoelastic effect in the sapphire windows hinders accurate polarization measurements. For the electric conductivity measurements, silver-paint electrodes were provided on the crystal surface, across which the conductivities were measured by the two-point method. Kerosene oil was used as the pressure-transmitting liquid in the conductivity measurements because it has higher electric resistivity than glycerin. To prevent chemical degradation of sample and surface leakage current, the crystal surfaces were coated with an insulating varnish paint, GE7031.

III. EXPERIMENTAL RESULTS

Pressure-induced changes in the reflectivity spectra are shown in Fig. 2(a). Temperature-induced changes of the same spectra in pure and impurity (trichloro-*p*-benzoquinone)-doped TTF-CA crystals investigated in the previous studies[4,6] are also reproduced in Figs. 2(b) and 2(c), respectively, for the sake of later discussion. At atmospheric pressure, there are two peaks, *B* and *C*, in the spectra at around 2.51 and 3.34 eV. They are both identi-

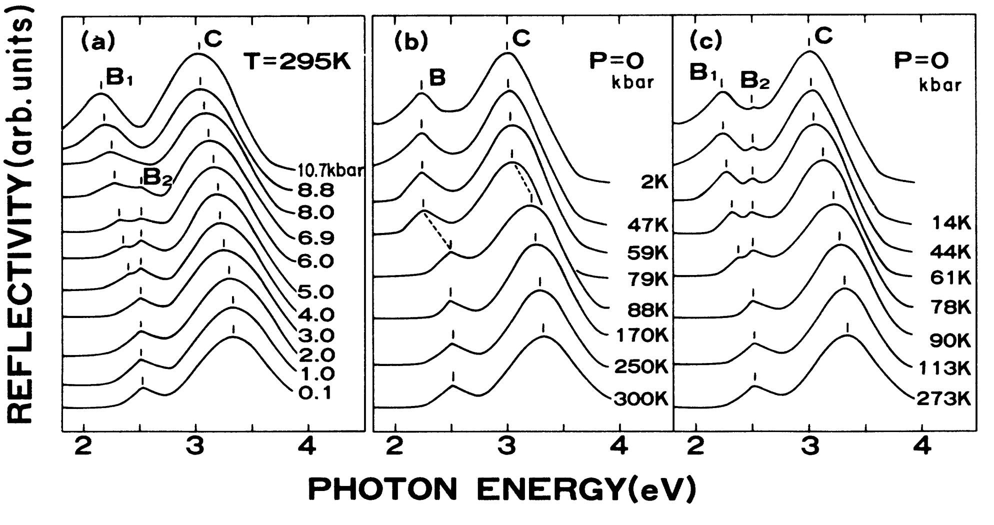

FIG. 2. Optical reflectivity spectra of TTf-*p*-chloranil crystal as a function of pressure at 295 K in (a), and as a function of temperature at $P=0$ kbar on pure crystal and impurity (7 mol % trichloro-*p*-benzoquinone)-doped crystals in (b) and (c), respectively. The spectra in (b) and (c) were taken from Refs. 4 and 6.

fied as intramolecular excitation bands in TTF molecules.[2–4] Their energies and intensities are dependent on the degree of CT in the crystal, so these spectra are utilized as a microscopic probe to detect the CT state of molecules in the lattice. (These two bands are usually assigned to the excitations of TTF^+ molecular ions, since their energies are close to those observed on radical cationic molecules; this assignment, however, is somewhat misleading, because the bands are actually due to the intramolecular excitations in the mixed-valent TTF molecules in the partially charge-transferred TTF-CA crystals.[4]) Besides the B and C bands, there is another band at about 4.1 eV which is also due to TTF molecules.[2–4] In the present measurements, this band could not be observed because of the strong optical absorption of the pressure-transmitting liquid, glycerin.

When hydrostatic pressure is applied to the crystal, the B and C bands show characteristic changes with pressure: The B band is found to split into two components, B_1 and B_2. At low pressures, the B_1 band appears as a shoulder on the low-energy side of the predominant B_2 band, but the B_1 band grows gradually with pressure, and finally dominates over the B_2 band above about 7 kbar. At higher pressures, only the B_1 band is observed; its intensity is larger than that of the original B band at ambient pressure. On the other hand, the C band appears to be continuously shifted to lower energy with increasing pressure, without showing any detectable splitting by pressure.

The pressure-induced change in the electric conductivity of the TTF-CA crystal at room temperature is shown in Fig. 3. The conductivity at atmospheric pressure is about $10^{-6}\,\mathrm{S\,cm^{-1}}$, but it increases remarkably with increasing pressure. It reaches a maximum value at about 8 kbar and decreases slightly at higher pressures. The maximum conductivity is nearly 10^5 times larger than the value at $P=0$ kbar.

IV. DISCUSSION

In Fig. 4(a), the peak energies of the $B_{1,2}$ and C bands of Fig. 2(a) are plotted as a function of pressure. To compare the pressure-induced changes in spectra with the temperature-induced changes shown in Figs. 2(b) and 2(c), we plotted the corresponding thermal shifts in pure and doped TTF-CA crystals by solid and open circles, respectively, against temperature in Fig. 4(b). The energy shifts of these intramolecular excitations manifest the change in ionicity of molecules as mentioned before. The red shifts observed in the B_1 and C bands indicate that the spatially averaged ionicity ρ of a mixed-valent molecule ($TTF^{\rho+}$) increases gradually with pressure. Another remarkable feature in the spectra is the splitting of the B band by pressure. The component B_1 is continuously shifted to lower energy with increasing pressure, while the other component B_2 remains almost unchanged in energy until it disappears at high pressures. The splitting of the B band suggests that there are two inequivalent TTF molecules in the lattice with different degrees of charge transfer. From the pressure-induced change in the intensities of the B_1 and B_2 bands in Fig. 2(a), the number of the quasineutral molecules is considered to decrease, whereas the ionic molecules increase in number at the expense of the quasineutral molecules, with increasing pressure. In the pressure range where both the B_1 and B_2 bands are observed, quasineutral and ionic TTF molecules are considered to coexist in the lattice. Such a binary CT

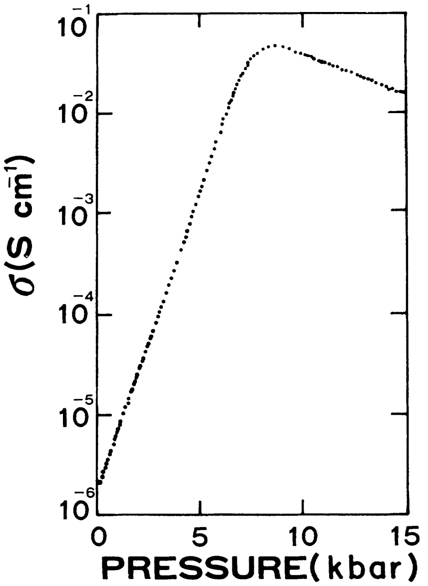

FIG. 3. Electric conductivity of TTF-p-chloranil crystal along the a axis (the stack axis) as a function of pressure at 295 K.

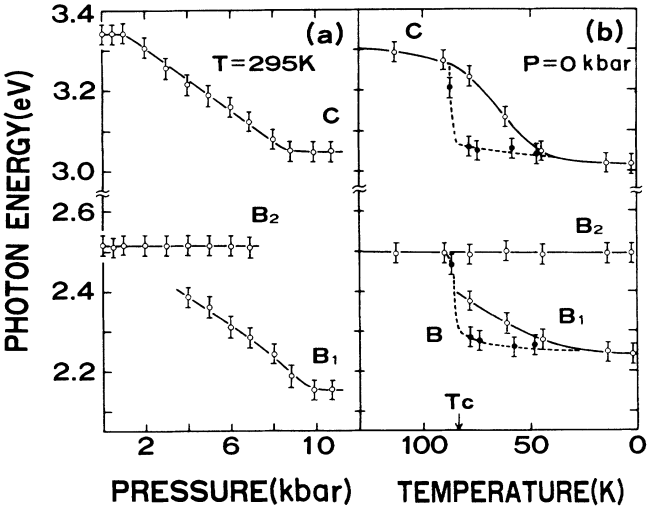

FIG. 4. Peak energies of intramolecular excitation bands in TTF-chloranil crystals (a) as a function of pressure at 295 K and (b) as a function of temperature at $P=0$. Solid and open circles in (b) represent the experimental points for pure and impurity (7 mol % trichloro-p-benzoquinone)-doped crystal, respectively. The data in (b) were taken from Refs. 4 and 6.

state cannot be due to any macroscopic inhomogeneity such as a nonuniform strain in the crystal, since there is no indication of an inhomogeneous broadening effect in the B band and the spectral changes are well reproducible for varying pressure. The reason why a splitting is not observed in the C band is discussed later.

This spectral change takes place gradually from the very beginning of pressure loading. This is quite consistent with the continuous increase of electrical conductivity with pressure shown in Fig. 3. More direct experimental support for the interpretation of the inhomogeneous PINIT is obtained by comparing the present pressure-induced changes in the spectra with the TINIT studied previously.[5,6] In the pure crystals, an abrupt change of spectra is observed at $T_c = 81$ K as shown in Fig. 2(b). However, when a small amount (several mol %) of a weaker acceptor molecule, trichloro-p-benzoquinone, is introduced in TTF-CA, the spectra show a gradual shift in a fairly wide temperature range near T_c as shown in Fig. 2(c). This is in marked contrast to the sharp shift in pure crystal shown in Fig. 2(b). A remarkable point in Fig. 2(c) is that the temperature-induced change in the B and C bands is very similar to the pressure-induced change in the same bands shown in Fig. 2(a): In either case, both B and C bands show a gradual change between the quasineutral phase and the quasi-ionic phase by increasing pressure [Fig. 2(a)] or by cooling [Fig. 2(c)]. The spectra of doped crystals also show a splitting of the B band into two components, B_1 and B_2, whereas the C band does not split, but shows a continuous shift like that in a pure crystal under pressure.

The thermal shifts of peak energies of the B and C bands are shown in Fig. 4(b) as a function of temperature. The experimental points for pure crystals (solid circles and dashed lines) show abrupt shifts at T_c in both B and C bands without showing any splitting in the B band. This clearly indicates that a homogeneous first-order transition takes place at T_c. It has been confirmed by x-ray study[11] and infrared molecular vibration spectroscopy[5,12] that the lattice is dimerized below T_c. In contrast, experimental results for doped crystals (open circles and solid lines) do not show a first-order-like behavior at T_c.

According to the picture we have presented in the previous paper,[6] the gradual thermal change in the spectra of doped crystals is interpreted as follows: In doped TTF-CA crystals, the substitutional impurity molecules are randomly distributed in the lattice, so that there is a microscopic inhomogeneity in the molecular ionicity. When temperature is lowered down to T_c, the host lattice tends to undergo the first-order TINIT. However, because of the presence of weaker acceptor impurity molecules, the N-I transition is suppressed in the vicinity of impurity molecules. (The TINIT is not observed in the mixed-stack pure crystal TTF-trichloro-p-benzoquinone.) As a consequence, when temperature is lowered below T_c, the doped crystal undergoes a gradual and inhomogeneous transformation into a binary phase in which the lattice is separated into two types of domains: one is free from the effect of impurities and can transform to the quasi-ionic state, the other remains in the quasineutral state due to the influence of impurities.

To explain the absence of temperature-induced splitting in the C band, it has been argued that the corresponding intramolecular excitation has a fairly large transition dipole moment compared with the B band, and hence this excitation is supposed to propagate in the lattice as a molecular (Frenkel-type) exciton. For such a delocalized excitation, an inhomogeneity of the ionicity on individual molecules will be averaged out in the motion, and the excitation (the C exciton) will behave as if the lattice is nearly homogeneous with an averaged ionicity which varies continuously with temperature. The observed intensity of the C band and the temperature variation of the peak energy are consistent with this interpretation, as discussed in a previous paper.[6] On the other hand, the excitation for the less intense B band is more localized on individual molecules and is split into two components in the binary N-I mixed phase. In this way, the temperature dependences of the B and C bands in a doped crystal can be consistently accounted for by this binary phase separation model.

There is a remarkable similarity between the pressure results and the doping results as seen before. The splitting of the B band by pressure is quite similar to the temperature-induced splitting of the same band in doped crystal, which strongly indicates that a binary phase separation occurs under pressure likewise as in a doped crystal at low temperatures. The absence of the splitting in the C band might be explained by the same model as applied to the doping results. It is difficult, however, to conclude that the C band in the spectra shown in Fig. 2(a) certainly does not split, because the C band in this case is considerably broad due to the high temperature (295 K) and also due to the 45° off-normal incidence geometry in the present reflectivity measurements under high pressure. If a small splitting (presumably less than 0.3 eV) exists in the C band also, it will not be resolved in the present spectra. However, irrespective of whether the C band is actually split or not, it is obvious that the PINIT is a gradual and inhomogeneous transformation, similar to that observed in a doped TTF-CA crystal by cooling, passing through a binary mixed state. In this sense, the PINIT cannot be explained solely by the effect of a contraction of a lattice and an increase of the long-range electrostatic (Madelung) energy by pressure, as originally suggested by McConnell *et al.*[1] and more recently by Metzger and Torrance.[13] Perhaps, the effect of electron-lattice coupling plays a substantial role, as is discussed below.

At this point, we would like to make the following remark: In spite of a remarkable similarity between the characters of the N-I transition in a pressure-loaded crystal and in a doped crystal at low temperatures, there is an essential difference between the two cases with respect to the following point. In the impurity-doped crystal, the inhomogeneous binary-phase structure is caused by the presence of randomly distributed impurities, so that it would be essentially static in nature. To the contrary, the inhomogeneously charge-transferred state under pressure is not considered to be static, since before application of pressure the lattice is in a uniform quasineutral phase. It is believed that the quasi-ionic regions formed within the surrounding quasineutral regions are not fixed to particular molecular sites but are supposed to be thermally fluctuating in the lattice. In other words, in the intermediate-pressure range, the lattice is considered to be separated into quasineutral and ionic domains which are both fluctuating in space and time. In the sense, the dynamical *N-I* mixed phase or fluctuating CT phase proposed here is substantially different from the staging phase proposed by Hubbard and Torrance[14] in which a static three-dimensional order is assumed to exist in the spatial array of the *N* and *I* regions. Experimental support for the fluctuating CT domain model is obtained from the electric conductivity data presented in Fig. 3 as discussed below.

In the pressure-induced variation of electric conductivity shown in Fig. 3, a notable point is that the experimental points fit a straight line very well in a semilogarithmic plot of $\log\sigma$ versus P in the pressure range from $P=0$ to 7 kbar only. Such an exponential increase in the conductivity with pressure implies that the thermal activation energy for the charge carrier generation (and also for the mobility perhaps) is diminished linearly with increasing pressure. After this initial exponential increase, the conductivity reaches a maximum at about 8 kbar, where most molecules are considered to be transformed into the quasi-ionic molecules [judging from the optical data shown in Figs. 2(a) and 4(a)]. Therefore, we consider that the maximum conductivity occurs around the crossover point where the energy difference between the quasineutral and quasi-ionic states becomes almost equal to zero. This implies that the thermal CT gap for the collective excitation of molecules vanishes at around 8 kbar with a help of the lattice relaxation after the CT process. On the other hand, the optical CT excitation energy, which corresponds to the Franck-Condon CT gap for a fixed molecular configuration, remains finite due to a finite Coulomb energy in the charge-transfer state even if the thermal CT gap becomes equal to zero.

The conductivity mechanism in TTF-CA crystals has been recently discussed from both experimental[15,16] and theoretical[17,18] viewpoints. It is suggested that the electric charge transport in the binary phase of the TTF-CA crystal is closely related with the dynamics of solitons[19] and neutral-ionic domain walls as well on the one-dimensional *D-A* stack.[17] These intrinsic defects form with greater ease in the *N-I* coexisting region as pressure is increased, until most molecules are eventually transformed to the quasi-ionic state. Since this PINIT takes place gradually below about 10 kbar, there is no abrupt change in the conductivity at any particular pressure. Such a pressure-dependent behavior is in contrast with a sharp jump of the conductivity at T_c when temperature is lowered.[19,20]

To sum up, the pressure effects on the visible reflectivity spectra and the electric conductivity can be consistently explained by assuming a binary phase separation of lattice into the quasineutral and more ionic molecular domains under pressure. In the intramolecular electronic excitation spectra in the visible region, we can detect the local charge-transfer states of individual molecules in a time scale shorter than the period of thermal fluctuation of the *N-I* domain walls. On the other hand, in the dc electric conductivity measurements, we observe a thermal average of the dynamical behavior of the *N-I* domain walls. Such a picture of dynamical *N-I* domain walls on the *D-A* stacks is analogous to the model of rapidly moving spin-solitons and antisolitons in the dimerized *I* phase, which has been presented before to explain a remarkable motional narrowing effect of the ESR lines observed below T_c.[19] These spin solitons are intrinsic defects formed at the boundaries between the oppositely dimerized ferroelectric domains (with the dimer unit of either D^+A^- or A^-D^+) which are degenerate below T_c. Likewise, the *N-I* domain walls are intrinsic defects associated with the boundaries between nearly degenerate *N* and *I* domains in the lattice under pressure.

When pressure is raised above 8 kbar, the spectral features shown in Fig. 2(a) approach those of a quasi-ionic crystal, which are observed below T_c at ambient pressure [cf. Fig. 2(b)]. At the same time, the electric conductivity becomes less sensitive to pressure after passing through a maximum at about 8 kbar. According to the results of infrared spectroscopy,[7] a weak 960-cm^{-1} a_g mode of the CA molecule, which is normally forbidden in a regularly stacked lattice, becomes observable around 10 kbar. Accordingly, in this region the predominantly ionic lattice is considered to be dimerized, presumably containing a small amount of thermally excited mobile quasineutral domains. With further increase of pressure, the intensity of the a_g mode of the CA molecule is abruptly enhanced at about 11 kbar. At the same time, the frequency of a b_{1u} $C=0$ stretch mode in the CA molecule shows a sharp red shift, indicating a discontinuous increase in the molecular ionicity from about 0.6 to a value higher than 0.8.[7] These results indicate that the crystal undergoes a first-order-like transition from a binary *N-I* mixed phase to a statically dimerized *I* phase at about 11 kbar. There is no discontinuous change in the electric conductivity at this pressure as seen in Fig. 3. More-detailed discussion of the *N-I* phase diagram as a function of temperature and pressure is presented in a separate paper.[20]

V. CONCLUSIONS

Intramolecular electronic excitation spectra of TTF-CA crystals show characteristic energy shifts and splitting under pressure up to 11 kbar. From comparison of these pressure data with previously studied temperature data on impurity-doped crystals, it has been concluded that TTF-CA crystals undergo a gradual transformation to the quasi-ionic phase through an inhomogeneous binary phase in which both quasineutral and quasi-ionic molecular domains coexist in the lattice. In the intermediate pressure range up to about 8 kbar, the ionic regions increase in volume with increasing pressure at the expense of the quasineutral region. Within the quasi-ionic domains, the *D-A* stacks are supposed to be dimerized, but a three-dimensional static order of the dimerization is hindered by a rapid thermal fluctuation of the domain walls at room temperature, until a first-order transition into the dimerized ionic phase takes place at about 11 kbar. Such fluctuations of *N-I* domain walls are suggested to be responsible for a remarkable increase in the electric conductivity by pressure observed in the same pressure range. The dynamical property of *N-I* domain walls in TTF-CA crystals is also supposed to be responsible for various novel features of TTF-CA such as transient optical response,[5] nonlinear electric conductivity,[15] and anomalous photoconductivity.[16] Further studies are obviously needed to establish a more-detailed picture of the interesting phenomena associated with the *N-I* transition of TTF-CA crystals.

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