Electric conductivity and phase diagram of a mixed-stack charge-transfer crystal: Tetrathiafulvalene-p-chloranil

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The electric conductivity has been measured on the mixed-stack charge-transfer crystal tetrathiafulvalene (TTF) -p-chloranil (CA) as a function of temperature ($T > 30$ K) and pressure ($P < 11$ kbar). On the basis of the experimental results, a P-T phase diagram is presented for the charge-transfer state in TTF-CA.

A mixed-stack organic charge-transfer (CT) crystal composed of tetrathiafulvalene (TTF) as the donor (D) and p-chloranil as the acceptor (A) exhibits a characteristic phase transition from the quasineutral (N) to quasiionic (I) state either by lowering temperature[1] or by applying hydrostatic pressure.[2] This so-called neutral-to-ionic (N-I) transition has been the subject of considerable interest in recent years. It has been revealed that when temperature is lowered at ambient pressure a sharp ionicity jump[3] and a simultaneous dimeric displacement of D-A molecules[4] take place at the critical temperature $T_c \simeq 81$ K. Formation of solitonlike paramagnetic defects in the dimerized one-dimensional D-A lattice has been observed by ESR measurements.[5] A sharp rise of electric conductivity has also been observed at T_c, and attributed to the formation of charged mobile solitons at the onset of dimerization.[5]

On the other hand, the pressure-induced N-I transition shows a rather complicated behavior. According to recent studies of infrared molecular vibration spectra under pressure,[6,7] the molecular ionicity increases continuously with pressure up to about 10 kbar, and then shows a discontinuous jump at 11 kbar.[6] (There is another recent report on the same subject.[8] The result is, however, substantially different from Refs. 6 and 7.) Thus, it is interesting to clarify the characters of temperature- and pressure-induced N-I transitions, which seem to be substantially different from each other; in other words, to investigate the phase diagram of TTF-CA crystal on the P-T plane. Such a P-T phase diagram has been discussed before by Torrance et al.,[1] but it could not be more than a schematic model, as there was no firm ground of quantitative experimental data at that time.

In this Rapid Communication, we report on the temperature dependence of electric conductivity of TTF-CA crystal under various pressures up to about 11 kbar. As compared with optical studies, electric conductivity measurements are more advantageous in making high-pressure studies at low temperatures, using well qualified single-crystal samples. An experimental N-I phase diagram is

presented for the first time on TTF-CA crystal on the basis of these high-pressure data.

In the measurements, a parallelepiped single crystal of TTF-CA, about $1 \times 1 \times 1$ mm^3 in size, was mounted in a small Be-Cu cylindrical high-pressure cell.[9] The crystal was provided with silver-paint electrodes, across which the electric conductivity was measured by the two-point method in the direction parallel to the stack axis (the a axis). (The conductivity in the perpendicular direction is about one order of magnitude smaller than the parallel value at normal state. The anisotropy becomes much larger at low temperatures and high pressures.) Hydrostatic pressures were exerted upon crystal through a 1:1 mixture of kerosene and diffusion pump oil. To prevent degradation of the crystal surface in the oil, it was coated with an insulating varnish, GE7031. After clamping the cell at a constant pressure, the cell was slowly cooled down to about 30 K in a cold helium gas flow. The pressure within the cell was monitored by a manganin wire pressure gauge. At low temperatures, the liquid in the cell became a glassy solid, but the change took place so slowly that there was no observable effect on the electric conductivity of the sample.

The normal state conductivity of TTF-CA crystal is of the order of $10^{-5} \sim 10^{-6}$ s cm^{-1} (several MΩ cm in resistivity). When temperature is lowered at ambient pressure ($P = 0$ kbar), the conductivity $\sigma(T)$ decreases monotonically until the first-order N-I transition takes place at $T_c \simeq 81$ K, as shown in Fig. 1(a). The conductivity $\sigma(T)$ shows a sharp jump by about one order of magnitude at T_c. On the other hand, when pressure is applied at room temperature, the conductivity $\sigma(P)$ shows a remarkable increase by more than four orders of magnitude in the pressure range from $P = 0$ to about 8 kbar, as shown in Fig. 1(b). Experimental points up to about 6 kbar fall fairly well on a straight line in the semilogarithmic plot of $\log_{10}\sigma$ vs P. At higher pressures, the experimental $\sigma(P)$ curve rounds off, reaches a maximum at about 8.7 kbar, and then slightly decreases with increasing pressure. There is no indication of a discontinuous jump in the $\sigma(P)$
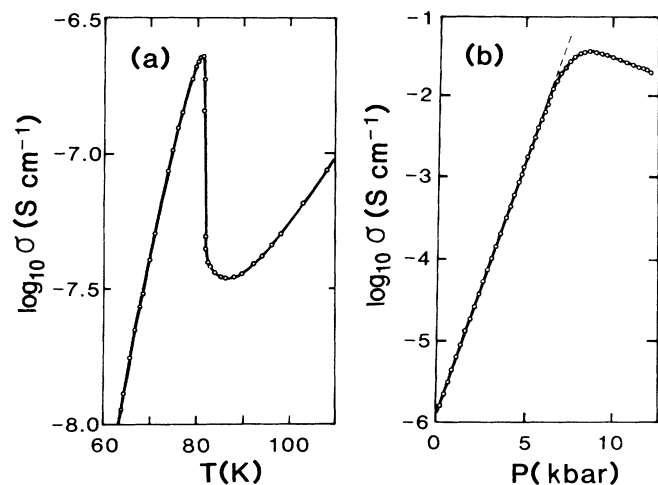
FIG. 1. Electric conductivity of TTF-CA crystal along the stack axis, (a) temperature dependence $\sigma(T)$ at ambient pressure ($P=0$), and (b) pressure dependence $\sigma(P)$ at room temperature (295 K).

curve at room temperature.

In Fig. 2, the experimental $\sigma(T)$ curves observed at various pressures are assembled in a sterographic plot upon the P-T plane. Several interesting features to be noted in this three-dimensional $\sigma(P,T)$ plot are summarized as follows: (1) In the low-P region, the $\sigma(T)$ curves show fairly sharp peaks at $T_c \cong 81$ K irrespective of the magnitude of P. The maximum σ values are also insensitive to pressure. (2) When pressure exceeds some critical value $P_c \cong 2.1$ kbar, the σ peak is suddenly broadened and shifted to the higher-T region. (3) In the high-T region, indicated by (a), the conductivities are remarkably enhanced with increasing pressure, whereas the conductivities in the low-T region (b) are almost independent of pressure. As a consequence, the anomaly of $\sigma(T)$ curve

tends to show an asymmetric humplike or shoulderlike shape. The $\sigma(P)$ curve presented in Fig. 1(b) corresponds to the intersection of $\sigma(P,T)$ surface at room temperature. The exponential dependence of σ upon P is one of the characteristic features of the $\sigma(P,T)$ surface in the region (a).

There is a clear ridge on the $\sigma(P,T)$ surface between the (a) and (b) regions. As the T and P dependences of conductivity are considerably different between the two regions as mentioned before, the projection of this ridge on the P-T plane will give an experimental phase diagram representing the thermodynamical states of TTF-CA crystal relevant to the electric conductivity. Such a projection of experimental points [peaks or humps on the $\sigma(P,T)$ surface] is plotted in Fig. 3 by open circles.

The experimental curve is composed of two parts, a vertical straight line in the low-P region and a slanted curve in the high-P region. There is a sharp turning point between them at about $T_c \cong 81$ K and $P_c \cong 2.1$ kbar. The straight line at T_c is assigned with no doubt to the first-order phase boundary between the N and I regions. From x-ray studies[4] and infrared spectroscopy,[10,11] it has been confirmed that the lattice is dimerized below T_c at ambient pressure. Although there are no low-temperature studies under pressure, it is quite likely that the lattice undergoes essentially the same first-order transition to the dimerized I phase when the system crosses the vertical line below P_c, since the sharp σ peaks are observed at the same temperature T_c. On the other hand, when pressure is higher than P_c, the nature of the N-I transition is supposed to be substantially different from that below P_c.

Before going on to further discussion of the experimental phase diagram, we shall discuss a qualitative picture of the pressure-induced N-I transition at room temperature, which has been revealed by the recent measurements on
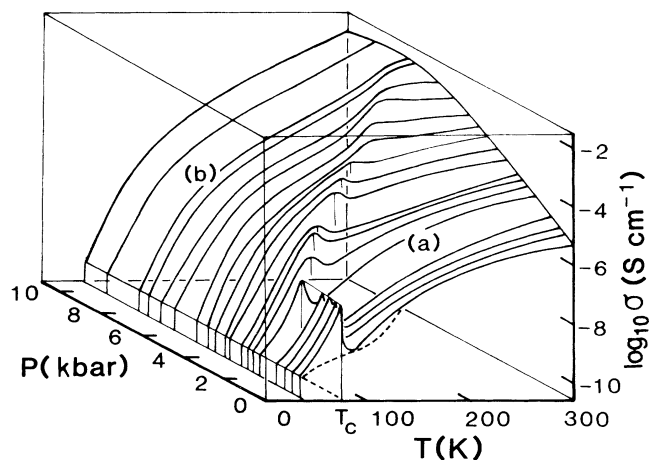

FIG. 2. A stereographic plot of temperature-dependent electric conductivity curves $\sigma(T)$ of TTF-CA crystal at various pressures. A dashed curve on the P-T plane is the projection of the $\sigma(P,T)$ peaks.
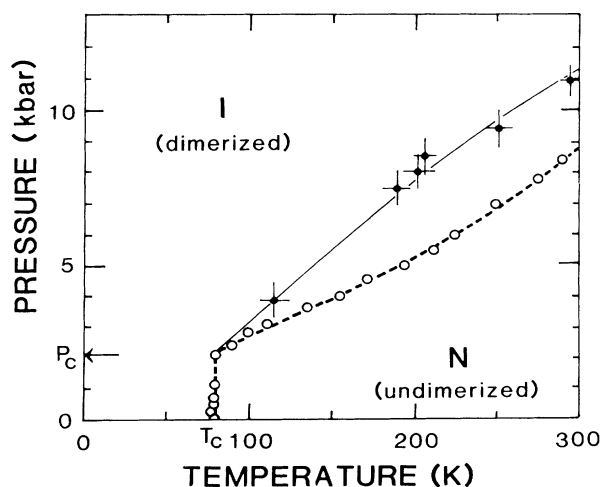

FIG. 3. Experimental phase diagram for netural-ionic transition in TTF-CA crystal. Open circles and dashed curve represent the projection of $\sigma(P,T)$ peaks in Fig. 2. Filled circles and solid curve represent the phase boundary between the dimerized ionic phase and the weakly (or dynamically) dimerized ionic phase detected by infrared molecular vibration spectra (Refs. 6 and 18).

pressure dependence of infrared[6,7] and visible[12] intramolecular excitation spectra. (There is also quite valuable yet unpublished data on x-ray[13] and neutron[14] diffraction studies under pressure.) According to the results of these studies, TTF-CA crystal shows a gradual and inhomogeneous change in ionicity with increasing pressure from $P=0$ to about 8 kbar.[12] In this pressure range, both quasineutral and quasi-ionic molecular domains are supposed to coexist. A remarkable exponential increase of electrical conductivity by pressure [Fig. 1(b)] is attributable to the increase of charged N-I domain wall density, as theoretically suggested by Nagaosa on the basis of a collective excitation model of CT states in TTF-CA crystal.[15,16] With further increase of pressure, the conductivity shows a weak maximum and becomes less dependent on pressure, indicating a saturation of the charged domain-wall density. This implies that the lattice is transformed through a mixed state of N and I domains to a predominantly ionic state. In the ionic region, molecules are supposed to be very weakly dimerized in the lattice.[6] When pressure is raised to about 11 kbar, the ionicity increases discontinuously, and at the same time the lattice shows a strong dimerization.

With the aforementioned picture in mind, we shall consider the experimental phase diagram presented in Fig. 3. A notable feature of the conductivity $\sigma(P,T)$ is that there is a clear distinction between its behaviors in the regions (a) and (b) in Fig. 2. In the region (a), the conductivity $\sigma(P,T)$ is strongly dependent on P, while it is nearly a function of T alone in the region (b) as seen in Fig. 2. In fact, when the $\sigma(T)$ curves are plotted against $1/T$, they fall on almost the same straight line in the low-temperature region below the peaks (or humps). From the slope of this line, the activation energy is estimated to be $0.06 \sim 0.09$ eV, which is considerably smaller than the lowest CT excitation energy of about 0.7 eV. Such

behavior may be attributed to the thermal excitation of charged solitonlike defects in the dimerized lattice. From these results, we consider that the lattice is dimerized in the region (b) likewise as observed in the I phase at $P=0$ kbar. To confirm the dimerization in this region, we attempted low-temperature infrared molecular vibration spectroscopy under pressure, similar to a previous study made at room temperature.[6] Leaving details in a separate paper,[17] we plotted the experimental results in Fig. 3 by filled circles. At these points, an optically forbidden a_g intramolecular vibration mode of CA has been found to become activated, indicating an occurrence of strong dimerization of D-A pairs. The solid line connecting these points therefore represents the boundary which separates the weakly (or dynamically) dimerized I phase and the statically dimerized I phase.

The two experimental phase boundaries (solid and dashed lines) are partly due to the different characters of the respective measurements; the solid line has been probed by microscopic optical molecular excitation, while the dashed line has been probed by macroscopic electric transport phenomenon, although both are associated with the same dynamics of the N-I domain walls or solitonlike defects at the pressure-induced N-I transition in the TTF-CA crystal. The detailed behaviors of the lattice in the region surrounded by the solid and dashed curves are particularly interesting in relation to the dynamical properties of TTF-CA crystal such as transient optical response,[11] nonlinear conductivity,[18] and photoconductivity.[19] These interesting aspects of the N-I transition in TTF-CA crystal will be treated in more detail in papers to follow.

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[1]J. B. Torrance, A. Girlando, J. J. Mayerle, J. I. Crowley, V. Y. Lee, P. Batail, and S. J. LaPlaca, Phys. Rev. Lett. **47**, 1747 (1981).

[2]J. B. Torrance, J. E. VAzquez, J. J. Mayerle, and V. Y. Lee, Phys. Rev. Lett. **46**, 253 (1981).

[3]Y. Tokura, T. Koda, T. Mitani, and G. Saito, Solid State Commun. **43**, 757 (1982).

[4]S. Kagoshima, Y. Kanai, M. Tani, Y. Tokura, and T. Koda, Mol. Cryst. Liq. Cryst. **120**, 9 (1985).

[5]T. Mitani, G. Saito, Y. Tokura, and T. Koda, Phys. Rev. Lett. **53**, 842 (1984).

[6]Y. Tokura, H. Okamoto, T. Koda, T. Mitani, and G. Saito, Solid State Commun. **57**, 607 (1986).

[7]A. Girlando, C. Pecile, A. Brillante, and K. Syassen, Solid State Commun. **57**, 891 (1986).

[8]C. W. Jurgensen and H. G. Drickamer, Chem. Phys. Lett. **125**, 554 (1986).

[9]H. Fugiwara, H. Kadomatsu, and K. Tohma, Rev. Sci. Instrum. **51**, 1345 (1980).

[10]A. Girlando, F. Marzola, C. Pecile, and J. B. Torrace, J. Chem. Phys. **79**, 1075 (1983).

[11]Y. Tokura, Y. Kaneko, H. Okamoto, S. Tanuma, T. Mitani, and G. Saito, Mol. Cryst. Liq. Cryst. **125**, 71 (1985).

[12]Y. Kaneko, S. Tanuma, Y. Tokura, T. Koda, T. Mitani, and G. Saito (unpublished).

[13]H. E. King, Jr., S. J. LaPlaca, P. Horn, R. Suter, and J. B. Torrance [quoted in R. M. Metzger and J. B Torrance, J. Am. Chem. Soc. **107**, 117 (1985)].

[14]P. Batail *et al.* (private communication from J. B. Torrace).

[15]N. Nagaosa, Solid State Commun. **57**, 179 (1986).

[16]N. Nagaosa, J. Phys. Soc. Jpn. **55**, 2757 (1986); **55**, 3497 (1986).

[17]K. Takaoka, Y. Kaneko, Y. Tokura, T. Koda, T. Mitani, and G. Saito (unpublished).

[18]Y. Tokura, H. Okamoto, T. Koda, T. Mitani, and G. Saito, Physica B (to be published).

[19]T. Mitani, Y. Tokura, Y. Kaneko, K. Takaoka, T. Koda, and G. Saito, Synth. Met. (to be published).