PHYSICAL REVIEW B VOLUME 36, NUMBER 7 1 SEPTEMBER 1987

Infrared molecular-vibration spectra of tetrathiafulvalene-chloranil crystal at low temperature and high pressure

K. Takaoka, Y. Kaneko,* H. Okamoto, Y. Tokura,† and T. Koda
Department of Applied Physics, University of Tokyo, Tokyo 113, Japan

T. Mitani
Institute for Molecular Science, Okazaki 444, Japan

G. Saito
Institute for Solid State Physics, University of Tokyo, Tokyo 106, Japan

(Received 10 February 1987)

Temperature (T) variations of the infrared molecular-vibration spectra of tetrathiafulvalene-chloranil (TTF-CA) crystalline powders have been measured at variable pressure (P). From the observed behavior of the spectra as a function of T and P, it is concluded that both quasi-ionic and quasineutral molecules coexist in an intermediate range of T and P, until the crystal undergoes a phase transition to the dimerized ionic phase at T_c which depends on P. These results are discussed in terms of a P-T phase diagram of TTF-CA crystal.

INTRODUCTION

Extensive studies have been made lately of the mixed-stack charge transfer (CT) crystal tetrathiafulvalene-*p*-chloranil (hereafter TTF-CA) to clarify the nature of the so-called neutral-ionic (NI) transition induced either by temperature or pressure.[1,2] Previous efforts were mostly concerned with the effect of lowering temperature at atmospheric pressure or applying hydrostatic pressure at room temperature. However, little has been discovered as yet on the effect of varying both temperature and pressure, except for a recent electric conductivity measurement by Mitani *et al.*[3] at low temperature and high pressure.

Of various experimental methods for the study of the NI transition, measurements of the infrared molecular-vibration spectra are particularly effective in obtaining microscopic information on the electronic and structural properties of charge transfer crystals. Detailed infrared spectroscopy studies have been made on TTF-CA crystals at low temperature[4,5] and at high pressure, [6-8] providing information on the CT states as a function of temperature and pressure. To obtain the phase diagram of TTF-CA crystal in the entire P-T plane, we need similar spectroscopic data in the low-temperature and high-pressure region. The purpose of this Brief Report is to present the first experimental data on infrared molecular-vibration spectra at low temperatures down to about 120 K and high pressures up to about 10 kbar.

EXPERIMENT

Fine crystalline powders of TTF-CA were made from purified single crystals. Measurements of the infrared transmittance spectra under hydrostatic pressure were made by using a diamond-anvil cell. The cell was mounted on a copper cold finger in a cryostat and cooled down to about 120 K by thermal conduction using liquid nitrogen as the refrigerant. A small amount of TTF-CA powder was sealed together with liquid paraffin within a 0.5-mm-diameter hole on a stainless-steel gasket which was sandwiched between a pair of diamond anvils.

The cell was clamped at a constant pressure P_0 at room temperature, and then cooled stepwise down to about 120 K. At each step of cooling, the temperature was held constant to within ± 1 K. Infrared transmittance spectra were measured at various temperatures by means of an optical system composed of a Nichrome wire heater as the light source, a 250-mm grating monochromator, and an Hg-Cd-Te infrared detector.

A quite troublesome problem in the present measurements was that the pressure in the cell drifted from the loaded pressure P_0 during cooling. For example, when the loaded pressure was, say, 7.3 kbar at room temperature, the pressure was found to increase to 9.0 kbar after the cell was cooled to 200 K. To make matters more complicated, the change in pressure upon cooling was different every time, probably depending on the gasket shape and the cooling speed. In order to monitor the instantaneous value of pressure in the cell, we have measured the R_1 emission line from a piece of ruby which was added to the cell. The pressure value could be determined with an accuracy of ± 0.5 kbar from the shift of R_1 emission line calibrated for pressure and temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

An example of the temperature variation of the infrared transmission spectra of TTF-CA crystalline powder under high pressure is presented in Fig. 1. The successive curves represent the spectra at various temperatures while cooling the diamond-anvil cell loaded at 8.6 kbar at room temperature. The spectra shown in Fig. 1(a) are assigned to

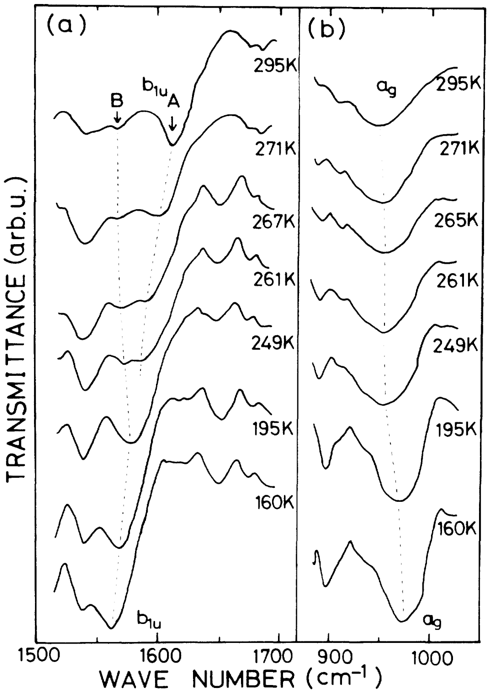

FIG. 1. Temperature-induced variation in molecular vibration spectra of TTF-CA powder crystal at high pressure for (a) the b_{1u} C=O stretch vibration and for (b) the a_g vibration both in CA molecule. The high-pressure cell was loaded at 8.6 kbar at room temperature and then slowly cooled.

the b_{1u} C=O stretching vibration mode in the CA molecule, while those in Fig. 1(b) are assigned to the a_g mode in CA. The spectra at room temperature (the topmost curves) are identical to those observed before[6] under high pressure at room temperature (see Fig. 1 in Ref. 6).

In the spectra shown in Fig. 1(a), the dips A and B are observed near room temperature. The main dip A is clearly identified with the b_{1u} C=O stretching mode of the CA molecule which is observed at about 1650 cm^{-1} at $P=0$ and room temperature. The dip is shifted to about 1615 cm^{-1} at 8.6 kbar. Another dip B, on the other hand, was not identified with any specific mode in the previous study, though it became observable at pressure higher than 7 kbar (cf. Fig. 1 in Ref. 6). This dip is also considered to be attributed to the b_{1u} mode of the CA molecule. When the temperature is decreased, the dip B is gradually enhanced and is shifted to higher frequency, whereas the dip A becomes weaker and shifts to lower frequency. As a consequence, the separation between the two dips diminishes with decreasing temperature and eventually seems to become zero around 250 K. At lower temperatures, only one dip is observed at about 1570 cm^{-1}. This frequency is close to that of the same b_{1u} C=O stretching mode in the quasi-ionic phase observed at high pressures ($P>20$ kbar) at room temperature. Contrary to these features, the frequencies of other structures in the spectra are almost independent of temperature. The remarkable dependence of frequency and intensity of the b_{1u} C=O stretching vibration mode in CA molecules upon temperature and pressure can be attributed to the fact that the electron transferred from the donor TTF molecule to the acceptor CA molecule is predominantly located on the carbonyl (C=O) groups in the CA molecule. Hence, a change in the degree of CT with temperature or pressure gives rise to an appreciable change in the force constants of the C=O group.

In the spectra shown in Fig. 1(b), a broad dip (absorption peak) at about 950 cm^{-1} at room temperature is assigned to the a_g mode in the CA molecule. This mode is not infrared active in a regularly stacked TTF-CA crystal because of the presence of centrosymmetry, but it becomes infrared active at low temperatures or high pressures due to molecular displacements from centrosymmetry. An x-ray study has proved that the lattice is dimerized when temperature is lowered below $T_c=81$ K at atmospheric pressure.[9] Appearance of the same a_g mode under high pressure indicates that lattice is also dimerized, either partly or totally, perhaps in the same manner as occurs at low temperatures below 81 K at ambient pressure. Looking at the spectra shown in Fig. 1(b), one finds that the a_g band already has a considerable intensity at 8.6 kbar at room temperature. Its intensity further increases with decreasing temperature, showing a gradual variation in the temperature range from 295 to about 250 K and a rather sharp change at about 250 K. Note that the two dips A and B in the b_{1u} spectra shown in Fig. 1(a) are fused together at this temperature to a single prominent dip.

Temperature variations of the infrared molecular-vibration spectra shown in Fig. 1 have been measured at several values of the loaded pressure P_0. The frequencies of the b_{1u} mode of the CA molecule are plotted in Fig. 2 against temperature for $P_0=4.0$, 7.3, and 8.6 kbar. However, it should be noted that the changes in frequencies of these dips were caused not only by temperature variations

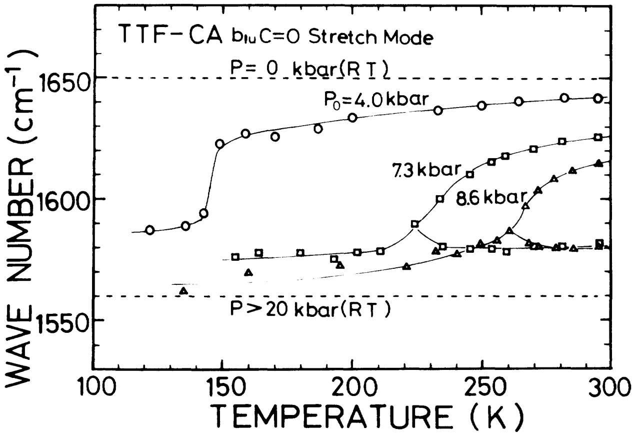

FIG. 2. Plot of the b_{1u} C=O CA bands of TTF-CA powder crystal under pressure against temperature. The data for loaded pressure $P_0=4.0$, 7.3, and 8.6 kbar are shown by open circles, squares, and triangles, respectively. Horizontal dashed lines indicate the positions of b_{1u} band at $P=0$ and $P=20$ kbar at room temperature (taken from Ref. 6).

alone but also by simultaneous pressure variations while cooling. For example, when the cell was loaded at 7.3 kbar, the pressure in the cell gradually increased by cooling to about 9.0 kbar below 200 K. Likewise, for $P_0=8.6$ kbar the pressure increased to 13.6 kbar at low temperatures. Therefore, in order to interpret these data, it is necessary to take account of both temperature and pressure variations during each measurement.

Keeping this in mind, let us examine the qualitative features of the experimental results plotted in Fig. 2. Near room temperature, the b_{1u} mode is observed as double structures A and B in the spectra for both $P_0=7.3$ and 8.6 kbar. The positions of these dips are located between 1560 and 1650 cm^{-1}. This range is just the region where the pressure-induced shift of the b_{1u} C=O band is observed at low temperature.[6] At $P=0$, the b_{1u} C=O band is observed at about 1650 cm^{-1}, but it is shifted to about 1558 cm^{-1} at pressures above 20 kbar. Two horizontal dashed lines in Fig. 2 indicate the frequencies of the b_{1u} C=O band in the quasineutral phase at $P=0$ (upper) and in the quasi-ionic phase at $P>20$ kbar (lower), both at room temperature. The molecular ionicity has been estimated to be about 0.3 and 0.9 for the respective cases.[6] Experimental points are found between these two dashed lines indicating an intermediate value of the molecular ionicity in the corresponding state.

The most remarkable feature in the b_{1u} spectra is an appearance of the double structures A and B near room temperature and a single structure below a specific temperature T_c which is dependent on pressure; for example, $T_c=220$ K for $P_0=7.3$ kbar, and $T_c=260$ K for $P_0=8.6$ kbar as seen in Fig. 2. T_c increases with increasing pressure. According to the previous study,[6] T_c reaches 290 K at $P=11$ kbar.

The presence of two different components A and B in the b_{1u} C=O spectra above T_c evidently indicates that there are two kinds of CA molecules which possess different values of molecular ionicity. Of these components, the A band is attributed to CA molecules having a smaller ionicity, while the other component B belongs to more ionic CA molecules. From these results, one can conclude that, when pressure is applied at room temperature, the lattice of the TTF-CA crystal is separated into two distinct regions having different ionicities. Such a binary phase separation continues to exist until the temperature is lowered to a critical value T_c. The vanishing separation between the two peaks at T_c indicates that all molecules in the lattice become quasi-ionic at T_c. In other words, this can be regarded as a phase transition from a neutral-ionic mixer state (N+I) to a homogeneous quasi-ionic (I) phase. Note that a remarkable enhancement of the a_g band is observed near T_c. This indicates that the quasi-ionic phase at low temperatures and high pressures is dimerized similarly to what is observed in the low-temperature phase at atmospheric pressure.

As a summary of these results, the experimental T_c values observed at various pressures are plotted in the P-T plane in Fig. 3. Open circles represent the experimental points obtained from a plot like Fig. 2. When the cell was loaded at a particular pressure P_0, say 8.6 kbar, at room temperature and then slowly cooled, the pressure inside the cell changed gradually following a dotted curve as shown in Fig. 3, for example. The critical point T_c can be likewise located on a similar P-T curve for each loaded pressure P_0. To compare the present infrared data, we have also plotted the experimental phase diagram determined from the electric conductivity data for the TTF-CA crystal[3] (open squares and a dashed curve). These results indicate that there is a distinct first-order phase boundary at $T_c=81$ K at low pressures ($P<2$ kbar), but at higher pressures the phase boundary becomes obscured due to a complicated mechanism of electric conductivity in the neutral-ionic mixed (N+I) region. Therefore, the electric conductivity data are not sufficient to determine whether the N+I region at intermediate pressures below room temperature is separated by any distinct boundary from the homogeneous quasi-ionic phase (I) which is supposed to exist in the high-pressure region. The present data could provide the first definitive information on the phase boundary separating the mixed (N+I) phase and the dimerized quasi-ionic (I) phase at high pressure and low temperature.

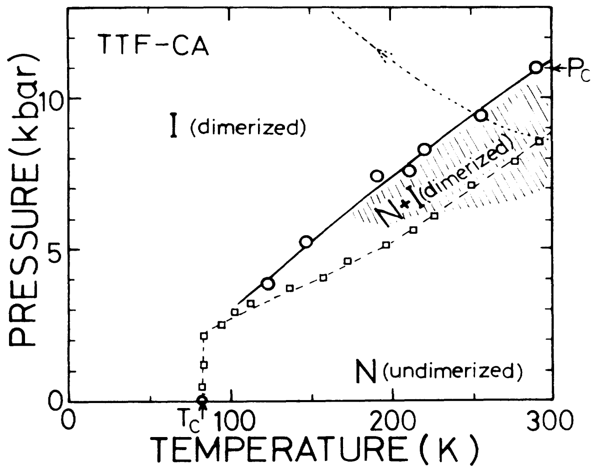

FIG. 3. Experimental phase diagram of TTF-CA crystal. Open circles and a solid curve represent the results of present infrared molecular vibration spectroscopy, while open squares and a dashed curve represent the electric conductivity data by Mitani *et al.* (Ref. 3). A dotted curve shows an example of experimental trace of P-T values in the cooling process. Hatched area represents the supposed N-I coexisting region.

Finally, we add the following two remarks: The present study has been made on powder samples because of an experimental limitation in the diamond-anvil cell. This might lead to some difficulty in the interpretation of experimental results, since the NI transition in TTF-CA crystal is apt to be affected by crystal quality. However, the phase boundary at room temperature proposed in the present study (solid curve in Fig. 3) coincides with the point P_c (marked by an arrow) where an anomaly has been observed in the pressure-induced lattice distortion by an x-ray study.[10] This may be regarded as support for the present interpretation. The second point to be noted is that the existence of the N+I mixed phase under pressure has been also suggested by Kaneko *et al.*[11] from pressure variation of intramolecular electronic excitation spectra of TTF-CA crystal at room temperature. However, the pressure-induced change in the molecular ionicity as viewed by intramolecular electronic excitation (the *B* band) is considerably different from that investigated by infrared molecular-vibration spectra (cf. Fig. 2 in the present paper and Fig. 2 in Ref. 11). To understand this difference, it is necessary to work out a more elaborate theory for the effect of CT processes in mixed-valance TTF-CA crystals upon various elementary excitations including molecular excitons and vibrational phonons.

---

[*] Present address: High-Technology Laboratories, Kawasaki Steel Corp., Chiba 260, Japan.

[†] Present Address: Physics Department, University of Tokyo, Tokyo 113, Japan.

[1] J. B. Torrance, A. Girlando, J. J. Mayerle, J. I. Crowely, 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] T. Mitani, Y. Kaneko, S. Tanuma, Y. Tokura, T. Koda, and G. Saito, Phys. Rev. B **35**, 427 (1987).

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

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

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

[10] H. E. King, Jr., S. J. LaPlaca, P. Horn, P. Dimon, R. Suter, and J. B. Torrance (unpublished). See Fig. 3 in the paper by R. M. Metzger and J. B. Torrance, J. Am. Chem. Soc. **107**, 117 (1985).

[11] Y. Kaneko, S. Tanuma, Y. Tokura, T. Koda, T. Mitani, and G. Saito, Phys. Rev. B **35**, 8024 (1987).