Bull. Chem. Soc. Jpn., ***63****, 897—900 (1990)*

Raman Spectra and Pressure-Induced Phase Transition of Phenothiazine Crystal

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(Received September 20, 1989)

The Raman spectra of the phenothiazine crystal were measured at high pressures up to 20 kbar in a diamond-anvil cell (DAC) at several temperatures. A pressure-induced phase transition was found to occur at 2.2 kbar and 297 K. The high-pressure phase was shown to be the same as the low-temperature ferroelastic phase previously found at atmospheric pressure. The wavenumber of the fluorescence band R_1 of ruby, used as the pressure monitor in DAC, was precisely measured to obtain its temperature dependence in the temperature region where the present Raman measurements were carried out.

The phenothiazine crystal undergoes a phase transition at T_c=248.8 K at atmospheric pressure.[1] The space group of the low-temperature phase (LTP) is considered to be $P2_1/n$,[2,4] while that of the high-temperature phase (HTP) is *Pbnm*.[2–4] LTP is ferroelastic.[5] The Raman spectra revealed that a small-wavenumber optical phonon shows a partial softening as the temperature approaches T_c in LTP.[1,5] The sound-velocity measurements revealed that the stiffness C_{55} shows an almost complete softening as it approaches T_c in HTP.[6] The phenomenological theory, in which the shear strain e_5 is taken as the order parameter, well-explains both the temperature dependence of C_{55} and that of the wavenumber of the above optical phonon.[6] Therefore, the phase transition of the phenothiazine crystal at atmospheric pressure is a proper ferroelastic transition which arises mainly from the instability of the acoustic phonon, but is accompanied by a slight participation of the optical phonon through the phonon–phonon coupling.

In this paper, we will report the results of high-pressure Raman measurements on phenothiazine crystals at several temperatures. The measurements were carried out in a diamond-anvil cell (DAC). We found a pressure-induced phase transition by monitoring the wavenumber shifts of lattice phonons as well as those of some intramolecular vibrations. It is concluded that the high-pressure phase is the same phase as LTP found at atmospheric pressure. However, the phonon-coupling strengths in the high-pressure region seem larger than those at atmospheric pressure. The difference in the wavenumber shifts of some intramolecular vibrations is discussed in connection with the character of the vibrational modes. It is pointed out that the transition curve on the temperature–pressure (T–P) plane is obviously curved around room temperature. The volume change at the phase transition at atmospheric pressure is estimated from the slope of the transition curve in the low-pressure region, and it is compared with the similar results for 1,3,5-triazine.

To estimate the pressure in DAC, the fluorescence band R_1 of ruby[7] is generally used.[8,9] However, the temperature dependence of the wavelength or the wavenumber of this band around room temperature has not yet been established, although some data have been reported.[9–11] Therefore, we carried out precise measurements of the ruby fluorescence over a wide temperature range, including the range where the present high-pressure Raman measurements were carried out. The results of these measurements are briefly reported and are then used to estimate the pressure in DAC at different temperatures.

Experimental

High-Pressure Raman Measurements. The Raman measurements under high pressures were carried out with the back-scattering geometry using a DAC, Toshiba Tungaloy Co., XK5582, operated with high-pressure nitrogen gas. The DAC was installed in a hand-made cryostat, and its temperature was controlled with cold nitrogen gas and an electric heater. A 0.2 mm-thick inconel plate with a 0.3 mm-diameter hole was used as the gasket. Liquid paraffin was used as the pressure medium, since phenothiazine is resolved into or reacts with other conventional fluids. The pressure was monitored by measuring the fluorescence of ruby[8,9] placed near the sample in DAC. Liquid paraffin was found to give an almost homogeneous pressure in the cell up to 16 kbar at room temperature. Above this pressure, liquid paraffin gave some Raman bands which are considered to arise from the lattice vibrations in the solidified paraffin. Therefore, liquid paraffin is not appropriate as the pressure medium in the ultrahigh pressure region.

The 514.5 nm radiation from an Ar^+-ion laser was used as the excitation light with the power of 100 mW. The equipments for the Raman measurements were almost the same as used in the previous study,[1] with a small modification of the lens system. A Spex 1403 monochromator was used both for the measurements of the Raman spectra and for the ruby fluorescence measurements to be described below.

Phenothiazine (Tokyo Kasei Kogyo Co.) was purified by recrystallization from methanol and by zone-refining. Small crystalline samples were cut from the zone-refined ingots,

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and the crystal orientation of the sample in DAC was determined by comparing the polarization behavior of the Raman spectra with that of known spectra.1)

Measurement of Temperature Dependence of Ruby R_1 Band Wavenumber. The wavenumber of the ruby-fluorescence band R_1 was measured as the function of the temperature in the temperature range of 93—439 K. A small portion of the ruby crystal synthesized at Shinkosha Co., Ltd., was mounted in an Oxford DN1704 cryostat, which was then charged with nitrogen gas as the heat conductor. The temperature of the sample was estimated with a chromel–alumel thermocouple placed near the sample. The power of the excitation light, the 514.5 nm radiation of the Ar^+-ion laser, was kept at 5 μW, as samll as possible to avoid the local heating of the sample. The R_1 band overlaps with the R_2 band in the high-temperature region above 400 K. Therefore, we deduced the wavenumber of the R_1 band by the least-squares fitting of the band shapes of these two bands. The scale of the wavenumber was determined with the vacuum wavenumber of the excitation laser light12) as the point of origin.

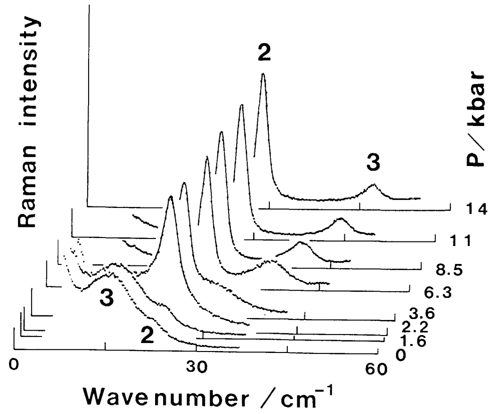

Fig. 1. The small-wavenumber Raman spectra of the phenothiazine crystal at different pressures at 332 K. The polarization of the measurement was **b**(**ac**)**b** before the pressure was applied. See the text about the numbering of the bands.

Results and Discussion

Temperature Dependence of Ruby Fluorescence. The temperature dependence of the wavenumber of the ruby R_1 band has been reported previously.9–11) However, the data reported so far are not given in the form of precise numerical data or are restricted to the temperatures below room temperature. The change in the wavenumber obtained in the present work is slightly larger than the result reported by McCumber and Sturge.10) A similar disagreement is seen in the room-temperature region in Fig. 1 in the paper of Buchsbaum et al.11) Our results were found to be represented by the following equation using the least-squares method:

$$\tilde{\nu}/\mathrm{cm}^{-1} = 14400.34 - 0.1413(T/\mathrm{K} - 300) - 0.000219(T/\mathrm{K} - 300)^2$$

The factor of the linear term agrees well with that reported tentatively by Barnett et al.9) The temperature dependence of the above equation around 300 K agrees well with that of the equation of Buchsbaum et al.,11) although there is a discrepancy of 2.4 cm^{-1} between the absolute wavenumbers given by these two equations at 300 K. Above 300 K, the equation of Buchsbaum et al. starts to deviate from the measured temperature dependence. Therefore, we use our own equation for the temperature dependence of the R_1 wavenumber between 250 and 370 K. In the following study, we assume that the R_1 wavenumber depends on both the pressure and temperature independently; the quadratic equation given by Piermarini et al.8) was used to estimate the pressure effect on the wavenumber shift.

Pressure Evolution of Raman Spectra of Phenothiazine Crystal in Lattice-Vibrational Region. Figure 1 shows the pressure evolution of the small-wavenumber Raman spectra observed at 332 K for the sample which had the **b**(**ac**)**b** orientation before the pressure was applied. We number the small-wavenumber bands according to the system of notation used in the previous paper.1) Band 3 is the characteristic band which shows a partial softening in the temperature-induced phase transition and which appears most strongly in the (**ac**) spectrum (B_{2g} in HTP and A_g in LTP). Band 2 is another characteristic band which appears in the (**cc**) spectrum with a very strong intensity (A_g both in HTP and LTP). The fact that Band 2 weakly appears in the (**ac**) spectrum before the pressure is applied is considered to be due to the imperfectness of the sample orientation.

When the pressure was increased to 2.2 kbar, Band 2 was suddenly observed with a very strong intensity. At this stage, we ascertained that no change in the sample orientation or in the sample shape occurred. As the pressure increased further, Band 3 obviously increased its wavenumber in contrast with Band 2 which showed only a small increase in the wavenumber. These changes in the spectra were reversible. The behavior of Band 3 is very similar to its partial softening in LTP at atmospheric pressure. We consider, therefore, that the crystal underwent a phase transition just below 2.2 kbar at 332 K. The fact that Band 2 appeared more strongly in the (**ac**) spectrum of the high-pressure phase than in that of LTP at atmospheric pressure might be due to the larger change in the molecular orientation accompanying the phase transition under high pressure.

Phase Diagram and Volume Change at Phase Transition. Similar spectrum evolutions were also observed by applying pressure at 272, 295, and 368 K. Figure 2 summarizes the wavenumber change of Band 3 on the T–P plane. Apparently, the phase found under high pressure is the same phase as LTP. The intersection of the two curved surfaces, which corre-

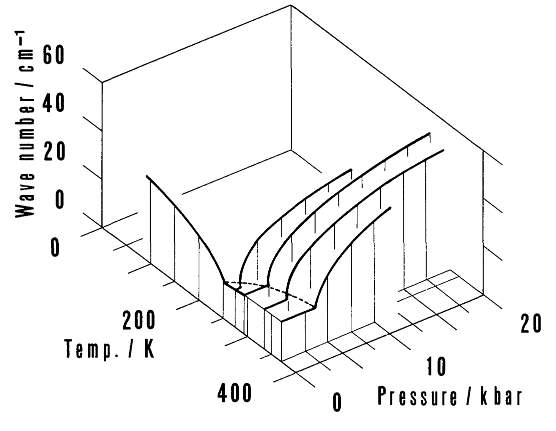

Fig. 2. The temperature and pressure dependences of the band 3 wavenumber. The dotted line is the phase boundary between the ferroelastic and paraelastic phases.

spond to the two phases respectively, gives the phase diagram. Obviously, the T–P phase diagram is curved around room temperature, although the accuracy of the critical-pressure estimation at each temperature is poor because of the poor resolution of the pressure monitor using the ruby fluorescence. The above curved diagram is in contrast with the almost linear transition curve seen for 1,3,5-triazine13) which has been known to show the ferroelastic transition at 198 K.14)

If we can assume the linearity of the curve of phenothiazine in the lowest-pressure region, we can estimate the volume change ΔV from LTP to HTP at atmospheric pressure by the Clausius–Clapeyron equation. The inclination of the transition curve, 0.04 kbar K^{-1} around 250 K, and the observed enthalpy of transition, 0.2 kJ mol^{-1},5) give the value of ΔV as 0.2 cm^3 mol^{-1}. The enthalpy of transition of 1,3,5-triazine, 74.5 J mol^{-1},15) and the inclination of the transition curve, 0.053 kbar K^{-1},13) give the value of ΔV as 0.071 cm^3 mol^{-1}. From the crystal data of phenothiazine3) and 1,3,5-triazine,16) the molar volumes of these crystals at room temperature are calculated to be 146.5 and 59.2 $cm^3 mol^{-1}$ respectively. Therefore, the volume changes at the phase transition relative to the molar volumes are almost the same for phenothiazine and 1,3,5-triazine.

Couplings between Phonons. Figure 3 shows the shifts of some small-wavenumber bands against the pressure at 295 K. The partial softening of Band 3 may be explained by the coupling with the acoustic phonon.6) Figure 3 indicates that Bands 10 and 12 show similar pressure dependences of their wavenumbers to that of Band 3. Therefore, it is considered that Bands 10 and 12 are also affected by the coupling with the acoustic phonon under high pressure. These bands have been found not to be affected at all or to be affected only slightly by the phase transition at atmospheric pressure.1) Therefore, the phonon-phonon couplings seem to increase under high pressure.

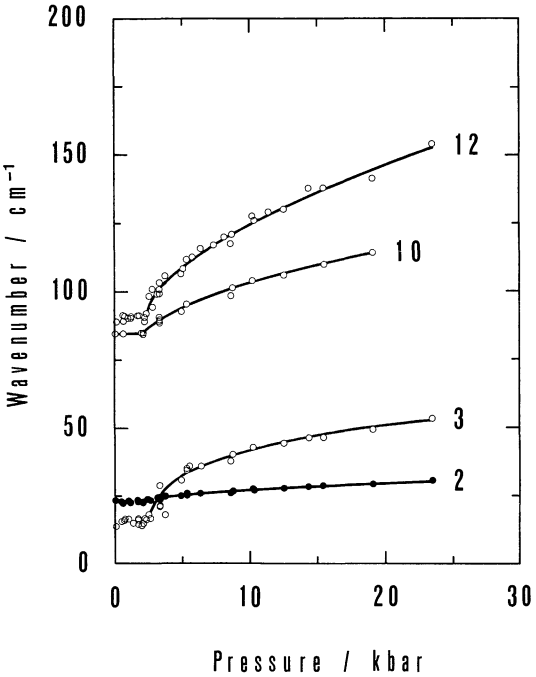

Fig. 3. The pressure dependences of the small-wavenumber bands of phenothiazine at 295 K. See the text about the numbering of the bands.

The temperature- or pressure-dependences of the phonon frequencies are due to the anharmonicity of the vibrational potential. Therefore, it is inferred that the change in the molecular conformations may be larger in the phase transition under high pressure than in that at atmospheric pressure, since the shifts of the Raman bands are much larger in the transition under high pressure.

In contrast with Bands 3, 10, and 12, Band 2 seems not to be affected by the phase transition at all, even under high pressure. This band has been found to show almost no change in the temperature-induced phase transition at atmospheric pressure.1) This band has been attributed to a vibrational mode which involves mainly the intramolecular bending at the S···N intersection of the phenothiazine molecule.1) It is an open question why this mode does not couple with other modes. However, the fact that the behavior of Band 2 in the pressure-induced transition is almost the same as that in the temperature-induced transition indicates that the symmetry around a phenothiazine molecule under high pressure is the same as that in LTP at atmospheric pressure. This supports our previous conclusion that the pressure-induced phase is the same phase as LTP.

Pressure Effects on Intramolecular Vibrations. In Fig. 4, the shifts of some intramolecular vibrational bands observed in the (aa) spectra are plotted against

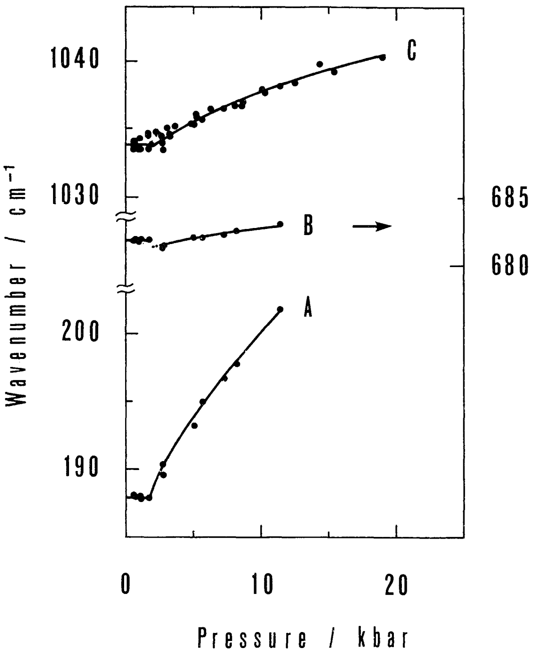

Fig. 4. The pressure dependences of the three intramolecular vibrational bands of phenothiazine at 295 K. See the text about the naming of the bands.

the pressure. Band A corresponds to that which has the smallest wavenumber among the Raman bands observed for phenothiazine in the liquid state.(17) This band is considered to arise from an intramolecular mode related to the deformation of the central ring.(17) Such a small-wavenumber intramolecular mode may mix with some lattice modes. Therefore, the shift of Band A under the high pressure is understandable as the results of lattice deformation.

Band B in Fig. 4 shows a very small pressure dependence up to 12 kbar. Such behavior is usually considered to be normal for large-frequency intramolecular modes, since the vibrational potentials of these modes may be mainly determined by the intramolecular potential. However, the behavior of Band C shown in Fig. 4 poses a question about the above ordinary explanation. This band shows a very large pressure dependence, although its wavenumber is much larger than that of Band B. It should be noted that Band B is considered to accompany the antisymmetric phenyl–sulfur–phenyl stretching in the central ring, while Band C is the symmetric breathing mode of the two phenyl rings.(17) Therefore, the former mode may not be accompanied by a large change in the molecular volume, while the latter mode is considered to change it very much. This explains the difference between the pressure dependences of the wavenumbers of these two bands. The assignments of the Raman bands of phenothiazine have not yet been established, although qualitative assignments have been given to some bands.(18) The behavior of the Raman bands under high pressure may offer a ground for checking the reliability of the assigments.

The authors wish to thank Mr. Hiroshi Iida for an assistance in measuring the Raman spectra. The ruby crystals were kindly provided by the Namiki Precision Jewel Co., Ltd. The present work was partially supported by Grant-in-Aid for Scientific Research (No. 61540334) from the Ministry of Education, Science and Culture.

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