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Observations During the Process of Transition and Melting for 1,2-Dibromoethane by Means of Raman Spectroscopy

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The Raman spectra of lattice and intramolecular vibrational bands were observed in the process of transition and melting for crystalline 1,2-dibromoethane. The Raman spectra in the lattice region for the low temperature phase changed into those for the high temperature phase, and small shifts in the frequencies of the intramolecular vibration occurred during the absorption of latent heat. In the melting process the Raman line of the lattice vibration disappeared and the Raman lines of the intramolecular vibration for the gauche form appeared. These variations in the Raman spectra were obtained as a function of the fraction transformed or melted.

INTRODUCTION

Many authors have discussed transition or melting in molecular crystals, and a large amount of experimental and theoretical work has been done on the heat capacity and other properties which show anomalies corresponding to order-disorder transitions or meltings in molecular crystals. It is found that at low temperatures the molecules in the crystal lattice may be vibrating with respect to each other about their equilibrium positions and orientations. As the temperature is increased, the order decreases until a transition (or melting) temperature is reached where usually a first-order transition to a translationally or orientationally disordered phase takes place. If the sample contains no impurity, the temperature of the sample may be maintained at constant temperature while the absorption of the heat of transition or fusion takes place. Today the process of the transition or melting is commonly interpreted as a sudden isothermal change in the molecular positions or

orientations. However, the motion of molecules in crystals has not been observed experimentally during the process of the heat absorption.

We previously studied the temperature dependence of the Raman lattice modes for 1,2-dibromoethane CH_2BrCH_2Br crystal in the region from 20 K to its melting point.[1] The frequency of the libration, which is associated directly with the transition, became lower than that of the other bands as the transition temperature was approached, and the linewidth broadened rapidly from about 100 K, which is 150 K below the transition point. The temperature dependence of this band is similar to a soft-mode behavior. On the other hand, the other Raman lattice modes exhibited no soft-mode behavior and were observed as normal lattice bands even at a temperature just below the transition point. In the high temperature phase, only one band due to lattice vibrations was observed and its frequency showed no shift over the whole temperature range of this phase.

In this paper we report the results of observations of the Raman lattice and intramolecular modes during the process of the transition and melting for solid CH_2BrCH_2Br. It will be possible to obtain the variations in the motion of the molecules during the orientational order-disorder transition and the melting in detail.

EXPERIMENTAL

CH_2BrCH_2Br was the same as that used in the previous measurement.[1] The Raman spectra were measured with the use of a Raman spectrometer, Kawaguchi Electric Works Ltd. model RL-62. The exciting light was 514.5 nm line of the Ar^+ laser, NEC model GLG2003. The power of the exciting light was kept constant during the measurement by means of the light feed back system for the GLG2003 laser made by Kawaguchi Electric Works Ltd. The cryostat has been fully described elsewhere.[1]

In order to observe the variations in the Raman spectra as a function of the fraction transformed or melted, we employed the following two techniques:

i) a continuous heating method which allows simultaneous measurements of the Raman spectra and the temperature of the sample as a constant current flows through the heater continuously; and

ii) a step heating method which allows measurements of the Raman spectra and the temperature of the sample directly after heating and at equilibrium as a constant current flows through the heater for a constant time on and off.

The emf of the thermocouple for the temperature measurements was measured by a precision digital meter (Yokogawa Electric Works. Ltd.

Type 2501). The monitoring and control of the adiabatic conditions were manually carried out.

RESULTS AND DISCUSSION

Figure 1a gives a plot of the temperature of the sample against time (t) obtained by method (i) during the process of melting in solid CH_2BrCH_2Br. We define the fraction melted (or transformed) which is dependent on time, $r(t)$, as follows:

$$r(t) = \frac{t - t_i}{t_{max} - t_i}; \qquad t < t_{max}$$
$$r(t) = \frac{t_f - t}{t_f - t_{max}}; \qquad t > t_{max}, \tag{1}$$

where t_i and t_f are the times at which melting begins and finishes, t_{max} given by the intersection of the extension of the plot as shown in Figure 1a.

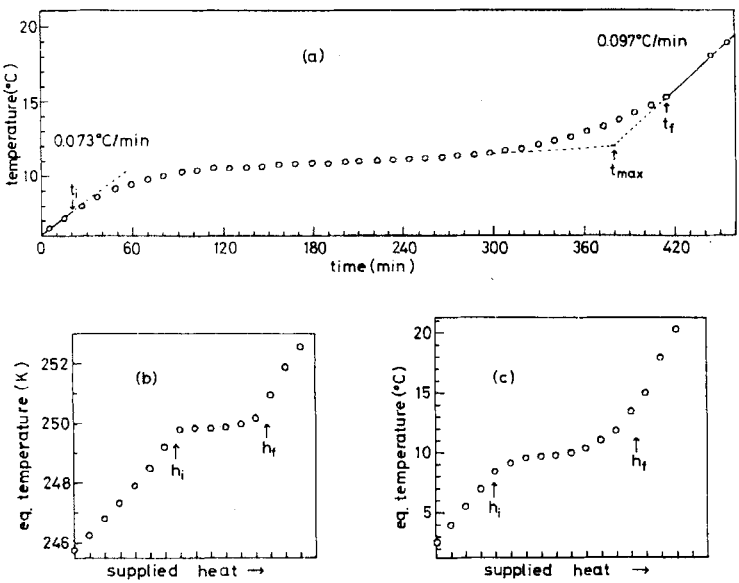

FIGURE 1 (a) time-temperature curve, (b) supplied heat-equilibrium temperature in the transformation process, and (c) supplied heat-equilibrium temperature in the melting process.

Variations in the Raman spectra of the intramolecular vibrations

It seems that the variations in the spectra of the intramolecular modes due to the phase transition are small in comparison with the lattice modes.

In the process of the β (low temperature phase)-to-α (high temperature phase) transition, larger frequency-shifts were observed in the bands in the 186 and 1252 cm^{-1} regions. The former shifted to a higher frequency and the latter to a lower frequency as the transition processed. These frequencies are plotted against $r(t)$ in Figure 2, and the Raman spectra in the 1252 cm^{-1} region are shown as a function of $r(t)$ in Figure 3. In the middle point ($r(t) = 0.4469$) of the transition, the peak of the band became flat and about 3 cm^{-1} wide which nearly corresponds to its frequency-shift. Probably this is to be interpreted as an effect induced by a distribution of molecules of different degree of transformation in the crystal. Thus, the band became sharp at $r(t) = 0.6303$, and this suggests that the molecules begin to position themselves in the α crystal-field.

The bands in the 187, 1056 and 1250 cm^{-1} regions for the trans form were measured during the melting process, and these frequency-shifts are given in Figure 4. The appearance of the Raman lines for the gauche form was also observed. The spectra in the 551 and 580 cm^{-1} regions for the gauche form are shown as a function of $r(t)$ in Figure 5 together with the spectra in the 1250 cm^{-1} region for the trans form. The band at 187 cm^{-1} shifted slightly to a higher frequency at about $r(t) = 0.2$ and the band at 1056 cm^{-1} to a lower frequency suddenly after $r(t) = 1.0$. The band in the 1250 cm^{-1} region shifted

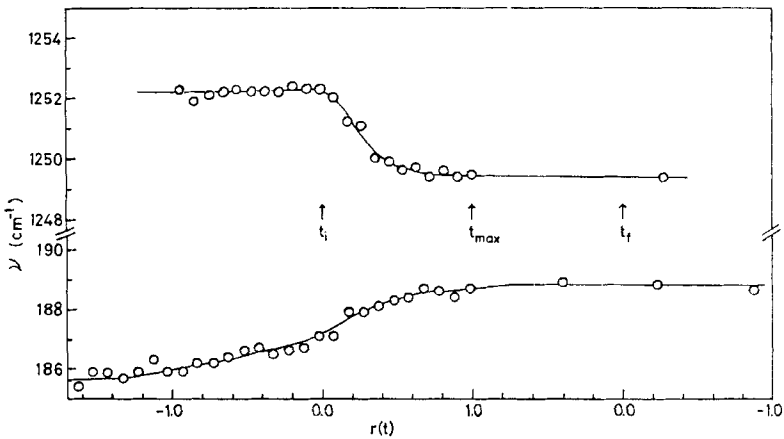

FIGURE 2 Plots of Raman frequencies of the intramolecular vibrations against $r(t)$ during the transformation process of CH_2BrCH_2Br crystal.

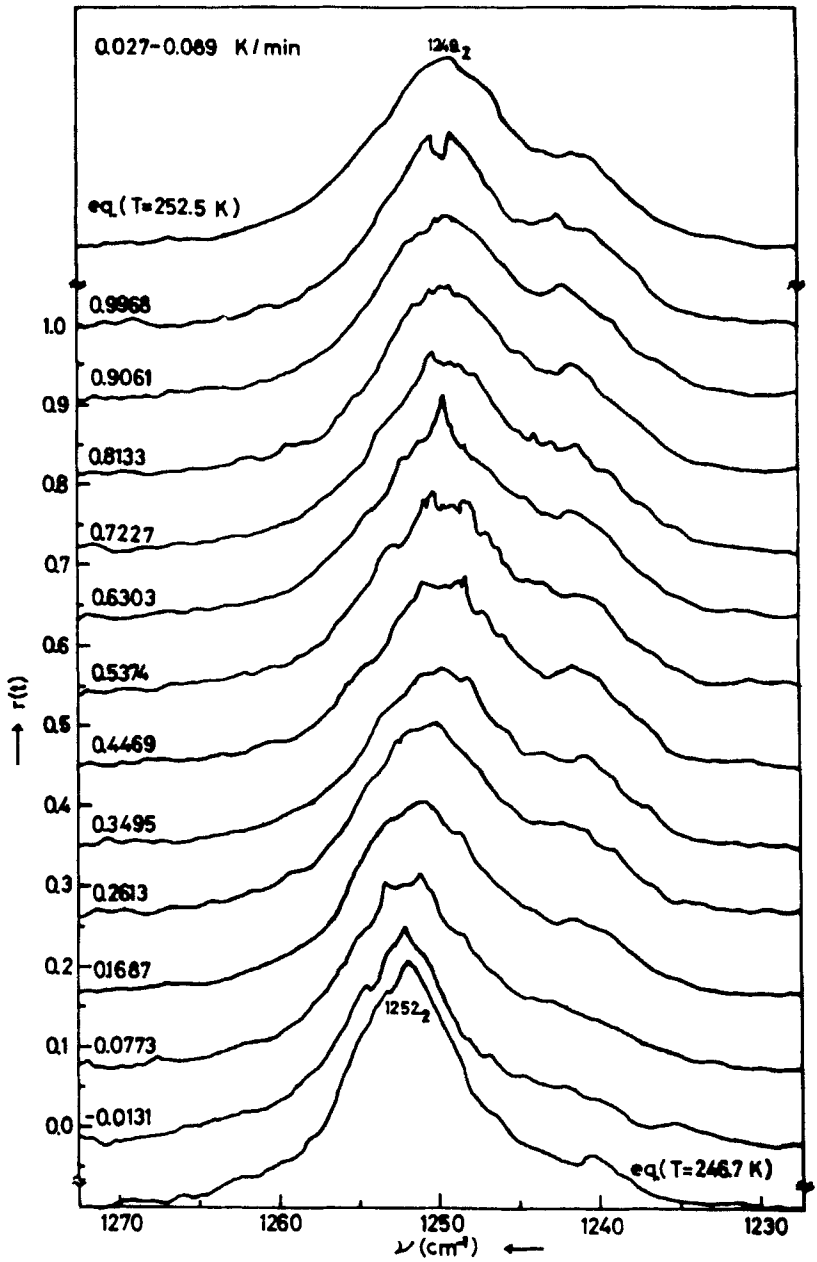

FIGURE 3 Intramolecular vibrational Raman spectra at various values of $r(t)$ during the process of transition of CH_2BrCH_2Br.

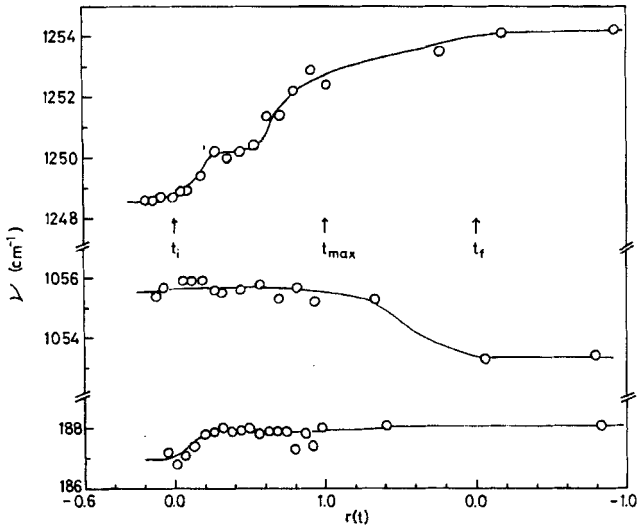

FIGURE 4 Plots of the Raman frequencies of intramolecular vibrations against $r(t)$ during the melting process of CH_2BrCH_2Br crystal.

to a higher frequency at about $r(t) = 0.2$ and at $r(t) = 0.6 \sim 0.8$, and these two points correspond to the appearance of the bands at 551 and 580 cm^{-1}, respectively.

The bands in the 187, 1056 and 1250 cm^{-1} regions are assigned to the CCBr deformation corresponding to the a_g mode, the CC stretching (a_g) and the CH_2 wagging or twisting corresponding to a_g or b_g, respectively. It is suggested that the large changes in molecular rotational or translational motion have an influence on the wagging or twisting frequency rather than on the stretching one for the intramolecular vibrations of light atoms, because the former forces are weaker than the latter ones. The skeletal stretching vibration shifts after the melting is finished. The bands at 551 and 580 cm^{-1} for the gauche form are assigned to the CBr stretching vibrations corresponding to the a and b modes, respectively. The former appears before the latter during the melting process. This may be due to the fact that the CBr stretching vibration corresponding to a is active in the Raman spectrum and the CBr stretching vibration corresponding to b is inactive for the trans form.

Variations in the Raman spectra of the lattice vibrations

It has been reported in the preceding paper[1] that two bands in the region of the lattice vibrations are observable at a temperature just below the transition point, while only one band was observed above the transition temperature.

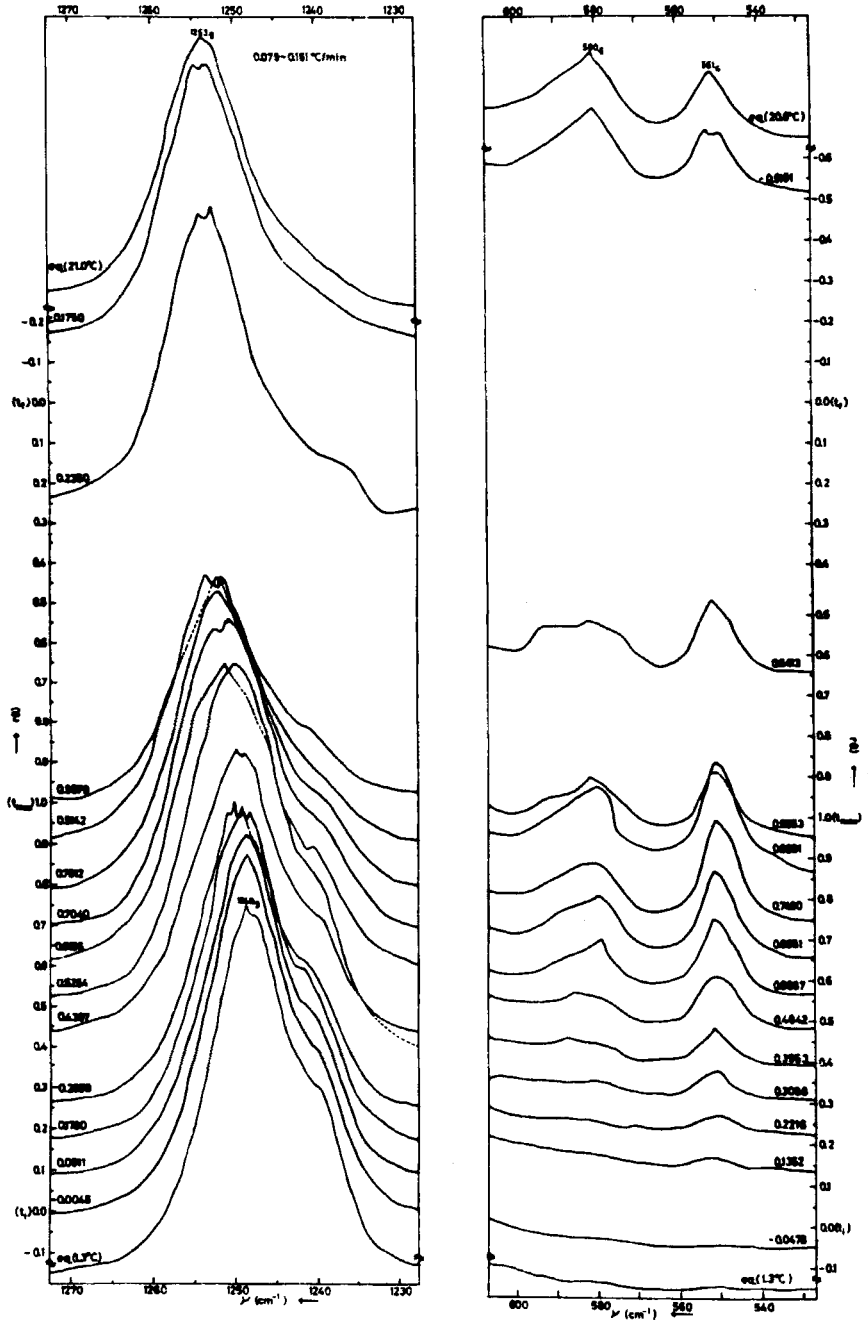

FIGURE 5 Intramolecular vibrational Raman spectra for trans and gauche forms at various values of $r(t)$ during the melting process of CH_2BrCH_2Br crystal.

The two bands of the β-phase may be the rotational lattice modes if the crystal structure of the β-CH_2BrCH_2Br is the same as that of the low temperature phase of solid CH_2ClCH_2Cl (C_{2h}^5—$P2_1/c$).[2]

The two bands of the β-phase are expected to disappear and a new band of the α-phase to appear during the transformation process. These variations in the Raman spectra were obtained by method (i) at two different heating rates, and the results are shown in Figure 6.

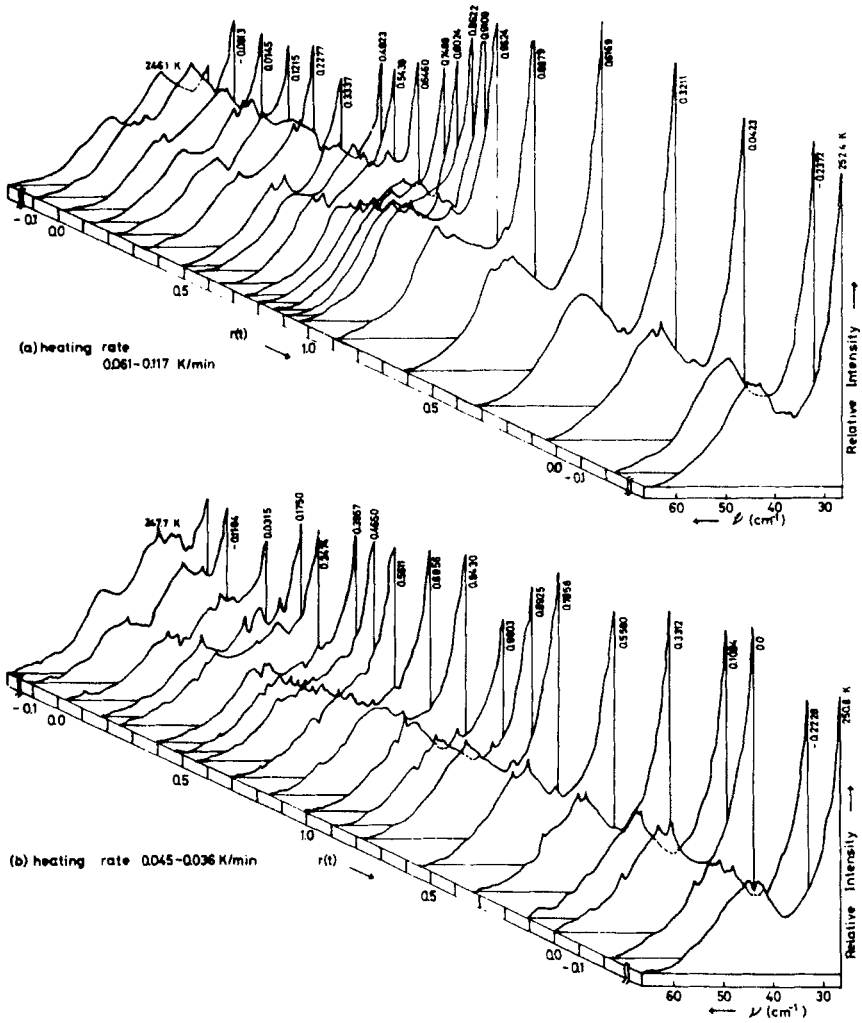

FIGURE 6 Lattice vibrational Raman spectra at various values of $r(t)$ during the process of transition of CH_2BrCH_2Br crystal.

It is seen that the disappearance of the spectrum of the β-phase takes place continuously and the appearance of one of the α-phase suddenly, and the transition point shifts to a larger value of $r(t)$ as the heating rate is increased. This suggests that there is a time lag between the supplied heat and the effect on the Raman spectrum due to this heat. In order to observe this time lag, an attempt was made to measure the Raman spectrum directly after heating and at its equilibrium by the step heating method (ii). Figure 1b gives a graph of the equilibrium temperature versus the supplied heat, h, obtained during the transformation process. We define the fraction transformed, which is dependent on the supplied heat, $r(h)$, as follows:

$$r(h) = \frac{h - h_i}{h_f - h_i}, \tag{2}$$

where h_i and h_f are given by means of the temperature rise due to the supplied heat as shown in Figure 1b. The observed Raman spectra in the lattice region are shown as a function of $r(h)$ in Figure 7, and the broken lines indicate the spectra observed directly after heating, the solid lines the spectra obtained after establishing an equilibrium and the numerals in parenthesis indicate the time required for the sample to reach equilibrium after heating (in minutes).

The Raman spectrum in the lattice region was also measured by method (i) during the melting process and the results are shown in Figure 8 as a function

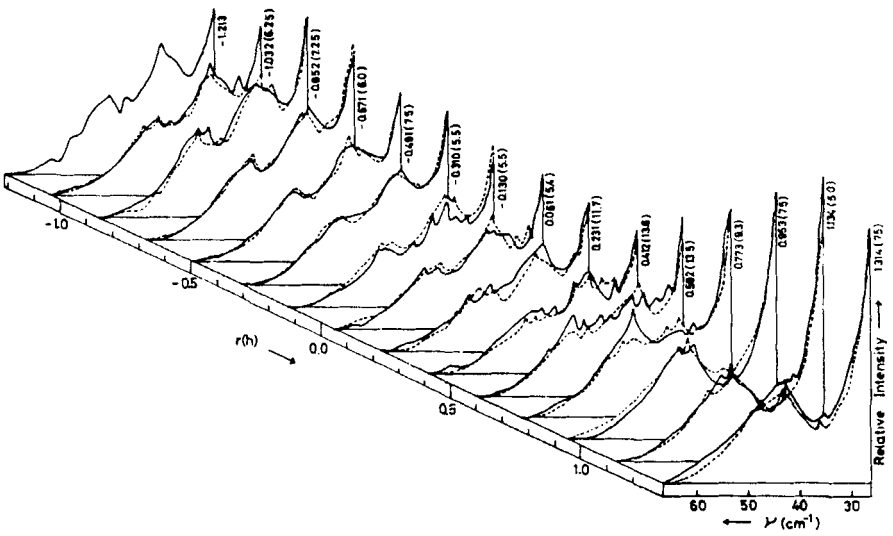

FIGURE 7 Lattice vibrational Raman spectra at various values of $r(h)$ during the process of transition of CH_2BrCH_2Br crystal.

of $r(t)$. The Raman spectra observed by method (ii) are illustrated in Figure 9 as a function of $r(h)$ (given on the graph shown in Figure 1c and by Eq. (2)).

The large discrepancy found in the spectrum between the solid and broken lines at the same value of $r(h)$ corresponds to the long time required for equilibrium after heating as seen from Figures 7 and 9. The longest time required for equilibrium occurs at $r(h)$ from 0.4 to 0.6 for the transition and at $r(h)$ from 0.2 to 0.6 for melting. The time required is the time to destroy the

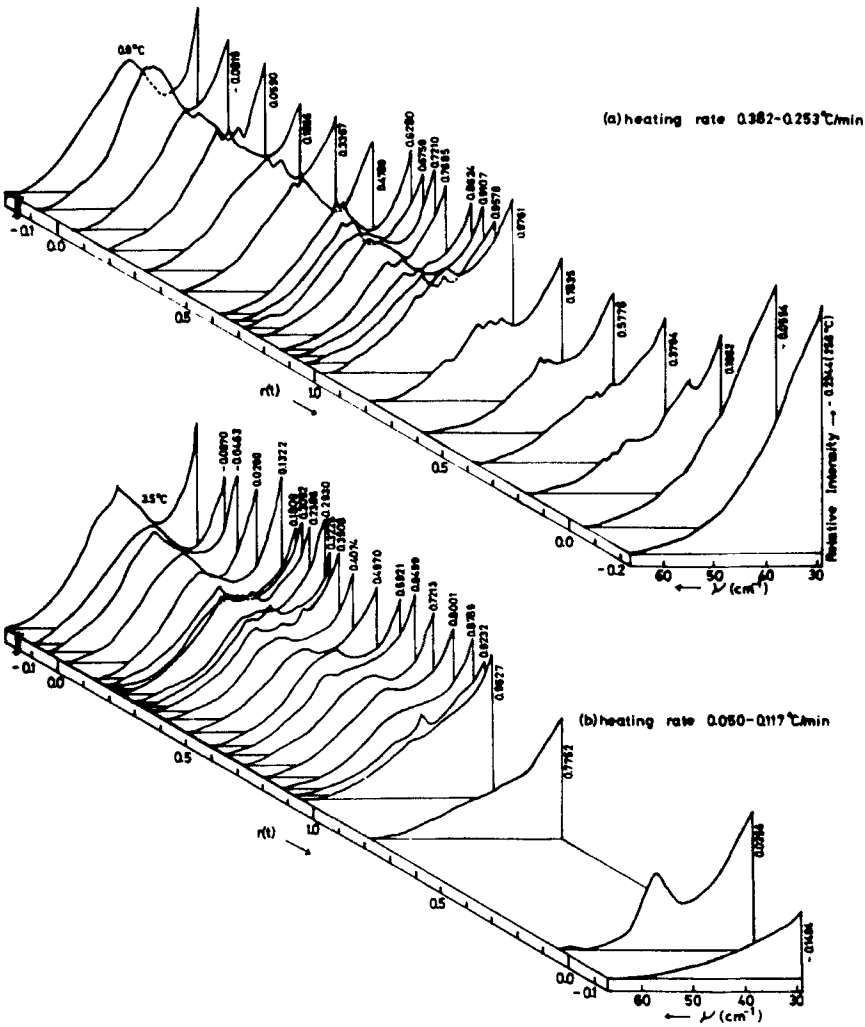

FIGURE 8 Raman spectra in the lattice region of CH_2BrCH_2Br crystal at various values of $r(t)$ during the melting process.

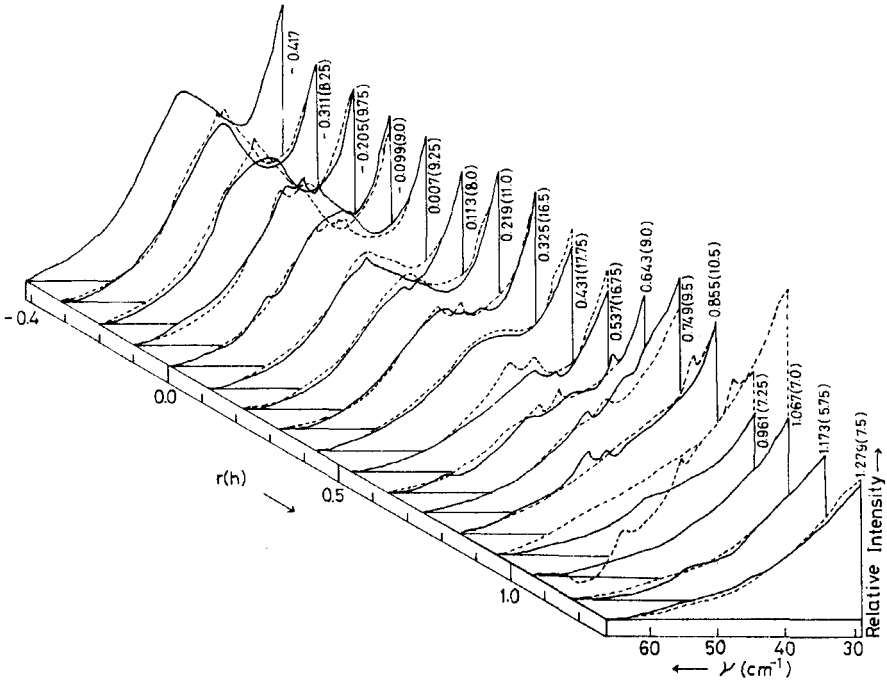

FIGURE 9 Raman spectra in the lattice region of CH_2BrCH_2Br crystal at various values of $r(h)$ during the melting process.

old phase rather than to form the new one. It is suggested that the molecules bound in the old crystal-field become free cooperatively by way of establishing the intermediate metastable states with the absorption of heat, and then the formation of the new molecular-field is begun by the molecules in similar states of motion after they are free from the old translational or orientational forces. In Figures 6 and 7, the appearance of the band for the α-phase begins at $r(t)$ of 0.6956 (b-curve) and at $r(h)$ of 0.773. It can be concluded that the time and energy required for the crystal to get out of the β-phase is longer and larger than those needed to form the α-phase. For melting, the corresponding values are at $r(t)$ or $r(h)$ of about 0.2 and the process continues until $t = t_f$ or $r(h) = 1.0$.

Observation of the Raman spectrum in the lattice region for CD_2BrCD_2Br crystal

It has been reported in the preceding paper[1] that CD_2BrCD_2Br crystal undergoes the same phase transition as CH_2BrCH_2Br, but the transition temperature shifts to about 256.0 K. Figure 10 shows the Raman spectra

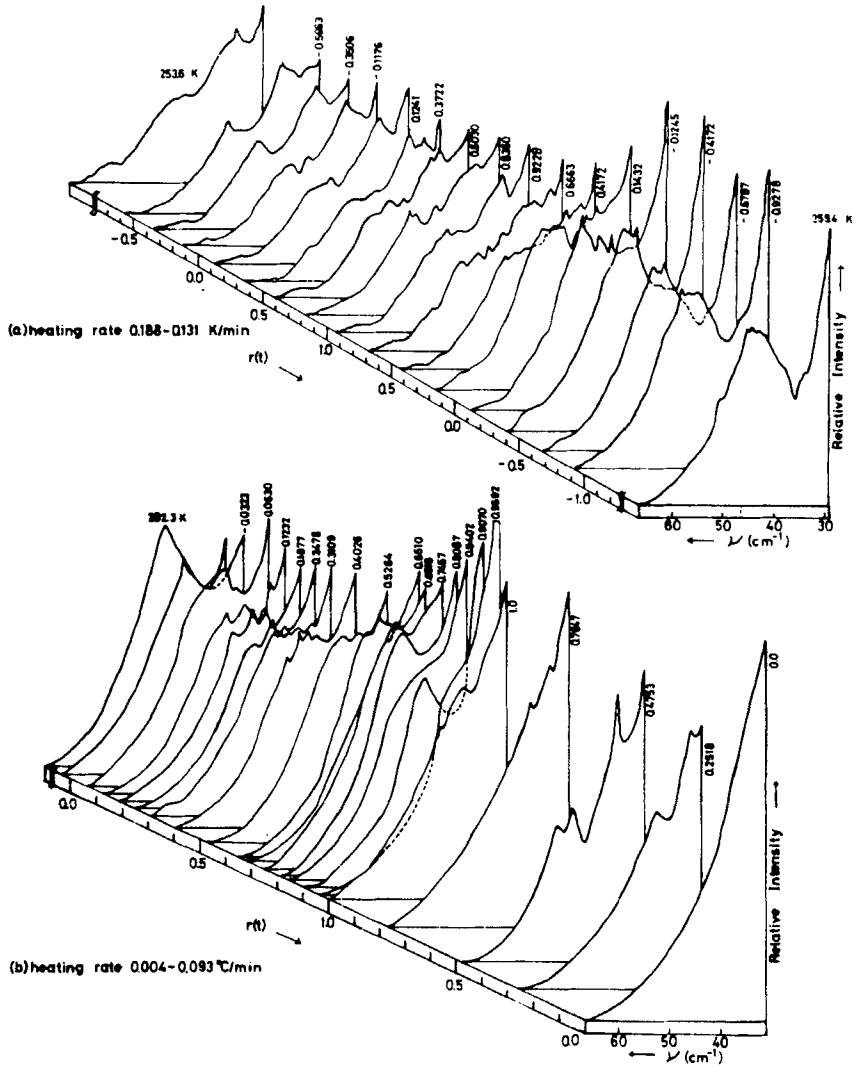

FIGURE 10 Raman spectra in the lattice region of CD_2BrCD_2Br crystal at various values of $r(t)$ during transition (a) and melting (b).

against $r(t)$ observed during the processes of transition (a-curve) and melting (b-curve) for CD_2BrCD_2Br crystal by using the same sample as that employed in the previous measurement.[1] Since the power of the exciting light was very much weaker than that employed in the measurement of CH_2BrCH_2Br, there is a temperature gradient in the sample, but the results are reasonably consistent with those obtained for the CH_2BrCH_2Br crystal.

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