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# Temperature-Induced Phase Transitions in 1,3,5-Trimethylbenzene Crystal

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The temperature effect on the Raman-active inter- and intramolecular vibrations of 1,3,5-trimethylbenzene crystal was studied. The spectral structure due to the intermolecular vibrations changed as the temperature was varied and the vibrational frequencies shifted discontinuously at about 95 and 195 K when the temperature rose from 77 K. For the intramolecular vibrations, a discontinuous shift of the vibrational frequencies of the $\nu_1$ and $\nu_{12}$ modes was observed at about 95 K. Thermograms obtained with a differential scanning calorimetry for the crystal show two endothermic peaks at 91 and 188 K as well as three endothermic peaks at 220, 222, and 227 K around the melting point. These observations indicate that the first-order phase transitions take place at 91 and 188 K under 1 atm in a 1,3,5-trimethylbenzene crystal, and that the crystal has three different crystal structures around the melting point between 220 and 227 K.

Valuable informations about the phase transitions in molecular crystals could be obtained by an observation of the Raman spectrum, because the intermolecular vibrations in crystals are generally observed in frequency regions lower than 150 $cm^{-1}$; these vibrational frequencies can be easily observed in the Raman spectrum with high degree of accuracy. Studies on the temperature- and pressure-induced phase transitions in molecular crystals were made for 1,4-dimethylbenzene,[1] hexamethylbenzene,[2] and halo-substituted benzene crystals[3—6] through an observation of the Raman spectra.

From these studies it was shown that (1) the spectral structure due to the intermolecular vibrations in methyl-substituted benzene crystals became diffuse and weak with increasing intermolecular forces, compared with the spectra observed in halosubstituted benzene crystals;[1—6] (2) when the methyl group is $CD_3$, coupling of the intermolecular and intramolecular methyl torsional vibrations in the crystals takes place and the spectral structure due to the intermolecular vibrations becomes complex.[1,2] It was reported that 1,3,5-trimethylbenzene crystal has three different structures around the melting point, and thus the crystal has three melting points at −44.8, −49.9, and −51.8 °C.[7]

In this work, the temperature-induced phase transition of 1,3,5-trimethylbenzene crystal was investigated based on observations of the temperature effects on the Raman spectra due to the inter- and intramolecular vibrations as well as on a differential scanning calorimetric observation.

## Experimental

**Material.** 1,3,5-trimethylbenzene, obtained from Wako Chemicals, was purified by repeated distillations under reduced pressure.

**Optical Measurement.** The Raman spectra of 1,3,5-trimethylbenzene crystal in the inter- and intramolecular vibrational regions were measured with a JEOL 400T Laser Raman Spectrophotometer and a Bio-Rad FT-Raman II NBR-9001 Spectrophotometer. The spectra were observed at various temperatures between 77 and 235 K under 1 atm by a backscattering observation method holding the sample in an OXFORD DN1704 cryostat. The temperature was raised from 77 K at heating rate of about 2 °C $min^{-1}$, and the observation was made after the temperature was remained constant for 20 min. Beams of 514.5, 488.0, and 476.5 nm from an $Ar^+$ ion laser (Spectra Physics Model 168B) and a 1064 nm beam from an Nd : YAG laser (Spectra Physics Model T10-106C) were used for excitation.

**Differential Scanning Calorimetry (DSC).** DSC measurements were carried out with a Seiko Denshi Model SSC5200. The calibration with respect to temperature and caloric was made using gallium and indium. After an appropriate amount of 1,3,5-trimethylbenzene crystal was weighed in a sample pan made of aluminum, the pan was sealed. Alumina was used as a reference material. The sample was set in the oven of the DSC apparatus and cooled down to 77 K using liquid nitrogen, and then heated to 250 K at a controlled heating rate. Different heating rates in the 0.5—5.0 °C $min^{-1}$ range were employed for several independent experimental runs.

## Results and Discussion

**Temperature Effect on Intermolecular Vibrations.** The low-frequency Raman spectra of 1,3,5-trimethylbenzene crystal observed at various temperatures between 77 and 210 K with a heating process from 77 K are shown in Fig. 1. The bands marked by L and H in the spectra are those having the lowest vibrational frequency and the highest intensity, respectively. The bands marked by * are the emission lines

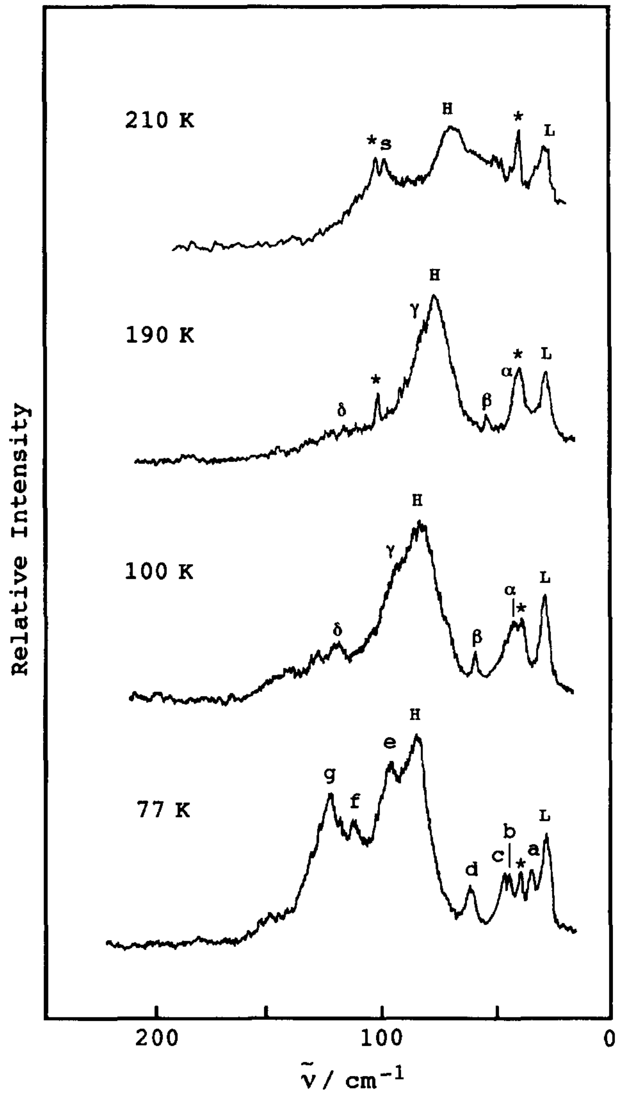

Fig. 1. The Raman spectra of 1,3,5-trimethylbenzene crystal in the intermolecular vibrational region observed at various temperatures between 210 and 77 K under 1 atm.

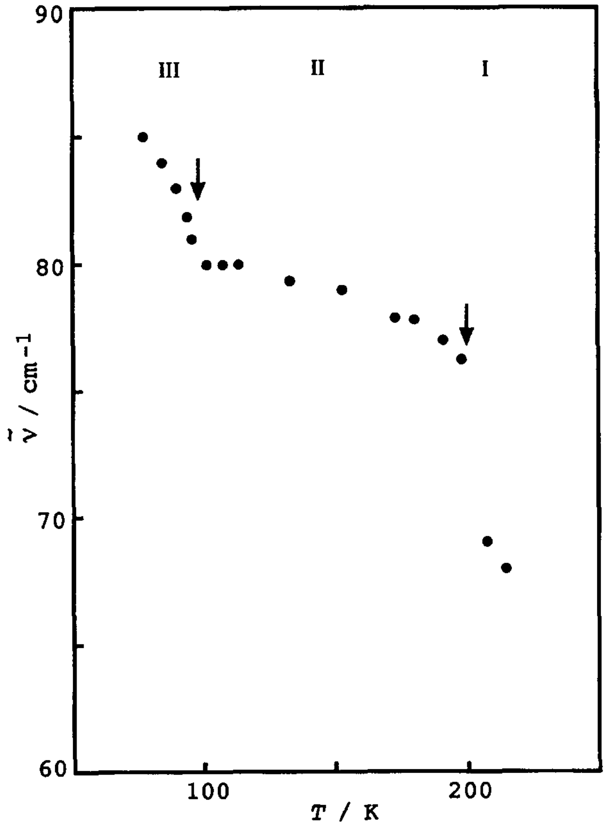

Fig. 2. Temperature-frequency curve for the Raman band H of 1,3,5-trimethylbenzene crystal in the intermolecular vibrational region observed at various temperatures between 217 and 77 K under 1 atm.

from Ar$^+$ ion. The curves for the temperature dependence on the vibrational frequency of the H band (temperature-frequency curves) are given in Fig. 2. The Raman spectrum observed at 77 K consists of several separated bands marked by L, a, b, c, d, H, e, f, and g. The spectral structure is kept unchanged up to 90 K; the structure changes at 95 K, where bands a, b, c, d, e, g are still observed with very weak intensity, while some new bands appear. The spectrum observed at 100 K consists of intensified versions of these new bands indicated by L, α, β, H, γ, and δ. Also the spectral structure does not change at temperatures from 100 to 190 K. The spectral structure changes again at 195 K, where the structure is almost the same as that observed at 210 K, except for the bands α, β, γ, and δ being very weakly observed. The spectrum observed at 210 K consists of the bands indicated by L, H, and s; the structure remains unchanged from 210 to 217 K. The crystal melts at 220 K.

It was shown previously[1,2] that the spectral structure of methyl-substituted benzenes, observed in the intermolecular vibrational region, becomes complex at temperatures below about 190 K, due to a coupling of the intermolecular and intramolecular methyl torsional vibrations when the methyl group is $CD_3$. However, when the methyl group is $CH_3$, coupling does not take place at a temperature above 77 K; therefore, the observed spectral bands in the low-frequency region up to 130 cm$^{-1}$ can be safely attributed to intermolecular vibrations.

Figure 2 shows that the vibrational frequency of the band H decreases discontinuously at 95 and 195 K as the temperature rises from 77 K. The observed change in the spectral structure shown in Fig. 1 and the temperature–frequency curve given in Fig. 2 suggest that the intermolecular interaction in the crystal changes as the temperature rises from 77 K, and that the phase transitions take place at 95 and 195 K under 1 atm. The crystal phases are referred to as phases I, II, and III downwards from the melting point.

The low-frequency Raman spectrum of the 1,3,5-trimethylbenzene crystal was also observed with a cooling process. The temperature was reduced from 235 K at a cooling rate of about 2 °C min$^{-1}$. The spectrum due to intermolecular vibrations could not be observed for the crystal of phase I, but the spectra could be observed for the crystals of phases II and III with the cooling process. This suggests that 1,3,5-trimethylbenzene liquid crystallizes to phase II via a supercooling liquid in this experiment.

The spectral structure of 1,3,5-trimethylbenzene crystal observed at 77 K is complex compared with the spectra of 1,4-dimethyl- and hexamethylbenzene crystals.[1,2] Because 1,4-dimethyl- and hexamethylbenzene crystals have an inversion point, only the rotational intermolecular vibrational bands can be observed in the Raman spectrum. The complex spectral structure observed in the 1,3,5-trimethylbenzene crystal suggests that no inversion point exists in the crystal, and therefore both the rotational and translational intermolecular vibrations are observed in the Raman spectra. The intermolecular vibrational frequencies of the Raman bands observed at 77, 100, 190, and 200 K under 1 atm are given in Table 1.

The Raman spectrum due to the intramolecular vibrations is shown in Fig. 3. The Raman bands observed at 578 and 998 cm$^{-1}$ were assigned to the $\nu_1$ and $\nu_{12}$ vibrations, respectively.[8] In Fig. 4 the relative frequency shifts defined by $(\nu_T - \nu_{77\ \mathrm{K}})/\nu_{77\ \mathrm{K}}$ are plotted against temperature for the $\nu_1$ and $\nu_{12}$ vibrations. Discontinuous changes in the slope were clearly detected in the curves at 195 K in this figure. This fact supports the idea that the phase transition takes place at 195 K, as pointed out in the discussion concerning the intermolecular vibrations.

Table 1. Vibrational Frequencies of the Intermolecular Vibrations of 1,3,5-Trimethylbenzene Crystal

| Band | 77 K | 100 K | 190 K | 200 K |
|---|---|---|---|---|
| | $\tilde{\nu}$/cm$^{-1}$ | $\tilde{\nu}$/cm$^{-1}$ | $\tilde{\nu}$/cm$^{-1}$ | $\tilde{\nu}$/cm$^{-1}$ |
| L | 28 | 26 | 25 | 25 |
| a | 33 | | | |
| α | | 42 | 40 | |
| b | 43 | | | |
| c | 46 | | | |
| β | | 57 | 53 | |
| d | 60 | | | |
| H | 85 | 82 | 77 | 69 |
| γ | | 90 | 85 | |
| e | 95 | | | |
| f | 111 | | | |
| δ | | 119 | | |
| g | 122 | | | |
| s | | | | 97 |

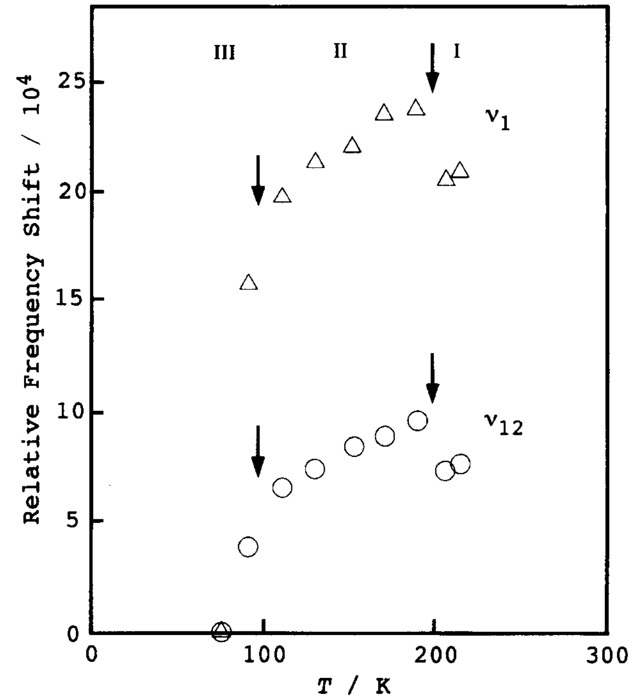

Fig. 4. Temperature-relative frequency shift curves for the intramolecular $\nu_1$ (△) and $\nu_{12}$ (○) vibrations of 1,3,5-trimethylbenzene. The relative frequency shift is defined by $(\nu_{77\ \mathrm{K}} - \nu_T)/\nu_{77\ \mathrm{K}}$.

The discontinuous changes in the vibrational frequencies of the Raman bands at about 95 and 195 K (Figs. 2 and 4) suggest that some structural change occurs in the 1,3,5-trimethylbenzene crystal at these temperatures. If the structural change is a first-order phase transition, it should accompany heat absorption. In order to examine this point, a differential scanning calorimetry (DSC) was applied for the crystal.

Figure 5 shows a typical thermogram obtained by a DSC heating scan. In this thermogram, two small endothermic peaks are observed in addition to a large endothermic peak,

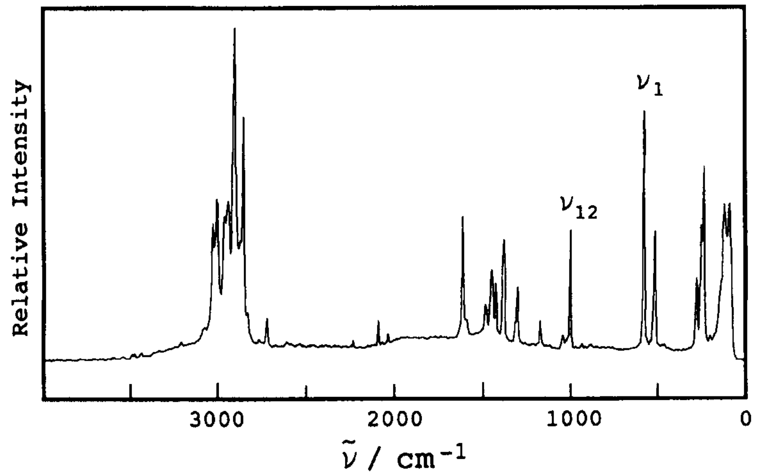

Fig. 3. The Raman spectrum of 1,3,5-trimethylbenzene crystal in the intramolecular vibrational region observed at 77 K under 1 atm.

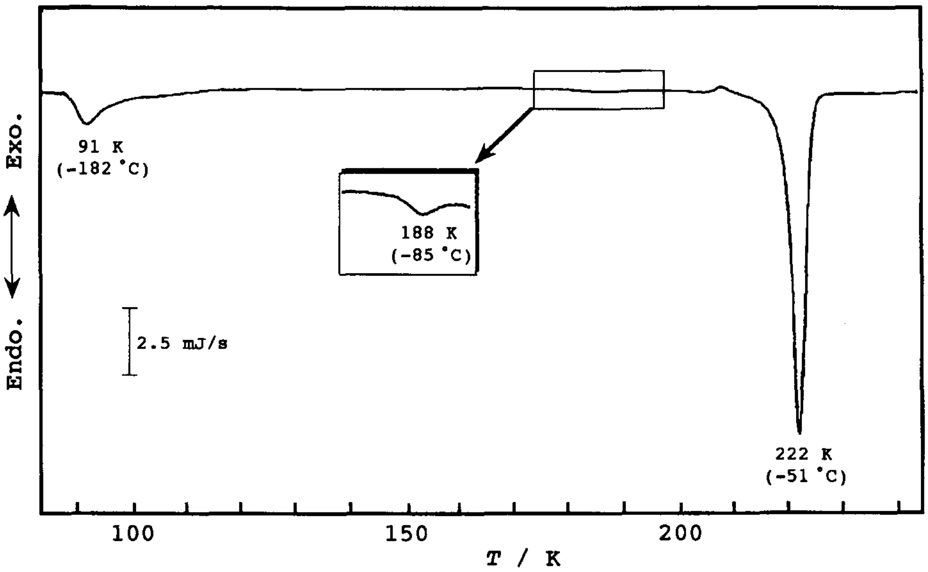

Fig. 5. DSC thermogram obtained by heating 1,3,5-trimethylbenzene crystal from 80 K at the rate of 1.0 °C min$^{-1}$. The sample weight is 53.02 mg. The inset figure represents the thermogram around 190 K drawn by expanding the vertical scale.

which is ascribed to melting of the 1,3,5-trimethylbenzene crystal. The temperatures for the small endothermic peaks, i.e., 91 and 188 K, correspond closely to those for the discontinuous change in the vibrational frequency of the Raman bands due to both the inter- and intramolecular vibrations due to the change in the temperature. Thus, the calorimetric study supports well the results that the 1,3,5-trimethylbenzene crystal has three different phases, depending on the temperature, i.e., phase III below 91 K, phase II between 91 and 188 K, and phase I above 188 K. The thermodynamic data for the phase transitions in a solid phase of 1,3,5-trimethylbenzene, obtained by DSC measurements, are summarized in Table 2.

As can be seen in Fig. 1, the spectral structure due to the intermolecular vibrations of 1,3,5-trimethylbenzene crystal changes more drastically for the case of the transition from phase III to phase II compared with that from phase II to phase I. It is considered from this fact that the change in the crystal structure accompanied by the phase transition is more remarkable for the phase III→phase II transition than for the phase II→phase I transition. This is in accord with the calorimetric results that the enthalpy change ($\Delta H$) and entropy change ($\Delta S$) associated with the phase III→phase II transition are much larger than those for the phase II→phase I transition (see Table 2). It is usual that the larger the structural change of crystalline lattice is, the more the energy required to cause a structural change is; also, the larger the increase in disorder is.

In addition to the solid state phase transition, the present DSC experiments revealed a complicated feature for the melting behavior of 1,3,5-trimethylbenzene crystal. We performed 28 independent experimental runs of DSC paying special attention to the melting temperature range. The DSC thermograms thus obtained are classified into three types with respect to the behavior in the melting temperature range as shown in Fig. 6. The first type of thermogram exhibits a simple endothermic peak due to the melting (curve (a) in Fig. 6). In the second type, a small exothermic peak appears prior to the melting (curve (b) in Fig. 6), and for the third type thermogram, a large exotherm is observed around 200 K (curve (c) in Fig. 6). The most frequently observed was the first type thermogram; it appeared 19 times in 28 experimental runs. The second type was observed 7 times, and the third type thermogram was obtained only twice.

During the course of these experiments, DSC measurements were made under several different experimental conditions: the weight of the sample in the range from 5 to 50 mg, the heating rate in the range from 0.5 to 5.0 °C min$^{-1}$, and the cooling rate in the range from 2.0 to 5.0 °C min$^{-1}$.

Table 2. Thermodynamic Data for Phase Transitions in Solid Phase and Melting of 1,3,5-Trimethylbenzene Crystal

| | $T$/K | $T$/°C | $\Delta H$/kJ mol$^{-1}$ | $\Delta S$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|
| Phase III → Phase II | 91.3 ± 1.2 | −181.9 ± 1.2 | 0.33 ± 0.04 | 3.6 ± 0.5 |
| Phase II → Phase I | 188.5 ± 1.8 | −84.7 ± 1.8 | 0.07 ± 0.03 | 0.4 ± 0.2 |
| Phase Iα → melt | 219.7 ± 0.9 | −53.5 ± 0.9 | 7.20 ± 0.4 | 32.8 ± 1.6 |
| Phase Iβ → melt | 222.0 ± 0.6 | −51.2 ± 0.6 | 7.21 ± 0.18 | 32.5 ± 0.8 |
| Phase Iγ → melt | 227.3 | −45.9 | 8.06 | 35.5 |

Figures are (mean)±(stand. dev.) estimated from 6 (Phase III→Phase II), 17 (Phase II→Phase I), 19 (Phase Iα→melt), and 7 (Phase Iβ→melt) data. The data for Phase Iγ→melt is the mean values determined from the two experimrntal runs.

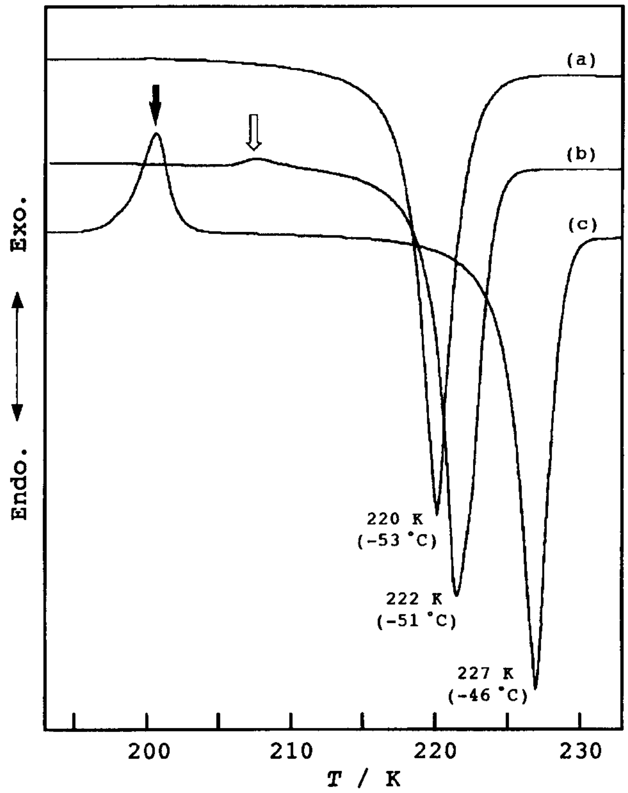

Fig. 6. Three types of DSC thermograms obtained for 1,3,5-trimethylbenzene crystal around the melting temperature. Curve (a) shows only a large endothermic peak due to a melting of 1,3,5-trimethylbenzene crystal. In curves (b) and (c), there appear small exothermic (white arrow) and large exothermic peaks (black arrow), respectively, prior to the melting.

No definite correlation was appreciable between the experimental condition and the type of thermogram that appeared, although there was a tendency that the second and third type thermograms were prone to appear when a large amount of sample, say 50 mg, was used for the DSC experiments. This complicated melting behavior of 1,3,5-trimethylbenzene might be caused by a trace amount of impurities included in the sample. For DSC measurements, we used several different samples, which were purified separately. No systematic difference was appreciable among the types of thermograms obtained with these different samples. Hence, the possibility of the impurity effect as an origin of the diverse melting behavior of the phase-I crystal would be eliminated. In several DSC experiments, the cooling-heating cycle was repeated twice using the same sample. The thermograms obtained by the second heating scan exhibited also three phase transitions, i.e., phase III→phase II, phase II→phase I, and phase I→melt, at the temperatures corresponding to those obtained by the first heating scan. Thus, it is unlikely that some interaction such as chemical reaction occurs between 1,3,5-trimethylbenzene and the DSC sample pan made from aluminum, because if such interaction takes place, the complicated melting behavior of this compound may be caused and a repeated scan should provide quite different thermograms. In any case, it was difficult to control the melting behavior of the 1,3,5-trimethylbenzene crystal for some unknown reason.

As can be seen in Fig. 6, the peak temperatures of the melting observed in different types of thermograms are definitely different from each other. This demonstrates clearly that there exist three crystal forms, i.e., polymorphs, in the temperature range corresponding to the phase I crystal of 1,3,5-trimethylbenzene. We denote the three crystal forms as phase I$\alpha$, phase I$\beta$, and phase I$\gamma$, in ascending order of the melting temperature. The thermodynamic data for melting these three crystal forms of 1,3,5-trimethylbenzene are summarized in Table 2. The existence of three crystal forms for 1,3,5-trimethylbenzene just below the melting temperature is consistent with the description in the literature, where three different temperatures (−44.8, −49.9, and −51.8 °C) have been reported as the melting point of this compound.[7] The melting temperatures obtained in the present DSC experiments for the three crystal forms are in good agreement with these melting points reported in the literature.

As mentioned above, in the thermograms corresponding to phase I$\beta$ and phase I$\gamma$, an exothermic peak appears prior to the endothermic peak of melting. It can be considered from this fact that the phase I$\alpha$ is thermodynamically metastable, and transforms into phase I$\beta$ or phase I$\gamma$ accompanying the exotherm during the course of the temperature rise. When the metastable form with high energy transforms to a lower energy state, the extra energy is released as heat; also the lower the energy of the final state is, the larger the released heat becomes. The exotherm for phase I$\gamma$ is much larger than that for phase I$\beta$. Thus, the phase I$\gamma$ is considered to be the most stable form in the three polymorphs. This is consistent with the results of heat of fusion ($\Delta H$); the value of $\Delta H$ for phase I$\gamma$ is significantly larger than those for the other two polymorphs. As for the phase I$\beta$, which is also metastable, it is more stable than the phase I$\alpha$, but their difference in the thermodynamical stability would be small, because the exotherm associated with the transformation from phase I$\alpha$ to phase I$\beta$ is quite small and the heat of fusion is comparable for the two forms.

Based on the above consideration, the free energy diagram for 1,3,5-trimethylbenzene in the temperature range between phase II and melt may be drawn schematically, as shown in Fig. 7. The complicated melting behavior of this compound can be explained according to this free energy diagram, as shown below. Upon heating 1,3,5-trimethylbenzene crystal from low temperature, a phase transition occurs from phase II to phase I$\alpha$ at 188 K, where the free energies of the two phases become equal. The free energy curve for phase I$\gamma$ intersects the free energy curve for phase II at a temperature lower than 188 K. It is thus expected that the phase transition from phase II to phase I$\gamma$ should occur at this temperature. Nevertheless, this phase transition is not observed at least under the present experimental condition. This may be attributed to a kinetic reason; i.e., a high activation energy would be required for a transition from phase II to phase I$\gamma$. The same situation may be also applicable to the relation between phase II and phase I$\beta$. When heating is continued after the transformation takes

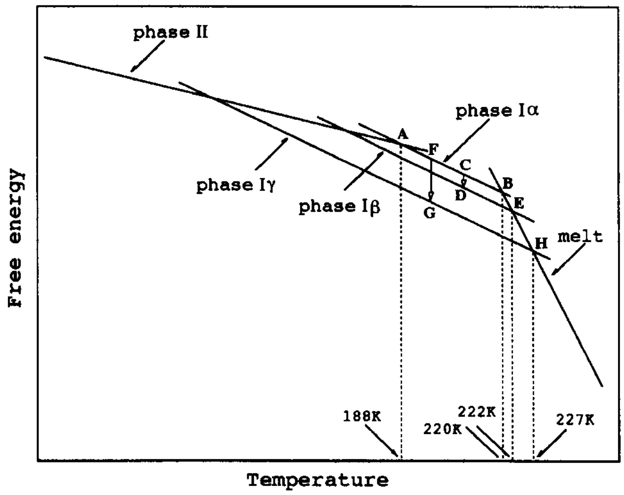

Fig. 7. Schematic free energy diagram for 1,3,5-trimethylbenzene crystal in the temperature range between phase II and melt.

place from phase II to phase Iα, the metastable crystal phase Iα continues to exist in some case until it melts at 220 K; in this case, the phase Iα melts passing through the route A→B as can be seen in Fig. 7. In some other case, the crystal phase Iα transforms to more stable phase Iβ form concomitantly with a small exotherm, and the phase Iβ crystal melts at its melting temperature (222 K); in this case, the melting occurs following path A→C→D→E, as shown in Fig. 7. The free energy difference between phase Iα and phase Iβ is not so large that the amount of the exotherm for this transformation process is small. In another case, although it is rare, the crystal phase Iα transforms to most stable phase Iγ form accompanying a large exotherm, and the phase Iγ crystal melts at the highest temperature (227 K); the phase Iα traces a path A→F→G→H, as shown in Fig. 7. The fact that the transformation from phase Iα to phase Iγ is quite rare in spite of the high thermodynamical stability of the phase Iγ may be also attributed to a kinetic reason, just as in the case that the phase transition from phase II to phase Iγ is forbidden.

The observed results for the temperature effect on the Raman spectra due to the inter- and intramolecular vibrations and for the thermogram obtained by the differential scanning calorimetry for 1,3,5-trimethylbenzene crystal are summarized as follows: (1) the first-order phase transitions take place at 91 and 188 K and (2) there exist three crystal forms, i.e., polymorphs, in the temperature range corresponding to melting.

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