Temperature dependence of Raman scattering in vapour-grown C$_{60}$ crystals

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Abstract. The temperature dependence of the Raman spectra of vapour-grown C_{60} crystals is investigated with deep-red excitation. The excitation using a deep-red laser can avoid a photo-induced transformation of C_{60} crystals during the Raman measurement. It is found that discontinuous changes occur in the Raman spectra at the SC–FCC phase transition temperature (260 K). Most intramolecular vibrational modes broaden drastically as the temperature exceeds 260 K. Crystal-field splitting of the intramolecular vibrational modes is observed below 260 K. The broadening of the Raman bands would be caused by the increase in the inhomogeneity of intermolecular force fields in the FCC phase. This broadening corresponds to the increase in the orientational disorder of C_{60} molecules above the phase transition.

1. Introduction

Since the discovery of a method to synthesize a large amount of C_{60} [1], much work has been done in order to clarify the physical and chemical properties of solid C_{60} as well as C_{60} molecules. Various natures of an isolated C_{60} molecule are retained in a crystal, because the C_{60} crystal is a molecular crystal in which quasi-spherical C_{60} molecules are attracted by weak intermolecular forces. Nevertheless, the rotational ordering transition occurs at a relatively high temperature in a C_{60} crystal [2].

C_{60} crystals undergo a first-order phase transition at about 260 K. The crystal has a face-centred-cubic (FCC) structure in the high-temperature phase where each C_{60} molecule rotates freely. In the low-temperature phase, the C_{60} molecules settle into four different orientations and the crystal structure becomes a simple-cubic (SC) structure with four orientationally inequivalent molecules per unit cell. In this phase, the molecules still jump between symmetrically equivalent orientations. At about 90 K, a glass transition, below which the molecular rotation is frozen out, has been observed by neutron diffraction [3], x-ray diffraction [4], calorimetry [5], dilatmetry [6] and thermal conductivity measurements [7]. Other anomalies have been observed at about 160 K by x-ray diffraction [4] and sound velocity measurements [8]. The origin of the anomalies at about 160 K was shown to be the same physical process as the glass transition at 90 K by elastic constant measurement [9].

Raman spectroscopy has played an important role since the beginning of the research on C_{60}. The observation of ten first-order Raman bands, two of which are polarized and eight

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of which are depolarized, agreed with the prediction of a factor group analysis [10]. This result is one piece of evidence for the soccer-ball structure of the C_{60} molecule. The Raman band of the $A_g(2)$ intramolecular vibrational mode softens when alkali metal is doped into C_{60} crystals or films [11–13]. This has been used to estimate the concentration of the doped alkali metal.

It was reported at an early stage of Raman spectroscopy studies on solid C_{60} that discontinuous changes in the frequencies and band widths of the intramolecular vibrational modes occur near the SC–FCC transition temperature [14, 15]. However, the reported values of frequency change were too large to explain this observation in terms of the structural phase transition, because the intermolecular force is a weak van der Waals bonding and only the rotational order of C_{60} molecules changes at the transition. Recently the photo-induced transformation has been found in solid C_{60}, which occurs more rapidly above the SC–FCC transition temperature [16]. The photo-induced transformation has been examined by Raman spectroscopy [17–20]. The photo-induced transformation is accompanied by mode softening and broadening in the Raman spectra. These observations suggest that the frequency changes reported at the early stage is associated with the photo-induced transformation caused by irradiation of an excitation laser.

In this work the effect of the phase transition on Raman bands has been investigated using deep-red excitation. Raman spectra of the intramolecular vibrational modes in C_{60} crystals have been measured over a wide temperature range. Crystal-field splittings are observed below the SC–FCC transition temperature. The intramolecular Raman bands discontinuously broaden as the temperature exceeds 260 K. The broadening is caused by the increase in the inhomogeneity of intermolecular force fields above the phase transition temperature, which arise from a large number of inequivalent relative orientations of adjacent C_{60} molecules allowed in the FCC phase. No marked frequency change is observed at the phase transition when using deep-red light to which C_{60} crystals are almost transparent.

2. Experimental details

C_{60} crystals were prepared by a sublimation method. Pure (99.9%) C_{60} powder was degassed at 300 °C and sealed in a Pyrex tube. The tube was placed in a horizontal furnace having a temperature gradient. The high-temperature side of the tube was kept at 600 °C and the low-temperature side was kept at 450 °C for 4–5 days. C_{60} powder was sublimed and crystallized at the low-temperature end of the tube.

C_{60} crystals were mounted on a sample holder of a cryostat in flowing He gas and the cryostat was evacuated immediately. The Raman spectra were measured using a Spex double monochromator equipped with a cooled CCD detector. In order to avoid the photo-induced degradation of the sample, near-infrared lines (about 780 nm) of a Ti:sapphire laser were used for excitation and the laser beam was line focused with a cylindrical lens. A maximum laser power of 1.5 mW (2.65 W cm^{-2}) was used for ordinary measurements except for the study of excitation power dependence. The spectral resolution was 0.4 cm^{-1} at 780 nm.

3. Results and discussion

The Raman spectra of the $A_g(2)$ mode were measured at various laser power levels to check the occurrence of the photo-induced transformation of C_{60} crystals under illumination with deep-red light. The Raman band of the $A_g(2)$ mode at 1467 cm^{-1} does not change

up to 100 W cm^{-2}. Since the frequency of the A$_g$(2) mode shifts down to 1460 cm^{-1} by photo-induced transformation [16–20], this observation indicates that no photo-induced transformation occurs with the illumination of deep-red light up to, at least, that power density.
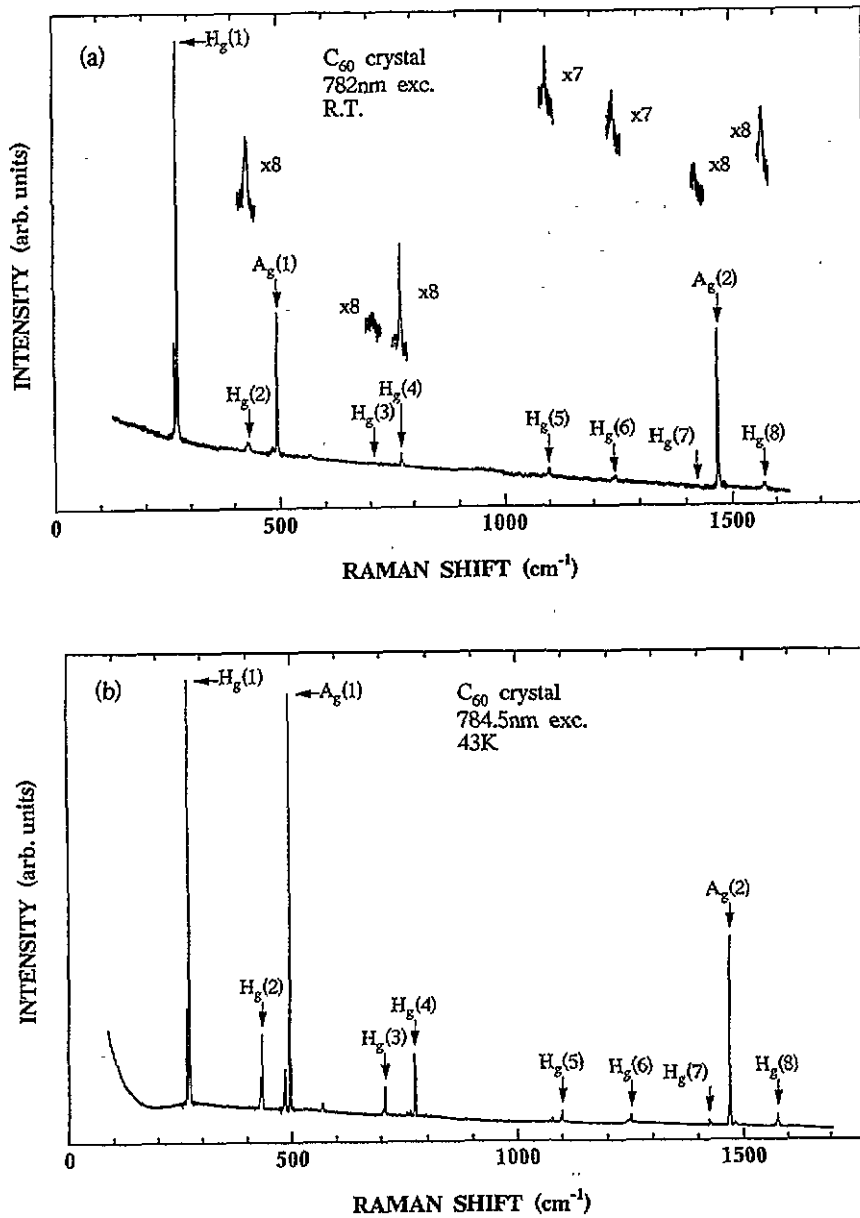

Figure 1. Raman spectra of a C$_{60}$ crystal measured at (a) room temperature and (b) 43 K.

Figure 1 shows the Raman spectra of the C$_{60}$ crystal over the frequency range 100 to 1700 cm^{-1}, which corresponds to the frequency region of the intramolecular vibrational
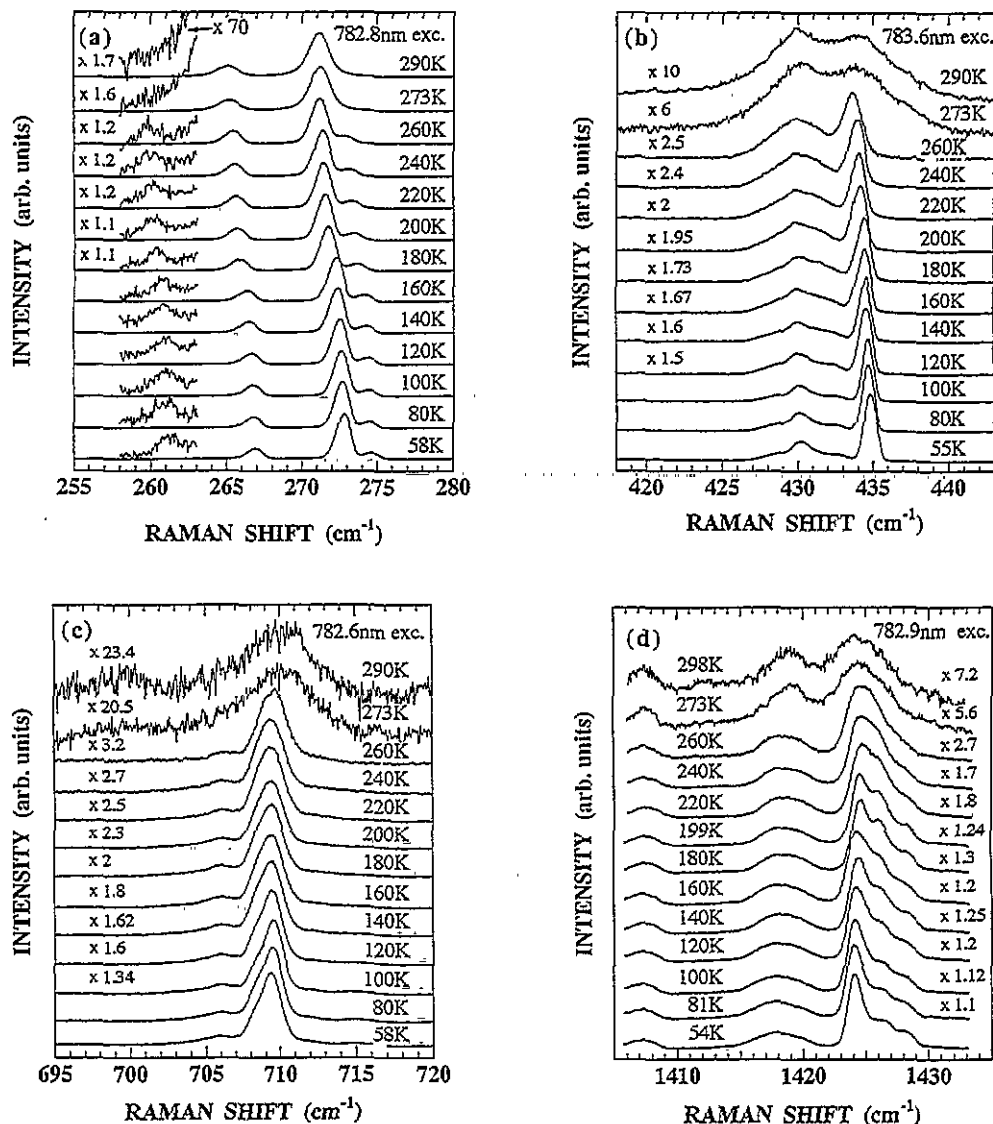
Figure 2. Temperature dependence of the Raman spectra of a C_{60} crystal: (a) $H_g(1)$ mode; (b) $H_g(2)$ mode; (c) $H_g(3)$ mode; (d) $H_g(7)$ mode; (e) $A_g(2)$ mode.

modes. 20 bands which include weak peaks are observed at room temperature and 49 bands which include shoulder bands are observed at 43 K. The factor group analysis of the C_{60} crystal predicts that 37 intramolecular vibrational modes are Raman active for the FCC phase (T_h^3) and 145 modes are Raman active for the SC phase (T_h^6) [21]. The increase in the number of observed peaks at low temperatures is consistent with this prediction. The ten peaks indicated by arrows in figure 1 have been assigned to the Raman-active intramolecular vibrational modes of a C_{60} crystal, which correspond to $2A_g$ and $8H_g$ modes of an isolated C_{60} molecule.

Other weak features may be second-order Raman bands or Raman bands activated by an isotope effect. The natural abundance of ^{13}C is 1.108%, so about 51% of the C_{60} molecules
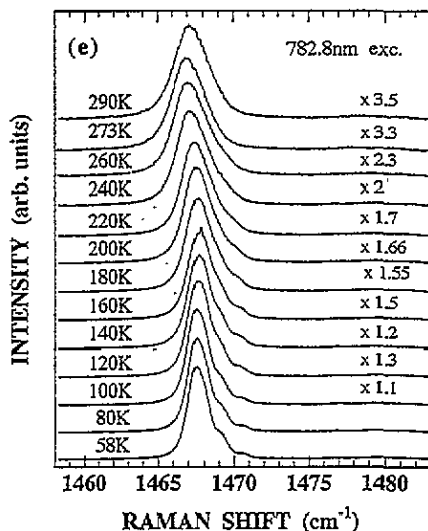
Figure 2. (Continued)

are composed of only ^{12}C and the remaining C$_{60}$ molecules contain one or more ^{13}C atoms. The substitution of ^{13}C for ^{12}C may provide two effects for the vibration of a C$_{60}$ molecule. One is a decrease in the frequency of molecular vibrations and the other is activation of otherwise Raman-inactive modes due to the symmetry lowering. For example, in the case of a C$_{60}$ molecule with a ^{13}C atom for which the symmetry of the molecule changes to C$_{1h}$ from I$_h$, the degeneracies of the vibrational modes are completely lifted and all the 174 vibrational modes become Raman active.

Raman spectra of the ten intramolecular modes (2A$_g$ + 8H$_g$) have been measured at various temperatures. The results for typical bands are shown in figure 2. In the low-temperature region, the Raman bands become narrow and shift toward the high-frequency side. Some bands show fine structures, sharpen drastically or increase their intensity as the temperature is decreased below 260 K. Discontinuous changes in the Raman spectra are observed at the SC–FCC phase transition temperature (260 K). We could not observe variation in the Raman spectra corresponding to the glass transition at about 90 K.

At room temperature, two bands are observed near the H$_g$(1) mode region as shown in figure 2(a), the intense band being at 271 cm^{-1} and the weaker band being at 265 cm^{-1}. As the temperature is decreased, the peak frequencies of the former and latter bands increase and reach 273 cm^{-1} and 267 cm^{-1}, respectively, at 58 K. A new weak band appears on the high-frequency side of the intense band below 260 K. The frequency of this band is 275 cm^{-1} at 58 K. The appearance of this band below 260 K is supposed to reflect the phase transition and may be due to a crystal-field splitting (Davydov splitting) in the low-temperature phase for which the unit cell contains four C$_{60}$ molecules. The intensities of the 275 cm^{-1} band and the 271 cm^{-1} band show similar temperature dependences below 260 K. The 271 cm^{-1} band was assigned to the first-order Raman band by many workers [10, 21, 22]. The 275 cm^{-1} band was assigned to the difference mode of the H$_g$(3) and H$_g$(2) modes by Love *et al* [22]. However, the 275 cm^{-1} band is not considered to be a second-order Raman band, because the temperature dependences of Raman bands are different for the first- and second-order bands [23].

In addition to the 275 cm^{-1} band, a weak feature is observed at about 261 cm^{-1}

below 260 K. This band is also characteristic of the SC phase and probably arises from the crystal-field splitting of the $H_g(1)$ mode. Love *et al* [22] pointed out that the weak feature at 261 cm^{-1} may be the E_2' vibrational mode (about 260 cm^{-1}) of C_{70} molecules contained in a C_{60} crystal. However, their assignment is excluded because the 261 cm^{-1} band disappears above 260 K, although the Raman band at 263 cm^{-1} in a C_{70} crystal is observed even above 260 K.

The intensities of the 265 and the 271 cm^{-1} bands show similar temperature dependences. This result indicates that the 265 cm^{-1} band is a first-order Raman band. However, Love *et al* [22] assigned this band to a second-order Raman band.

Figure 2(b) shows the Raman spectra in a frequency region near the $H_g(2)$ mode. The spectra are composed of two bands at 430 and 434 cm^{-1}. These two bands are broad and weak in the FCC phase. As the temperature is decreased, the intensity of the 434 cm^{-1} band increases by two to three times and the width of the 434 cm^{-1} band is reduced abruptly just below 260 K. The 430 cm^{-1} band also becomes narrow. This band seems to consist of a few peaks and a fine structure is observed at lower temperatures. The 430 cm^{-1} band may be a second-order Raman band, because its relative intensity to the first-order Raman band at 434 cm^{-1} decreases as the temperature is lowered. The same assignment was given by Love *et al* [22], who suggested that the 430 cm^{-1} band is a difference band between the G_g mode (1530 cm^{-1}) and the $H_g(5)$ mode (1100 cm^{-1}).

Raman spectra in a frequency region near the $H_g(3)$ mode are shown in figure 2(c). The $H_g(3)$ mode shows a broad band at 710 cm^{-1} above 260 K. This band becomes narrow abruptly below this temperature and is resolved into two bands at 706 and 709 cm^{-1}. The 709 cm^{-1} band becomes asymmetric as the temperature is decreased. This band seems to be composed of a few bands. The peak intensity of the $H_g(3)$ band increases by about seven times at 260 K as the temperature is decreased. The weak band is observed at about 715 cm^{-1} at low temperatures. The bands at 706 and 715 cm^{-1} seem to be the crystal-field splitting components of the $H_g(3)$ mode. However, this assumption is not confirmed because the broad band at 710 cm^{-1} extending over the wide frequency range prevents the observation of these weak bands in the FCC phase. Another explanation of the 706 cm^{-1} band may be a combination band of the $H_g(1)$ mode (273 cm^{-1}) and $H_g(2)$ mode (435 cm^{-1}).

Figure 2(d) shows the Raman spectra in the vicinity of the $H_g(7)$ mode. At low temperatures, Raman bands corresponding to the $H_g(7)$ mode are composed of several components. Three peaks, which are located at 1407, 1419 and 1424 cm^{-1}, are observed in the FCC phase. Below 260 K, the Raman band at 1424 cm^{-1} becomes narrow and two shoulder bands appear on the high-frequency side of the 1424 cm^{-1} band as the temperature is decreased. We consider the 1407 and the 1418 cm^{-1} bands as the second-order Raman bands, because their relative intensity to the 1424 cm^{-1} band, which is certainly the first-order Raman band ($H_g(7)$ mode), decreases with decreasing temperature. The 1407 cm^{-1} band was assigned to a combination band of the $F_{1g}(2)$ mode (974 cm^{-1}) and $H_g(2)$ mode (433 cm^{-1}) by Dong *et al* [24]. They also reported that the 1418 cm^{-1} band is a combination band of the $F_{1g}(1)$ mode (502 cm^{-1}) and $F_{2g}(3)$ mode (916 cm^{-1}) [24]. Another possibility for the 1418 cm^{-1} band is an overtone band of the $H_g(3)$ mode (709 cm^{-1}). The shoulder bands on the high-frequency side of the 1424 cm^{-1} band may arise from the crystal-field splitting of the $H_g(7)$ mode in the SC phase, because the splitting occurs below 260 K. However, Love *et al* [22] explained that the 1418 cm^{-1} band and two shoulder bands on the high-frequency side of the 1424 cm^{-1} band are isotopically activated components of the $H_g(7)$ mode.

Figure 2(e) shows the Raman spectra of the $A_g(2)$ mode (pentagonal pinch mode) measured at various temperatures. In the high-temperature region, the single peak is

observed at 1467 cm^{-1}. Two bands appear on the high-frequency side of the main band as the temperature is decreased. The frequencies of these bands are about 1469 and 1470.5 cm^{-1} at 58 K. There are two conceivable causes for the appearance of these bands. One is an isotope effect and the other is crystal-field splitting.

The frequencies of molecular vibration are decreased by substitution of ^{13}C atoms for ^{12}C atoms in a C$_{60}$ molecule. The probability of finding the isotopically substituted C$_{60}$ molecules can be deduced from the natural abundance of ^{13}C (1.108%). The probability of finding the C$_{60}$ molecule including zero, one and two ^{13}C atoms are calculated to be 0.51, 0.34 and 0.11, respectively. Raman bands of the isotopically substituted C$_{60}$ molecules should be observed on the low-frequency side of the Raman band of the C$_{60}$ molecule formed from only ^{12}C. The intensity of Raman bands of isotopically substituted C$_{60}$ molecules should be proportional to the number of the isotopically substituted C$_{60}$ molecules. As mentioned above, the two weak additional bands appear on the high-frequency side of the 1467.5 cm^{-1} band in the present work. This result indicates that the Raman bands at 1469 and 1470.5 cm^{-1} in the sublimation-grown C$_{60}$ crystal do not arise from the isotopically substituted C$_{60}$ molecules. We suppose that these two bands are caused by crystal-field splitting and their appearance is a characteristic phenomenon of the SC phase.

The isotope splitting of the A$_g$(2) band was reported in a frozen solution of C$_{60}$ in CS$_2$, in which Raman bands of the A$_g$(2) mode were observed at 1471, 1470 and 1469 cm^{-1} [25, 26]. These bands were assigned to the A$_g$(2) mode of the C$_{60}$ molecule containing no ^{13}C, one ^{13}C and two ^{13}C, respectively. These observations are different from the present result observed for the sublimation-grown C$_{60}$ crystal. This spectral difference might arise from the difference in the surroundings of a C$_{60}$ molecule; a frozen solution of C$_{60}$ in CS$_2$ is supposed to be isolated C$_{60}$ molecules. Recently, Raman measurement has been carried out for sublimation-grown C$_{60}$ crystals with a higher ^{12}C content by Horoyski *et al* [26]. Their spectral profile and frequency of the A$_g$(2) mode are nearly the same as our spectra. They suggested that the splitting of the A$_g$(2) mode results not only from the crystal-field effect but also from the isotopic effect [26].

Raman spectra of the other intramolecular vibrational modes which are not described here show a temperature dependence similar to the vibrational modes shown in figure 2. The peak frequencies and the linewidths (FWHM) of the ten intramolecular modes (2A$_g$ + 8H$_g$) are plotted versus temperature in figure 3. The frequencies decrease with increasing temperature because of the anharmonicity of the intramolecular potential. The band widths increase continuously as the temperature rises and increase abruptly just above 260 K, while the frequencies show no drastic change in the vicinity of the phase transition temperature.

An abrupt spectral change at the phase transition temperature reported so far may be caused by the photo-induced transformation of C$_{60}$ crystals. There is a threshold temperature for the photo-induced transformation, above which the photo-induced transformation occurs more rapidly. Zhou *et al* [16] reported that the SC–FCC transition temperature corresponds to the threshold. The photo-induced transformation introduces the softening and broadening of the intramolecular vibrational mode [17–20]. The amounts of mode softening and broadening are comparable to the values of the change in frequency and width at 250 K, which are obtained from the Raman study of a C$_{60}$ crystal using the 514 nm line of an Ar$^+$ laser by van Loosdrecht *et al* [14]. They reported that the intramolecular vibrational modes soften in the order of 2–11 cm^{-1} and broaden by a factor of 3–4 when the temperature exceeds 250 K [14]. The photo-induced transformation occurs readily under the illumination of the 514 nm line of an Ar$^+$ laser [17] above the threshold temperature. Hence, the mode softening and broadening observed at about 250 K in their study may be due to the photo-induced transformation by the excitation laser. Matus and Kuzmany [27] also reported an
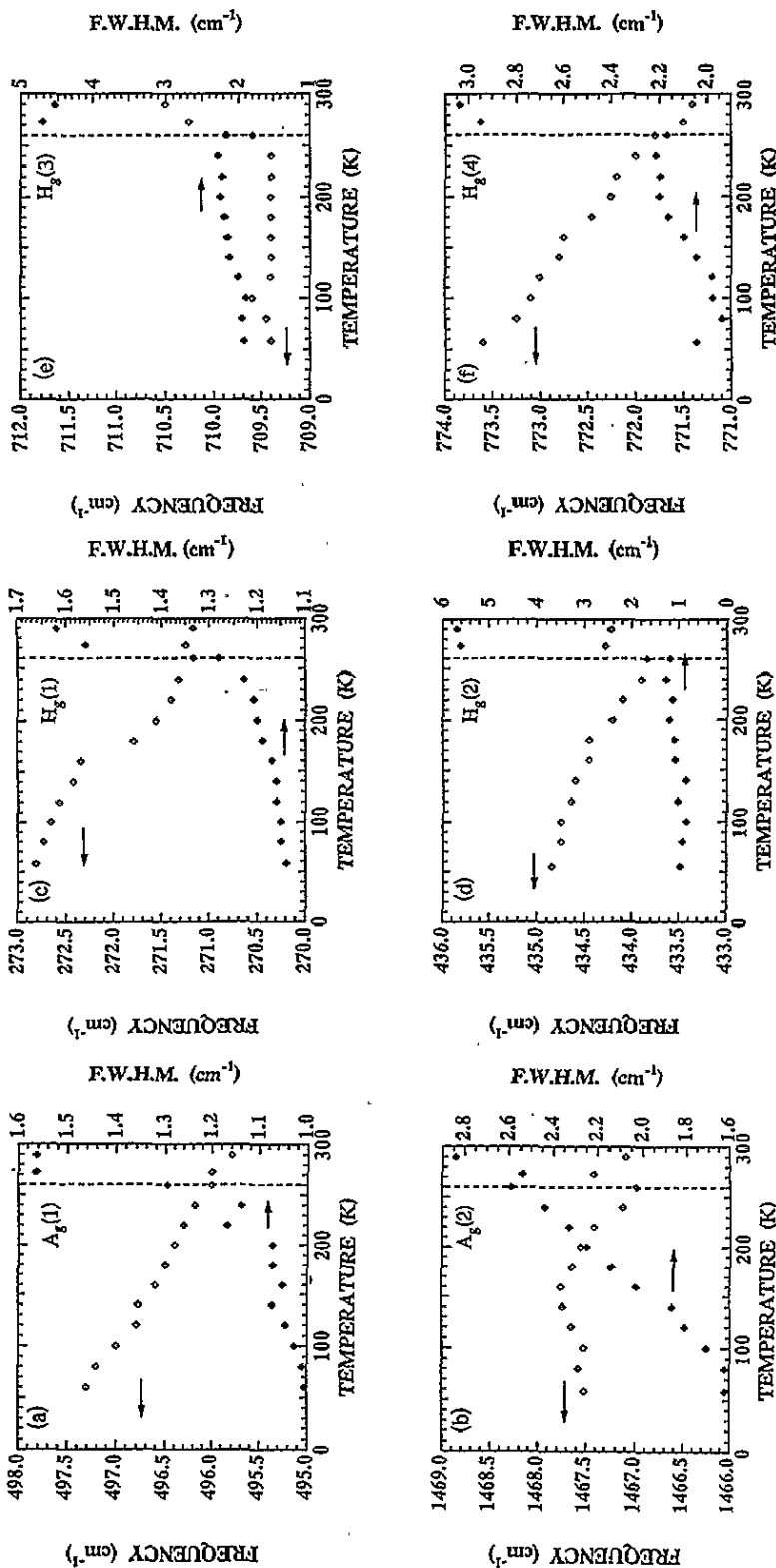
Figure 3. Temperature dependence of the peak frequencies and the linewidths (FWHM) of the ten intramolecular modes: (a) $A_g(1)$ mode; (b) $A_g(2)$ mode; (c) $H_g(1)$ mode; (d) $H_g(2)$ mode; (e) $H_g(3)$ mode; (f) $H_g(4)$ mode; (g) $H_g(5)$ mode; (h) $H_g(6)$ mode; (i) $H_g(7)$ mode; (j) $H_g(8)$ mode.
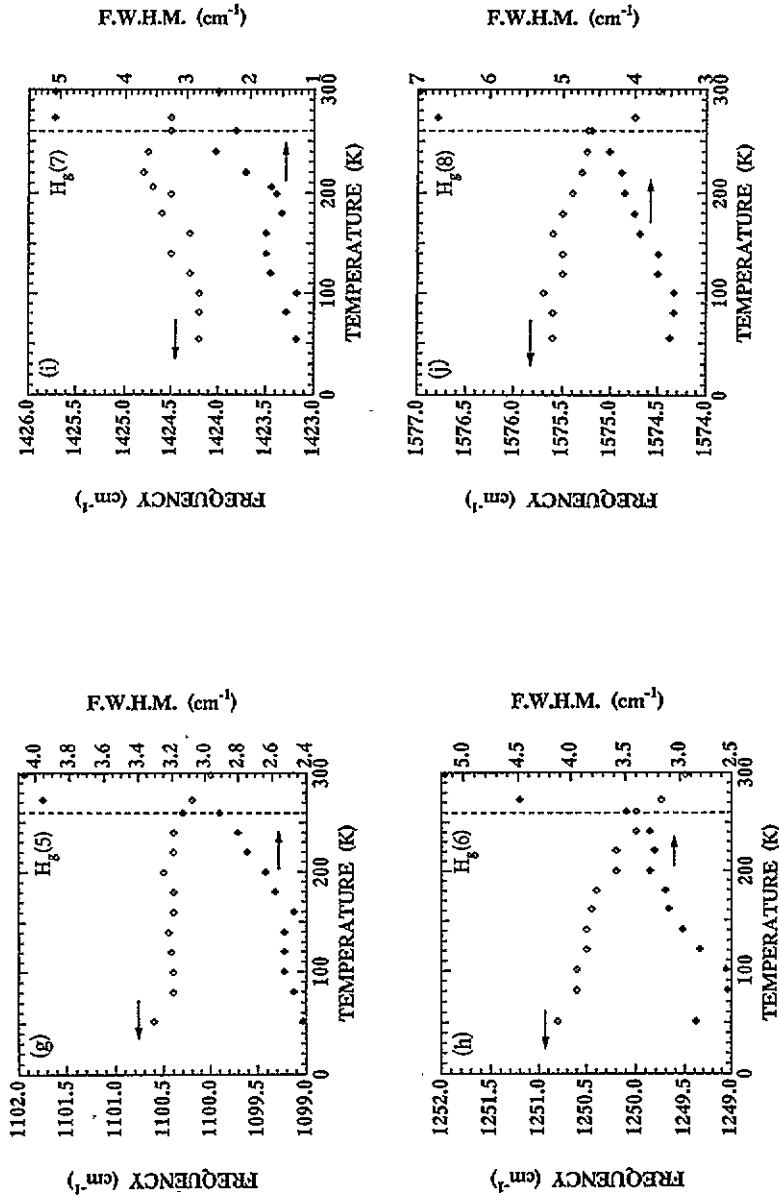
Figure 3. (Continued)

experimental result which supports this probability.

The striking changes in the band widths observed at 260 K which are shown in figure 3 are qualitatively explained by considering the rotational motion of the C_{60} molecule in a crystal lattice. The magnitude of the intermolecular forces depends on relative orientations between neighbouring molecules. The most stable orientation is achieved in the case when the electron-rich double bond of a C_{60} molecule faces the electron-poor pentagonal face of a neighbouring C_{60} molecule [3]. Each C_{60} molecule jumps between symmetrically equivalent orientations below 260 K and rotates more freely above 260 K. So, there are a number of combinations in relative orientation between neighbouring molecules above 260 K. In other words, orientational disorder of the C_{60} molecule exists. This brings about random force fields for each molecule. Below 260 K, the number of combinations is limited. So, variation in the force fields is also limited. The vibrational frequencies of a C_{60} molecule vary from molecule to molecule owing to the difference in the surrounding intermolecular forces for each C_{60} molecule. The broadening of the Raman bands observed in the FCC phase is due to inhomogeneous broadening. It results from the large variation in the vibrational frequencies caused by the large number of combinations in relative orientations between the neighbouring C_{60} molecules. Below 260 K, the number of these combinations is limited and the variation in the intermolecular force field is small. Therefore, the inhomogeneous broadening is small and the Raman bands become narrow. The broadening of the intramolecular mode has also been observed in solution-grown C_{60} crystals [28]. This broadening is due to a random force field arising from non-uniform distribution of solvent molecules contained in the crystals.

The band widths of the $H_g(2)$ mode and $H_g(3)$ mode change drastically by factors of 2–3 and 7, respectively, at 260 K, while the band width of the $A_g(2)$ mode shows no significant change at 260 K. Probably, the amount of the broadening would be related to the atomic displacement pattern of a molecular vibration. According to Stanton *et al* [29], carbon atoms forming a C_{60} molecule move in the tangential direction for the $A_g(2)$ mode. On the other hand, atomic motions are 90% radial in the $H_g(2)$ mode and 96.5% radial in the $H_g(3)$ mode [29]. The distance between carbon atoms belonging to two adjacent C_{60} molecules does not vary much for vibrations in the tangential direction. Accordingly, the contribution of intermolecular forces to the frequency of vibrations in the tangential direction is small compared with those of vibrations in the radial direction. These considerations suggest that the amount of the broadening at the SC–FCC transitions is small for the $A_g(2)$ mode and large for the $H_g(2)$ mode and $H_g(3)$ mode.

The amount of crystal-field splitting is estimated using a simple model (coupled-oscillator model). In this model, a molecular crystal is represented by a linear chain of molecules in which molecules are coupled by weak intermolecular forces [30]. The amount of the splitting of the intramolecular vibrational mode is approximately given as follows:

$$\Delta\omega \approx \omega_1^2/2\omega_0 \qquad (1)$$

where ω_1 is the frequency of the intermolecular vibration and ω_0 is the frequency of an isolated molecule. The frequencies of the intermolecular vibrational mode in the C_{60} crystal have been measured by inelastic neutron scattering [31], Raman scattering [32] and infrared absorption [33]. The frequencies of the intermolecular vibrational modes are 54 and 41 cm^{-1} for the translational modes and 18, 21 and 24 cm^{-1} for the librational modes. Using average values of translational (librational) modes, the amounts of the splitting $\Delta\omega$ are calculated and plotted versus ω_0 in figure 4 together with the splitting observed experimentally. The experimental values are comparable to or larger than the calculated values. This disagreement between the experimental values and the calculated values suggests that the
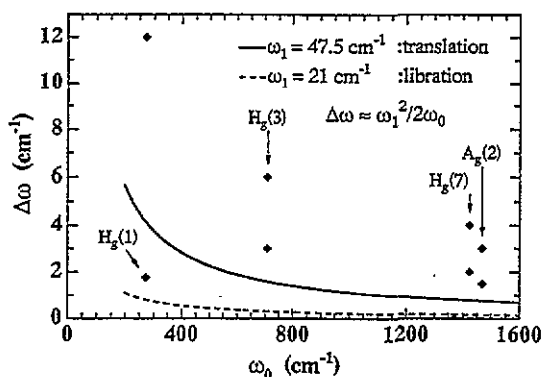
Figure 4. The experimental values (♦) and the calculated values (——, – – –) for the crystal-field splitting of the intramolecular modes of a C$_{60}$ crystal.

intermolecular forces acting on intramolecular modes are larger than the intermolecular forces estimated from the frequencies of the translational and librational modes using the coupled-oscillator model. The amounts of the splitting observed experimentally decrease as the frequency of the corresponding mode increases. A similar tendency is seen in the calculated curves in figure 4. It follows from the above discussion that the splitting of the intramolecular vibrational modes shown in figure 2 are probably caused by the crystal-field splitting.

4. Summary

The Raman spectra of vapour-grown C$_{60}$ crystals have been measured over a wide temperature range. Excitation by a deep-red laser has enabled us to measure the Raman spectra without photo-induced transformation of C$_{60}$ crystals. Discontinuous spectral changes of the intramolecular vibrational modes are observed at the SC–FCC phase transition temperature. Broadening of most of the intramolecular vibrational modes occurs abruptly as the temperature exceeds 260 K. Crystal-field splitting of the intramolecular modes is observed below 260 K. We conclude that the broadening of the Raman bands above 260 K is caused by the increase in the inhomogeneity of intermolecular force fields and reflects the increase in the orientational disorder of C$_{60}$ molecules above the phase transition.

Acknowledgments

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