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Raman study of a structural phase transition in C_{60} crystals

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Raman spectra of purified C_{60} single crystals are measured over a wide temperature range. It is found that above 400 K the high-frequency A_g mode (pentagonal pinch mode) changes in frequency and becomes sharp compared with the A_g mode at room temperature. This spectral change is reversible. The results indicate that structural change occurs and the intermolecular interaction for each C_{60} molecule is isotropic above 400 K. A reversible spectral change is observed as the intensity of the excitation laser varies. The similarity between the spectral change at 400 K and the spectral change at high laser intensity levels suggests that the photoinduced spectral change observed in the present study is due to the thermal effects of laser irradiation.

Recent developments in the method for obtaining large C_{60} crystals with high quality[1-3] have led to experimental studies that clarify the physical and chemical properties of solid C_{60}. Earlier powder x-ray diffraction and differential scanning calorimetry studies indicated that C_{60} crystals undergo a phase transition at 249 K.[4] The crystal forms a face-centered-cubic (fcc) structure above the transition temperature (249 K) and a simple-cubic (sc) structure below the transition temperature. This transition is classified as an order-disorder phase transition with the development of orientational order in the sc phase. Powder neutron diffraction studies confirm that each C_{60} molecule rotates isotropically and randomly in the fcc phase and rotates uniaxially about the $\langle 111 \rangle$ direction in the sc phase.[5] This reorientational motion is frozen with some disorder below 90 K, where the glass transition occurs.[6,7] The results of the neutron diffraction measurements[5] are compatible with those from NMR (Ref. 8) which show that the rotational correlation time for the molecules at room temperature is only three times as long as that for the free molecules and becomes much longer below the transition temperature. More recently, a synchrotron x-ray study using single crystals has shown that the C_{60} molecules orient anisotropically and do not rotate freely at room temperature.[9]

Much work on Raman scattering of C_{60} crystals has been done so far.[10-20] The nature of the intermolecular and intramolecular forces and influence of the phase transition on the spectra have been discussed. However, there still remain unresolved problems in Raman scattering of C_{60} crystals. One is the effect of oxygen on the Raman spectra of C_{60} solids. When C_{60} solids are exposed to oxygen, the A_g pentagonal pinch mode shifts rapidly from 1458 to 1469 cm^{-1} (Ref. 10) which is almost equal to the frequency of the A_g mode in the sc phase.[11-13] This fact prevents analyses of the spectral change at the transition temperature. The origin of the frequency shift by the incorporation of oxygen is still controversial.[13-17]

Another unresolved issue is the change in Raman spectra at the phase transition. van Loosdrecht and coworkers[11,12] have reported that in the sc phase a shift, splitting, and narrowing of the intramolecular modes occurs. Several new modes including intermolecular vibrational modes have also been observed. However, such behavior would not be expected if the intermolecular forces are very weak van der Waals forces.

Recent Raman studies[12,13,16,17] have shown that the A_g pentagonal pinch mode softens when the crystal is irradiated with an intense laser beam. Zhou *et al.*[17] reported that the frequency of the A_g mode changes from 1469 to 1460 cm^{-1} after intense laser irradiation. A similar result has been reported by Matus and Kuzmany.[16] Zhou *et al.*[17] explained that the 1469-cm^{-1} band originates from a pristine C_{60} molecule and the 1460-cm^{-1} band originates from a phototransformed C_{60} molecule. Rao *et al.*[18] suggested that the polymerization of the C_{60} molecules occurring under strong UV and visible radiation causes this spectral change. van Loosdrecht *et al.*[12] observed that the frequency shifts reversibly from 1466 to 1456 cm^{-1} as the laser intensity is increased and that this spectral change is irreversible for laser intensities above 10 $\mathrm{W/cm}^2$. They explained the result as follows.[12,13] The lower frequency band (at about 1456–1460 cm^{-1}) is associated with the photoexcited $C_{60}{}^*$ whose population increases with the laser intensity, whereas the higher-frequency band (at about 1466–1470 cm^{-1}) is associated with the ground-state C_{60} molecule. Therefore, the lower-frequency band grows reversibly as the excitation laser intensity increases. The excited state of C_{60} is an antibonding state and intramolecular forces relevant to the excited state will be weak. Hence appearance of the lower-frequency band in the photoexcited C_{60}^* does not conflict with this expectation.

It was found that the presence of oxygen hardens the C_{60} films against phototransformation.[17] This hardening is explained if one considers that photopolymerization is induced through the excited triplet state of C_{60} as suggested by Rao *et al.*[18] and also that oxygen molecules effectively quench the excited triplet state.[21]

In this work, we have measured Raman spectra of oxygen-free C_{60} single crystals at various temperatures in order to clarify the effect of crystal structure on the vibrational properties. We have found a remarkable spectral change at about 400 K. The spectral change suggests that a phase transition occurs at this temperature.

We have measured the Raman spectra of the A_g pentagonal pinch mode at various excitation laser intensities in order to understand the relation between the spectral change at high temperature and the photoinduced effect.[12,13,16–18] The spectral change has been observed at high laser intensity levels. The similarity between the spectral changes with temperature and with irradiation intensity suggests that this change is induced by a partial temperature rise of the C_{60} crystals owing to the strong laser irradiation.

C_{60} crystals were prepared by a sublimation method. Pure C_{60} powder (99.9%) was used as the starting material. This powder was degassed at 300 °C and sealed in an evacuated Pyrex tube. The tube was placed in a furnace having a temperature gradient. The source at one end of the tube was heated up to 600 °C and the other thin end (capillary) was kept at about 450 °C for 5–6 days. C_{60} crystals with shiny faces grew at the thin end. The capillary part containing the crystals was sealed off and mounted on the sample holder of a cryostat or a heater. This procedure made it possible to maintain the C_{60} crystals in vacuum after the sublimation.

The Raman spectra were taken by a SPEX double monochromator equipped with a charge-coupled device detector using the 488-nm line of an Ar-ion laser as an excitation light source. In order to avoid sample degradation in normal measurement except for the study of photoinduced transition, a laser power below 0.1 mW was used with a focusing spot size of 50 μm.

Figures 1(a) and 1(b) show the room-temperature Raman spectra of the C_{60} crystal maintained in vacuum and that exposed to air after sublimation. The latter sample was also measured in vacuum. Spectrum (a) shows a strong peak at 1460 cm^{-1} which is assigned as the A_g pentagonal pinch mode because this band is highly polarized. The spectrum of the crystals exposed to air shows striking growth of the 1467-cm^{-1} band, whose intensity exceeds that of the 1460-cm^{-1} band. It is to be noted that the 1467-cm^{-1} band is sharp compared with the 1460-cm^{-1} band of the oxygen-free crystals. These results agree well with the previous results of Duclos *et al.*,[10] who explained that the 1458-cm^{-1} band originates from pristine C_{60} solids and that the 1467-cm^{-1} band originates from C_{60} solids perturbed by oxygen. Recent experiments have revealed that molecular oxygen is incorporated into the crystal lattice of C_{60} when the crystal is exposed to oxygen.[22,23]

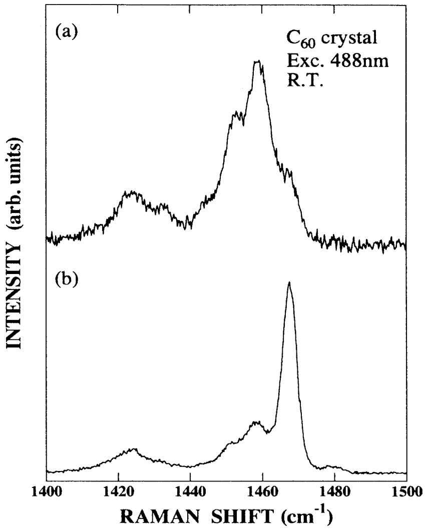

FIG. 1. Room-temperature Raman spectra of the A_g pentagonal pinch mode in C_{60} crystals (a) maintained in vacuum and (b) exposed to air after growth. The peaks at about 1420–1430 cm^{-1} are the H_g mode.

Raman spectra of the oxygen-free C_{60} crystals have been observed at various temperatures. Representative Raman spectra obtained at three different temperatures are shown in Fig. 2 for the frequency region between 200 and 1750 cm^{-1}. The middle and bottom spectra of this figure correspond to those of the fcc and sc phases, respectively. All Raman modes existing in this frequency

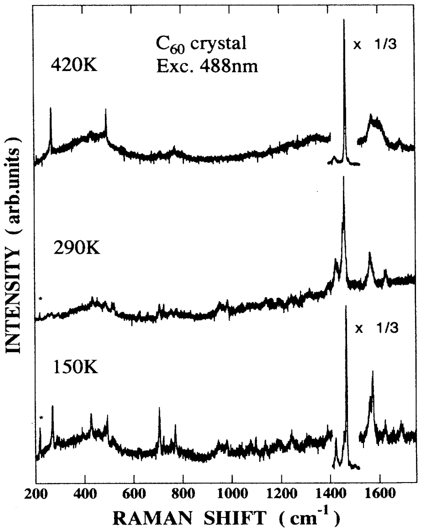

FIG. 2. Raman spectra of C_{60} crystals at 420 (top), 290 (middle), and 150 K (bottom). The broad background around 400 cm^{-1} is from the Pyrex tube. Laser plasma lines are denoted by an asterisk.

region are the intramolecular vibrational modes. Only ten Raman-active modes ($2A_g + 8H_g$) are expected for an isolated C_{60} molecule owing to its icosahedral symmetry.[24] In the case of the crystal, ten Raman-active modes are also expected to be dominant because of the weak intermolecular interaction between adjacent molecules. These ten modes assigned by Bethune *et al.*[19] are observed at the three temperatures as shown in Fig. 2. In the sc phase (bottom spectrum in Fig. 2), a number of bands are observed in addition to ten Raman bands. More than 30 Raman bands, including the splitting of some bands, are observed. In the fcc phase (middle spectrum), the number of Raman bands decreases. However, most of the bands observed in the sc phase still remain above the transition temperature, though their intensities are weak, their linewidths are large, and frequency shifts occur. This result implies that the intramolecular vibrations of the C_{60} crystals are much affected by the sc-fcc transition. According to the results of factor-group analysis,[25] 145 Raman-active modes are expected in the sc phase and 37 modes are expected in the fcc phase. The result that some bands observable in the sc phase disappear in the fcc phase reflects the change in the number of inequivalent molecules per unit cell. At 420 K (top spectrum), the number of Raman bands decreases remarkably and only 14 bands are observed. Two A_g modes at 1466 and 494 cm^{-1} and one H_g mode at 270 cm^{-1} are sharp and intense. The other modes are broad. This result indicates that the structure of the C_{60} crystal differs at 290 and 420 K.

In Fig. 3, the spectral features for the A_g pentagonal pinch mode are shown for various temperatures. This mode shows a remarkable change with temperature. The sharp and intense 1468-cm^{-1} band appears predominantly in the sc phase (150 K). Its linewidth is about 4 cm^{-1}. At room temperature, the broad 1460-cm^{-1} band with a shoulder band at 1453 cm^{-1} is dominant. The linewidth of the 1460-cm^{-1} band is about 8 cm^{-1}. Upon heating the crystal, the intensity of the 1453-cm^{-1} band is decreased gradually. At about 400 K, a new band with a linewidth of about 5 cm^{-1} appears at 1467 cm^{-1}, which grows and shifts slightly towards low frequency with rising temperature. The polarization measurement shows that the band at 1467 cm^{-1} is highly polarized and has an A_g character. At 470 K, the peak frequency is 1465 cm^{-1} and its intensity is about one order of magnitude larger than that of the 1460-cm^{-1} band at 290 K. Such spectral changes with temperature are reversible.

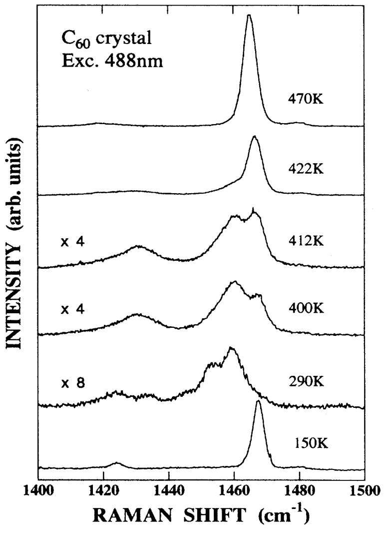

FIG. 3. Raman spectra of the A_g pentagonal pinch mode in C_{60} crystals at various temperatures. The peaks at about 1420–1430 cm^{-1} are the H_g mode.

David *et al.*[5,26] and Pintschovius *et al.*[27] reported that the intermolecular interaction of solid C_{60} cannot be explained as a van der Waals interaction and depends on the relative orientation of adjacent molecules through the electrostatic interaction between the electric charges on adjacent molecules because of the nonuniform charge distribution on a C_{60} molecule. The Raman frequency of the A_g pentagonal pinch mode may depend on the relative molecular orientation. Since in the low-temperature sc phase, C_{60} molecules are in the orientationally ordered state, the force fields acting on individual molecules are identical. Accordingly, a sharp band appears. In the room-temperature phase (fcc), the orientational disorder increases as compared with the sc phase. However, the orientational order partly remains and each C_{60} molecule forming a crystal does not rotate freely and isotropically.[9] Hence molecules suffer anisotropic force fields. In addition, the structural disorder in this phase may cause variation of the force fields acting on molecules and the frequency of the intramolecular vibration differs from molecule to molecule. Consequently, the broad Raman band is observed. Above 400 K, each molecule rotates freely and isotropically, so the molecules feel the isotropic force field and the variance of the force field among molecules is very little. This results in the sharp Raman band. Arai *et al.*[23] indicated that the electrical resistivity of oxygen-free single crystals changed with a broad hump at about 450 K, which might be related to the structural change occurring at about 400 K.

Raman spectra of the A_g pentagonal pinch mode measured at various excitation laser intensities are shown in Fig. 4. The measurement was performed at room temperature using the 488-nm line with laser intensities between 8 μW and 1.6 mW. As the intensity of the laser is increased up to 1.1 mW (55 W/cm^2), the relative Raman intensity of the shoulder band at 1453 cm^{-1} decreases and the 1460-cm^{-1} band becomes dominant. Above 1.2 mW, however, a new sharp and intense band appears. This band, which has a peak at 1465 cm^{-1}, shifts slightly towards low frequency with increasing laser intensity. At 1.5 mW, the 1460-cm^{-1} band disappears. Such spectral changes with the excitation laser intensity are reversible for all intensity levels used here and resemble the spectral changes observed in the high-temperature region above 400 K (Fig. 3). The linewidth of the 1465-cm^{-1} band is about 5 cm^{-1}, being comparable to that of the 1467-cm^{-1} band observed above 400 K at low laser intensity levels.

The similarity between the A_g mode spectra obtained at high laser intensities and above 400 K suggests that the spectral change at high laser intensity levels is not due to a direct photoassisted effect induced by the photoexcited C_{60}^* but due to a partial temperature rise of the C_{60} crystal heated by strong laser irradiation. The 1467-cm^{-1} band cannot be ascribed to a vibrational mode of the photoexcited C_{60} molecules, because the vibrational frequency of the excited C_{60} is expected to be lower than that of the ground state C_{60} (Ref. 13) (1460 cm^{-1} at 300 K).

An alternative explanation for the spectral change at high laser intensity levels is photopolymerization.[18] From this viewpoint, the spectral change above 400 K might be attributed to the dissociation of polymerized C_{60} molecules which already exist at room temperature under low laser power. The polymerization of the C_{60} molecules will hinder the rotational motion of the molecules and the phase transition at about 250 K no longer occurs. However, on decreasing the laser intensity from any intensity levels used here, the Raman spectrum of the A_g pentagonal pinch mode measured at low laser intensity levels showed the same temperature dependence as that shown in Fig. 3, and the spectral change associated with the sc-fcc transition is always observed at about 250 K. Accordingly, the effect of photopolymerization of the C_{60} molecules and their dissociation is considered to be small on the Raman spectra of the crystals examined in this study, although the possibility of photopolymerization cannot be completely ruled out.

In summary, we have presented Raman spectroscopic evidence of a structural change occurring in oxygen-free C_{60} crystals at about 400 K. Above 400 K, the Raman band of the A_g pentagonal pinch mode, which is broad at room temperature, disappears and a sharp and intense band appears at a higher frequency. This reversible spectral change with temperature indicates the presence of a phase transition. Variation in the linewidth of the A_g pentagonal pinch mode is explained by assuming that C_{60} molecules performing a hindered rotation in a room-temperature region begin to rotate more freely and isotropically above 400 K.

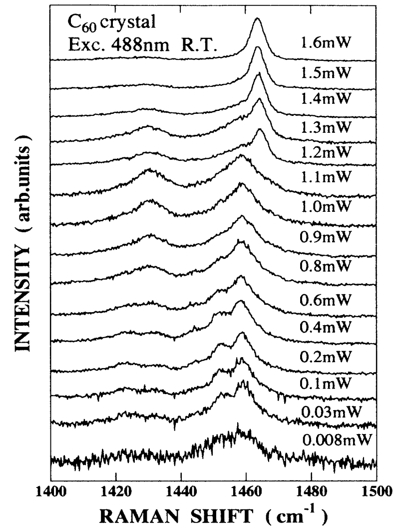

FIG. 4. Room-temperature Raman spectra of the A_g pentagonal pinch mode in C_{60} crystals at various excitation laser intensities. Each spectrum is normalized to respective maximum intensity.

The Raman band of the A_g pentagonal pinch mode at room temperature changes at high laser intensity levels. The spectral change is reversible. A partial temperature rise is considered to play an important role in the irradiation-induced phase transition because of the similarity between the spectral change at 400 K and that at high laser intensity levels.

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