

Orientalional phase transitions in a C₇₀ crystal at high pressure

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The Raman spectra of C₇₀ crystals have been studied at pressures up to 17 GPa. The frequency Ω of most of the optical vibrations increases linearly with the pressure P . The pressure-induced shift $\partial\Omega/\partial P$ itself has jumps at $P_1 \approx 2 \pm 0.2$ and $P_2 \approx 5.5 \pm 0.5$ GPa. The jumps observed in $\partial\Omega/\partial P$ are correlated with a sharp change in the half-width of the Raman line for several optical modes. These spectral features of the Raman scattering are linked with phase transitions caused by an orientational ordering of the C₇₀ molecules in the crystal lattice as the pressure is raised.

Theoretical work on the molecular dynamics of the new carbon molecules known as fullerenes was developing rapidly even before a technique was devised for producing these materials in macroscopic amounts.¹ The vibrational spectra of the C₆₀ and C₇₀ molecules were calculated, bond lengths were determined, and the frequencies, shape, and symmetry of the IR- and Raman-active vibrations were found.^{2–4} The first detailed measurements of the Raman and IR spectra of thin films of C₆₀ and C₇₀ were carried out in Ref. 5. The subsequent development of these studies was primarily research on the phonon spectra of various phases of the fullerene C₆₀ intercalated with alkali metals,^{6,7} because it was discovered that these compounds exhibit a superconducting transition at a fairly high temperature.⁸ The recent progress in the preparation of single-crystal samples of a fullerite of C₇₀ has spurred research on the physical properties of these crystals. Phase transitions in C₇₀ crystals with various crystallographic structures grown from the gas phase have been studied by x-ray and electron diffraction.^{9,10} Raman spectra have been measured, and the frequencies of intra- and intermolecular phonons have been determined. Characteristic changes caused in the Raman spectra in the region of intermolecular libration modes by a phase transition of the orientational order of C₇₀ molecules at $T=276$ K have been studied for the first time.¹¹

In this letter we are reporting the first results of measurements of the Raman spectra of C₇₀ crystals at pressures up to 17 GPa. The purpose of this study was to determine the pressure-induced shift of intramolecular phonon modes and the behavior of these modes near phase transitions at high pressure. There is particular interest in phase transitions of the orientational order at high pressures, because of the particular shape of the C₇₀ molecule, which resembles a rugby ball. One would expect that the phase transition of the orientational order at high pressure should occur in two steps, corresponding to the onset of an orientational order with respect to rotations

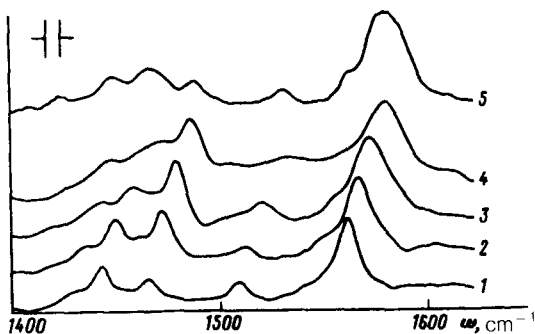


FIG. 1. Raman spectra of a C_{70} crystal over the frequency interval $1400\text{--}1600\text{ cm}^{-1}$ at several pressures: 1—0.2; 2—1.2; 3—2.2; 4—3.4 GPa. The sample was excited by an Ar^+ laser with $\lambda=488\text{ nm}$. The upper spectrum (5) was recorded during excitation by a He-Ne laser with $\lambda=632.8\text{ nm}$ at a pressure $P=3.4\text{ GPa}$. For this spectrum the spectral resolution is twice that indicated in the figure.

around short and long axes of the molecule. The phase transition would differ from that in C_{60} .

The measurements were carried out on C_{70} single crystals grown from a supersaturated benzene solution of C_{70} . The typical dimensions of the crystals were $50 \times 50 \times 15\ \mu\text{m}$. The measurements were carried out in a diamond-anvil pressure chamber; a mixture of alcohols was used as the pressure-transmitting medium. The pressure was determined from the luminescence in the R_1 line of a ruby crystal, with $\approx 0.1\text{ GPa}$. The samples were excited by the beam from an argon laser ($\lambda=488\text{ nm}$) or a helium-neon laser ($\lambda=632.8\text{ nm}$). The Raman spectra were measured on a DILOR XY triple Raman spectrometer with a multichannel optical recording system.

In the Raman spectra of C_{70} crystals at standard pressure, up to 16 Raman modes were observed, with frequencies of $1562, 1508, 1465, 1442, 1429, 1364, 1255, 1225, 1180, 1058, 767, 732, 709, 567, 407,$ and 251 cm^{-1} . These frequencies are essentially the same as those reported in Ref. 11 for hexagonal C_{70} crystals at $T=23\text{ K}$. We should point out these frequencies are slightly lower than those found in Ref. 5 for thin films of C_{70} . All the Raman modes observed are intramolecular; the intermolecular rotational and vibrational modes lie in the frequency interval $10\text{--}60\text{ cm}^{-1}$ (Ref. 11) and were not investigated in the present study. Figure 1 shows fragments of Raman spectra of C_{70} crystals in the region of high-frequency intramolecular vibrations at several pressures. These experiments were carried out at room temperature, but our estimates, carried out as in Ref. 12 and assuming that the thermal conductivity of C_{70} crystals is approximately the same as that measured for C_{60} crystals,¹³ indicate that the heating due to the laser excitation under these experimental conditions was $\approx 100\text{ K}$, i.e., that the temperature in the excitation region was $T \approx 400\text{ K}$. It is easy to see that the frequencies of all the phonons increase with increasing pressure. There is also a redistribution of the relative intensities of the phonons at $1562, 1465,$ and 1442 cm^{-1} in the Raman spectrum as the pressure is raised. A change in the excitation wavelength from $\lambda=488\text{ nm}$ to $\lambda=632.8\text{ nm}$ also causes a redistribution of the in-

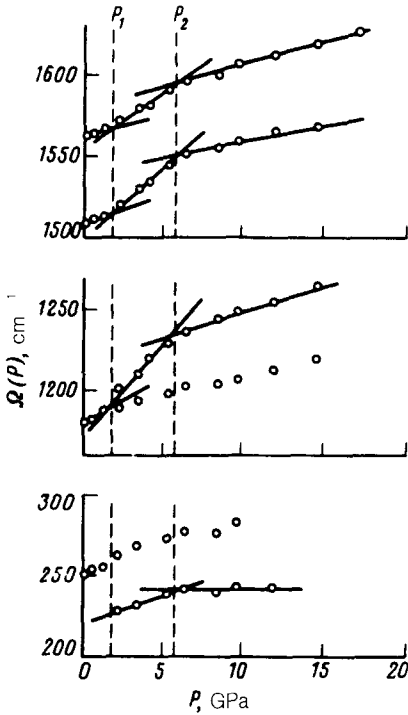


FIG. 2. Frequency of optical phonons, $\Omega(P)$, versus the pressure for several intramolecular vibrations of the C_{70} crystal. The dashed lines mark the pressures $P_1=1.8$ GPa and $P_2=5.8$ GPa. The solid lines are least-squares fits in three pressure regions: $P < P_1$, $P_1 < P < P_2$, and $P > P_2$.

tensities of the optical vibrations throughout the Raman spectrum (in the frequency interval $1400\text{--}1600\text{ cm}^{-1}$, these changes can be seen easily by comparing spectra 4 and 5 in Fig. 1). The intensity redistribution observed for several of the optical modes may be due to changes in the excitation resonance conditions because of the significant pressure-induced shift of the optical absorption spectrum.¹⁴ Incidentally, we observe a significant shift of the intrinsic luminescence band of the C_{70} crystal in the long-wave direction as the pressure was raised. A particular consequence of this shift is that, beginning at a pressure $P \geq 3$ GPa, it becomes possible to use a helium-neon laser with $\lambda=632.8$ nm as the excitation source. At lower pressures it was difficult to record Raman spectra because of an intense luminescence in the frequency interval of interest.

Figure 2 shows the pressure dependence of the phonon frequency, $\Omega(P)$, for several intramolecular modes. We can distinguish three pressure regions within which the $\Omega(P)$ dependence is linear, with abrupt changes in the slope at the boundaries between regions, $P_1 \approx 2 \pm 0.2$ GPa and $P_2 \approx 5.5 \pm 0.5$ GPa. Several modes (e.g., the mode at 1180 cm^{-1}) also undergo a splitting at $P > P_1$, or a new mode ($\Omega=230\text{ cm}^{-1}$) appears in the spectrum. The pressure-induced shift $\partial\Omega/\partial P$ is different for the different phonon modes and the different pressure regions, ranging from $8 \pm 0.5\text{ cm}^{-1}/\text{GPa}$ to $-0.3 \pm 0.1\text{ cm}^{-1}/\text{GPa}$. Figure 3 shows the pressure dependence of the width of the most intense line, for the 1562-cm^{-1} phonon. Here we can clearly see abrupt increases in the linewidth at the boundaries between the three pressure regions, while the behavior in intermediate regions is described by essentially the same linear

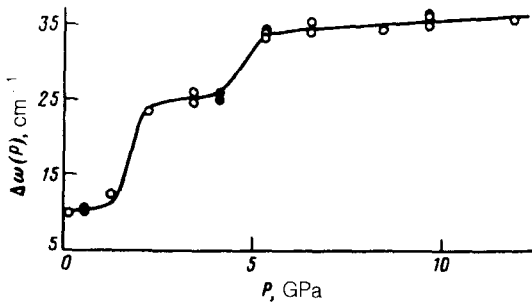


FIG. 3. Half-width of the Raman line, $\Delta\omega$ (P), for the phonon with frequency $\Omega = 1568 \text{ cm}^{-1}$ versus the pressure. Filled circles—Measurements during the first loading cycle; open circles—during the second.

function. These results are unambiguous evidence that two phase transitions occur in the C_{70} crystal, at pressures $P_1 \approx 2 \pm 0.2 \text{ GPa}$ and $P_2 5.5 \pm 0.5 \text{ GPa}$. We should point out that the high-pressure measurements were carried out in two loading cycles, during a forward change in pressure. In a first loading cycle, we carried out measurements at pressures of 0.55 and 4.1 GPa (the filled circles in Fig. 3). The pressure was then reduced to 0.1 GPa, and a second loading cycle was carried out. It terminated at 17 GPa. The fact that the values found for the position and half-width of the line in the two cycles are approximately the same means that the phase transition at $P_1 \approx 2 \pm 0.2 \text{ GPa}$, at least, is reversible in terms of pressure.

In contrast with the case of C_{60} crystals, the orientational-order phase transitions for the C_{70} crystals occur in two steps. These steps correspond to a freezing of the rotations around the short and long axes of the molecule, respectively, at $T_1 = 335 \text{ K}$ and $T_2 = 276 \text{ K}$ at standard pressure.^{9,15} It would be natural to suggest that the phase transitions observed at $T \approx 400 \text{ K}$ in our experiments correspond to phase transitions of the orientational order. A change in the slope of the pressure-induced shift of the phonon frequencies may be due to abrupt changes in the matrix elements of the intermolecular interaction at the point of the phase transition, since the orientational-order transitions in C_{70} are accompanied by abrupt changes in structural properties.⁹ The abrupt increase in the width of the 1562-cm^{-1} line may be due to the doublet nature of this line.¹¹ If the width of the components of a doublet is sufficiently large, an abrupt increase in the distance between them upon a phase transition would be perceived as a broadening of the line, and this broadening should be reversible in terms of pressure. A similar behavior is observed for other doublet lines, in particular, for the phonons at 1180 and 1225 cm^{-1} , but this behavior is not seen in the case of single lines.

In summary, these results indicate that two phase transitions occur, at pressures $P_1 \approx 2 \pm 0.2 \text{ GPa}$ and $P_2 \approx 5.5 \pm 0.5 \text{ GPa}$, and that these transitions may be due to the particular features of the orientational order of the C_{70} molecules in a crystal.

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