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RAMAN STUDY OF PHASE TRANSITIONS IN C₇₀ CRYSTAL AT HIGH PRESSURE

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Abstract The Raman spectra of C₇₀ single crystals have been measured at pressures up to 17 GPa. The frequency Ω of most of the optical intramolecular phonons increases linearly with pressure P . The slope of the pressure shift $d\Omega/dP$ itself has jumps at 2 ± 0.2 and 5.5 ± 0.5 GPa. These jumps are correlated with a sharp change in the half-width of the Raman line for several optical modes. The peculiarities 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.

INTRODUCTION

The first detailed measurements of the Raman and IR spectra of thin films of C₆₀ and C₇₀ were carried out in 1991¹. The progress in the preparation of single-crystal samples of C₆₀ and C₇₀ has spurred research on the crystal properties². Raman spectra of C₇₀ crystals have been measured and characteristic changes caused in the region of external libration and internal vibration modes by a phase transition of orientational order of C₇₀ molecules at $T=276$ K have been studied^{3,4}. Phase transitions in C₇₀ crystals have been studied also by x-ray and electron diffraction^{2,5}. In this paper we are reporting the 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 orientational order at high pressure

should occur in two steps, corresponding to the onset of the orientational order with respect to rotations around short and long axes of the molecule. The phase transition would differ from that in C_{60} .

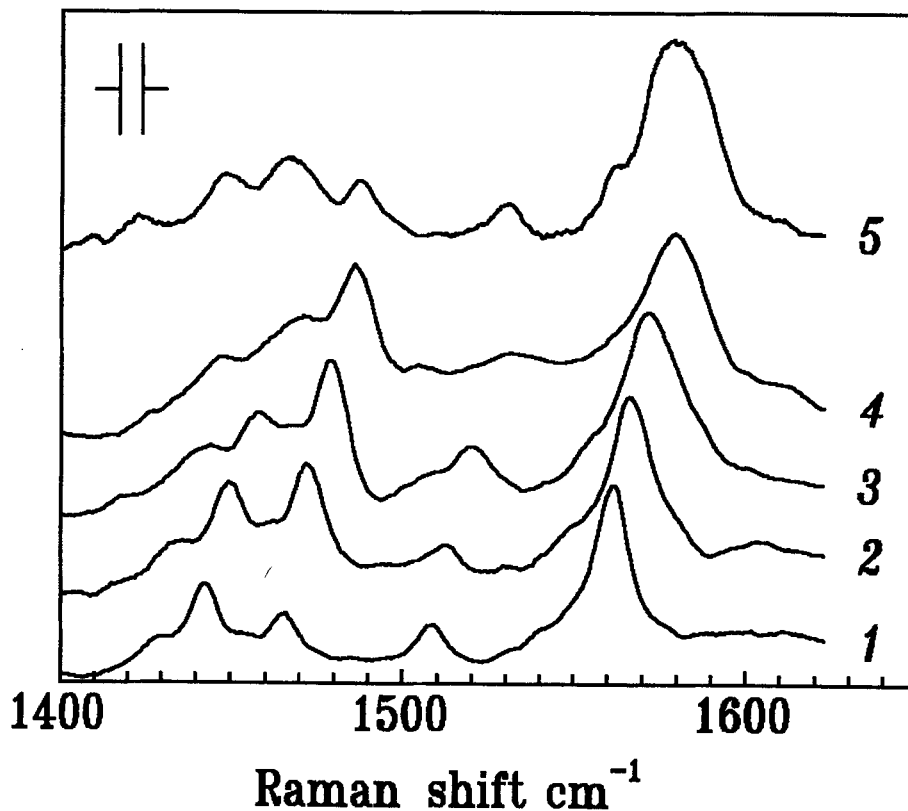


FIGURE 1 Raman spectra of a C_{70} crystal at several pressures: 1 - 0.12; 2 - 1.2; 3 - 2.2; 4 - 3.4 GPa. The sample was excited by Ar⁺ laser with $\lambda=488$ nm. The upper spectrum (5) was recorded during excitation by a He-Ne laser with $\lambda=632.8$ nm at a pressure $P=3.4$ GPa.

EXPERIMENT

The measurements were carried out on C_{70} crystals grown from an supersaturated benzene solution of C_{70} . The typical dimensions of the crystals were $50 \times 50 \times 15$ μm . The measurements were carried out in a diamond-anvil pressure cell; 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 the ac-

curacy ≈ 0.1 GPa. The samples were excited by the beam from an argon laser ($\lambda=488$ nm) or helium-neon laser ($\lambda=632.8$ nm). The Raman spectra were measured on a DILOR XY triple Raman spectrometer with a multichannel recording system.

In the Raman spectra of C₇₀ crystals at normal pressure, up to 16 Raman modes were observed, with frequencies of 1562, 1508, 1465, 1442, 1364, 1255, 1225, 1180, 1058, 767, 732, 709, 567, 507, 407, and 251 cm⁻¹. These frequencies are essentially the same as those presented in Ref.3 for hexagonal C₇₀ crystals at T=23 K. We should point out these frequencies are slightly lower than those found in Ref.1 for thin films of C₇₀. All the Raman modes observed are intramolecular; the intermolecular rotational and vibrational modes lie in the frequency interval 10-60 cm⁻¹ and were not investigated in this work³. Figure 1 shows fragments of Raman spectra of C₇₀ crystals in the region of

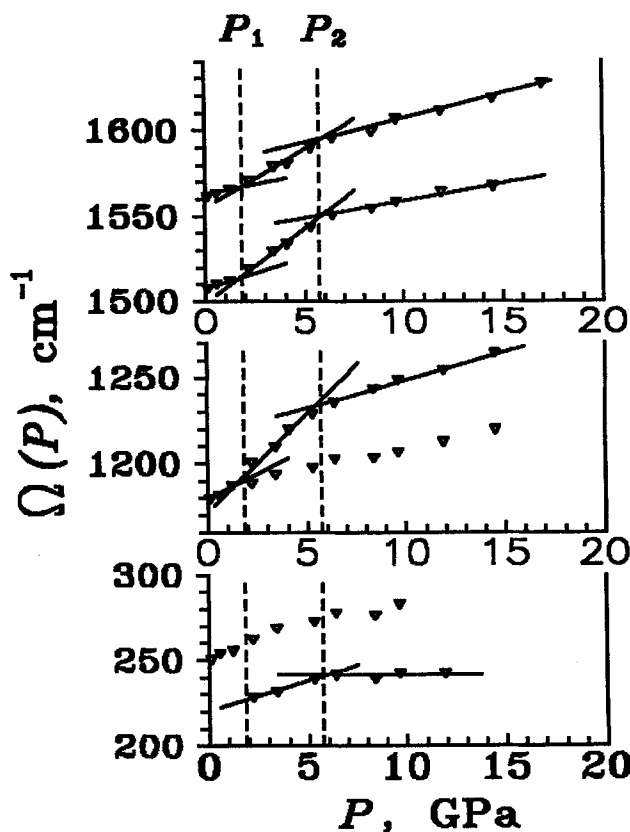


FIGURE 2 Frequency of optical phonons, $\Omega(P)$, versus the pressure for several intramolecular phonons of the C₇₀ crystal. The dashed lines mark the pressures $P_1 = 2$ GPa and $P_2 = 5.5$ GPa. The solid lines are fits in pressure regions: $P < P_1$, $P_1 < P < P_2$, and $P > P_2$.

high-frequency intramolecular vibrations at several pressures. These experiments were carried out at room temperature, but our estimates, carried out as in Ref. 6 and assuming that the thermal conductivity for C₇₀ crystals is approximately the same as that measured for C₆₀ crystals, indicate that the heating due to the laser excitation under these experimental conditions was ≈ 100 K, i.e., that the temperature in the excitation region was $T \approx 400$ 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 $\lambda = 488$ nm to $\lambda = 632.8$ nm also causes a redistribution of the intensities of the optical phonons throughout the Raman spectrum (in the interval of 1400–1600 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. Incidentally, we observe a significant shift of the luminescence band of the C₇₀ 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, $P_1 \approx 2.0 \pm 0.2$ 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 $P \geq P_1$, or a new mode ($\Omega = 230$ cm^{-1}) appears in the spectrum. The slope of the pressure-induced shift $d\Omega/dP$ is different for the different phonon modes and the different pressure regions, ranging from 8.0 ± 0.5 $\text{cm}^{-1}/\text{GPa}$ to -0.3 ± 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 function. These results are unambiguous evidence that two phase transitions occur in the C₇₀ crystal, at pressures $P_1 \approx 2.0 \pm 0.2$ GPa and $P_2 \approx 5.5 \pm 0.5$ 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 the 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 $P_1 \approx 2.0 \pm 0.2$ GPa, at least, is reversible in terms of pressure.

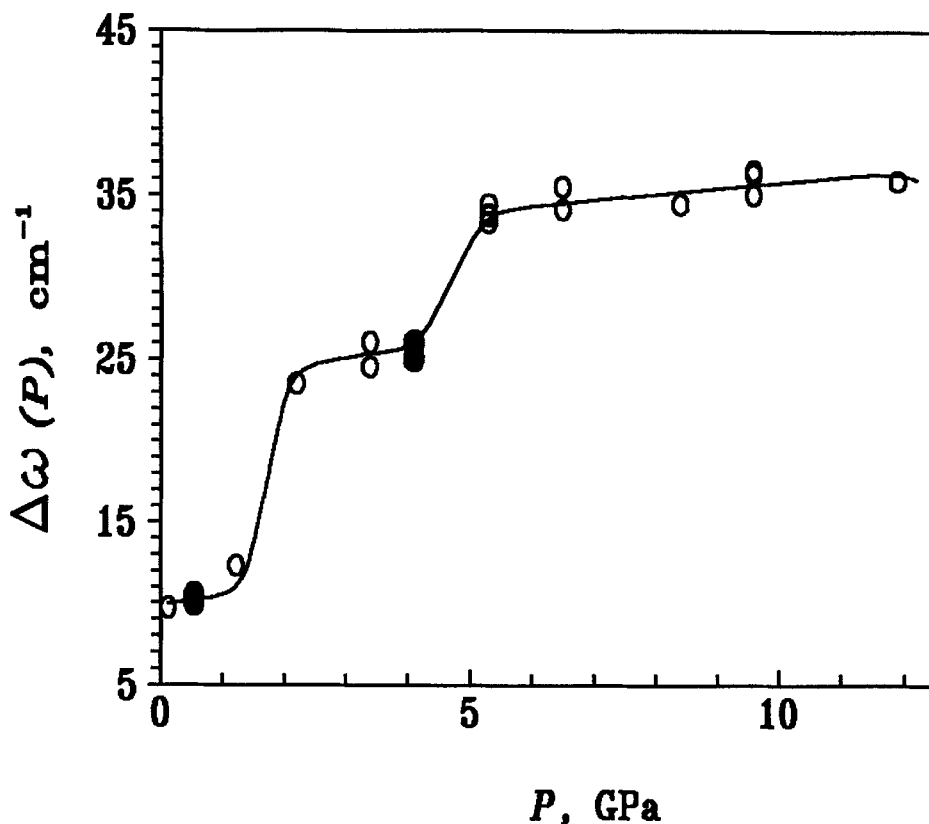


FIGURE 3 Half-width of the Raman line, $\Delta\omega(p)$, for the phonon 1568 cm^{-1} versus the pressure. Filled circles - measurements during the first loading cycle; open circles - during the second.

DISCUSSION

In contrast with the case of C₆₀ crystals, the orientational-order phase transitions in C₇₀ crystals occur in two steps. These steps correspond to a freezing of the rotations along short and long axes of the molecule, respectively, at $T_1 = 335\text{ K}$ and $T_2 = 276\text{ K}$ at ambient pressure^{2,9}. 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 crystal structure parameters². The abrupt increase in the width of the 1562 cm^{-1} line may be due to the doublet nature of this line³. 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 $P_1 \approx 2.0 \pm 0.2\text{ GPa}$ 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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