RAMAN STUDY OF PHASE TRANSITIONS IN C_{70} CRYSTAL AT HIGH PRESSURE

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Abstract The Raman spectra of C_{70} single crystals have been measured at pressures up to 17 GPa. The frequency $\Omega$ 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 $2\pm0.2$ and $5.5\pm0.5$ 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 C_{70} 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 C_{60} and C_{70} were carried out in 1991. The progress in the preparation of single-crystal samples of C_{60} and C_{70} has spurred research on the crystal properties. Raman spectra of C_{70} 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 C_{70} molecules at $T=276$ K have been studied. Phase transitions in C_{70} crystals have been studied also by x-ray and electron diffraction. In this paper we are reporting the results of measurements of the Raman spectra of C_{70} 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 C_{70} 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 C₆₀.

FIGURE 1 Raman spectra of a C₇₀ 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 λ=488 nm. The upper spectrum (5) was recorded during excitation by a He-Ne laser with λ=632.8 nm at a pressure P=3.4 GPa.

EXPERIMENT

The measurements were carried out on C₇₀ crystals grown from an supersaturated benzene solution of C₇₀. The typical dimensions of the crystals were 50×50×15 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 R₁ line of a ruby crystal with the ac-
Accuracy $\approx 0.1$ 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 C$_{70}$ 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 C$_{70}$ crystals at $T=23$ K. We should point out these frequencies are slightly lower than those found in Ref.1 for thin films of C$_{70}$. All the Raman modes observed are intramolecular; the intermolecular rotational and vibrational modes lie in the frequency interval 10-60 cm$^{-1}$ and were not investigated in this work. Figure 1 shows fragments of Raman spectra of C$_{70}$ crystals in the region of

![Graph](image)

FIGURE 2 Frequency of optical phonons, $\Omega(P)$, versus the pressure for several intramolecular phonons of the C$_{70}$ 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 $P>P_2$. 

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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 C_{70} crystals is approximately the same as that measured for C_{60} 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=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 λ=488 nm to λ=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 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=3 GPa, it becomes possible to use a helium-neon laser with λ=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, Ω(P), for several intramolecular modes. We can distinguish three pressure regions within which the Ω(P) dependence is linear, with abrupt changes in the slope at the boundaries between regions, P_1≈2.0±0.2 GPa and P_2≈5.5±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 (Ω=230 cm^{-1}) appears in the spectrum. The slope of the pressure-induced shift dΩ/dP is different for the different phonon modes and the different pressure regions, ranging from 8.0±0.5 cm^{-1}/GPa to -0.3±0.1 cm^{-1}/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 C_{70} crystal, at pressures P_1≈2.0±0.2 GPa and P_2≈5.5±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 \( P_1 = 2.0 \pm 0.2 \) GPa, at least, is reversible in terms of pressure.

![Graph showing the relationship between pressure (P) and half-width of the Raman line (\( \Delta \omega(p) \)), for the phonon 1568 cm\(^{-1}\) versus the pressure. Filled circles represent measurements during the first loading cycle; open circles during the second.](image)

**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 \( C_{60} \) crystals, the orientational-order phase transitions in \( C_{70} \) crystals occur in two steps. These steps correspond to a freezing of the rotations along short and long axes of the molecule, respectively, at \( T_1 = 335 \) K and \( T_2 = 276 \) K at ambient pressure\(^2,9\). It would be natural to suggest that the phase transitions observed at \( T = 400 \) 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 parameters. The abrupt increase in the width of the 1562 cm$^{-1}$ line may be due to the doublet nature of this line. 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 $P_1 \approx 2.0 \pm 0.2$ GPa and $P_2 \approx 5.5 \pm 0.5$ 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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