

Pressure dependence of the external mode spectrum of solid C_{60}

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Using inelastic neutron scattering we have investigated the external mode spectrum of solid C_{60} in the orientationally ordered phase. Hydrostatic pressures 1 bar $< P < 9$ kbar and temperatures 180 K $< T < 335$ K were covered. The entire density of states shows a pronounced pressure dependence. In accordance with theory¹ translational phonons have larger pressure coefficients ($d\hbar\omega/dP \approx 0.2$ meV/kbar) than librions ($d\hbar\omega/dP \approx 0.06$ meV/kbar). Anharmonic frequency shifts become smaller upon increasing the pressure. It is conjectured that they are related to the orientational disorder in the system arising from competing H and P orientations. A direct link between libron softening and the order-disorder phase transition cannot be established. [S0163-1829(99)10205-4]

C_{60} possesses the highest molecular point group (I_h) and, in this sense, may be considered the most spherical of all molecules. Under normal conditions the molecular cages in solid C_{60} are uncharged, highly polarizable and not covalently linked to each other. The intermolecular bonding, therefore, should share many similarities with the Van der Waals bonding encountered in the noble gases. The Van der Waals picture allows, e.g., one to explain certain properties of solid C_{60} like the low cohesive energy or the existence of a high-temperature rotator phase with rapidly reorienting cages.^{2,3} It fails, however, to account for the details of the static and dynamic properties. Various efforts have been undertaken to improve the description of the intermolecular potentials, e.g., by including the nonspherical electron distribution around the carbon atoms.^{1,4-6} As the physical properties depend crucially upon the distance between the cages, experiments using pressure as an external control parameter are ideal benchmarks for these models. Changes in the intermolecular potentials are particularly well reflected in the external mode spectrum. This has been demonstrated successfully by Raman experiments.^{7,8} The librions at the zone center show a pronounced dependence both upon pressure and molecular orientation. Being subjected to stringent selection rules optical spectroscopy cannot give complete information on the external mode spectrum of C_{60} . Using small C_{60} single crystals the dispersion relations of C_{60} have been determined successfully⁹ by inelastic neutron scattering (INS). Repeating these measurements as a function of pressure is experimentally a formidable task as the scattering from the pressure cell leads to a further reduction of the already weak signal-to-noise ratio. Information on the excitation spectrum can fortunately already be obtained by experiments on C_{60} powder yielding the vibrational density of states $G(\omega)$. Even these experiments are experimentally demanding. On one hand, large sample quantities are needed to obtain sufficient data statistics. Large samples, on the other hand, imply big pressure cells creating strong background scattering. We will show in this article that despite these difficulties it is possible

to obtain reliable data on the pressure dependence of the entire external mode spectrum of C_{60} by adapting both the cell material and its dimensions to the scientific case.

For pressures of up to 10 kbar a cylindrical steel cell of 6 mm inner and 12 mm outer diameter turns out perfectly suited for the study of C_{60} : (1) Due to the mechanical strength of steel reasonable sample volumes can be obtained with a limited amount of cell material in the beam. (2) The phonon spectrum of steel is hard giving strong scattering only above 10 meV, while the external mode spectrum of C_{60} is confined to energies below 10 meV. (3) The neutron absorption by the cell is negligible. As can be seen in Fig. 1 the signal from the sample reasonably exceeds the back-

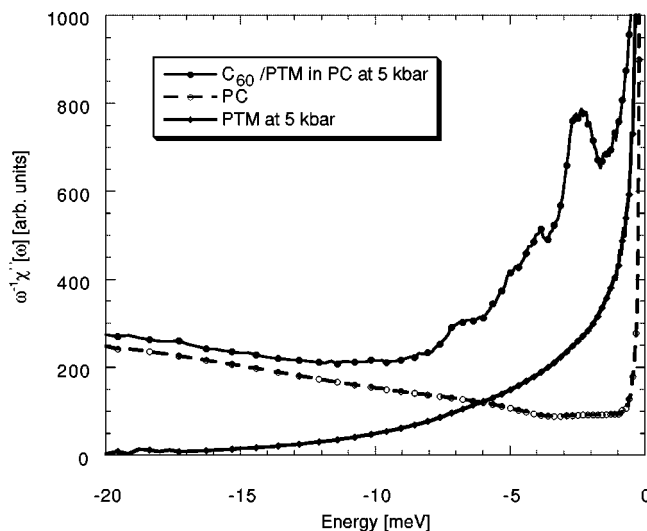


FIG. 1. Generalized susceptibility $\omega^{-1}\chi''(\omega)$ of the C_{60} /PTM mixture at 290 K and 5 kbar. $\hbar\omega < 0$ indicates up-scattering. For the energies shown $\omega^{-1}\chi''(\omega)$ is proportional to the scattering law $S(\omega)$. Integration has been carried out over all scattering angles. The combined scattering of the C_{60} /PTM mixture in the pressure cell is compared to the contributions from the pressure cell (PC) and PTM. As can be seen the sample scattering dominates for energies below 10 meV.

ground from the cell despite the fact that carbon is only a medium scatterer.

Pure C_{60} powder is found unsuitable to transmit pressure. The internal friction blocks the movement of the piston already at rather low pressures making a homogeneous pressure distribution impossible. We, therefore, mixed the C_{60} powder with an external pressure transmitting medium (PTM). Our choice was a commercial product with the brand name Fluorinert (obtained from 3M Cergy, France). The exact composition of Fluorinert is unknown. Fluorinert contains only medium scatterers like carbon and fluor but no hydrogen. This is important as the PTM adds to the background (see Fig. 1). In addition, C_{60} does not chemically dissolve in Fluorinert. The molecular units of Fluorinert are rather large. Penetration of the C_{60} matrix by PTM molecules can, therefore, be excluded even at elevated temperatures. We have checked this assertion by performing temperature scans of the C_{60} /PTM mixture at ambient pressure. The transition temperature from the ordered low-temperature phase towards the plastic crystal phase is observed at about $T_c = 255$ K, i.e., close to the literature values for pure C_{60} . As T_c reacts strongly to impurities¹⁰ this indicates that the physical properties of C_{60} are preserved in the mixture.

The INS experiments have been performed using the time-of-flight instrument IN6 at the Institute Laue-Langevin in Grenoble (France). The instrument IN6 provides a very high flux of cold neutrons which is an essential requirement for the present study. The incident energy E_i was chosen to be 4.75 meV. Data were collected in 235 ^3He counters covering the angular range from 10 to 113 degrees. These angles translate into an elastic wave-vector range of $0.3 \text{ \AA}^{-1} \leq Q_{el} \leq 2.6 \text{ \AA}^{-1}$. The elastic resolution amounts to 170 μeV full width at half maximum when time focusing on the elastic line. The energy region of interest between 0.5 and 10 meV can be covered in the neutron energy gain mode (up-scattering) down to temperatures of about 100 K. Typical counting times were 12 h.

Precompacted C_{60} powder was saturated with the PTM and sealed into the pressure cell. The temperature range from 180 to 335 K was explored at pressures between ambient and 9 kbar. Pressure was in all cases applied above 280 K and the sample cooled subsequently at a rate of 1 K per minute. This is necessary to obtain hydrostatic pressure conditions as the PTM freezes at low temperatures and high pressures. The pressure was monitored by a dilatation sensitive resistance mounted on the outside of the cell. Calibration was obtained from the applied load after correction for the friction between piston and cylinder leading to an absolute error on the high-pressure values of ± 0.5 kbar.

The raw data are corrected for the contributions of the pressure cell and PTM. To this effect first the empty cell spectrum is recorded at various temperatures and ambient pressure. Then the cell is filled with PTM and the scans are repeated at the chosen temperatures and pressures. This is necessary as the spectrum of the PTM changes both with temperature and pressure. The absolute amount of PTM present in the C_{60} /PTM mixture was determined by comparison with pure C_{60} at 180 K and ambient pressure.

After corrections for the energy dependence of the detector efficiency the scattering law $S(2\theta, \omega)$ is obtained from the data. The generalized phonon density of states $G(\omega)$ is

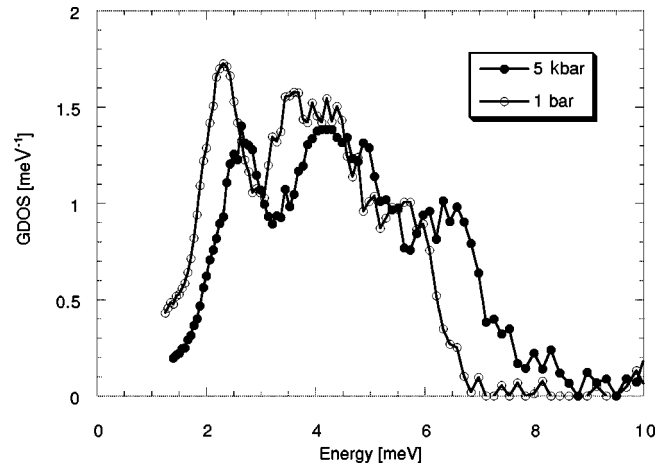


FIG. 2. Pressure dependence of the external mode spectrum of C_{60} as a function of pressure. Shown are the phonon density of states at ambient pressure and 5 kbar. The temperature is 180 K. There is a strong shift of the entire spectrum towards higher frequencies. Translational phonons have higher pressure coefficients than librions.

extracted from $S(2\theta, \omega)$ using the incoherent approximation.¹¹ Despite the rather long wavelength of the incoming neutrons the incoherent approximation works reasonably well for fullerene systems giving all the main features of $G(\omega)$. The largest errors concern the absolute intensity of the lowest libron peak.

Before going into the discussion of the experimental results it is important to recall some facts about the molecular orientations in solid C_{60} . It is well known that without external pressure the molecules in the low-temperature phase of C_{60} order predominantly in such a way that the electron-rich short bonds face electron-poor pentagons of neighboring molecules¹² (P orientation) thus minimizing the interaction energy. There is a competing H orientation defined by short bonds facing hexagons. At standard pressure the free-energy minimum corresponding to the H orientation lies only about 10 meV above the global minimum of the P orientation. Thermally activated hopping leads to disordered states at finite temperatures. At ambient pressures the H orientation has a about 1% smaller volume¹³ if compared to the P orientation. It, therefore, becomes energetically more favorable upon application of external pressure due to the work term $p\Delta V$ in the Gibbs free energy.

The critical temperature T_c associated with the transition from the orientationally ordered low-temperature phase to the high-temperature rotator phase seems not to be influenced by the details of the molecular orientation.¹⁰ It is directly observable in the INS spectra by the onset of quasielastic signals arising from the statistical reorientation of the molecules on the ps time scale. We observe $T_c = 280$ K at $P = 1.75$ kbar and $T_c = 335$ K at $P = 4.5$ kbar. The coefficient dT_c/dP which can be extracted from these values is in close agreement with the literature value of 16 K/kbar¹⁰ confirming our pressure calibration.

In Fig. 2 we compare the density of states of C_{60} at 180 K for ambient pressure and 5.0 kbar. There is a strong up-shift of all the external modes. Numerical values for some prominent spectral features are given in Table I.

The libronic spectrum of C_{60} is composed of several

TABLE I. Temperature and pressure dependence of selected features of $G(\omega)$: S_1 denotes the low-frequency shoulder of the first peak; Max_1 the first maximum; Min_1 the first minimum; Max_2 the second maximum; Min_2 the second minimum and Max_3 the third maximum. Frequency units are meV. The errors range from ± 0.05 meV at low frequencies to ± 0.1 meV at the upper cutoff. High-pressure values are accurate to ± 0.5 kbar.

T(K)	180			290	
P(kbar)	0.001	5.0	3.0	5.0	9.0
S_1	1.9	2.1	1.9	2.0	2.5
Max_1	2.3	2.6	2.3	2.5	3.1
Min_1	3.1	3.6	3.1	3.5	3.9
Max_2	3.5	4.1	3.9	4.0	4.7
Min_2	5.1	5.9	5.4	6.0	7.0
Max_3	5.5	6.4	6.2	6.6	7.8

bands.³ The lower band is centered at about 2.3 meV at 180 K and ambient pressure. It can easily be separated from the translational contribution to $G(\omega)$, which in this region shows a Debye-like behavior [$G(\omega) \propto \omega^2$]. In the Raman spectra two peaks can be discerned within the lower libron band.^{14,8} The upper peak (2.4 meV at ambient pressure and 180 K) is close to the center position of the band while a second even stronger excitation at 1.9 meV can be identified with a shoulder on the low-frequency side of the band (see Fig. 2). The fact that Raman peaks coincide with typical features in $G(\omega)$ can be explained by the flatness of the libron dispersion curves.⁵ The higher libron band at about 4 meV is close to a band of translational excitations and, therefore, not separable in $G(\omega)$ without model calculations. This band is hardly visible in the Raman spectra.^{14,8} Under pressure both libron bands shift towards higher frequencies. The numerical value for the shift of the peak position is 0.06 ± 0.01 meV/kbar at 180 K. This is in good agreement with theoretical calculations¹ and slightly less than the coefficient observed by the Raman experiments.⁸ The low-frequency shoulder of the first libron peak shifts somewhat less than the band center in accordance with the optical data. When comparing our INS data with the Raman data⁸ one has to be aware of the different thermal histories. While we cool under pressure leading to H-oriented equilibrated states, Horoyski *et al.* apply pressure at low temperature this way staying in the P-oriented glassy state.

The absolute changes as a function of hydrostatic pressure are larger for translational phonons than for librations. As translational modes probe directly the repulsive part of the intermolecular potential this may intuitively be expected. Rotational modes reflect the difficulty of the molecule to reorient as a consequence of the nonsphericity of the C_{60} cage and are, therefore, more indirectly concerned by an increase in pressure. This intuitive picture has been corroborated by numerical calculations¹ and is now confirmed experimentally. E.g., the cutoff of the external mode band which is purely of translational character (Fig. 2) moves by about 0.2 meV/kbar in quantitative agreement with theory.

At ambient pressure the order-disorder phase transition is preceded by a pronounced softening of the lower libron band. To check to which extent these anharmonic signatures are present at higher pressures we examined the temperature

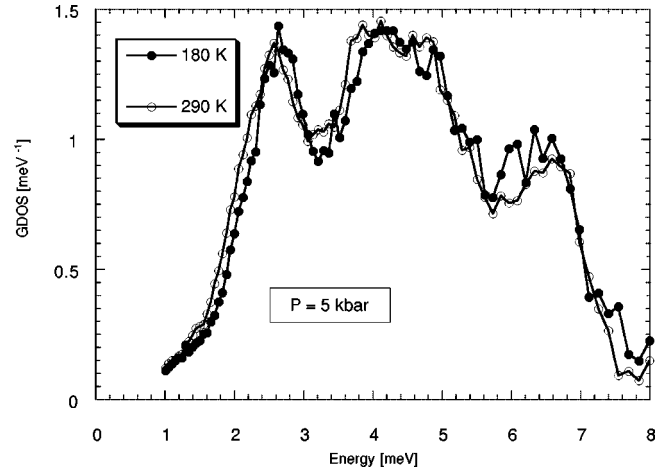


FIG. 3. Temperature dependence of the external mode spectrum in the hexagon phase ($p = 5$ kbar). Shown are the phonon density of states at 180 and 290 K. Besides a general small downshift there are little or no indications of anharmonicities.

dependence of the phonon spectrum at 5 kbar. As seen in Fig. 3 the external mode spectrum behaves quasiharmonically between 180 and 290 K. Frequencies change by less than 0.1 meV. These are small variations which can be explained by thermal expansion. For comparison, the frequency of the libron peak drops from 2.5 meV at 100 K to 2.2 meV at 200 K at ambient pressure.^{3,8} As the degree of anharmonicity changes with pressure it follows directly that the pressure coefficients of the librations are nonlinear at higher temperatures. For the understanding of the phase transition it is interesting to determine the energies $\hbar\omega_{\text{lib}}^{\text{crit}}$ towards which the libron peak extrapolates when approaching T_c . It is found that $\hbar\omega_{\text{lib}}^{\text{crit}}$ is not constant but increases with pressure. At 4.5 kbar $\hbar\omega_{\text{lib}}^{\text{crit}} \approx 2.4$ meV, while at ambient pressure $\hbar\omega_{\text{lib}}^{\text{crit}} \approx 1.8$ meV.

The following picture emerges from these observations: As the change from P towards H orientation must be reflected in the spectra⁷ the quasiharmonic behavior observed at 5 kbar precludes a change of orientation from H - to P -type in the investigated temperature range. This is in agreement with the currently accepted phase diagram. The absence of strong anharmonic precursors in the H -oriented phase directly challenges models of the phase transition which, like orientational melting, attribute a dominant role to libron softening.¹⁵ We conjecture to the contrary that the anharmonicities observed at lower pressures are mainly a manifestation of the disorder arising from competing H and P orientations. The argument is as follows. Extrapolating the pressure dependence of the libron peak towards zero we obtain the libron energy of a hypothetical hexagon phase at ambient pressure $\hbar\omega_{\text{lib}}^{\text{hex}} \approx 1.9$ meV. This extrapolation is confirmed by the Raman data.⁷ $\hbar\omega_{\text{lib}}^{\text{hex}}$ is close to $\hbar\omega_{\text{lib}}^{\text{crit}}$ at ambient pressure and inferior to the libron peak position $\hbar\omega_{\text{lib}}^{\text{pent}}$ of the pentagon phase at ambient pressure and low temperatures. Therefore, as the amount of H orientations increases with temperature the following changes take place: (1) Cages featuring H orientations librate at lower frequencies. (2) Due to their smaller specific volume H ordered cages create a negative pressure on the predominantly P ordered environment leading to mode softening in the host matrix. The result

is an overall softening of the libron band which originates from static disorder (on the time scale of the libron frequency) and not from inherent anharmonicities of the intermolecular potentials.

In summary, we have presented extensive experimental information on the pressure dependence of the external mode spectrum in orientationally ordered C_{60} . All external modes show large pressure coefficients. In absolute terms and in accordance with theory¹ translational phonons react stronger to pressure than librations. Concerning the temperature behav-

ior, anharmonic frequency shifts become less important with increasing pressure. At sufficiently high pressures the spectra remain quasiharmonic up to T_c . The libron mode softening at ambient pressure is conjectured to be mainly due to an increase of H orientations and is not a direct precursor of the phase transition. High-pressure Raman experiments close to T_c allowing us to determine line broadening are needed to confirm the above postulated correlation between libron anharmonicities and orientational competition, which may be of relevance for the study of disordered systems in general.

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