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A high-pressure investigation of C₆₀ by diffuse neutron scattering

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Abstract. Results of a diffuse neutron scattering experiment on C₆₀ powder under pressure are presented. A sapphire anvil pressure cell was used and pressures up to 1.6 GPa were applied. The results confirm that an orientational order–disorder transition occurs at room temperature under high pressure. The data indicate a 70% occupancy of the 38° orientational variant in C₆₀ under high pressure. The presence of elastic diffuse scattering shows that static orientational disorder persists at least up to 1.3 GPa which is the highest pressure up to which the diffuse scattering was investigated. The compressibility at room temperature was determined to be $5.4 \times 10^{-2} \text{ GPa}^{-1}$ in agreement with results of Duclos *et al.*

1. Introduction

The first evidence for the occurrence of a pressure-induced ordering transition in C₆₀ was obtained by differential thermal analysis [1] showing that the anomaly in the latent heat connected with the 260 K orientational order–disorder transition [2, 3] drastically shifts to higher temperatures under hydrostatic pressure. It was conjectured that application of pressure will lead to an orientational ordering transition at room temperature qualitatively similar to that known to occur near 260 K with temperature.

At present the orientationally ordered state below T_c is described within the framework of a model where each C₆₀ molecule adopts one of two orientational variants corresponding to anticlockwise rotations through 98 and 38°, respectively, about a cubic [111] direction [4, 5]. The two orientations are energetically nearly degenerate and the fraction of the 98° orientation is reported to increase from about 60% below T_c to about 80% at 100 K. At room temperature the C₆₀ molecules are dynamically disordered [6].

Theoretical models predict an orientational ordering transition under pressure and claim that at room temperature and at about 1.2 GPa the orientational order is complete and is characterized entirely by the 38° orientation [7]. This preference for the 38° orientation under pressure is generally related to the smaller volume of this configuration where a double bond of one molecule is oriented parallel to a hexagon of the neighbouring molecule whereas in the 98° orientation a double bond is parallel to a pentagonal face.

Only a few diffraction experiments on C₆₀ under hydrostatic pressure are described in the literature. A recent experiment on C₆₀ powder performed by synchrotron radiation suffered from very small sample volumes and, consequently, incomplete powder averaging [8]. The authors came to the rather surprising conclusion that at 2.5 GPa their data are compatible

Table 1. A survey of investigations on volume changes of C₆₀ powder as a function of pressure at ambient temperature. Experiments at other temperatures are not included. The phase transition is reported to occur between 0.25 and 0.4 GPa and information on a discontinuous change in volume can only be derived from data covering this pressure range. Therefore, the first measured point above ambient pressure has been indicated. The term 'quasi-continuous' signifies a relatively large number of data points in the pressure range around the phase transition. In order to compare our data with earlier work we have chosen the volume change between ambient pressure and 1 GPa. This quantity is most directly related to the data actually measured, while published data on compressibilities (or bulk moduli) have been obtained in various ways and for various pressures thus rendering comparison difficult. Of course, the volume change at 1 GPa is numerically equal to the compressibility derived from two measurements of the volume at 0 and 1 GPa, respectively. Note that, unlike all other numbers given, the value of Schirber *et al* [22] refers to only 0.56 GPa.

Experiment	This work	Duclos (1991) [13]	Fischer (1991) [15]	Lundin (1992) [17]	Haines (1994) [18]
Technique	Neutron diffraction	X-ray diffraction (synchrotron)	X-ray diffraction	Volume change (piezometer)	X-ray diffraction
Pressure cell	Diamond anvil	Diamond anvil	Diamond anvil	Piston cylinder	Diamond anvil
Pressure transmitter	—	—	Ethanol/methanol	—	NaCl or none
Pressure range (GPa)	0–1.6 First point at 0.6 GPa	0–20 First point at 0.5 GPa	0–1.2 Only 1 point at 1.2 GPa	0–1.1 (quasi-continuous)	0–28 First point at ~2.3 GPa
Volume jump observed at phase transition	?	?	?	No	?
$\Delta V/V$ between 0 and 1 GPa (including volume jump if observed)	0.054	0.045	0.069 (interpolation between 0 and 1.2 GPa)	0.078	0.052 (interpolation between 0 and 2.3 GPa)
Remarks				Powder sample contained ~20% C ₇₀	

with the occurrence of the 98° orientation as the predominant variant whereas at 1.5 GPa their data are more likely to be explained by the presence of the 38° orientational variant. Moreover, helium gas was used as the pressure-transmitting medium and the question arises of whether helium atoms introduced under pressure into the C₆₀ lattice will possibly perturb its structural state [9].

A further diffraction experiment under pressure was reported by David and Ibberson [10] showing that at 150 K where C₆₀ is found in the ordered state the application of pressure induces an increased occupation of the 38° variant.

Recently, a neutron scattering experiment on C₆₀ powder revealed the presence of elastic

Table 1. (Continued)

Experiment	Lundin (1994) [19]	Ludwig (1994) [20]	Jephcoat (1994) [8]	Bashkin (1994) [21]	Schirber (1995) [22]
Technique	Volume change (piezometer)	X-ray diffraction	X-ray diffraction (synchrotron)	Volume change (piezometer)	Neutron diffraction
Pressure cell	Piston cylinder	Diamond anvil	Diamond anvil	Piston cylinder	Aluminium pressure cell
Pressure transmitter	—	None or NaCl, FC87	He	—	Ar
Pressure range (GPa)	0–1 (quasi-continuous)	0–13 (quasi-continuous)	0–2.5 First point at 0.4 GPa	0–2 (quasi-continuous)	0–0.56 (quasi-continuous)
Volume jump observed at phase transition	Smooth	~1% at ~0.3 GPa	?	No	~1% at ~0.25 GPa
$\Delta V/V$ between 0 and 1 GPa (including volume jump if observed)	0.076	0.060	0.060 (interpolation from neighbouring values)	0.060	0.053 at 0.56 GPa (!!) (highest pressure data available)
Remarks			Data influenced by He diffusion into sample (see also [22])		Ar does not diffuse into C_{60} ; further data for He and Ne available

diffuse scattering below the 260 K transition in addition to the presence of the Bragg reflections characterizing the ordered state [11]. Upon cooling below T_c the intensities of most of the reflections increase in accordance with the higher occupation of the 98° variant thus approaching a state of higher orientational order while the elastic diffuse scattering does not decrease within the same temperature range. The elastic diffuse scattering therefore gives evidence for additional orientational static disorder.

In this communication we present results of a diffuse neutron scattering investigation of C_{60} under hydrostatic pressure up to 1.3 GPa (13 kbar). Additional data for the determination of the compressibility were obtained at 1.6 GPa.

2. Experimental details

The neutron scattering investigations were performed on the triple-axis spectrometer VALSE located at a cold neutron guide position of the Orphée reactor in Saclay (France). During the measurements the spectrometer was operated in the elastic mode where both monochromator and analyser were set to the same energy. Pyrolytic graphite crystals were used both as monochromator and analyser. The incident neutron energy was 14.7 meV and a pyrolytic graphite filter was put into the incident beam in order to eliminate higher-order

contaminations.

A sapphire anvil pressure cell [12] with a sample volume of about 20 mm³ was used. The gasket was made of aluminium and the pressure was measured by the ruby fluorescence technique.

Sublimed C₆₀ powder (99.9% purity) was taken as starting material for the sample. The powder was mechanically compressed in order to obtain a sample of spherical shape which was mounted into the cell. The compaction of the powder induced a plastic deformation of the powder grains as shown by broadened Debye–Scherrer lines. The application of pressure induced a corresponding shift of the Debye–Scherrer lines—however, without further line broadening.

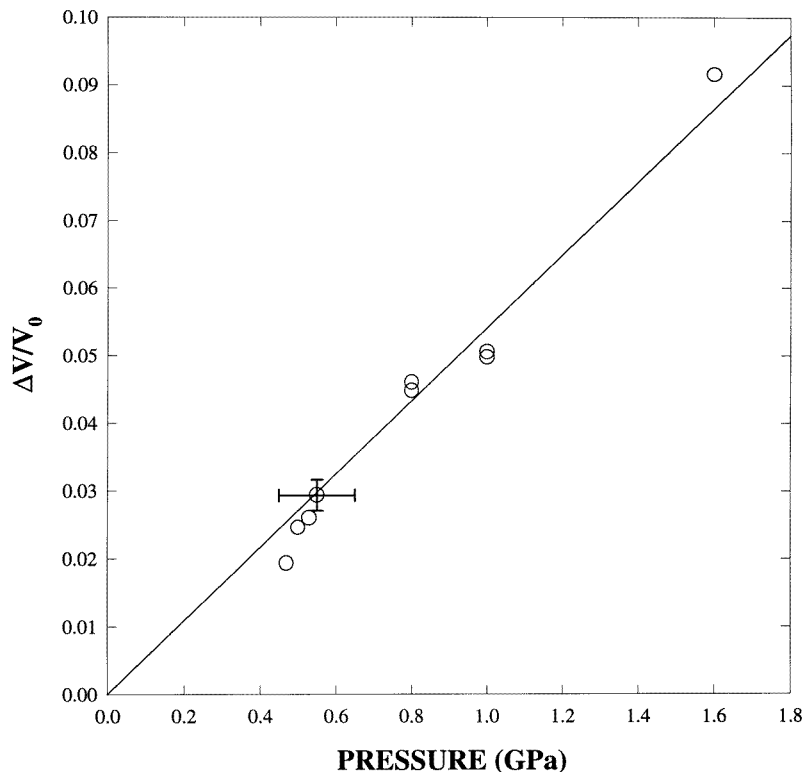


Figure 1. The relative change of unit cell volume versus pressure at room temperature. The straight line shows a linear fit to the data yielding a value of $(V/V_0) = 0.95$ at 1 GPa. V_0 is the measured unit cell volume at room temperature and zero pressure. From this the compressibility at room temperature was determined to be $5.4 \times 10^{-2} \text{ GPa}^{-1}$.

Pressure gradients were monitored by several ruby chips within the compressed sample. The pressure could be determined with an accuracy of ± 0.1 GPa.

No pressure-transmitting medium was used in this experiment as described in [12]. The ruby fluorescence technique confirmed the hydrostatic nature of the pressure in the sample. A similar technique of pressure application was also used in one experiment of Duclos *et al* [13] where, without using a medium, the pressure within a C₆₀ powder sample remained hydrostatic up to 4 GPa. The use of a pressure-transmitting liquid was avoided in order to reduce the sample background in this diffuse scattering experiment on a powder sample.

3. Results

In a first series of measurements the positions of the strong fundamental reflections (220), (311), (222), (331) and (420) were determined at different pressures, i.e. 0.5, 0.8, 1.0 and 1.6 GPa. The corresponding pressure-induced decrease of the unit cell volume is shown in figure 1 yielding a volume change of about 5% at 1 GPa. Within the accuracy of the measurements the data in figure 1 indicate a roughly linear change of $\Delta V/V_0$ with pressure up to 1.6 GPa yielding for the compressibility a constant value of $5.4 \times 10^{-2} \text{ GPa}^{-1}$.

The structural state of the C_{60} sample was investigated in more detail at 1.3 GPa. The reflections characterizing the ordered state occur at higher Q -values and their intensities are low when compared to the reflections from which the compressibility data were taken. The results obtained from a series of scans at 1.3 GPa are shown in figure 2. For comparison the scattering data obtained with a sublimed powder at 150 K and ambient pressure are shown in figure 3.

Figure 2(a) shows that the scattering observed under pressure at room temperature is similar to the one displayed in figure 3 for the sublimed powder at 150 K and ambient pressure. In figure 2(a) the reflections are broadened due to the initial plastic deformation but most of the reflections found at 150 K can also be seen under high pressure, especially the reflections of the ordered phase occurring near 3.5 \AA^{-1} . Figure 2(a) therefore shows that under pressure an orientational ordering transition occurs at room temperature.

Furthermore, the data in figure 2(a) show the presence of diffuse elastic scattering with a similar characteristic Q -modulation as observed without pressure at temperatures below the order–disorder transition [11].

The present measurements were performed using the triple-axis mode, and therefore within the limits of experimental resolution (0.5 meV) the observed diffuse scattering is of elastic origin. The elastic diffuse scattering is absent under ambient conditions but appears with high pressure.

A more detailed analysis of the data in figure 2(a) was performed by calculating the Debye–Scherrer line intensities within the framework of the two-orientation model of David (see [4, 5]). The initial increase of the linewidth due to the compaction of the powder sample was taken into account. Moreover, we calculated the diffuse scattering related to the orientational disorder of C_{60} molecules [14] which is given by

$$I_D(Q) \sim \overline{|F(Q)|^2} - |\langle F(Q) \rangle|^2$$

where $F(Q)$ is the structure factor of the C_{60} molecule. The angle brackets indicate an average over the molecular orientations and the overbars denote a powder average. The calculated diffuse scattering was used to describe the background of the data and added to the calculated Debye–Scherrer line intensities. The results of these calculations for two different occupations of the 98° and 38° orientations are shown in figure 2(b). A comparison of figure 2(a) with figure 2(b) indicates that the measured high-pressure data are significantly better reproduced by the calculations where it is assumed that the 38° orientation corresponds to the majority variant. In particular the measured intensity distribution near the Q -regions marked by the arrows A, B and C in figure 2(a) are highly significant in this respect since they show that the high-pressure data are in rather good agreement with the calculations where a 70% occupation of the 38° orientation is assumed. On the other hand the arrow D in figure 2(a) indicates the absence of a Debye–Scherrer line characteristic of the 98° orientational variant. The better agreement of the data with calculations where a 70% occupation of the 38° orientation is taken into account is also depicted in figure 2(c) where the data and the calculations are drawn on a logarithmic scale.

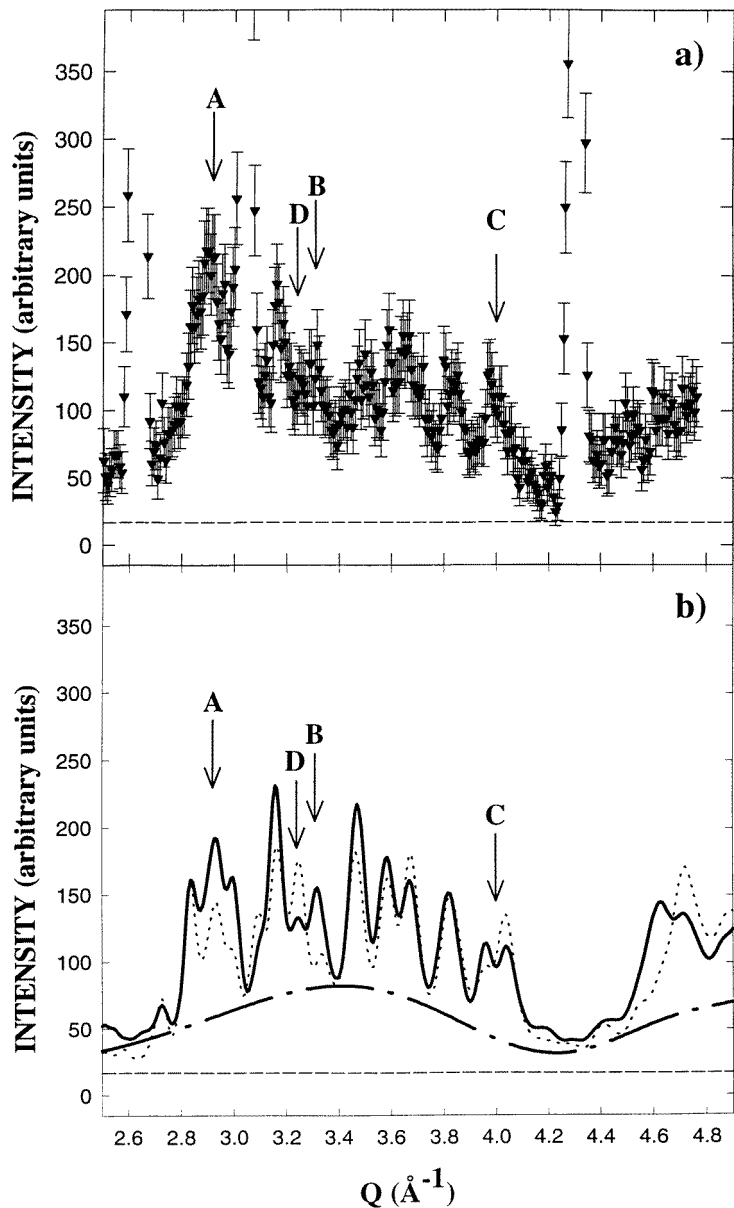


Figure 2. See facing page.

In order to illustrate the degree of accuracy to be expected in our simulations we have performed calculations in order to describe the experimental data obtained at ambient pressure and 150 K, the results of which are displayed in figure 3. The calculations were done for a 30% occupation of the 38° orientation which holds for 150 K according to available experimental data [5], and the agreement with the measured scattering intensity distribution can be considered satisfactory.

The present results therefore indicate that C_{60} orders under pressure in agreement with

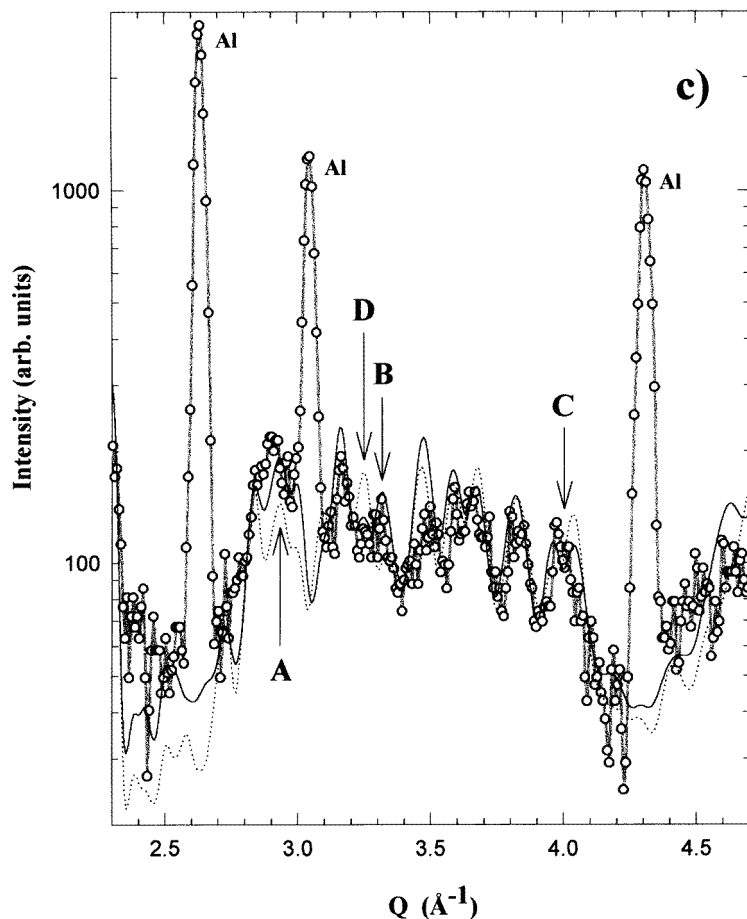


Figure 2. (Continued) The elastic scattering intensity observed in C_{60} powder under hydrostatic pressure of 1.3 GPa in comparison with calculations. (a) The measured scattering intensity at 1.3 GPa. The dashed line indicates the background level under ambient conditions. The three strong peaks rising above the intensity distribution are due to Debye–Scherrer lines of the aluminium container. The arrows A, B, C and D indicate regions in Q -space where significant differences between the 38° and 98° majority orientational occupations can be observed (see the text). (b) Calculated Debye–Scherrer line intensities. Full line: 70% of the molecules are found in the 38° orientation and 30% in the 98° orientation; dotted line: 30% of the molecules are found in the 38° orientation and 70% in the 98° orientation. The dash-dotted line indicates the calculated elastic diffuse scattering. A fit of the calculated full and dotted lines to the data gives normalized chi-square values of 1.3 and 2.2 ± 0.2 , respectively, for the Q -region between 2.8 and 3.4 \AA^{-1} comprising the features marked A, B and D where the differences between the two models are most pronounced. Likewise, a fit for the Q -range around C gives superior results for the full line. (c) The data (circles) and the calculations as shown in (a) and (b) respectively reproduced on a logarithmic scale.

the David model but with a higher occupation of the 38° variant than at low temperatures. The order, however, is not perfect and a significant static orientational disorder persists under high pressure as borne out especially by the elastic diffuse scattering observed.

Our value of the compressibility obtained at 1 GPa and room temperature by determining

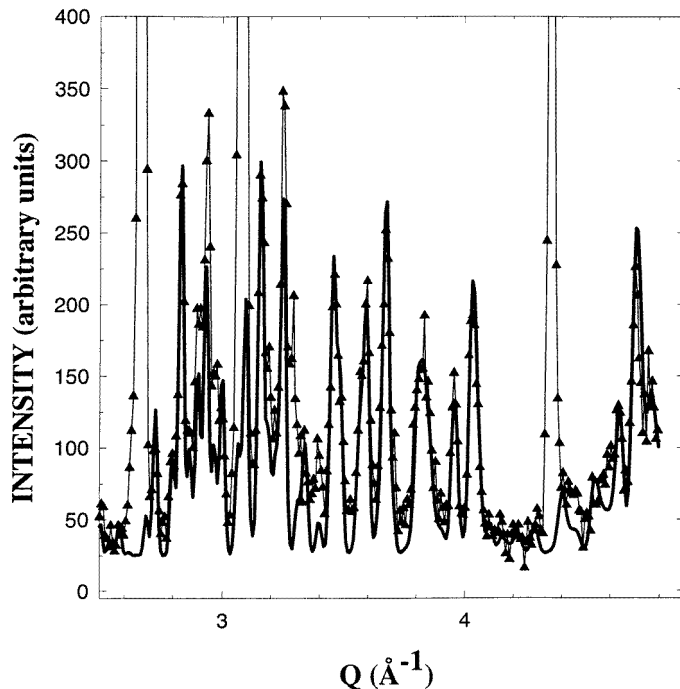


Figure 3. The elastic scattering intensity observed for C_{60} powder at 150 K and ambient pressure in comparison with calculations. Again, as in figure 2(a), the three strong peaks visible in the experimental data but not in the calculations are due to the sample containment. Triangles: measured data points; full line: calculated intensities corresponding to a 30% occupation of the 38° orientation.

the positions of a series of fundamental Bragg peaks at different pressures is in good agreement with several values in the literature [13, 8, 21] (see table 1). Other measured values of the compressibility are about 20% higher [15, 16, 19, 17, 18]. We are unable to deduce from our data a jump in the unit cell volume at the order–disorder transition occurring near 0.3 GPa as reported by Ludwig *et al* [20] and Schirber *et al* [22]. The data of Schirber *et al* show a well pronounced volume jump near 0.3 GPa, but the total volume change observed between 0 and 0.6 GPa is significantly larger than all other values found in the literature.

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