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High-pressure, low-temperature structural studies of orientationally ordered C₆₀

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Abstract. The low-temperature orientationally ordered structure of C₆₀ consists of rapid reorientation between two structurally distinct configurations. At ambient pressure, the lower-energy orientation, described by pentagons facing $\langle 110 \rangle$ bonding directions, has a larger volume than the second orientation, described by hexagons facing $\langle 110 \rangle$. In this paper, it is shown that application of a modest pressure of around 2 kbar is sufficient to make the 'hexagon orientation' the more energetically favourable, indicating that the structural ground state of C₆₀ is highly pressure dependent.

1. Introduction

The crystal structure of C₆₀ has been extensively studied at ambient pressure as a function of temperature. The existence of a first-order phase transition at around 260 K was first confirmed by differential scanning calorimetry (Heiney *et al* 1991). The transition involves a reduction of space group symmetry from $Fm\bar{3}m$ to $Pa\bar{3}$. In the high-temperature phase, the C₆₀ molecules reorient quasi-isotropically resulting in a scattering density that is close to a spherical shell. Departures from isotropy are no more than 16% (Chow *et al* 1992, David *et al* 1993). In the low-temperature phase, each molecule reorients between two energetically similar but crystallographically distinct orientations (David *et al* 1992a). These orientations are best described in terms of the inter-molecular bonding configurations. In the more energetically favourable ambient pressure configuration, the bonding motif may be described by pentagons facing C=C double bonds in a neighbouring molecule. In the less favourable orientation hexagons face the C=C bonds. The energy difference has been calculated to be around 122 K (David *et al* 1992, Bürgi *et al* 1992, David *et al* 1993). These two orientations may be reached by hopping $\sim 42^\circ$ about $\langle \bar{1}10 \rangle$ directions over an activation energy of some 2600 K. The magnitude of this activation energy has significant implications for the reorientational correlation times, which follow an Arrhenius behaviour. Around the order-disorder transition at 260 K, the reorientational correlation times are of the order of 10^{-9} s; at 86 K, however, the reorientation is so slow ($> 10^3$ s) that an orientational glass transition occurs (David *et al* 1992a, Matsuo *et al* 1992, Gugenberger *et al* 1992). From the analysis of the lattice constant behaviour at the glass transition, it is evident that the lower-energy 'pentagon' orientation rather unusually has the larger volume. This is most likely a consequence of the fact that a facing hexagon, because of its larger area, may more easily accommodate a closer approach of neighbouring C=C bonds than a facing pentagon (Gugenberger *et al* 1992). Careful lattice parameter measurements (David *et al* 1993) have been modelled in a manner analogous to specific heat measurements using a combined

Debye–Einstein model. From this model fit, the effective lattice constant difference Δa between a hypothetical ‘pentagon only’ orientation and a ‘hexagon only’ orientation structure is estimated to be $0.0439(10) \text{ \AA}$ at ambient pressure. This corresponds to a rather large fractional volume change of $0.94(2)\%$ which implies that the relative stabilities of ‘pentagon’ and ‘hexagon’ orientations should be highly pressure dependent. This observation provided the motivation for the present work. Indeed, a straightforward calculation of the free energy difference $\Delta G^{\text{HP}}(p) = \Delta G_{(p=0)}^{\text{HP}} + p\Delta V^{\text{HP}}$ indicates that the two orientations will be of equal energy at a pressure given by the equation $p_{(H'=P')} = -\Delta G_{(p=0)}^{\text{HP}}/\Delta V^{\text{HP}}$. Given that $\Delta G_{(p=0)}^{\text{HP}}$ is $\sim 122 \text{ K}$ and ΔV^{HP} is $-6.43(15) \text{ \AA}^3$ for a single C_{60} molecule (David *et al* 1993) then it may be estimated that only 2.6 kbar is required to make the ‘pentagon’ and ‘hexagon’ sites equivalent. At all pressures above 2.6 kbar therefore the more preferred stable orientation of C_{60} should be the ‘hexagon’ orientation. This has significant implications for understanding the high-pressure transformations in C_{60} .

Previous work has already shown that modest pressures have a profound effect on the structure of solid C_{60} . The order–disorder transition in C_{60} has been studied as a function of pressure using the techniques of DTA and ^{13}C NMR (Samara *et al* 1991, 1993) and x-ray diffraction (Fischer *et al* 1991, Duclos *et al* 1991). These studies established that the ordered simple cubic phase is stabilized by pressure. Using helium as the pressure transmitting medium, Samara *et al* (1993) report $dT_c/dp = 10.4(2) \text{ K kbar}^{-1}$. This result is not surprising and is consistent with a substantial reduction in the molecular separation since the C_{60} – C_{60} interactions are relatively weak and reminiscent of interlayer interactions in graphite. No compression of the C_{60} molecule has been detected. It is clear that increased pressure will hinder the reorientational motion of the C_{60} molecules thus frustrating the disordering process and raising the order–disorder phase transition temperature. The initiation of orientational ordering with pressure is observed in many well characterized molecular solids such as methane, CH_4 (Constantino and Daniels 1975), molecular hydrogen, H_2 (Sivera 1980), and adamantane, $\text{C}_{10}\text{H}_{16}$ (David and Ibberson 1993).

2. Experimental details

Time of flight powder diffraction data were recorded at high pressure using the high-resolution powder diffractometer (HRPD) at ISIS (Ibberson *et al* 1992). Approximately 1 cm^3 of pure C_{60} was contained in an aluminium gas pressure cell in a standard ‘orange’ cryostat. The cell utilizes a Bridgeman seal and has a maximum operating pressure of 4.0 kbar. Hydrostatic pressure is achieved by means of a gas intensifier system. On a pulsed neutron source, diffraction data are optimally recorded when using constrained sample environment equipment, such as a pressure cell, at a scattering angle of 90° . In this case, collimation can be used to define a scattering lozenge entirely within the sample volume. However, in the present experiments, high-resolution backscattering data were required and so contamination by Bragg scattering from the cell was inevitable. The incident beam size was reduced to that of the sample cross section; no collimation was used around the cell. The regions in which aluminium Bragg peaks occur were subsequently excluded during the profile refinement. Because of the high-resolution nature of the diffraction patterns, the total excluded regions represented only 25% of the diffraction pattern.

Following the work of Samara *et al* (1993), who report modifications to the structural behaviour of C_{60} as a function of pressurizing gas, argon was selected as the pressure transmitting medium. The van der Waals radius of argon is sufficiently large, 2.86 \AA , so as not to be accommodated in the tetrahedral and octahedral interstices of the C_{60} structure.

The use of argon, however, introduces additional technical problems. Around 90 K at the ambient pressure orientational glass transition, argon becomes solid at very modest pressures. Problems were experienced in achieving a reliable sample pressure in the solid region of the argon phase diagram. Indeed, data were ultimately only obtained within the liquid regime of the argon phase diagram. The first datasets were recorded at 150 K as a function of pressure. Measurements were subsequently collected at 2.8 kbar and then at 2.0 kbar as a function of temperature between 150 K and 200 K. Following a change in temperature, a manual adjustment was made to maintain constant pressure (± 25 bar) in the cell. Data were recorded over a time-of-flight window of 30–130 ms corresponding to a d spacing range of ~ 0.6 – 2.6 Å. The experiment collection times were of the order of 3 h (~ 120 μ A h).

3. The 150 K structure as a function of pressure

Despite the modest hydrostatic pressures of the present measurements, significant structural changes are evident. At 150 K, the lattice parameter reduces to 13.960 74(12) Å at 2.8 kbar compared with 14.066 39(10) Å under ambient pressure conditions. The equation of state of C₆₀ at 150 K was determined using the Murnaghan (1944) equation. The bulk modulus K is calculated as 127.4(8) kbar, which compares with two previous measurements of (i) $K = 181(18)$ kbar and $K'_0 = 5.7$ (Duclos *et al* 1991) from a fit of ambient temperature data at pressures up to 200 kbar and (ii) $K = 140(20)$ kbar reported by Fischer *et al* (1991) who measured at room temperature up to a pressure of 120 kbar. Because of the restricted pressure range of the present data, deviations from a straight line behaviour were not statistically significant and therefore, refinement of the derivative K'_0 of the bulk modulus could not be justified. The expression of bulk modulus as a linear function of pressure over this limited pressure range is quite reasonable and agrees with the variations observed over the more extensive range of data collected by Duclos and co-workers (1991).

A full Rietveld analysis of the 150 K data as a function of pressure was performed using the CCSL refinement package (David *et al* 1992b). Following the two orientation model described previously, the relative proportions of 'pentagon' and 'hexagon' orientations were refined as a function of pressure. The results for the fraction of 'pentagon' orientations are presented in figure 1(a) and clearly show that the expected increased stabilization of the smaller-volume 'hexagon' orientation occurs as a function of pressure. The free energy difference (in K) $\Delta G^{\text{HP}} = -\ln[1/n_p] - 1$ is given as a function of pressure in figure 1(b). The free energy pressure variation $\Delta G^{\text{HP}} = \Delta F^{\text{HP}} + p\Delta V^{\text{HP}}$ is, as expected, a straight line to within experimental errors. The fitted parameters (in K) give

$$\Delta G^{\text{HP}} = 128.4(2.0) - 67.1(1.6)p.$$

The slope of the fit may be equated to the volume difference between a single C₆₀ molecule in the 'hexagon' and 'pentagon' orientations. The fractional volume change is 0.0135(3), which is equivalent to a lattice constant difference of 0.0630(15) Å. This is some 50% larger than the value of 0.0439(10) Å obtained from extrapolation of the lattice constant as a function of temperature at ambient pressure. Although these values differ by around 10σ , it must be noted (i) that they have been obtained from orthogonal variations in p - T space, (ii) that the lower value is a model extrapolation based upon the assumption that the lattice constant a is a linear sum $a = n_p a_p + n_H a_H$, and (iii) that there may be a small degree of argon incorporation within the C₆₀ structure in the high-pressure experiments.

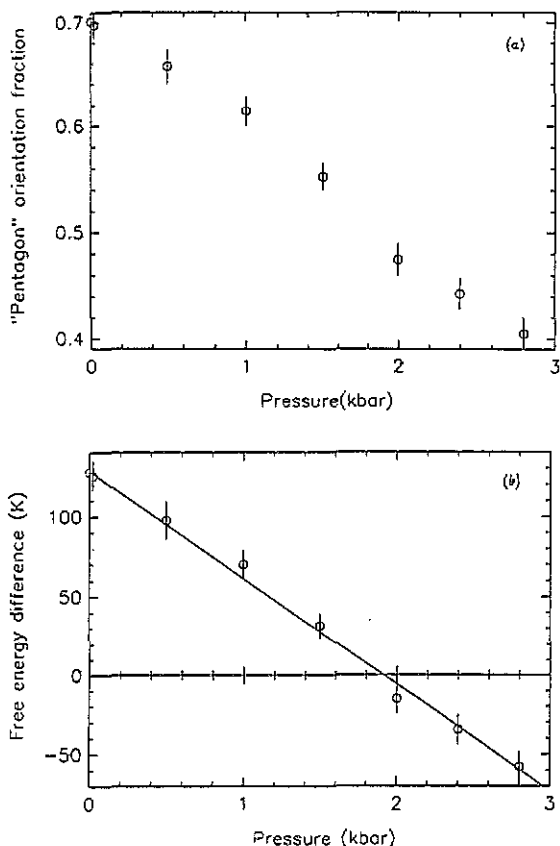


Figure 1. (a) Fractional occupation of the major 'pentagon facing' orientation as a function of pressure at 150 K. (b) The derived free energy difference ΔG expressed in degrees kelvin between the two orientations as a function of pressure at 150 K. This was obtained from the equation $\Delta G = -kT \ln[(1/p_p) - 1]$. The straight line is a least-squares fit giving $\Delta G = 128.4(2.0) - 67.1(1.6)p$.

The discrepancy does not appear to be caused by a differential compressibility between 'pentagon' and 'hexagon' orientations (i.e. $\Delta a_p(p) \neq \Delta a_H(p)$). Within experimental errors the compressibilities appear to be identical from the absence of a p - T cross term in the evaluation of the lattice constant as a combined function of temperature and pressure. The following equation was found to fit the lattice parameter data to sufficient precision in the temperature range 150–200 K and a pressure range 0–2.8 kbar:

$$a = 14.0619(30) - 1.39(30) \times 10^{-4}T + 1.12(10) \times 10^{-6}T^2 \\ - 0.0442(6)p + 2.36(20) \times 10^{-3}p^2 + 3(3) \times 10^{-5}pT$$

(the precision of the cell constants derived at elevated pressures was typically an order of magnitude less precise than previous ambient pressure results (David *et al* 1993). It is therefore reasonable to conclude that the simple two-orientation model is an adequate description of the behaviour of the solid as a function of pressure and temperature in the ordered simple cubic phase. The analysis of the temperature variations of the relative populations of 'pentagon' and 'hexagon' orientations at ambient pressure and at 2.0 kbar

and 2.8 kbar, however, indicate that the assumption of a single potential minimum associated with each of these orientations may be an over-simplification. This is supported by more comprehensive recent measurements (David *et al* 1993) as a function of temperature at ambient pressure, which indicate that in the 110–200 K temperature range, the free energy difference only approaches a constant value above 160 K (figure 2). There is also additional experimental evidence from specific heat measurements (Matsuo *et al* 1992). The anomalous excess specific heat above the orientational glass transition may be modelled to a variable degeneracy Schottky anomaly (Matsuo 1993) and leads to a relative degeneracy g_H/g_P of 3.4 ± 0.9 .

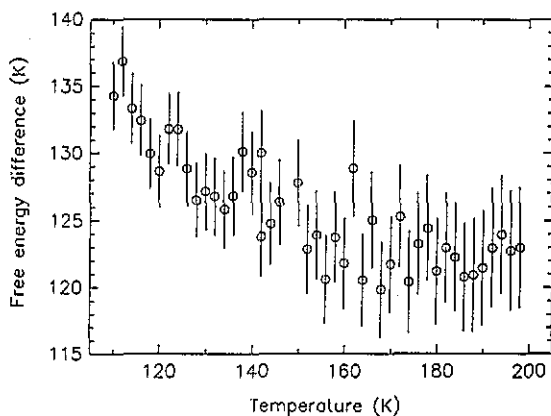


Figure 2. The derived free energy difference ΔG expressed in degrees kelvin between major and minor orientations as a function of temperature at ambient pressure. Note that ΔG is independent of temperature only in the region 160–200 K.

4. Conclusions

In this paper, the structure of C_{60} has been studied at simultaneous high pressure and low temperature. The main conclusion of the present work is that the most stable orientation state at ambient pressure, involving a pentagon face opposite the C=C double bond of the adjacent molecule, is destabilized in preference to the orientation involving a hexagon facing an adjacent C=C bond. This result is clearly expected from a straightforward analysis of the ambient pressure behaviour as a function of temperature, which indicates that the 'pentagon' orientation, although more favourable in energy than the hexagon orientation, has a larger associated volume. The application of pressure thus stabilizes the 'hexagon' orientation. In the temperature range investigated at elevated pressures, no evidence was found for the orientational glass transition. On the one hand, applied pressure might reasonably be expected to increase the activation energy of hopping, thus raising the orientational glass transition temperature T_g . On the other hand, at only a few kbar, the 'hexagon' orientation will completely dominate, thus making T_g difficult to observe. Within the 'pentagon'/'hexagon' orientation model, the observed pressure dependence indicates that T_g will effectively disappear above 10 kbar. More precise, higher-pressure data are required to ascertain this. Consideration of the ambient pressure behaviour of the relative occupancies of 'pentagon' and 'hexagon' orientations indicates that the derived free energy

difference between the two distinct orientations varies in a non-linear manner as a function of temperature. These measurements indicate that ordered C_{60} has a rich structural variation even at modest pressures (< 3 kbar) at low temperatures. Further studies of the high-pressure structure and dynamics of C_{60} up to 100 kbar should be equally rewarding.

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