

## High pressure study of the C<sub>84</sub> fullerene

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### Abstract

The structural properties of solid C<sub>84</sub> (mixture of two isomers, D<sub>2</sub>(IV) and D<sub>2d</sub>(II) in a 2:1 abundance ratio) were studied by synchrotron X-ray powder diffraction at ambient temperature and elevated pressures. The structure remains strictly cubic to 9.2 GPa with no evidence of a structural phase transition, analogous to those encountered in C<sub>60</sub> and C<sub>70</sub>. The pressure behavior of the intramolecular phonon modes studied by Raman spectroscopy is consistent with the structural results. © 2002 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

Following the breakthrough in producing macroscopic quantities of C<sub>60</sub>, a number of higher fullerenes has also been synthesized. Among these, C<sub>84</sub> is the third most abundant member of the series after C<sub>60</sub> and C<sub>70</sub> [1]. It has 24 structural isomers obeying the isolated pentagon rule. Early <sup>13</sup>C NMR studies [2,3] revealed that it can be isolated as a mixture of two major isomers with D<sub>2</sub>(IV) and D<sub>2d</sub>(II) symmetry which occur in a 2:1 abundance ratio. Tight-binding calculations [4,5] showed that these isomers are close in energy and

energetically the most stable. A remarkable feature of their structural properties is their quasi-spherical shape and their small aspect ratios, as derived from theoretical calculations (D<sub>2</sub>(IV):  $d_x = 7.79 \text{ \AA}$ ,  $d_y = 8.45 \text{ \AA}$ ,  $d_z = 8.16 \text{ \AA}$ ; D<sub>2d</sub>(II):  $d_x = 7.90 \text{ \AA}$ ,  $d_y = 8.30 \text{ \AA}$ ,  $d_z = 8.50 \text{ \AA}$ ) (Fig. 1) [6]. High-resolution synchrotron X-ray powder diffraction has shown that the structure of the isomer-mixture solid C<sub>84</sub> is face-centered cubic (FCC) in the temperature range 5–295 K [7]. The combination of this result with the fact that both isomers possess low-lying LUMOs [8] makes C<sub>84</sub> a highly promising candidate as a host for the synthesis of intercalation compounds in analogy with C<sub>60</sub>. Indeed successful separation of C<sub>84</sub> in single isomer forms [9] allowed the synthesis of potassium intercalation compounds of C<sub>84</sub> whose electronic properties depend on the particular

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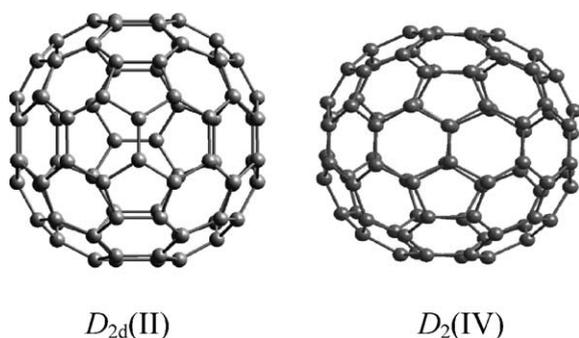


Fig. 1. The  $D_{2d}(\text{II})$  isomer of  $C_{84}$  viewed along the unique  $\bar{4}$  axis of the molecule (left). The  $D_2(\text{IV})$  isomer of  $C_{84}$  viewed along one of the three two-fold axes (right).

isomer of  $C_{84}$  used as host [10]. In addition, preliminary structural investigations also reveal a rich crystal chemistry of the isomer-pure forms of solid  $C_{84}$  with evidence of phase transitions to low-symmetry structures in the vicinity of 180 K [11].

In this report, we present synchrotron X-ray powder diffraction measurements on the 2:1  $D_2(\text{IV}):D_{2d}(\text{II})$  mixture of  $C_{84}$  as a function of pressure at room temperature (up to 9.24 GPa). In this range of pressures, there is no evidence of a phase transition neither to an orientationally ordered nor to a low-symmetry phase. In addition, the structural results were complemented by following the pressure response of the intramolecular phonon modes by means of Raman spectroscopy.

## 2. Experimental details

The  $C_{84}$  material under study was a mixture with 2:1 abundance ratio of the two major isomers  $D_2(\text{IV})$  and  $D_{2d}(\text{II})$ . Separation of  $C_{84}$  was achieved by recycling HPLC using a Cosmosil 5PYE column and toluene as eluent. The crystalline samples for X-ray and Raman analysis were recrystallized from toluene with subsequent removal of residual solvent at  $\sim 550$  K under vacuum  $10^{-5}$  Torr for 12 h and sublimed at  $\sim 950$  K.

High-pressure X-ray diffraction experiments at ambient temperature were performed on beamline

ID09 at the European Synchrotron Radiation Facility, Grenoble. The powder sample was loaded in a DAC, which was used for the high pressure generation and was equipped with an aluminum gasket. The sample was introduced in a hole made in the gasket 70  $\mu\text{m}$  deep and 200  $\mu\text{m}$  in diameter. Silicone oil loaded in the DAC was used as a pressure-transmitting medium and the ruby fluorescence technique was used for pressure calibration. The diffraction patterns were collected using an image plate detector ( $\lambda = 0.49953$  Å). Masking of the strong Bragg reflections of the ruby chip and integration of the two-dimensional diffraction images were performed with the local ESRF FIT2D software. The data analysis was performed with the Rietveld refinement and the LeBail [12] pattern decomposition techniques.

The Raman spectra were recorded using a triple monochromator (DILOR XY-500) equipped with a CCD liquid-nitrogen-cooled detector system. The spectral width of the system was  $\sim 5$   $\text{cm}^{-1}$ . The 514.5 nm line of an  $\text{Ar}^+$  laser was used for excitation. The laser power was kept lower than 5 mW, measured directly before the cell, in order to avoid laser heating effects and related changes in the phonon spectrum. Measurements of the Raman spectra at high pressure and room temperature were carried out using the DAC of Mao-Bell type [13]. A 4:1 methanol–ethanol mixture was used as pressure-transmitting medium and the ruby fluorescence technique was used for pressure calibration.

## 3. Results and discussion

Synchrotron X-ray powder diffraction profiles of  $C_{84}$  were collected at pressures between ambient and 9.24 GPa. Inspection of the diffraction data indicated that all patterns could be indexed as FCC at all pressures. All peaks observed to a momentum transfer  $Q = 3.06$  Å $^{-1}$  (where  $Q = 4\pi \sin \theta / \lambda$ ) indexed with Miller indices either all odd or all even. The only exception is a significant peak on the leading edge of the (1 1 1) reflection at  $\approx 2.95^\circ$ , which we ascribe to the presence of hexagonal stacking faults in the FCC structure, as observed in other fullerene solids.

Profile refinements of the dataset at 0.06 GPa were thus attempted in space group  $Fm\bar{3}m$ , which necessitates the presence of orientationally disor-

dered quasi-spherical  $C_{84}$  molecules placed at the origin of the unit cell. In this approach, the carbon atom motion is confined to the surface of sphere,

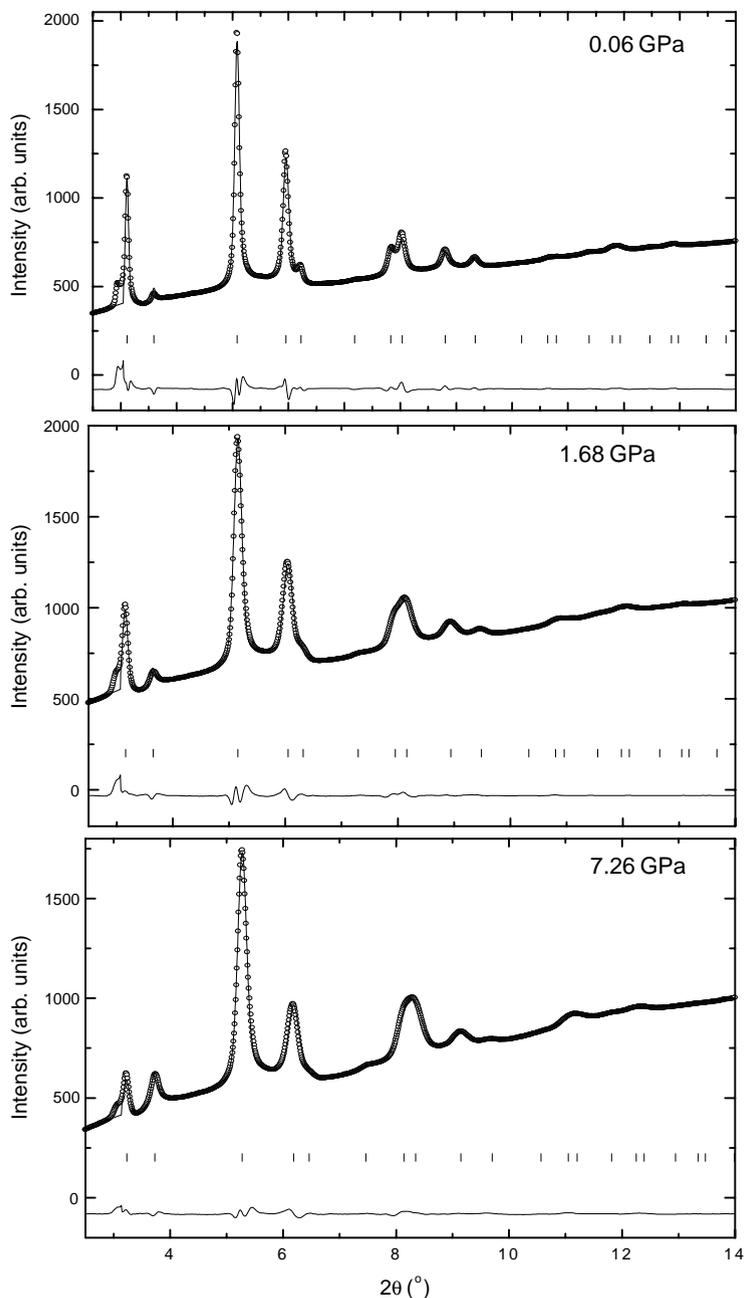


Fig. 2. Refinements of the ambient-temperature synchrotron X-ray ( $\lambda = 0.49953 \text{ \AA}$ ) powder diffraction profiles of  $C_{84}$  at pressures 0.06 GPa (Rietveld), 1.68 GPa (LeBail) and 7.26 GPa (LeBail). The observed data are shown as points and the calculated fits as solid lines. The difference curves are included at the bottom of each diagram with the vertical marks indicating the Bragg reflections.

as described before for the high temperature FCC phase of  $C_{60}$ . Each fullerene molecule is modelled by a simple spherical shell of electron density with a form factor given by

$$f(Q) = (84/\sqrt{4\pi}f_c[\sin(QR)/QR],$$

where  $Q$  is the momentum transfer,  $f_c$  the carbon atom form factor and  $R$  the radius of the shell. Rietveld refinement of the data ( $2\theta$  range =  $2.5$ – $14^\circ$ ) proceeded smoothly (Fig. 2), leading to value for the cubic lattice constant,  $a = 15.935(5)$  Å, and the diameter for the spherical shell,  $d = 8.35(3)$  Å at 0.06 GPa ( $R_{wp} = 1.8\%$ ,  $R_{exp} = 1.3\%$ ). No full profile refinements were performed for the datasets measured at higher pressures. Instead LeBail refinements (Fig. 2) were employed to extract accurate values of the cubic lattice parameter as a function of pressure. The refined values of the cubic lattice constants are  $a = 15.702(6)$  Å at 1.68 GPa ( $R_{wp} = 1.6\%$ ,  $R_{exp} = 1.2\%$ ) and  $a = 15.349(1)$  Å at 7.26 GPa ( $R_{wp} = 1.2\%$ ,  $R_{exp} = 1.4\%$ ).

Fig. 3 shows the pressure evolution of the volume of the cubic unit cell of  $C_{84}$  together with a least-squares fit of its ambient-temperature equation-of-state (EOS) to the semi-empirical

second-order Murnaghan EOS [14]:

$$P = (K_0/K'_0)[(V_0/V)^{K'_0} - 1], \quad (1)$$

where  $K_0$  is the atmospheric pressure isothermal bulk modulus,  $K'_0$  is its pressure derivative ( $= dK_0/dP$ ), and  $V_0$  is the unit cell volume at zero pressure. The fit results in values of  $K_0 = 20(2)$  GPa and  $K'_0 = 16.1(6)$ . The extracted value of the volume compressibility,  $\kappa = 0.050(5)$  GPa $^{-1}$  is comparable to those measured for other pristine fullerene solids ( $C_{60}$ : 0.055(6) GPa $^{-1}$ ,  $C_{70}$ : 0.040(14) GPa $^{-1}$ ). The somewhat smaller compressibility of  $C_{70}$  may reflect its anisotropic shape compared to the quasi-spherical  $C_{60}$  and  $C_{84}$  units, which can pack much more efficiently.

The Raman spectrum of  $C_{84}$  was also measured at pressures up to 10 GPa. The spectra are considerably richer than those of pristine  $C_{60}$  due to the lower symmetry of the two  $C_{84}$  isomers and larger number of the Raman active modes. The Raman peaks are also broadened with respect to those of the pristine  $C_{60}$  and  $C_{70}$ , which may be associated mainly with the two-isomer nature of the present sample. The positions of the observed peaks are in agreement with those reported at ambient pressure for the single  $D_2(IV)$  and  $D_{2d}(II)$

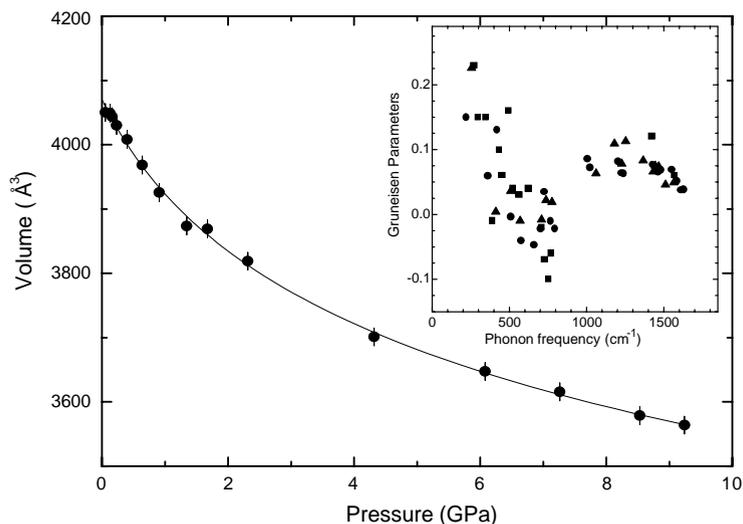


Fig. 3. Pressure evolution of the volume of the cubic unit cell of solid  $C_{84}$  (closed circles) and the least-squares fit to the semi-empirical second-order Murnaghan EOS (solid line). Inset: the Grüneisen parameters of the phonon modes of  $C_{84}$ ,  $C_{70}$  and  $C_{60}$  (circles, triangles, and squares, respectively).

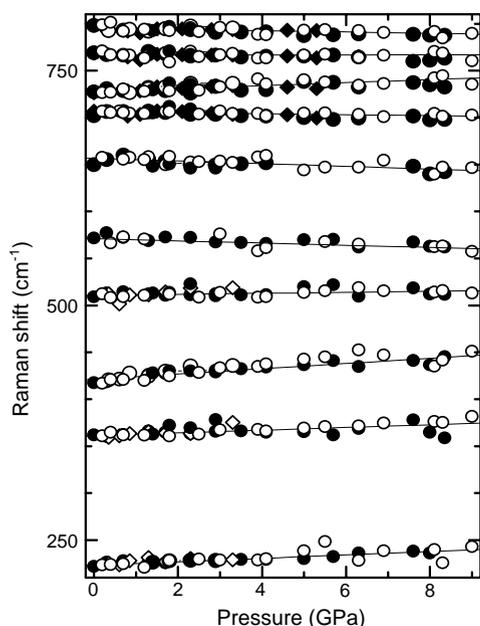


Fig. 4. Pressure evolution of the low-energy intramolecular phonon modes of  $C_{84}$  for increasing (open symbols) and decreasing (closed symbols) pressure.

isomers [15]. The pressure dependence of the low-energy Raman modes is shown in Fig. 4. The open (closed) symbols represent the data for increasing (decreasing) pressure. Similar pressure dependence was also obtained for other Raman modes. No singularity is present and the data are entirely reversible under release of pressure. The extracted Grüneisen parameters of the intramolecular phonon modes of  $C_{84}$  (solid circles) are shown in the inset of Fig. 3 together with those of  $C_{60}$  (solid squares) and  $C_{70}$  (solid triangles). Their frequency dependence is very similar for all three fullerene solids, which is consistent with their common origin.

#### 4. Conclusions

In conclusion, we have employed synchrotron X-ray powder diffraction to characterize the structural properties of pristine  $C_{84}$  as a function of pressure to 9.24 GPa at ambient temperature.  $C_{84}$  does not show any phase transition or

irreversible transformation, being stable up to the highest pressure used in the present study and its structure remaining strictly face-centered cubic (space group  $Fm\bar{3}m$ ). The results were corroborated by complementary pressure-dependent Raman spectroscopic studies on the same material. Such behavior can be presumably associated with the disordered nature of the material, arising from the coexistence on the same lattice sites of  $C_{84}$  molecules with differing molecular symmetry. This is a persistent problem with structural studies of higher fullerene solids, which invariably occur in more than one isomeric form. The incipient frozen-in disorder suppresses phase transitions driven by subtle orientational ordering effects modulated by the interfullerene van der Waals interactions. As such effects also govern the electronic properties of both the pristine solids and their intercalated derivatives, they make essential the availability of isomer-pure materials for a proper understanding of the properties of these systems.

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