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Neutron-diffraction study of the rare-gas interstitial fullerene ArC_{60}

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Neutron powder diffraction studies have been carried out between room temperature and 15 K on C_{60} powder, which has been hot isostatically pressed (HIPed) under 170 MPa of Ar and at 300 °C to give ArC_{60}. Rietveld analysis of the neutron diffraction patterns confirms the stoichiometry, in agreement with our earlier x-ray analysis. This analysis shows the Ar to be trapped in octahedral interstitial sites of a fcc lattice with a unit cell of ~14.230 Å at 285 K, which is unexpectedly close to that of pure C_{60}~14.218 Å. A phase transition from an orientationally disordered fcc structure to an ordered simple cubic structure occurs on cooling between 245 and 250 K, which is lower than found for pure unHIPed C_{60} (255–260 K). The Rietveld refinement of the diffraction pattern at 15 K indicates that the Ar does not influence the orientation of the C_{60} molecules. [S0163-1829(97)00222-1]

Over the last few years the trapping of gases interstitially in fullerite materials has received considerable attention.[1–4] Recently,[5] we have shown through a Rietveld analysis of x-ray diffraction patterns from C_{60} hot isostatically pressed (HIPed) between 200 and 400 °C under 170 MPa of Ar, that Ar is forced into the face center cubic (fcc) lattice to form the stoichiometric compound ArC_{60}. The Ar was shown to be confined in octahedral lattice sites as similarly found for the intercalation of O_2.[1] The compound was found to be quite stable against loss of Ar at room temperature, with x-ray patterns several weeks later showing no change. In this paper we confirm this result using neutron diffraction. We are also able to show, through a temperature study, that a phase transition from fcc to simple cubic (sc) occurs between 240 and 245 K, in close analogy to that of pure C_{60} and similarly studied with neutron and x-ray diffraction by Heiney *et al.*[6]

Four grams of brown fcc C_{60} powder (ultra pure 99.95+%) was HIPed for 12 h at 300 °C under 170 MPa of Ar to form ArC_{60}. Both x-ray and neutron diffraction patterns were recorded before and after HIPing the C_{60} powder. Transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS) confirmed the presence of Ar in the sample after HIPing and the x-ray pattern from the HIPed sample was the same as previously found for ArC_{60}.[5] The neutron study of the pure C_{60} before and after HIPing was carried out over a temperature range of 15–285 K, using a neutron wavelength of 1.668 Å, a 2θ range of 4°–138° and with a stepsize of 0.1°. Diffraction patterns were recorded using the medium resolution powder diffractometer (MRPD) on the HIFAR nuclear reactor at ANSTO.[7] The samples were mounted in a closed cycle helium refrigerator allowing cooling down to 15 K. The neutron measurement of the C_{60}, before and after HIPing, allowed the phase transition temperature for pure C_{60} to be compared with that of the HIP produced ArC_{60}, both materials being measured under the same experimental conditions. It should be noted that the literature values for the fcc↔sc phase transition temperature for pure C_{60} are varied and both the presence of impurities[8–10] and the effects of stacking disorder[11] contribute to this. The use of ultrahigh-purity C_{60} and the dual study as described above circumvent some of these problems.

Figure 1 shows the neutron diffraction patterns from the Ar HIPed C_{60} sample over a range of temperatures from 15 to 285 K. The diffraction pattern changes between 245 and 250 K, indicating a phase change. Many more reflections are apparent at low temperature, due to a lowering of symmetry. This change is most salient in the 2θ range above 80°.

Figure 2 shows the fit of the neutron diffraction pattern from the Ar HIPed C_{60} sample taken at 285 K. A Rietveld refinement that fitted 130 reflections shows a reasonably good fit ($R_{\mathrm{Bragg}}=12\%$) for a cubic structure model of C_{60} in space group $Fm3m$, as previously found by our x-ray analysis.[5] The C_{60} molecules were similarly modeled using a spherical Bessel function $j_0=\sin(\kappa\cdot r)/(\kappa\cdot r)$which is tantamount to spreading the C atoms uniformly over the surface of a sphere of radius 3.54 Å, reflective of the unhindered rotational dynamics of the C_{60} molecules. The Ar occupied octahedral sites at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. The main error in the fit is in the reflections at low 2θ. This can be attributed to hexagonal stacking disorders which are generally associated with C_{60}.[11,12] the refinement is an improvement over that from the x rays which fitted only 21 reflections. The slower fall off of the neutron form factor allows reflections to be fitted over a wider 2θ range. The x-ray pattern also showed some indication of preferred orientation that was not adequately modeled in the fit, but this problem is absent in the neutron diffraction pattern due to the larger effective sample volume on account of the penetration of the neutron beam. The Rietveld analysis confirms that Ar sits in octahedral interstitial sites and the fit shows an occupancy of 100%, in agreement with the stoichiometry of ArC_{60}. Asterisks mark the position of two unidentified impurity lines which were present before HIPing, and which show no discernible changes with temperature. They have been ignored in the analysis.

What is also apparent are the broad diffuse peaks centered at ~50° and ~90° (2θ). These peaks are rather weak below the phase transition but are equally evident in the neutron diffraction patterns of pure C_{60}. The elastic diffuse scattering as observed in pure C_{60} has been thoroughly investigated by several groups both theoretically[13–15] and experimentally.[16–19,21–23] The expression for diffuse scattering can be broken into a term relating to a single molecule

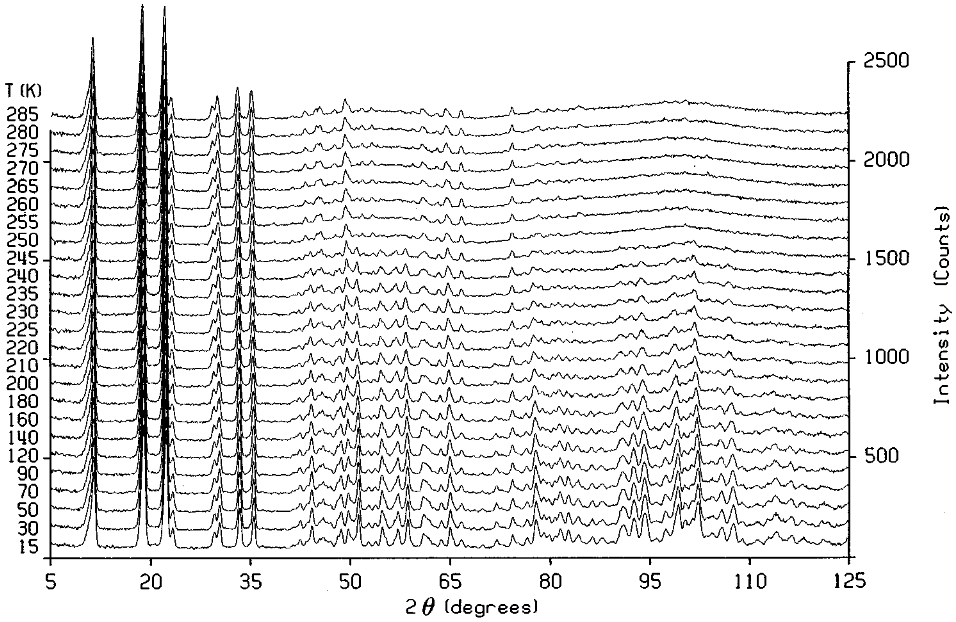

FIG. 1. The neutron diffraction patterns of ArC_{60} taken over the temperature range 15–285 K with a neutron wavelength of 1.668 Å and over a 2θ range of 5°–125°.

''self'' component and a so-called ''distinct'' component relating to the orientational correlations between the C_{60} molecules at different sites.[13] Without using such a more complete analysis utilizing multipole expansions for the molecular mass density and residual preferred orientation multipole expansions for the molecular mass density and residual preferred orientation we found we could reasonably model the diffuse scattering by just using pair correlation functions within an individual C_{60} molecule. A more detailed analysis as based on the current data is not warranted but will be the subject of a further study.

Figure 3 shows the neutron diffraction pattern for the HIPed sample at 15 K. To refine this pattern, we implemented a cubic structure model for C_{60} in the space group $Pa3$ based on that of David *et al.*[20] and 620 reflections were fitted. The C_{60} molecules were assumed to be nonrotating and the individual C atom positions were refined. The refinement showed a good fit ($R_{\mathrm{Bragg}}=8.0\%$) but the C atom positions were found to change slightly from the initial input positions of David *et al.*[20] Closer inspection of the refined atomic positions indicated that the shifts from the positions of David *et al.* do not significantly change the molecular shape or the orientations of the C_{60} molecules within the molecular lattice.

In all refinements the thermal vibrations were modeled with isotropic thermal parameters. This should be adequate for the thermal motion of argon atoms in a cubic environment, but is an oversimplification in the case of the carbon atoms in C_{60}. In the low-temperature phase this equates to a spherical thermal parameter at each carbon site, whereas in the high-temperature phase it equates to a spherical parameter for each C_{60} molecule in the unit cell. In fact a complete model of the carbon thermal motions in the low-temperature phase would include both librational and rotational components. A number of studies on the dynamics of C_{60} using neutron quasielastic and diffuse scattering, NMR, and optical

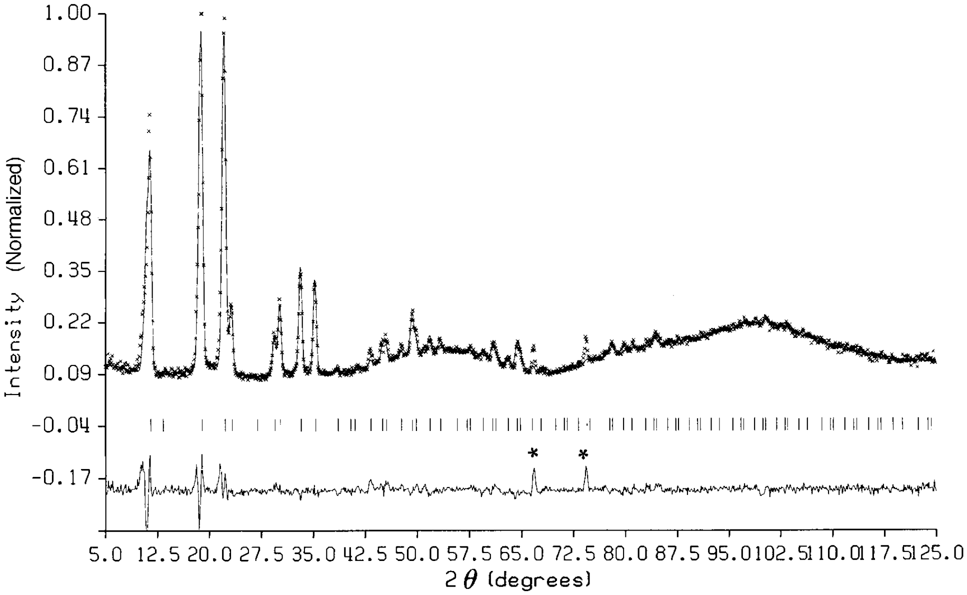

FIG. 2. The neutron diffraction pattern and Rietveld fit (superimposed) of ArC_{60} taken at 285 K, with a neutron wavelength of 1.668 Å and over a 2θ range of 5°–125°. Position markers for the allowed reflections are shown below the data. A plot of the difference between observed and fit is shown at the bottom of the figure. The two lines asterisked are associated with some undefined impurity phase which was initially present in the starting C_{60} material. Incidentally they are not associated with Cu, Al, or Ti and therefore cannot be associated with the neutron experiment.

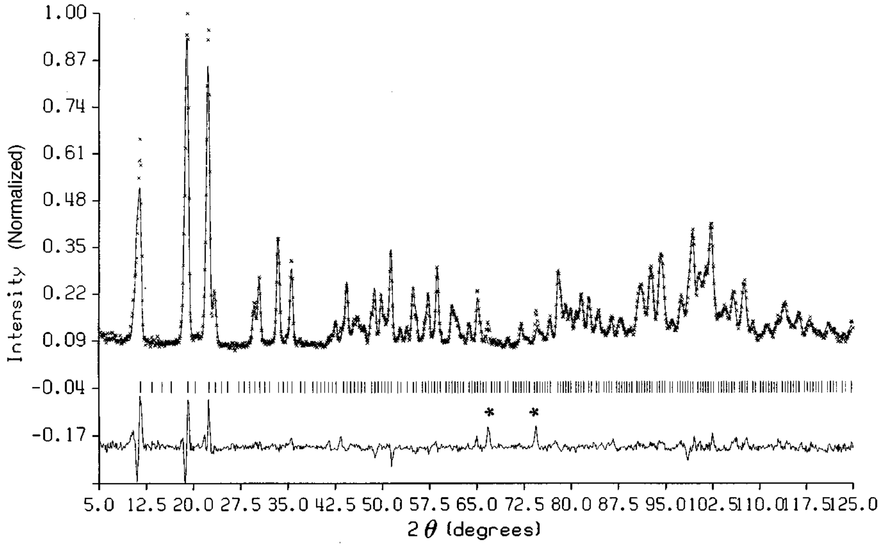

FIG. 3. The neutron diffraction pattern and Rietveld fit (superimposed) of ArC_{60} taken at 15 K, with a neutron wavelength of 1.668 Å and over a 2θ range of 5°–125°. Position markers for the allowed reflections are shown below the data. A plot of the difference between observed and fit is shown at the bottom of the figure. The two lines asterisked are explained in the figure caption for Fig. 2.

spectroscopy have been reported.[16–19,21–23] However, neutron powder diffraction is not sensitive to the details of these thermal motions and so a more sophisticated thermal model is unwarranted from the data presented here.

Initial refinements of the ArC_{60} patterns indicated that the value of the root mean square (rms) thermal displacement of argon was quite large at low temperature (~0.17 Å). Refinement at higher temperatures showed very little increase with increasing temperature and no significant discontinuity at the transition temperature. This is not surprising considering that the electrostatic interaction between argon and C_{60} is negligible, so we may reasonably expect the argon thermal excursions to vary only with the thermal expansion of the unit cell. Consequently the rms value of the thermal displacement of argon was fixed at the average value (0.25 Å) and refinements at all temperatures were repeated to obtain more reliable values of the carbon rms thermal displacements.

The molecular radius for C_{60} obtained from the high-temperature refinement, using a spherical shell, is found to be ~3.54(1) Å, in good agreement with the literature.[12,20,24] There is a disparity with our x-ray study which showed a slightly higher value of 3.58(1) Å. From the neutron study we find evidence for expansion on addition of Ar to the lattice of C_{60} in the fcc phase but surprisingly this is rather small (0.012±0.003 Å, at 285 K). The expansion as observed at 285 K, is actually less than the zero point motion of the C atoms at that temperature, which is of the order of 0.07 Å.[25,26] At 15 K in the simple cubic phase there is no evidence for expansion.

Figure 4(a) shows the trend of the lattice parameter with temperature for both pure C_{60} and ArC_{60}. The plots show a distinct jump at the fcc↔sc phase transition for both materials and the transition temperature for ArC_{60} occurs ~10 K lower. The data indicate that just above the fcc↔sc transition, the lattice parameter for ArC_{60} is very close to that of pure C_{60}, and is ~14.214±0.003 Å for ArC_{60} compared to 14.211±0.003 Å for pure C_{60}. This reflects the fact that the Ar does not interfere significantly with the van der Waals potential between neighboring C_{60} molecules, so the C_{60} molecules lock at the same separation as in pure C_{60}. Because the Ar seems to exert a gas pressure forcing the C_{60} molecules apart, the phase transition in ArC_{60} occurs at a lower temperature.

As the C_{60} molecules lock into their preferred orientation there is a noticeable reduction of the lattice parameter. This is clearly seen in Fig. 4(a). For pure C_{60} the change in the lattice parameter for the fcc↔sc transition is about 1.1% of the van der Waals radius of a C_{60} molecule (5.01 Å).[1] For ArC_{60}, the corresponding change is ~1.0%. Figure 4(a)

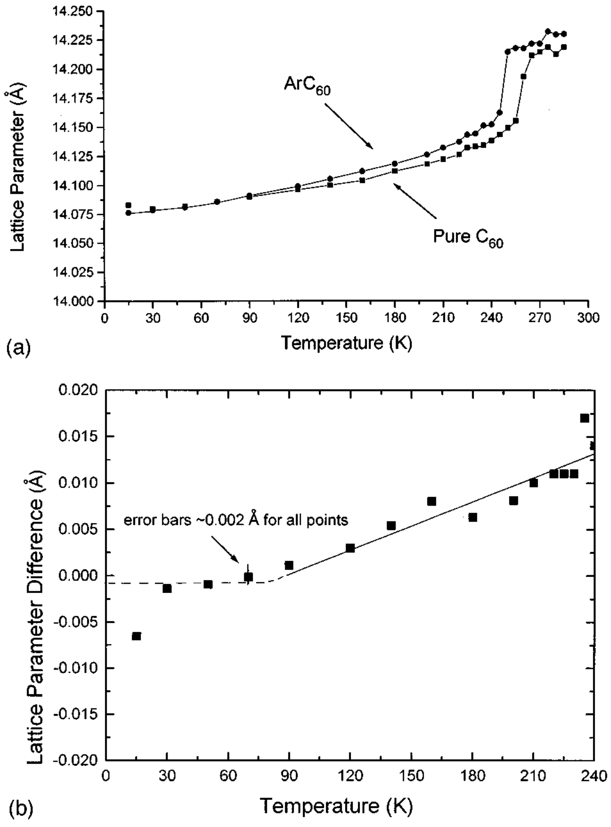

FIG. 4. (a) A plot of the lattice parameter for both ArC_{60} (●) and pure C_{60} (■), with temperature. (b) The difference in lattice parameter between ArC_{60} and pure C_{60} with temperature.

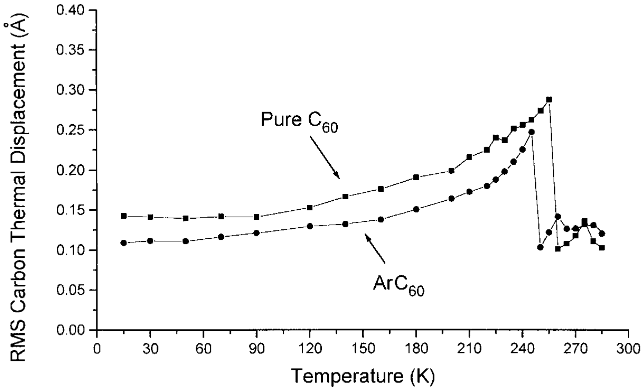

FIG. 5. A plot of the rms displacements for the carbon atoms with temperature for both ArC_{60} (●) and pure C_{60} (■).

shows that the lattice parameter below the phase transition is nearly the same for both solids. If we consider the reverse melting of sc→fcc a clearer picture for this phenomenon can be gained. At the lowest temperatures (15–30 K) the lattice parameter for both solids in the sc phase is the same within experimental error, but as we warm the sc solid phase the lattice begins to expand as the increased thermal energy of the lattice opposes the van der Waals attraction between the C_{60} molecules. Figure 4(a) shows beautifully that the lattice for ArC_{60} expands at a faster rate, which can be considered as due to increasing gas pressure inside the octahedral interstitial site (or increasing thermal energy associated with the free motion of the Ar atoms). Once the C_{60} molecules reach a critical separation, however, the C_{60} molecules unlock and the free rotating fcc phase ensues. It therefore appears that the Ar, apart from creating an internal pressure within the sc lattice, does not drastically interfere with the C_{60} interpotential.

The expansion of the sc lattice of ArC_{60} due to the internal pressure or thermal energy of the Ar alone is presented in Fig. 4(b), in which we have plotted the difference between ArC_{60} lattice parameter and that of C_{60} against temperature. The plot is linear above ~90 K and from a least-squares fit the thermal expansion above this temperature is 8×10^{-5} Å K^{-1}. If we assume the Ar to behave as an ideal gas in a fixed volume, then we can estimate the lattice expansion with respect to the internal pressure due to the Ar. Assuming that the available volume for the Ar is the volume of the octahedral interstitial site (2.06 Å radius, volume 37 $Å^3$), and using the ideal gas equation we obtain for dP/dT the value ~0.37 MPa K^{-1}. This used in conjunction with the Ar only thermal expansion gives a lattice expansion with internal Ar pressure of 2.2×10^{-4} Å MPA^{-1}. Considering the crudity of this calculation, the value compares favorably with the experimental value of 3.6×10^{-4} Å MPa^{-1} obtained by Schirber *et al.*,[2] studying the compressibility of C_{60} with gases.

In Fig. 4(b) it appears that the gas pressure is zero below 90 K, indicating that the rare gas atom is experiencing the shallow well region of the van der Waals potential and at

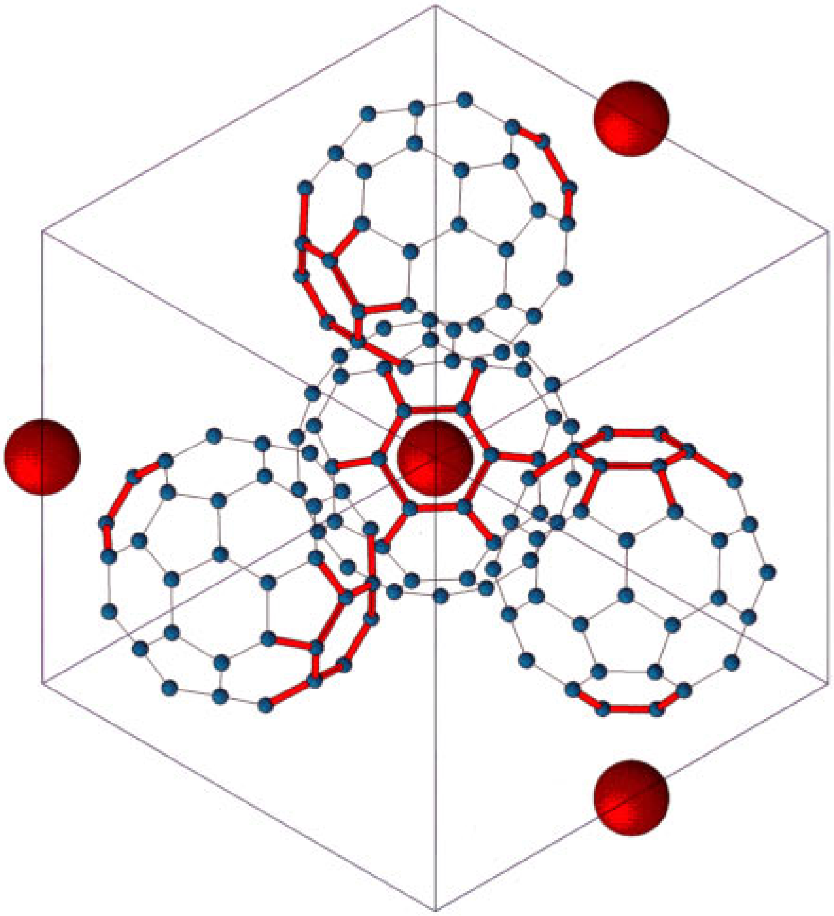

FIG. 6. (Color) A view along the ⟨111⟩ axis, with each C_{60} molecule rotated 98° counterclockwise about the ⟨111⟩ axis giving the lattice cell in a $Pa3$ space group, as found at low temperatures by David *et al.* (Ref. 20) for pure C_{60}. This structure fits the Rietveld refinement of the low-temperature (15 K) neutron diffraction pattern of ArC_{60}. The position of the interstitial argon atoms is shown.

temperatures below 90 K the motion of the Ar is best described as a large amplitude vibration. Above 90 K the motion is one of translational motion within the interstitial site with basically hard body collisions with the carbon atoms.

Figure 5 shows a plot of the carbon rms displacements with temperature for both ArC_{60} and pure C_{60}. They are positive and increase from ~ 0.1 Å to the transition temperature. The increase is nonlinear and at the transition temperature attains a value of ~ 0.3 Å for both materials. At the transition temperature there is a sharp drop of ~ 0.15 Å. The extreme change over the fcc↔sc phase transition indicates that the structural transition coincides with a discontinuity in the vibrational modes. The thermal displacements for carbon reflect that in the fcc phase, near the transition temperature, the motion of the C_{60} molecules is one of free rotation with little intermolecular vibration. On locking into position in the simple cubic ratchet phase, there is an appreciable amount of librational motion vibrations (~ 0.25 Å) of the Ar atoms (even at 15 K where the Ar is not apparently exerting any pressure) indicate the freedom of argon atoms to move inside the octahedral site. As a consequence, the contribution of Ar to peak intensities diminishes rapidly with increasing angle, making it difficult to accurately determine the value of the rms thermal displacement.

Although there is a small discrepancy between the carbon atom positions for the low-temperature phase as found in our refinement as compared to that of David *et al.*,[20] the overall alignment of the C_{60} molecules is not changed from the 98° rotation about the [111] direction from the ideal $Fm3m$ configuration. Figure 6 shows the unique alignment of the C_{60} molecules in this $Pa3$ structure of ArC_{60}, looking down the [111] axis. The interstitial nature of the Ar atoms is seen as well as the threefold nature of the lattice which is reduced from $Fm3m$ to $Pa3$ by the 98° rotation of the C_{60} molecules from the standard $Fm3m$ arrangement.[8,27] David *et al.*[28] have also incorporated a percentage of molecules with a 38° rotation to obtain a better fit for the low-temperature phase. We have not considered this variation in this preliminary study but it would be interesting to see if the Ar in any way subtly affects such a more complex model.

We conclude by saying that these initial neutron diffraction studies confirm not only the stoichiometry of the compound ArC_{60}, but also the octahedral confinement of the trapped Ar in the lattice of C_{60}. The study shows a phase transition from fcc to primitive cubic to occur between 245 and 250 K, which is 10 K lower than that found for pure C_{60}.[6] The rare gas fullerene bears an interesting comparison to the ionic counterparts formed between the alkali metals (e.g., Na, K, Rb, Cs) and C_{60}.[29–31] Whereas the alkali metals are able to transfer electrons to the C_{60} cage structure forming a whole range of negative ions, e.g., the C_{60}^{3-} anion in K_3C_{60}, there is no evidence for this in the rare gas fullerene, as one would intuitively expect. The behavior of the rare gas fullerene is very much like that of the parent C_{60} material even though it has an atom trapped interstitially which is of reasonable size. The orientational dynamics of the C_{60} molecules are hardly affected by the presence of the Ar rare gas atoms and the C_{60} molecules orientationally freeze as in pure C_{60}, when the lattice reaches some nominal value. In ArC_{60}, because the gas exerts an interstitial pressure, a colder temperature is needed to contract the lattice to this value, resulting in a lower transition temperature. On the contrary, if we consider A_3C_{60}, for example, the behavior of the lattice is changed completely. Because of the electron transfer, electrostatic forces become very important in controlling the behavior and structure of the lattice. The forces acting on the C_{60} molecules result in only two orientations with respect to the cubic lattice, where a six-membered ring is pointed towards a tetrahedral site. In these configurations the tetrahedral sites are larger, allowing their occupancy. In the rare gas fullerene material the guest-host forces do not exist due to the absence of electron transfer and we only observe octahedral occupancy. Unlike the rare gas fullerene and pure C_{60} materials, the alkali-doped materials exhibit larger angular barriers in the potential and the C_{60} anions are not freely rotating at room temperature although NMR shows evidence for hopping between the two orientations on a 50 μs timescale.[32] Because of this the usual phase transition characteristics of C_{60} is not observed and the material at room temperature exists as a completely three-dimensional disordered material with 50% of the C_{60} molecules in each orientation.

In a recent paper, Morosin *et al.*[33] have reported the intercalation of Ne into C_{60} at room temperature and using high pressures of Ne gas (0–3 kbar). Through a Rietveld analysis of time-of-flight neutron powder diffraction, they have also shown that the Ne only occupies the octahedral interstitial sites. Their quoted lattice expansion for a full occupancy of the octahedral sites with Ne (0.02 Å) is significantly higher than what we found for Ar (0.012 Å), and until we reproduce their experiment no further comparison will be made.

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