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Ne-intercalated C_{60}: Pressure dependence of Ne-site occupancies

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We report the Rietveld refinement of the structures of inert gas (Ne)-intercalated C_{60} using time-of-flight neutron powder diffraction data. Various pressures to ~2.5 kbar at room temperature were employed. We find that only the octahedral interstices are occupied by the Ne intercalate. The pressure dependence of the Ne occupancies in the octahedral site has been determined. The cubic lattice parameter increases linearly with the amount of intercalated Ne.

I. INTRODUCTION

We recently reported measurements to 6 kbar of the room-temperature compressibilities of C_{60} using He, Ne, and Ar as pressure media.[1] For He and Ne, the compressibilities are reduced by intercalation of the noble gas atoms into the C_{60} lattice. These results were consistent with earlier literature studies[2,3] in that He was found to intercalate easily, resulting in a substantially higher transition pressure for the $Fm3m$(fcc)-$Pa3$(sc) orientational ordering pressure, while Ar did not penetrate the lattice, yielding a transition pressure typical for other nonpenetrating media such as pentane or N_2. Ne was shown to slowly penetrate the lattice and the transition pressure was intermediate to that found with He and Ar. The lattice parameters were consistent with the change in the transition temperature in that the values were slightly larger for He, and smaller for Ar, than those for Ne at a particular pressure. The transition takes place with all three gases at a lattice parameter $a \cong 14.065$ Å with increasing pressure at room temperature[1] compared with the value of David *et al.*[3] measured on cooling at 1 bar, $a = 14.150$ Å.

Such lattice parameter differences might be the result of differences in the occupancy of the octahedral and tetrahedral interstices of the C_{60} lattice. It was learned soon after the discovery of C_{60} that this material could be intercalated with alkali metals to form superconductors in which both of these sites are occupied.[4] In our previous study, most of the data were collected for a length of time (~1 h) adequate for lattice parameters within a typical statistical standard deviation of 0.0005 Å (0.0007 Å in our 10-min runs), but not adequate for full refinement of structural models to determine which sites the inert gas atoms were occupying.[1] We report here Rietveld structural refinement using neutron-powder-diffraction data on Ne-intercalated C_{60} at various pressures to ~2.5 kbar at room temperature.

II. EXPERIMENT

C_{60} (99.6% nominal purity) from commercial sources was subjected to slow progressive heating in vacuum up to 400 °C for several days in order to remove all solvents and occluded N_2 and O_2. The powdered sample (~3 g) was loaded into a thin walled vanadium tube that was inserted into the aluminum pressure cell described in detail elsewhere.[5] Data were collected at room temperature (296 K) on the 90-degree detector banks of the Special Environment Powder Diffractometer at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS).[6] Due to shielding that is an integral part of the pressure cell, this scattering angle provides data that are completely free from direct diffracted scattering from the walls of the cell which would contribute to the background scattering. However, multiple scattering events contribute about 3–4 % of the background scattering at higher q's in addition to the expected large disorder background scattering[7] for C_{60}. Corrections for both of these contributions to the background were included in our Rietveld refinements.

In the previous series of experiments in which Ne was used as the pressure medium,[1] it was established that intercalation occurred over hours, requiring up to 24 h to reach equilibrium at the highest pressures (~6 kbar) and substantially less time (~5 h) at pressures within the range of the fcc phase. For the present study, after making sudden changes in pressure (for example, from either a beginning 1-bar pressure or some other already attained pressure), diffraction data were collected in sequential runs to monitor the time-dependent change of lattice parameters as they approached equilibrium values. Figure 1 shows an example of the lattice parameter change from such a sequence of runs. Data for times where the lattice parameters were constant (within 2 standard deviations) were then summed to produce a data set with enough statistics for full Rietveld refinement. Such data

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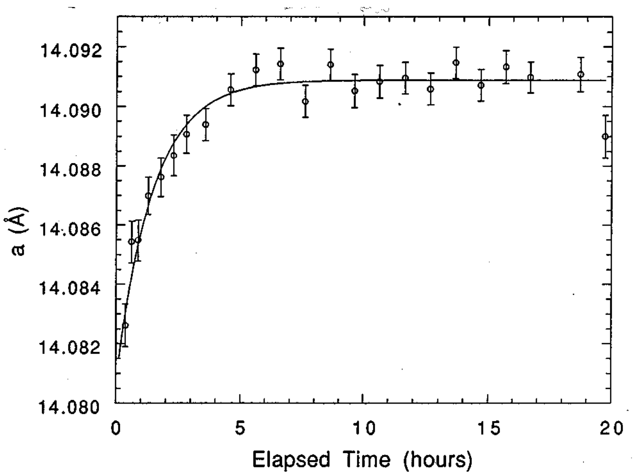

FIG. 1. Lattice parameter vs time for a C_{60} sample exposed to 2.1-kbar Ne. The material remains in the fcc phase with increasing lattice parameter as the Ne intercalates and appears to saturate after about 6 h. In this case, the data set used in the refinement was the sum of data collected after 5 h.

sets contained 5–17 h of data.

For the least-squares refinement of the structure, we used a modified version of the time-of-flight Rietveld code available at IPNS.[8] The modifications included the use of a molecular spherical shell scattering form factors for the rotating C_{60} balls and a contribution to the background derived from the expected diffuse scattering arising from disorder as has been previously used by Copley *et al.*[7] These modifications allowed reasonably good refinements to be done, but the background was still not adequately modeled at d spacings below about 1.3 Å. To extend the d-spacing range of our refinements to about 0.55 Å, we used Fourier-filtered background fitting techniques as described by Richardson and Faber.[9] An example of a refinement using these procedures is shown in Fig. 2.

III. RESULTS AND DISCUSSION

From our least-squares refinements, it was immediately learned that all of the Ne was in the octahedral sites. Tetrahedral site occupancies were essentially zero for all pressures. Thus, the tetrahedral site occupancy was set to zero in the final refinements. It was found that even with the inclusion of data to a d spacing of 0.55 Å we could not independently refine the site occupancy and the temperature factor for the Ne in the octahedral site. We speculate that this occurs because the vibration of the Ne in the large irregularly shaped "box" bound by the six C_{60} molecules, essentially a "square-well" system, cannot be perfectly modeled by any harmonic model, as used in the Rietveld code. The situation is somewhat different in alkali-metal C_{60} compounds in that electrostatic forces maintain the cation in essentially a deep harmonic well about its equilibrium position. In those cases, successful refinement of both the occupancies and thermal parameters using synchrotron x-ray data is also aided by the more favorable scattering (form) factor ratio between the alkali metals and the carbons forming C_{60}.[10] Thus, to refine site occupancies, we fixed the temperature factor for Ne at $B=13$ Å^2. This gives a site occupancy approaching one at the highest pressures. Values higher than one are not physically allowed,[11] so the choice of a larger value of B would lead to unphysical results. Smaller values of B_{Ne} would lead to smaller site occupancies. For example, if we assume a probably low value of $B_{Ne}=5$ Å^2, at the highest pressures we obtain $n_{Ne}=0.67$. This uncertainty in our determination of the absolute values of the Ne site occupancy cannot be avoided. However, the behavior of the site occupancy versus loading pressure is clear.

On the 14 new data sets, $R(p)$ and $R(wp)$, the usual

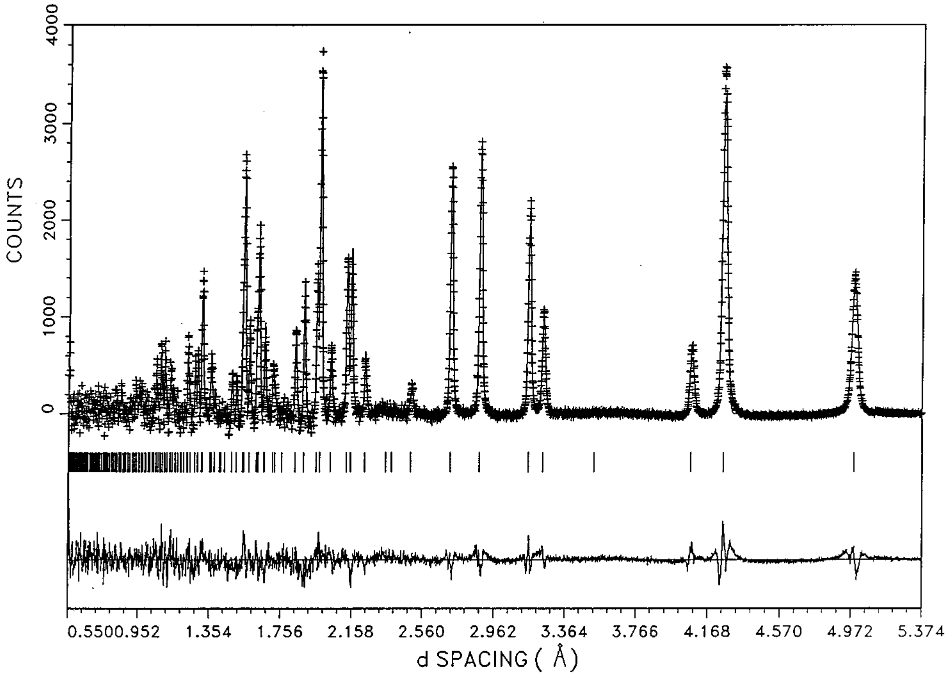

FIG. 2. Neutron diffraction data for C_{60} Ne at 1.55-kbar pressure. The continuous line through the sets of points is the calculated profile from the Rietveld refinement, the set of tick marks below the data indicate the positions for the allowed reflections, and the lower curve represents the difference between observed and calculated profiles.

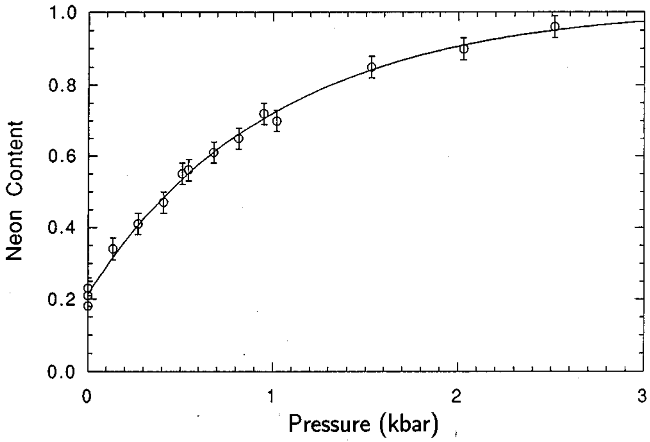

FIG. 3. Ne octahedral site occupancy vs pressure. The temperature factor, B(Ne), is set to 13.0 Å^2 in these refinements.

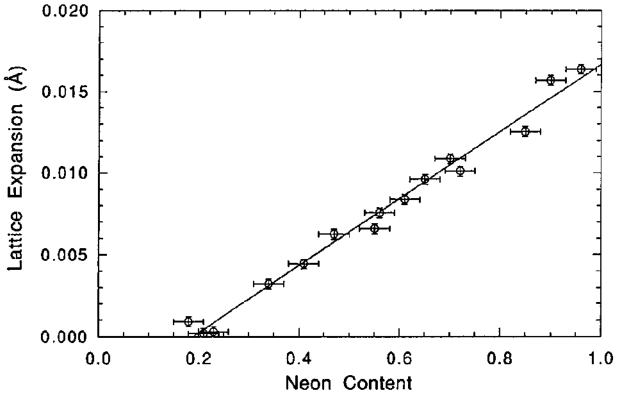

FIG. 4. Lattice parameter expansion due to Ne intercalation vs the amount of intercalated Ne. The expansion is determined by subtracting the lattice parameter for a C_{60} sample pressurized in Ar to the same pressure (Ref. 1).

residuals for the peaks in the spectra for unweighed and weighted intensities, respectively, expressed as a percentage averaged 2.49(17) and 4.87(22), respectively, and ranged from 2.19 to 2.75 and 4.38 to 5.21, being correlated, as expected, with hours of run time. The thermal parameter for C_{60} averaged 1.34(11) Å^2 (range 1.13–1.57) and does not appear to correlate with either run time or gas pressure. An interesting observation is that the incremental change in the lattice parameter is largest between our 1 bar and the lowest pressurized point at 0.14 kbar, with the corresponding Ne occupancy increasing from 0.21 to 0.34, also the largest increment. The most rapid loading occurs at the lowest pressures. Our 1-bar Ne pressure points (3 data sets) average 14.16043(27) Å and can be compared with a value of 14.16076(20) Å from a similarly refined 1-bar data set with an identical d-space span from a sample exposed only to Ar.[12]

The Ne octahedral site occupancy versus loading pressure is shown in Fig. 3. The Ne octahedral site occupancy increases smoothly from near 0.21 to 0.96 as Ne pressure is increased from 1 bar to ~2.5 kbar. The data demonstrate an apparent concentration saturation as the number of intercalates approach 1.0, the limit based on space considerations.[11] These data have been fit with the equation

$$n_{\mathrm{Ne}}(P)=n_0+\Delta n\ \exp(-P/P_0),$$

where the best-fit values for the coefficients are $n_0=1.01(4)$, $\Delta n=-0.80(4)$, and $P_0=0.99(11)$ kbar. All the points fit on such a curve within the experimental standard deviations for the octahedral site occupancies.

One puzzling feature of the behavior we observe is that the refined Ne content at 1 bar is not zero. There may be several possibilities for this result. We believe the most probable one is that there may be some residual gas, Ne itself, but most probably N_2 as an impurity in the Ar and Ne gases, which does not leak out in the time scale of the present experiments.[13] We also note that the scattering length for N ($b_{\mathrm{N}}=0.930$) is larger than that for Ne ($b_{\mathrm{Ne}}=0.455$) and that as a N_2 entity, only a 5% intercalation would be necessary to explain the observed scattering content of the 1-bar samples. On the other hand, thermogravimetric analysis (TGA) experiments to 300 °C to confirm such an idea have not shown any evidence for intercalated gas atoms. However, our sample preparation procedure usually employed 400 °C in vacuum to remove occluded gases. Further, there may be a systematic error in the analysis due to something we have not modeled correctly. This is supported by the fact that there are differences between the actual and modeled line shapes as seen in the Rietveld refined models (see Fig. 2) and, as pointed out previously, the harmonic potential model for the thermal parameters is admittedly not adequate for this material. With so few structure parameters available in the problem, errors might accumulate on the Ne-site occupancy parameter.

As we noted in our earlier paper,[1] the presence of Ne (or He) in the interstitial sites gives systematically larger lattice parameters at a particular gas pressure than in their absence (Ar pressurized values; within the experimental uncertainty of these lattice parameter values, a perfectly straight line is found to ~2.5 kbar). The dependence of these lattice parameter differences on Ne site occupancy is shown in Fig. 4. This lattice parameter difference, or offset, proves interesting in that it, rather than a cell volume difference, scales with Ne-site occupancy.

Since the octahedral site is much larger than the intercalated Ne and since only one Ne can occupy each site,[11] we would expect the Ne to be attracted to the walls of the cage by weak van der Waals forces in the low-temperature limit. As the temperature increases to values larger than the van der Waals well depth, the Ne atom will begin to move freely within the cage and its kinetic energy will exert a proportionate pressure on the walls that scales with occupancy. In the high-pressure limit, the expected behavior is similar to the problem of packing of hard spheres with a large size dissimilarity, which has been addressed with molecular dynamics calculations.[14] The increasing internal pressure, just like decreasing external pressure, is expected to give essentially the linear expansion that we have observed. We believe that this is the first observation of this effect in a realistic physical system.

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[11] The occupancy of the octahedral *O* site and probable zero occupancy of the tetrahedral *T* site may be justified by considering the radii for He, Ne, and Ar. Values obtained from the known low-temperature solids [J. D. H. Donnay and H. M. Ondik, *Crystal Data,* 3rd ed. (National Bureau of Standards/Joint Committee on Powder Diffraction Standards, Washington, D.C., 1973), Vol. II] are 1.499, 1.572, and 1.878 Å, respectively, for He, Ne, and Ar. The *O* sites (radius ∼2.06 Å) are sufficiently large to even accept an Ar atom, but only one atom. With Ne, the *O* site is sufficiently large with excess space (≅0.6 Å) and the weak forces suggests that the intercalated inert gas atom probably acts as a particle in a box. The temperature factors may also be expected to have a large contribution from the zero point B_0 [see, for example, Table 3.3.5.1c in Int. Tables X-ray Crystallogr. **III**, 238 (1959)]. The *T* sites (radius ∼1.1 Å), on the other hand, are too small even for a He atom. The real issue might be transport through the cavity channels between the *O* and *T* sites (radius ∼0.82 Å).

[12] The previous experimental history of this sample at this point included a 6-day soak at over 5-kbar Ar pressure, subsequent series of ∼1-h runs for the lattice parameters reported in Ref. 1 to a point when pressure was released to 1 bar. Subsequently, after further Ar runs, a few 3–4-kbar He runs were followed by release to 1 bar.

[13] The "half life" of H_2 and O_2 in C_{60} have been determined by NMR; see R. A. Assink, J. E. Schirber, D. Loy, B. Morosin, and G. A. Carlson, J. Mater. Res. **7**, 2136 (1992). TGA-type measurements suggest the half life of N_2 is of the order of 7 h; see J. E. Schirber, R. A. Assink, G. A. Samara, B. Morosin, and D. Loy, Phys. Rev. B **51**, 15 552 (1995).

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