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Ne intercalated C_{60}: Diffusion kinetics

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In situ neutron powder-diffraction has been used to probe the Ne content and diffusion kinetics in C_{60} by monitoring the C_{60} lattice parameter vs time following step changes in applied Ne pressure. In the face-centered-cubic phase where the C_{60} molecules are freely rotating, diffusion is slower for higher Ne pressure. In the primitive cubic phase where the C_{60} molecules are orientationally ordered, the diffusion rate is slower and is essentially independent of pressure. These observations can be understood in terms of three unequal competing effects: (1) Increasing the external Ne pressure increases the driving force for diffusion; (2) compression of the C_{60} lattice slows diffusion with increasing pressure; and, the major one, (3) C_{60} molecular dynamics enables and enhances diffusion by a thermally activated ''paddle wheel'' effect. The activation energy for such Ne intercalated C_{60} reorientational hopping or rotation (~1500 K or 13 kJ/mole) is less than that in pure C_{60} (~2600 K or 22 kJ/mole), suggesting the Ne atoms act as ''roller bearings.'' [S0163-1829(99)01309-0]

INTRODUCTION

Fullerenes have been shown to intercalate various gases at different rates and this has raised the possibility of employing these materials as filters for gas separation.[1–3] Early data also showed that the orientational ordering transition temperature is affected by the gases used under such pressure experiments and intercalated into the interstices.[3–6] At the face-centered-cubic (fcc in $Fm3m$) to simple cubic (sc in $Pa3$) orientational ordering transition (260 K at ambient pressure; between ~2.4 and 3.2 kbar at room temperature), the motion of the C_{60} molecules changes from essentially free, uncorrelated rotation to hopping between two similar energy, but distinct, orientations.[7–9] For the inert gases He, Ne, and Ar at 0–6 kbar pressure and room temperature, this transition was shown to occur at a pressure which is highest for He, intermediate for Ne, and smallest for Ar, but at the same lattice parameter, equal to 14.042 Å, the average of the fcc and sc values at the transition.[4–6] This may be compared with the corresponding 14.125 Å value[9] found on cooling pure C_{60} at 1 bar. At room temperature, Ar did not intercalate while He was shown to do so easily.[10] With Ne, the intercalation kinetics were of the order of hours, so that insertion could be monitored using lattice parameter changes as a function of time following step changes in Ne pressure. Some unusual diffusion kinetics during loading and unloading Ne were observed prompting the present studies to better understand the contribution of the C_{60} dynamics to intercalation kinetics.

EXPERIMENTAL AND DATA EVALUATION

C_{60} (99.6% nominal purity) from commercial sources was sieved to remove larger particles (>0.105 mm) and then subjected to slow progressive heating in vacuum up to 500 °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 which was inserted into the aluminum pressure vessel cooled by a Displex refrigerator (described in detail elsewhere[11]). Data were collected at various temperatures on the 90 degree detector banks of the Special Environment Powder Diffractometer at Argonne National Laboratory's Intense Pulsed Neutron Source (IPNS).[12] 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. Corrections were included in our Rietveld refinements for the expected large disorder background scattering[13] resulting from the motion of the C_{60}.

In our previous series of experiments in which Ne was used as the pressure medium, it was established that intercalation occurred over times of hours, requiring more than 24 h to reach equilibrium at the highest pressures (~ 6 kbar) and

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substantially less time (~ 5 h) at pressures within the range of the fcc phase (<2.4 kbar at 300 K).[5–7] Further, our previous study showed that the lattice parameter value at a given pressure was reproducible from either direction, increasing or decreasing pressure of arbitrary step size after waiting for the intercalation to proceed to completion. For the present study, after making step changes in pressure (for example, from either a beginning 1 bar pressure or some other already attained pressure), time-of-flight diffraction data were collected in sequential short-time runs to monitor the time-dependent change of the lattice parameter as it approached an equilibrium value (for an example, see Fig. 3 of Ref. 5).

The entire set of points for the lattice parameter a at time t for a particular pressure change run were least-squares fit to the function

$$a(t)=a_0+(a_f-a_0)\exp(-t/\tau),$$

where a_0 is the lattice parameter for C_{60} at the beginning of the run (usually that with no intercalated Ne), a_f is the final lattice parameter at long times, achieved when C_{60} is loaded to its solubility limit with Ne at the experimental pressure, and τ is a time constant for the intercalation. a_0, a_f, and τ are all functions of pressure. This function is the simplest form of the standard equation that expresses the average concentration of a diffusing species inside a spherical particle as a function of time as the diffusing species enters the particle from the surface. This equation may be applied to the problem of Ne diffusion into C_{60} and fits the lattice parameter data reasonably well. It is based on the following assumptions:

(a) The C_{60} particle size is nominally the same for all particles in the sample and does not change during the course of the experiment. It is believed that this assumption is fairly well met after the first loading to maximum pressure (6 kbar) and subsequent release at room temperature (see below).

(b) The lattice parameter of intercalated C_{60} is a linear function of the Ne content. Our previous study (Fig. 4 of Ref. 5) showed a linear expansion of the lattice when the repulsive contribution of the Ne exceeded that of the attractive force between the C_{60} at a Ne content of ~20%.

(c) The gradient of Ne concentration from the surface to the interior of the particle can be ignored. This gradient gives rise to a strain in the particles during the loading process as the volume increases which results in broadening of the diffraction peaks and is evident during early times of typical runs. As the particles become homogeneous, the peaks sharpen. Figure 1 shows such peak width broadening vs time for a typical run. The peak width increases by about 50%, reaching a maximum at an elapsed time of approximately $\tau/2$ and then relaxes to its normal value at longer times. This change in peak width is easily fit as part of the data analysis, and the refined lattice parameter is a valid measure of the average Ne concentration inside the C_{60} particle at all times. This behavior of the peak width confirms that diffusion inside the C_{60} particle, not a surface barrier effect, is the limiting step in the intercalation process.

(d) No subtle phase transitions nor changes in the mechanism by which Ne intercalates occur as a function of concentration or pressure. This assumption may not be met completely. On the higher pressure runs some reproducible oscillatory patterns of a vs t were noted during the intercalation process. Figure 2 illustrates this behavior for several runs at pressures above 3.5 kbar in the sc phase. The changing lattice parameter appears to hesitate at particular values as if the system is undergoing a ''staging'' process. It is noted, however, that no weak diffraction lines indicating a multiple cell nor intensity changes suggesting a structural modification were seen in any of the data.

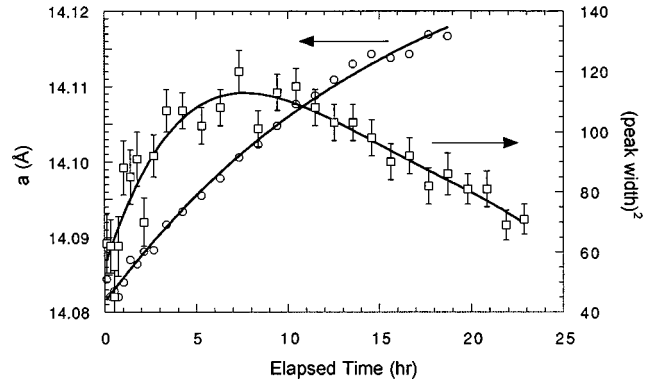

FIG. 1. Peak width parameter vs time for a typical run. Peak broadening occurs during early times of the intercalation process but narrows again as the particles become homogeneous in Ne concentration.

The study is instrument-time-intensive which limited the number of runs. In addition there were constraints set by the cell with respect to its high pressure and high-temperature limit, by the phase diagram with its fcc-sc transition, and by the slower kinetics of the sc phase at lower temperatures. Our data reported here primarily consist of runs at room temperature with various increasing and decreasing pressure jumps, but also include selected experiments at 200, 240, 265, and 340 K, which allow an estimate of the activation energy of the intercalation process to be made.

RESULTS AND DISCUSSION

A. Intercalation dynamics

Several qualitative features of the intercalation process were immediately seen in our early room-temperature work:

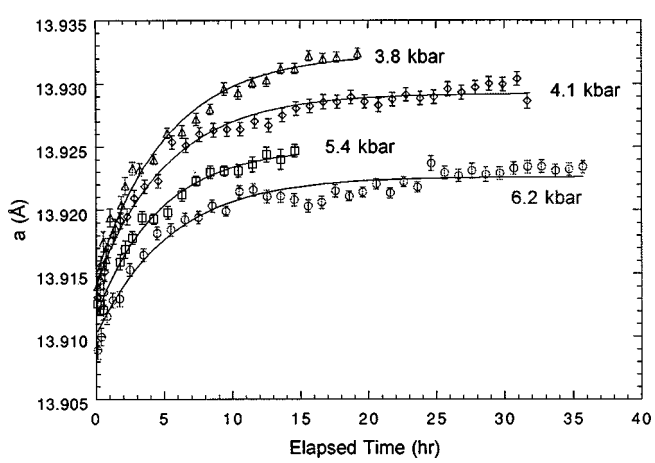

FIG. 2. Lattice parameter vs time for C_{60} samples exposed to Ne at pressures above 3.5 kbar in the sc phase. Note the oscillatory behavior of a vs t in several experimental runs.

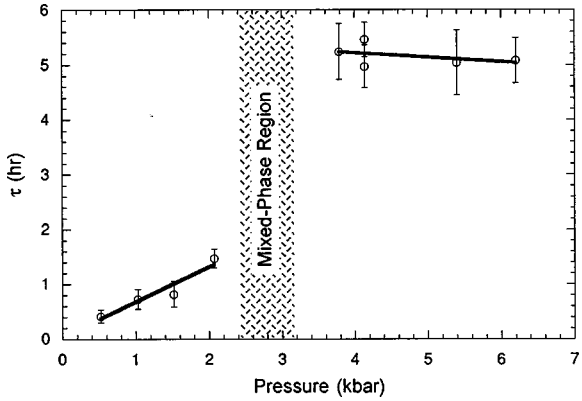

FIG. 3. Time constant for loading Ne into C_{60} at room temperature as a function of loading pressure. An increase in τ values is noted at the $Fm3m$(fcc)-$Pa3$(sc) orientational ordering transition. The width of the two-phase region is taken from our previous study (Ref. 4).

Namely, that the diffusion of the Ne into C_{60} (loading) in the fcc phase is slower for larger Ne pressure steps, that the diffusion in the sc phase is much slower than in the fcc phase, and that the diffusion out of the pressurized C_{60} (unloading) is extremely rapid. Figure 3 compares the time constants obtained in fitting runs of the lattice parameters for various loading steps from 1 bar at room temperature (300 K). There is a marked difference in the behavior of the time constants τ with respect to Ne pressure in the two phases; the large pressure dependence seen in the fcc phase is absent in the sc phase. Within the error of the measurements, the data for τ vs pressure in the fcc phase can be fit by a straight line. Based on the ideas used to explain the pressure dependence discussed below, it is likely that τ becomes rapidly larger as the fcc-sc transition is approached; but, no data to test this hypothesis is available. Figure 3 also shows our τ values in the sc phase. These τ values are significantly larger than those determined for the fcc phase. Also the τ values show somewhat larger statistical errors than those for the fcc phase. This may result, in part, from run truncation at long times and/or from unexplained jitter of the lattice parameter points at the beginning of some, but not all, of the high-pressure runs; the other possible contributing factor was the possible ''staging'' effect noted above. The least-squares-fit line shown in Fig. 3 through these sc τ values shows essentially no pressure dependence.

With no intercalated Ne, the fcc-sc transition occurs over the pressure range 2.4–2.7 kbar.[4] With Ne intercalation at the solubility limit, the transition occurs over the pressure range 2.9–3.2 kbar. Thus, for partial intercalation, the transition can be anywhere in the pressure range 2.4–3.2 kbar. Measurements of the intercalation kinetics cannot be made in this pressure range because the fcc-sc transition will occur at some time during the intercalation process, producing a change in the lattice parameter that has a larger effect than that resulting from the intercalation process. This pressure range is indicated as a mixed-phase region in Fig. 3.

The intercalation process can be understood in terms of competing pressure-dependent effects: Increasing the external Ne pressure (a) increases the driving force for diffusion (the usual definition of diffusion of the flux being proportional to the gradient of concentration) but also (b) reduces the space between the nearly incompressible C_{60} molecules constricting the paths for Ne diffusion. Additionally, pressure could have a pronounced effect on the contribution of C_{60} rotational motion to the Ne diffusion. The rotating C_{60} molecules may be viewed as ''paddle wheels,''[14] which assist the Ne through the narrow channels between the octahedral sites (and through tetrahedral sites, which remain empty[5]). In the fcc phase below 2.4 kbar, the C_{60} molecules are essentially rotating freely. Results at 1 bar demonstrate that even at 280 K, the C_{60} molecular rotation is very rapid, with reorientational correlation times[8] around 9×10^{-12} s.

In the sc phase, the C_{60} molecules no longer rotate freely; they are hopping between two positional orientations of approximately equal energy.[7] One of these orientations corresponds to a structural packing arrangement with the lower energy (though curiously larger volume) which involves having electron-rich interpentagon double bonds pointing towards electron-poor pentagonal faces of neighboring C_{60} molecules. For the marginally higher energy ($\sim$122 K or 1.06 kJ/mole) orientation, these double bonds point towards electron-poor hexagonal faces.[7] These two orientations were shown to be reached by hops of $\sim$42° about $\langle 110\rangle$ directions with an activation energy of some 2600 K (22.6 kJ/mole), a magnitude with significant implications for the reorientational correlation times which followed an Arrhenius behavior.[7] At 1 bar and 260 K, the reorientational correlation times[7] are of the order of 10^{-9} s; thus, the onset of the transition involves a hundredfold increase of the reorientational correlation times.

The most important contribution to Ne diffusion is the C_{60} molecular rotation. While in the fcc phase, there is a rapid free rotation; in the sc phase, there are rapid hops of limited rotational angle separated by comparatively long times when the molecule rotationally liberates around a particular orientation. The next hop is just as likely to be in the positive direction (i.e., same direction as the last hop) or negative direction. Thus, regardless of the reorientational correlation time, such a hopping does not contribute to Ne diffusion in a way that is qualitatively the same as for complete free rotation. This means that the paddle wheel mode of diffusion is not operative in the sc phase. This lack of rotation in the sc phase provides a qualitative explanation for the longer diffusion time constants (Fig. 3).

Data for the sc phase provide a measure of the competing pressure-dependent effects of increased driving force for the diffusion and constriction of the diffusion paths with increasing pressure. The near zero pressure dependence of τ in the sc phase suggests that these two effects cancel one another. Since the lattice compression is essentially identical in the fcc and sc phases $[(da/dP)/a=0.0026\,\mathrm{kbar}^{-1}$ in the fcc phase and 0.0023 kbar^{-1} in the sc phase], it is logical to assume that these two effects also cancel one another in the fcc phase. Note that since the C_{60} molecules are nearly incompressible, most of this lattice compression is subjected upon the channel dimensions corresponding to a significant reduction of $\sim$10% over the pressure range of our experiments (0–6 kbar). Thus, the pressure dependence of τ in the fcc phase must be attributed to the effect of pressure on the contribution of C_{60} molecular rotation to the Ne diffusion process. It is proposed that increased pressure reduces the rotation rate, decreasing the Ne loading rate. Although there

are no measurements of the rotation rate vs pressure, it is clear that it must decrease upon approaching the fcc-sc transition, where free rotation stops altogether. Measuring the pressure dependence of τ just below the fcc-sc transition, where the pressure dependence of the rotation rate would be expected to be largest, would provide a better test of this hypothesis, but data cannot be taken in this pressure range because of the mixed-phase region created by the fcc-sc transition (as discussed above).

As noted above, the intercalation of the Ne of nominal radius 1.12 Å (as well as He with a nominal radius of 0.93 Å)[15] involves its passage through the narrow channels (radius ~0.82 Å if C_{60} molecules are considered as rigid spheres) between the octahedral sites. Near room temperature, thermal motion normal to the rotating molecule is present with a root-mean-square displacement of the order of 0.03 Å, but would only account for a small contribution to the channel radius. However, the C_{60} molecules are not actually rigid spheres. The center of the pentagonal faces are ~0.29 Å inside the surface of the sphere defined by the maximum radius. Thus, if the C_{60} molecules rotate, the channel size can vary from 0.82 Å to a radius which probably exceeds ~1.11 Å, sufficient to allow Ne but not Ar (nominal radius 1.54 Å) to intercalate near room temperature.[16] In fact, since the centers of these pentagonal faces are electron poor, there should be dimples into the polyhedra of size somewhat deeper than the 0.29 Å just mentioned. This significant departure from a sphere for the C_{60} molecules may be viewed as slots or buckets in a ''paddle wheel'' which effectively sweeps the Ne either into or out of the lattice. The C_{60} molecular dynamics is responsible for enabling and enhancing diffusion by this paddle wheel effect and is the major contribution to the observed diffusion rates. As the phase transition is approached, either the rotation rate decreases or the effectiveness of the paddle wheels is hindered in some other way; this results in the increase in the τ values.

As indicated above and irrespective of pressure (or phase), the unloading runs of Ne from C_{60} at room temperature (five runs from the sc phase; four from the fcc phase) were all sufficiently rapid to yield lattice parameters which, though showing large scatter at early times, always were in the vicinity of the 300 K, 1 bar value. This fast unloading is expected. Figure 3 predicts a very fast diffusion at zero pressure. In addition, as the unloading process is initiated, the lattice is expanded because of the intercalated C_{60} with its very high internal Ne pressure further increasing the unloading rate. For modestly lower temperatures where both the Ne jump frequency and paddle wheel dynamics are significantly slower, unloading times are sufficiently long that they can be experimentally measured and employed to determine the activation energy of this process (see below); with decreasing temperature, τ increases.

The reorientation correlation times given above are determinations at 1 bar and the magnitude of their pressure dependence could only be qualitatively inferred; thus, an alternate approach towards accounting for the lower limits for Ne diffusion might be useful. Assuming our particles of nominal 0.1 mm size are spherical, one can determine that the number of octahedral sites on the surface is $\sim 3.3\times 10^{10}$, which act as the sites for the injection of the Ne atoms into the particle interior with its $\sim 0.6\times 10^{15}$ empty octahedral sites. Thus, the ratio of empty to injector sites or the number of injections needed ($\sim 2\times 10^4$) poses no problem, even with the 260 K 10^{-9} s reorientation correlation time rate in the sc phase, as long as hops are driven towards empty sites. Our longer τ values (~6 h or 2×10^4 s in the sc phase) would require hopping times to be only of the order of 10^{-5} s to fill the sites. The external Ne pressure serves as a driving force for intercalation as long as the empty space within the lattice remains. This space, including the channel, octahedral, and tetrahedral sites, can be determined from the lattice parameter and the size of the C_{60} molecule and is $\sim 160\,\text{Å}^3/C_{60}$, sufficiently large to accept the Ne atoms. However, the presence of the Ne contributes a small repulsive force within the lattice. This was determined in our previous study on site occupancy,[5] which showed after 20% occupancy, a linear expansion of 0.1% over the 3 kbar range to completely fill the octahedral sites. This expansion is only 1/6th of that resulting from the compression by 1 kbar pressure. However, this empty lattice space is a sufficient driving force to overcome the repulsive force that the Ne atoms contribute to the lattice at occupancy levels of ~20%. The atomic level details for the lattice suggest that the paddle-wheel C_{60} dynamics dominate the other effects contributing to the intercalation process.

From our loading and unloading runs and the comments above, a physical picture emerges. When C_{60} is initially pressurized with Ne at room temperature and low pressures (<2.4 kbar), the C_{60} molecules are compressed, but remain freely rotating, with their reorientation rate slightly reduced and, hence, a reorientational correlation time which is increased. The lattice remains fcc. The τ values are small. Ne atoms are intercalated into the crystallites by the paddle wheel effect, resulting from the small departure from perfect sphericity of the C_{60} molecules. With Ne introduction in the outer portions of the C_{60} crystallite, a slight volume expansion occurs which broadens the diffraction lines of the inhomogenously distributed Ne crystallite. Intercalation and paddle wheel induced hopping continue until equilibrium of the appropriate Ne occupancy is attained throughout the crystallite volume for the given gas pressure (Fig. 3, Ref. 5). At this point, the C_{60} lattice becomes homogenous and the diffraction peak widths reduce to a value similar to their initial value. As the pressure approaches that of the fcc-sc transition, the pressure effect becomes more nonlinear with respect to the molecular rotation rate, which is significantly decreased or impeded. The τ values rapidly increase. The onset of the transition is occurring with a marked reduction of the rotation rate. At pressures greater than 3.2 kbar, the C_{60} molecules have become more ordered with a transition from the fcc to the sc lattice accompanied by a small, 1% volume reduction and a discontinuous drop in the reorientation correlation time. Rather than freely rotating, the C_{60} molecules now hop between the two positional orientations, at a much slower, at approximately onehundredth the rate. The continuous paddle wheel mode of diffusion is not operative in the sc phase. Thus, the intercalation times become much longer, with τ about three times that for the higher fcc values. Here, there is little pressure dependence of the C_{60} molecular hopping rate. The τ values remain constant as the other effects contributing to diffusion cancel each other. For the intermediate pressure range between 2.4 and 3.2 kbar, the

gas pressure is initially sufficient to force the transition to sc to occur, but as Ne is intercalated and reaches equilibrium with near full occupancy of the octahedral sites, the lattice reverts to the fcc phase. Overall, increasing the external Ne pressure increases the driving force for intercalation, but the resulting compression of the C_{60} lattice slows the diffusion into the crystallites. However, these effects are small compared to the C_{60} paddle wheel dynamics. Temperature also alters the reorientation times and the lattice size, with lower temperatures having a similar, but not identical, effect as increasing pressure.

Upon pressure release at room or higher temperatures from either the fcc or sc phase, the Ne intercalated C_{60} lattice expands to a value slightly larger than that for pure C_{60} at the appropriate Ne pressure. Simultaneously, the reorientational correlation time is dramatically decreased to the 1 bar (or possibly a lower value) with a corresponding increase in the paddle wheel rate; the Ne is unloaded from the C_{60} in a time comparable to the lower limit of diffraction data acquisition (300–600 s). For modestly lower temperatures, unloading times are sufficiently longer that they can be determined, and these are employed in determining the activation energy (see below). As expected on unloading, τ increases with decreasing temperature.

B. Activation energy

Only limited data are available to obtain an activation energy for Ne intercalation into C_{60}. For the sc phase, this consists of the τ values for runs at 240 and 265 K together with that from an extrapolated point (for 300 K, 1.5 kbar), which may be obtained by extrapolating the sc phase behavior into the fcc phase (see Fig. 3). Since the τ pressure dependence in the sc phase is near zero, this should introduce no error. From the Arrhenius equation,

$$\tau(T) = A \exp(-E/kT),$$

where τ depends on the temperature T,A is a constant related to frequency factor in the diffusion process, E is the activation energy, and k is the Boltzmann constant. The least-squares fit (Fig. 4) of our τ values yields $E = 1400(400)$ K [12(3) kJ/mole] for the sc phase, the large uncertainty in E resulting from the use of only three τ values. The E value is smaller than that for pure C_{60}, but is quite reasonable. The presence of the Ne expands the C_{60} lattice compared with that for pure C_{60} pressurized by a nonpenetrating gas,[4] such as Ar, and this should reduce the energy barrier for hopping between the two different orientational configurations. Note that this lattice expansion occurs despite the fact that the octahedral site can easily accommodate the Ne, i.e., the Ne is acting as a repulsive rather than an attractive force. One might alternatively view the presence of Ne as ''roller bearings'' between the C_{60} molecules in reducing the activation energy. A similar situation exists in methane[17] intercalated C_{60}. In this case, pressure is not necessary to maintain the intercalant in the lattice sites,[16] so that the lattice expansion from repulsive interaction is evident at ambient pressure, and the roller-bearing effect results in an orientational ordering temperature depressed 20–25 K.[17]

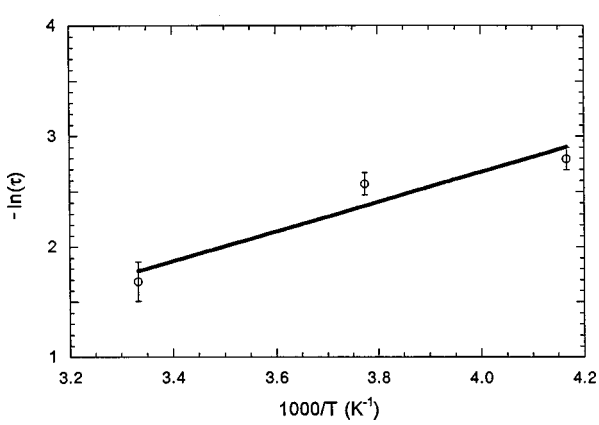

FIG. 4. Qualitative determination of the activation energy on loading Ne into C_{60} for the low-temperature $Pa3$ structure. The solid line is a least-squares fit to the data.

For the fcc phase, our experimentally determined τ value is limited to that for 340 K (loaded to 4.1 kbar). One then must again extrapolate a point (at 300 K, 4.1 kbar) in the ''extended'' fcc phase in order to obtain a qualitative value for the activation energy in this phase. In this case, τ is pressure dependent and the least-squares fit line shown in Fig. 3 was used for the extrapolation. It is noted that the 340 K point is sufficiently away from the phase boundary, taken as the midpoint between that determined with He and a nonpenetrating fluid, that it cannot be considered within the onset of the transition.[3] Using only these two values of τ results in $E = 1600(1000)$ K [14(9) kJ/mole]; notwithstanding large fitting errors, this qualitative value is similar to that determined for the sc phase.

As indicated above, the unloading runs of Ne from C_{60} at room temperature were all too rapid to yield τ values. On the other hand, for runs below 265 K, lattice parameter values on three runs were obtained which could be fit with the lattice parameter expression given above yielding τ values on unloading. These τ values yield an extremely qualitative least-squares fit; hence, this results in an expected large error with respect to the resulting E value. On unloading of Ne from the C_{60}, $E = 1200(1800)$ K [10(16) kJ/mole], lower than upon loading. One would have expected that the lattice, due to the essentially filled octahedral site, would expand upon pressure release, as indeed the early time values of the lattice parameter data shows, and that this would increase the paddle wheel rate of the C_{60} molecules. Thus, the magnitude for E on unloading is reasonable.

CONCLUSIONS

Although the present study may be viewed as only an initial look at the diffusion kinetics of Ne in C_{60}, several interesting facts have emerged. The significant pressure dependence of τ on loading in the fcc phase is in sharp contrast to that in the sc phase as is the diffusion kinetics during loading compared to unloading. The C_{60} molecular dynamics plays a major role in explaining our observed intercalation rates. In addition, competing effects involve the increase in the external Ne pressure increasing the driving force for diffusion while compression of the C_{60} lattice primarily reduces channel dimensions, slowing diffusion with increasing pressure. As the Ne pressure approaches pressures required to induce the orientation ordering transition, the C_{60} molecular

dynamics are strongly affected, with a marked decrease in the C_{60} molecular rotation rate. The pressure dependence on the C_{60} molecular dynamics near the onset of the transition explains the large differences in the diffusion kinetics. On unloading, the intercalated Ne present in the C_{60} expands the lattice, enhancing the ''roller-bearing'' effect.[18] At room temperature the C_{60} molecular dynamics quickly unloads the Ne at times too rapid to be experimentally determined by our diffraction technique; at lower temperatures, this unloading occurs with a marked increase in the C_{60} reorientational correlation times, allowing an assessment of the activation energy for this process.

There are several interesting observations which need further study. For example, the deviations of our loading data from the lattice parameter expression used to fit it are significant and reproducible. In particular, in the runs at higher pressure, the lattice parameter, $a(t)$, oscillates in a reproducible way around the smooth curve expected for a single diffusion mechanism. Such oscillations could result from subtle transitions between different configurations for the intercalated Ne—perhaps analogous to the staging transitions that occur for various species incorporated into graphite. Unfortunately, no direct evidence for the superstructures that would be associated with such phases have been observed in our diffraction data. A more sensitive structural probe will be required to investigate this.

Understanding gained on considering the C_{60} molecular dynamics on the Ne intercalation suggest that this is also the reason for the large 20% Ne octahedral site occupancy at 1 bar.[5] This puzzling Rietveld refinement result was originally explained by us as scattering from possible impurities in our gas source, though other conflicting experimental details were offered which counter this.[5,19] From our present understanding, the octahedral site occupancy results from the ease by which the paddle wheels intercalate Ne atoms in the fcc phase. This rapid intercalation is aided by the empty volume within the lattice and is eventually balanced by the repulsive force, contributed by the Ne presence as the concentration reaches ~20%, which begins to expand the lattice.

The C_{60} molecular dynamics enables and enhances diffusion by a thermally activated ''paddle wheel'' effect assisting diffusion of Ne through the narrow 0.82 to 1.11 Å channels between the octahedral sites. Within our expressed limitations, the process for both phases yield about equal values of the activation energy on loading; this value is in reasonable agreement to that for the reorientational barrier between the structural configurations of pure C_{60} in the sc phase. Our much lower value (~1500 K or 13 kJ/mole) for the activation energy compared with that for pure C_{60} (~2600 K or 22 kJ/mole) (Ref. 7) may be rationalized on the basis of the slightly expanded lattice when Ne is present, in which Ne may be viewed as acting like ''roller bearings'' between the C_{60} molecules.

ACKNOWLEDGMENTS

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(NBS & JCPDS, Washington, D. C., 1973), these radii are 1.499, 1.572, and 1.878 Å, respectively, for He, Ne, and Ar.

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[19] Data subsequently taken on a sample of the vacuum heat treated C_{60} at the Los Alamos Neutron Science Center (LANSCE) proved that the initial octahedral site occupancy was zero on the material employed in the study.