Intercalation of fullerite C_{60} with N_2 molecules.
An investigation by x-ray powder diffraction

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The lattice parameter a of fullerite C_{60} intercalated with N_2 molecules is investigated in the temperature interval 6–295 K by x-ray diffraction. It is found that the interstitial molecular N_2 has a considerable effect on both the temperatures, T_c of the orientational phase transition and T_g of the orientational glass formation. Hysteresis of $a(T)$ has been detected in the T_c and T_g regions, besides, the abrupt change in the volume over the region defining T_c. Complete intercalation of C_{60} with N_2 molecules results in a 0.2% increase in the lattice parameter, which persists over the whole temperature range. Evidence is also obtained that the interstitial guest molecular N_2 induces a slight deformation of the cubic symmetry of the host C_{60} lattice.

Introduction

Intercalation of fullerite C_{60} with dielectric admixtures can cause significant changes in its properties. These changes are predominantly related to the considerable accompanying expansion of the crystal volume that occurs with this interaction, as though a negative pressure was applied to the solid matrix. An experimental condition such as this is hardly possible to apply to a pure substance in any real situation. The most interesting and important alterations of the properties are observed at the temperature of the orientational phase transition T_c and in the region of existence of the orientational glass. Normally, when inert gas atoms and simple molecules occupy the octahedral and even sometimes the tetrahedral sites of the fcc lattice, the noncentral molecular interactions grow weaker, with the effect that the rotational motion of the C_{60} molecules gain more freedom. As a result, the temperature of the orientational phase transition decreases [1–4]. This is illustrated clearly by the experimental results in Table 1. At temperatures above a respective T_c most molecular impurities (N_2, O_2, CO, CH_4, etc.) are orientationally disordered and rotate quite freely in the interstitial sites of the lattice [7,12–15]. However, below T_c the nonspherical S_6 symmetry of the force field associated with the octahedral sites, with its specific noncentral interaction with the surrounding C_{60} molecules, promote localization of the interstitial guest molecule, as well as inducing it to align in certain orientations with respect to the symmetry axes of the C_{60} lattice [13–15]. This in turn can influence the lattice dynamics, the phase transition and even the structure of the C_{60} host matrix. The latter is illustrated most clearly by the $(CO_2)_x C_{60}$ system, in which the interstitial CO_2 molecule modifies the nature of the phase transition and below 200 K it is found that these solid solutions form a monoclinic lattice exhibiting $P2_1/n$

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Table 1. Lattice parameter a, orientational phase transition temperature T_c and glass formation temperature T_g for pure C_{60} and C_{60} intercalated with atomic and molecular impurities.

Substance	T_c, K	a, Å	T_g, K	Source
Pure C_{60}	260	14.161	90	[25,26]
He_1C_{60}	246	14.223	85	[4,5]
$Ne_{0.49}C_{60}$	258	14.168	90	[5,27]
Ar_1C_{60}	251	14.173	80	[2–4]
$Kr_{0.8}C_{60}$	238	14.207	–	[2]
$Xe_{0.34}C_{60}$	230	14.240	70	[6]
$Xe_{0.46}C_{60}$	220	14.236	–	[2]
$Xe_{0.66}C_{60}$	210	14.36	–	[2]
$(N_2)_{0.6}C_{60}$	239	14.183	80	[7]
$(O_2)_{0.7}C_{60}$	240	14.174	–	[5,11]
$(CH_4)_{0.92}C_{60}$	241	14.187	–	[1,13]
$(CD_4)_{0.88}C_{60}$	235	14.184	–	[1]
$CO_{0.67}C_{60}$	245	14.179	–	[5,8–9,14–15]
$(CO_2)_{0.67}C_{60}$	< 200	14. 224	–	[16]
$NO_{0.1}C_{60}$	245	–	–	[5,9–10]

symmetry [16]. The «negative» pressure (lattice volume expansion) is therefore not the only factor responsible for property modifications of the C_{60} lattice when intercalated with various, molecular species. In developing an understanding of such a system, it is important to consider not only the distribution of the guest molecules over all the possible interstitial sites but also to consider all the energetically allowed orientations of the molecule within these crystal sites and what effect these can have on the noncentral interaction in the solid solution. Small-size atomic or molecular impurities such as He atoms or H_2 molecules produce rather weak effects, and their vibrational and, for the case of H_2, also rotational motion in the octahedral sites of the C_{60} lattice are relatively free even at the lowest temperatures. In contrast to this, an example of where the interaction between C_{60} and molecular species in the solid state is very strong, having a dramatic influence on both the final solid state structure and its associated properties, is the example of C_{60} interacting with cubane C_8H_8 [17–19]. In this case a hetero-molecular crystal results with «immovable» molecules of cubane and with «free» rotation of the C_{60} molecules! On cooling the sample just below 140 K, the rotation of the C_{60} molecules freezes out, with a lowering of the crystal symmetry to orthorhombic.

The intercalation with van der Waals species has other effects in addition to the suppression of the orientational

phase transition temperature T_c. For example, no glass phase transition was detected in C_{60} intercalated with either CO or NO molecules [8–10]. A similar result (a much lower T_c and a nearly completely suppressed glass formation) was observed in dilatometric and neutron diffraction measurements [11] of C_{60} intercalated with N_2 and O_2 molecules. It was found [8–12] that at the lowest (liquid helium) temperatures studied, nearly all of the C_{60} molecules (90%) in the solid solution formed the lower energy pentagon–pentagon arrangements between neighboring C_{60} molecules. Over this temperature region, the presence of atomic and molecular species can also significantly alter the temperature behavior of the thermal expansion as compared to that of the pure C_{60} lattice, as well as introducing hysteresis effects [20,21].

Although N_2 and O_2 have closely similar vdW molecular diameters and lengths (3.0 and 4.1 Å for N_2; 2.8 and 4.0 Å for O_2, respectively) it is found that N_2 molecules diffuse much more slowly into the C_{60} lattice as well as being much harder to remove from it, as compared to O_2 molecules. It is proposed that the O_2 molecules interact less strongly with C_{60} molecules and subsequently behave more freely within the C_{60} lattice. It is interesting note that their atomic spacing are reversed in the order of their size length: N–N 1.095 Å, O–O — 1.208 Å [22–24].

In this study we have investigated the effect of N_2 upon the phase transitions, the processes of orientational ordering and glass formation in C_{60} by the x-ray powder diffraction method and over the temperature range of 6–295 K. Data were taken during both the heating and cooling of the samples. The XRD patterns obtained were analyzed to detect possible effects of a nonspherical guest molecule on the structure of the C_{60} host matrix.

Experimental technique

Polycrystalline C_{60} powder was saturated with N_2 using hot isostatic pressing (HIP) and under a gas pressure of 200 MPa at $T = 723$ K. It was then compacted into pellet form using hydrostatic compression at $P = 1$ GPa. The pellet samples prepared (8 mm high, 10 mm in diameter) were used to investigate the thermal expansion, the hardness and structural characterization as in this study. The chosen technique of saturation made it possible to achieve, as validated by thermo-gravimetric analysis (TGA) and measured weight loss, a 100% occupancy of the octahedral sites in the C_{60} crystal.

The x-ray investigation was performed using a DRON–3M diffractometer (K_α emission with $\lambda = 1.54178$ Å from copper anode). The low temperature measurement was made using an x-ray helium cryostat for 2–293 K. The temperature measurement and stabilization were accurate within ± 0.1 K. The error in the lattice parameter was ± 0.02 %.

Results and discussion

A typical x-ray diffractogram of the compacted polycrystalline C_{60}–N_2 samples is shown in Fig. 1. Apart from the distinct intensity reflections from the fcc C_{60} lattice, the diffraction pattern contains several additional weak ones that are not typical for pure fcc C_{60}. Among them are the rather weak (200) and (400) reflections, which account firstly for the occupancy of the octahedral sites in C_{60} with N_2 molecules and, secondly, for a noticeable deformation of the C_{60} crystal. According to [28], pertaining to the x-ray diffraction of pure nondeformed C_{60}, the reflections from (h00) planes have nearly zero intensity at room temperature. The other weak reflections observed are marked with arrows in Fig. 1, and these may correspond to diffraction by an additional phase formed (like in [6]) by partial polymerization of the C_{60} as a result of the high-pressure compaction. This assumption is supported by the fact that the x-ray diffraction patterns taken of the powder resulting from gently crushing a compacted samples showed only the reflections from fcc C_{60}–N_2 alloys, with these weak reflections now absent.

The intensity distributions of the medium to strong x-ray reflections from both solids of the C_{60}–N_2 solution and pure C_{60} are very similar quantitatively. However, the half–widths of the reflections from C_{60}–N_2 ($0.4 \pm 0.01^{°}$) are between 2.0 and 2.5 times larger than those for annealed pure C_{60}. These higher half-widths are typical for both substitutional and interstitial solid solutions and are due to nonuniform static displacements of the trapped atomic or molecular species in the host lattice. An additional contribution could also be made from residual plastic deformation of the samples as a result of the high-pressure compaction.

The magnitude of the lattice parameter of the C_{60}–N_2 solution at room temperature was estimated from the pro-
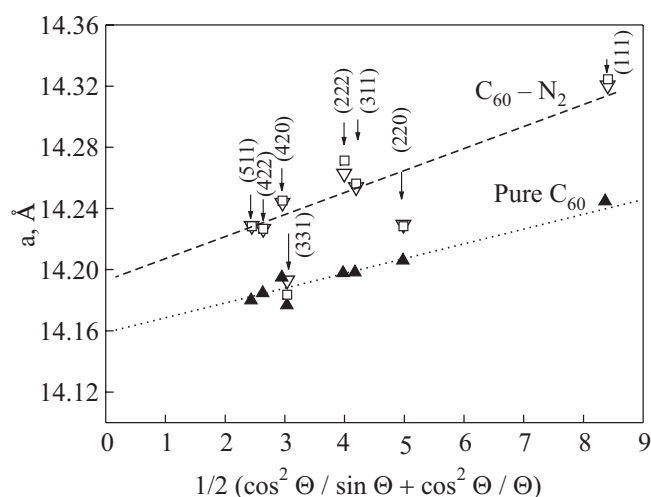
Fig. 2. Lattice parameters calculated from individual experimental reflections as a function of diffraction angle: two different measurements on C_{60}–N_2 alloy (∇, $\square$); pure C_{60} ($\blacktriangle$).

cessing of all the x-ray diffraction patterns taken at this temperature. The derived lattice parameters, with one calculated from the Θ_{hkl} of each reflection, were plotted against the extrapolation function $1/2(\cos^2 \Theta/ \sin \Theta + \cos^2 \Theta/\Theta)$ [29] (Fig. 2). The set of points was linearly fitted, and then extrapolated to intercept the vertical lattice parameter axis. The intercept was taken as the lattice parameter of the $(N_2)_x C_{60}$ solution. This procedure minimizes random and systematic errors and yields a highly accurate estimate of the true parameter. Using this procedure, we processed results of several experiments and obtained the average lattice parameter $a = 14.1906 \pm 0.003$ Å for the $(N_2)_x C_{60}$ solution. This exceeds the value for pure C_{60} by 0.029 ± 0.003 Å [25,26].

Figure 2 reveals considerable scatter of the calculated a_{hkl} — values about the linear fit. Scatter like this is impossible for a nondeformed fcc lattice. Indeed, as follows from our experiments on pure C_{60}, the lattice parameters calculated from individual (hkl) reflections fall quite accurately (within the experimental error) on the extrapolated straight line (Fig. 2). Besides, the linear dependence $a = f(\Theta)$ is also typical for binary solutions of C_{60} with spherically symmetrical species such as rare gas atoms. We have analyzed in the same way as above, diffraction parameters of C_{60} solutions with He, Ne, Ar and Kr and have found that the scatter of points is no worse than that of pure C_{60}.

The above results suggest that certain inhomogeneous systematic changes in the interplaner spacing of the fcc lattice of C_{60} occurs when intercalated with linear N_2 molecules. It is most likely that the intercalation with the linear N_2 molecule causes a weak tetragonal deformation of the cubic C_{60} lattice. The largest deviations from the extrapolated linear dependence are observed for the

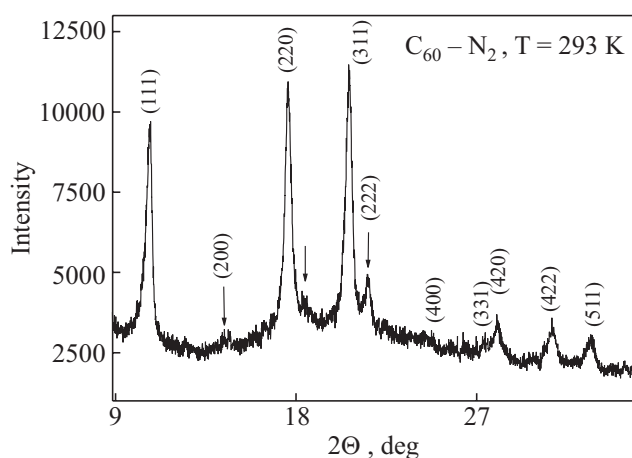*Fig. 1.* Typical x-ray diffraction pattern of the compacted polycrystalline $(N_2)_x C_{60}$ samples. The arrows show an unknown second phase.

(hk0), (hk1), and other reflections which bifurcate in the case of tetragonal deformation. It is also known that linear molecules (e.g., N_2) in simple substitutional solid solutions cause local tetragonal distortions of the host lattice [30–32]. The weak tetragonality assumed for the $(N_2)_x C_{60}$ lattice offers another possibility for explaining the comparatively large broadening of individual reflections that can exhibit a weak doublet splitting. Attributing the cubic symmetry violation to a noncentral component in the N_2–C_{60} molecular interaction, we might expect enhancement of the effect in the low–temperature region, where the N_2 molecules will become orientationally ordered. Surprisingly, with this ordering of the N_2 molecules, no further distortion is observed at the coldest temperature studied from the observed distortion at room temperature.

The temperature dependence of the lattice parameter measured on cooling and heating the C_{60}–N_2 solutions are shown in Fig. 3. An appreciable hysteresis of $a(T)$ is observed in the region of the orientational phase transition T_c. The temperatures of the orientational phase transition on cooling and heating the C_{60}–N_2 solution differ nearly by 10 K, and T_c values are 245 and 255 K, respectively (the phase transitions are marked with solid arrows in Fig. 3). This also applies to heating and cooling the sample in the temperature region where an orientational glass exists, below $T = 60$ K. It is important to realize that these differences observed between the lattice parameters measured on cooling subsequent heating exceed the possible error in the measurement. These effects, when converted into thermal expansion coefficients, agree with the directly measured dilatometric data for this solution [33]. As well as these observed phenomena, it is also found that both T_c and T_g are displaced considerably towards lower
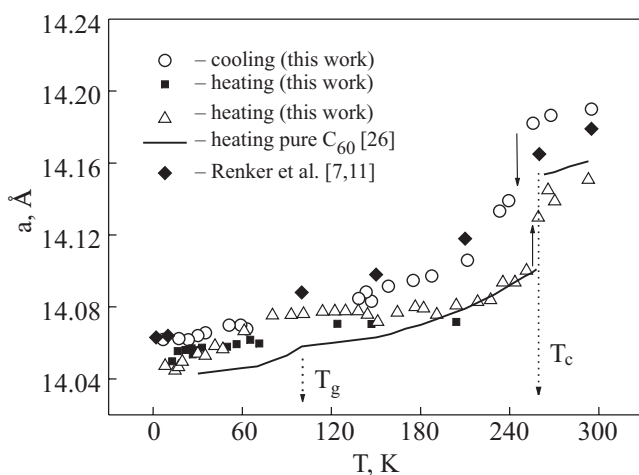
temperatures for the C_{60}–N_2 solutions in comparison to the corresponding values for pure C_{60} (Fig. 3). The lattice parameters we have measured on cooling agree quite well (within the total error of both experiments) with the data from Renker et al. for $(N_2)_{0.6} C_{60}$ [7], also measured over a similar temperature range in this work. On cooling over this temperature interval the lattice parameter of our $(N_2)_{0.85} C_{60}$ solution changes by $\triangle a = 0.129_4$ Å, whereas the $(N_2)_{0.6} C_{60}$ solution of Renker et al. [7] shows a somewhat smaller change of $\triangle a = 0.126_9$ Å, though comparable within experimental error. Both of the values, however, slightly exceed the lattice parameter change typically observed for cooling of pure C_{60} over a similar temperature change, namely $\triangle a = 0.119_0$ Å, for [26]. This means that the thermal expansion of nitrogen-doped C_{60} within the temperature range studied is 8.5% larger compared to pristine fullerite. However, on heating the thermal expansion of the sample appeared to be much smaller than that on cooling. The change in the lattice parameter is comparable with or even slightly lower than in the case of pure C_{60} (Fig. 3). As a result, at room temperature the lattice parameter does not reach its initial value observed at the beginning of the cycle. It is likely that the hysteresis loop is closed at higher temperatures. At the same time we could observe the effect of the lattice parameter relaxation. During the exposure of the sample to room temperature (15–20 hours) the lattice parameter returns to its initial value. However, no relaxation of the parameter a was observed during the same period at temperatures below that of the phase transition. We are planning a detailed investigation of the relaxation processes in the C_{60}–N_2 solution.

It is interesting to compare the lattice parameters for the solutions of C_{60} with N_2 to those of C_{60} with other species. This comparison is very illuminating when we compare the dependences of the room temperature lattice parameter with occupancy of the octahedral sites by these species. The room-temperature lattice parameters for both our C_{60}–N_2 and the C_{60}–60 % N_2 solution of Renker et al. [7] are shown in Fig. 4, together with the room temperature values arising from a range of other C_{60} solutions with differing trapped species as well as varying stoichiometry. It is seen that the linear lattice parameter versus concentration relationship holds for C_{60} with Ne, as was thoroughly investigated by Morosin et al. [27]. The value of the lattice parameter obtained in this study, if assumed to fall on another straight line formed between the data point formed from the lattice parameter and occupancy of the sample of [7], predicts the occupancy of our sample to be 85 % (Fig. 4). This value was confirmed by analyses of integral diffraction intensities of studying alloy. The decrease in the concentration N_2 of our samples from 100 to 85 % might come from rather long (several weeks) exposure of the sample to vacuum during its prep-

Fig. 3. Temperature dependences of lattice parameters of C_{60}–N_2 solution on cooling (O) and heating ($\triangle$, ■) (results this work). For comparison, the data by Renker et al. [7,11] (◆) and for pure C_{60} [26] (——) are shown.
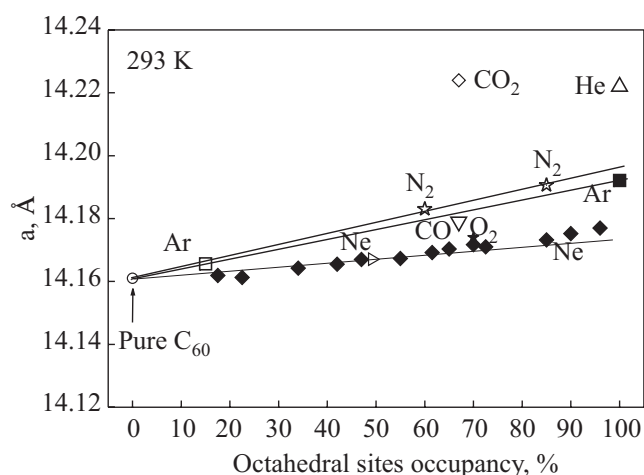
Fig. 4. The FCC lattice parameter of C_{60} at 293 K as a function of the occupancy of octahedral sites by inert gas atoms and sample molecules: He ($\triangle$) [4], Ne ($\blacklozenge$) [27], Ne ($\triangleright$) [35],Ar ($\blacksquare$) [3], ($\square$) Ar [4], CO_2 ($\diamondsuit$) [16], CO ($\triangledown$) [14,15], O_2 ($\bigstar$) [5,11], N_2 ($\stackrel{\star}{\diamond}$) [7] and this study, pure C_{60} ($\bigcirc$) [26].

Fig. 5. Effects of increasing the cubic unit cell parameter of C_{60} on T_c in binary substitutional solid solutions for different atomic and molecular species: $Ne_{0.49}C_{60}$ ($\blacktriangle$) [27]; $Ar_{1.0}C_{60}$ ($\bigstar$) [3]; $CO_{0.67}C_{60}$ ($\bullet$) [15]; $(O2)_{0.7}C_{60}$ ($\triangle$) [5,11]; $(CH_4)_{0.92}C_{60}$ ($\square$) [1]; $(CD_4)_{0.88}C_{60}$ ($\blacksquare$) [1]; $He_{1.0}C_{60}$ and He_xC_{60} ($\triangledown,\nabla$) [4,34]; $(N_2)_{0.6}C_{60}$ ($\stackrel{\star}{\diamond}$) [7,11]; $(N_2)_{0.85}C_{60}$ ($\stackrel{\star}{\diamond}$) [this study]; $Kr_{0.84}C_{60}$ ($\diamondsuit$) [2]; $Xe_{0.35,0.44,0.66}C_{60}$ ($\blacklozenge$) [2]; $(C_8P_8)_{1.0}C_{60}$ ($*$) [17 –19]; pure C_{60} ($\bigcirc$) [26,37].

aration and measurement of the thermal expansion coefficients [33]. The obtained linear dependence is slightly higher but still close to the $a(x)$ values for C_{60}–Ar [2–4] solutions. The similarity of the lattice parameters of the C_{60}–N_2 and C_{60}–Ar solutions may indicate nearly equal effects of these species with very similar gas–kinetic diameters [23] upon the lattice of C_{60}. Also of interest is the lattice parameter for C_{60}–He [4], which if plotted with a 100 % occupancy appears to be rather high compared to the other gases.

The increase in the parameter a and volume of the C_{60} lattice by intercalation with van der Waals species suppresses the C_{60}–C_{60} intermolecular interaction, which in turn enhances the rotational motion of the C_{60} molecules and lowers the temperature of orientational ordering.

Using the presently available data on the structure of binary C_{60} solutions with atomic and molecular species, we have been able to plot in Fig. 5 the dependence of the orientational phase transition temperature (T_c) for C_{60} on the size of the lattice parameter (a), measured at the onset of the phase transition, when cooling the sample down from room temperature. Figure 5 illustrates the general tendency of T_c to decrease with growing lattice parameter for C_{60}. The tendency holds within a single system (e.g., Xe–C_{60}) and for the whole collection of binary solutions. Only one value (for C_{60}–He [4]) appears outside the smooth dependence $T_c(a)$ (see the He_x point in the inset in Fig. 5). The reason can be as follows. In the course of a prolonged exposure of the samples to the He atmosphere, the atoms have enough time to occupy not only the octahedral sites but also the tetrahedral ones [4,34–36]. It is most likely that the larger-than-expected lattice parameters of these solutions is a direct result of this ability of He
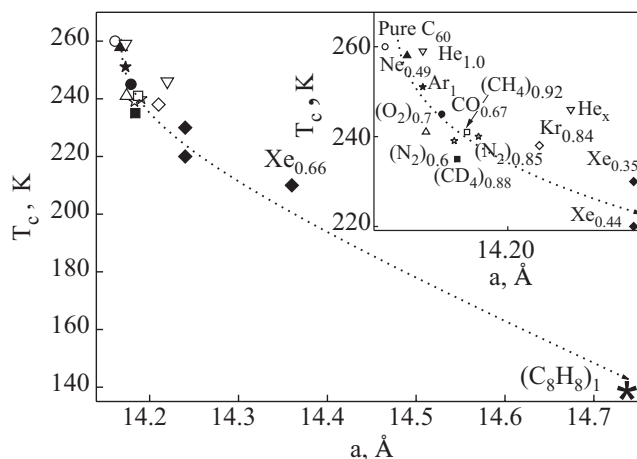
to be able to occupy both types of interstitial sites and therefore exert a greater than normal internal pressure on the C_{60} lattice. When a monatomic species (such as Ne or Ar) occupies (completely) only octahedral sites, the changes in a and T_c are much smaller. Indeed, assuming that the initial part of the curve shown in reference [4] that describes the time variation of the parameter a during intercalation of C_{60} with He [4], corresponds to occupation of the octahedral sites only, we obtain the smallest lattice parameter change measure for intercalating species with C_{60} and if assumed to be occupying 100 % of the octahedral sites. The lattice parameter changes by only $\triangle a = 0.012$ Å, whilst T_c decreases only by 2 K. The point $He_{1.0}$ in Fig. 5 corresponds to these results [4,5] and falls quite accurately on the averaged smooth dependence. When He atoms occupy 100 % of only the octahedral sites, their effect on both the lattice parameter and the T_c of the C_{60} matrix is very close to that arising from Ne atoms occupying the C_{60} lattice but with a 49 % occupancy.

Conclusions

C_{60}–N_2 solid solutions have been investigated over in a wide temperature range (6–293 K) using the x-ray diffraction method. It is found that an interstitial molecular species has a considerable effect upon the structural properties, the orientational phase transition (T_c) and the orientational glass temperature (T_g) in C_{60}. In contrast to atoms the N_2 molecules intercalated into the C_{60} lattice cause some deformation of the cubic cell as well as ap-

proximately a 0.2% increase in the lattice parameter at room temperature. This excess over the value for pure C_{60} persists when cooling the sample down to a temperature of $T = 6$ K. On heating the sample back to ambient temperatures, the lattice parameter of the solid solution approaches the a value of pure C_{60} in the region of T_c. It is observed that the onset of the phase transition at T_c, as observed on the C_{60}–N_2 sample from room temperature, is lower than that corresponding to pure C_{60}. Both T_c and the associated change in the lattice parameter exhibit hysteresis. The distinct behavior of solid C_{60}–N_2 solutions and solutions with atomic species is largely determined by the noncentral component in the C_{60}–C_{60} intermolecular interaction, as well from possible ordering of the molecular species in the octahedral sites at lower temperatures.

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