Intercalation of molecular gases into C_{60}

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The intercalation of N_2 into solid C_{60} has been studied by high-resolution dilatometry, neutron diffraction, and quasielastic neutron scattering. Favored by weak binding forces between C_{60} molecules in the bulk, $N_2(O_2)$ molecules trapped on octahedral sites of the host lattice are found to cause significant structural changes. Thermal expansion of bulk samples as well as peculiarities in the molecular ordering are followed over a wide range of temperatures and compared to pristine C_{60} . Rotational diffusion and the inelastic excitation spectra of guest and host molecules that had been studied in detail in a previous paper [B. Renker *et al.*, Phys. Rev. B. **61**, 13 960 (2000)] are brought in relation to the structural results. In addition, results of magnetic excitations in paramagnetic O_2C_{60} are presented.

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I. INTRODUCTION

The ordering of large icosahedral C_{60} balls in a Van der Waals crystal² is an interesting question that has been subjected to many investigations.³ As a consequence of the big outer diameter (10.02 Å) (Ref. 3) of the molecule the cubic crystal lattice contains large voids. These voids feature diameters of 4.14 Å (octahedral sites) (Ref. 3) and 2.24 Å (tetrahedral sites) (Ref. 3) and can be accessed via channels in the lattice.⁴ This opens up a whole range of possible guest-host systems that may find application as storage media.^{5,6} The physics of the loading and storage of guests such as O_2 and N_2 in a C_{60} matrix depends on a delicate balance of energetic and steric constraints. In this sense we can consider O_2C_{60} and N_2C_{60} as simple model systems for binary molecular crystals with constituents of appreciably different size. In particular, the aspect of how much these systems differ from one in which the smaller guest is considered as an isolated molecule in the matrix of the far larger host is of importance. Here, paramagnetic O_2 offers the additional possibility to study the influence of the environment on the magnetic excitation spectrum. The present work addresses the intercalation of O_2 and N_2 in C_{60} both from the structural and dynamic perspective. To this end a large number of different experimental techniques have been combined.

Intercalation of atoms or small molecules into bulk C_{60} has been known for quite some time.⁷ In several cases the intercalation is accompanied by a decrease of the transition temperature T_0 from the simple cubic (sc) phase, featuring orientationally ordered C_{60} molecules, to a high-temperature state where these molecules perform almost free rotations.

The transition temperature is ≈ 260 K for pristine C_{60} and drops to ≈ 240 K in the case of N_2C_{60} . Differential scanning calorimetry (DSC) measurements, therefore, offer an easy way to monitor the process of intercalation and it has been used for quite a number of different systems.⁸⁻¹⁰ Guided by the general observation that T_0 increases if an external pressure is applied to bulk C_{60} the decrease of T_0 on intercalation of gas has been assimilated to a “negative-pressure” effect. To our knowledge a detailed structural analysis has so far only been performed for ArC_{60} ,¹¹ CO_2C_{60} ,¹² and CO_2C_{60} .¹³ The molecular dynamics has been studied by NMR^{8,9,14,15} and IR spectroscopy¹⁵ and in a previous paper for the compounds N_2C_{60} and O_2C_{60} by quasielastic and inelastic neutron scattering.¹ In this paper we present results concerning high-resolution dilatometry, a detailed structural analysis of N_2C_{60} , and magnetic-neutron-scattering investigations of O_2C_{60} . Quasielastic and inelastic-neutron-scattering investigations that augment our previous work will only be discussed to a limited extent.

II. SAMPLE PREPARATION

Molecular oxygen can be intercalated almost stoichiometrically into pellets of C_{60} , which have been compacted under high pressure.¹⁶ For our experiments gold grade C_{60} was milled, passed through a 75 mesh sieve and heated in dynamic vacuum at 570 K. Small pellets with 8 mm diameter and about 1 mm thickness were produced in a standard pressure cell at a pressure of 15 kbar. Intercalation of $O_2(N_2)$ was obtained by the exposure to high purity $O_2(N_2)$ gas at 300 K (500 K) at pressures of ≈ 500 bar for about seven

FIG. 1. Full heating/cooling cycle in DSC measurements of virgin and annealed N_2C_{60} samples and pristine C_{60} for reference. N_2 diffuses out of the sample at ≈ 600 K (normal pressure, see text) causing an upshift of the sc-fcc transition temperature by ≈ 20 K (see the difference between curves I and II).

days. An attempt to intercalate N_2 into a C_{60} single crystal failed and led to a decomposition of the crystal. A downshift by 20 K (21 K) of the sc-fcc transition temperature for the intercalated samples was measured by DSC analysis. The loss in weight observed after annealing of the gas-loaded samples in a dynamic vacuum typically corresponded to an occupation of $\approx 70\%$ of the octahedral sites. Not well understood is an exothermic reaction for O_2 -loaded samples starting at temperatures of ≈ 450 K that is observed in DSC measurements and that prevented us from performing a full cycle of the thermal-expansion measurements for O_2C_{60} . Figure 1 shows full heating/cooling cycles in DSC measurements (normal pressure, N_2 atmosphere) for the indicated samples. The position of the peak at ≈ 600 K (curve I) depends on the heating rate (here $10^\circ\text{C}/\text{min}$) and is supposed to be caused by N_2 diffusing out of the pellet as proved by a second measurement on the same sample. Pristine C_{60} is shown for reference. Loss of C_{60} due to evaporation is minimal for the chosen heating rate,¹⁷ which can also be concluded from the good correspondence of the cooling curves. A shift in the transition temperature T_0 is clearly visible (changes in enthalpy are typically 6 Jg^{-1}).

III. THERMAL EXPANSION OF N_2C_{60}

A main feature of C_{60} intercalation compounds is the “negative pressure” effect, i.e., an expansion of the host lattice upon intercalation. In order to study this effect extensively we have performed measurements with a high-resolution capacitance dilatometer capable of measuring length changes down to $\approx 0.1\text{ \AA}$ (Ref. 19). The systematic error (general shift in the scale) is largely due to an uncertainty in the total length of the sample (typically $4 \times 10^{-3}\text{ m}$) and is assumed to be less than 10% for this measurement. An advantage of these studies in comparison to our structural analysis by neutron diffraction is that subtle changes with temperature can be followed continuously. It

has been shown in previous papers on C_{60} single crystals and fullerene derivatives that the order-disorder transition around 260 K as well as the glass transition near 100 K are clearly resolved in such measurements.^{18–20}

In Fig. 2, we present results for the linear thermal expansion $\Delta L(T)/L_{295K}$ and the thermal expansivity $\alpha(T) = d(\ln L)/dT$ of N_2C_{60} . The first part of the investigation covers the temperature region from slightly below the orientational ordering transition at 240 K and reaches up to 500 K. During the measurement the sample is exposed to dynamic vacuum and both heating and cooling curves are obtained with rates of 10 mK/s. Cooling (1 $\rightarrow$ 2) and heating (3 $\rightarrow$ 4) cycles locate the sc $\rightarrow$ fcc phase transition in N_2C_{60} at 240 K. Above 350 K the heating curve flattens off and for $T > 500$ K we observe the normal thermal expansion of C_{60} that can be interpreted as a sign for complete loss of N_2 from our sample. A general decrease of $\approx 0.22\%$ is observed in the subsequent cooling curve (4 $\rightarrow$ 5). The loss of N_2 is equally demonstrated by the upshift of the transition temperature to 260 K characteristic for pristine C_{60} . The same transition temperature and a minimal hysteresis is observed in the subsequent heating curve (5 $\rightarrow$ 6). Thus, both a lattice expansion on N_2 intercalation as well as a downshift of the ordering transition by ≈ 20 K show up clearly in the dilatometry data. Remarkably, we observe pronounced precursors of the transition that have the shape of an λ anomaly although the transition is of first order. All these features correspond well to the previous results from DSC measurements and will be discussed in greater detail together with data obtained by quasielastic neutron scattering. We register that the shape of the curves for the N_2 intercalated and the annealed sample are very similar and conclude that the N_2 molecules do not interfere significantly with their C_{60} matrix. The fact that the diffusion of N_2 out of the sample is observed at considerably lower temperatures than in the previous DSC measurements could be understood by the very different experimental conditions: A much lower heating rate in dynamic vacuum com-

FIG. 2. High-resolution dilatometry measurements on a N₂C₆₀ sample. (a) The loss of N₂ upon heating in dynamic vacuum causes a contraction of the lattice and an upshift of the sc-fcc transition temperature. (b) Suppression of the glass transition anomaly in N₂C₆₀ (upper curves) and its recovery after annealing (loss of N₂) (lower two curves). Due to its weakness the transition is hardly visible in the normal thermal expansion.

pared to N₂ atmosphere and normal pressure in the DSC study.

Pristine C₆₀ displays a glass transition around 90 K, where a residual disorder of C₆₀ molecular orientations is frozen in. This transition is due to the competition between so-called pentagon orientations of neighboring molecules that require a larger volume and hexagon orientations with a smaller volume but a ≈ 11 meV higher ground-state energy. This particular feature results from the fact that a C-C double bond can penetrate deeper into a neighboring C hexagon than into the smaller C pentagon. Therefore, we might expect that due to its larger unit cell N₂C₆₀ on cooling will order to a much larger extent in the pentagon phase than pristine C₆₀. This is, indeed, observed in a second series of thermal-expansion measurements performed on N₂C₆₀ at low temperatures (Fig. 2b). Only a very small anomaly invisible in the thermal ex-

pansion $\Delta L(T)/L_{295\text{ K}}$ and indicative of a glass transition remains in $\alpha(T)$. The strength of the anomaly increases strongly for the annealed sample albeit with a reduced magnitude when compared to a C₆₀ single crystal.¹⁸ The principal shape of the anomaly, a decrease in the expansivity at T_g on heating, is the same for both N₂C₆₀ and reference C₆₀. Its position is connected to the dynamics of reorientational jumps that become very slow at low temperatures. It is found at a somewhat lower temperatures, at ≈ 80 K, in the N₂C₆₀ sample. Detailed studies of the glass transition for a single crystal and a pressed pellet of C₆₀ by high-resolution dilatometry have been presented elsewhere.^{18,19}

IV. DIFFRACTION

More detailed results on the structure are obtained from neutron-diffraction studies performed on the high-resolution diffractometer D2B at the Institut Laue Langevin in Grenoble (France). Measurements on N₂C₆₀ were performed at temperatures 2 K, 100 K, 150 K, 210 K, and 260 K and for a C₆₀ reference sample that was processed in the same way but not annealed under high N₂ pressures. For an accurate calibration of the instrument an additional measurement of a pure Silicon sample was performed at 100 K. The same sample holder, a thin-walled Indium-sealed Vanadium tube of 6 mm diameter, was used for all measurements. Diffraction angles between $7.5^\circ \leq 2\theta \leq 162^\circ$ and a wavelength of $\lambda = 1.594$ Å together with the natural collimation of 0.45° for the incident neutron beam were chosen. In order to have the highest possible contrast we have taken a N₂C₆₀ sample for these measurements, where we profit from the much larger scattering length $b_{coh}^N = 0.94$ b nitrogen (oxygen: $b_{coh}^O = 0.58$ b, carbon: $b_{coh}^C = 0.661$ b). A full diffraction pattern measured at 2 K together with refinement data from our Rietveld analysis (Fullprof 1999 version²¹) are shown in Fig. 3. Typical R values are $R_{Bragg} = 3.63\%$ and $R_p = 4.5\%$.

The C₆₀ molecule (present in two different orientations on the same site) was treated as a rigid body with idealized icosahedral symmetry using an appropriate set of distance-constraints. A general problem is that—due to the particular kind of sample processing but also due to the intrinsic, temperature-dependent molecular disorder—there are relatively high contributions of background scattering that render the data processing for high-scattering angles with weak and overlapping Bragg peaks difficult. A particular problem in our case are strong correlations between background scattering, the overall temperature factor, and the occupation probabilities for different molecular orientations of the C₆₀ molecule in the Rietveld refinements. We are particularly interested in temperature-dependent changes and got the impression that uncertainties in the background contribution at high angles would introduce unacceptable errors in the most interesting parameters, i.e., the occupation probability of the majority orientation of C₆₀. Therefore, for the purpose of determining occupation parameters, we have omitted the data for $2\theta > 66^\circ$. We will show that already from this reduced data set we get occupation numbers for the majority orientation of the C₆₀ reference sample that compare well to the literature values. Furthermore, we have convinced our-

FIG. 3. Neutron-diffraction profiles of N_2C_{60} at 2 K ($\lambda = 1.594$ Å) as observed (crosses), as calculated (line), the difference (displaced line), and Bragg positions (vertical bars).

selves that the addition of data from the higher-scattering angles does not influence our main conclusions. For comparison, we have additionally analyzed the 10 K data from our previous measurement on O_2C_{60} (Ref. 1) under identical conditions. We find very similar results although with larger standard deviations since oxygen is a less efficient neutron scatterer.

A first clear result is that the refinements are sensitive to the presence of $N_2(O_2)$, i.e., the R values get significantly larger if $N_2(O_2)$ is omitted. We find an occupation of the octahedral site by N_2 of 65% (78%), which compare well with the value of $\approx 70\%$ determined from the loss in weight for an annealed sample. The N_2 occupation turned out to be the same for the data sets at different temperatures as it should be. Figure 4 shows the refined lattice parameters for N_2C_{60} and reference C_{60} for some temperatures. An expansion of the C_{60} lattice due to the intercalation of N_2 is obvious. The expansion at 150 K is 0.2% and corresponds to our thermal-expansion measurements. In Fig. 5 we present the results for the occupation of the major orientation of the C_{60} molecule. As a consequence of the larger available volume the occupation of the pentagon orientation at low tempera-

tures increases that explains our previous dilatometry result indicating that the glass transition—where a residual disorder of molecular orientations is frozen in—is strongly suppressed in N_2C_{60} and O_2C_{60} .

The scattering power of N_2 is clearly localized at the octahedral site of the host lattice for all investigated temperatures. A refinement of the positional parameters of nitrogen, however, turns out to be difficult since the maximally obtainable resolution d of this diffraction experiment is of the order of 0.81 Å ($d = 2 \sin \Theta / \lambda \approx 0.62$ for $2\Theta_{\max} = 162^\circ$). For the space group $Pa\bar{3}$ the point symmetry of the octahedral site is S_6 if all C_{60} molecules are in the major orientation. With this restriction, we find an equal probability for nitrogen atoms on the corners of a small octahedron, where the distance measured along a diagonal through the center is 1.18 Å that is favorably close to the N-N bond length of the free molecule of 1.098 Å. N-N separations of 0.8 Å that is the length of the edge of the small octahedron are not realized in nature. Thus, the experiment gives evidence for the presence of $N_2(O_2)$ molecules on the octahedral sites that, however,

FIG. 4. Refined cubic lattice parameters. (i) solid squares: N_2C_{60} , (ii) open squares: reference sample of compressed pellets of C_{60} , and (iii) up triangle: O_2C_{60} (10 K).

FIG. 5. Occupation of the major orientation of C_{60} molecules (pentagon phase). (i) solid squares: N_2C_{60} sample, (ii) open squares: reference sample of C_{60} , and (iii) up triangle: O_2C_{60} (10 K).

FIG. 6. Refined low-temperature structure of N_2C_{60} for the space group $Pa\bar{3}$ with C_{60} molecules in the major orientation. N_2 molecules are found on the corners of a small octahedron centered on the octahedral sites of the host lattice. The octahedron is roughly aligned along the cubic $\langle 100 \rangle$ axes with N_2 molecular axes disordered over directions given by the diagonals of the octahedron.

are disordered over three possible orientations. To our surprise, we find that irrespective of our starting coordinates the molecules move away from a $\langle 111 \rangle$ orientation (which was our first guess) into an orientation where the molecular axis is roughly oriented along a crystal axis, i.e., along $\langle 100 \rangle$ (Ref. 22) (see Fig. 6). This was a “stable” result in a number of different refinements and is obtained for all investigated temperatures. Thus, it seems that the temperature-dependent orientational disorder of the C_{60} balls has negligible influence on the molecular orientation of N_2 . In order to obtain an impression to what extent these results depend on our particular model we have performed a differential Fourier synthesis with “observed” structure factors extracted from the complete powder pattern between 7.5° and 162° . These results that are shown in Fig. 7 (2 K) are compatible with our previous refinements but imply a more isotropic orientation of the N_2 molecule. Here, however, we have to realize that a sizable “smearing out” of the nuclear density must already be expected due to the limited value of $(\sin \Theta/\lambda)_{\max}$ of the experiment. Hence, at least a larger part of the obtained isotropic distribution is due the limited resolution. Disorder of the C_{60} molecules, thermal displacements, and at low temperatures possibly also zero-point motion further contribute to this “smearing.”

V. NEUTRON SCATTERING

A detailed analysis of rotational-diffusion excitations in N_2C_{60} is shown in Fig. 8. Very similar results had been obtained before, for O_2C_{60} .¹ The data have been collected on the time-of-flight instrument IN6 of the Institut Laue Lange-

FIG. 7. Occupation probability of nitrogen in N_2C_{60} as obtained from the Fourier difference calculated from observed intensities (full range of 2Θ) and scattering intensities calculated for pristine C_{60} in the sc phase (2 K).

vin with an incident wavelength of $4.1 \text{ \AA}$. In order to improve data statistics we have summed intensities over scattering angles (high-angle bank) close to the maximum of the structure factor of the C_{60} molecule ($3.4 \text{ \AA}^{-1}$).^{23,24} Since defects in the lattice structure such as stacking faults may have significant influence on the rotational dynamics, we compare our data with those obtained on a C_{60} reference sample that was prepared in exactly the same way but not exposed to N_2 gas at high pressures. The onset of rotational diffusion shows up by a disappearing of the C_{60} librational mode near 2 meV and the rising up of a broad quasielastic line. In agreement with the previous results, we observe a clear down shift of the transition temperature T_0 for the N_2 -loaded sample. Large precursor effects exist below $T_0 = 240 \text{ K}$ as demonstrated by the intensity remaining within the gap region around 1 meV. From its temperature dependence, we conclude that this intensity is not due to static disorder but must correspond to reorientational jumps of the C_{60} molecules below T_0 .

Next, we present results for the similar system O_2C_{60} , which due to the magnetic groundstate of O_2 ($S=1$) offers the unique possibility of observing magnetic scattering contributions from this molecule. We want to investigate whether there are indications of fast reorientations of O_2 molecules at temperatures lower than the orientational transition temperature of the host matrix. In Fig. 9 we show a comparison of raw data obtained on a O_2C_{60} sample ($\approx 70\% O_2$) at $T=200 \text{ K}$, i.e., close to T_0 , before and after the removal of oxygen (annealing at 200° in dynamic vacuum for 12 h, O_2 content $< 10\%$). The contributions from C_{60} balls have been partly suppressed by omitting higher-detector angles ($Q_{el} > 2 \text{ \AA}^{-1}$) in the summation. Statistically fluctuating intensities in the difference spectrum close to the center of the elastic line arise from the subtraction of very large elastic counting rates and are limited to the

FIG. 8. Generalized susceptibility $\omega^{-1}\chi''(\omega)$ of N_2C_{60} (dots) and a reference sample of C_{60} (line). The sc-fcc phase transition at $T=T_0$ is characterized by the vanishing of C_{60} libron modes near 2 meV and the concomitant rise of quasielastic scattering. A decrease of T_0 , strong fluctuations below T_0 and identical rotational dynamics above T_0 (260 K result, crosses show the measured instrumental resolution) can be deduced from the figure.

narrow region defined by the experimental resolution (indicated in the figure). The internal mode spectrum lies between the time-of-flight channels 100 and 230 (see also the crude energy scale on top of the figure). A strong peak at ≈ 270

channels on the energy-loss side is due to a contamination from the cryostat walls. As can be seen there are no clear indications for quasielastic scattering, which means that the O_2 molecules do not seem to reorient on the time scale of picoseconds.

Distinct excitations at ± 0.4 meV show up in the magnetic scattering at low temperatures (Fig. 10). For this experiment an incident neutron wave length of 5.12 Å was chosen that allowed for a resolution of 0.08 meV and the advantage to work below the Bragg cutoff of Al. Only intensities of detectors at scattering angles with $Q_{el} < 0.7 \text{ Å}^{-1}$ were summed up and the spectra obtained at different temperatures were normalized with respect to the elastic line. Contributions of pure-elastic scattering were removed by subtraction of a vanadium spectrum. Remaining intensities close to zero energy might be an artifact since they arise from differences of very high counting rates. The magnetic nature of the inelastic peaks becomes evident from the fact that the scattering intensity decreases by a factor of ≈ 2 within a region of $0.3 < Q < 1.8 \text{ Å}^{-1}$. Nothing similar was observed for the system N_2C_{60} with a nonmagnetic ground state. For temperatures > 20 K we register a broadening of the peaks, a decrease in intensity, and a complete vanishing for $T > 50$ K, where a quasielastic component slowly starts to show up (50 K and 70 K results). The Q dependence of the quasielastic component, however, implies that it originates from reorientational jumps of C_{60} molecules.

VI. DISCUSSION

Gases such as O_2 and N_2 with molecular dimensions of $2.8 \times 4.0 \text{ Å}$ and $3.0 \times 4.1 \text{ Å}$ can diffuse into pressed powder samples of C_{60} . At most, one $\text{N}_2(\text{O}_2)$ molecule per C_{60} unit can be trapped on the octahedral site. Since the minimum diameter of the open channels between the octahedral sites measures $\approx 1.56 \text{ Å}$ the intercalation depends sensitively on external parameters such as temperature, pressure, and time.

The exclusive occupation of octahedral sites in the C_{60} host lattice is an indisputable result of our structural refinements as well as distinct changes observed for the C_{60} host:

FIG. 9. Neutron time-of-flight spectra of O_2C_{60} showing the spectral changes on annealing. (i) solid circles: virgin sample, (ii) open circles: the same sample after annealing, (iii) solid triangles: the difference, and (iv) dots: the instrumental resolution. Contributions of C_{60} librational modes have partly been suppressed by the selection of a particular Q region for the integration of data (see text). No clear evidence for quasielastic scattering due to O_2 rotational diffusion is observed.

FIG. 10. Magnetic scattering from molecular oxygen in O_2C_{60} for the indicated temperatures. Elastic scattering has been removed by the subtraction of a Vanadium line.

A lattice expansion, an almost suppression of the glass transition near 90 K, and a predominant ordering in the energetically more favorable pentagon phase. Within the generally accepted $Pa\bar{3}$ symmetry of the low-temperature structure (S_6 symmetry of the octahedral sites) we obtain a 65% (78%) occupation by $N_2(O_2)$ molecules with the molecular axes roughly aligned parallel to the $\langle 100 \rangle$ axes of the cubic lattice. A differential Fourier analysis reproduces these alignments but points to a considerable “smearing” of the ideal orientations. Although, the analysis reaches the limits set by our experimental resolution, the “smearing” is in line with the anharmonic behavior of $N_2(O_2)$ optic modes discussed in our previous paper. Keeping the $N_2(O_2)$ molecular alignments fixed in $\langle 110 \rangle$ or $\langle 111 \rangle$ direction does not significantly worsen the R values of the Rietveld fits.

A careful analysis of the spectra in Figs. 8 and 9 gives no evidence for $N_2(O_2)$ quasielastic scattering. The guest molecules, therefore, do not reorient on the time scale of picoseconds. This is in line with the density of states where we got evidence for well-defined translational vibrations of the encapsulated $N_2(O_2)$ molecules near 8 meV and a broad distribution of librational modes at finite energies¹ (see also

Fig. 9). Although we found from model calculations¹ a preference for equilibrium orientations along the $\langle 111 \rangle$ directions in contrast to the present structural analysis, it is a common result that the potential that is experienced by the guest molecules must be rather shallow. These model calculations predicted a larger dispersion of $N_2(O_2)$ vibrational modes for alignments along the $\langle 110 \rangle$ and $\langle 100 \rangle$ axes, which, according to our impression, did not show up in the density of states.¹ With respect to the present results, we must conclude that the actual potential that is experienced by the guest molecules is more isotropic and that very weak interactions with the surrounding C_{60} molecules favor an alignment not far away from one of the nearest-neighbor axes. The finding that we did not see any influence of the fraction of hexagon/pentagon orientations on the alignment of the guest molecules could support this conclusion.

Further details might be concluded from the magnetic-scattering results. For an isolated molecule the even parity of the total ground-state wave function requires the rotational and the spin quantum numbers to take on the values $J=1$ and $S=1$. This state is ninefold degenerate and is supposed to split in a crystalline electric field of octahedral symmetry. The scenario of an O_2 molecule in a crystalline electric field (CEF) has been worked out to quite some extent in the literature.^{25,26} There the results have been compared to specific heat measurements of O_2 dissolved in noble-gas crystals. The observation of only one CEF excitation at ± 0.4 meV requires a crystal-field constant $K_4 > 0$, where the molecule is oscillating and far away from the limit of free rotation. The observed temperature dependence below $T < 20$ K would correspond to a two-level scheme and support this picture. However, for $20 \text{ K} < T < T_g$ the observed spectra do not correspond to a normal CEF scenario, i.e., no new excitations are observed with increasing temperature. Reorientational jumps of C_{60} molecules that would lead to an averaging of the CEF potential become important for $T \geq 70$ K (Fig. 10), which is in agreement with the almost-suppressed glass transition around 70 K (Fig. 2). The observed decrease and broadening of magnetic excitations already for $T > 20$ K could be due to slow reorientational motions of the O_2 molecules. We might add that we did not observe indications for a collective behavior in the sense that the excitation at ± 0.4 meV did not depend on momentum transfer.

Favored by the weak Van der Waals binding forces of the C_{60} lattice we register significant and interesting changes in the cage dynamics for the intercalated samples. Most evident is a downshift of the $sc \rightarrow fcc$ ordering temperature. In our case δT_0 is $-21/-20$ K for $N_2(O_2)$ intercalation, respectively. An obvious explanation for this decrease of T_0 is the lattice expansion. Using the known pressure dependence of T_0 for N_2 of 160 K/GPa^{3,27} the observed down shift would require an internal pressures of ≈ -1.25 kbar for our samples. This value, however, is not fully compatible with the results from dilatometry measurements presented before. For $\Delta L(T)/L_{295K} = 0.0022$ we obtain an internal pressure of only 0.581 kbar based on the literature value for the Bulk modulus of 8.8 GPa.^{3,27} This implies that the changes in the molecular dynamics can not be solely attributed to negative

pressure. Intercalation must have a more profound influence on the ordering of the cages. In this context, one has to keep in mind that negative pressure already implies a shift in ordering towards the energetically more favorable pentagon orientation as this orientation requires a larger volume. This statement is confirmed indirectly by the strong suppression of the glass transition anomaly in the dilatometry measurements and directly by the diffraction data. The nearly exclusive ordering in the pentagon configuration equally explains²⁸ why the libron frequency is found to harden with respect to pure C₆₀ at low temperatures.¹ This requires that the intercalation of guests molecules has an influence on the barrier-height distribution that has to be overcome by the cages in the process of reorientation.

All investigations (DSC, thermal expansion, and quasi-elastic neutron scattering) give evidence for large precursors of the order-disorder transition (240 K) which, as it can be concluded from the neutron data, are dynamic in nature and prove reorientational jumps of C₆₀ molecules on a time scale of $\approx 10^{-10}$ s. These precursors set in at lower temperatures in the intercalated samples. There are no signs of strong hybridization between energetically corresponding external C₆₀ and optic N₂(O₂) modes. To a good approximation the total density of states can be understood as a superposition of the C₆₀ spectrum and that of the host particle (see also the discussion in Ref. 1). The barrier heights enter exponentially into the expressions for the reorientation times of the cages. These expressions in addition are sensitive to the path taken by the cages in the energy landscape. Small changes may, therefore, lead to appreciable reductions in T_0 .

VII. CONCLUSIONS

The structure and dynamics of O₂ and N₂ intercalated into bulk C₆₀ has been investigated via high-resolution dilatom-

etry, neutron diffraction, quasielastic, and inelastic neutron scattering in the present and a preceding paper.¹ Concerning the C₆₀ host we find that the main structural and dynamic characteristics remain unchanged. Details concerning the transition towards the high-temperature rotator transition, the merohedral disorder in the low-temperature phase as well as the low-temperature glass transition are strongly affected by the intercalated molecules and can only partly be explained by "negative pressure." The inelastic-excitation spectrum of the C₆₀ host is not significantly affected by the intercalated particles. The well-resolved rotational line near 2 meV slightly hardens at low temperatures, a fact that can be attributed to the nearly exclusive ordering in the pentagon orientation. It, however, drops stronger with temperature, a fact compatible with the reduction in the ordering temperature. We have taken special effort to explore the dynamics of the guest molecules and in none of our measurements we obtain evidence for reorientation on the picoseconds time scale. In this context, our observation of distinct magnetic excitations for encapsulated O₂ is quite interesting and these investigations will be carried on.

Although, the subject has not been addressed explicitly it turns out that the morphology of the samples does not play an important role in the phenomena discussed here. Weak Van der Waals bonds could promote the formation of stacking faults that might have some influence on molecular ordering. However, from a large number of investigated samples obtained under different conditions, we conclude that the main results presented here are general in nature and can be applied to the whole class of these compounds. On the other hand, the sensitivity of diffusion on morphology as well as on the external control parameters of gas, loading may allow to find conditions where such systems become interesting for applications, an aspect that will be addressed in a forthcoming paper.

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