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Structure and dynamics of C_{60} intercalation compounds: N_2C_{60} and O_2C_{60}

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We have studied the dynamics of polycrystalline C_{60} intercalated with O_2 and N_2 by inelastic and quasielastic neutron scattering. Complementary neutron diffraction investigations have been performed for O_2C_{60}. The diffraction pattern of the low-temperature phase can be refined with the structural parameters of crystalline C_{60} (space group $Pa\overline{3}$). All oxygen molecules are found on octahedral sites and an expansion of the host lattice is registered with respect to pristine C_{60}. The samples show a reduction in the order-disorder transition temperature T_0 of about 20 K with respect to bulk C_{60}. This is demonstrated by differental scanning colorimetry measurements and the onset of quasielastic scattering. The fact that quasielastic intensity is observed appreciably below T_0 indicates the presence of large fluctuations in the ordered phase. Above T_0 we find the same quasielastic response as for pristine C_{60}. The phonon spectrum of the host is only weakly perturbed by the presence of the guest molecules. Vibrations of the trapped O_2/N_2 molecules give rise to well pronounced peaks at 7 and 8 meV, respectively. The external molecular vibrations show a highly anharmonic temperature behavior. There are, however, no signs of rapid reorientational jumps of the guest molecules on the ps time scale. Model calculations indicate a predominant alignment of the guest molecules along the [111] directions combined with appreciable orientational disorder.

I. INTRODUCTION

Pristine C_{60} shows a well-known first-order phase transition. Above 260 K the C_{60} cages are orientationally disordered (fcc phase $Fm\overline{3}m$). At lower temperatures the rotational degrees of freedom freeze in a simple cubic (sc) arrangement (sc phase $Pa\overline{3}$).[1,2] Despite considerable experimental and theoretical efforts a comprehensive understanding of the intermolecular potentials responsible for molecular ordering and molecular reorientation is still awaited.[3–5] Due to the combination of weak interactions with multiple interaction sites the transition is very sensitive to the details of the potential and can be altered appreciably by the application of pressure or the intercalation of guest molecules.

Intercalation of atoms into fcc C_{60} is well known from the alkali-metal doped systems. It generally increases the ordering temperature T_0 in the same way as the application of external pressure.[2,6] Apart from alkali-metal ions many other atoms and small molecules diffuse into the C_{60} matrix more or less readily as long as their diameter does not exceed the diameter of the octahedral interstitial sites in fcc C_{60} of ≈ 4.1 Å (Refs. 7–11). Diffusion obviously takes place via hopping between these sites and is enhanced by temperature and pressure.[12] These systems, therefore, have the potential of becoming lightweight solid gas storage devices.[7]

van der Waals atoms or molecules are particularly well-suited candidates for intercalation. As no large structural changes of the host matrix are expected upon their intercalation they allow us to tune the C_{60} interaction potential in a controlled way for a detailed study of the molecular dynamics.[13] Surprisingly, intercalation of van der Waals atoms or molecules into the octahedral voids reduces the temperature of molecular ordering. This effect may be assimilated to ‘‘negative pressure.’’ Using a mechanical analog the van der Waals guests may be termed molecular lubricants. The magnitude of the change in T_0 depends on the system details. For ArC_{60} shifts $\Delta T_0 \approx -10$ K are observed[14] while 0.14 kbar of He produce a rather small shift of only $\Delta T_0 \approx -2$ K.[9,15] O_2C_{60} features one of the most pronounced shifts $\Delta T_0 \approx -20$ K.[16] A still larger value of $\Delta T_0 \approx -22$ K is measured for N_2C_{60}. Once loaded the intercalated gases can be preserved by quenching the samples to 77 K where the diffusion process becomes extremely slow.

Because of their large ΔT_0 we concentrate in this paper on the investigation of C_{60} intercalated with O_2 or N_2. Up to now the intercalation of O_2 has been studied extensively using x-ray diffraction[11,16] (XRD), differential scanning calorimetry,[11,16,17] internal friction,[15] NMR,[16–18] and dielectric spectroscopy.[12,18] Nearly stoichiometric samples of N_2C_{60} have been prepared in the course of our investigations. Indications for an intercalation of N_2 into C_{60} had been obtained before via dielectric and NMR spectroscopy.[18]

The molecular motions in these systems have, however, been given little attention despite the fact that they play an important role for a comprehensive understanding of the reduction in T_0. Neutron scattering is an ideal tool for the study of molecular motions of both the C_{60} host as well as the guest molecules. It offers the possibility to observe the dynamics of rotational diffusion both in time and space. Si-

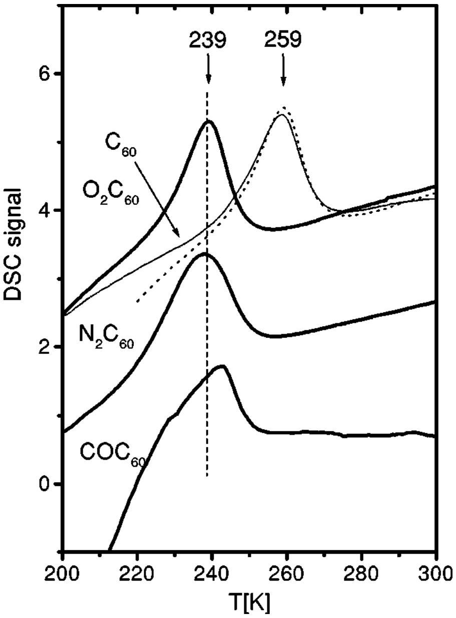

FIG. 1. Differential scanning calorimetry (DSC) scans showing a significant downshift in the sc-fcc phase transition temperature of C_{60} on intercalation of O_2, N_2, and CO. The dotted curve is the O_2C_{60} result shifted by 20 K and shows that the enthalpy remains essentially unchanged. The two lower curves have been downshifted for better presentation.

multaneously the frequency spectrum of the lattice modes can be studied[19] yielding the interactions between guest molecules and the host lattice. Neutron diffraction in addition is a bulk probe which is an advantage over surface-sensitive methods as intercalated molecules may be lost easily from the surface region.

II. SAMPLE PREPARATION

C_{60} compacted in pellets under high pressure has been reported to be an effective medium for O_2 intercalation.[16] Intercalated O_2 is readily lost from its host matrix in loose powder samples where the diffusion between the crystallites is high. No comparable intercalation of molecular gases has been reported for single crystals. For our experiments gold grade C_{60} was further purified by heating in a dynamic vacuum. The polycrystalline powder was milled and passed through a 75 mesh sieve. Small pellets of 8 mm in diameter and 1 mm in thickness were produced in a standard pressure cell between pistons at 15 kbar pressure. For oxygenation the pellets were kept in a furnace at 300 K and an oxygen pressure of 200 bar was applied over seven days. Different conditions, 500 K and 390 bar pressure, were used for the intercalation of N_2. Subsequently the pellets were stored in closed sample containers under liquid nitrogen.

The sc-fcc transition temperatures were measured by DSC analysis for pellets of C_{60} loaded with O_2, N_2, and CO (Fig. 1). No significant changes in the enthalpy of the transition are observed as a function of intercalation. This can best be seen from the dotted line in Fig. 1 which shows the DSC signal for O_2C_{60} shifted by 20 K along the temperature axis. The absolute value for the enthalpy change is in good agreement with the literature values for C_{60}, if taking into consideration the uncertainty in determining the baseline discussed in Ref. 13. $\Delta H \approx 6.3$ kJ/mol for $C_{60}O_2$ ($M = 743$ g/mol for $x = 0.7$). Thus, no additional energetic contributions to the transition, e.g., arising from the rotational degrees of freedom of the guest molecules, are observed (of course this measurement might not be sensitive enough).[20] Scans performed with different heating rates give evidence for the rapid loss of the intercalated gas around 440 K. After annealing of the samples in dynamic vacuum at 500 K for two days we found a loss in weight corresponding to an occupation of about 70% and 60% of the octahedral sites by O_2 and N_2, respectively.

III. EXPERIMENTAL DETAILS

Neutron diffraction studies were performed on the high resolution diffractometer D2B at the Institut Laue-Langevin in Grenoble (France) for temperatures of 10 and 300 K. Diffraction angles between $7.5° < 2\Theta < 162°$ and a wavelength of $\lambda = 1.5938$ Å were chosen. The accumulation time for the 300 K measurement had to be reduced because of possible oxygen losses but was sufficiently long to allow for a determination of the lattice constants.

Inelastic neutron scattering (INS) experiments were performed on the IN6 time-of-flight spectrometer at the same site using an incident neutron energy of 4.72 meV and an elastic energy resolution of $\Delta E \approx 200$ μeV [full width at half maximum (FWHM)] in a slightly inelastic focusing mode. The data were analyzed in the up-scattering (neutron energy gain) region allowing for measurements down to temperatures $T \approx 100$ K with a very good resolution in the important low-energy domain. Due to the instrument's low incident neutron energy only small momentum transfers ($\leqslant 2.6$ Å^{-1} for elastic scattering) are possible. For instance, at 2 meV, which is the position of the librational mode in sc C_{60}, we do not reach the first maximum of the inelastic structure factor at 3.5 Å^{-1}. Librational intensities are therefore underestimated, which is of no importance for the discussion in this paper. Our data will be presented in two forms: The generalized phonon density of states $G(\omega)$ and the generalized dynamical susceptibility $\chi''(\omega)$. ''Generalized'' means that the vibrational contribution of each kind of atom is weighted by its neutron scattering power σ/m. $G(\omega)$ is obtained from the time-of-flight data by means of the incoherent approximation (for details see Ref. 19). Multiphonon contributions are corrected for in a self-consistent way. Rotational diffusion, which is a statistical process, is not correctly described by $G(\omega)$ and better studied via $\chi''(\omega)$. Here we will present our data in the form $\omega^{-1}\chi''(\omega)$ which for energies small compared to the temperature is proportional to the scattering law. An integration is carried out over the angular region accessible to the experiment allowing for good data statistics. The fact that we lose in this way information concerning the Q dependence is irrelevant for the conclusions drawn.

IV. STRUCTURAL PROPERTIES

Figure 2 shows the diffraction pattern of O_2C_{60} obtained at 10 K. It is compared to a Rietveld fit form the refinement package FULLPROF.[21] In the calculation the C_{60} molecule is treated as an ideal, truncated icosahedron (symmetry $m\bar{5}m$).

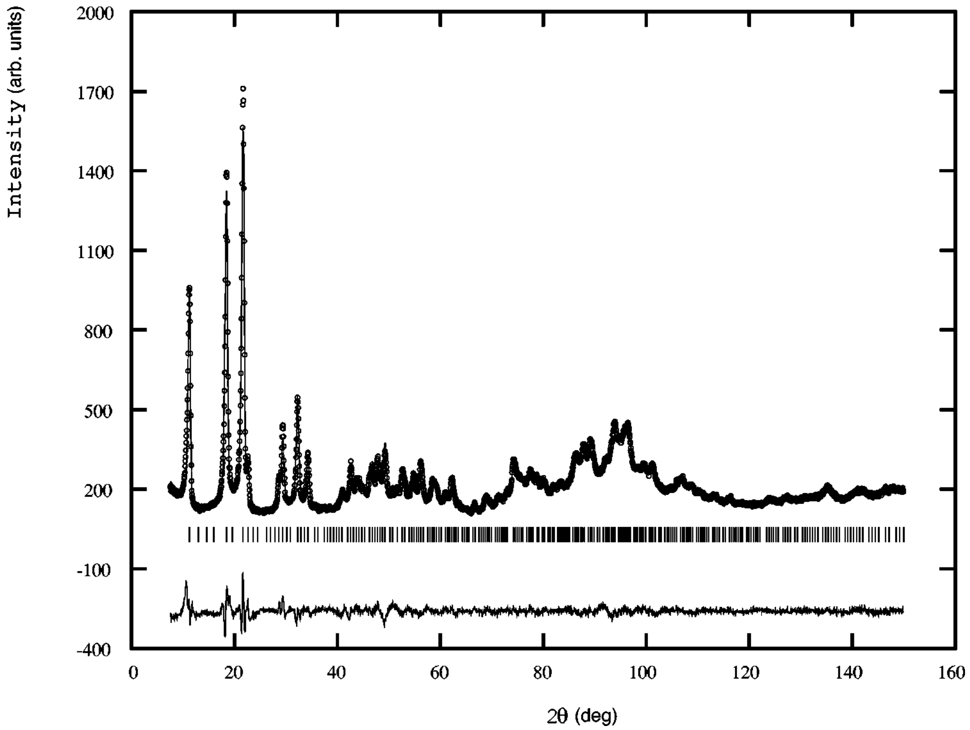

FIG. 2. Powder neutron diffraction profiles observed (open dots), calculated (lines), and difference (solid lines) for O_2C_{60} at 10 K.

Only the radius and the orientation of the molecule are refined within the space group $Pa\overline{3}$. We obtain molecular radii ($r = 3.54$ Å) and molecular orientations very close to those found by David *et al.* for pure C_{60} in the major orientation.[22] O_2 is placed on the octahedral sites oriented along [1 1 1] and disordered over all three equivalent positions. No attempt is made to refine the position of the O_2 molecular axis. The occupation probability of O_2 on octahedral sites is found to be close to 80% which corresponds well to the 70% determined gravimetrically. Thus, it can be concluded that the O_2 molecules are exclusively trapped in the large octahedral cavities of the sc lattice of C_{60} and not at zone boundaries in the polycrystalline sample. As the fit is already very good ($R_p = 0.364$, $R_w = 0.051$, $R_{\text{Bragg}} = 0.0026$, and a χ^2 of 5.3) we do not attempt to improve the refinement by allowing for orientational disorder. Due to the high overlap of reflections it is not easy to determine in a precise way the background contribution. Nevertheless the existence of structure in the background can be observed even with the naked eye. We treat the background iteratively by using a Fourier filtering technique and obtain a shape which at large Q strongly resembles the diffuse scattering found in pure C_{60} just above the ordering temperature.[23] We take this as a hint for orientational disorder due to C_{60} cages in the minority orientation. The shape of the peaks in addition contains clear Lorentzian components indicating that we are not dealing with large ideal crystals.

Of particular importance for the present work is the lattice expansion. At 10 K we obtain $a = 14.050$ Å as compared to the literature value $a = 14.041$ Å in pure C_{60} (Ref. 22) which leads to a linear lattice expansion of $\Delta a = 0.009$ Å. It has to be noted that the lattice constant is strongly correlated with the instrumental zero of the scattering angle 2Θ which has not been refined separately in the present work. At 300 K $a = 14.174$ Å, i.e., $\Delta a = 0.022$ Å if comparing with pure C_{60}.[24] The expansion found here for O_2C_{60} is very similar to that determined for COC_{60}.[13] In the latter system orientational parameters for CO have also been refined.[25,26] It is well known that the lattice parameter shows a distinct jump to larger values at the first-order sc-fcc phase transition.[2] For the intercalated systems this jump is observed at lower temperatures in agreement with the reduced value of T_0. Thus, favored by weak interball binding forces the C_{60} lattice reacts noticeably to the occupation of the octahedral sites by O_2 in the same way as to the application of negative pressure. Using the uniaxial compressibility of C_{60}, $da/dp = 0.033$ Å/kbar (Ref. 2) we may estimate that an internal pressure of about 0.7 kbar would be necessary to produce the observed lattice expansion of $\Delta a \approx 0.022$ Å. This pressure can be converted into a T_0 reduction via the pressure dependence[2] of T_0. Using $dT_0/dp = 16$ K/kbar, which is the maximum value published in the literature,[27] we obtain $\Delta T_0 \approx 11$ K far smaller than the measured downshift. Negative pressure on its own, therefore, is unable to explain the T_c reduction.

Similar results have been found for other systems, e.g., structural refinements give $\Delta a = 0.012$ Å at 285 K for intercalated Ar.[14]

V. LATTICE DYNAMICS

A. Inelastic neutron scattering results

In Fig. 3 we show the experimental[28] $G(\omega)$ of O_2C_{60} together with the C_{60} reference at 210 and 260 K. For optimum comparison the reference sample underwent exactly the same treatment as the intercalated samples apart from oxygen loading.

The spectrum for O_2C_{60} below ≈ 4 meV is very similar to that of the C_{60} reference.[29] The first band in the C_{60} spectrum at 2 meV is of librational origin.[30,31] The second band at 4 meV contains both transverse-acoustic and librational

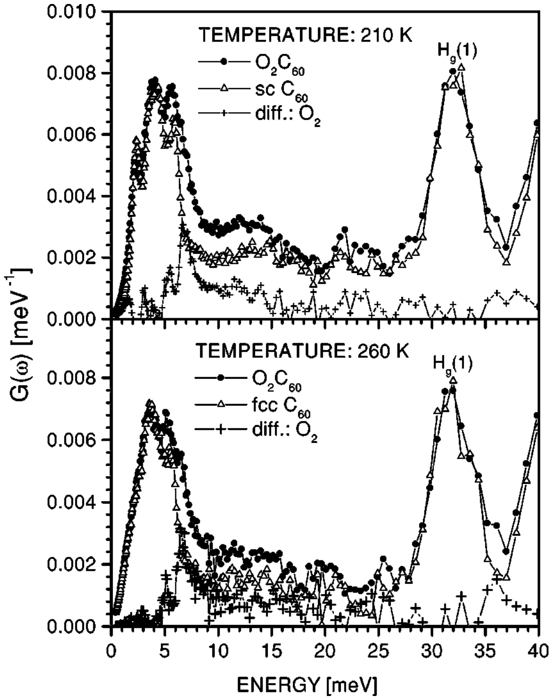

FIG. 3. Low-energy part of the generalized phonon densities of states of O_2C_{60} and C_{60} below ($T=210$ K) and above ($T=260$ K) the sc-fcc phase transition. The difference pattern gives evidence for vibrations of the oxygen molecule with a distinct peak at 7.0 meV.

C_{60} contributions whereas the smaller peak at 6 meV is caused by longitudinal-acoustic modes.[30,31] The excess intensity between 5 and 15 meV may be attributed to vibrations of the oxygen molecule. The difference spectrum is shown by crosses in Fig. 3 and gives—in the approximation of vanishing host-guest coupling—the O_2 partial density of states. Apart from a distinct peak at 7.0 meV there is evidence for a broad underlying distribution. The integration of the excess intensities up to 15 meV yields 5 degrees of freedom in agreement with the expected three translational and two rotational modes of molecular oxygen. For this estimation the difference in the neutron scattering powers and the reduced O_2 occupation have been considered. The O_2 stretching vibration is much higher in energy. The partial O_2 density of states in O_2C_{60} occupies the same energy region as the density of states of solid oxygen (α-O_2).[32] The later exhibits two major translational bands around 5 and 9 meV and a broader libronic band between 9 and 15 meV. Thus, the strength of the restoring forces encountered by O_2 in solid oxygen is not very different from that encountered by intercalated O_2 in C_{60}.

Nitrogen has a significantly larger neutron scattering power σ/m(barn/amu) than oxygen and carbon: 0.8187 (N) compared to 0.2644 (O) and 0.4631 (C). This leads to an improved contrast when it comes to determining the N_2 contributions. The difference spectrum with the C_{60} reference (Fig. 4) shows a prominent peak at 8 meV which is attributed to vibrations of N_2 trapped in the octahedral cavities. Assuming similar restoring forces and taking into consideration the different masses it may be identified with the O_2 peak in O_2C_{60} at 7 meV. As in O_2C_{60} an underlying broad band of intensity is found in N_2C_{60} which reaches up to 17 meV. Taking into account that N_2 occupies 60% of the octahedral sites we estimate that the difference spectrum corresponds to roughly 5 degrees of freedom. The moments of inertia for N_2 and O_2 are very similar (0.156×10^{-40} g cm^2). Thus from the experimental comparison it is not possible to discriminate translational from librational excitations.

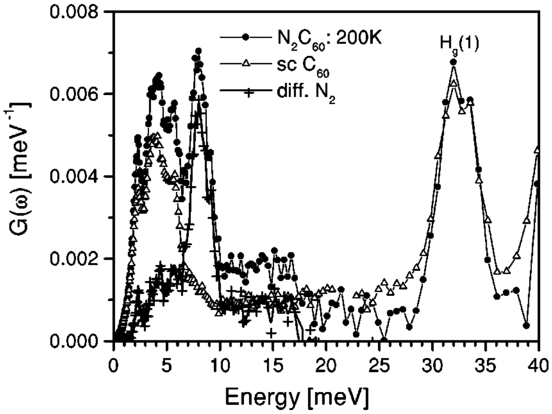

FIG. 4. Low-energy part of the generalized phonon densities of states of N_2C_{60} at 200 K. The well localized peak at 8.0 meV is due to external vibrations of the N_2 molecule. An underlying broader band of excitations shows up in the difference spectrum (crosses).

We concentrate in this paper on the external modes. Due to the weak interaction between the guest and host the internal modes are only marginally affected by intercalation. To support this point we present the Raman scattering result for N_2C_{60} (Fig. 5). The influence of the host matrix on the bond-stretching frequency of N_2 is indeed small. Compared to the free N_2 gas we register a decrease by 3.5 cm^{-1} which is only slightly larger than the calibration error of the spectrometer (≤ 2 cm^{-1}). Shifts and splittings of lines in the internal mode spectrum of C_{60}, which are commonly observed in systems with charge transfer[33] or with covalent intramolecular bonding, are not registered in the present case.[34]

B. Quasielastic scattering results

Figure 6 shows in detail the evolution of $\omega^{-1}\chi''(\omega)$ between 210 and 260 K for samples $(O_2)_xC_{60}$ with $x=0$, $x\approx0.4$, and $x=0.75$. To obtain these spectra we have summed up the intensities recorded in the highest scattering angles (1.5 Å $\leq Q_{el} \leq 2.6$ Å) in order to give a higher weight to rotational excitations. It is seen from the temperature evolution of $\omega^{-1}\chi''(\omega)$ how the intercalation of O_2 facilitates reorientational jumps of C_{60}. The 210 K patterns show the librational mode of the host cages around 2 meV. This librational mode is already broadened and shifted by 0.1 meV to lower energies—with respect to the pristine reference—for the fully oxygen loaded sample. In addition a small quasielastic component is present at 210 K and fills part of the gap around 1 meV. This component is absent at 100 K (inset) and therefore due to anharmonicity in the sample. With further increasing temperature the librational peak at 2 meV loses intensity in favor of a broad quasielastic line, indicating that an increasing number of C_{60} molecules participate in rapid reorientational jumps. At 245 K the librational peak has completely disappeared in the loaded samples while the spectrum of pure C_{60} shows only a very

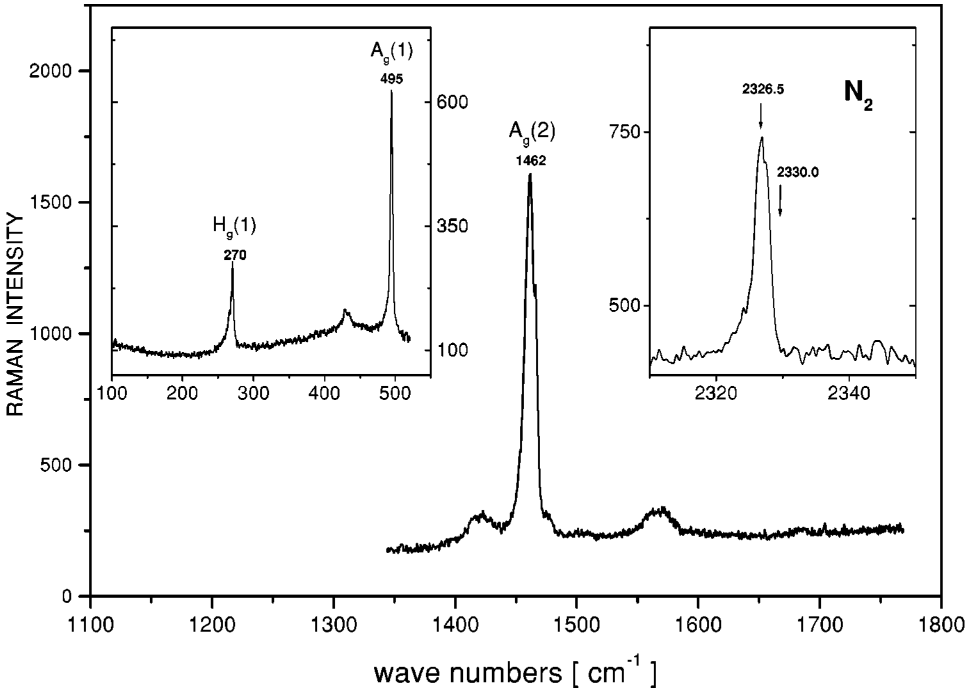

FIG. 5. Selected regions of the Raman spectrum of N_2C_{60}. No significant changes in the internal mode spectrum of C_{60} and only a small downshift of the N_2 stretching mode with respect to the gas phase (2330 cm^{-1}) are found.

small quasielastic contribution. In the loaded samples the dynamics is, therefore, already dominated by rotational diffusion which has been studied in detail for pure C_{60}.[31,35] At 260 K, which is just above T_0 for pure C_{60}, all three spectra become indistinguishable in the quasielastic region. For constant Q, $\omega^{-1}\chi''(\omega)$ can be expressed by a sum of Lorentzians. The Q dependence of the quasielastic linewidth and intensity allows us to extract a constant for rotational diffusion[31,35] which is of the order of $D_r = 1.6\times 10^{10}\ s^{-1}$ for C_{60} at $T = 320$ K. From the coincidence of all three spectra at 260 K we conclude that the intercalation of O_2 has a negligible influence on the reorientation times of the C_{60} cages in the plastic phase. The same kind of dynamic behavior is registered for N_2C_{60}.

In contrast to O_2C_{60} where the guest vibrations are not clearly separated from the external host spectrum we may follow the spectral evolution of the main N_2 band in N_2C_{60} as a function of temperature. Similar to the librational excitations of C_{60} near 2 meV the N_2 band at 8 meV softens strongly and broadens when approaching the phase transition (Fig. 7). However, the band persists in the rotator phase while the librational peak at 2 meV disappears. This is consistent with the fact that no additional quasielastic scattering due to rotational diffusion of O_2 or N_2 could be observed at temperatures less than T_0. At higher temperatures such contributions would be masked by the strong changes in the dynamics of C_{60}. NMR investigations[26] of COC_{60} using C^{13}-enriched CO give evidence for rapid reorientational movements of CO at temperatures above ≈ 240 K which is close to the transition temperature T_0. Due to the very similar properties of O_2/N_2 we would expect a comparable behavior also for these molecules. What remains, however, is a big difference in the time scale of both experimental techniques which is much shorter in the case of neutrons (10^{-12} s).

C. Model calculations for the low-temperature phase

In order to estimate the potential influence of the guest molecules on the host dynamics we performed lattice-dynamical calculations. As these are based on the harmonic approximation they are only meaningful in the low-temperature sc phase. In our calculations all carbon and oxygen atoms are considered independent dynamical units. The molecular cages (short bond 1.4 Å, long bond 1.45 Å) are

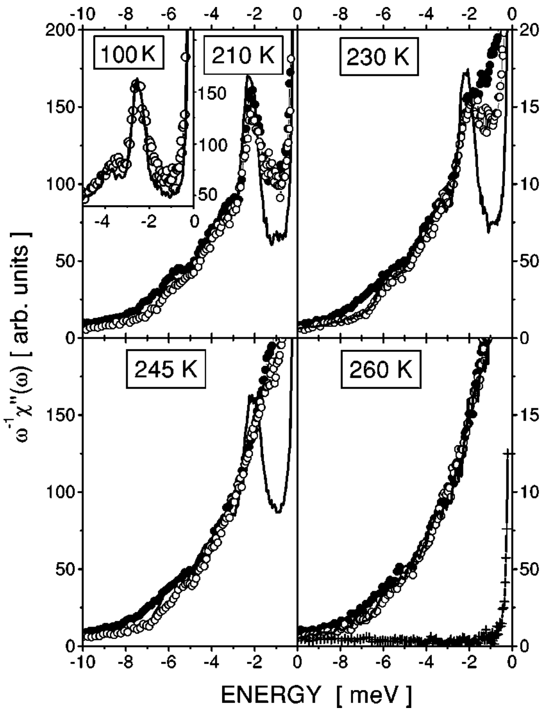

FIG. 6. Generalized susceptibility $\omega^{-1}\chi''(\omega)$ of $(O_2)_xC_{60}$ for $x=0$ (solid line), $x\approx 0.4$ (open symbols), and $x=0.75$ (full symbols). The sc-fcc phase transition is characterized by the vanishing of the C_{60} libron modes near 2 meV and the concomittant rise of quasielastic scattering. (i) A decrease of T_0, (ii) strong fluctuations well below the nominal tranition temperature, as well as (iii) identical rotational dynamics above T_0 (the 260-K result) can be directly deduced from the figure.

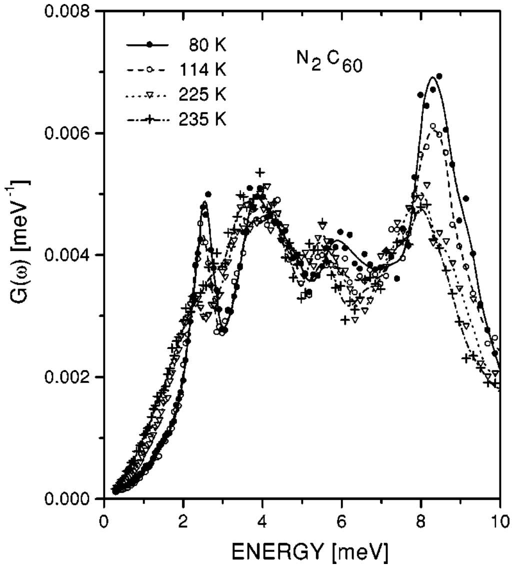

FIG. 7. Temperature dependence of the external mode spectrum of N_2C_{60}. A pronounced anharmonic behavior is found both for the C_{60} spectrum as well as the N_2 vibrations at 8 meV.

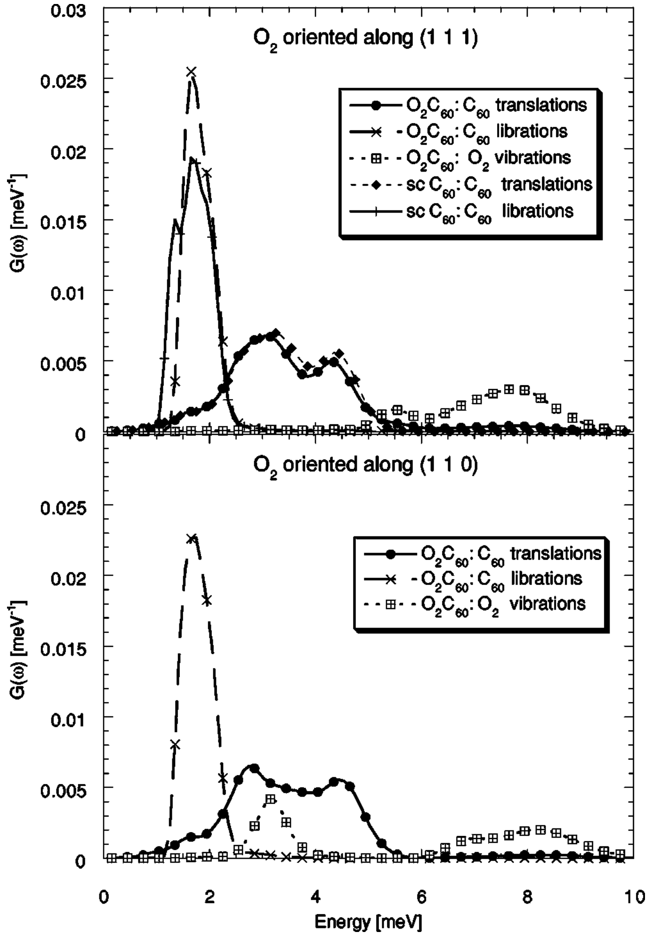

FIG. 8. Calculated $G(\omega)$ for O_2C_{60} in the sc phase with C_{60} cages in the major orientation, O_2 on octahedral sites oriented along [111] (upper frame) and [110] (lower frame). O-C interactions were modeled by a Lennard-Jones potential which was adjusted to yield frequencies in the observed region (see the parameters in Table I).

stabilized by the same force field used previously to reproduce the dynamical properties of C_{60}.[19] They interact with each other through Lennard-Jones potentials. It is well known that such a simple model cannot reproduce the details of the rotational dynamics in C_{60}.[36] E.g., the model calculations give only one librational band in contradiction to the experiment.[37] For the ensuing comparison intended to study the influence of the guest molecules on the host lattice dynamics these shortcomings are, however, acceptable.

The geometry chosen for the host lattice corresponds to space group $Pa\bar{3}$ with the cages rotated around equivalent [111] directions anticlockwise by 100°, i.e., all cages are in the major orientation. In order to isolate the influence of the guest atoms from a pure negative pressure effect we keep the same lattice constants for the loaded and pristine systems. It can safely be assumed that there is little correlation between the movements of guest atoms on distinct sites. We, therefore, may do the calculations on a hypothetically ordered system. The center of gravity of the ordered guest molecules is fixed on the octahedral site. The coordinates of the individual atoms are chosen such that different alignments of the molecular axis can be investigated. As the symmetry of the molecule is incompatible with the site symmetry $(\bar{3})$ the ordering of the guest molecules implies a reduction of the space group from $Pa\bar{3}$ to Pbca. Like the C-C interaction the O-C and N-C interactions are modeled by Lennard-Jones potentials. We have not considered any magnetic or polar interactions that might arise from a small quadrupole moment of O_2. In a first step the O-C potential is adjusted to yield O_2 vibrational frequencies that correspond as close as possible to the experiment. For fixed potential parameters we have considered alignments of the guest molecule along the [111], [110], and [100] axes and we find the most satisfying correspondence to the experiment for the [111] arrangement. In the [111] direction the guest molecules have maximum distances to the surrounding carbon atoms. For the two other orientations we obtain a partial O_2 density of states with two separated maxima and an extension of modes to higher energies. The calculated spectra are shown in Fig. 8 and the model parameters are listed in Table I. Concerning the comparison with experiment the broad underlying intensity due to vibrations of the guest molecules cannot be described by the lattice-dynamical models. This fact indicates substantial disorder in the guest molecule's orientation which according to Sec. V B should be static on the time scale of ps.

The calculations demonstrate that the original spectrum of C_{60} is little influenced by the presence of the guest mol-

TABLE I. van der Waals parameters for the different types of bond used in the model calculations. We use a Lennard-Jones parametrization of the form $V(r)=D[(\sigma/r)^{12}-2(\sigma/r)^{6}]$. The parameter d_s indicates the shortest distances between ions ([111]/[110] direction, respectively). C-C interactions on the cage are not considered, but are described through the force field of Jishi *et al.*[40] The two oxygen ions forming a molecule ($d=1.23$ Å) are coupled to each other via a longitudinal force constant of 114 N/m in order to give the correct stretching frequency.

Bond	σ (Å)	D (meV)	d_s (Å)
C-C	3.85	2.85	3.11
O-C	4.00	1.0	3.24/3.14

ecules. In particular the librational bands do not soften as a result of the interaction. This contrasts with the intercalation of alkali-metal atoms where due to charge transfer the presence of Coulomb forces causes significant changes in the $G(\omega)$ spectrum of the C_{60} host.[37] The fact that we can describe O_2C_{60} and N_2C_{60} with the same potentials is consistent with the experimental finding that the frequencies of the guest molecule's vibrations scale roughly with the molecular mass.[38] Despite the fact that the vibrational modes are concentrated in bands the dynamics of the intercalated gas molecules differs from what is expected for a simple local oscillator in the details. We explain this by a high degree of translational-rotational coupling leading to rather complex eigenvectors for the guest molecule.

VI. DISCUSSION

In agreement with earlier investigations we find that molecular O_2, and from the present work equally N_2, can be intercalated into solid C_{60} almost stoichiometrically. The intercalation is promoted if C_{60} is present in the form of compressed pellets. Microcrystalline cracks may favor the diffusion under pressure whereas O_2/N_2 losses under ambient conditions are reduced for the compacted material. We have verified that grinding of the pellets leads to a rapid loss of O_2. However, in compacted form a major part of the gas molecules remains trapped in the C_{60} matrix for hours even at 300 K. Therefore, it seems possible to find conditions that allow for an effective use of these systems as solid-state storage media.

The literature value for the transition temperature of crystalline C_{60} (Ref. 2) is 261 K which corresponds to the maximum at 259 K in the DSC signal of Fig. 1. This maximum is shifted for the oxygen intercalated sample (70% occupation of the octahedral sites) by $\Delta T_0 = -20$ K. For N_2 and an occupation of 60% we obtain a record shift of $\Delta T_0 = -22$ K and a slightly smaller value of $\Delta T_0 = -16$ K for CO. The onset of the transition in the DSC measurements is found about 20 K below T_c. This holds both for pristine C_{60} and for the intercalated systems. The onset in the DSC measurement scales with the onset of an anomalous lattice expansion and the observation of extra ''quasielastic'' intensity at low frequencies. The latter is evident from Fig. 6. The quasielastic signal indicates that large reorientational fluctuations are present in the low-temperature phase. Therefore the reorientational fluctuations on the ps time scale do not freeze out completely as the system crosses the first order T_c. This phenomenon may be related to the fact that we are dealing with potentially ''dirty'' powder samples. As, however, only powder samples can be efficiently loaded with van der Waals gases the finding is relevant for the present work. The pronounced anharmonic behavior of the C_{60} librations starts already at much lower temperatures (Fig. 7) and seems not to be directly correlated with the excess intensities at lower frequencies.

Both the inelastic neutron measurements and the theoretical calculations demonstrate that the influence of the intercalated O_2 and N_2 molecules on the lattice dynamics of the host remains small. E.g., the energy of the main librational peak of the C_{60} cages is found at 2.6 meV at 100 K within $\leq \pm 0.05$ eV for all four investigated samples: C_{60}, COC_{60}, O_2C_{60}, and N_2C_{60} (Fig. 9). Thus the rotational force field which is experienced by a C_{60} molecule is essentially determined by interactions with neighboring C_{60} cages. Note that at 100 K we exclusively probe the curvature at the bottom of the potential well. Naturally at least the expansion of the host lattice—equally found for Ar (Ref. 14) and CO (Ref. 25)—must influence the vibrational spectrum of the host. Here we expect similar effects for the intercalation of CO, O_2, and N_2 since the ''van der Waals diameters'' of these molecules are very similar (4.36, 4.29, and 4.3 Å). However the effects are small. The pressure dependence of the main librational peak in C_{60} has been determined as $d(\hbar\omega)/dP \approx 0.06$ meV/kbar (Ref. 39) for a hexagon (minority) oriented sample. Negative pressures between 300 and 700 bar, as obtained from the structural investigations, would therefore lead to a softening of the libron peak frequency in the range 0.02–0.04 meV. This is within the experimental uncertainties involved in measuring absolute energies on different samples. In addition, this small effect may be offset by changes in the molecular ordering. Negative pressure favors the pentagon (major) orientation that has the smaller free energy but requires a larger volume.[24] It has been argued that the libron frequency for C_{60} in the pentagon orientation is slightly higher than that expected for a hypothetically hexagon oriented system at ambient pressure.[39] Therefore, the fact that we see no softening at all may be related to an increase in pentagonal ordering of the cages due to the presence of the guest molecules. Further structural investigations will be undertaken to clarify this point.

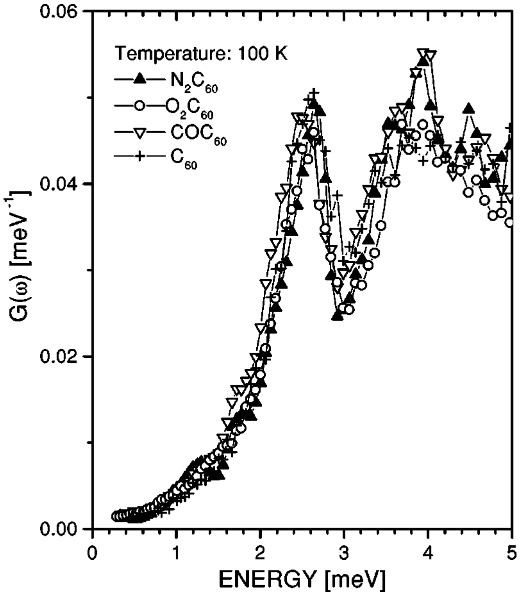

FIG. 9. Energy of the C_{60} libron mode near 2.6 meV at 100 K for different systems: pristine C_{60} host and samples intercalated with O_2, N_2, and CO.

Despite the small influence of the van der Waals guests on the C_{60} dynamics at low temperatures, the guests strongly react to the anharmonicity inherent to the librational motion of the host cages. This is most clearly observable for N_2C_{60} where the N_2 external modes soften significantly in the same way as the C_{60} librations. As in an ordinary material the slow down of the guests's motion should contribute to the higher thermal expansion observed in doped systems below T_c via the concomitant increase in the guest's mean-square displacement. In addition the anharmonic coupling of the cage libration with the guest vibration must modify the potential surface. We conjecture that the effective barriers which have to be overcome for molecular reorientation are reduced, explaining in this way the decrease in T_c beyond what is expected from negative pressure. Further investigations including MD simulations and pressure dependent INS experiments will be necessary to support the conjecture.

VII. CONCLUSION

The observation that the free rotation of the C_{60} cages in the crystalline state is promoted by intercalated gas molecules has been investigated essentially by the technique of neutron scattering. The host lattice is found to expand upon loading and the lattice expansion increases with temperature. No influence of the van der Waals molecules on the cage dynamics can be observed at low temperature. The temperature evolution of the cage dynamics is very similar for all systems investigated if scaled properly to the respective transition temperatures. In particular, all systems show strong fluctuations already far below the actual first order transition. The dynamics of the guest molecules is intriguing indicating both orientational disorder and strong anharmonicities. The lubricant effect, i.e., the reduction in T_c upon gas loading, is explained via a combination of ''negative'' pressure and anharmonic guest-host coupling.

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