Rotational order in CO-intercalated C_{60} crystals

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(Received 5 September 1997)

The structure of $(CO)_x C_{60}(x=0.67)$ has been determined by x-ray powder diffraction at 25 K. CO is found distributed over six equivalent orientations on the octahedral sites of the cubic close-packed structure of C_{60}. The C_{60} molecules are orientationally ordered in almost exclusively the major orientation. Evidence is presented for a weak electrostatic interaction between C_{60} and CO. [S0163-1829(98)01408-8]

The properties of solid C_{60} can be influenced through intercalation of atoms or small molecules. In many instances, the face-centered-cubic (fcc) arrangement of C_{60} is not altered, and the intercalated species occupies the octahedral or tetrahedral sites between the C_{60} molecules. For example, many of the alkali metal (A) intercalates $A_3 C_{60}$ become superconducting at low temperatures.[1] Simultaneously, the orientational order of C_{60} is modified. In most of the alkali-metal intercalates C_{60} has been found to occupy two or three equivalent orientations, which are different from the orientations present in pure solid C_{60}.[1-3]

Recently it was shown that the compound ArC_{60} can be made by exposing C_{60} powder to Ar gas at 1.7 kbar pressure.[4] Argon atoms occupy the octahedral sites, but the orientational order of C_{60} could not be determined unambiguously. In a previous paper, Holleman *et al.*[5] showed that CO can be intercalated into C_{60} by exposing microcrystalline powder of C_{60} to CO gas at a pressure of 200 Bar and a temperature of 200 °C. Both infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) were used to study the rovibrational motion of CO in solid C_{60} as a function of temperature. In the present paper we report results of x-ray powder diffraction on CO-intercalated C_{60}. It is shown that CO occupies the octahedral sites of cubic close-packed C_{60}, and detailed information is obtained about the order and the remaining disorder at $T=25$ K of both CO and C_{60} molecules.

$(CO)_x C_{60}$ was synthesized in a high-pressure cell using microcrystalline C_{60} (Hoechst Super Gold Grade, purity $>99.9\%$) from which the residual solvent was removed by heating under vacuum, and CO gas (purity 2.0).[5] Without further treatment, the resulting powder was loaded into glass capillaries of 1.0 mm diameter and sealed. The measurement was started about 36 h after removing the sample from the high-pressure cell. Pure C_{60} from the same batch, but not exposed to CO, was measured under the same conditions. X-ray powder diffraction was performed at beamline X3B1 at the National Synchrotron Light Source at Brookhaven National Laboratories, using monochromatized synchrotron radiation of wavelength 1.15030(1) Å. The samples were placed in a closed-cycle helium cryostat. During cooling, a single peak was repeatedly scanned, from which the cubic

lattice constants were determined (Fig. 1). For C_{60} the glass transition at $T_g \approx 90$ K is clearly revealed.[6] With the same experimental resolution, a glass transition could not be identified for $(CO)_x C_{60}$.

At a temperature of 25 K, scattered intensity was collected for the scattering angle 2θ varying from 5° to 75°. Well-defined reflections were found over the whole measured range, thus allowing the determination of detailed aspects of the structure. Indexing of the data revealed $Pa\bar{3}$ symmetry for both C_{60} and $(CO)_x C_{60}$. For C_{60} the lattice constant at $T=25$ K was determined as a = 14.0478(1) Å. For $(CO)_x C_{60}$ the lattice constant at T = 25 K was found as $a = 14.0605(1)$ Å, which is significantly larger than for pure C_{60}. Rietveld refinements of the structures were performed with the program GSAS,[7] with peak-profile functions suitable for the synchrotron.[8,9] An icosahedral C_{60} molecule was
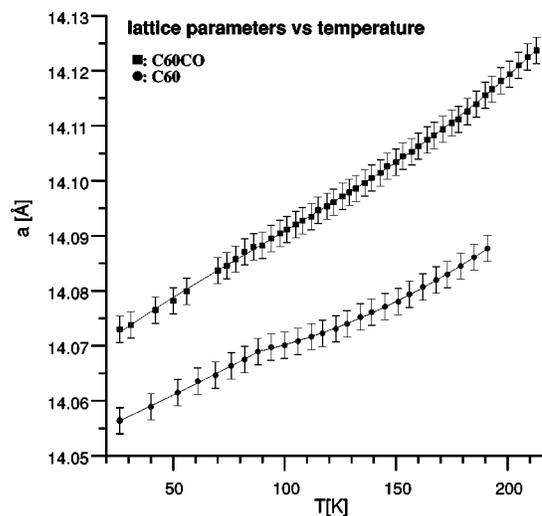
FIG. 1. The cubic lattice constant of $(CO)_x C_{60}$ and C_{60} as a function of the temperature. The values were determined from the varying position of a single peak, and they were not corrected for the zero-point error. Error bars pertain to the standard deviations including the zero-point error. Relative values within one temperature run will be much more accurate, as the same zero-point error applies for all data points from a single run. The lines are a guide for the eye.
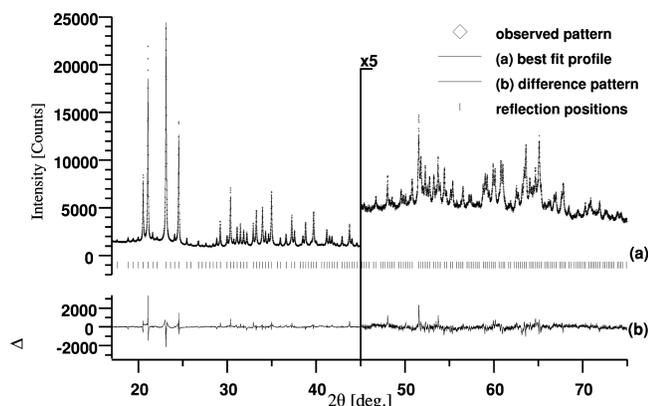
FIG. 2. Experimental data and the fit through the x-ray powder diffraction diagram of $(CO)_x C_{60}$ at $T = 25$ K.

used with bond lengths of 1.4526 Å and 1.3925 Å. In the refinements the orientation of this molecule, as well as its radius of initially 3.5459 Å, were varied. The value for the latter refined towards 3.5363(7) Å, resulting in bond lengths of 1.45(2) Å and 1.39(2) Å. At low angles, the Bragg peaks exhibited a complicated asymmetrical shape, probably due to stacking faults. Because the shape of these maxima could not be fitted by any of the available peak-shape models, the part of the pattern between $2\theta = 5°$ and $2\theta = 17°$ was excluded from the refinement.

For C_{60} the final fit was obtained at $R_p = 0.044$ ($R_{wp} = 0.062$ and $R_{Bragg} = 0.045$), with 83.3(2)% major orientation (rotation angle $\phi = 98.8°$), and 16.7% minor orientation (rotation angle $\phi = 98.8° - 60°$) of C_{60} centered at the (0,0,0) position, in accordance with results of David and co-workers.[6] Using this structure model as input, the refinement against the data of $(CO)_x C_{60}$ resulted in $R_p = 0.055$ ($R_{wp} = 0.123$ and $R_{Bragg} = 0.062$), while the occupation of the minor orientation decreased to 7.4(8)%. The difference electron density map revealed the CO molecule on the octahedral site. A CO molecule disordered over six equivalent positions was introduced into the structure model. After refinement of the position, the orientation and the occupation of CO on the octahedral site, the best fit was found at $R_p = 0.034$ with $R_{wp} = 0.059$ and $R_{Bragg} = 0.045$ (Fig. 2). The orientation of C_{60} was found to be the same as for pure C_{60} powder. Other models, including CO with complete orientation disorder, gave a worse fit to the diffraction data. A similar x-ray diffraction experiment at room temperature did not reveal CO in the exposed sample, although its presence was confirmed by IR and NMR. (Experiment at beamline BM16 of the European Synchrotron Radiation Facility in Grenoble.) From this we conclude that at room temperature CO is highly disordered, in full agreement with the results from IR and NMR.[5]

IR spectroscopy on the CO-intercalated C_{60} revealed a splitting of the CO resonance at temperatures below 10 K.[5] Two components were found at frequencies of 2123.3 cm^{-1} and 2124.1 cm^{-1}, with a relative intensity at 4 K of 1:2, respectively. A straightforward explanation is that there is more than one environment for CO, while the intensity of each maximum will be proportional to the fraction of CO in a particular coordination. Assuming a disordered distribution of both orientations of C_{60}, the probability can be calculated of octahedral holes with different environments. A fraction

of 92.6% major orientation determines that 63% of the octahedral holes are surrounded by six C_{60} molecules in the major orientation, while 30% of the octahedral holes have precisely one C_{60} molecule in the minor orientation. Together they comprise almost all octahedral holes, while their probability ratio is about 2 to 1. The fraction of C_{60} in the major orientation as determined by x-ray diffraction then quantitatively matches the intensity ratio of the two resonances in IR spectroscopy.

The splitting of lines in IR spectroscopy was interpreted as the result of the splitting of degenerate levels due to tunneling motion of the CO molecules.[5] Degenerate levels are only found in the octahedral sites with full S_6 symmetry (all six C_{60} in the major orientation). The tunnel splitting is expected to result in two peaks with approximately the same intensity, with the high-frequency component gaining slightly in intensity at the cost of the low-frequency component, on approaching zero temperature. The additional intensity in the high-frequency component is then attributed to the remaining fraction of CO that is in less symmetric environments (one of the C_{60} in the minor orientation).[5] In the same way as for the first model, the major/minor ratio observed in the x-ray experiment is in accordance with the observed intensity ratio of the two peaks in IR. However, more recent spectroscopic measurements indicate that tunneling motion might be quenched due to zero-point motion of C_{60}, and that the tunnel splitting might be much less than the observed splitting, thus favoring the interpretation in terms of different environments. The combination of spectroscopic measurements and the present x-ray diffraction results then shows that a correlation does not exist between the environment of of the octahedral holes by different numbers of C_{60} in the major and minor orientations, and the occupation of this site by CO molecules.

Both models require that the fraction of C_{60} in the minor orientation is the same at 25 K and at lower temperatures, thus requiring the glass transition to be above 25 K. No anomaly characteristic for such a transition was found in the temperature dependence of the lattice constant (Fig. 1), so that a possible transition must be either close to 25 K or above 200 K. Alternatively, it might be possible that the final major:minor ratio is already obtained at the rotational ordering transition, and the glass transition is suppressed altogether. It is difficult to assess whether the glass transition of $(CO)_x C_{60}$ should be expected at lower or at higher temperatures than in C_{60}. The larger lattice constant of $(CO)_x C_{60}$ indicates weaker interaction between C_{60} molecules, and would lead to a lower T_g. The interaction between CO and C_{60} will lead to additional stabilization of the major orientation, and would lead to an increase of the T_g. The ratio major:minor below T_g then might be either larger or smaller than in C_{60}.

The best fit to the diffraction data was found for a CO molecule in a 24-fold position of $Pa\bar{3}$ with an occupancy of 0.112(7). This implies an average occupation of the octahedral sites of $x = 0.67(4)$, where there is disorder over six positions in each octahedral site. Further refinements with additional CO on the octahedral sites, aligned with the threefold axis, lead to a set of dependent refinement parameters. Fixing the temperature factors then gave an occupation of this new orientation of 0.10(5), while the R factors were the

same as for the original refinement. The conclusion must be that the presence of CO can only be confirmed on the sixfold disordered positions in the octahedral holes, while it cannot be excluded that a small fraction of the order of the standard deviation of 0.04 is found in other orientations.

A simple model with only van der Waals interaction between linear CO and spherical C_{60} leads to minima in the lattice energy for CO aligned with one of the four $(1, \pm 1, \pm 1)$ directions. The mid-point between the van der Waals radii then should coincide with the octahedral site. As either O or C may point towards the positive direction, eight equivalent orientations are possible for CO. Theoretical calculations taking into account the nonspherical symmetry of the C_{60} molecules, showed that the two orientations for which CO coincides with the threefold axis of $Pa\overline{3}$ are local minima with a slighly higher energy than the six equivalent minima for CO oriented along one of the other axes through the octahedral site. Furthermore, the direction of CO in the conformation of minimum energy did deviate by only a few degrees from the $(1, \pm 1, \pm 1)$ directions, and CO was shifted with the oxygen atoms displaced towards C_{60}.[5]

The present refinement gave a different result. It was found indeed that at 25 K CO is not present along the three-fold axis, and that six orientations are occupied with the same probability. However, CO is not aligned with the $(1, \pm 1, \pm 1)$ directions. The initial structure model included CO molecules with bond lengths of $d_{CO} = 1.131$ Å (not varied) aligned along the three directions $(1, \pm 1, \pm 1)$, and with the midpoints between the van der Waals radii (0.315 Å off the C atoms) located on the octahedral sites. The refinement then resulted in a rotation of the molecule to an orientation, with a smallest angle with respect to one of the $(1, \pm 1, \pm 1)$ axes of 34.8°. Also, the molecules were shifted, with the C atom displaced towards the C_{60} molecule (Fig. 3). Two short distances are found between C of CO and atoms of C_{60} in the major orientation, amounting to 2.39(5) Å and 2.55(4) Å, the next shortest distance being 2.93(5) Å. These two distances are considerably shorter than the van der Waals distance between C atoms (3.04 Å), and we interpret this result as the presence of a weak bond between CO and C_{60}. This bonding can be understood as the result of electrostatic interactions between CO and C_{60} in addition to the normal van der Waals interaction. CO has a permanent dipole moment with the C atom as negative side.[10] The two short distances imply that CO is bonded towards one of the long bonds of C_{60}, i.e., that a negative charge is bonded towards an electron-poor bond.

The relative conformation of CO and C_{60} in the minor orientation is similar, with two short bonds between C of CO and the two atoms comprising a long bond in C_{60}, of 2.33 Å and 2.71 Å, respectively. Because of this still shorter bond, we interpret this conformation as less favorable than the bonding of CO towards C_{60} in its major orientation. It should
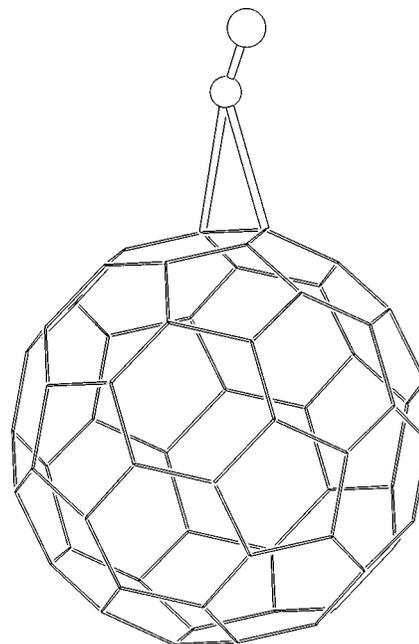
FIG. 3. Relative orientations of C_{60} and CO molecules in the $(CO)_x C_{60}$ crystal, as resulted from the best fit.

be noted that in all octahedral holes there is the possibility for CO to be bonded to a C_{60} molecule in the major orientation. Whether or not the disorder is dynamic or static cannot be determined from the present experiment. However, we do find that CO is exclusively found in one of six positions. It follows that, if the disorder is dynamic, the reorientations must be jumplike.

In conclusion, we have shown that CO can be intercalated on the octahedral sites in C_{60}, without disturbing the cubic close packing of the C_{60} molecules themselves. The major and minor orientations are found to be the same as in pure C_{60}, but at 25 K a larger fraction is found of the major orientation. A glass transition could not be identified, but the results indicate that it should be above 25 K. Evidence is presented for weak electrostatic interaction between CO and C_{60}.

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[1] M. S. Dresselhaus, G. Dresselhaus, and P. C. Ecklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).

[2] J. E. Fischer and P. A. Heiney, J. Phys. Chem. Solids **54**, 1725 (1993).

[3] C. A. Kuntscher, G. M. Bendele, and P. W. Stephens, Phys. Rev. B **55**, 3366 (1997).

[4] G. E. Gadd, M. James, S. Moricca, P. J. Evans, and R. L. Davis, Fullerene Sci. Technol. **4**, 853 (1996).

[5] I. Holleman *et al.*, Phys. Rev. Lett. **79**, 1138 (1997).

[6] W. I. F. David, R. M. Ibberson, T. J. S. Dennis, J. P. Hare, and K.

Prassides, Europhys. Lett. **18**, 735 (1992).

[7] R. B. von Dreele and A. C. Larson, *Los Alamos National Laboratory Report LAUR 86-748*, 1990.

[8] P. Thomson, D. E. Cox, and J. B. Hastings, J. Appl. Crystallogr.

20, 79 (1987).

[9] L. W. Finger, D. E. Cox, and A. P. Jephcoat, J. Appl. Crystallogr. **27**, 892 (1994).

[10] J. S. Muenter, J. Mol. Spectrosc. **55**, 490 (1975).