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Electronic and geometric structure of La@C_{82} and C_{82}: Theory and experiment

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Core-level and valence-band photoemission studies of films of La@C_{82} and C_{82} demonstrate charge transfer from La to the fullerene cage and the formation of a nonmetallic solid with the uppermost band centered 0.64 eV below the Fermi level. Comparison to results for C_{82} demonstrates that there are modifications to the electronic-state distribution throughout the valence band. Bonding of the molecular radicals in the pure solid is found to be significantly stronger than in empty fullerene solids which sublime at much lower temperatures. Detailed calculations for isolated La@C_{82} molecules allow comparison with the experimental results. They show the tendency of the La ions to move from the center of the molecule toward the cage. Comparisons of calculations for La@C_{82} based on C_{3v} and C_2 structures show that much of the energy difference between the two structures is lost upon La incorporation. Bond-length analyses allow comparison with extended x-ray-absorption fine-structure data for the metal-carbon coordination which has been measured for Y@C_{82}. They show sizable La-induced effects on the structure of the carbon cage in the proximity of the La ion.

INTRODUCTION

Early studies of the fullerenes demonstrated that metal atoms can be trapped within these closed carbon cage structures to form endofullerenes.[1] The fact that the internal voids of most fullerenes are large enough to accommodate any element of the Periodic Table has led to speculation about the properties of solids derived from endofullerenes.[2,3] Some have suggested, for example, that a trivalent metal atom, such as La, within C_{60} would donate its valence electrons to the cage, partially filling the lowest unoccupied molecular orbitals of C_{60}. By analogy to the fullerides of K and Rb, this might give rise to conducting and superconducting materials.[3] Endofullerene lasers, ferroelectrics, and capsules for transuranic materials have also been suggested.[3] In general, it has not been possible to test most of these ideas experimentally because the production and separation of the endofullerenes has proven to be exceptionally difficult. Very recently, however, sufficient amounts of several endofullerenes have been prepared so that some of their properties could be examined in solution,[3,4] in mixed-fullerence solid state environments,[5] and in phase-pure solid-state form.[6]

From a theoretical perspective, the difficulty of investigating the endofullerenes is evident from Fig. 1 where we show the structures of two isomers of La@C_{82}, as discussed below. To undertake a reasonable calculation of the electronic states of the undoped cage, it is necessary to know the geometric arrangement of the carbon atoms. Without experimental guidance as to the isomer that is actually produced, it is prohibitively time consuming to categorize the many possibilities. This difficulty is exacerbated for the endofullerene because not only the cage structure must be optimized but also an optimization of the location of the entrapped atom is required for each cage. The ultimate goal, of course, is to determine the electronic properties of the solid-state lattice adopted by the endofullerenes.

In this paper, we discuss theoretical and experimental investigations of La@C_{82} and C_{82} with emphasis on the geometric and electronic structures in isolated molecular form (theoretical) and in solid-state form as solvent-free thin films (experimental). Comparisons demonstrate sizable La-induced modification of the orbital distribution and of the C-C bond lengths of the C_{82} cage. In particular, calculations show that the cage center is an unstable position for the La ion and that its relaxed position is close to the carbon cage. This gives rise to strong La-fullerene bonds and to a large dipole moment. Both experiment and theory demonstrate La^{3+} character. This leads to a singly occupied molecular orbital (SOMO) in the isolated molecule. In the solid, there is a splitting of the SOMO-derived band and spectroscopic results show that the occupied portion of this band is centered 0.64 eV below the Fermi level. Hence, the material is nonmetallic. This suggests that an important rearrangement of the electronic structure takes place in the solid, likely due to the formation of chemical bonds between the molecules. Such bonding would account for the reduced vapor pres-

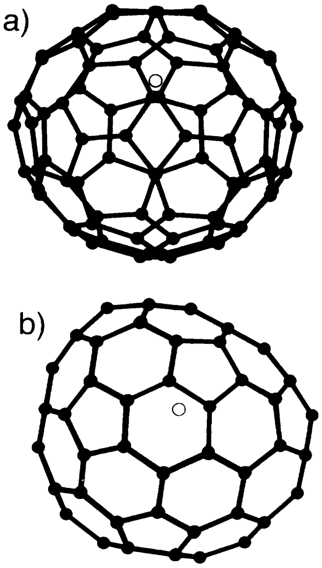

FIG. 1. Calculated structures of La@C_{82} relaxed from the (a) C_2 and (b) C_{3v} cage geometries of C_{82}. In (a), the La atom (open circle) is offset from the center along the C_2 axis which is vertical in this depiction. In (b), the molecule is shown with the former mirror plane parallel to the page. In this case, the La atom is also off center and is out of the plane.

sure (enhanced cohesive energy) of La@C_{82} compared to empty fullerene solids.

THEORETICAL PROCEDURES

Calculations were performed for isolated molecules of C_{82} and La@C_{82}. The first results were reported in Ref. 7. As explained there, we have used the local-density approximation (LDA) pseudopotential based on the Car-Parrinello method, whose accuracy has been proved in several calculations of fullerenes and fullerene-derived materials.[8,9] The LDA norm-conserving atomic pseudopotentials for C(4+) and La(11+) are from Refs. 10 and 11, respectively. The Bachelet-Hamann-Schlüter pseudopotential for La was derived from fully relativistic all-electron calculations. We retain scalar relativistic effects in the pseudopotential description of the core-valence interaction but neglect spin-orbit coupling. This approximation is common to all calculations performed to date on La-doped fullerenes, but it is not expected to alter the conclusions regarding the bonding character of these materials. The La 5*s* and 5*p* core electrons are allowed to relax in the molecular calculations. Atomic calculations show that the relaxation of these states is often crucial for an accurate determination of valence state properties because of the overlap of the 5*d* electron orbitals with the other orbitals of the $n=5$ shell. For example, the energy required for the removal of the 5*d* electron is underestimated by as much as 1 eV when electronic relaxation is neglected.[7] We notice that the relaxation of the La $n=5$ core electrons is neglected in the calculations of Rosén and Wästberg[12] on La@C_{60}, where they constrained the La atom to lie at the center of the molecule and predicted a (3+) charge state for La. The frozen-core approximation could, in part, explain the discrepancy between this result and that of all-electron unrestricted Hartree-Fock (UHF) calculations of Chang, Ermler, and Pitzer[13] which, for the same system and for the same geometry, predicted a (2+) charge state for La. As we shall discuss below, our own result for the La-centered configuration agrees with that of Chang, Ermler, and Pitzer and is independent of the specific fullerene, be it C_{60} or C_{82}. In the molecular calculations, we expand the wave functions in plane waves to an energy cutoff of 35 Ry and use periodic boundary conditions with a fcc unit cell of edge 21.16 Å. This separation renders negligible the interaction between the molecule and its repeated images. The atomic positions are relaxed for both the empty and endohedrally doped molecules until the interatomic forces become smaller than 1×10^{-4} a.u.

Nagase and co-workers[14,15] recently considered the electronic state distribution for La@C_{82}. They used effective core-valence potentials and allowed the outermost ($n=5$) core electrons of La to relax, as in our procedure. However, the present calculations differ from those of Nagase and co-workers in three main points that can alter the resulting physical picture. First, Nagase and co-workers used the UHF method so that, while taking into account spin polarization (which we do not), they neglected the effects of electronic correlation. The former does not change the characteristics of the electronic structure in a significant way, as also demonstrated by the agreement between UHF (Ref. 13) and LDA in C_{60}.[9,16] Moreover, the UHF ground state is a doublet, showing that mixing with states of higher spin multiplicity is negligible and supporting the assumption of the present LDA calculations. Electron correlation effects, on the other hand, are crucial for a correct determination of the bonding and structural characteristics of carbon systems in general, and in particular of the bond-length alternation pattern in fullerenes.[8] Second, although they optimized the structure of the empty molecule, they did not reoptimize the carbon positions in the presence of La. Freezing the ionic system to the structure of the undoped molecule amounts to neglecting its response to the relaxation of the electronic system due to doping. This implies, *a priori,* that there are no deformations of the carbon-carbon bonds such as those induced by charge transfer. This assumption is rather unrealistic for carbon systems. Third, while we use a plane-wave basis set for the expansion of the electronic wave functions, their scheme makes use of Gaussian orbitals. The set used for La is very limited and causes intrinsic limitations for the description of the La-C interaction. The combination of the LDA approach and full structural relaxation gives us confidence that a better description is obtained of the chemical bonding in the La@C_{82} molecules.

EXPERIMENTAL TECHNIQUES

La@C_{82} and C_{82} were prepared and purified as described in Refs. 17 and 18, respectively. For La@C_{82} preparation, a carbon arc was struck between composite rods of graphite and La_2O_3 (Toyo Tanso Co, Ltd.) under

200 Torr of He pressure. The fullerenes and endofullerenes that were produced were first extracted from the soot by dissolution in CS_2. Thereafter, La@C_{82} was isolated by a two-step high-performance liquid chromatography process. It has been observed that at least two species of La@C_{82} can be produced by the carbon arc method.[19,20] The chromatography employed here appears to favor the major La@C_{82} species, as indicated by electron spin resonance (ESR) measurements.[17] However, we note that time and solvent dependences of ESR spectra suggest that the amounts of minority species may be underestimated and may even be dynamic.[19]

Ultraviolet photoemission spectroscopy (UPS) studies were conducted in an ultrahigh vacuum chamber using He I radiation ($h\nu=21.2$ eV, overall experimental resolution ~60 meV). These studies allowed comparisons of electronic features within 12 eV of the Fermi level for La@C_{82} and C_{82}. This chamber was equipped with a nonmonochromatic Al K_α x-ray source ($h\nu=1486.6$ eV) for parallel x-ray photoemission spectroscopy (XPS) investigations of core level signatures. Higher resolution XPS measurements performed in a separate spectrometer using monochromatized Al $K\alpha$ radiation allowed an investigation of the C 1*s* and La 3*d* core-level emission (resolution 0.6–0.8 eV). They also allowed comparison of valence-band signatures measured at high photon energy with those obtained at low energy. This offered the opportunity to assess any contributions from La-derived levels and to examine the carbon *s* and *p* character of the valence-band features. The resolution was 0.8 eV for the XPS valence-band spectra. All of the measurements were done at room temperature.

La@C_{82} and C_{82} molecules were evaporated from powders that were heated in alumina crucibles. These molecules were condensed at room temperature onto GaAs(110) substrates that had been cleaved *in situ*. The films were ~150 Å thick, based on the attenuation of the XPS signal from the GaAs substrate. The XPS spectra showed that these sublimed films were contamination free with no evidence of oxygen, residual solvents, or other species. After these measurements were completed, the samples were characterized with UPS and valence-band spectra were acquired. The samples were then transferred through air to the higher-resolution XPS system. Comparison of results before and after transfer made it possible to assess the tendency to degrade due to exposure to the atmosphere. While normal emission XPS measurements showed O 1*s* emission for both La@C_{82} and C_{82} after the transfer, measurements done at shallow photoelectron takeoff angles indicated that the oxygen was concentrated in the ~10 Å surface region. Subsequent heating of the La@C_{82} film to ~400 °C *in vacuo* reduced the O 1*s* contribution to ~0.2 at. % We conclude that weakly bound oxygen-bearing species, such as H_2O, O_2, CO_2, or CO, were confined to the near-surface region. No changes were observed in the C 1*s* emission spectra after heating and no elements other than C, La, O, and substrate GaAs were detected. Finally, there were minimal changes in La 3*d* core-level spectra obtained before and after transfer and after heating to ~400 °C. This implies that the endofullerenes were stable under these conditions, an effect reported earlier for fullerene-endofullerene mixtures.[5]

High-resolution XPS was also performed on two samples prepared *ex situ*. For one, some of the as-separated La@C_{82} powder was dispersed on an oxidized Al surface, using CS_2 that was allowed to evaporate. The La 3*d* signature was slightly modified from that of the vacuum-deposited sample and indicated the presence of some La oxide. The carbon-to-lanthanum intensity ratio suggested a composition of about 500:1 instead of 82:1 for this highly impure sample, even after annealing to 450 °C. A second sample was prepared by dispersing with CS_2 some residue that remained in a tantalum boat after La@C_{82} had been vacuum evaporated. The La signal was essentially that of La_2O_3 and the C to La ratio exceeded 800. These results suggest that La@C_{82} degradation will occur but also that sublimation separates the intact molecules and facilitates the formation of pure films. We suspect that heat and light generated during sublimation may increase the rate of deterioration. Exposure to light, especially in the presence of solvents or other species, has been observed to result in the degradation of empty fullerenes.[21]

RESULTS AND DISCUSSION

Molecular structures of C_{82} and La@C_{82}

Fowler and Manolopoulos[22] enumerated nine isolated-pentagon isomers of C_{82}. ^{13}C NMR of the C_{82} material chromatographically separated from the soot extract[23] has revealed four isomers of C_2, C_{2v}, C_{3v}, and C_2 symmetry with ratios 8:1:1:1. For the La endofullerenes, ESR has detected two isomers.[19,20] We present here the theoretical results for two isomers of C_{82} and a study of the La@C_{82} structures derived from them. We have optimized the atomic positions of empty C_{82} in two geometries, one of C_2 symmetry and the other of C_{3v} symmetry.[24] We find the energy of the C_2 isomer to be lower than that of C_{3v} by about 0.93 eV per molecule or about 0.01 eV per atom. The bond lengths vary between 1.35–1.47 Å in the C_{3v} isomer and between 1.37–1.47 Å in the C_2 isomer. The relative energy stabilization of the structure of lower symmetry is accompanied by a larger gap (0.74 vs 0.13 eV) between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). This is in agreement with predictions of Hückel calculations.[22] The HOMO-LUMO gaps are much smaller than in C_{60} and C_{70}, for which the LDA value is about 1.7 eV.[25]

Starting from these optimized structures for the empty molecules, we allowed a relaxation in response to La incorporation. The resulting relaxed structures are shown in Figs. 1(a) and 1(b). As first demonstrated in Ref. 7, configurations with La in off-center positions are strongly preferred energetically and the off-center displacement is accompanied by a change in the charge state of La from (2+) to (3+). In both C_2- and C_{3v}-derived structures we find that La donates two electrons to cage states when it is confined to the cage center. Such configurations, however, are unstable. The HOMO lies in the quasifivefold degenerate "5*d*" La state. The transition to the quasi-(3+) state is accompanied by a "repulsion" of the *d* states to higher energy and a lowering of cage states to accommodate the unpaired electron. (The details of the resulting electronic structure are described in the following section). Thus, endohedral doping with La changes the electronic nature of the molecule from closed-shell to radical and it induces sizable variations in the bond-lengths for C atoms close to the La ion. This appears to be independent of the specific fullerene since we find it in both structures of C_{82} and also in C_{60}.[9,16] Here, we focus on the isomer with the C_2-derived structure. The C_{3v}-derived structure is also considered for the sake of comparison.

Following Nagase *et al.*,[14] we considered a configuration with La located on the symmetry axis of the C_2 molecule, as shown in Fig. 1(a). We found that there is a local energy minimum and did not search for others of lower energy. This energy is lower by about 4 eV than the cage-centered configuration. This difference amounted to 2.6 eV in the calculations of Nagase *et al.* The distance of La from the cage center is 1.49 Å or about 0.17 Å smaller than in the more recent calculations of Nagase and Kobayashi.[15] The closest shell of neighbors is formed by an irregular hexagon with La-C distances ranging between 2.53–2.56 Å. The second shell of neighbors is formed by six atoms at distances of 2.95–3.02 Å.

While no structural determination exists for La@C_{82}, extended x-ray absorption fine structure (EXAFS) measurements for Y in the Y@C_{82} system were recently made.[26] These were fitted with a model of two carbon shells around the metal ion, each containing 6±1 atoms, at distances of (2.40±0.05) and (2.85±0.05) Å, respectively. Taking into account the difference of the ionic radii of Y^{3+} and La^{3+} (Ref. 27), the fit is clearly consistent with the above structure. However, as stated in Ref. 26, the resolution of the data does not allow for a unique determination of the structure.

Comparison of the empty cage to the La-doped one shows a nontrivial displacement of the atoms that depends primarily on their distance from the La ion. The main result of La-doping is an enlargement (by 0.1 Å) of the closest hexagon as shown in Fig. 2(a). However, the lengths of the carbon-carbon bonds involving atoms in at least two shells are significantly modified. Figure 2(b) reports such displacement $\Delta(C)$ as a function of the La-C distance, d(La-C). The units are Å and the results show relaxation that extends throughout the cage structure.

In Ref. 7, we considered a few endohedral configurations for La in the C_{3v}-like cage of C_{82}. Among the off-center positions, we found that the configuration with La on the symmetry plane was more than 1 eV lower in energy than that with La near the symmetry axis. Using molecular dynamics, we have now searched for other low-energy configurations and found at least one with an energy minimum that is ~0.5 eV lower than the geometry described as "*K*" in Ref. 7. This structure corresponds to a closest La-C coordination of 6, although La is not aligned with the center of a hexagon, the distances being in the range 2.45–2.63 Å. The next shell is more diffuse and we can count eight carbon atoms in the range 2.75–3.17 Å from La. The changes in the carbon-carbon pattern are similar to those of the C_2-derived isomer. We note that this structure is also compatible with the EXAFS data for Y@C_{82}.[26] These results reflect the local character of the La-C interaction and suggest very similar chemistry in the two different cages.

More interestingly, the calculated energies of the two isomers of La@C_{82} are very close, with the C_2-like one lower by only 0.12 eV. This suggests that much of the stability difference between the empty isomers is removed by the presence of the endohedral ion. The nontrivial electronic and structural rearrangements induced by endohedral doping may even alter the energy ordering. This implies that the most abundant carbon cage structures may vary for the endohedral species compared to the empty fullerenes if such variations are allowed by the kinetics of La@C_{82} formation. Within one type of cage, several almost-isoenergetic positions may exist for La, separated by low-energy barriers. On the other hand, the barrier for the transformation between isomers having different cage structures will be very high since this would involve rearrangement of carbon bonds.

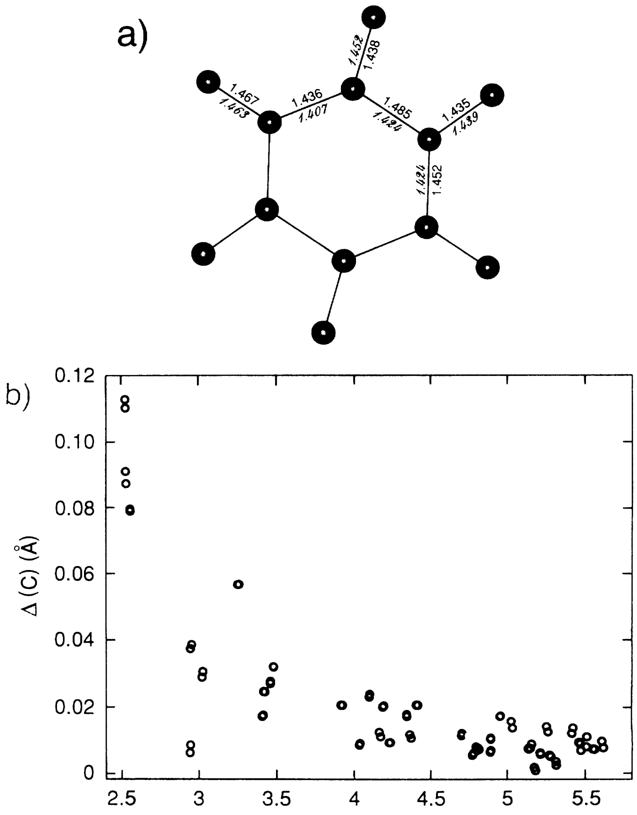

FIG. 2. Distortion of the empty C_{82} structure upon La incorporation. The calculated bond lengths (in Å) of C_2-derived La@C_{82} nearest the La ion are given in (a). The corresponding bond lengths in empty C_{82} are given in italics. In (b), the displacements of carbon atoms of La@C_{82}, Δ(C), relative to atomic positions in empty C_{82}, are plotted as a function of their distance from the La ion, d(La-C).

The large displacement of La from the center of the molecule is expected to produce a large dipole moment. We have estimated values of 3–4 D. This large dipole moment, as well as the presence of higher multipoles, may have an effect on the solubility of this molecule. Experimentally, it has been observed that La@C_{82} is soluble in CS_2, toluene, 1122-tetrachloroethane, and *o*-dichlorobenzene.

Electronic structure

Figure 3 shows the results of the LDA calculations for the two isomers of C_{82} with and without La. The bottom panel is a diagram of the Kohn-Sham eigenvalues for relaxed C_2- and C_{3v}-derived structures, while the top shows broadened eigenvalue spectra for C_2-derived species. We include broadened eigenvalue spectra for C_{82}, for La@C_{82} with La off center, and for the highly improbable La-in-center position (curves *a*, *b*, and *c*, respectively). We take this as a reference for comparison with the experimental data discussed below.

Figures 4 and 5 provide an overview of the electronic structure of La@C_{82} and C_{82}. The spectrum in the center of Fig. 4 is the valence-band region of La@C_{82} as measured with XPS and referenced in energy to the Fermi level. The dotted curve overlapping this spectrum in the binding energy range from 17 to 30 eV shows the emission from C_{82} to highlight the contributions from the La 5*p* states in La@C_{82}. Figure 5 compares the leading portion of the valence-band spectra of C_{82} and La@C_{82} measured by UPS. The two curves are offset for clarity. The differences are emphasized by the bottom spectrum, a curve obtained by subtracting data points for C_{82} from those for La@C_{82} after shifting the C_{82} spectrum by -0.18 eV to obtain the best overall agreement.

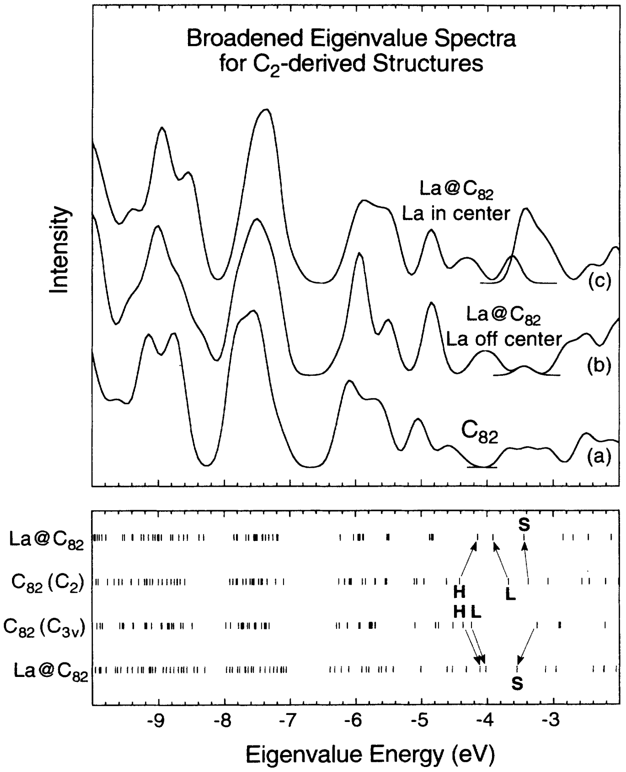

FIG. 3. Lower panel: the calculated eigenvalues for the two C_{82} isomers considered and for the endohedral molecules derived from them. HOMO, LUMO, and SOMO levels are indicated, abbreviated *H*, *L*, and *S*. The C_2-derived structure of C_{82} shows a larger HOMO-LUMO gap and was found to be the more stable isomer by 0.93 eV. Upper panel: broadened eigenvalue spectra for (a) the C_2-derived empty fullerene, (b) the C_2-derived endohedral with La in the low-energy, off-center position and (c) the C_2-derived endohedral with the La constrained to the molecular center. The broadening was done with a Gaussian of 0.3 eV full width at half maximum. Filled and empty state curves are overlaid in the vicinity of the SOMO. For (b), SOMO is well separated from adjacent energy levels so that the state density is that of a single electron in the occupied and empty portions of SOMO. For (c), SOMO lies within a group of closely spaced levels, some of which have La 5*d* character. The La 5*d* orbitals become less bound in the off-center geometry (b) and their contribution is evident only at the edge of the figure.

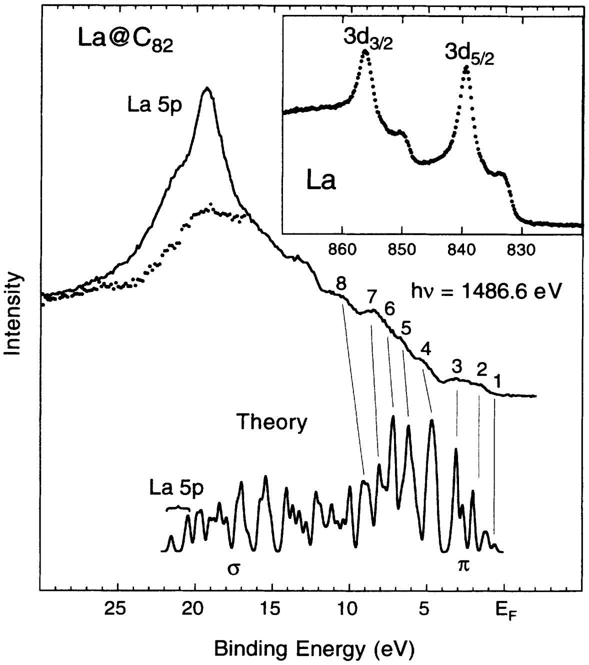

FIG. 4. Comparison of the La@C_{82} valence-band spectrum measured with $h\nu = 1486.6$ eV to the calculated eigenvalue spectrum. The calculated results were broadened with a Gaussian of 0.3 eV full width at half maximum. The dotted curve overlying the XPS spectrum is a portion of the C_{82} valence-band spectrum that helps define the La 5*p* emission. This is emphasized because of the high 5*p* photoionization cross section. The C 2*s* character of the valence band is similarly emphasized over the C 2*p* character. The main features of the valence-band spectra are numbered to facilitate comparison to the spectra of Figs. 5 and 7. The lines relate measured and calculated features. The inset shows the La 3*d* spectrum measured by XPS which indicates a formal valence of +3 for La.

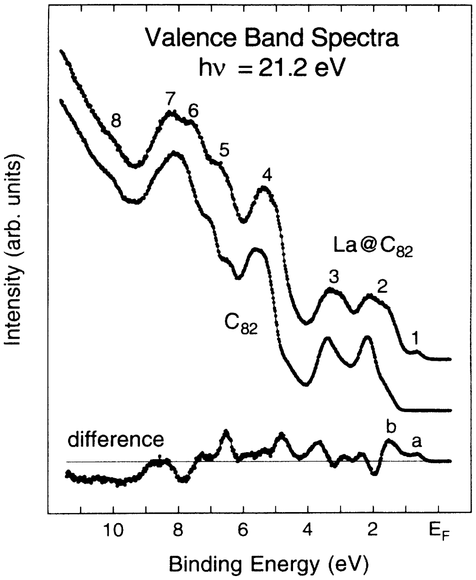

FIG. 5. Comparison of valence band spectra for C_{82} and La@C_{82} measured at 21.2 eV. The main features are numbered as in Fig. 4. The difference curve at the bottom was obtained after shifting the C_{82} spectrum by −0.18 eV for the best overall alignment. Significantly, the difference curve shows spectral changes throughout the valence band. This is consistent with theoretical results that indicate that La produces significant rearrangement of the energy levels and not simply a rigid filling of C_{82} empty states. Feature 1 is attributed to SOMO-derived levels centered 0.64 eV below the Fermi level. Its onset at 0.35 eV indicates insulating character for solid La@C_{82}.

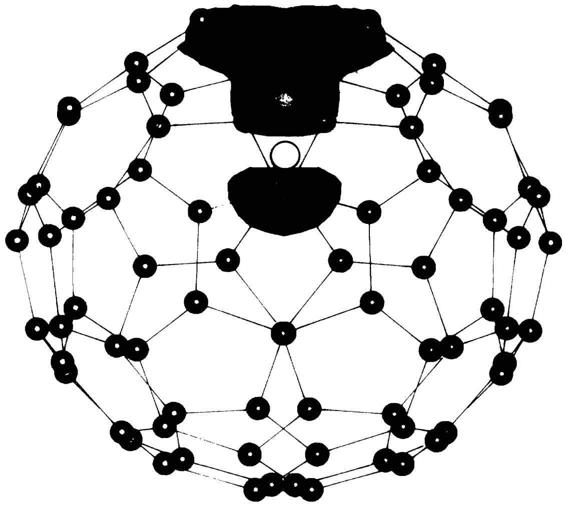

FIG. 6. Constant electron density surface [$\rho=0.008\ e/(\text{a.u.})^3$] corresponding to one of the four molecular orbitals of C_2-derived La@C_{82} that contains significant La 5*p* character. The orbital is much more localized than the purely carbon-derived orbitals and is clearly associated with the La ion. However, much of the state density is found on the fullerene cage. The La ion is positioned between the lobes of the La 5*p*–C 2*s* hybrids.

Figure 4 shows that the valence-band width is ~24 eV for La@C_{82} and for C_{82}, extending from the *p*-derived states near the Fermi level through the deeper *s*-derived states. The bandwidth is essentially the same as for other fullerenes studied to date,[28] as expected. This similarity in bandwidth is also found in our LDA calculations, since they predict the same valence bandwidth for C_{60}, C_{70}, and C_{82} to within a few tenths of an eV. The XPS results in Fig. 4 are dominated by the *s* states because the photoionization cross section for the *s* states is ~13 times larger than that of the *p* states for 1486.6-eV photons.[29] Spectra obtained at lower photon energy show much enhanced *p* character. Comparison to equivalent results for C_{60} shows that much of the high orbital degeneracy of C_{60} is lost in C_{82} or La@C_{82} so that the sharp and well-separated spectral features are broadened.

The presence of La in the endofullerene is obvious because of the contribution from the La 5*p* states. These states overlap the carbon-derived valence bands. In XPS, they are emphasized because of their very high relative photoionization cross sections. From the molecular calculations it is apparent that the 5*p* states of La mix with the lowest cage state. The nature of such mixing is illustrated in Fig. 6 for one of these states, where a surface of constant electron density is shown, corresponding to a high value. The energies of the four hybridized states span 1.2 eV in the calculation. The greater width of this manifold in the experiment can be attributed to spin-orbit splitting (~2.5 eV, Ref. 30), lifetime broadening, and solid-state broadening. In the calculations, the mean La 5*s* to La 5*p* separation was 14.6 eV. Experimentally, we find a separation of 16.2±0.5 eV since the La 5*s* levels appeared at 36.7-eV binding energy. The agreement between the broadened Kohn-Sham eigenvalues and experiment is comparable with what has been found previously with other fullerenes.[25]

Comparison of the valence-band spectra for C_{82} and La@C_{82} in Fig. 5 makes it clear that both are rich in structure, but also that the structure differs throughout the leading 10 eV of the valence band. This is emphasized by the difference spectra shown in Fig. 5. Hino *et al.*[6] recently showed a difference spectrum within ~2 eV of E_F that was obtained by normalizing the spectra to the peak height of feature 3. In that case, they deduced that there were spectral changes but that they were limited to the range between E_F and 2 eV, suggesting that the C_{82} and La@C_{82} cage structures were identical. They pointed out that the structure near the valence-band edge is composed of two features with an intensity ratio of about 1:2. These are labeled "*a*" and "*b*" in Fig. 5. They attributed this to the three electrons transferred from La, with two electrons filling an orbital 1.6 eV below E_F and one electron occupying an orbital 0.9 eV below E_F. The origin of the difference between their spectra and ours may reflect a cleaner sample in our case since our results show sharper structure with greater distinction between features. Moreover, we have been able to resolve more spectral features. Indeed, our high-resolution results show that La incorporation introduces more profound changes than simple charge transfer to rigid electronic states of the carbon cage, but we agree that there are two structures within 2 eV of E_F. We note also that the relative intensities of fullerene photoemission features vary with $h\nu$ because of dipole matrix elements[31] so that the 1:2 area ratio may be fortuitous.

For La@C_{82}, the small but very important feature at 0.64-eV binding energy has no analog in the spectrum for C_{82} and, clearly, is due to states derived from the SOMO of La@C_{82}. The parentage of this orbital, C or La derived, was tested experimentally through a study based on the strongly disparate photoionization cross sections of La and C at UPS and XPS photon energies.[32] In particular, the ratio of La 5*d* to C 2*p* intensities would range from 0.7 at $h\nu=21.2$ eV to 76 at $h\nu=1486.6$ eV, making it possible to amplify any La 5*d* contribution by a factor of ~100. Comparison of the leading portions of the measured La@C_{82} valence-band spectra in Fig. 7 indicates that these orbitals are almost entirely C derived and contain minimal La 5*d* admixing. This is fully consistent with the results of our calculations for both isomers. In fact, the La 5*d* states turn out to be ~1.2 eV above the SOMO and the nature of the SOMO is that of a π state of the cage. This is emphasized in Fig. 8 where we show a constant electron density surface for the SOMO.

In their electrochemical investigation of La@C_{82}. Suzuki *et al.*[4] found small reduction and oxidation potentials compared to those of C_{60}. This is consistent with the fact that La@C_{82} is a radical, in contrast to C_{60}.

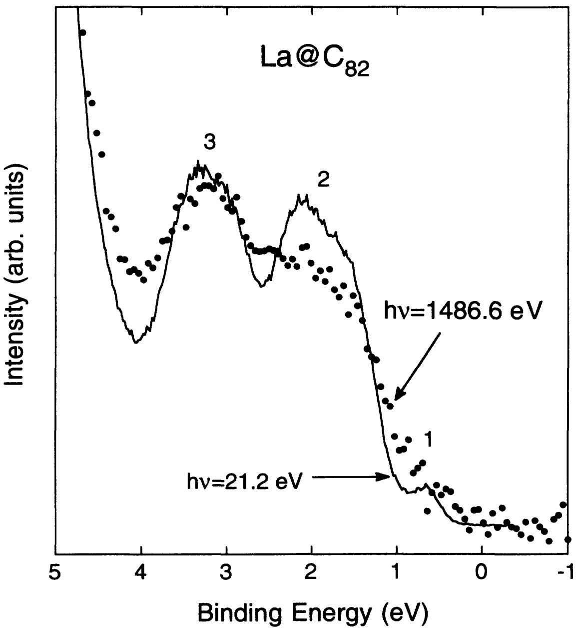

FIG. 7. Leading valence-band features of La@C_{82} measured at high and low photon energies. Any La 5*d* character should be magnified by a factor of ~100 in the spectrum obtained at 1486.6 eV due to the relative photoionization cross sections of C 2*p* and La 5*d* electrons. The intensity of feature 2 relative to feature 1 varies with photon energy, as demonstrated in Ref. 6, and is near a maximum at $h\nu=21.2$ eV. After considering this and the differences in experimental resolution, it is apparent that there is essentially no La 5*d* character in the occupied states of La@C_{82}. This is consistent with the theoretical finding that the La 5*d* orbitals are well above SOMO in the low-energy La@C_{82} isomers.

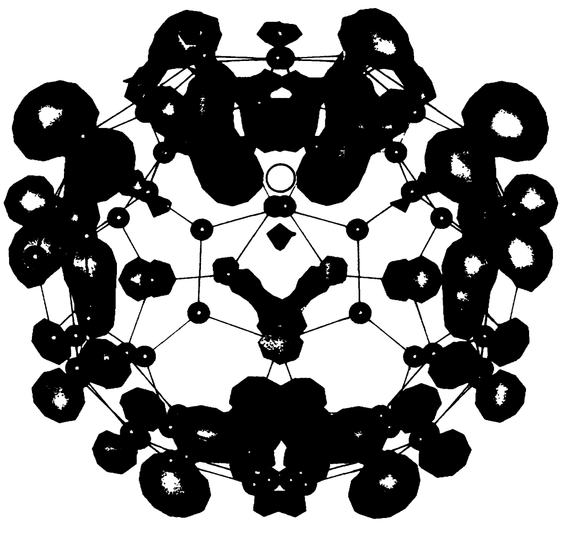

FIG. 8. Constant electron density surface [$\rho=0.001$ *e*/(a.u.)^3] of SOMO for the C_2-derived structure of La@C_{82}. The SOMO is delocalized over the carbon cage, attesting to its carbon π character and confirming that there is no La 5*d* admixing.

The delocalized character of the SOMO was first indicated by ESR measurements that revealed, for the unpaired electron, a very small hyperfine coupling (1.2 G) to the ^{139}La nuclear moment.[33] The measured *g* value of 2.001 is in the range found for empty fullerene radicals, namely 1.95–2.001.[34] This led to the conclusion that the unpaired electron occupies an orbital primarily located on the carbon cage. This was supported by a comparison of the small La@C_{82} hyperfine coupling constant to the observed value of 50 G for La^{+2} substitutionally incorporated in place of Ca in a CaF_2 crystal[35] and to the calculated value of −186 G for an isolated La^{+2} ion. However, as Nagase and Kobayashi pointed out,[15] an unpaired electron residing in a metal *d* orbital, with very little *s* character, can also have small hyperfine coupling. Furthermore, if the *d*-orbital degeneracy is lifted by interaction with the cage, then the shift in the electron *g* value can be small. Hence, the extent of metal-to-cage charge transfer could not be ascertained conclusively from the ESR data. Nonetheless, the original interpretation is supported by the photoemission experiments described above.

Additional evidence for a La^{+3} charge state is provided by the La 3*d* spectrum (inset Fig. 4) because the 3*d* line shape provides a clear indication of the electronic environment sensed by La in the C_{82} cage.[36] This is due to the sensitivity of the 3*d* electrons to the distribution of valence electronic charge surrounding the La atom, as discussed previously in the context of an XPS study of a mixture of La endofullerenes and empty fullerenes.[5] Here, we find that the high-resolution La 3*d* core-level spectrum for pure La@C_{82} is almost identical to that for the mixture, suggesting either that the previous results were dominated by a La@C_{82} contribution or that La bonding is always 3+ regardless of the cage size or specific symmetry. The former possibility is supported by observations that La@C_{82} is the dominant endofullerene in air exposed mixtures.[37] The latter possibility is supported by theory since La takes on a formal valence of three and resides off center in both of the La@C_{82} isomers tested as well as in La@C_{60}.

The La 3*d* core-level spectrum shows two dominant structures, each with weaker shoulders at lower energy. These signatures are easily distinguished from those of other La-bearing species, notably La_2O_3 and La metal, as examined in detail elsewhere.[5] Comparison of the La 3*d* signature for La@C_{82} to that for the trihalides of La shows very similar line shapes, supporting the picture that the La ion within the cage is in a trivalent state of charge.[5,38] For these trihalides, the relative magnitude of the lower-energy doublet has been shown to decrease as the electronegativity of the halide decreases.[38] By comparison, we can deduce that the carbon cage environment of La@C_{82} has an effective electronegativity less than that in $LaBr_3$.

Carbon 1*s* spectra (not shown) were also measured for C_{82} and La@C_{82}. A symmetric C 1*s* main line [full width at half maximum (FWHM) 0.86 eV] was found for C_{82} while an asymmetric feature (FWHM 1.13 eV) was found for La@C_{82}. The widths of these spectra undoubtedly reflect the inequivalence of the carbon atoms within each molecule. The larger width for La@C_{82} suggests greater inequivalence, probably due to the close approach of the La ion to one side of the carbon cage. Unfortunately, distinct peaks were not resolved that could be assigned to carbon atoms that were La coordinated. A clear π-plasmon feature was present in both materials, displaced ~ 6.0 eV from the main line. Two clear π-π^* satellite peaks were also observed for C_{82} at ~ 3.7 and ~ 1.4 eV. The π-π^* satellite intensity of La@C_{82} was spread more evenly and individual peaks were not resolved.

The fact that the SOMO of La@C_{82} is derived and is centered 0.64 eV below the Fermi level has implications as far as the conducting nature of the solid is concerned. In a simple one-electron picture, the half filling of a single band by one electron would result in a metallic solid. However, the onset of emission at ~ 0.35 eV below the Fermi level indicates insulating character for solid La@C_{82}. This could be explained by a crystal structure with an even number of molecules per primitive unit cell. Crystal-field splitting of the band might then result. Such a situation would be analogous to the dimerization typical of a Peierls distortion. Unfortunately, solid-state structural information for pure La@C_{82} is not available. A cocrystal precipitated from CS_2 has been identified and has been found to possess the space group $I\bar{4}3d$. It contains 16 La@C_{82} molecules and 24 CS_2 molecules per unit cell.[39] In contrast, recent transmission electron microscopy studies for Sc_2@C_{84} show a simple hcp lattice with the c/a ratio expected for ideal spherical molecules.[40] The observed nearest-neighbor distance, 11.2 Å, is the same value found previously for fcc crystals of empty C_{84}.[41] The presence of solvent in the first case and the nonradical nature of the endofullerenes in the latter, prevent an assessment of the implications for pure, solid La@C_{82} as measured in our experiments.

Simple crystal-field splitting might be a questionable explanation of the insulating nature of solid La@C_{82} since a gap of at least 0.35 eV has been opened with the occupied portion of the band exhibiting a spectral full width at half maximum of only about 0.3 eV. Indeed, Peierls distortions are generally found only in low-dimensional materials due to the difficulty of opening a gap throughout an entire three-dimensional Brillouin zone. A possibility that should always be considered for fullerene-based materials, where electron correlation effects are found for pure or doped solids,[2] is that solid La@C_{82} may be a Mott-Hubbard-type insulator.

Finally, we note that sublimation of the fullerenes and endofullerenes, as described above, made it possible to form contamination-free thin films. To investigate the sublimation characteristics in more detail, we used XPS to monitor the thickness of the solvent-free La@C_{82} film as a function of temperature. These measurements showed no significant La@C_{82} sublimation after 1 h at 410 °C. At 480 °C, however, the desorption rate was ~ 22 Å per h, corresponding to a vapor pressure for La@C_{82} of approximately 5×10^{-10} Torr. For comparison, the vapor pressure of C_{60} at 480 °C can be estimated to be 3×10^{-3} Torr by extrapolation from results obtained at lower temperature.[42] This implies that the cohesive energy of the endofullerene solid is much higher than the empty fullerene solid and that there are rather strong intermolecular interactions, probably dipole-dipole interactions given the large predicted molecular dipole moment for these endofullerenes. The vapor pressure disparity has been used by Yeretzian *et al.*[37] to separate endofullerenes and fullerenes from arc generated soot without the use of solvents. They found that air exposed soot, even when partially separated by gradient sublimation instead of with solvents, had a higher abundance of La@C_{82} than other endofullerenes, suggesting that solvent effects do not "filter" the endofullerene distribution to make La@C_{82} the most abundant.

CONCLUSIONS

In conclusion, the theoretical and experimental results presented here for La@C_{82} help to establish the following.

(i) There is strong bonding between La and the carbon cage of the fullerence that leads to extensive differences between the properties of the doped and undoped molecules.

(ii) There is a clear distinction in the electronic properties of configurations with La occupying on-center and off-center endohedral locations. These can easily be probed by photoemission experiments. The photoemission results confirm a formal 3+ valence state for La, predicted by calculations and inferred from previous ESR and XPS data.

(iii) The states occupied by the electrons donated by La are π-cage orbitals that do not mix with the La 5*d* states. Calculations for the molecules indicate that 5*d* states remain localized on La and lie ~ 1.2 eV above the

SOMO. This prediction awaits confirmation from inverse photoemission or other empty state measurements.

(iv) The 5*p* core states of La are not passive spectators of the doping process but, instead, mix to a considerable extent with the lowest σ state of C_{82}.

(v) Solid state bonding in La@C_{82} is considerably stronger than in empty fullerenes as indicated by the drastically reduced vapor pressure.

(vi) Solid-state effects split the molecular SOMO level of La@C_{82} and produce a nonmetallic solid.

Because of the strong bonding between La and the cage, and in contrast with the case of alkali-metal doping, the La-induced changes in the C-C bond alternation are localized and relatively large. This leads to variations in the isomeric energy ordering such that the abundance of the endohedral structures may well change with respect to the empty fullerence distribution. Further work requires the establishment of the crystal structure as well as explicit calculations of the solid-state effects.

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[1] J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto, F. K. Tittl, and R. E. Smalley, J. Am. Chem. Soc. **107**, 779 (1985).

[2] For a detailed review of the properties of fullerenes and fullerence-based materials, see J. H. Weaver and D. M. Poirier, in *Fullerene Fundamentals,* edited by H. Ehrenreich and F. Spaepen, Solid State Physics Vol. 48 (Academic, New York, 1994), Chap. 1, pp. 1–108.

[3] Endofullerene research was recently reviewed by D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries, and C. S. Yannoni, Nature **366**, 123 (1993).

[4] T. Suzuki, Y. Maruyama, T. Kato, K. Kikuchi, and Y. Achiba, J. Am. Chem. Soc. **115**, 11 006 (1993).

[5] J. H. Weaver, Y. Chai, G. H. Kroll, C. Jin, T. R. Ohno, R. E. Haufler, T. Guo, J. M. Alford, J. Conceicao, L. P. F. Chibante, A. Jain, G. Palmer, and R. E. Smalley, Chem. Phys. Lett. **190**, 460 (1992); T. Guo, M. D. Diener, Y. Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. R. Ohno, J. H. Weaver, G. E. Scuseria, and R. E. Smalley, Science **257**, 1661 (1992).

[6] S. Hino, H. Takahashi, K. Iwasaki, K. Matsumoto, T. Miyazaki, S. Hasegawa, K. Kikuchi, and Y. Achiba, Phys. Rev. Lett. **71**, 4261 (1993).

[7] K. Laasonen, W. Andreoni, and M. Parrinello, Science **258**, 1916 (1992).

[8] W. Andreoni, in *Electronic Properties of Fullerenes and Other Novel Materials, Proceedings of the International Winterschool,* edited by J. Fink, H. Kuzmany, M. Mehring, and S. Roth, Springer Series in Solid State Sciences, Vol. 117 (Springer, Berlin, 1993), p. 85.

[9] W. Andreoni, in *Physics and Chemistry of Fullerenes,* edited by K. Prassides (Kluwer, Dordrecht, 1994), p. 169.

[10] W. Andreoni, D. Scharf, and P. Giannozzi, Chem. Phys. Lett. **173**, 449 (1990).

[11] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[12] A. Rosén and B. Wästberg, J. Am. Chem. Soc. **110**, 8701 (1988); Z. Phys. D **12**, 387 (1989).

[13] A. H. H. Chang, W. C. Ermler, and R. M. Pitzer, J. Chem. Phys. **94**, 5004 (1991).

[14] S. Nagase, K. Kobayashi, T. Kato, and Y. Achiba, Chem. Phys. Lett. **201**, 475 (1993).

[15] S. Nagase and K. Kobayashi, Chem. Phys. Lett. **214**, 57 (1993).

[16] W. Andreoni, K. Laasonen, and M. Parrinello (unpublished).

[17] K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto, and Y. Achiba, Chem. Phys. Lett. **216**, 67 (1993).

[18] K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, T. Moriwaki, S. Suzuki, H. Shiromaru, K. Saito, K. Yamauchi, I. Ikemoto, and Y. Achiba, Chem. Phys. Lett. **188**, 177 (1992).

[19] M. Hoinkis, C. S. Yannoni, D. S. Bethune, J. R. Salem, R. D. Johnson, M. S. Crowder, and M.S. DeVries, Chem. Phys. Lett. **198**, 461 (1992).

[20] S. Suzuki, S. Kawata, H. Shiromaru, K. Yamauchi, K. Kikuchi, T. Kato, and Y. Achiba, J. Phys. Chem. **96**, 7159 (1992).

[21] R. Taylor, J. P. Parsons, A. G. Avent, S. P. Rannard, T. J. Dennis, J. P. Hare, H. W. Kroto, and D. R. M. Walton, Nature **351**, 277 (1991); L. P. F. Chibante, C. Pan, M. L. Pierson, R. E. Haufler, and D. Heymann, Carbon **31**, 185 (1993).

[22] P. W. Fowler and D. E. Manolopoulos, Nature **355**, 428 (1992).

[23] K. Kikuchi, N. Nakahara, T. Wakabayashi, S. Suzuki, H. Shiromaru, Y. Miyake, K. Saito, I. Ikemoto, M. Kainosho, and Y. Achiba, Nature **357**, 142 (1992).

[24] The C_2 structure examined corresponds to the pentagon-hexagon arrangement labeled C_2 (a) in Ref. 14, although our optimization procedure results in different bond lengths. The C_{3v} structure is the one suggested by Manolopoulos and Fowler (Ref. 22) to be the stable isomer of a so-far-hypothetical anion $C_{82}{}^{2-}$.

[25] W. Andreoni, F. Gygi, and M. Parrinello, Chem. Phys. Lett. **189**, 241 (1992).

[26] C.-H. Park, B. O. Wells, J. DiCarlo, Z.-X. Shen, J. R. Salem, D. S. Bethune, C. S. Yannoni, R. D. Johnson, M. S. de Vries, C. Booth, F. Bridges, and P. Pianetta, Chem. Phys. Lett. **213**, 196 (1993).

[27] The ionic radii are 1.06 Å (La^{3+}) and 0.893 Å (Y^{3+}). Values are from *Handbook of Chemistry and Physics,* 72nd ed. (CRC, Boca Raton, FL, 1991), pp. 12–18.

[28] For C_{60}, see J. H. Weaver, J. L. Martins, T. Komeda, Y. Chen, N. Troullier, T. R. Ohno, G. H. Kroll, R. E. Haufler, and R. E. Smalley, Phys. Rev. Lett. **66**, 1741 (1991). For a comparison of the valence-band widths of C_{60}, C_{84}, and graphite, see D. M. Poirier, J. H. Weaver, K. Kikuchi, and Y. Achiba, Z. Phys. D **26**, 79 (1993).

[29] U. Gelius, in *Electron Spectroscopy,* edited by D. A. Shirley (North-Holland, Amsterdam, 1972), p. 311.

[30] S. Hüfner, in *Photoemission in Solids I,* edited by M. Cardona and L. Ley, Topics in Applied Physics, Vol. 26 (Springer-Verlag, New York, 1978), p. 271.

[31] P. J. Benning, D. M. Poirier, N. Troullier, J. L. Martins, J. H. Weaver, R. E. Haufler, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **44**, 1962 (1991).

[32] J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).

[33] R. D. Johnson, M. S. de Vries, J. R. Salem, D. S. Bethune, and C. S. Yannoni, Nature **355**, 239 (1992).

[34] P. J. Krusic, E. Wasserman, B. A. Parkinson, B. Malone, and E. R. Holler, J. Am. Chem. Soc. **113**, 6274 (1991); P.-M. Allemand, G. Srdanov, A. Koch, K. C. Khemani, and F. Wudl, J. Am. Chem. Soc. **113**, 2780 (1991); A. Penicaud, J. Hsu, C. A. Reed, A. Koch, K. C. Khemani, P.-C. Allemand, and F. Wudl, J. Am. Chem. Soc. **113**, 6698 (1991); S. G. Kukolich and D. R. Huffman, Chem. Phys. Lett. **182**, 263 (1991).

[35] O. Pilla and H. Bill, J. Phys. C **17**, 3263 (1984).

[36] For photoemission with $h\nu = 1486.6$ eV, the La $3d_{3/2,5/2}$ direct emission overlaps a La MNN Auger feature so that the background beneath the $3d_{3/2}$ component is enhanced.

[37] C. Yeretzian, J. B. Wiley, K. Holczer, T. Su, S. Nguyen, R. B. Kaner, and R. L. Whetten, J. Phys. Chem. **97**, 10097 (1993).

[38] S. Suzuki, T. Ishii, and T. Sagawa, J. Phys. Soc. Jpn. **37**, 1334 (1974).

[39] H. Suematsu, Y. Murakami, T. Arai, H. Kawata, Y. Fujii, N. Hamaya, O. Shimomura, K. Kikuchi, Y. Achiba, and I. Ikemoto (unpublished).

[40] R. Beyers, C.-H. Kiang, R. D. Johnson, J. R. Salem, M. S. de Vries, C. S. Yannoni, D. S. Bethune, H. C. Dorn, P. Burbank, K. Harich, and S. Stevenson (unpublished).

[41] Y. Saito, T. Yoshikawa, N. Fujimoto, and H. Shinohara, Phys. Rev. B **48**, 9182 (1993); J. F. Armbruster, M. Roth, H. A. Romberg, M. Sing, M. Schmidt, M. S. Golden, P. Schweiss, P. Adelmann, J. Fink, R. Michel, J. Rockenberger, F. Hennrich, and M. M. Kappes, Phys. Rev. B (to be published).

[42] D. M. Poirier, D. W. Owens, and J. H. Weaver (unpublished). We note that our estimate of the C_{60} vapor pressure is within an order of magnitude of that measured by thermogravimetric analysis [J. Abrefah, D. R. Olander, M. Balooch, and W. J. Siekhaus, Appl. Phys. Lett. **60**, 1313 (1992)].

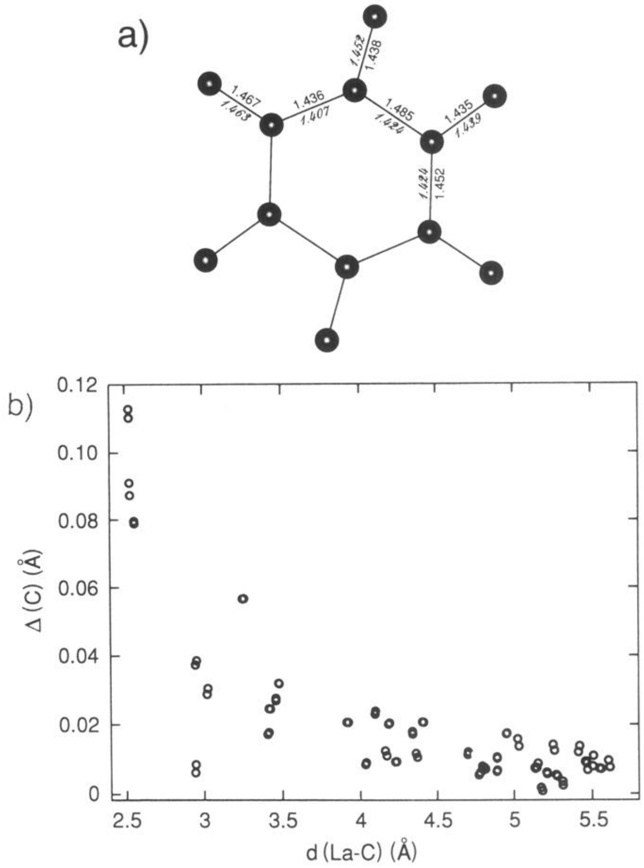

FIG. 2. Distortion of the empty C_{82} structure upon La incorporation. The calculated bond lengths (in Å) of C_2-derived La@C_{82} nearest the La ion are given in (a). The corresponding bond lengths in empty C_{82} are given in italics. In (b), the displacements of carbon atoms of La@C_{82}, Δ(C), relative to atomic positions in empty C_{82}, are plotted as a function of their distance from the La ion, *d*(La-C).

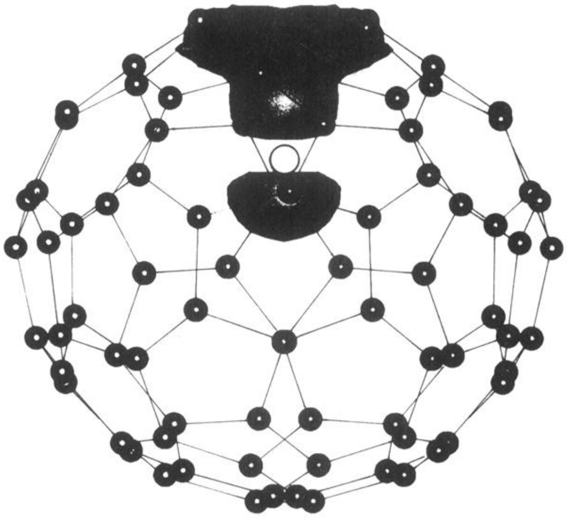

FIG. 6. Constant electron density surface $[\rho=0.008\ e/(\text{a.u.})^3]$ corresponding to one of the four molecular orbitals of C_2-derived La@C_{82} that contains significant La $5p$ character. The orbital is much more localized than the purely carbon-derived orbitals and is clearly associated with the La ion. However, much of the state density is found on the fullerene cage. The La ion is positioned between the lobes of the La $5p-$C $2s$ hybrids.

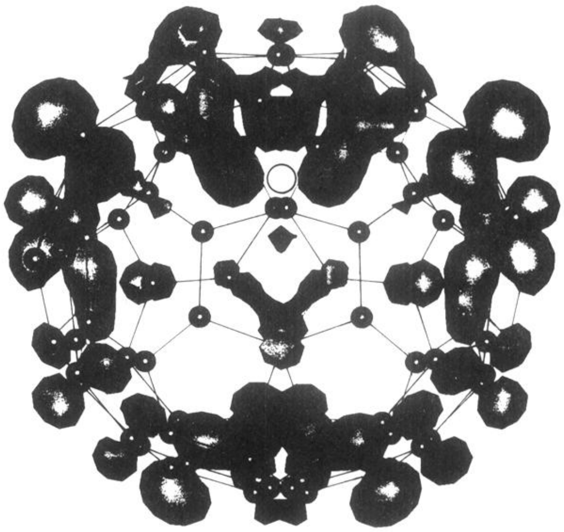

FIG. 8. Constant electron density surface [$\rho = 0.001\ e/(\text{a.u.})^3$] of SOMO for the C_2-derived structure of La@C_{82}. The SOMO is delocalized over the carbon cage, attesting to its carbon π character and confirming that there is no La 5*d* admixing.