Structural and Electronic Properties of La@C₈₂

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The structural and electronic properties of the La@C₈₂ fullerene have been investigated by means of the Car-Parrinello method, which is based on the local density approximation of the density functional theory. The topological arrangement of the C₈₂ cage was assumed to be a C_{3v} symmetry isomer. Three configurations were considered, one with the lanthanum atom at the center of the cluster, one with it along the threefold axis, and one with it at a low-symmetry, highly coordinated site. The structure was fully relaxed and it was found that the last of these configurations is energetically preferred. In this position, the lanthanum atom is nearly in a La³⁺ state and the unpaired electron is somewhat delocalized on the cage, in agreement with available experimental data. This arrangement suggests that the chemical shifts of the 5*s* and 5*p* lanthanum states can be used as a structural probe and as a way of further validating this picture. It is argued that this conclusion is not affected by the assumed fullerene structure.

Almost simultaneously with the discovery of C_{60} (1), the investigation of cluster beams obtained with laser vaporization techniques revealed that La (and a few other metal atoms) could be trapped in the hollow fullerene cage (endohedral doping) (2). Since then, several other endohedral fullerene complexes have been obtained [such as K@C60, K@C59B, and Fe@C60 (3)] as well as, most spectacular of all, metallofullerenes with group IIIB (La, Y, Sc) (4-9) and rare-earth elements (10). In fact, the latter can now be synthesized in macroscopic amounts with a simple variant of the Krätschmer-Huffman procedure (11), making possible detailed experimental investigations of these compounds. They have been confirmed to be endohedral complexes on the basis of chemical reactivity and the thermally induced "shrink wrap' decay process of the fullerene cage (4).

The interest in these molecules also reflects practical considerations. They are expected to have novel chemical properties as well as unusual electron-phonon coupling and vibrational properties. Here we focus our attention on La@ C_{82} , the first of these compounds to have been isolated, the one most intensely subjected so far to experimental study, and one that exhibits apparently unexpected and still unexplained behavior.

The accepted wisdom on the stability of fullerenes is based essentially on a few simple criteria, some geometrical, such as the rule that a fullerene must have 12 isolated pentagons (12), and some electronic (13), such as the criterion that there be a large HOMO-LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap. Electronic stability has been related to the complete filling of shells and consequent opening of large HOMO-LUMO gaps. This sort of analysis led Manolopoulos and Fowler (13) to predict that the C_{82}^{2-} isomer of C_{3v} symmetry is stable. On the basis of these considerations, La@C₈₂ was believed to be stable with two 6s electrons transferred from La to the cage to form a stable C_{82}^{2-} C_{3v} isomer. The unpaired 5*d* electron would be left behind, localized on La, which would thus assume a formal charge of 2+. These expectations were apparently heightened by earlier Hartree-Fock electronic calculations by Chang *et al.* (14), who predicted this type of scenario in the case of La@C₆₀ with La at the center of the molecule.

Thus the experimental findings of Johnson et al. (5) came as a surprise: electron paramagnetic resonance and hyperfine splitting [electron spin resonance (ESR)] data are only consistent with a picture in which the La 5d electron is also almost completely transferred to the cage in a rather delocalized state, thus leading to a formal charge on La of close to 3+. Successive x-ray photoemission spectroscopy measurements by Weaver et al. (6) have confirmed this picture, showing line shapes similar to those of such fairly ionic La compounds as LaBr₃ or LaI₃. To reconcile this fact with the assumed explanation for stability, these investigators suggested that the unpaired electron is not part of the π -electron system but is in an orbital that is primarily diffused inside the cage, in disagreement with ESR data. This situation shows that the simplistic arguments presented above need to be corrected and the full complexity of the problem treated if we are to understand the system.

We present here a calculation based on the use of the Car-Parrinello method (15), which shows that the behavior of the La@C₈₂ cluster cannot be explained unless the interaction between La and the cage is taken into account. Such interactions lead to a lowering of the symmetry and to the almost complete transfer of the La 5*d* electron into a diffuse state on the cage.

We summarize here some of the technical details of the calculation. Our computational scheme is similar to that used several times in Car-Parrinello-like simulations of fullerenes (16). We use the local density approximation to the density functional theory, adopt pseudopotentials to integrate out core electrons, and expand the Kohn-Sham orbitals in plane waves using a cutoff of 35 Ry. Therefore, we are forced to use periodic boundary conditions. In the present calculation they are of the face-centered-cubic type, and a lattice constant of 21.16 Å is used to decouple each cluster as far from its periodically repeated images as possible.

The pseudopotential for C and the form of the local density functional are the same as those used by Feuston et al. (16). In the case of La, the choice of the pseudopotential is more complex. The ground-state configuration is $5s^25p^66s^25d^1$, and we found it necessary to treat all 11 of these electrons explicitly. The necessity for this procedure was pointed out by Bachelet et al. (17), who noted that the 5s and 5p core states cannot be considered frozen without a significant loss of accuracy. In particular, we have verified that freezing them out would lower the third ionization potential, corresponding to the loss of the 5d electron, from 19.1 to 18.2 eV [experimental value: 19.2 eV (18)]. We took the La scalar-relativistic pseudopotential from the Bachelet-Hamann-Schlüter tables (17) and recast it in the Kleinman-Bylander form (19) with the *p*-component as the local part. A test calculation on a LaC_2 molecule predicted a formal charge state close to 2+ for La (and gave a La-C bond length of 2.33 Å, that is, about 10% less than the bond length in solid LaC_2). This is consistent with the structure assumed in the solid phase, namely, the CaC2 structure, typical of C compounds with divalent cations such as Ca and Sr.

At present the equilibrium structure of La@C₈₂ is not experimentally known, and it is not clear whether the C_{3v} structure is the most stable one. Recent nuclear magnetic resonance experiments (20) have shown that in the undoped C₈₂ case several isomers are stable and that the C_{3v} isomer is not the most abundant one. This may also be the case for La@C₈₂. However, as we explained above, this is the only structure for which the argument based on the stability of the C_{82}^{-} ion would apply (13). If it fails here, then another mechanism must be invoked to explain the stability of $La@C_{82}$ that may well be not structure-specific. We thus focus here on the C_{3v} structure. Given the similarity of the C network in all possible fullerene isomers (21), we believe

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that our choice does not imply a loss of generality.

The C_{3v} structure has three mirror planes and a threefold symmetric rotation axis. As a start, we optimized the atomic positions on this undoped molecule and calculated its electronic structure. The energy level structure around the HOMO turns out to be qualitatively as expected from Hückel calculations (13). There is a small HOMO-LUMO gap of 0.1 eV, whereas a much larger gap (1.0 eV) appears between the LUMO and the LUMO+1. In a rigid energy level scheme this becomes the HOMO-LUMO gap of C_{82}^{2-} and leads to the prediction of its stability. First, we performed a calculation on La@C₈₂ by relaxing the cage but keeping the La atom at the center (we denote this the "O" configuration). This retains the C_{3v} symmetry. Upon doping, the cluster relaxed with atoms moving no more than 0.05 Å, and the energy level diagram was in close agreement with the rigid energy level scheme (13). In fact, two electrons move from La to the C_{82} cage forming a C_{82}^{2-} anion while the third electron remains localized on La in an approximately $d_{3z^2-r^2}$ (a1) state, as illustrated in Fig. 1A. This arrangement is in agreement with the picture of Chang et al. for La@C₆₀ (14), but it contradicts the experimental data on La@ C_{82} (5, 6). The LUMO and LUMO+1 have predominantly d-like character, and a small HOMO-LUMO gap exists (<0.1 eV) owing to the crystal field effect.

Next, we displaced the La atom offcenter along the threefold axis, thus retaining the C_{3v} symmetry, and again relaxed the cage. The La position that corresponds to a local energy minimum is ~ 1.6 Å from the center, that is, 2.5 Å from the cage (which we call the "A" configuration). In this neighborhood, the cage atoms relax significantly (by ~0.16 Å) as a consequence of the fact that La does not simply behave as an electron donor but actually forms a strong bond with the C atoms (the first coordination is 6). The La displacement from the O to the A configuration corresponds to an energy gain of ~ 2.5 eV. However, the A configuration implies an electronic structure that is still in disagreement with the picture emerging from experiments. In fact, the nature of the high occupied states is almost unaltered with respect to the O configuration, which has a doubly degenerate HOMO-1 belonging to the cage and a $d_{3z^2-r^2}$ -like HOMO localized around La. In parallel with the gain in energy, the HOMO-LUMO gap increases (to $\sim 0.2 \text{ eV}$) as a result of the stronger crystal field.

Finally, we considered other possible configurations with La residing at lower symmetry C_s sites on symmetry planes and



Fig. 1. Constant electron density surface $[0.01 e/(au)^3]$ (au, atomic unit) corresponding to the HOMO state (**A**) in the O and (**B**) in the K configurations (see text). The cluster is seen from a direction perpendicular to a mirror symmetry plane. The La atom is the red sphere, enlarged for better visibility.

having high coordination (coordination number 10 within a cutoff of ~ 2.86 Å). There are three equivalent positions (which we call the "K" configuration). The optimized configuration corresponds to a minimum distance of ~ 2.5 Å between La and the cage, to a relaxation (by 0.12 Å) of the atoms bound to La, and to an energy gain of ~3.5 eV with respect to the O configuration. The nature of both the HOMO and the LUMO now changes dramatically. As shown in Fig. 1B, the HOMO is not localized on La and has no d character. Instead, it is diffuse on the cage in the region close to La, thus leading to a formal charge state close to 3+ for La, in agreement with experimental data. Similarly, the LUMO has no d character either and is localized on the cage. The HOMO-LUMO gap is larger, namely, ~0.4 eV. Consistent with experimental evidence (5), La@C₈₂ in the K configuration is a doublet with the unpaired

Fig. 2. Contour plots of the valence charge density in the mirror symmetry plane of La@C_{a2}. The contour levels correspond to values with densities of $0.3, 0.27, \ldots 0.03, 0.008$ e/(au)³. The four electron states deriving from the atomic 5s and 5p states have not been included in the evaluation of the valence charge density.

electron in a fairly delocalized orbital. This result suggests that the interpretation of the special stability of this radical is not trivial. In Fig. 2 we present a contour plot of the valence electron density in the mirror symmetry plane in which La lies. Some small s-like component of the density is left on the La ions in agreement with hyperfine data. There is, however, substantial charge transfer to the cage, so that La can best be described as being in a 3+ state.

Our results show that the electronic structure, at least in the vicinity of the HOMO-LUMO gap, is strongly dependent on the atomic configuration. The low-lying energy levels of the La core electrons are "not frozen" as anticipated but are rather sensitive to the chemical environment. The "5s" - "5p" energy difference changes by as much as 1.6 eV from the central position to the off-center ones. Furthermore, the splitting of the "5p" levels increases from $\sim 0.2 \text{ eV}$ in the O to $\sim 0.8 \text{ eV}$ in the A to $\sim 1.2 \text{ eV}$ in the K configuration. This result suggests that measurements of the chemical shift may constitute a useful structural tool.

The type of La-cage bonding that we have found here, a rather localized and strong one, is independent of the specific global structure of the fullerene. For this reason, we argue that the present choice of the $C_{3\nu}$ -like isomer for the metallofullerene does not affect our conclusions. If anything, the $C_{3\nu}$ structure should bias the results toward the La²⁺ charge state. This argument is further supported by our preliminary results on La@C₆₀, which show a tendency toward a similar bonding pattern.

Because La is relatively close to the C_{82} cage, it is possible to incorporate other La

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atoms inside it. Indeed, $La_2@C_{82}$ (4) has been synthesized. Even more interesting in view of our findings is the recent synthesis of $Sc_3@C_{82}$ (7, 8), for which the three Sc atoms have been experimentally identified as occupying three equivalent positions. Because Sc has the same electronic configuration as La and is significantly smaller, it is not surprising that an endohedral threeatom cluster can form. The equivalency of the three positions strongly suggests that the cage does have C_{3v} symmetry and that the Sc atoms have the K configuration.

The behavior we have discovered for $La@C_{82}$ is consistent with the available experimental data. Moreover, the behavior of the other group IIIB metal atoms is similar to that of La; they form similar endohedrally doped fullerenes and, in the case of C_{82} , give three electrons to the cage. Thus we believe that our results are qualitatively valid for those systems also and that they provide insight into them. Contrary to the structure in alkali-intercalated compounds such as K3C60, endohedral doping of fullerenes with a threevalent atom such as La results not in mere electron donation but in a strong modification of the metal and cage electron states. This modification changes the electronic and vibrational properties of these systems significantly. Particularly interesting would be the properties of solid Ladoped fullerenes.

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Scanning Tunneling Microscopy of **Electrodeposited Ceramic Superlattices**

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Cleaved cross sections of nanometer-scale ceramic superlattices fabricated from materials of the lead-thallium-oxygen system were imaged in the scanning tunneling microscope (STM). The apparent height differences between the layers were attributed to compositiondependent variations in local electrical properties. For a typical superlattice, the measured modulation wavelength was 10.6 nanometers by STM and 10.8 nanometers by x-ray diffraction. The apparent height profile for potentiostatically deposited superlattices was more square than that for galvanostatically deposited samples. These results suggest that the composition follows the applied potential more closely than it follows the applied current. The x-ray diffraction pattern of a superlattice produced under potential control had satellites out to the fourth order around the (420) Bragg reflection.

Quantum confinement of carriers in nanometer-scale materials leads to size-dependent optical and electrical properties that are intermediate between those of molecules and those of extended network solids (1-3). As the dimensions of these materials

approach the nanometer scale, characterization becomes increasingly more difficult. In multiple quantum wells the composition profile is often designed to be square, yet this profile can only be inferred from x-ray diffraction (4-6). We have used the STM to measure the modulation wavelength and estimate the squareness of the composition profile in cleaved cross sections of superlattices by mapping out the electronic proper-

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ties in real space on a nanometer scale. We define a superlattice as a crystalline multilayer structure with coherent stacking of atomic planes and periodic modulation of the structure or composition, or both.

Operation of the STM is based on the tunneling of electrons due to an applied bias voltage between a conductive sample and a sharp metal tip that are separated by a few nanometers (7, 8). The current density for free electron tunneling through a planar barrier with an applied voltage less than the work function of either the probe tip or the sample is given by

$$J = \left(\frac{e^2}{h}\right) \left(\frac{\kappa}{2\pi s}\right) V \exp(-2\kappa s) \quad (1)$$

where s is the effective tunneling distance, κ is the inverse decay length of the wave function density outside the surface, V is the bias voltage, e is the electronic charge, h is Planck's constant, and $2\kappa = 1.025\phi^{1/2}$. The effective barrier height, ϕ , is, to a first-order approximation, the average of the probe tip and sample work functions (9). In the case of nonfree electrons and nonplanar barriers, the tunneling current can no longer be expressed in such simple closed form. The prefactor will be altered as a result of density of states effects (7). However, the tunneling current will still have the same exponential dependence on both the sample-to-probe tip separation and the work function.

The work function of a semiconductor is strongly dependent on doping. Using Si as a prototypical material, we find that the calculated work function shifts from 4.6 eV for intrinsic Si to 4.3 eV when the material is doped with only 2 \times 10⁻⁵ atomic percent (that is, 10^{16} atoms/cm³) of an *n*-type dopant such as P (10). Hence, small changes in doping levels could bring about large contrasts or apparent height differences in the STM.

Another possible source of contrast in semiconducting samples is the local resistance. The surface potential in a nonmetallic sample can be appreciably different from the applied potential resulting from *iR* (current multiplied by resistance) drop in the sample. Again using the example of Si, we find that the resistivity shifts from 2×10^5 ohm-cm for intrinsic Si to 0.4 ohm-cm when the Si is doped with only 2×10^{-5} atomic percent of an *n*-type dopant. Flores and Garcia have estimated that the spreading resistance (resistivity of the semiconductor divided by four times the tip radius) during an STM experiment will be 4×10^8 ohms for a Si sample with a resistivity of 10 ohm-cm (11). The relevant V in Eq. 1 is the difference in local surface potentials for the tip and the sample rather than the applied bias.

The sensitivity of the STM to surface

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