La@C_{60}: A metallic endohedral fullerene

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We have produced an endohedrally doped fullerene that shows a metal-like density of states at the Fermi level. Individual La@C_{60} clusters deposited onto graphite exhibit a zero band gap as observed by scanning tunneling spectroscopy on single clusters at room temperature. Moreover, we find that an isolated La@C_{60} cluster on graphite shows a reversible opening of a band gap at a transition temperature of ~28 K. The transition is associated with a freezing of the vibrational motion of the La atom inside the fullerene cage. The metallic behavior of La@C_{60} is attributed to the presence of a dynamical dipole in the single cluster. © *2001 American Institute of Physics.*
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I. INTRODUCTION

Endohedral fullerenes are of great interest due to their diversity and plans for numerous applications.[1] Because of the robust carbon cage and its large hollow interior, endohedral fullerenes represent a new class of technologically relevant composites as they incorporate possible metallic and fullerenelike properties. One of the most intriguing aspects of endohedral fullerenes is the expected metallic or even superconducting character.[1,2] Charge transfer from the metal (M) into the unoccupied carbon cage orbitals, which is fostered by the high electron affinity of the fullerenes,[3] raises expectations for M@C_{60} and other endohedral fullerenes to exhibit metallic properties. In spite of tremendous efforts spent on the isolation of endohedral fullerenes from carbon soot, only a few endohedral fullerenes have been isolated in macroscopic amounts. The chromatographic extraction of endohedrally doped M@C_{60} seems particularly difficult, as only Eu@C_{60} has been isolated in pure form.[4] However, it turns out that all these endohedral fullerites reveal a zero density of states at the Fermi level in contrast to the intuitive metal-to-carbon charge transfer picture. Metallic conductivity has only been observed for C_{60} when doped within a very narrow stoichiometry range and some of these metallic phases exhibit remarkable high superconducting transition temperatures.[1,2,5–13] None of the other fullerenes are found to be metallic regardless whether dopants are introduced externally or encapsulated endohedrally into the cage. The failure to produce metallic endohedral fullerides might be attributed to the fact that charge transfer in endohedrally doped fullerenes is more complex than that in the exohedral alkali-metal-doped systems. This is most likely due to the hybridization of metal *d* orbitals with the carbon orbitals causing a donor–acceptor type of bonding. This hybridization has been proven experimentally for a thin film of La@C_{82} by resonant photoemission experiments.[14]

Endohedral M^{3+}@C_{60}^{3-} clusters containing trivalent metal atoms are of special interest as these are isoelectronic to the high-T_c superconducting fullerides A_3C_{60} (A=alkali metal). As proposed by Weaver *et al.*, crystals of pure La@C_{60} are expected to be metallic due to a charge transfer best described as 3+.[15] This has not been experimentally demonstrated so far, because La@C_{60} has not been isolated in pure form. However, by using a laser vaporization cluster source, a wide range of endohedral lanthanide fullerenes from 30 to about 150 carbon atoms, including endohedrally doped M@C_{60}, are available for deposition from a mass-selected metal–fullerene cluster beam.[16,17] Combining this deposition technique with scanning tunneling spectroscopy (STS), we have probed the local density of electronic states near the Fermi level of single La@C_{60} and Ce@C_{60} fullerenes on highly oriented pyrolytic graphite (HOPG). As STS gives information on both the occupied and unoccupied orbitals the band gap of the individual clusters on HOPG is immediately revealed by these measurements.

II. EXPERIMENT

The clusters were synthesized by pulsed laser vaporization of a graphite-metal rod (100:1) and condensation in He atmosphere.[16,17] After supersonic expansion, the cluster cations were mass-selected by a magnetic sector field ($m/\Delta m \approx 250$) and deposited onto a sample area of $\sim 1\times 1$ mm^2. In order to avoid damage upon surface impact, the clusters were deposited softly at an ion kinetic energy of <200 meV/atom. Following deposition, the cluster-covered samples were transferred into a variable-temperature scanning tunneling microscope (STM) under ultra high vacuum conditions.[18] The STS spectra have been taken with a chemically etched tungsten tip on top of individual clusters.

III. RESULTS AND DISCUSSION

Figure 1(A) shows a STM overview of the mass-selected endohedral clusters on HOPG. A mean coverage density of ~1/100 nm^{-2} can be inferred from the STM figure, which corresponds to ~1% of a monolayer. Thus the deposited clusters are separated several times their diameter as clearly seen for La@C_{60} in Fig. 1(B). The intactness of the deposited fullerene cages has been verified by the height of La@C_{60} and Ce@C_{60}, which is very similar to pristine C_{60} as demonstrated in Fig. 1(C). Both endohedral clusters appear slightly higher than C_{60}, which is attributed to a different

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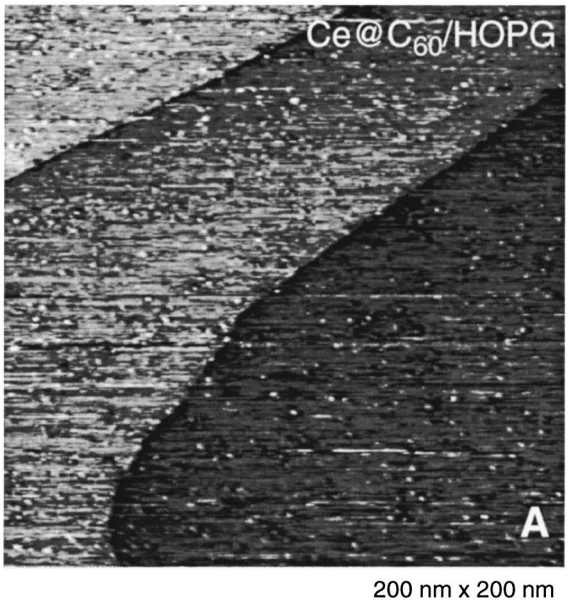

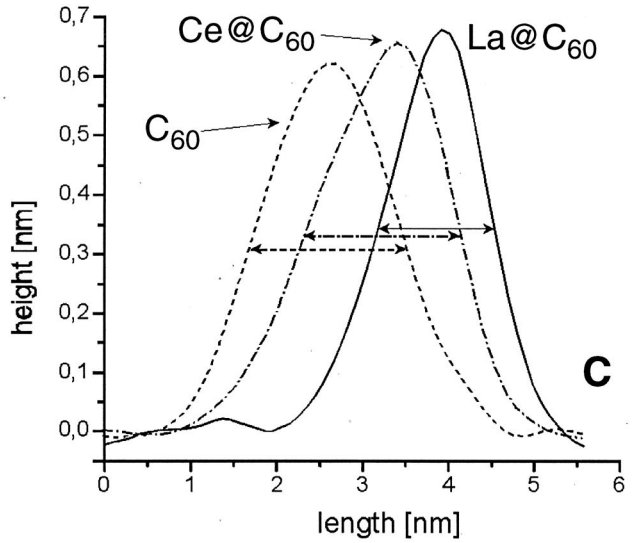

FIG. 1. STM images of mass-selected (A) $Ce@C_{60}$ and (B) $La@C_{60}$ on HOPG. The cluster coverage is about 1% of a monolayer. Profile plots are shown in (C) and are compared to the height of undoped C_{60}.

tunneling conductivity owing to the different electronic structures. At room temperature, $La@C_{60}$ shows an enhanced mobility on the HOPG surface with respect to $Ce@C_{60}$.

Figures 2 and 3 show the normalized STS curves of single C_{60}, $La@C_{60}$, and $Ce@C_{60}$ clusters on HOPG at room

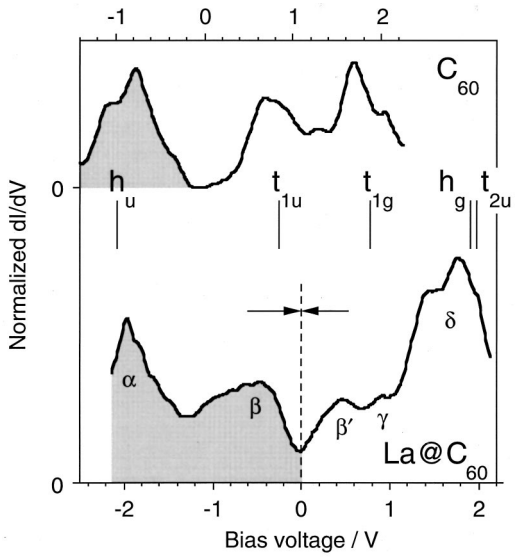

FIG. 2. The normalized differential tunneling conductivity $(dI/dV)(V/I)$ as a function of the negative and positive bias voltages of C_{60} (top) and $La@C_{60}$ (bottom) on HOPG at room temperature. For $La@C_{60}$ a metal-like density of states at the Fermi level (zero voltage) is revealed. The orbital assignment in the center of the plot refers to the orbitals of free C_{60} from a local density approximation calculation.

temperature, respectively. The most prominent difference between $La@C_{60}$ and $Ce@C_{60}$ is the density of states in the immediate vicinity of the Fermi level. While $Ce@C_{60}$ shows a gap of ~0.3 eV, which is distinctly smaller than that of deposited C_{60} on HOPG (Fig. 2) and reconstructed Si(100),[19] no gap is obvious for $La@C_{60}$. As can be seen in Fig. 4 the tunneling current of $La@C_{60}$ at room temperature increases linearly with the bias voltage for a large energy region around the Fermi level. Therefore the density of states at the Fermi level of $La@C_{60}$ is different from zero. The zero band gap identifies $La@C_{60}$ to be metal-like. In contrast, $Ce@C_{60}$ has a semiconductorlike electronic structure as revealed by the sharp drop of the normalized STS signal distinctly below and above the Fermi level. The small peak at −0.1 V in

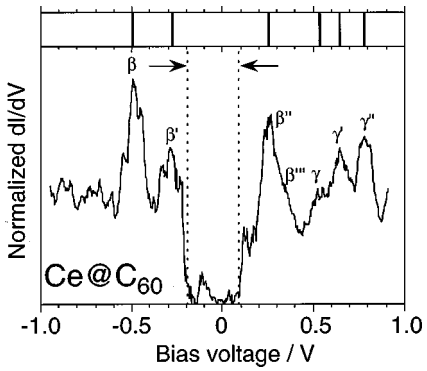

FIG. 3. The normalized differential tunneling conductivity $(dI/dV)(V/I)$ as a function of the negative and positive bias voltages for $Ce@C_{60}$ on HOPG at room temperature. The distinct gap of ~0.3 eV at the Fermi level identifies $Ce@C_{60}$ as a ''semiconducting'' cluster. The reproducible STS features are marked by the bars at the top of the spectrum. β,β',β'' (and β''') are derived from the C_{60} LUMO (t_{1u}), while γ,γ',γ'' are derived from the empty LUMO+1 of C_{60} (t_{1g}).

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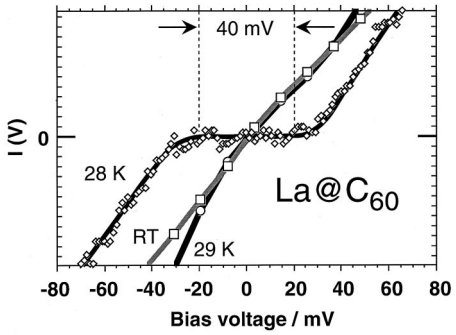

FIG. 4. Temperature-dependent scanning tunneling spectra of a single La@C_{60} cluster on HOPG. The plot shows the $I(V)$ curve at room temperature (RT), ~29 K, and ~28 K, respectively. Note the occurrence of an energy gap below the transition temperature of ~28 K.

Ce@C_{60} is attributed to poor statistics emphasized by normalization near zero bias. Up to now, all endohedral compounds, e.g., La@C_{82}, have been found to be semiconducting when deposited as solid films. La@C_{60} is the first endohedral fullerene found to have a metal-like density of states. Moreover, the moleculelike peak structure of the STS curve demonstrates that the metal-like character is an intramolecular property of the La@C_{60} cluster itself.

The metal-like density of states in La@C_{60} can be interpreted in terms of charge donation from the La atom into C_{60}-derived π orbitals. Figure 2 shows a comparison of STS curves of C_{60} (top) and La@C_{60} (bottom) on HOPG. The C_{60}-derived lowest unoccupied molecular orbital (LUMO) is expected to be split in La@C_{60} by symmetry reduction owing to both a noncentrosymmetrical position of the La atom[20,21] and charge donation. Upon charge transfer from the trivalent La atom into the empty LUMO of C_{60}, the t_{1u}-derived orbital in La@C_{60} is only partially filled. The Fermi level is thus located within this Jahn–Teller split orbital. Consequently, the peaks immediately below (β) and above (β') the Fermi energy can be assigned to the t_{1u}-derived orbitals while the Fermi energy in C_{60} is located between the h_u and t_{1u} orbitals. Peak γ at +0.9 V is interpreted to be derived from the t_{1g} orbital (C_{60} LUMO+1), which is broadened by Jahn–Teller distortion. The same holds true for the C_{60}-derived highest occupied molecular orbital (HOMO) (h_u) around −2 V (α) and the h_g/t_{2u}-derived peak at +1.9 V (δ). Though the degeneracy of the C_{60}-derived orbitals is lifted upon doping, the overall valence-electron structure of La@C_{60} is principally similar to that of pristine C_{60}. However, due to the charge transfer from the La dopant into the empty "conduction" band of C_{60}, the LUMO-derived orbital of La@C_{60} is only partly filled, a necessary condition for a metal-like level density.

The electronic level density at the Fermi level of La@C_{60} changes upon cooling as demonstrated in Fig. 4. While the electronic structure is not altered very much from room temperature down to ~29 K, a distinct gap is opened around the Fermi level at ~28 K as deduced from the $I(V)$ curve. A gap of ~40 mV is revealed by fitting a flat base line through the data around the Fermi level in Fig. 4. In contrast, the $I(V)$ curves at room temperature and ~29 K exhibit a nearly constant slope throughout the entire vicinity of the Fermi level. Thus, the $I(V)$ curve of La@C_{60} reveals a metal-like characteristic above ~29 K, while a semiconductorlike behavior is obvious below ~28 K. The "metal-to-semiconductor" transition in La@C_{60} is reversible at the transition temperature of ~28 K. We note that the gap of 40 mV is too small to be caused by a Coulomb blockade, which amounts to more than 1 eV for a sphere of 10 Å diameter. Since no Coulomb blockade is observed at any temperature we conclude that the endohedral fullerene is not locally charged, making a sufficient orbital overlap and Ohmic contact to the HOPG substrate evident. Moreover, no effect related to the HOPG substrate is known to occur in this temperature region.

We attribute the opening of the gap to the freezing of the dopant's vibrational motion within the fullerene cage. The period of circular motion at room temperature has been calculated by Andreoni and Curioni to be 1.1 ps.[20,21] This La motion is expected to freeze at a temperature that corresponds to an energy smaller than the potential barrier. Our measured freezing temperature of ~28 K corresponds to an energy of ~2.4 meV, which defines the minimum energy for movement. This potential barrier agrees quite well with the calculations of Andreoni and Curioni,[20,21] who predict vibrational frequencies involving La to be as small as 30 cm^{-1} (3.7 meV). The motion of La inside the C_{60} cage is associated with a dynamical dipole moment of La@C_{60}. In contrast to the dynamical Jahn–Teller distortion above ~29 K where the dipole averages to zero on a picosecond time scale, the dipole is locked in the frozen state that gives rise to a static Jahn–Teller distortion. Obviously, the La dynamics introduces electronic states at the Fermi level that are well separated by 40 meV in the static state. This agrees with the calculated splitting of the C_{60} t_{1u}-derived levels for the ground-state geometry of La@C_{60}.[22] Both the freezing of the low-frequency modes involving the La atom and the resulting gap opening is consistent with the nonmetallic electronic structure of La@C_{82} for which a fixed position of La has been predicted at room temperature.[20,21]

The question why Ce@C_{60} behaves like a semiconductor at room temperature in contrast to La@C_{60} can be attributed to a formal 4+ charge state due to the extra *4f* electron in Ce. In this case the Fermi level is expected to be located somewhere between the split t_{1u}-derived C_{60} orbitals (β, β', β'' in Fig. 3), and the existence of the gap follows from a closed shell structure of the t_{1u}-derived levels. As the Jahn–Teller distortion of the t_{1u} band is much less than the splitting of the h_u and t_{1u} frontier orbitals of C_{60}, the reduced HOMO-LUMO gap in Ce@C_{60} is consistent with this interpretation. Considering an on-site two-electron Coulomb repulsion similar to the Hubbard *U*, a gap might occur even in the case of a noninteger charge transfer. Three electrons occupying the t_{1u}-derived levels would then give rise to four peaks in the spectrum. Peaks β' and β'' below and above the Fermi level, respectively, represent the same single-particle orbital, split by the Coulomb interaction *U*. The other t_{1u}-derived levels are represented by β and β''', the latter indicated as a shoulder of peak β''. The Jahn–Teller distortion then amounts to ~0.2 eV ($\beta - \beta'$) and ~0.1 eV ($\beta'' - \beta'''$). Note that for a detailed understanding of the charge transfer the

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exact hybridization between the Ce $5d/6s$ and fullerene orbitals has to be taken into account. Nevertheless, the presence of the additional *4f* electron will definitely have an effect on the hybridization. Moreover, Ce is located in a more eccentric off-center position which is ~10% larger than that in $La@C_{60}$.[20,21,23] This and the larger charge transfer could lead to a permanent dipole moment in $Ce@C_{60}$ in contrast to the dynamical dipole moment of $La@C_{60}$.

IV. CONCLUSIONS

In conclusion, endohedral doping can lend metallic properties to a single C_{60} cluster by intramolecular orbital hybridization, whereas intermolecular band overlap will cause a line of several adjacent C_{60} clusters to form a conducting wire.[24] The deposition from a mass-selected cluster beam opens the possibility for a systematic exploration of diverse physical properties such as metallicity, superconductivity, and ferromagnetism on a vast number of endohedral fullerenes doped with rare-earth-metal atoms. If a method of large-scale synthetic production can be found, this could open the pathway for the design of technologically novel endohedral fullerene-based materials such as molecular metals of extremely low weight with magnetic or superconducting properties or as novel catalyst materials.

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