Testing the magnetism of polymerized fullerene

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We present band structure calculations of rhombohedral C_{60} performed in the local-spin-density approximation. Rhombohedral C_{60}(Rh-C_{60}) is a two-dimensional polymer of C_{60} with trigonal topology. No magnetic solution exists for Rh-C_{60} and energy bands with different spins are found to be identical and not split. The calculated C $2p$ partial density of states is compared to carbon K-edge x-ray emission and absorption spectra and shows good agreement. It is concluded that the rhombohedral distortion of C_{60} itself cannot induce magnetic ordering in the molecular carbon. The result of magnetization measurements performed on the same Rh-C_{60} sample corroborates this conclusion.

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A recent report on ferromagnetic ordering in samples synthesized at high pressures and temperatures, on the basis of the rhombohedral polymerized phase,[1] has stimulated interest in carbon systems as possible new magnetic materials made exclusively of light elements. Reports on magnetism in organic compounds and systems composed of nonmagnetic constituent elements are naturally met with skepticism due to the possible influence of magnetic impurities,[2–4] whereas an intrinsic origin of the ferromagnetism in both graphite and rhombohedral (Rh)-C_{60} has been demonstrated.

In order to investigate the possibility of long-range magnetic ordering in the rhombohedral C_{60} polymer we have performed electronic structure calculations that employ density functional theory in the local-spin-density approximation (LSDA).[5,6] The results, consistent with x-ray fluorescence measurements, do not show a magnetic solution and we conclude that a simple distortion of C_{60} molecules in the Rh-C_{60} polymer cannot induce magnetic ordering in the system.

Spin-polarized band structure calculations have been performed for rhombohedral C_{60} molecules using a self-consistent linearized muffin-tin orbital (LMTO) method within the local density approximation (computer code TBLMTO-47, see Ref. 7). This method has been successfully used for different C_{60} compounds.[8,9] For comparison, non-spin-polarized band structure calculations of C_{60} have been carried out. We tried, as a first iteration, different sets of initial spin polarizations of $2p$ carbon states corresponding to different hypothetical magnetic structures, but this polarization inevitably tends to zero at the iterations of self-consistency procedure and the final state turns out to be nonmagnetic (Fig. 2). The isolated C_{60} molecule has an icosahedral symmetry and it is usually assumed that the same holds for each molecule in the solid, monomeric fcc and simple cubic phases.[8] The positions of atoms in cubic C_{60} are taken from Ref. 8. Rh-C_{60} clusters form a trigonal lattice in each layer, and the space group of this system is $R\overline{3}m$. The crystal lattice structure in this case is usually expressed by using hexagonal system parameters: $a=9.19$ and $c=24.5$ Å; the interlayer distance is $c/3$.[10] The electronic structure calculations have been carried out in a standard way, but two important points should be mentioned. First, this is a problem of an optimal choice of atomic radii, numbers of empty spheres, and overlap parameters. We have used the method described in Ref. 9 to solve this problem. Second, a large sized elementary cell in real space permits us to use fewer k points. It appeared that 13 k points in the irreducible part of the Brillouin zone are sufficient for convergence of the density of states picture. One can see in Fig. 3 that the latter is in a good agreement with the experimental data.

Soft x-ray emission measurements of cubic and rhombohedral C_{60} were carried out at Beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. For the emission spectra, the emitted radiation is collected in a Rowland-circle type spectrometer with spherical gratings and recorded with an area-sensitive multichannel detector.[11] This combination provides an instrumental resolution of about 0.4 eV at C $K\alpha$ emission energies.

The x-ray photoemission spectroscopy (XPS) measurements were carried out with a PHI 5600 ci multi-technique spectrometer using monochromatized Al $K\alpha$ radiation ($E_{\mathrm{exc}}=1486.6$ eV). The estimated energy resolution is 0.35 eV and the base pressure in the vacuum chamber during measurements was about 5×10^{-9} Torr.

The measured Rh-C_{60} sample has a cylinder geometry, mass $m=16$ mg, and was synthesized at the limit of thermal stability of the rhombohedral polymerized C_{60} phase at $T=800\,^{\circ}$C and pressure P$=6$ GPa from the powder fullerite C_{60} using a toroid-type high-pressure apparatus. Complementary magnetization $\vec{M}(\vec{H},T)$ measurements were performed using the SQUID magnetometer MPMS5 (Quantum

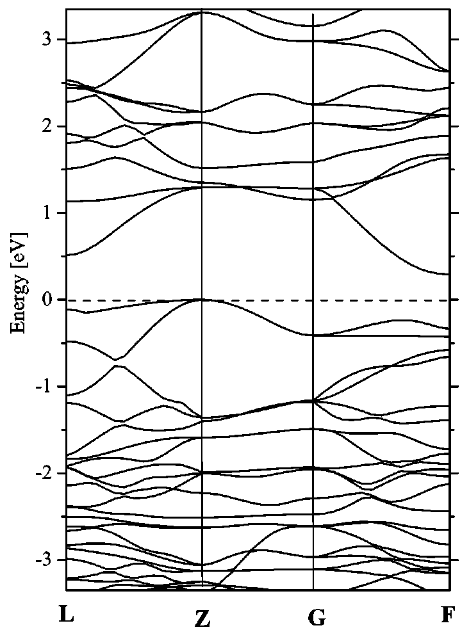

FIG. 1. Energy bands for rhombohedral C_{60}.

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The calculated electronic band structure for the rhombohedral polymer of C_{60} is shown in Figs. 1 and 2 (the Fermi level is set to zero in both figures). The energy gap between the top of the valence band and the bottom of the conduction band is 0.29 eV, which is in accordance with previous band structure calculations.[12] No stable ferromagnetic solutions showing energy splitting between spin-up and spin-down electrons were found. Thus, the pure rhombohedral polymerized phase of C_{60} does not appear to be magnetic according to the LSDA approach.

Generally speaking, the applicability of the LSDA to fullerene-based systems is not obvious because of the possible contribution from correlation effects (for example, see Ref. 13). In order to verify the accuracy of our conclusions we compared the calculated C $2p$ density of occupied states to carbon $K\alpha$ XES of cubic and rhombohedral C_{60} as shown

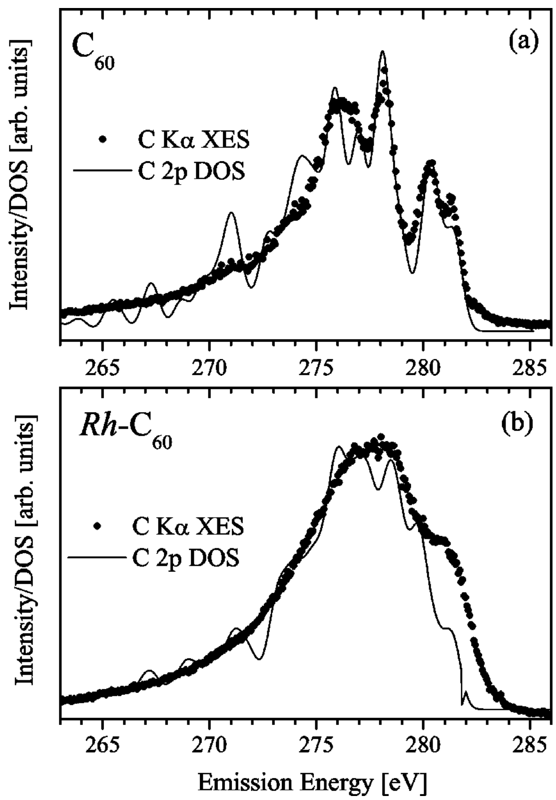

FIG. 3. Comparison of C $2p$ density of states (DOS) and C $K\alpha$ XES of (a) cubic and (b) rhombohedral C_{60}. Calculated C $2p$ DOSs are smeared by Gaussian curves with full widths at half maximum of 0.35 eV.

in Fig. 3. Clearly, experimental carbon K-emission spectra are reproduced quite well by theoretical C $2p$ density of states calculations for both structural modifications of C_{60}. The broader features present in the measured spectra are due to life-time broadening and not an instrumental effect. As displayed in Fig. 4 there are more sharp features in the cubic C_{60} XPS valence-band (VB) spectrum than that of the rhombohedral phase. This is due to the higher space symmetry in cubic $C_{60.}$ The sharp features are more characteristic of small

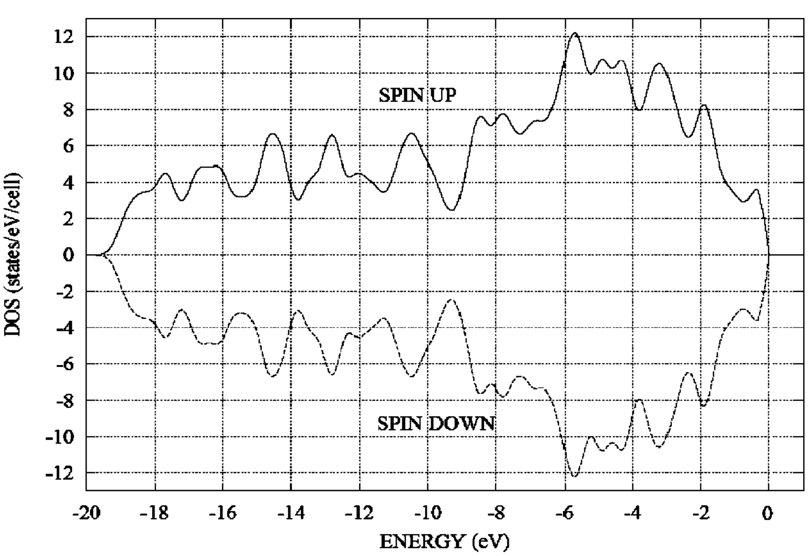

FIG. 2. Density of states for Rh-C_{60}.

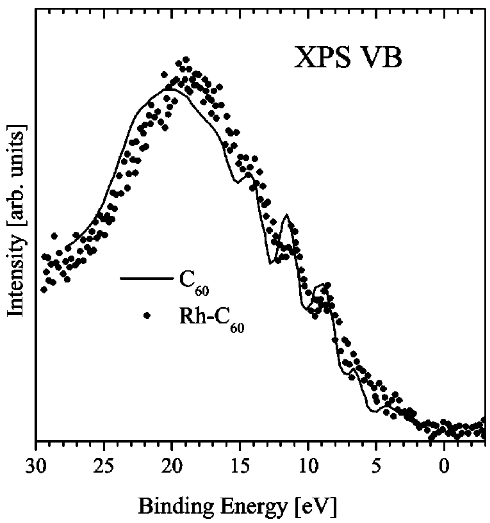

FIG. 4. Comparison of XPS VBs with calculated DOS of cubic and rhombohedral C_{60}. Calculated DOS are weighted by atomic C $2s$ and C $2p$ photoionization cross sections. The XPS VB of cubic C_{60} is taken from Ref. 15.

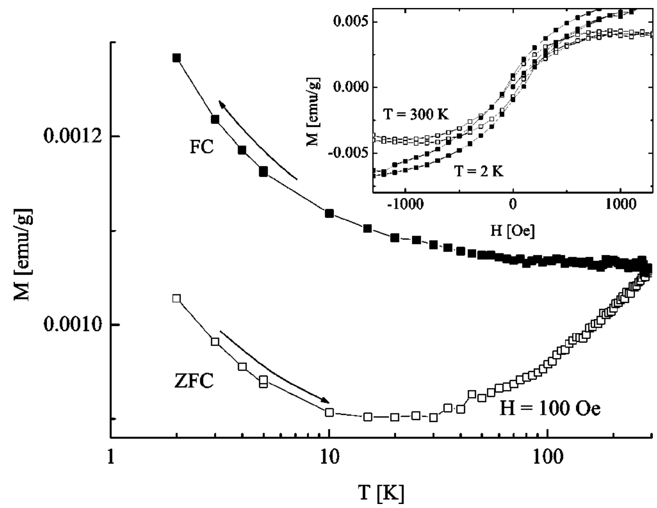

FIG. 5. $M(T,H)$ measured in both ZFC and FC regimes at an applied magnetic field $H = 100$ Oe; the inset demonstrates low-field portions of ferromagnetic-type $M(H)$ hysteresis loops obatined at $T = 2$ and 300 K.

molecules than of solids, showing that the weak intermolecular interactions have only a slight effect on the density of states. The main effect of the interactions between C_{60} molecules in the polymer is a broadening of subbands located at the top of the valence band, which is seen in carbon K-emission spectra. According to the orbital analysis, the subbands at the top of the valence band largely stem from π states and the deeper subbands are almost entirely σ derived. Both experimental C $K\alpha$ XES and XPS VB spectra are very close to the calculated energy bands of occupied electronic states, which demonstrates reasonable agreement between theory and experiment. Thus, LSDA band structure calculations are adequate for this case and our conclusion about the absence of ferromagnetic solutions is reliable. This conclusion agrees with the results of magnetization measurements[14,15] as well as theoretical calculations,[16] which indicate that the ferromagnetic behavior of fullerenes and related materials may originate from various defects.[14–16]

The magnetization measurements performed on the Rh-C_{60} sample studied in this work provide additional information about the inhomogeneous character of the ferromagnetism. Figure 5 presents $M(T)$ measured at $H = 100$ Oe in both zero-field-cooled (ZFC) and field-cooled (FC) cooling regimes. The magnetization data corresponding to the ZFC regime, $M_{ZFC}(T,H)$, were taken on heating after the sample cooling at $H = 0$, and the magnetization in the FC regime, $M_{FC}(T,H)$, was measured as a function of decreasing temperature in the applied field. The difference between $M_{ZFC}(T,H)$ and $M_{FC}(T,H)$ together with the observation of ferromagnetic-type $M(H)$ hysteresis loops (Fig. 5, inset) suggests that our sample possesses a disordered magnetism originating from isolated ferromagnetic clusters. The results of x-ray structural analysis performed on this sample, shown in Fig. 6, reveal the coexistence of a Rh-C_{60} phase and clusters of graphitelike layers, which may be a source of the local ferromagnetism in the nominal Rh-C_{60} compound.[14]

To conclude, we have performed *ab initio* spin polarized band structure calculations and found that Rh-C_{60} cannot be ferromagnetic in the LSDA approach. The calculated energy bands are confirmed by x-ray fluorescence measurements, which demonstrate the applicability of the LSDA. Also, the Rh-C_{60} phase is not magnetic; the ferromagnetism occurring in the nominal Rh-C_{60} samples is associated with other carbon structures that formed when the fullerene cages collapsed.[1,14]

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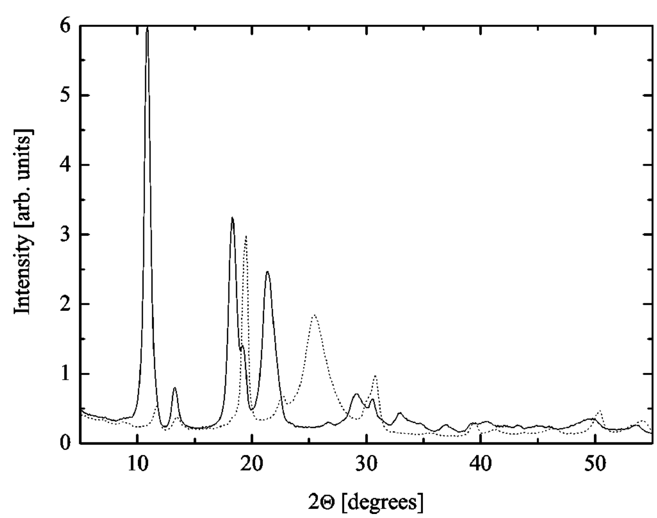

FIG. 6. X-ray diffraction patterns measured for two mutually perpendicular orientations of the sample.

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