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Electronic Structure of Crystalline K_6C_{60}

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First-principles electronic-structure calculations for crystalline K_6C_{60} are reported, based on the geometry determined by x-ray-diffraction measurements. The ground state is found to be insulating, with an indirect gap of 0.48 eV. The character of both occupied and unoccupied states near the valence-band maximum is completely carbonlike. The K atoms are almost fully ionized, and the C_{60} molecule is stabilized in an unusually high charge state with six additional electrons. Implications of the distribution of excess charge on the C_{60} molecule for orientational ordering are discussed.

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The recent discovery of superconductivity [1] in potassium-doped fullerenes, K_xC_{60}, has stimulated considerable interest in the electronic structure and likely mechanisms for superconductivity for this new class of materials. For $x \neq 0$, the only ordered pure phases that have been unambiguously indexed to date are K_3C_{60} [1] and K_6C_{60} [2]. The undoped phase, $x=0$, has been experimentally observed to exist in an fcc structure [3], in which each Bravais-lattice site is occupied by a single C_{60} "fullerene" molecule. Molecular-dynamics simulations have recently been used to investigate the rotational-vibrational properties of solid fcc C_{60} [4], and ground-state total-energy calculations have been used to predict the cohesive energy and electronic structure of this phase [5]. In this Letter, we report on our theoretical studies of the electronic structure of solid K_6C_{60}.

X-ray-diffraction experiments [2] performed on C_{60} powders that have been doped to saturation with potassium show a single highly crystalline doped phase, with no evidence for an amorphous doped phase. Indexing of the diffraction data shows the Bravais lattice to be bcc, with lattice constant $a=11.39$ Å; a C_{60} molecule occupies each bcc site, and is surrounded by a "cage" of 24 K atoms located at $(0.00,0.50,0.28)a$ and symmetry-related positions. Together with weight uptake and chemical analysis, this is consistent with stoichiometric K_6C_{60}. The structure may alternatively be described by a conventional cubic unit cell as shown in Fig. 1, with C_{60} molecules occupying the corners and center of the cube, and twofold-symmetric planar "crosses" of K atoms lying in the cube faces. The bond lengths of the C atoms are essentially the same as in the isolated C_{60} molecule; the C positions are stable, indicating the absence of orientational disorder, in contrast to the undoped phase. The point group of solid K_6C_{60} is T_h, which is the largest common subgroup of the full cubic group (O_h) and the icosahedral group (Y).

Using the experimentally determined C and K positions, we have performed first-principles electronic-structure calculations on solid K_6C_{60}, using the local-density approximation (LDA) to density-functional theory. We use a Gaussian-orbital method, which expands the Bloch wave functions in terms of a fixed set of Gaussian basis functions, and then minimizes the LDA total energy by traditional matrix methods. By forming combinations of simple Gaussian functions to represent the occupied atomic orbitals and using additional Gaussian functions for greater variational freedom, compact basis sets can be used (average of fifteen basis functions per atom in the present case) to perform accurate all-electron calculations, including relaxed self-consistent core wave functions. For the K basis, five s-type and four p-type contracted functions were formed from fourteen Gaussians with exponents ranging from 0.20000 to 128908.9; for the C basis, four s-type and three p-type functions

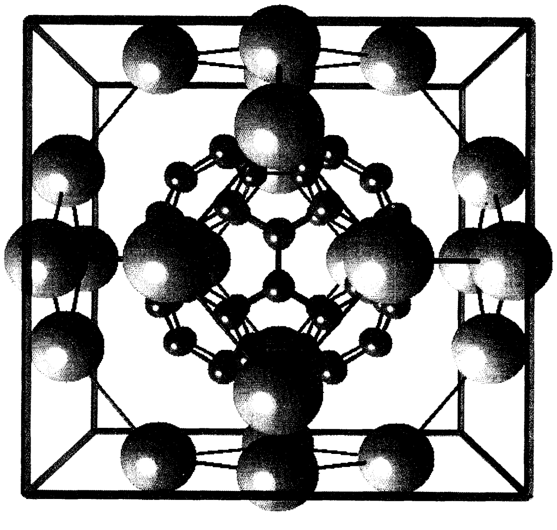

FIG. 1. Conventional unit cell for K_6C_{60}. The C_{60} molecule is surrounded by a cage of 24 K atoms, which form twofold-symmetric crosses on the faces of a cube.

were formed from thirteen Gaussian exponents in the range 0.248050 to 9470.52. The form of the potential and electronic charge density is completely general and without shape approximations. This method, as well as the basis sets, have been extensively tested, and give eigenvalue spectra and charge densities essentially indistinguishable from those given by other first-principles methods. Further details describing the numerical methods, choice of basis, and comparison with other methods may be found in Ref. [6]. The electronic charge density was iterated to self-consistency using the Γ point for Brillouin-zone integration; this is sufficient for such a large unit cell. Electron correlation effects were included through the Ceperly-Alder exchange-correlation functional.

The electronic energy-band structure for solid K_6C_{60} is shown in Fig. 2. Our calculation predicts K_6C_{60} to be insulating, with an indirect gap of 0.48 eV, a valence-band (VB) maximum at Γ, and a conduction-band (CB) minimum at N. The direct gap at Γ is 0.54 eV. Since the LDA is well known to underestimate band gaps by (20–50)%, a similar factor must be taken into account when comparing this value with experiment (inverse photoemission data [7] for empty states in undoped solid C_{60} suggest an estimated K_6C_{60} gap of approximately 1 eV). The width of the highest occupied (t_{1u}) band is approximately 0.5 eV, and the lower-lying bands show appreciable dispersion, in the range of 1.0–1.5 eV. In the far right-hand panel of Fig. 2, we show a superposition of Gaussian-broadened discrete levels of the isolated fullerene molecule [8]. The close correspondence between the density of states (DOS) of solid K_6C_{60} (middle panel) and the broadened fullerene levels is clear. Evidently there is very little contribution to these states from K basis functions. This is borne out by a Mulliken decomposition of the bands shown in the figure; the character of these states is almost entirely C-like, with a K admixture of at most 4% in this energy range. The unoccupied K 4*s* states mix with unoccupied C *p*-type basis functions to form a relatively dispersive band in the energy range 3.9–5.2 eV. *These results strongly suggest that bonding in crystalline K_6C_{60} is almost entirely ionic and, moreover, implies that each C_{60} molecule binds as many as six excess electrons.* In contrast, isolated C_{60} is known to bind one [9] or possibly two additional electrons; it is not known whether more highly charged species are stable. An analogous situation is found in the strongly ionic solid MgO: Although the free O atom can bind at most one excess electron, the crystal environment provides six nearest-neighbor Mg^{+2} ions, which stabilize the O^{-2} ion. Our present theoretical finding of a highly charged C_{60} molecule stabilized by the Madelung field—which arises primarily from the surrounding cage of 24 K^+ ions—has a similar origin. We can give further support to this prediction by calculating the LDA total energies of isolated K and C_{60} as a function of charge state. For a lattice of well-separated K atoms and C_{60} molecules, we obtain, for the charge-transfer reaction $C_{60}+6K \rightarrow C_{60}{}^{-6}+6K^{+1}$, an energy cost in the range of 53.9–62.1 eV for self-consistent and non-self-consistent $C_{60}{}^{-6}$ wave functions, respectively. The energy gain (Madelung energy) from the interaction of classical point charges at the atomic positions is 71.4 eV per formula unit (corrected for the classical self-energy of a single cluster of sixty charges). In the solid, the bands are sufficiently well separated and bandwidths sufficiently narrow to justify the above description, and the total energy gain of 9.3–17.5 eV indicates that full ionization is expected. Moreover, because of the internal structure of the C_{60} molecule, this charge transfer has several additional implications, to which we now turn.

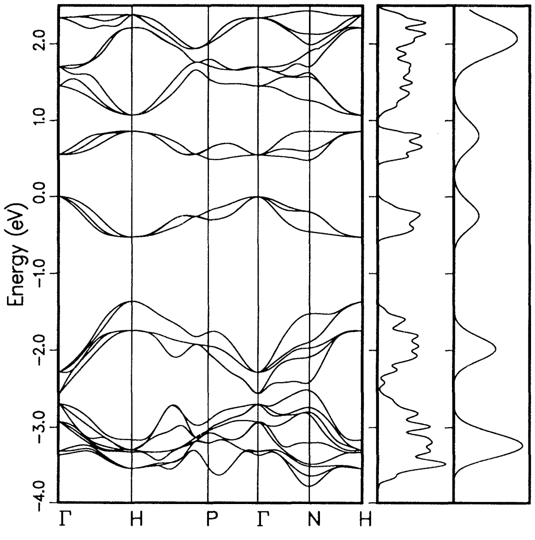

FIG. 2. Left-hand panel: Self-consistent electronic band structure of crystalline K_6C_{60}. The zero of energy is set to the valence-band maximum. Middle panel: Theoretical density of states for K_6C_{60}. Far right-hand panel: Theoretical Gaussian-broadened energy levels from the isolated C_{60} molecule.

Although a high degree of orientational disorder is observed in the undoped phase, incorporation of K is found to strongly suppress this disorder [2]. One might argue this effect as arising from the formation of C-K bonds; however, we believe that the stabilization mechanism is entirely electrostatic in origin. First, the description of bonding in K_6C_{60} as ionic can be made more quantitative by calculating the charge Q_n associated with each atom n in the unit cell. The point-group symmetry T_h implies that there are three inequivalent C atoms, C_1, C_2, and C_3. Complete ionization of all six K atoms and equipartitioning of this charge on each of the sixty C atoms would correspond to $Q_1^{eq}=Q_2^{eq}=Q_3^{eq}=6.1$, with $Q_K^{eq}=18$ the charge on the single unique K atom; the superscript label "eq" denotes the ideal case of equipartitioning. We have used the LDA eigenfunctions and a standard Mulliken-population technique to calculate the self-consistent charges Q_i^{sc}, and have listed the results in Table I. The near equality of the Q_i^{sc} and Q_i^{eq} confirm the ionic description of K_6C_{60} that was suggested by the purely C-like character of the bands. Second, there is a small deviation from ideal behavior, in that the excess charge on the C_{60} shows a slight preference (0.05 extra electron) for associating with C_1 atoms. The reason for this is again primarily electrostatic in origin, and can be understood by considering the classical interaction (Madelung) energy $E_M(\{q_i\})$ of the periodic array of point charges $\{q_i\}$; here $q_i = Z_i - Q_i$, Z_i is the atomic number, and Q_i is an assumed electronic charge, for atom i. For the ideal case of $Q_i = Q_i^{eq}$, $E_M = -8.82$ eV per unit cell. This energy gain is of course the mechanism primarily responsible for the charge transfer from K to C_{60}, along with an additional band-structure energy gained by occupying the threefold-degenerate t_{1u} states of C_{60} with the six donated electrons. Alternatively, one can calculate the values $\{q_i^m\}$ that simultaneously minimize $E_M(\{q_i\})$ and satisfy the constraints $q_i^m \leq 0$ $(i=1,2,3)$ and $0 \leq q_K^m \leq 1$. In this way one finds that the distribution of charges that minimizes the classical interaction energy and is physically reasonable corresponds to $Q_1^m = 6.50$, $Q_2^m = Q_3^m = 6.00$, $Q_K^m = 18.00$. In other words, all of the available excess charge prefers to reside on the twelve equivalent C_1 atoms. This distribution is a simple consequence of the orientation of the C_{60} molecule relative to the crystal axes; i.e., C_1 atoms are the C atoms closest to the K ions. For this distribution of point charges, $E_M = -18.15$ eV per unit cell, a substantial energy gain relative to the equipartitioning scheme. Of course, there is a quantum-mechanical energy penalty to be paid for localizing charge, and so one finds that the self-consistent C-atom charges Q_i^{sc} arrange for a compromise, and fall between the limiting values of Q_i^{eq} and Q_i^m. *We propose that this coupling of the C_{60} orientation to the nonuniform distribution of excess charge is largely responsible for the observed suppression of orientational disorder in K_6C_{60}.* However, we emphasize that full charge transfer and equipartitioning do not necessarily imply a barrier to rotation, since the excess electronic density could conceivably distribute itself uniformly on the C_{60} surface. It is the deviation of the Q_i^{sc} from equipartitioning that suggests that there exists a barrier to rotation, and, moreover, that it arises primarily from the simple ionic attraction of charged C_1 atoms and nearby K ions.

In gaseous as well as in solid C_{60}, there are two symmetry-inequivalent C-C bonds. Their bond lengths are found experimentally to be 1.46 and 1.40 Å [10], and are generally described as single and double bonds, respectively. A similar bonding configuration persists after incorporation of K. In Fig. 3(a) we show the self-consistent valence-charge density in the plane of one of the C_{60} hexagons in K_6C_{60}. The hexagon contains the three inequivalent C atoms (C_1 at the bottom, C_2 in the middle, and C_3 at the top of the figure) as well as the two alter-

TABLE I. Charge associated with each of the four inequivalent atoms in the K_6C_{60} unit cell. Q_i^{eq} denotes the (ideal) charge on each atom that would result from full ionization of K and equipartitioning of the excess charge on the sixty C atoms. Q_i^{sc} is the self-consistent charge on each atom, calculated from the LDA eigenfunctions. Q_i^m is the (ideal) charge distribution that minimizes the Madelung energy, subject to constraints discussed in the text.

Atom	Equivalent atoms per cell	Q_i^{eq}	Q_i^{sc}	Q_i^m
C_1	12	6.10	6.12	6.50
C_2	24	6.10	6.08	6.00
C_3	24	6.10	6.07	6.00
K	6	18.00	18.17	18.00

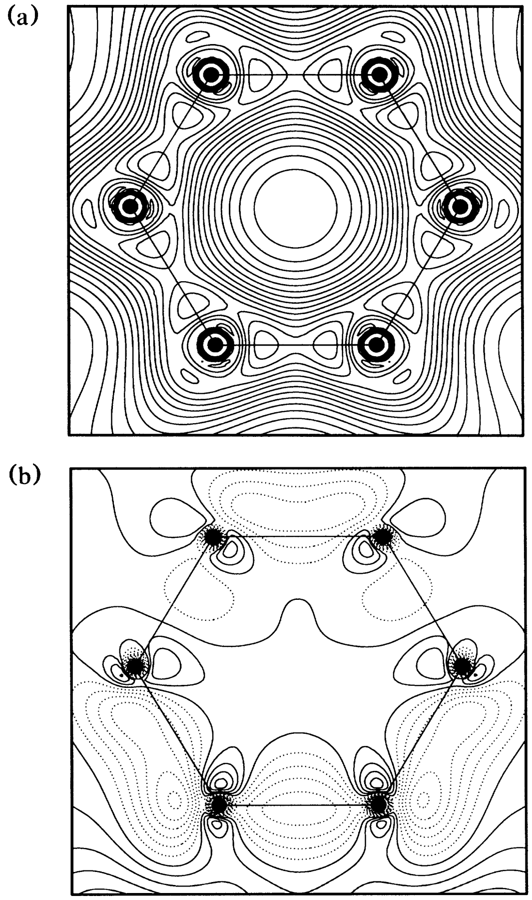

FIG. 3. (a) Self-consistent valence-charge density in the plane of a hexagon containing the three inequivalent carbon atoms C_1, C_2, and C_3. Contours are separated by 0.020 a.u., which is also the value of the lowest contour. (b) The same as in (a), minus the self-consistent valence charge of solid bcc C_{60} (without potassium). Solid contours denote positive values, and dotted contours denote negative values. Adjacent contours are separated by 0.005 a.u.

nating inequivalent bonds (long bonds are C_1-C_2 and C_3-C_3, short bonds are C_1-C_1 and C_2-C_3). It is clear from the figure that the short bonds indeed show a greater accumulation of electron density than the long bonds. A more detailed analysis, however, reveals that the presence of the K ions induces a rearrangement of the valence density. In Fig. 3(b) we show the charge-density difference $\rho^{K_6C_{60}}(\mathbf{r})-\rho^{C_{60}}(\mathbf{r})$, where $\rho^{C_{60}}(\mathbf{r})$ is the self-consistent valence-electron density of solid bcc C_{60} with no K present. The effect of the K ions is to draw charge out of the bonds that are closest to the ions (the bottom of the figure) and to redistribute it, partly on the face of the hexagon and partly by forming small dangling-bond-like structures on all six C atoms, in directions perpendicular to the C-C bonds. Apparently, the effect of K incorporation is to weaken some of the bonds in the C_{60} molecule; this effect may be observable in photofragmentation measurements or in distortion of the C_{60} molecule itself.

In summary, we find that the ground state of crystalline K_6C_{60} is insulating, with an indirect gap of 0.48 eV from Γ to N. The density of states around the VB maximum is very similar to that of the isolated C_{60} molecule, consistent with our conclusion from charge analysis that the K atoms are almost completely ionized. The excess charge of six electrons is distributed over the sixty C atoms, resulting in an unusual highly charged C_{60} molecule stabilized by the Madelung field. Deviations from uniform distribution can be traced to contributions from the Madelung energy, and may be partly responsible for the observed suppression of orientational disorder in solid K_6C_{60}.

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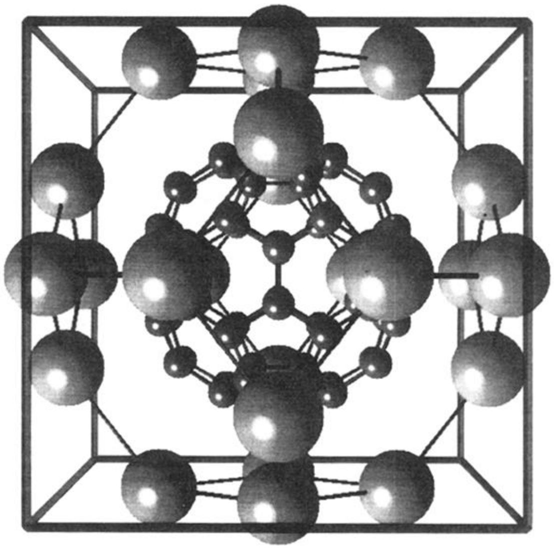

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