Sr_6C_{60} and Ba_6C_{60}: Semimetallic Fullerides

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We have studied the electronic structure of the recently discovered superconducting body-centered-cubic alkaline-earth fullerides Sr_6C_{60} and Ba_6C_{60} using the local-density approximation in the density-functional theory. Both fullerides are found to be the novel semimetallic compounds of alkaline-earth atoms and C_{60} clusters in which the hybridization between the alkaline-earth-atom states and the C_{60} π states is essential for their metallic electronic structure, and consequently for the occurrence of the superconductivity.

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The macroscopic production of the C_{60} cluster with the simultaneous discovery of solid C_{60} where C_{60} clusters crystallize like atoms [1] realized the dream to use C_{60} and other fullerenes as atomlike constructing units of new materials [2,3]. The electronic structure of solid C_{60} was actually confirmed to be hierarchical: each cluster state forms a solid-state energy band as in a usual solid where an atomic state forms an energy band [4]. The potassium atom, which is one of the largest atoms on the periodic table, was found not to see an individual C atom on the C_{60} cluster but to interact with the whole cluster to form a charge-transfer complex in the case of the endohedral $C_{60}K$ cluster [3,5] and ionic metal K_xC_{60} in the case of the interstitial-site–doped face-centered-cubic (fcc) solid C_{60} [6]. The superconductivity observed in K_3C_{60} [7] and other alkali-metal–doped fullerides A_3C_{60} [8,9] with high transition temperatures up to 33 K [9] demonstrated the rich potential abilities of such new types of materials. In these A_3C_{60} superconductors, valence electrons of the alkali-metal atoms transfer to the C_{60} cluster almost completely and the half-filled conduction band consists of the lowest unoccupied t_{1u} state of the C_{60} cluster [6,10,11].

In addition to A_3C_{60}, several alkaline-earth-doped superconductors have been reported recently [12–14]. In the case of Ca, the C_{60} clusters also form a fcc lattice as in A_3C_{60}, and Ca_5C_{60} is considered to be the superconducting phase [12]. In Ca_5C_{60}, the second-lowest unoccupied (t_{1g}) state of the C_{60} cluster hybridized with the Ca 4s states is found to form a conduction band [15]. However, the heavier alkaline-earth-metal–doped C_{60} superconductors, Sr_6C_{60} [13] and Ba_6C_{60} [14], have a body-centered-cubic (bcc) C_{60} lattice. Similar bcc fullerides with alkali-metal atoms, A_6C_{60}, have been already discovered [16] but are insulating with a finite energy gap between the occupied t_{1u} band and the empty t_{1g} band [11,17]. A further electron transfer expected in Sr_6C_{60} and Ba_6C_{60} results in the occupation of the t_{1g} band, and the complete transfer from the alkaline-earth-atom s state could cause the insulating electronic structure in apparent contradiction to their superconductivity. Hence, the electronic structure of these alkaline-earth bcc fullerides is now of high interest.

In this Letter, we report the electronic structure of Sr_6C_{60} and Ba_6C_{60} obtained using the local-density approximation in the density-functional theory (LDA) [18]. Results show that C_{60} electronic states in both fullerides are hybridized strongly with alkaline-earth-atom states and consequently the hybridized bands have significant dispersions. This results in the new semimetallic electronic structure with a finite overlap between the t_{1g} valence band and the h_g conduction band in these otherwise insulating fullerides. Hence, hybridization plays an essential role in their metallic and superconducting behaviors, and both fullerides are the first example of compound semimetals consisting of atomlike fullerenes and metal atoms where carriers are distributed both on C_{60} clusters and on alkaline-earth-metal atoms. The hybridization also strengthens the cohesive force and explains the observed short interfullerene distances in Sr_6C_{60} and Ba_6C_{60}.

In the present calculation, we have used the Ceperley-Alder exchange-correlation potential [19]. The C_{60} cluster with 1.46 Å and 1.40 Å for the pentagon bonds and for the hexagon bonds, respectively, is assumed as in our previous works on (doped) solid C_{60} [4,6,10,15,20,21]. The bcc lattice constants for Sr_6C_{60} and Ba_6C_{60} used are 11.010 Å and 11.182 Å, respectively. The highest-symmetry (T_h) orientation of the icosahedral C_{60} clusters on the cubic lattice points [4] is assumed and is expected to be valid in Sr_6C_{60} and Ba_6C_{60} as has been confirmed in A_6C_{60} [16]. The norm-conserving pseudopotentials and the Gaussian basis functions are used [22]. Pseudopotentials for Sr and Ba have been generated by solving the atomic Dirac equation, and the j-averaged potential for each l is used in the present calculation. Exponents of Gaussian orbitals for C atoms (0.299 and 2.908 for s-type and 0.362 and 2.372 for p-type orbitals in atomic units,

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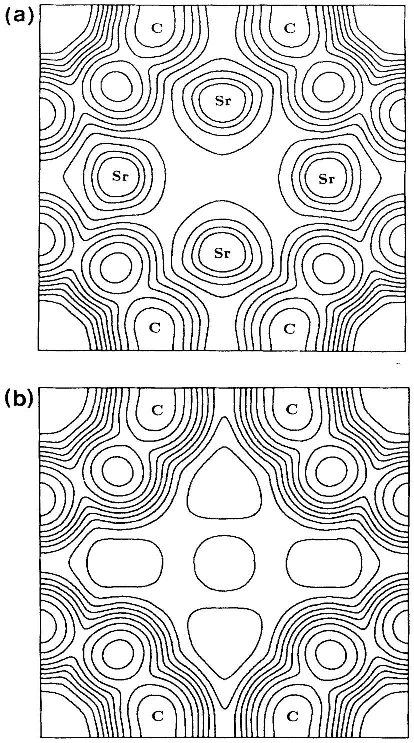

FIG. 1. Contour maps of the valence-electron densities of (a) Sr_6C_{60} and (b) pristine bcc solid C_{60} on the (100) plane. The center of the C_{60} cluster is located at each corner. "C" and "Sr" indicate the atomic positions on the plane. Each contour represents twice (half) the density of the neighboring contours. In each figure, the highest-density contours correspond to 0.95 (1/Å^3) and appear around the C atoms and the C-C bonds. Although the Sr-ion center is at the lowest-density area, it is apparent that there are considerable densities around Sr in contrast to the wider empty tetrahedral sites in the pristine solid C_{60}. The density at the intercluster site (the center of the figure as well as the middle point of each side) in Sr_6C_{60} is about 4 times higher than that in the pristine solid C_{60}.

respectively) are the same as used in the previous calculations [4], and those for Sr (Ba) are 0.060, 0.180, and 1.270 (0.060, 0.101, 1.500) for *s*-type, 0.060 and 0.195 (0.060 and 0.121) for *p*-type, and 0.100 (0.100) for *d*-type orbitals, respectively. These exponents have been chosen so that the pseudo-orbitals can be reproduced well. Moreover, in order to improve the basis set further and to describe possible intracluster and intercluster states in both Sr_6C_{60} and Ba_6C_{60}, we have placed Gaussian orbitals with the exponents of 0.020, 0.040, and 0.080 for *s*-type, 0.020 and 0.040 for *p*-type, and 0.040 for *d*-type orbitals at the center of the C_{60} cluster and those with 0.100 for *s*-, *p*-, and *d*-type orbitals at each middle point of the second-nearest-neighbor pair of the bcc C_{60} lattice ("intercluster site"), i.e., the center of the rhombus of alkali-earth atoms on the (100) plane. Although the further refinement of the basis may affect the higher unoccupied bands, the band structures in the important regions, i.e., around and below the Fermi level, have well converged as will be discussed below. In addition to Sr_6C_{60} and Ba_6C_{60}, we have also studied the electronic structure of the hypothetical pristine bcc solid C_{60} to show the role of the doped alkaline-earth atoms clearly. Its lattice constant is set equal to that of Sr_6C_{60}, and the same Gaussian orbitals as used in Sr_6C_{60}, including the Sr orbitals at the empty tetrahedral interstitial sites as well as the orbitals at intracluster and intercluster sites, are used.

In Fig. 1 the valence-electron densities of Sr_6C_{60} and the pristine bcc C_{60} are shown. There are two main differences between these two densities: one is the presence of the considerable charge around the Sr sites and the other is also the higher density at the intercluster area in Sr_6C_{60} than in the pristine bcc C_{60}. The charge around the Sr sites clearly shows the incomplete charge transfer from the Sr atom to the C_{60} cluster, implying the presence of the hybridization between the Sr states and the C_{60} π states. From the LDA calculation, the 4*d* state of the Sr^{2+} ion is found to be lower in energy than the 5*s* state. Hence, the Sr 4*d* state can partially accept the electrons originally donated from the Sr 5*s* state to the C_{60} cluster. Therefore, the Sr 4*d* state is hybridized with C_{60} π states more than the 5*s* state.

The presence and the importance of the hybridization between the Sr states and the C_{60} π states can be seen more clearly from the band structures of Sr_6C_{60} and the pristine bcc solid C_{60} shown in Figs. 2(a) and 2(b). Most bands in Sr_6C_{60} show more dispersions than the corresponding bands in the pristine bcc C_{60}, giving several prominent differences in their electronic structure. For example, the energy difference between the h_u-band top and the t_{1u}-band bottom in solid C_{60} (more than 0.7 eV) becomes almost zero in Sr_6C_{60}. More drastically, the t_{1g} (valence) band and the higher h_g (conduction) band overlap each other in Sr_6C_{60} and the system becomes semimetallic with holes around the N point and electrons near the H point. On the other hand, the t_{1g} band in bcc C_{60} where the intercluster distance is the same as that of Sr_6C_{60} is well separated both from the lower t_{1u} band and from the upper h_g band. This contrast clearly demonstrates that it is the hybridization between the Sr states and the C_{60} π states that gives a metallic electronic structure in Sr_6C_{60}.

The valence-electron density of Ba_6C_{60} is found to be very similar to that of Sr_6C_{60}, although the density at the intercluster site is slightly lower than that of Sr_6C_{60} because of the longer intercluster distance. Also the same interchange of *s* and *d* states is found in the Ba^{2+} ion in the LDA. Although the lattice constant in Ba_6C_{60} is longer than that assumed in the pristine bcc C_{60}, the band dispersions are still much more prominent than those in the pristine solid C_{60} [Fig. 2(c)]. The t_{1g} valence-band top at the N point is again found to be

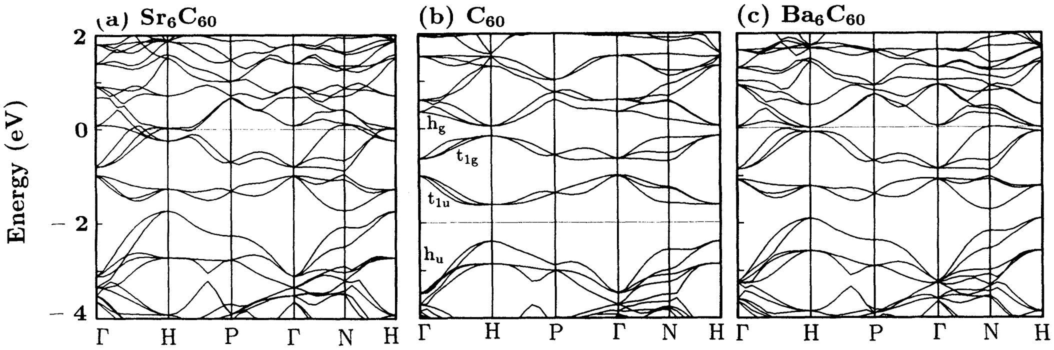

FIG. 2. Band structures of (a) Sr_6C_{60}, (b) hypothetical pristine bcc solid C_{60}, and (c) Ba_6C_{60}. Energy is measured from the Fermi level denoted by the horizontal line. In (b), energy bands are shifted downward by 2 eV for the sake of easier comparison to (a) and (c), and each bunched band is labeled according to the corresponding state of the C_{60} cluster. In each figure, energy eigenvalues on more than forty **k** points are connected sequentially by segments. Especially in (a), **k** points are taken densely in the vicinity of band (anti)crossing points near E_F.

higher than the conduction-band bottom at the H point, and the electronic structure is also semimetallic. Since the overlap between the valence band and the conduction band in Ba_6C_{60} is small (about 0.01 eV in width), intracluster orbitals as well as the intercluster orbitals are found to be important. Addition of only the intercluster orbitals to the basis set gives a considerable downward shift of the conduction bands, but the system remains insulating. Inclusion of the intracluster orbitals gives a further shift and the system finally becomes semimetallic. Actually, the nondegenerate band, which is located only 1 eV above the Fermi level (E_F) at the Γ point and has a coupling with nearby lower conduction bands, is found to have the amplitude both well inside the hollow C_{60} cage and outside the cage around the intercluster site. The state has shown the most prominent downward shift by the inclusion of the intracluster orbitals. Since its amplitude in the intercluster region is higher, it is considered to be an intercluster state coupled with the intracluster state [23]. The corresponding nondegenerate band appears at even lower energy in the case of Sr_6C_{60}. Of note is a similar role of the interlayer state in graphite intercalation compounds [24].

The interfullerene distances in Sr_6C_{60} and Ba_6C_{60} are the shortest and the second shortest among all the known fullerides and are considerably shorter than that in the pristine fcc solid C_{60}. The hybridization is expected to give further attractive interaction in addition to the electrostatic interaction and should be responsible for their short interfullerene distances.

In K_3C_{60} and Rb_3C_{60}, the universal linear relationship between the calculated Fermi-level density of states [$N(E_F)$] and the observed superconducting transition temperature (T_c) under the pressure has been found [10]. Although the full explanation for this unusual relationship may await a more elaborate theory than the conventional treatment with the Eliashberg equation, qualitatively the same electronic structure around E_F in both K_3C_{60} and Rb_3C_{60}, i.e., a half-filled t_{1u} conduction band without hybridizaiton with alkali-metal states, is considered to be essential for the relationship to hold. However, in the case of Sr_6C_{60} and Ba_6C_{60}, crossing and anticrossing of energy bands near E_F are very complicated in Sr_6C_{60} but Ba_6C_{60} is a rather simple semimetal without such (anti)crossings. The degree of hybridization is also expected to be different in these two fullerides since the Sr $4d$ state is lower in energy than the Ba $5d$ state. Therefore, the T_c may show a more complicated relationship with the applied pressure as well as with $N(E_F)$. Actually, the reported T_c for Sr_6C_{60} (4 K) is lower than that of Ba_6C_{60} (7 K) although the calculated $N(E_F)$, in the same way as in A_3C_{60} [10], is found to be higher in Sr_6C_{60} (11.6 states/eV) than in Ba_6C_{60} (4.3 states/eV).

In Fig. 3, the distributions of the states near E_F [21], $\rho_{E_F}(\mathbf{r}) = -(1/\pi)\mathrm{Im}\sum_{n,\mathbf{k}}\int_{E_F-\Delta}^{E_F+\Delta} dE|\psi_{n\mathbf{k}}(\mathbf{r})|^2/(E-\epsilon_{n\mathbf{k}}+i\delta)$, in Sr_6C_{60} and Ba_6C_{60} are shown. Here Δ=0.1 eV, which is the typical phonon energy in fullerides, and $\delta=\Delta/3$ are used, and 64 **k** points on the uniform mesh in the first (whole) Brillouin zone are taken for the **k** summation. Although their overall distributions are similar to each other, Ba_6C_{60} has a more uniformly spread distribution in the intercluster region than Sr_6C_{60}. This may be related to the higher T_c in Ba_6C_{60}. Such considerable distributions of ρ_{E_F} around the alkaline-earth sites given by the hybridization discussed above may result in the coupling of the carriers not only with intracluster phonons but also with the optical phonons between the alkaline-earth ions and the C_{60} cluster. Even in A_3C_{60} superconductors, the residual electron correlation beyond the LDA may be unimportant because the intersite Coulomb repulsion energy of the C_{60} lattice is of the same order as the intrasite repulsion energy and the effective intrasite repulsion should be much smaller [25]. A more delocalized feature of the carriers in Sr_6C_{60} and

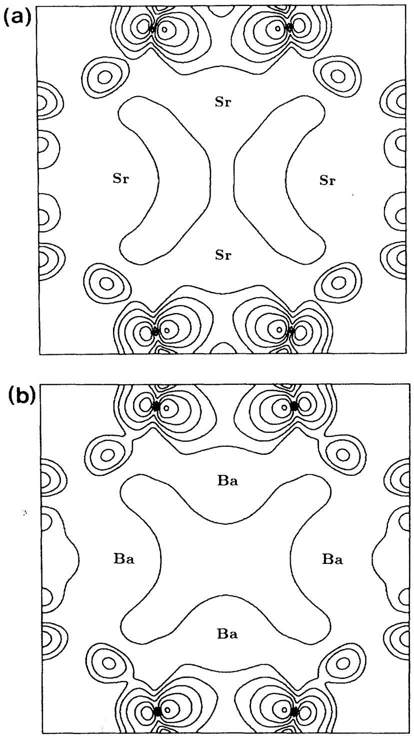

FIG. 3. Contour maps of the distributions of the states near the Fermi level, $\rho_{E_F}(\mathbf{r})$, in (a) Sr_6C_{60} and (b) Ba_6C_{60} on the same (100) plane as in Fig. 1. Each contour again represents twice (half) the value of the neighboring contours. Although the high ρ_{E_F} regions are near the C atoms or the C-C bonds, the much broader area around the alkaline-earth-atom sites ("Sr" and "Ba") and the intercluster sites also has considerable ρ_{E_F} values.

Ba_6C_{60} due to the hybridization may make the residual correlation even less important [15].

In A_3C_{60} and Ca_5C_{60}, the conduction bands which are responsible for the superconductivity mainly consist of the t_{1u} band and the t_{1g} band, respectively. It is now found that the even higher energy band as well as the t_{1g} band are responsible for the superconductivity in Sr_6C_{60} and Ba_6C_{60}. Such diversities of the electronic structure of the C_{60} superconductors indicate the high possibility of the future discoveries of new fulleride superconductors. It also implies the presence of the hole-doped (h_u-band) superconducting fullerides [20,21].

The present work has clarified that bcc Sr_6C_{60} and Ba_6C_{60} are the novel semimetallic fullerides where the hybridization between the alkaline-earth-metal d state and the C_{60} π states plays an essential role in their metallic properties and, consequently, in their superconducting properties. Their unusually short interfullerene distances should be also due to the hybridization. Carriers are distributed not only on the C_{60} clusters but also around the alkaline-earth atoms because of the hybridization. These new compound semimetals of atomlike C_{60} fullerenes and ordinary atoms, Sr and Ba, show the great potential abilities of C_{60} and other fullerenes for producing a variety of new materials.

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