

Electronic structure of superconducting Ba_6C_{60}

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We report the results of first-principles electronic-structure calculations for superconducting Ba_6C_{60} . Unlike the A_3C_{60} superconductors, this new compound shows strong Ba-C hybridization in the valence and conduction regions, mixed covalent-ionic bonding character, partial charge transfer, and insulating band structure, with a very small or zero gap within the local-density approximation.

Most of the known superconducting C_{60} fullerenes exhibit the stoichiometry A_3C_{60} or A_2BC_{60} ($A, B = \text{alkali metal}$), form fcc lattices, and are known (or believed) to exhibit essentially complete charge transfer from alkali metal to C_{60} . Broadly speaking, all of these compounds exhibit similar electronic structure, in which the half-filled conduction band (CB) is formed primarily from C orbitals of p_z symmetry. Superconductivity has also been observed in 5:1 solid solutions of Ca in C_{60} .¹ In contrast to the A_3C_{60} compounds, theoretical studies of hypothetical (stoichiometric) Ca_nC_{60} indicate substantial hybridization of C and Ca orbitals in the CB regime,² but the relevance of these results to the real (nonstoichiometric) material is difficult to gauge.

Recently, synthesis of a crystalline, stoichiometric, Ba-intercalated fullerene superconductor, Ba_6C_{60} , has been reported, with $T_c = 7$ K.³ Naive electron counting, assuming divalent Ba and rigid K_6C_{60} -like band structure, would suggest this new compound to be a 0.2-eV gap insulator consisting of very highly charged C_{60}^{12-} molecules. Here, we present first-principles electronic structure results for Ba_6C_{60} that definitively predict *strong Ba-C hybridization near the Fermi level, incomplete charge transfer, and, surprisingly, an insulating band structure with a very small or zero gap* (within the local-density approximation).

Like the alkali metal A_6C_{60} compounds, Ba_6C_{60} forms a bcc Bravais lattice, with twofold planar crosses of Ba ions decorating the faces of the conventional unit cell. The aspect ratio of the crosses is identical to that in K_6C_{60} ,⁴ and the lattice constant of 11.171 Å is 2% smaller than for K_6C_{60} . As with K_6C_{60} , Rietveld refinement of x-ray powder patterns for Ba_6C_{60} indicate rotationally ordered C_{60} molecules.

We have studied the electronic structure and energetics of crystalline Ba_6C_{60} using the local-density approximation (LDA) to density-functional theory. The computational methods were identical to those used in previous studies of K_6C_{60} and K_3C_{60} ,^{5,6} with a few modifications. The charge density and potential are completely general and without shape approximation, and were iterated to self-consistency using the Γ point. All 696 electrons were explicitly included in the calculation and were treated on equal footing, without the need for pseudopotentials. The Ceperly-Alder exchange-correlation functional was used. Lowest-order relativistic effects were accounted for

perturbatively, as described below. In our local-orbital method,⁷ basis functions are expanded on a set of 14 Gaussian exponents contracted into four s -type and three p -type functions for C, and 21 exponents contracted into seven s -type, five p -type, and four d -type functions for Ba. The smallest Gaussian exponents were 0.24 for C and 0.15 for Ba; these basis sets give eigenvalue spectra converged to a tolerance of ~ 0.02 eV for core, valence bands (VB), and low-lying CB. We have exhaustively tested the quality of our basis set: for a variety of different sets of Gaussian exponents, the longest-ranged of which was 0.12 for C and 0.10 for Ba, the VB and CB varied by at most 0.02 eV, and by less than this near the Fermi level.

The resulting band structure and density of states (DOS) are shown in Fig. 1, plotted along the same high-symmetry lines as for our previous study of K_6C_{60} (cf. Fig. 2 of Ref. 5). Although the correspondence between the two is clear, substantial differences arise from strong hybridization of C $2p$ and Ba $5d$ wave functions in the

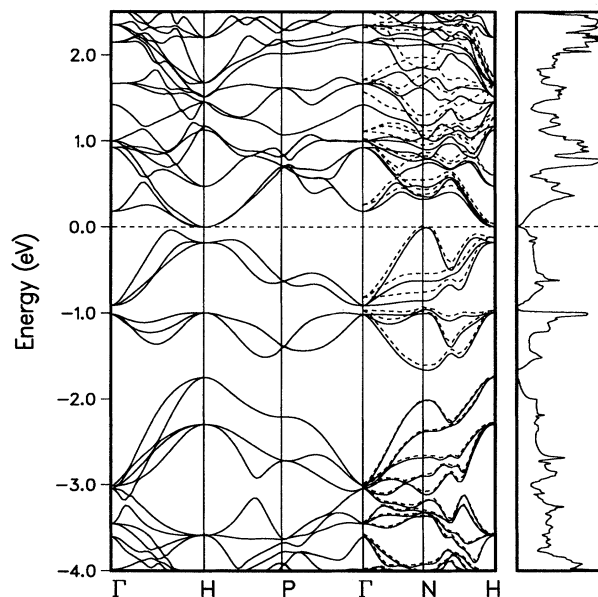


FIG. 1. Self-consistent electronic band structure for Ba_6C_{60} . The Fermi level is the energy zero. The dotted curves (for clarity shown only along the directions Γ - N - H) are the relativistically corrected bands described in the text.

valence and conduction regions. Both the t_{1u} band (filled in K_6C_{60}) and the t_{1g} band (empty in K_6C_{60}) are filled in Ba_6C_{60} . Surprisingly, the electronic structure is again insulating, since there are no partially filled bands and the Fermi-level DOS is indeed zero. The magnitude of the LDA gap is zero, to within the limits of accuracy of our calculation. This is strikingly at odds with the experimental finding of superconductivity (and therefore a metallic normal state) in Ba_6C_{60} . We note further that the LDA is known generally to give semiconductor band gaps *smaller* than experiment; indeed, previous work on self-interaction corrections⁸ and quasiparticle corrections⁹ to the LDA has shown that such improvements to the Hamiltonian have always resulted in *larger* semiconductor band gaps. We have also considered the possibility of separate B and C self-energy shifts, and find that such shifts further favor an insulating filled-band electronic structure.¹⁰ We are unaware of any other instance for which the LDA band structure of a known metal is insulating.

An enlarged view of the DOS near the Fermi level is shown in Fig. 2, along with atom- and symmetry-projected partial DOS. States within 1 eV of E_F have approximately 75% C $2p$ character and 25% Ba $5d$ character, with a very small admixture of C s character in the low-lying CB. The contribution from Ba s and p basis functions to bands in this energy region is negligible.

We have also simulated relativistic corrections to the bands, by appending to the Hamiltonian a nonlocal operator diagonal in the atomic-orbital Bloch basis. These atomic shifts were taken over directly from differences between relativistic and nonrelativistic atomic eigenvalues

for Ba (the shifts for C are negligible). For Ba core states, the shifts are large and resulted in purely rigid shifts of the corresponding bands. For the $5d$ states, which contribute to the VB and lower CB, we used the degeneracy-weighted average of the atomic $5d_{3/2}$ and $5d_{5/2}$ shifts,¹⁰ giving a single shift of +0.44 eV. Since the upper VB and lower CB states have comparable Ba $5d$ admixture, diagonalization of this new Hamiltonian resulted in nearly rigid band shifts in this energy region. Indeed, within 1 eV of E_F , the changes were at most 0.1 eV, and the zero-gap insulating character of the band structure was unchanged (the relativistically corrected bands are shown in two of the panels of Fig. 1, and the partial DOS in Fig. 2 includes this correction). Relativistic shifts for the Ba $6s$ atomic orbitals are quite small (-0.16 eV), and since these states contribute only to bands several eV above E_F , these shifts have a negligible effect on the occupied eigenvalue spectrum and charge density.

We have not systematically attempted to include spin-orbit (SO) effects here. The atomic SO splitting of the Ba $5d_{3/2}$ and $5d_{5/2}$ states is 0.11 eV.¹⁰ To a first approximation, one expects the resultant band splitting also to be proportional to the amount of $5d$ character, and so we estimate the SO splitting in both the upper VB and lower CB to be of order 0.05 eV or less. Shifts of ± 0.05 eV to E_F would result in a Fermi-level DOS, $N(E_F)$, of order 1–2 states/eV-cell-spin. This is 3–6 times lower than what we have previously calculated for K_3C_{60} .⁶ If the pairing mechanism is the same in both materials and the coupling strengths are comparable, then such values for $N(E_F)$ are far too low to account for the measured T_c of 7 K. This suggests a number of possible scenarios: (1) If SO splitting is indeed responsible for making the bands metallic, then either the Ba_6C_{60} superconducting mechanism itself or the pairing strength (or both) is quite different from the standard fullerene superconductors. (2) If the one-electron (mean-field) approximation of the LDA does not apply to Ba_6C_{60} , then it is conceivable that a full accounting of electron-electron correlation leads to a metallic normal state. We view this as unlikely, since the standard result of treating electron correlation more accurately is to increase the band gap (see Refs. 8 and 9), or even to give an insulating ground state when the single-particle ground state is metallic. (3) In principle, it is possible that a self-consistent *spin-polarized* calculation would lead to a metallic ground state. Such magnetic instabilities generally have as a prerequisite a large value for $N(E_F)$ in the paramagnetic (spin-unpolarized) state. Since we find a paramagnetic solution with $N(E_F) \approx 0$, we view this scenario as unlikely. (4) If stoichiometric Ba_6C_{60} is indeed an insulator at $T = 0$, then the possibility arises that superconductivity occurs as a result of off-stoichiometric doping effects. Indirect evidence for this scenario is found in recent measurements of resistivity in thin-film Ba_xC_{60} , $0.5 < x < 5.8$, for which the highest positive temperature coefficient of resistivity occurred at $x = 5.0$, and for which further doping resulted in an *increase* in the resistivity.¹¹ We also note that a similar off-stoichiometric argument was recently advanced on theoretical grounds for superconducting K_3C_{60} (Ref. 12) (although the single-particle spectrum for this material

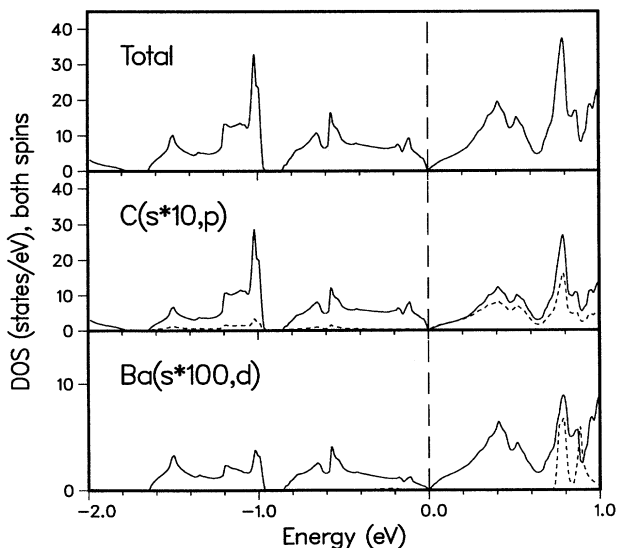


FIG. 2. Total DOS near the Fermi level (top panel); atom- and symmetry-projected partial DOS for carbon (middle panel) and barium (bottom panel). For the partial DOS, s components are shown as dotted curves and are magnified by a factor of 10 (100) for C (Ba); there are only negligible contributions from Ba p states in this energy region. Note also the factor of 3 scale difference between the C and Ba graphs.

TABLE I. Integrated muffin-tin (MT) charges, $Q(R)$, and charge differences, $\Delta Q(R)$, for the four inequivalent atoms in the Ba_6C_{60} cell. C atoms are numbered by increasing distance from the nearest Ba atom. Charge differences are defined with respect to overlapping neutral atom electronic configurations.

Atom	MT radius, R (Å)	$Q(R)$	$\Delta Q(R)$
C_1	0.70	4.05	+0.10
C_2	0.70	4.04	+0.10
C_2	0.70	4.06	+0.11
Ba	2.37	59.24	-0.65

is unambiguously metallic). (5) If we take seriously the *zero-gap* insulating state, then the possibility also exists that BCS-like pairing occurs not between states on the Fermi surface, but rather between states whose energies lie in some small interval $E_F \pm \Delta E$. Clearly, this picture would be favored by the existence of an extremely small, or zero, gap. Interestingly, this scenario also requires some minimum "threshold" coupling strength, below which pairing does not occur (in contrast to pairing of states on the Fermi surface, for which *any* nonzero coupling suffices).

We consider now the question of charge transfer from Ba to C_{60} . In a previous study of K_6C_{60} , we used Mulliken population analysis to compute the charge associated with each atom in the cell, and found essentially complete charge transfer from K to C_{60} .⁵ For Ba_6C_{60} , Mulliken analysis associates 55.57 electrons with each Ba, suggesting a loss of only 0.43 electrons per atom. We caution, however, that Mulliken charges may not be meaningful when there is large wave-function overlap, and so we turn to direct methods. Integration of the total charge density within touching muffin-tin (MT) spheres, of radius R , gives the charges, $Q(R)$, listed in the third column of Table I. Of course, these spheres do not represent the entire cell volume, nor are they the only plausible choice of integration volumes. Thus, the total integrated charges are less meaningful than the difference charges (relative to overlapping neutral atoms), $\Delta Q(R)$, shown in the fourth column. These values suggest that ~ 0.7 electrons are transferred from each Ba atom, in rough agreement with the Mulliken result.

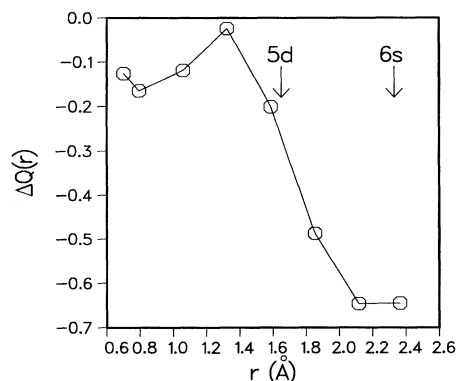


FIG. 3. Charge-difference function, $\Delta Q(r)$, in a sphere centered on a Ba atom. The arrows denote the expectation values of r for atomic Ba $5d$ and $6s$ states.

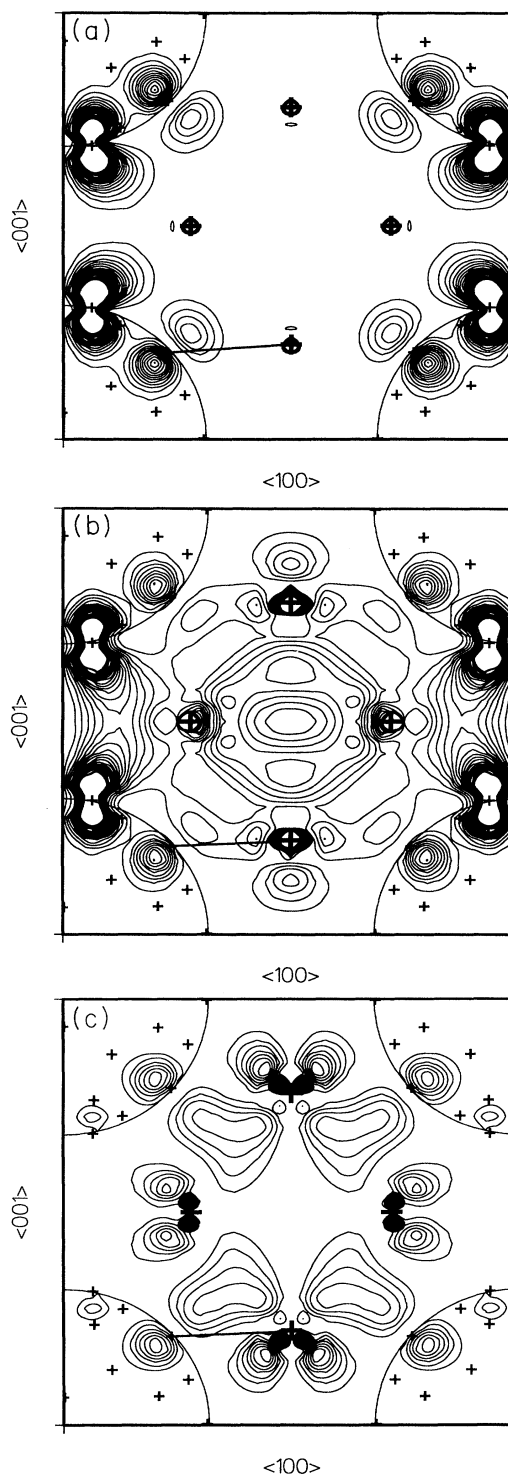


FIG. 4. Valence-electron densities for (a) the t_{1u} band of K_6C_{60} , (b) the t_{1u} band of Ba_6C_{60} , and (c) the t_{1g} band of Ba_6C_{60} . Each plotting plane contains four C_{60} molecules (at the corners of the plot area) and four K^+ ions (marked by large crosses). The projected C positions are marked by small crosses, and the C_{60} cage radius is shown by quarter circles. A heavy solid line marks the nearest-neighbor C-Ba internuclear axis. Adjacent contours are separated by 0.0005 a.u.

A more detailed description of the spatial distribution of Ba charge is given by the function $\Delta Q(r)$ for values of r less than the touching MT radii. For Ba, this function is shown in Fig. 3, for $R_C \leq r \leq R_{Ba}$. It is clear that most of the 0.6 electron is lost from the region $1.6 \text{ \AA} \leq r \leq 2.2 \text{ \AA}$. Moreover, we find that the Ba $5d$ and $6s$ atomic expectation values of r are 1.65 \AA and 2.33 \AA , respectively.¹⁰ These observations are consistent with a picture in which charge is lost from the Ba $6s$ state, and donated partially to Ba $5d$ states and partially to C p states. This description is also consistent with our prediction of the mixed $5d/2p$ character of the highest-lying occupied bands.

Some insight into the differences between the K- and Ba-intercalated fulleride crystals can be gained by examining the breakdown of an ionic model that was found to successfully describe K_6C_{60} . Since the details of this model have been described elsewhere,¹³ we only present a brief qualitative discussion here. For a system of nonoverlapping entities, the charge transfer can be predicted by properly accounting for the Madelung contributions and the density-functional-based electron affinities (for the C_{60} molecule) and the ionization energies (for the metallic dopants). When such a model is applied to K_6C_{60} , full charge transfer is expected at the experimental lattice constant of 11.39 \AA . Furthermore, since at this lattice constant the smallest C-K distance (3.2 \AA) is large compared to the sum of the ionic radii (2.1 \AA), corrections due to banding are expected to be small. Results from this ionic model were in excellent agreement with the charge transfer calculated self-consistently for K_6C_{60} .⁵ In contrast, when the same ionic model is applied to Ba_6C_{60} , we find that the Ba atoms are expected to lose 1.2 electrons, roughly twice as much as calculated self-consistently in the crystal. This discrepancy can be understood by noting that a Ba atom in such a charge state would still have excess valence charge available for bonding with the C atoms. Further, for this charge state, the Ba $5d$ states exhibit a maximum at a radius of approximately $1.5\text{--}1.6 \text{ \AA}$ and exhibit appreciable tails as far out as $2.6\text{--}2.8 \text{ \AA}$. Since the nearest-neighbor C-Ba distance is only 3.1 \AA , the partially filled Ba $5d$ orbitals overlap strongly with the neighboring C $2p$ states, which allows for the formation of a covalent bond. This covalent bonding can

be further strengthened by allowing stronger overlap between the Ba and C states. At self-consistency, this is accomplished by reducing the ionicity of the Ba atoms over what is expected from the ionic model leading to longer ranged Ba d states. While the covalent bonds are strengthened, the Madelung stabilization decreases and the actual degree of charge transfer is arrived at by compromising between a purely covalent and purely ionic system.

To further characterize the degree of covalent vs ionic bonding character, we compare the valence-electron density in Ba_6C_{60} to that of K_6C_{60} . In Fig. 4(a) we show the electron density from the filled t_{1u} band of K_6C_{60} . The radially directed C-centered density lobes are plainly evident, and very little contribution from K states appears. (We also note a slight but definite polarization of charge toward the K^+ ions.) In Fig. 4(b) we show the density from the corresponding (t_{1u}) band of Ba_6C_{60} , and in Fig. 4(c) the t_{1g} density. A substantial amount of Ba-derived density is evident in each. Nearest-neighbor C-Ba pairs clearly show a substantial off-axis "bent" covalent bond, accompanied by strongly polarized back-bonding lobes. Weaker bonds are formed between next-nearest-neighbor C-Ba pairs. Given the substantial covalent character accompanied by (incomplete) charge transfer, we conclude that bonding in Ba_6C_{60} is best described as mixed covalent-ionic.

In summary, we have performed first-principles LDA calculations on superconducting Ba_6C_{60} and find a number of unusual features. In contrast to the structurally identical compound K_6C_{60} , in which we predicted full charge transfer and ionic bonding, for Ba_6C_{60} we find only partial charge transfer and mixed covalent-ionic bonding. In contrast to the A_3C_{60} superconductors, we calculate an insulating band structure, which appears to be at odds with the experimental finding of superconductivity, suggesting the possibility of off-stoichiometric doping effects in the superconducting material.

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¹A. R. Kortan, N. Kopylov, S. Glarum, E. M. Gyorgy, A. P. Ramirez, R. M. Fleming, F. A. Thiel, and R. A. Haddon, *Nature (London)* **355**, 529 (1992).

²S. Saito and A. Oshiyama, *Solid State Commun.* **83**, 107 (1992).

³A. R. Kortan *et al.*, *Nature (London)* **360**, 566 (1992).

⁴O. Zhou, J. E. Fischer, N. Coustel, S. Kycia, Q. Zhu, A. R. McGhie, W. J. Romanow, J. P. McCauley, A. B. Smith, and D. E. Cox, *Nature (London)* **351**, 462 (1991).

⁵S. C. Erwin and M. R. Pederson, *Phys. Rev. Lett.* **67**, 1610 (1991).

⁶S. C. Erwin and W. E. Pickett, *Science* **254**, 892 (1991).

⁷S. C. Erwin, M. R. Pederson, and W. E. Pickett, *Phys. Rev.*

B **41**, 10437 (1990).

⁸R. A. Heaton, J. G. Harrison, and C. C. Lin, *Phys. Rev. B* **28**, 5992 (1983); S. C. Erwin and C. C. Lin, *J. Phys. C* **21**, 4285 (1988).

⁹W. E. Pickett and C. S. Wang, *Phys. Rev. B* **30**, 4719 (1984).

¹⁰S. C. Erwin and M. R. Pederson (unpublished).

¹¹R. C. Haddon *et al.*, *Chem. Phys. Lett.* **203**, 433 (1993).

¹²R. W. Lof *et al.*, *Phys. Rev. Lett.* **68**, 3924 (1992).

¹³M. R. Pederson, S. C. Erwin, K. A. Jackson, and L. L. Boyer, in *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, edited by P. Jena *et al.* (Kluwer Academic, Dordrecht, The Netherlands, 1992), Vol. II, p. 1323.