

then the ionic sizes fall between Na^+ and K^+ . Even if the charge transfer is not complete (as suggested by the photoemission results on Sr) (7), it is clear that Ca and Sr will be good fits for the tetrahedral sites, and we speculate that Ca_2C_{60} and Sr_2C_{60} are structurally similar to Na_2C_{60} (21). In the case of Ca, the weak resistivity maximum probably reflects disorder in the film or a tendency toward disproportionation as a result of the poor size match of the third Ca ion to the interstitial octahedral site. We note that Ca^{2+} is similar in size to Na^+ , there is evidence of disorder in the Raman spectrum of Na_3C_{60} films (22), and bulk Na_3C_{60} has been shown to undergo a low-temperature disproportionation (21).

Beyond $x = 3$ it is therefore apparent that the conductivity is due to carriers in the t_{1g} level, perhaps hybridized with Ca and Sr s states as suggested in the photoemission studies (7). Thus, the superconductivity observed in bulk Ca_5C_{60} (6) apparently originates in bands derived from the t_{1g} level of the C_{60} molecule.

Note added in proof: See the recent photoemission studies (23).

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Charge Donation by Calcium into the t_{1g} Band of C_{60}

G. K. Wertheim, D. N. E. Buchanan, J. E. Rowe

Photoemission spectra of compounds prepared by the reaction of C_{60} films with calcium show two distinct metallic phases, whereas alkali-doped C_{60} films have only one. In the first phase the bulk t_{1u} band, derived from the lowest unoccupied molecular orbital of C_{60} , is partially occupied. This is followed by an insulating phase that has the composition Ca_3C_{60} in which the t_{1u} band is filled and has properties analogous to those of K_6C_{60} . Continued exposure to calcium produces a second metallic phase in which electrons are donated into the t_{1g} band. The superconductivity of Ca_5C_{60} is associated with the t_{1g} band.

According to a recent report (1), Ca_5C_{60} is a superconductor like the A_3C_{60} compounds formed by the alkali metals $\text{A} = \text{K}$, Rb , and Cs . In view of the divalent character of Ca, it seems unlikely that the charge donated to the C_{60} is the same in both materials. However, it is not clear from transport measurements alone (1) whether the mechanism for conductivity and for superconductivity is the same in Ca-doped fullerides as in alkali compounds.

Photoemission spectroscopy can answer this question by providing a direct view of the occupied electronic structure. Care must be exercised, however, because this technique probes a surface layer comparable in thickness to the layer spacing of C_{60} . Nevertheless, we can identify the band responsible for the superconductivity, that is, whether it is the t_{1u} band as in the alkali metal compounds or the second empty band derived from the t_{1g} orbitals.

The prospect that the t_{1g} band is occupied at first seemed remote because Chen *et*

al. (2) report a hybridized band involving only the t_{1u} states of C_{60} and the outer n s levels of Mg, Sr, and Ba ($n = 3, 5$, and 6) in other alkaline earth compounds of C_{60} . We report here that Ca_xC_{60} does not conform to this pattern, exhibiting the sequential filling of the t_{1u} and t_{1g} bands with increasing Ca content. We find that the superconductivity is associated with the second unoccupied band of C_{60} , which has t_{1g} symmetry.

Calcium differs from the heavier alkali and alkaline earth ions for which metallic C_{60} intercalation compounds have been reported in having a significantly smaller ionic radius, 0.99 Å, as compared to 1.33, 1.47, 1.67, 1.12, and 1.34 Å for K, Rb, Cs, Sr, and Ba, respectively. Other elements with small ionic radii, for example, Na (0.97 Å) and Mg (0.66 Å), are reported to form insulating compounds with C_{60} (2, 3). The tetrahedral sites in C_{60} have a radius of 1.12 Å and can readily accommodate the small Ca^{2+} ion. The octahedral sites are much larger and can accommodate an atom with a radius of 2.06 Å. A small ion like Ca^{2+} will be displaced from the center of the site along one of the eight (111) directions, toward one of the neighboring tetrahedral sites (1). It will then contact only three of the six C_{60} molecules that define the octahedral site. Multiple occupancy by up to four ions has been suggested (1). However, the incompletely screened Coulomb repulsion between these ions probably makes the site energetically less favorable for additional ions.

The Ca-doped fulleride samples used in this study were prepared as thin films on a W(100) substrate that had been cleaned by sputtering and annealing. Two procedures were used: (i) films of C_{60} 100 to 200 Å thick, deposited from a Knudsen cell onto the room-temperature substrate, were subsequently exposed at room temperature to Ca vapor from another furnace with a BN crucible and (ii) a thick Ca layer was deposited at 78 K followed immediately by a layer of C_{60} 100 Å thick. In the first method data were taken both immediately after exposure and after a brief anneal to 425 K. In the second method measurements were made as this Ca- C_{60} sandwich was annealed at temperatures up to 400 K. We took the photoemission data with 21.2-eV He I resonance radiation, using a 50-mm hemispherical electron-energy analyzer (Vacuum Science Workshop). A nominal instrumental resolution of 100 meV was used throughout. This is sufficiently small compared to the width of the spectral features of both C_{60} and Ca_xC_{60} that the data show no discernible instrumental broadening, except at the Fermi cutoff.

Figure 1 demonstrates the importance of annealing on C_{60} films after exposure to Ca

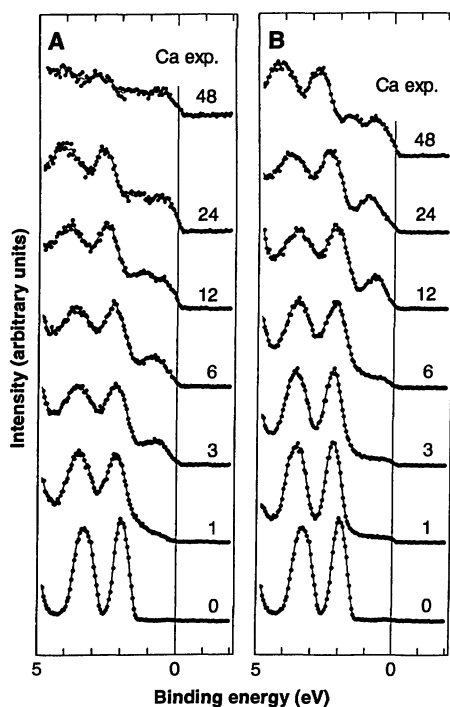


Fig. 1. Valence-band spectra of C_{60} film exposed to Ca vapor at room temperature (**A**) and annealed at 425 K (**B**). The total exposures are proportional to the numbers shown.

vapor. The data in Fig. 1A were obtained after room-temperature exposure to Ca and those in Fig. 1B after a subsequent 425 K anneal. The sample was then exposed to additional Ca at room temperature, and the process repeated. Comparison of the pre- and post-anneal data shows significant changes. The scan taken after the first exposure to Ca vapor shows substantial broadening of the deeper lying levels as well as a new broad response between the Fermi level and the h_u band. Upon annealing, the spectrum narrows and most of the new response converts into a step at the Fermi level. The appearance of a Fermi cutoff after the anneal indicates that the unsplit t_{1u} band of the bulk has become partially occupied. With continued exposure and annealing, the Fermi edge step grows but remains weak as compared to the h_u band. Before the anneal, the Ca is associated with the outermost layer of molecules in which the t_{1u} band is split by the lower symmetry at the surface. This makes possible a partially doped but nonmetallic surface layer of composition CaC_{60} or Ca_2C_{60} in which one of the subbands is filled. This is similar to the behavior of the conduction band in K_xC_{60} , with regard to both the nonmetallic surface layer and the weakness of the Fermi edge step (4). The latter is a result of the fact that the photoelectron escape depth in C_{60} is significantly smaller than the spacing of the molecular layers (5). The signal from the bulk is consequently always a minor

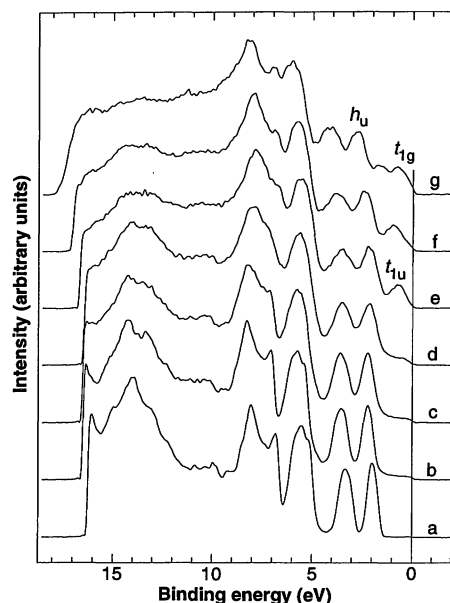


Fig. 2. Valence-band spectra of C_{60} film exposed to Ca vapor at room temperature and then annealed at 425 K. The exposures are the same as in Fig. 1.

part of the photoemission spectrum of C_{60} compounds. Annealing produces significant changes throughout the Ca deposition sequence. This behavior is quite different from that of K, which diffuses so rapidly in C_{60} at room temperature that subsequent annealing produces only minor changes.

The complete scans for the annealed samples are shown in Fig. 2. In spectra b and c the metallic Fermi cutoff is apparent. For divalent intercalated ions the half-filled t_{1u} band does not correspond to a limiting composition; in K_3C_{60} , the half-filled bands obtains when all the interstitial sites of the face-centered-cubic structure are occupied. As a result, Ca doping can proceed smoothly through the half-filled band, making it very difficult to prepare a uniform sample with this composition. A stoichiometric metallic phase may exist when only the tetrahedral sites are filled, corresponding to the compound Ca_2C_{60} , but there is no proof that the data in spectra b and c correspond to this composition. (The absence of t_{1u} band superconductivity in Ca_xC_{60} may be understood in terms of these distinctions between it and K_3C_{60} .) In spectrum d the signal at the Fermi level has become weaker, indicating that the bulk t_{1u} band is becoming filled. The filled band is reached in spectrum e, where the t_{1u} band becomes quite strong and peaks well below the Fermi level. This spectrum corresponds to the insulating compound Ca_3C_{60} in which the tetrahedral and octahedral sites are each occupied by one Ca^{2+} ion. The spectrum is similar to that of body-centered-cubic K_6C_{60} in which the t_{1u} band is filled.

The fact that the t_{1u} band in spectrum e

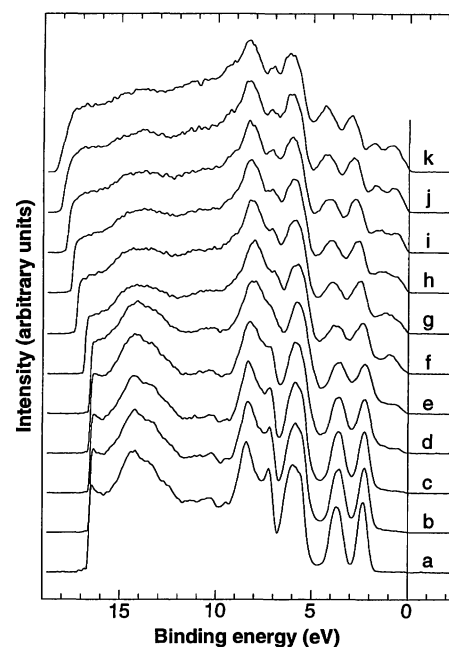


Fig. 3. The valence-band spectra of a C_{60} layer deposited on a metallic Ca film at 78 K after warming to the following temperatures: spectra a through g, 95, 200, 222, 245, 265, 290, or 300 K, and after annealing for 1 min, spectra h through k, at 325, 350, 375, or 400 K.

has an amplitude commensurate with the degeneracies of the h_u and t_{1u} bands indicates that the surface now contributes to the t_{1u} peak. The behavior is reminiscent of that of K_xC_{60} . A clue to the origin of this change in the surface spectrum is found in the work function cutoff. After an initial decrease in the work function, associated with the pinning of the empty t_{1u} band at the Fermi level, there is little change as the bulk t_{1u} level becomes partially occupied (see Fig. 2, spectra b through d). This is an indication that there is no Ca left on the surface after the anneal, presumably because a fully coordinated bulk interstitial site is energetically more favorable than a surface site. Under these conditions the surface molecules are asymmetrically coordinated by Ca. Because C_{60} interacts much more strongly with the alkaline earth ions than with the neighboring C_{60} molecules, the splitting of the surface t_{1u} band mentioned above is due to the neighboring Ca. (Spectra of C_{60} itself give no evidence of such splitting.) With increasing exposure to Ca, at spectrum e, the work function begins to decrease further, an indication that now Ca remains on the surface, giving the surface molecules a more symmetric Ca environment. As a result, the splitting of the surface t_{1u} band vanishes; the surface spectrum becomes similar to that of the bulk; and the intensity of the filled band becomes comparable to that expected on the basis of the degeneracies.

Continued exposure to Ca results in a shift of the t_{1u} band to greater binding energy and to the development of a tail that intersects the Fermi level (see Fig. 2, spectrum f). This tail gives the initial indication of the filling of the t_{1g} band. Doubling the exposure (spectrum g) results in a shift of the entire spectrum to larger binding energy and in the appearance of a new peak associated with the t_{1g} band. At this exposure the rounded cutoff indicates an inhomogeneous surface, that is, that excess Ca is left on surface after annealing. The separation of the peaks of the two bands in spectrum g is ~ 1 eV, in accord with the separation in the empty bands in the calculation of Saito and Oshiyama (6). If the Ca atoms are fully ionized, four atoms in the octahedral site, together with one in each of the two tetrahedral sites per C_{60} , can provide 12 electrons to fill both the t_{1u} and t_{1g} bands without a structural phase transition. In spectrum g the t_{1g} band clearly intersects the Fermi level, indicating that the composition has not quite reached that of Ca_6C_{60} or is not quite ionic. The data show that the system is metallic both as the t_{1u} band is filling and subsequently as the t_{1g} band is occupied.

Because the escape depth in C_{60} is smaller than the molecular diameter, we must consider the possibility that the two peaks in Fig. 2, spectrum g, are due, not to the t_{1u} and t_{1g} bands as proposed above, but to a splitting of the surface t_{1u} band. We have invoked this splitting to account for the weakness of the Fermi cutoff in Fig. 2, spectra b to d. The fact that the two peaks in spectrum g have comparable intensities is incompatible with the split-band picture, which requires to a 2:1 intensity ratio. It is in accord with the two-band picture, because both bands are threefold degenerate (6). Moreover, the total area of the two components is too large as compared to that of the h_u band to be due the split t_{1u} band alone. We therefore rule out the split surface-band interpretation.

Data taken with the C_{60} -Ca sandwich are shown in Fig. 3. The sample was allowed to warm up from liquid N_2 temperature to room temperature, was held there for some time, and was then annealed for 1 min at progressively higher temperatures. The data taken at low temperature fail to show a Fermi edge. This is no surprise because an anneal was required to produce a Fermi edge after room-temperature exposure to Ca. A spectrum indicative of a filled t_{1u} band is reached just below room temperature in Fig. 3, spectrum f, where the work function indicates that Ca has reached the surface. By 375 K, the t_{1g} state appears to be fully occupied, corresponding to the compound Ca_6C_{60} . The metallic character is not apparent in these spectra, suggesting that there is rapid conversion to the fully

doped compound Ca_6C_{60} when Ca is plentiful. The work function cutoff continues to move to larger energy, indicating that Ca is accumulating on the surface.

Finally we must consider the possibility that the filled t_{1g} band is a surface phenomenon associated with the presence of excess Ca on the surface. The data in Fig. 2 do not suffice to rule this out, because the filled t_{1g} band is seen only in spectrum g where the broadened work function cutoff indicates an inhomogeneous surface. However, the data in Fig. 3, spectra h through k, show the t_{1g} band filled well before excess Ca has accumulated on the surface, indicating that it is not a surface phenomenon. We conclude that the photoemission spectra show the progressive occupancy of the bulk t_{1u} and t_{1g} bands, with evidence of metallic conductivity for the incompletely filled bands. It is

then clear that the superconductivity of Ca_5C_{60} is due to the t_{1g} band, which can be filled without a structural change because of the small size of the Ca ion.

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Electronic, Magnetic, and Geometric Structure of Metallo-Carbohedrenes

B. V. Reddy, S. N. Khanna, P. Jena

The energetics and the electronic, magnetic, and geometric structure of the metallo-carbohedrene Ti_8C_{12} have been calculated self-consistently in the density functional formulation. The structure of Ti_8C_{12} is a distorted dodecahedron with a binding energy of 6.1 electron volts per atom. The unusual stability is derived from covalent-like bonding between carbon atoms and between titanium and carbon atoms with no appreciable interaction between titanium atoms. The density of states at the Fermi energy is high and is derived from a strong hybridization between titanium 3d and carbon *sp* electrons. Titanium sites carry a small magnetic moment of 0.35 Bohr magneton per atom and the cluster is only weakly magnetic.

Recently Guo, Kerns, and Castleman (1) reported the observation of an unusually stable cage-like network consisting of eight Ti and twelve C atoms (Ti_8C_{12}). This cluster, known as metallo-carbohedrene or "met-car," shares a common shape with buckminsterfullerenes (2). However, there are fundamental differences between these two clusters. In the fullerenes all the atoms are C atoms and they are arranged in pentagonal and hexagonal rings, whereas in met-cars there are only pentagons whose vertices are occupied by metal and C atoms. It is likely that the presence of metal atoms may give the met-cars unusual electronic and magnetic properties. Possible applications of met-cars for new electronic materials, pollution control, and chemical tracers, and in site-specific protein chemistry in living organisms are being envisioned.

Guo *et al.* (1) assigned a dodecahedral structure to the met-cars that is characterized by twelve pentagons with Ti occupying

eight identically coordinated sites. Each Ti is bonded to three C atoms, and each C is bonded to two Ti and one C atom. Guo *et al.* arrived at this structure by studying its reaction with NH_3 and by following the general rules of chemical bonding.

Aside from the proposed structure of met-car and its apparent stability, little is known about its electronic structure, the reasons for its unusual stability, its geometrical parameters, and its electronic and magnetic properties. To provide some understanding of these quantities, we undertook a series of fully self-consistent total energy calculations of Ti_8C_{12} . Our method is based on the self-consistent field-linear combination of atomic orbitals-molecular orbital (SCF-LCAO-MO) theory and the density functional approximation (3). Our results show that the unusual stability of Ti_8C_{12} is derived from a large binding energy (~ 6.1 eV per atom) owing to covalent bonding between C atoms and between Ti and C atoms. There is virtually no interaction between Ti atoms. The electron density of states at the Fermi energy is high

Physics Department, Virginia Commonwealth University, Richmond, VA 23284.