Cohesive Mechanism and Energy Bands of Solid C_{60}

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We present microscopic total-energy calculations which provide a cohesive property and electronic structures of a new form of solid carbon, the face-centered-cubic C_{60} crystal (fcc C_{60}). We find that C_{60} clusters are condensed by van der Waals force, and that the resulting fcc C_{60} is a novel semiconductor with direct energy gap of 1.5 eV at the Brillouin-zone boundary (X point). We also find that an "impurity" C_{60}K cluster induces a shallow donor state in fcc C_{60}.

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Since the interesting proposal of the truncated-icosahedron structure for the C_{60} observed as a "magic" cluster in carbon-cluster mass spectra and named "buckminsterfullerene" several years ago,[1] many theoretical and experimental works have been done to confirm the proposed structure and to study the physical properties of C_{60} clusters.[2] Recently, a macroscopic quantity of C_{60} clusters has been produced and C_{60} has been shown to bear the truncated-icosahedron structure indeed.[3] More surprisingly, C_{60} clusters are found in a crystallized form (solid C_{60}). In addition to C_{60}, cage-structure C_{70} and C_{84} clusters have been produced in large quantities and are also found in crystallized forms.[4] These new forms of solid carbon are now being studied intensively since they have a great potential of application as new materials. Moreover, these cage-structure carbon clusters C_N are expected to trap atoms and molecules inside,[1,5] and such C_NX clusters (X represents trapped atoms or molecules) may exhibit a variety of electronic structures. Therefore, C_N and C_NX clusters provide a new set of atomlike units which could be used not only to construct new materials but also to make small molecular devices.

In this Letter, we report a cohesive property and electronic structures of face-centered-cubic (fcc) solid C_{60} in which truncated-icosahedron C_{60} clusters are held together on the lattice sites. [Both the fcc phase[6] and the hexagonal-close-packed (hcp) phase[3] of solid C_{60} have been reported experimentally so far.] We have found that, in fcc C_{60}, clusters are condensed by rather weak van der Waals force, and that fcc C_{60} exhibits peculiar optical excitations, and it is *a semiconductor with direct energy gap at the Brillouin-zone boundary (X point).* We have also calculated donor and acceptor impurity levels using the effective-mass theory, and the C_{60}K cluster is proposed as a candidate for a "donor cluster" in fcc C_{60}.

Total energies and the one-electron energies (band structure) are calculated using the local-density approximation[7] (LDA) in the density-functional theory.[8] For the exchange-correlation potential, we have used the parametrized Ceperley-Alder potential.[9] The norm-conserving pseudopotentials[10] are constructed to describe the electron-ion interaction. The wave functions are expanded in terms of the Gaussian-orbitals basis set,[11] whose exponents used, 0.299 and 2.908 for s and 0.362 and 2.372 for p orbitals, are determined by fitting the numerically obtained pseudoatomic orbitals. It has been confirmed that the present method successfully describes both the strong bond formation and the weak van der Waals force between C atoms: For graphite, the calculated bond length within the layer agrees with the experimental value with a difference of 1.7%, and the optimized interlayer distance is 94.7% of the experimental value. For diamond, the difference between the calculated lattice constant and the experimental one is 0.2%. The C_{60} cluster consists of twenty hexagons and twelve pentagons (Fig. 1). The former involve the sp^2 hybridization and the latter the sp^3 hybridization. (The bond angle 108° in the pentagon is very close to the angle 109°28′ in the ideal sp^3 hybridization.) Since the present method is reliable both for the sp^2 configuration (graphite) and for the sp^3 configuration (diamond) as well as for describing the weak van der Waals force, we

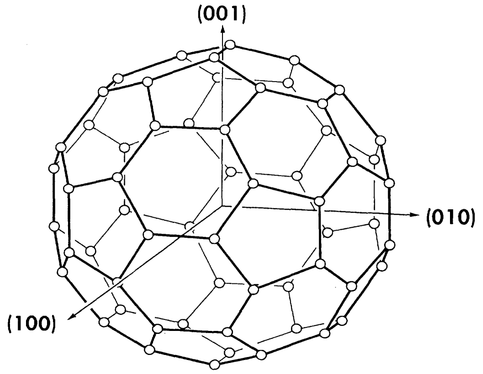

FIG. 1. Geometry of the C_{60} cluster. There are two different types of C-C bonds; one is on the regular pentagon (single bond) and the other is shared by two hexagons (double bond). Crystal axes of the fcc lattice assumed in the calculation of fcc C_{60} are also shown. Each crystal axis crosses the double bond at the midpoint.

expect that it also provides reliable results for the C_{60} cluster and solid C_{60}.

In Fig. 1, the geometry of the system studied is shown. Each C_{60} cluster has two different bonds within the icosahedral symmetry. One is those which constitute regular pentagons (with the length r_1), and the other those which are shared by two hexagons (r_2). The latter thirty bonds are believed to be the so-called "double bonds." Actually, a recent nuclear-magnetic-resonance experiment[12] has shown the existence of two different bond lengths in the C_{60} cluster, 1.46 and 1.40 Å, which we have used for r_1 and r_2 in the present work. On each fcc lattice site, we have placed the C_{60} cluster so that the point group becomes the highest symmetry, T_h. The point group T_h is one of subgroups of both I_h and O_h. In this choice of the orientation of C_{60} clusters on fcc lattice sites, each cluster has twelve equivalent nearest-neighbor clusters.[13] Then, each pentagon in a C_{60} cluster has two C atoms which are nearest to the neighboring C_{60} cluster. (There are three kinds of C atoms in each cluster: 24 C atoms which are the nearest neighbors of other clusters, 12 C atoms closest to the three crystal axes in Fig. 1, and the remaining 24 C atoms.)

In Fig. 2, the calculated total energies of fcc C_{60} are shown, measured from the total energy of the isolated C_{60} cluster, as a function of the fcc lattice constant (a) around the experimental value ($a_0=14.198$ Å).[6] The isolated cluster has been simulated by a much larger lattice-constant calculation, $a=1.2a_0$, and is found to have the cohesive energy of 7.4 eV per atom. As can be seen from Fig. 2, C_{60} clusters are condensed by rather weak van der Waals force. Even though each cluster has twelve nearest-neighbor clusters, the calculated cohesive energy per C_{60} cluster is 1.6 eV, which is much smaller than the typical C-C bond energy (more than 3 eV). This feature is visible in the contour map of the valence-electron density (Fig. 3). There is no chemical bond between C_{60} clusters. Also, the difference between the double bond and the single bond within a cluster can be seen. The valence-electron density between C_{60} clusters is much lower than the densities at single and double bonds within a C_{60} cluster.

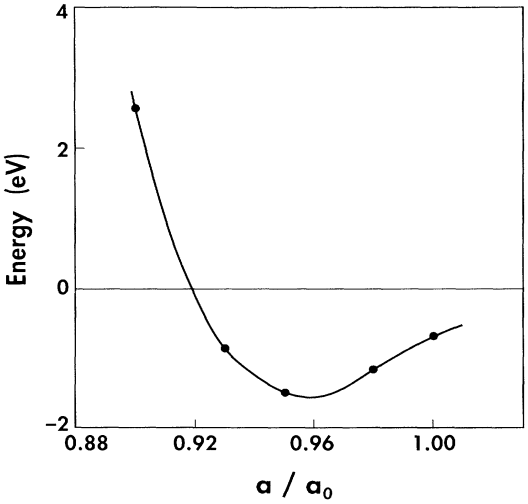

FIG. 2. Total energy per C_{60} cluster in the fcc C_{60} crystal, measured from the total energy of the isolated C_{60} cluster, as a function of the lattice constant a. a_0 is an experimental lattice constant. The solid line is a guide for the eye.

In Fig. 4(a), the calculated energy levels of the C_{60} cluster and the band structure of fcc C_{60} at the experimental lattice constant are shown. The isolated C_{60} cluster has an icosahedral symmetry (I_h) and its energy levels have up to fivefold degeneracies. It can be seen that the deeper levels of the C_{60} cluster have very little dispersion even when they form an fcc crystal. These levels are considered to be the bonding states of σ bonds. On the other hand, most levels between -6 and $+7$ eV have considerable dispersion in fcc C_{60}. We can assign these bands as the π-bond states since the π bond spreads outside the cluster more than the σ bond and has larger intercluster overlap. Levels above 7 eV again have little dispersion in fcc C_{60} and they correspond to the antibonding states of σ bonds. The valence-band structure is in excellent agreement with the recent x-ray photoemission studies of solid C_{60},[14] and is consistent with the plane-wave basis-set calculation with very soft pseudopotentials.[14]

The highest-occupied state of the C_{60} cluster is the h_u state and is completely occupied by ten electrons. The energy gap between the h_u and the lowest unoccupied

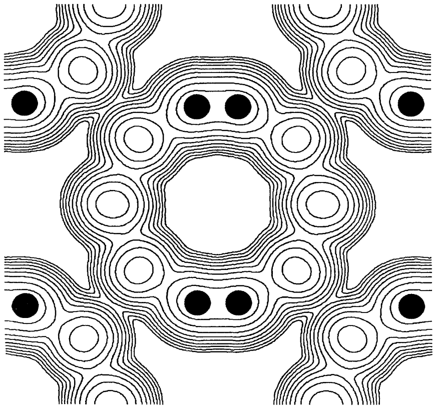

FIG. 3. Contour map of the valence-electron density of the fcc C_{60} crystal on the (010) plane. Solid circles denote C atoms. The highest-density contour around each C atom represents the equal-density line of 2.04×10^{-2}/Å^3. Each contour represents twice (or half) the density of the neighboring contours. In addition to the two double bonds formed by the C atoms shown, the (010) plane vertically cuts four single bonds and two double bonds at their midpoints in each C_{60} (see Fig. 1). The highest-density region of the double bond is slightly wider than that of the single bond.

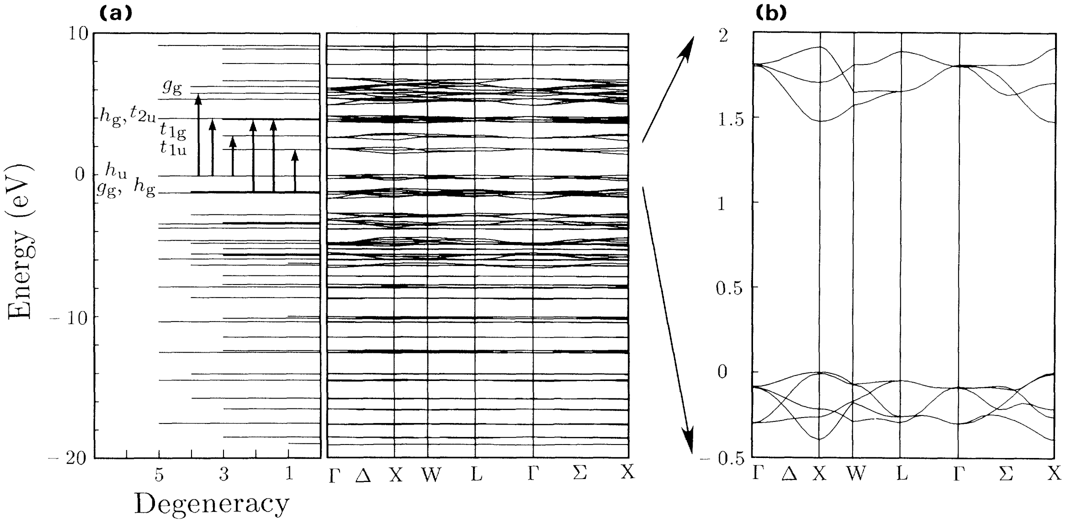

FIG. 4. (a) Electronic energy levels of the C_{60} cluster (left panel) and the band structure of the fcc C_{60} crystal (right panel). fcc C_{60} is found to be a semiconductor and the valence-band top at the X point is defined as the zero energy. The cluster energy levels have been shifted so that the highest occupied state (h_u) is aligned at the mean value of the five highest occupied bands of fcc C_{60} at the Γ point. The optically allowed transitions with excitation energies less than 6 eV are indicated by arrows. (b) Band structure of fcc C_{60} around the energy gap. Both the valence-band top and the conduction-band bottom are at the X point.

state, t_{1u}, is about 1.9 eV. In the energy levels of the C_{60} cluster, the lowest six optically allowed excitations, $h_u \rightarrow t_{1g}$, $h_g \rightarrow t_{1u}$, $h_u \rightarrow h_g$, $g_g \rightarrow t_{2u}$, $h_g \rightarrow t_{2u}$, and $h_u \rightarrow g_g$, are shown by arrows in Fig. 4(a). The calculated excitation energies are 2.87, 3.07, 4.06, 5.09, 5.17, and 5.87 eV, respectively. The experimental photoabsorption spectrum of the C_{60} cluster[15] exhibits peaks at 3.06, 3.76, 4.82, and 5.85 eV, some of which agree well with the present results. If the system has a perfect spherical symmetry, the energy levels can be characterized by angular momentum number l, and the optically allowed transitions are from l to $l \pm 1$ states ($\Delta l = 1$). The second and the third highest occupied states of C_{60}, g_g and h_g, correspond to the $l = 4$ state of the spherical symmetry. The highest occupied state h_u is one of the substates of the $l = 5$ state. The optical transitions listed above correspond mostly to $\Delta l = 1$ transitions in spherical symmetry and are expected to have considerable oscillator strength. Since there are clear correspondences between the energy levels of the C_{60} cluster and the energy bands of fcc C_{60}, we can expect that the optical spectra of fcc C_{60} are similar to those of the C_{60} cluster.

The energy gap of the C_{60} cluster remains finite when C_{60} clusters form the solid. In Fig. 4(b), several energy bands of fcc C_{60} near the energy gap are shown. Both the valence-band top and the conduction-band bottom are located at the X point. The present LDA calculation indicates that the fcc C_{60} crystal is a direct-gap semiconductor with an energy gap of 1.5 eV. The transition between the valence-band top and the conduction-band bottom is optically forbidden.[16]

The calculated effective mass of the conduction band is $1.3m_e$ (m_e is the bare electron mass). Then, it gives a rather shallow donor state with the ionization energy of 60 ± 30 meV. Here, we have used the static dielectric constant $\epsilon_0 = 18 \pm 4$ which is estimated from an approximate formula,[17] $\epsilon_0 = 1 + 4\pi N e^2 \hbar^2 / m_e E_g^2$, where N is the valence-electron density. E_g is a typical excitation energy of the system. From the experimental photoabsorption spectra,[15,18,19] we have assumed $E_g = 5.3 \pm 0.6$ eV.

There are two valence bands relevant to the hole states. Their effective masses are $1.5m_e$ and $3.4m_e$. The light-hole state is found to locate slightly lower in energy than the heavy-hole state (about 10 meV). The acceptor levels associated with the lower and the upper valence bands have the ionization energies of 60 ± 30 and 170 ± 70 meV, respectively.

In our previous work,[20] we have calculated the energy levels of C_{60} and $C_{60}K$ clusters using the numerical atomic orbitals with Slater's $X\alpha$ exchange-correlation potential. The calculated energy levels of the C_{60} cluster are very similar to those of the present result. The $C_{60}K$ cluster has already been produced as a cluster beam,[5] and the K atom is believed to be inside the C_{60} cage. In the $C_{60}K$ cluster, the $4s$ valence electron of the K atom is found to be transferred to the outer C_{60} cage. If the $C_{60}K$ cluster is in fcc C_{60}, the additional electron of the C_{60} cage should be bound around the $C_{60}K$ cluster, but extended due to the screening effect: the donor state discussed above. Hence, the $C_{60}K$ cluster may be used as a "donor cluster" in the semiconductor C_{60}. The bare K-atom impurity in fcc C_{60} may also act as a donor. Interstitial sites of solid C_{60} have enough space for various atoms to sit. Halogen atoms and halides may act as acceptors in solid C_{60}.

In conclusion, the present work has revealed that the new form of carbon crystal, fcc C_{60}, is a novel semiconducting material with a direct energy gap at the Brillouin-zone boundary. In addition, donor and acceptor impurity levels have been calculated using the effective-mass theory, and the $C_{60}K$ cluster has been proposed as a donor cluster in the solid C_{60}, showing the great possibilities of application of the cage-structure clusters (buckminsterfullerenes), C_N and C_NX.

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[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature (London) **318**, 162 (1985).

[2] For a review, see H. W. Kroto, Science **242**, 1139 (1988).

[3] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Hoffman, Nature (London) **347**, 354 (1990).

[4] R. L. Whetten *et al.*, *The MRS Late News Session —Buckeyballs: New Materials Made from Carbon Soot,* videotape (Materials Research Society, Pittsburgh, 1990).

[5] R. F. Curl and R. E. Smalley, Science **242**, 1017 (1988).

[6] The fcc C_{60} single crystal has been obtained by sublimation (R. Fleming *et al.*, in Ref. 4), while the report of the hcp phase in Ref. 3 is based on the results for powder crystal with a few percent of C_{70}.

[7] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[8] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[9] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[10] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979); G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[11] Y. Miyamoto and A. Oshiyama, Phys. Rev. B **41**, 12680 (1990); A. Oshiyama and M. Saito, J. Phys. Soc. Jpn. **56**, 2104 (1987).

[12] R. D. Johnson, N. Yannoni, G. Meijer, and D. S. Bethune, in Ref. 4.

[13] Recent experiment has suggested that C_{60} clusters are rotating rapidly at room temperature in fcc C_{60} and the rotation is much slower at lower temperature [C. S. Yannoni *et al.*, J. Phys. Chem. **95**, 9 (1991)]. It has also been supported theoretically (Q. Zhang, J.-Y. Yi, and J. Bernholc, in Ref. 4). Therefore, the total-energy difference between the different cluster orientations is expected to be small and the cohesive property of solid C_{60} we have found based on a particular orientation holds in other orientations.

[14] J. H. Weaver *et al.*, Phys. Rev. Lett. **66**, 1741 (1991).

[15] H. Ajie *et al.*, J. Phys. Chem. **94**, 8630 (1990). The absorption spectrum of solid C_{60} has been also reported in Ref. 4, although it is modified due to the presence of C_{70}.

[16] Delicate band structures such as degeneracies at points of high symmetry may be different for other choices of the C_{60} orientation on fcc lattice sites.

[17] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[18] R. Taylor, J. P. Hare, A. K. Abdul-Sada, and H. Kroto, J. Chem. Soc. Chem. Commun. **20**, 1423 (1990).

[19] Y. Achiba (private communication).

[20] S. Saito, in "Clusters and Cluster Assembled Materials," edited by R. S. Averback, D. L. Nelson, and J. Bernholc, MRS Proceedings (Materials Research Society, Pittsburgh, to be published), and also in Ref. 4.