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Condensed phases of all-pentagon C_{20} cages as possible superconductors

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C_{20} cages consisting only of pentagons have been synthesized in a gas phase. [H. Prinzbach *et al.*, Nature (London), **407**, 60 (2000)]. By performing first-principles calculations, we have found that the C_{20} cages can form condensed phases in several dimensions. The most stable phase among the investigated ones is a simple-cubic-like (SCL) phase, which shows a metallic property. Meanwhile, a metastable one-dimensional phase (1D chain) is found to be a semiconductor. The computed band structure of a 1D chain shows high density of states near the Fermi level compared to the SCL phase, which is a promising sign of superconductivity under carrier doping.

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Doped fullerenes (C_{60}, C_{70}, and C_{84}, etc.) are superconductors with transition temperatures (T_C's) of the order of a few tens of kelvins. Such high T_C's are partly due to a high density of state (DOS) at the Fermi level (E_F) under doping,[1] and due to the strong electron-phonon coupling constant ($V_{e\text{-}p}$). The recent discovery of C_{36} fullerenes[2] and the improvement in their purification[3] have attracted much attention to smaller fullerene superconductors. A density functional study of possible solid phases of C_{36} (Ref. 4) showed that Na atoms are good candidates of donors. Meanwhile, $V_{e\text{-}p}$ was found to increase when a diameter of a fullerene decreases.[5] The origin of the larger $V_{e\text{-}p}$ in smaller fullerenes is stronger localization of π electrons. Because of this fact, the doped solid C_{36} is expected to have a higher T_C than that of alkali-doped C_{60}.

If fullerenes smaller than C_{36} can be synthesized to form stable solid phases, T_C is expected to be increased. The smallest fullerene is a C_{20} cage only with pentagons. There are other isomers of C_{20}, such as a ring and a bowl. Theoretical investigations[6] showed that the computed relative stabilities of these C_{20} isomers are dependent on treatments of the many-body effect. So, the most stable structure among these C_{20} isomers is still under debate. Recently, Prinzbach *et al.*[7] succeeded to synthesize the C_{20} cages by starting with the stable $C_{20}H_{20}$ molecules, i.e., the C_{20} cages with each C atom terminated by a H atom. An experimental evidence of the cage shape is a measured photoelectron spectrum, which is far different from those of a ring and a bowl.[7] Agreement between experimental data and theoretical calculations of the photoemission spectrum of the cage has been confirmed by us.[8] By the analogy with large fullerenes, C_{20} cages are expected to form condensed phases, so it is worth exploring possible condensed phases of C_{20} cages by performing first-principles calculations prior to further experimental works. The question is whether the condensed phases have high DOS near E_F like other solid fullerenes, which can be superconductors.

By performing the first-principles total-energy and band-structure calculations, we have found that two C_{20} cages can make a dimer as shown in Fig. 1(a), in which two C-C bonds are formed at the cage-cage junction. We call this dimer a double-bonded dimer. From this dimer structure, one can easily imagine the formation of the chain structure as shown in Fig. 1(b) and the two-dimensional network that is assembled by condensing the one-dimensional chains in parallel orientation, and the three-dimensional network as shown in Fig. 1(c), which is a simple-cubic-like (SCL) lattice of double-bonded C_{20} cages. The SCL phase has the highest cohesive energy among the investigated phases, and the computed energy band structure indicates that this phase is a metal. Meanwhile, a chain structure (we call this a double-bonded chain) shows semiconducting property and has a high DOS near E_F compared to the SCL phase. From this fact, it is expected that high DOS at E_F is realized by carrier doping into the chain, and thus the chain is likely to show superconductivity.

The present calculations were performed within the density functional theory using the local density approximation (LDA) and the pseudopotentials (PP's). (Calculations based on various methods, for example, the Hartree-Fock, LDA, and GGA, gave contradicting results on the stability of C_{20} isomers,[6] but we believe this fact should not affect the computed condensed phases of the C_{20} cages.) The Perdew-Zunger interpolation[9] fitted to the Ceperley-Alder calculation[10] was adopted in taking the exchange-correlation energy of electrons into account. In some cases, the generalized gradient approximation (GGA) with use of the Perdew and Wang functional[11] was also used, to ensure the validity of the LDA. (We note here that the application of GGA was not for a case of formation of the double-bonded dimer but for a case of a single-bonded dimer, which will appear later.) Interactions between ions and valence electrons were expressed by soft PP's (Ref. 12) with a separable form.[13] The *s*-orbital component was used for the nonlocal part. The plane-wave basis set with a kinetic cutoff energy of 40 Ry was used to express valence electrons. In the present band-structure calculations, we used periodic boundary conditions which separate nonbonding cages by around 4 Å. Although

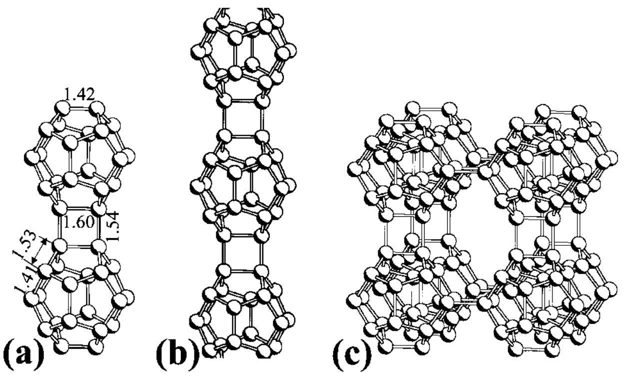

FIG. 1. Possible condensed phases of C_{20} cages. (a) A dimer optimized to minimize the total energy. Numbers show C-C bond lengths in units of Å. (b) A one-dimensional chain, whose atomic coordinates and the period along the chain axis were optimized to minimize the total energy. (c) Atomic structure of a SCL phase, whose atomic coordinates were optimized while its lattice constant was set 3% shorter than the period of the chain shown in (b).

this separation does not affect the energetics of dimerization and chain formation, tiny dispersions in the energy bands remain because of the wave function interaction through this distance. To prevent this, the separation was increased to 6 Å in computing the band structure and DOS of the 1D chain.

First of all, we show that two neutral C_{20} cages can be dimerized forming two C-C bonds at the junction. Figure 1 (a) shows the optimized geometry of the dimer. A significant feature of this dimer is a variation in bond lengths and angles. As indicated in Fig. 1(a), the C-C bond lengths vary from 1.5 to 1.6 Å at the junction, while the lengths of C-C bonds away from the junction are around 1.4 Å. Small bond angles of 90° are seen at the junction, similar to those at junctions of polymerized C_{60} fullerenes.[14,15] We have not calculated the activation barrier for forming the double-bonded dimer from isolated C_{20} cages, but it is expected that this dimer formation occurs easily like a case of photopolymerized C_{60} fullerenes[14] and a case of alkali-doped polyfullerenes.[15] This geometrical feature at the cage-cage junction also appears when the double-bonded dimer evolves into a double-bonded chain, as seen in Fig. 1(b). This chain structure was determined by optimizing both of internal atomic coordinates and the period along the chain axis.

At junctions of the chain, the coordination numbers of C atoms are four. While other C atoms apart from the junction are three-hold coordinated. The chain therefore can bond additional C_{20} cages forming two-dimensional, and finally, three-dimensional phases. One possible three-dimensional phase is a SCL phase, as shown in Fig. 1(c). A structure shown in Fig. 1(c) was actually determined by performing the geometry optimization under a fixed lattice constant which is 3% smaller than the period of the 1D chain. Twenty-four symmetry operations keep the SCL phase invariant. This number of the symmetry operations is half that of the *true* simple cubic lattice, which is because the present SCL phase lacks the C_4 symmetry along with one of the three principal axes. When the lattice constant of the SCL phase was also optimized to reach the minimum of the total energy, the internal atomic coordinates finally relaxed to a configuration as shown in Fig. 2(a), in which the C_{20} cages are opened. The optimum lattice constant is 5.36 Å, which is 4% smaller than that shown in Fig. 1(c). According to the computed cohesive energies of several condensed phases of C_{20} cages, listed in Table I, the SCL phase is the most stable among the investigated phases. Figure 2(b) shows band dispersion along high symmetric lines in the first Brillouin zone (BZ) of the SCL phase and the corresponding DOS. (Here the standard linear tetrahedron scheme was used to obtain the DOS. Seventy-six irreducible k points, which correspond to 1726 k points in the whole BZ, were used.) The computed band structure and DOS show that the SCL phase is a metal. As far as we know, this is the first example of metal fullerene with neither dopants[1] nor external pressure.[16] In the case of the polymerized C_{60} fullerenes, the fullerene chains prefer to form the orthorhombic phase.[15,17] From this fact, it can be speculated that the present SCL phase of the C_{20} fullerene may not be the most stable phase. Further investigation is therefore necessary to explore the most stable three-dimensional condensation of C_{20} fullerenes.

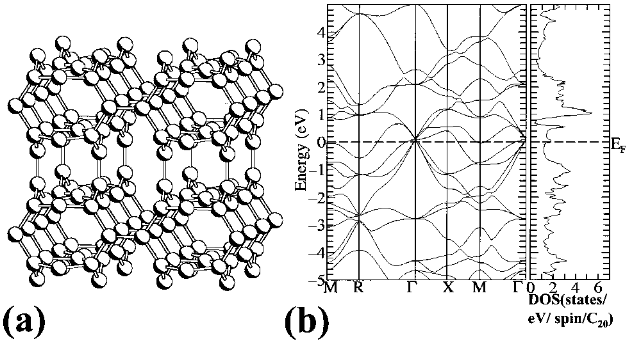

FIG. 2. (a) A SCL phase of C_{20}, whose lattice constant and atomic coordinates were optimized to minimize the total energy. (b) The associated energy-band structure and the density of states. The notations of M, R, Γ, and X mean the high symmetric points in the first Brillouin zone of the simple cubic; $M=(1,1,0)$, $R=(1,1,1)$, $\Gamma=(0,0,0)$, and $X=(1,0,0)$ in unit of π/a where a is the optimized lattice constant of 5.36 Å.

On the other hand, we also explored the electronic property of the metastable double-bonded chain whose electronic

TABLE I. Cohesive energies of condensed C_{20} cages, obtained by the LDA total energy calculations. Each value, in units of eV per C_{20}, was obtained by subtracting a total-energy of a condensed C_{20} cages from that of an isolated cage.

Structure	Cohesive energy
Single-bonded dimer	1.38
Double-bonded dimer	2.41
Single-bonded chain	1.88
Double-bonded chain	4.25
SCL	8.56

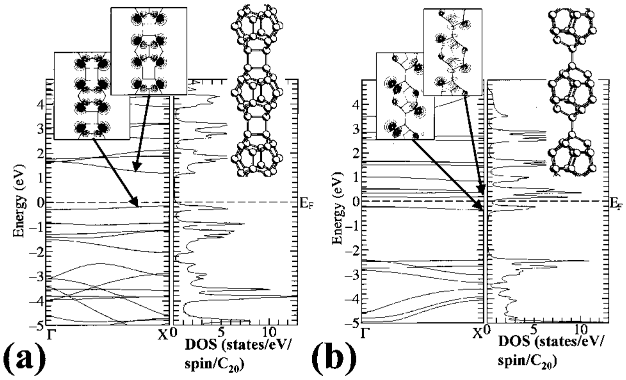

FIG. 3. (a) Band structure and the DOS of the double-bonded chain. Atomic structure is shown on the rightmost inset, while the charge contour maps of the HO and the LU bands are shown in the leftmost and middle insets, respectively. (b) Band structure and the DOS of the single-bonded chain. Atomic structure is shown on the rightmost inset, while the charge contour maps of the HO and the LU bands are shown in the leftmost and middle insets, respectively.

property is different from that of the SCL phase. As mentioned before, the structure of the double-bonded chain was determined by optimizing the internal atomic coordinates and the period of the chain to reach the total energy minimum. [As shown in Fig. 1(b), the cage structure was preserved contrary to the SCL lattice of Fig. 2(a).] Figure 3(a) shows the calculated energy-band structure and DOS of the chain.[18] The band structure shows a semiconducting property. The width of the highest occupied (HO) band is around 0.2 eV, while that of the lowest unoccupied (LU) band is around 0.6 eV. Both of HO and LU bands are associated with π electrons, whose amplitudes are localized on each cage and are away from the junction, see charge contour maps in the leftmost and middle insets of Fig. 3(a). These localized characteristics are due to the fact that the π electrons do not prefer to sit on the four-coordinated sites at the cage-cage junction. This fact causes low transfer probability of electrons from one cage to its neighbors, and thus results in small dispersions of the HO and LU bands. By injecting carriers, the location of E_F can be shifted close to peaks of the DOS originating from LU and HO bands.

Furthermore, we point out another possible way of the formation of a C_{20} dimer and a 1D chain, which have one C-C bond per cage-cage junction. We call these the single-bonded dimer and chain. Since it was difficult to consider a higher-dimensional single-bonded network due to a geometrical property of the C_{20} cages, we focus on the 1D chain. As seen in Table I, the cohesive energies of the single-bonded dimer and chain are less than a half of those of the double-bonded dimer and chain, respectively. But we expect that the formation of the single-bonded dimer and chain is possible, although they may be the minority. We found that an upper bound of an activation barrier for formation of the single-bonded dimer is 0.4 eV by performing LDA total energy calculations, while the corresponding value became 0.8 eV when GGA was applied. Once single-bonded dimers are formed, these dimers can evolve to a single-bonded chain as shown in the rightmost inset of Fig. 3(b); We have computed the total energies of an array of the single-bonded dimers by changing the interdimer distances under the periodic boundary conditions, and observed a presence of a tinny barrier of 10 meV per C_{20} before the dimer array becomes to a single-bonded chain. If the GGA calculation is performed, the computed barrier may be higher but cannot be in the different order of magnitudes. Similar to the double-bonded chain, there are high peaks of DOS near E_F, originating from very localized π electrons on each cage; see the contour maps in the inset of Fig. 3(b).

From the computed electronic structures of the several condensed C_{20} cages, we discuss the possibility of the superconductivity. In the SCL phase, the computed heights of the DOS peaks at E_F are close to that of the alkali-doped C_{60} fullerene[1] under normalization with respect to the number of C atoms. However, the breakage of the cage structure may result in small $V_{e\text{-}p}$ compared to that of C_{60} fullerenes. The SCL phase of the C_{20} cages might be a superconductor, but it is unlikely that the T_C is higher than those of C_{60} fullerene superconductors.

On the other hand, both of single-bonded and double bonded chains show semiconducting properties, so either electrons or holes must be injected to obtain high DOS at E_F. Since the cage structures in these chains are preserved, strong $V_{e\text{-}p}$,[5] and therefore, high T_C compared to those in the SCL phase are expected. Recently, external electrical field has been used to inject carriers in films of polyacene and fullerene.[19] If this method is used, carrier injection in single-bonded chain is rather easy because of its small band gap compared to that of the double-bonded chain. However, we should avoid energy-gap opening due to Peierls-type lattice distortion. Actually, we found energy-gap opening in the band structure of the single-bonded chain; the gap of 0.1 eV appears when we use double-size unit cell and inject a single electron (or hole) per C_{20}. Therefore, the E_F should be determined to avoid the energy-gap opening.

Compared to the SCL phase, both single-bonded and double-bonded chains are less stable, see Table I. But we expect that these chains are fabricated in porous materials as in the boron nitride nanotube, and zeolite, whose band gaps are so wide as to retain the original electronic property of the chains. Recently, nanotubes with a diameter of 4 Å were found to be synthesized inside zeolite.[20] Since the diameter of the C_{20} cage is in the similar order, the C_{20} chain is expected to be synthesized in the same manner.

In summary, we have investigated possible superconducting phases of the recently discovered C_{20} cages by performing the first-principles calculations. The most stable condensed phase is a SCL phase of the C_{20} cage, but the T_C of this phase is unlikely to be higher than those of C_{60} superconductors. Two types of C_{20} 1D chains were found to have a high DOS near E_F, and thus to be candidates for superconductors under carrier injection. Since the structure of the C_{20} cages is preserved in these chains, strong $V_{e\text{-}p}$ as well as high T_C compared to those of C_{60} are expected.

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$$\frac{1}{\pi}\sum_{n,k}\frac{\delta}{(E_{n,k}-E)^2+\delta^2}$$

with use of 33 sampling k points on the wedge of the one-dimensional Brillouin zone. Here $E_{n,k}$ is an eigenvalue of the nth band with a wave vector k. The value δ was set as 0.03 eV.

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