

Orientalional Ordering of Solid C₇₀

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(Received 18 August 1995)

We investigate the ground state structures and orientational ordering of face-centered-cubic, hexagonal-close-packed, rhombohedral, orthorhombic, and monoclinic lattices of solid C₇₀. We find that the calculated lattice constants of the hexagonal phases and face-centered-cubic lattice are in excellent agreement with the observed experimental values and further provide the exact orientational ordering of the crystals. The driving force for the phase transformation of various orientational orderings is an effective contact area between C₇₀ molecules. Phase transformation associated with orientational ordering is also discussed.

PACS numbers: 61.50.Jr, 61.50.Em, 61.50.Lt, 64.70.Kb

The development of efficient synthesis procedures for massive quantities of fullerenes has accelerated the basic research, in particular, on C₆₀ and C₇₀ [1]. Unlike the spheroidal shape of the C₆₀ molecule, the shape of the C₇₀ molecule is ellipsoidal. This gives an additional degree of freedom in solid packing, implying that the orientational ordering of the oblong C₇₀ in solid is much more complex. In solid C₆₀, the face-centered-cubic (fcc) lattice at room temperature and simple-cubic (sc) lattice at low temperature have been observed experimentally [2–4], although the fcc lattice is predicted to be the ground state structure theoretically [5–7], suggesting that more complex orientational ordering is involved in solid C₆₀.

Vaughan *et al.* [8] reported hexagonal-close-packed (hcp) ($a = 10.62$ Å, $c = 17.32$ Å) and fcc ($a = 15.01$ Å) structures for C₇₀ crystals. Fleming *et al.* [9] also reported fcc and monoclinic (mono) phases. Verheijen *et al.* [10] found four types of phases: fcc ($a = 14.96$ Å) at high temperature, rhombohedral (rh), an ideal hcp ($c/a = 1.63$), and a deformed hcp ($c/a = 1.82$) around room temperature, and the mono phase at low temperature. Several groups also reported similar structures [11–14]. It is clear now that several phases exist in solid C₇₀, depending on the sample preparation conditions and cooling rates. However, the experimental data do not, in general, provide the information for orientational ordering of each phase. A comprehensive study of the ground state structures is required in order to understand the correct phase transformation associated with orientational ordering. Furthermore, the orientation and stacking of fullerenes are extraordinarily important for transport properties of both pure and intercalated crystals.

Although the local density approximation based first principles calculations describe accurately the interatomic interactions between carbon atoms in fullerene molecules, it fails to describe van der Waals interactions between fullerene molecules. Girifalco [15] has derived an analytical Lennard-Jones (LJ) type potential between C₆₀ molecules based on atom-atom interactions, which has

been successfully used to compute the clusters [16] and the phase transformation of solid C₆₀ [17]. We adopt the Girifalco's LJ potential (GLJ) in this study to describe various ground state structures of solid C₇₀. In this Letter we provide a comprehensive study of both translational and orientational ground state structures of various solid C₇₀ phases. We find that the calculated lattice constants of the fcc and hcp phases are in excellent agreement with experimentally observed values and further provide the detailed orientational ordering of each phase. This enables us to predict a possible phase transformation associated with orientational ordering. The orientational ordering is determined mostly by the minimization of the steric hindrance between the C₇₀ molecules such that an effective contact area between C₇₀ molecules is maximized.

We generate the ground state structure of the C₇₀ molecule by the tight-binding total energy scheme developed by Wang *et al.* [18]. The generated C₇₀ has the long axis of 7.9 Å, about 1 Å longer than its short axis. It has eight characteristic bond lengths, ranging from 1.40 to 1.45 Å, where some of intermediate bonds are not distinguishable. This structure is used to describe the intermolecular interactions with GLJ. We tested the ordering of solid C₆₀. The calculated binding energy and the lattice constant for the fcc lattice are 2.01 eV/cluster and 14.01 Å, respectively, in good agreement with the experimental value of 1.739 eV/cluster [19] and 14.04 Å [4], and theoretical values of 1.988 eV/cluster and 14.049 Å [20].

We first generate the fcc supercell with 108 C₇₀ molecules by placing the center of the mass of the C₇₀ molecule at the fcc lattice points. We calculate the intermolecular interaction on four internal C₇₀ molecules. We introduce various orientational orderings. For instance, the long axes of all C₇₀ molecules are aligned to the [100] direction (fcc I). The total energy is calculated with varying the lattice constant. This calculation is repeated for different orientations where (i) the long axes of the molecule at the corner of the fcc are aligned to the [100]

direction but those at the faces are aligned to the $[010]$ direction such that the long axes of the adjacent C_{70} molecule are perpendicular to each other (fcc II); (ii) the long axes of all the molecules are aligned to the $[110]$ direction (fcc III); (iii) the long axes of the molecules at the corners and at the faces are aligned to the $[110]$ and $[1\bar{1}0]$ directions, respectively (fcc IV); and (iv) the long axes of all the molecules are aligned to the $[111]$ direction (fcc V). Figure 1(a) shows the total binding energies per C_{70} molecule for various orientational orderings. The lattice constant of the fcc II is 15.2 \AA , as compared to the experimental value of 14.96 \AA at room temperature [9] and 15.01 \AA at 400 K [8]. The binding energies of all C_{70} phases are higher than that of C_{60} [21]. This is expected from the larger lattice constant of 15.2 \AA , as compared to 14.01 \AA of solid C_{60} . Steric hindrance of the ellipsoidal shape of the C_{70} molecule expands the lattice constant in solid phase. The energies and the lattice constants between different orientations do not differ significantly with each other except the fcc III, suggesting that the mixed orientational orderings might be observed at high temperature near the phase transformation.

In the hcp lattice, two lattice constants (a and c) in addition to the orientational ordering have to be determined. We vary the values of a and c alternatively until we get the true minimum energy. We search for the minimum with five orientations: (i) the long axes of all the molecules are aligned to the $[0001]$ direction (hcp I); (ii) the long axes of the molecules at the bottom face ($c = 0$) and at the middle of the c axis are aligned to the $[0001]$ and $[1000]$ directions, respectively (hcp II); (iii) the long axes of all the molecules are aligned to the $[1000]$ direction (hcp III); and (iv) the long axes of the molecules at the bottom face and at the middle of the c axis are aligned to the $[1000]$ and $[0100]$ directions, respectively (hcp IV). The calculated values of the c/a ratio range from 1.5 to 1.84 as shown in Fig. 1(b). The hcp I gives the minimum energy, which is even lower than that of solid C_{60} . In this case, the lattice constant a is the shortest value of other phases, giving the largest effective contact area between neighbors in the plane, whereas c is the longest one. The ratio c/a is 1.85, which is severely deformed from an ideal of 1.633, in excellent agreement with the experimental values of 1.85 [12] and 1.82 [11]. This distorted phase is also observed from a constant-pressure molecular dynamics simulation [22]. The binding energies of other phases are much higher than that of the hcp I. The hcp II, where the long axes of the C_{70} molecules in the middle of the c axis are rotated to the $[1000]$ direction, which is perpendicular to the others, gives the value of $c/a = 1.61$, close to an ideal value of 1.633. Because of this rotation the value c becomes shorter to 17.5 \AA and a becomes longer to 10.9 \AA . The value of the c/a ratio 1.61 is in good agreement with the experimental value of 1.62 [11,12] although the orientational ordering is different from the experimental prediction where the long axes of all the molecules are aligned along the

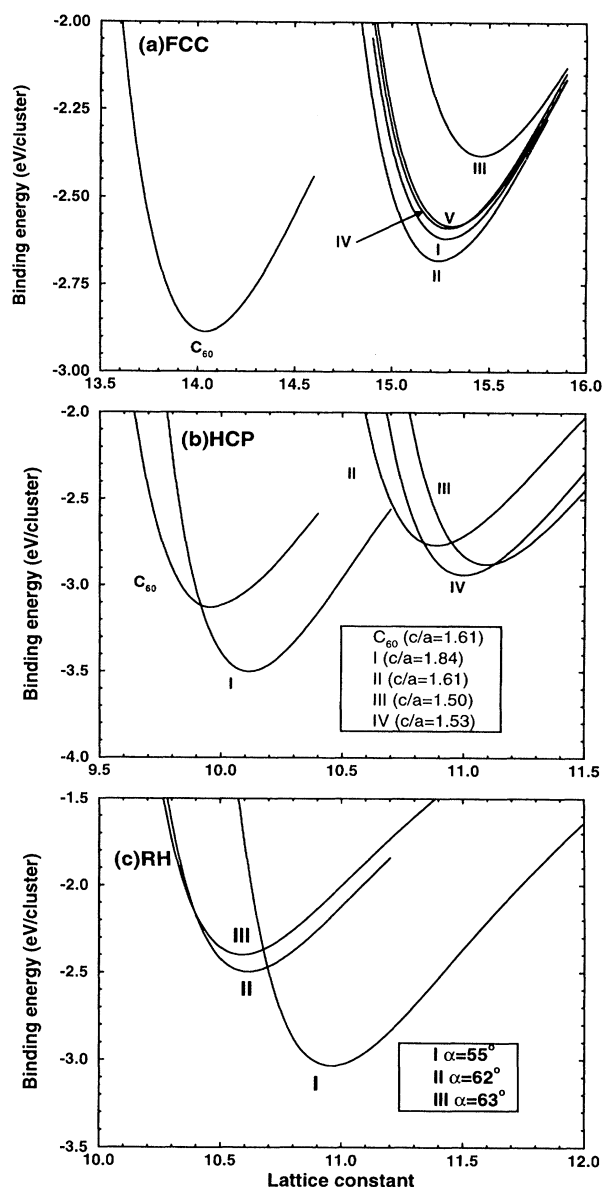


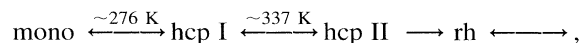
FIG. 1. The binding energy curves of various phases and orientations. Each orientation is explained in the text. The curve for the corresponding solid C_{60} is drawn for comparison. The binding energy is with respect to isolated molecules.

$[1000]$ direction. Further rotation of the molecule towards the $[1000]$ direction from the c axis will reduce the ratio. Since the binding energies between the hcp phases except ground state hcp I are not significantly different, the orientational ordering should be observed as the mixed states at relatively high temperature. The value of the c/a ratio will be the criteria to determine the mixed degree of orientations of these phases, i.e., more ordering of the long axes of the molecule towards the $[1000]$ direction will give the lower value.

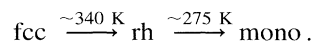
The rh phase is obtained by stretching or pressing the primitive rh cell of the fcc lattice along the [111] direction. The rh phase has an abcabc... packing rule along the [111] direction similar to the fcc phase. The lattice constant a and angle α between two atoms on the {110} faces are the controlling parameters to minimize the binding energy. In the case of $\alpha = 60$, it is a fcc. We consider three orientational orderings for the rh phase: (i) the long axes of all the molecules are aligned along the [111] direction (rh I) as shown in Fig. 1(c); (ii) the long axes of the molecule are aligned along the $[1\bar{1}0]$ direction (rh II); and (iii) the long axes of the molecules are aligned along the [100] direction (rh III). The rh I phase gives the lowest energy at $\alpha = 55^\circ$. The lattice constant is 11.0 Å, in good agreement with the observed one of 10.9 Å [23]. The energy is lowered by maximizing the contact area of the long axes of the molecules along the [111] direction. The rh phase is also reported experimentally although the exact orientation and the nearest neighbor distance are not known. The angle $\alpha = 55^\circ$ agrees well with the observed one of 55.1° [23].

The rh phase transforms to the fcc lattice with increasing temperature. We may expect intermediate phases between the rh and the fcc phases. We search for orthorhombic (orth) phases by changing a , b , and c separately. We find orth I ($a = 16.2$ Å, $b = c = 14.4$ Å), which is transformed from the fcc I. This gives a slightly lower binding energy than the rh lattice with the nearest neighbor distance of 10.18 Å, a little larger than that of the rh. We also find orth II ($a = 16.0$, $b = 14.4$, $c = 14.8$ Å), which is transformed from the fcc II. The nearest neighbor distance is 10.32 Å with a little higher binding energy compared to the orth I phase. Table I summarizes the calculated lattice constants and the relative strength of various phases.

Figure 2 illustrates the orientation of various solid C_{70} phases and the corresponding binding energy curves which give the minimum energy of each lattice. One may consider the phase transformation of orientational ordering based on our ground state structures. Tendeloo *et al.* [11] proposed the phase transformation as follows with increasing temperature:



and Sprik *et al.* [24] also observed similar transformation from a constant-pressure molecular dynamics simulation with decreasing temperature:



There are two types of mono phases. One is from a rotationally distorted hcp phase which involves the long-range rotational ordering which is observed from the experiment [11] and another is from the lattice-distorted hcp phase (mono II). The energy gain of such mono phases from hcp I is about 30 meV/cluster in both cases.

TABLE I. Various solid C_{70} phases and their lattice parameters. The values in parentheses are observed ones.

Phase	Lattice parameters (Å)	Binding energy (eV/cluster)
mono	$a = 10.2(10.04)$, $b = 10.0(9.90)$ $c = 18.6(27.77)$, $\gamma = 120^\circ(119.64^\circ)$	-3.5230
hcp I	$a = 10.1$, $c = 18.6$; $c/a = 1.84$ (1.85 ^b , 1.82 ^c)	-3.4991
hcp II	$a = 10.9$, $c = 17.5$; $c/a = 1.61$ (1.62 ^{b,c})	-2.7647
hcp III	$a = 11.1$, $c = 16.7$; $c/a = 1.50$	-2.8762
hcp IV	$a = 11.0$, $c = 16.8$; $c/a = 1.53$	-2.9385
rh	$a = 11.0(10.9^a)$, $\alpha = 55^\circ(55.1^\circ)$	-3.0279
orth I	$a = 16.2$, $b = c = 14.0$	-3.0636
orth II	$a = 16.0$, $b = 14.4$, $c = 14.8$	-2.9230
fcc I	$a = 15.3$	-2.6183
fcc II	$a = 15.2(14.96^d, 15.01^e)$	-2.6768

^aReference [23].

^bReference [12].

^cReference [11].

^dReference [9].

^eReference [8].

It is clear that the ground state structure is a mono phase at low temperature from our calculation although the binding energy difference from the hcp I is not so appreciable. The nearest neighbor distance of the mono II is 10.0 Å, the shortest of other phases, as compared to 9.9 Å of fcc-like (or centered) mono phase [24]. With increasing temperature, the mono phase easily transforms to the hcp I. Two pathways may exist for the phase transformation from the hcp I. Because the hcp has abab layer stacking, whereas the rh and the fcc lattices have abcabc layer stacking, a shear stress for the stacking fault must be applied for the hcp I to transform into the rh lattice. This may be achieved by a rapid thermal annealing. By increasing the temperature further, the long axes of the C_{70} molecules at the faces align along the [010] direction, perpendicular to those at the corners. This increases the nearest neighbor distance to 10.75 Å and forms the fcc II lattice. One may also observe intermediate phases such as orth I, II lattices during this transformation. Another pathway may be chosen without a shear stress from the hcp I. In this way the molecules rotate along the [1000] direction such that the hcp III can be observed. By increasing the temperature further the molecules in the middle of the c axis may rotate, which give the hcp IV phase. Further rotation of molecules will eventually form the hcp II phase. This transformation may be monitored by measuring the c/a ratio as discussed before. The transformation from the hcp to the fcc lattice requires a shear stress due to the different stacking rule. The stacking fault may occur by the rotation of the C_{70} molecules, but the exact origin for such a transformation in the experiment is not certain from our calculations. We

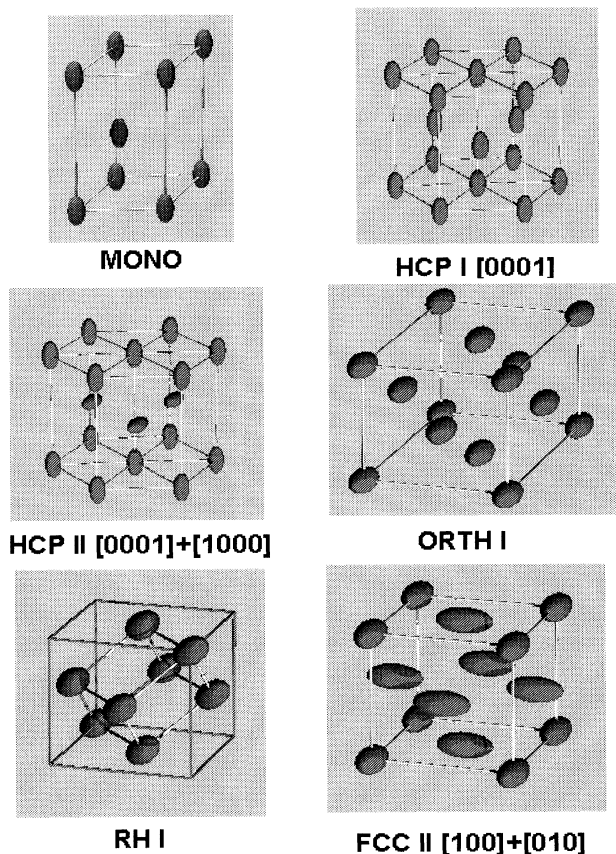
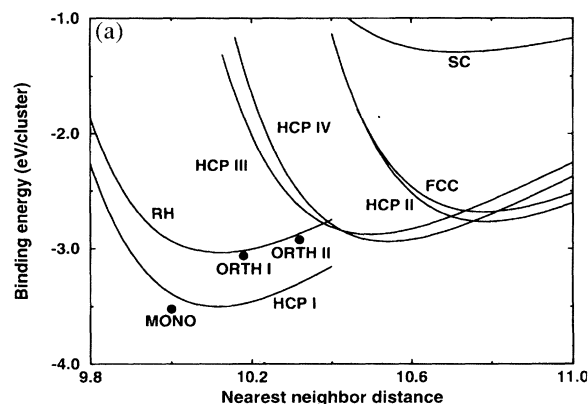
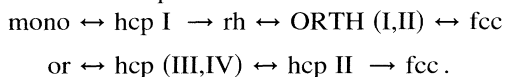


FIG. 2. (a) The binding energy curves and (b) the corresponding orientational orderings of various phases which give lower binding energy or agree with experimental observation. The binding energy is with respect to isolated molecules.

thus summarize the phase transformation as follows:



In summary, we have calculated the binding energy curves for various orientational orderings of solid C_{70} . The calculated lattice constants and the orientational ordering of fcc and hcp I are in excellent agreement with the observed values although the orientational ordering of the hcp II is different from the previous suggestion. In addition to the previously observed phases, we predict other phases which give relatively strong binding energies. We propose two pathways of phase transformation associated with orientational ordering. Careful studies for the phase transformation are required to observe many intermediate phases of solid C_{70} .

This work was supported by the Korea Science and Engineering Foundation (KOSEF) and in part through the Semiconductor Physics Research Center at Jeonbuk National University.

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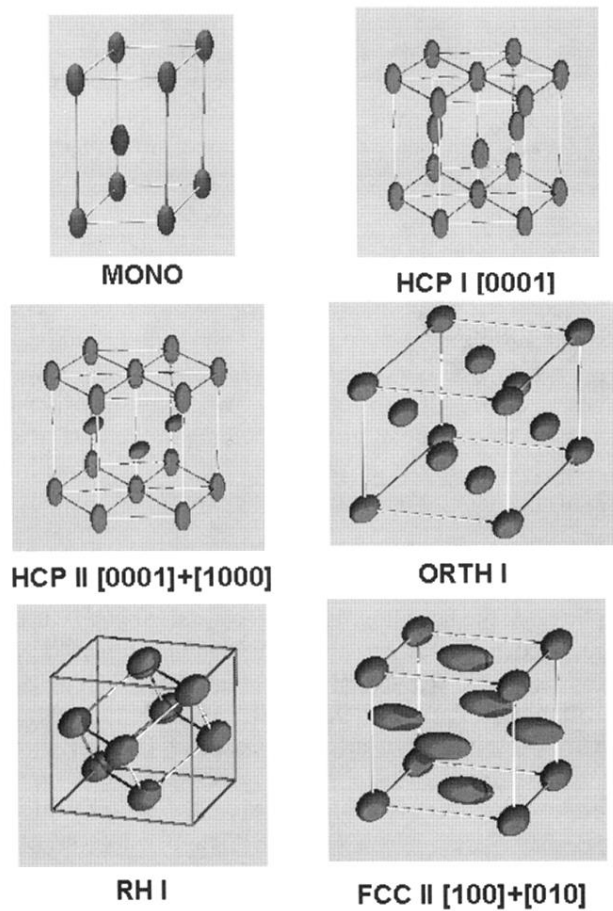
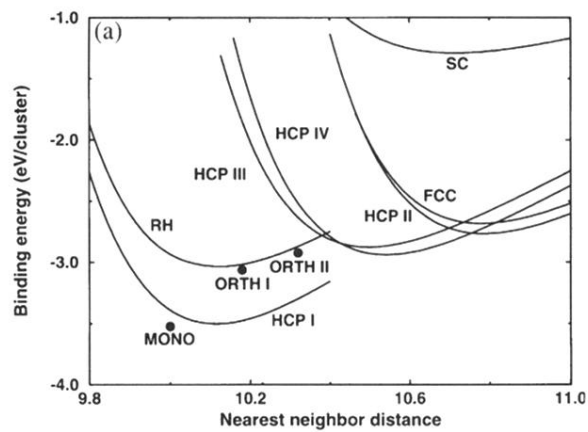


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