Electron-Phonon Interactions in Solid C_{36}

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Among the experimentally observed structures of molecular C_{36}, our calculations show that the structure with D_{6h} symmetry is one of the two most energetically favorable. Based on this result and the fact that D_{6h} is conducive to forming a periodic system, we propose a new solid phase of carbon using C_{36} fullerenes as a basis. Full structural relaxations and electronic density of states are evaluated using an *ab initio* pseudopotential plane wave method within the local density approximation. The calculated electron-phonon interaction potential is found to be substantially enhanced compared to C_{60}, leading to the possibility of larger superconducting transition temperatures than in alkali-doped C_{60} solids. [S0031-9007(98)06606-X]

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The discovery of high superconducting transition temperatures in the alkali-doped C_{60} solids ($T_c = 10-40$ K) has contributed to the intense research effort to study this class of materials [1–14]. Experimental evidence suggests that the current maximum value for T_c is 40 K in Cs_3C_{60} compounds [15], and theoretical studies indicate that electron-phonon interactions are responsible for superconductivity in these materials [9–14]. Simple models based on the curvature of the fullerenes have been proposed to explain their high T_c compared to intercalated graphite [8,9,16]. Solids based on *smaller* fullerenes, which are even more curved than C_{60}, suggest the possibility of enhancing T_c and further enriching this class of materials.

In this Letter, we propose a new solid phase of carbon made from C_{36} fullerenes. *Ab initio* total energy calculations of the isolated molecules show that the high-symmetry (D_{6h}) structure is energetically favorable and conducive to forming a crystal. Our calculations predict that the C_{36} crystal, after full relaxation within the local density approximation (LDA), is stable with a binding energy per atom similar to that of C_{60}. Furthermore, the electron-phonon coupling, evaluated directly within LDA, is significantly enhanced compared to C_{60}.

The C_{36} molecules have been observed experimentally [17], and characterized using mobility measurements [18–20]. We have carried out *ab initio* pseudopotential [21] density functional calculations for six different possible ground state structures: the D_{6h}, D_{2d}, C_{2v}, and D_{3h} fullerenes, a corranulenelike bowl, and a monocyclic ring [22]. Our calculations, using both the LDA and gradient corrected B-PW91 [23] functionals, predict the D_{6h} and D_{2d} fullerenes to be the most energetically favorable structures and to have the same binding energy within 0.04 eV (0.001 eV/atom). Of these two near isoenergetic geometries, the higher symmetry (D_{6h}) structure can form simple solids and will therefore be the focus of the rest of this Letter. The C_{36} (D_{6h}) is a good prototypical system for our theoretical study since it is small yet highly symmetric. Furthermore, the D_{6h} structure has the advantage that higher degeneracy in the electronic levels, because of its higher symmetry, can lead to a potentially large density of states.

Experimentally observed C_{60} and C_{70} fullerene van der Waals crystals have fcc and hcp structures, respectively. The C_{36} molecule resembles C_{70} since both possess a stretched c axis, and so its possible crystal structures which preserve the close packing requirement are hcp and rhombohedral. In order to lessen computational demands, we investigate the rhombohedral lattice since it involves only one fullerene per unit cell (Fig. 1), although we note that the difference between the rhombohedral and hcp structures is in the second nearest neighbor [24]. In

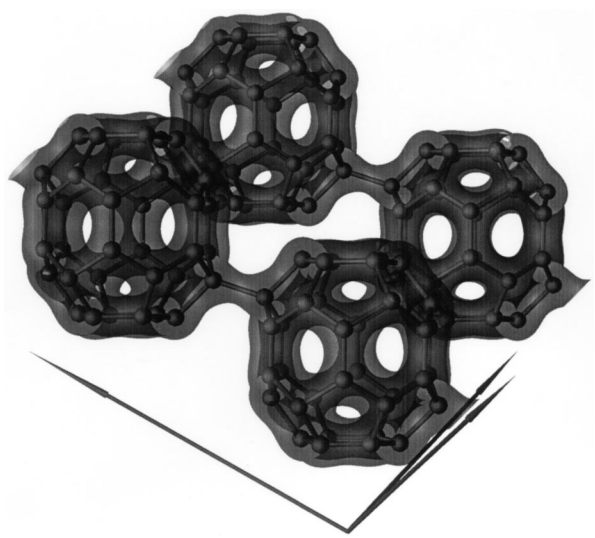

FIG. 1. Ball and stick model of the crystal structure of rhombohedral C_{36}. The length of the lattice vectors is 7.68 Å and the rhombohedral angle is 98.4°. The surface of constant charge density shows covalentlike bonding between the molecules.

addition, the orientation of the fullerenes in the crystal must be determined. Apart from the obvious orientation of the c axis of the fullerenes along the (111) direction of the lattice, there is also the freedom of rotating the unit along this axis within the cell which determines how the fullerenes interact with their neighbors. There are two different orientations: either the planes of the pentagon rings are face to face or the bonds on the pentagon belt face bonds on the neighboring fullerenes. Full structural relaxations [25], using six irreducible k points ($3 \times 3 \times 3$ shifted grid), in both orientations show that the case of bonds facing each other is energetically preferable.

As depicted in Fig. 1, we find that the C_{36} molecules bind together covalently with a distance of 1.56 Å between the closest atoms of neighboring molecules. Hence, this rhombohedral C_{36} solid will not be a van der Waals crystal but rather one where the fullerenes polymerize, similar to what is observed for A_1C_{60}. Any closed structure consisting of threefold coordinated atoms that form only pentagons and hexagons have 12 pentagons due to Euler's relations. Thus, the pentagons in C_{36} must touch, leading to more reactive sites than in C_{60} and favoring polymerization in the solid. Apart from this bonding, the basic shape of the fullerenes remains the same as in the isolated molecule. Our calculated equation of state gives a bulk modulus of 60 GPa, which is 4 times larger than that of solid C_{60}; the difference can be attributed to the extra covalentlike bonding in the C_{36} solid. The binding energy per C_{36} molecule in the solid is 2.2 eV, and the total cohesive energy for this solid is roughly 0.6 eV per atom higher than graphite, compared with that of 0.4 eV for solid C_{60}.

Figure 2 shows the density of states (DOS) per eV per C_{36} per spin, which has been calculated using a $4 \times 4 \times 4$ unshifted k-points grid in the Brillouin zone. Within the LDA, undoped rhombohedral C_{36} is metallic with a half-filled conduction band. The Fermi level E_F falls within a DOS peak, with a value comparable to that of the doped C_{60} superconducting materials (e.g., $\sim$6–14 states per molecule per eV per spin [1]). A closer look at the DOS reveals that, unlike the case of C_{60}, the ordering of the electronic levels near E_F is changed compared to the isolated C_{36} molecule. This is attributable to the intermolecular bonding. In the isolated case, the highest occupied and lowest unoccupied states are both singlets as shown in the inset of Fig. 2. In contrast to C_{60}, these states are reordered in solid C_{36} so that the conduction band arises from the broadened doublet states (E_{1g} and E_{2g}). Despite these orbital level order changes, the dispersion of the energy levels in the solid is about 1 eV, indicating that the solid is still mostly a molecular type crystal.

It has been argued that the curvature of the C_{60} fullerene is thought to be responsible [8,9] for the substantial increase in T_c in its solid phase compared

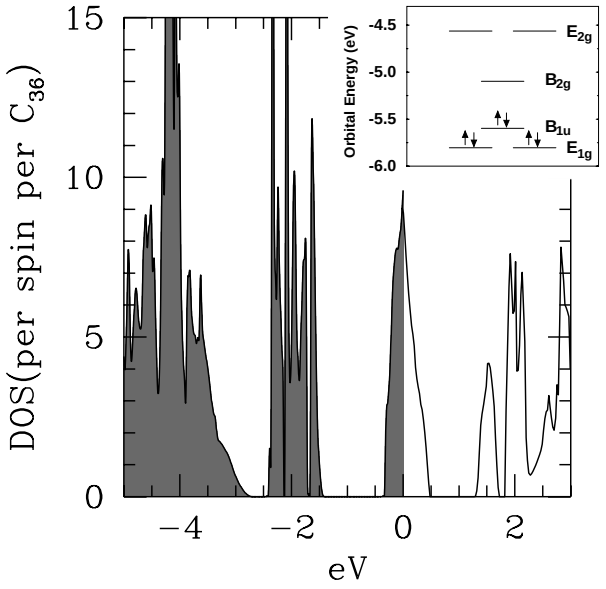

FIG. 2. Calculated density of states for the rhombohedral C_{36} structure. States near the Fermi energy are shown. The darker (lighter) region represents the occupied (unoccupied) states. The upper right inset shows the energy levels for the isolated molecule.

to intercalated graphite. Since C_{36} is even more curved than C_{60}, this argument is suggestive of even higher transition temperatures in C_{36} based solids. To explore this possibility, we have carried out state of the art calculations of the electron-phonon interaction potential, V_{ep}, which is used in the definition of the coupling parameter $\lambda = N(0)V_{ep}$, where $N(0)$ is the DOS at E_F.

One can extract V_{ep} from the electron-phonon spectral function [26], which is a double average over the Fermi surface connecting states due to the change in the potential caused by a phonon. For fullerene crystals, the computation is greatly simplified because of the small dispersion in both the electronic and phononic spectra. Therefore, one can use the electronic states and vibrational modes of the isolated molecule to approximate those found in the solid [9,10,13]; this implies that only the intramolecular modes are considered in the evaluation of V_{ep}. In the case of solid C_{36}, because of the intermolecular covalent bonds, one should carry out the full average over the Fermi surface. While such a calculation is prohibitive in practice, fortunately the C_{36} crystal is mostly molecularlike which allows us to use the procedure described above for the calculation of V_{ep}. Since the states of the isolated C_{36} molecule rearrange in the crystal, we evaluate V_{ep} for the four molecular states which are nearest in energy to E_F.

The dynamical matrix is constructed using the forces on the atoms where only nonequivalent atoms are moved along the three Cartesian directions, and the rest of the information is obtained from the symmetry properties of this matrix. Diagonalizing the dynamical matrix yields

the 3N dimensional polarization vectors, $\boldsymbol{\epsilon}_\alpha$, with normalization $\boldsymbol{\epsilon}_\alpha \cdot \boldsymbol{\epsilon}_\beta = \delta_{\alpha\beta}$ which means that we have to use the DOS per unit cell in the expression for λ. Using the approach outlined in the preceding paragraph, one can write

$$V_{ep} = \sum_\alpha \frac{1}{M\omega_\alpha^2} \frac{1}{g^2} \sum_{i,j=1}^{g} |\langle i|\boldsymbol{\epsilon}_\alpha \cdot \nabla V| j\rangle|^2, \quad (1)$$

where M is the mass of a carbon atom, i and j are degenerate electronic states in the isolated molecule for which we are evaluating the coupling, and g is the degeneracy of these states. The quantity $\langle i|\boldsymbol{\epsilon}_\alpha \cdot \nabla V| j\rangle$ is obtained by means of a finite difference approach. The application of selection rules to the matrix elements can be used as a consistency check to determine which vibrational modes should produce nonzero contributions. Within the LDA framework, we make no approximations or fits in our evaluation of V_{ep}.

Table I lists our calculated electron-phonon coupling values for several electronic states near E_F. The couplings due to the different phonon modes are listed separately since the A_g contribution to V_{ep} is expected to be screened out in A_3C_{60}. This effect has been observed by Raman-scattering experiments [27,28], as well as demonstrated theoretically within the random phase approximation for static screening [11].

Our results for C_{60} are in good agreement with previous LDA calculations [9–12]. The results show that the coupling in C_{36} is substantially larger than in C_{60} for the E_{1g} and E_{2g} degenerate states. The increase in V_{ep} for C_{36} supports arguments based on curvature. Note that, although the A_g phonon modes comprise a slightly larger percent contribution of V_{ep} for C_{36} than for C_{60}, even without the inclusion of these modes the coupling strength of the E_{2g} electronic state is still enhanced by more than a factor of 2 compared with C_{60}. Of course, for the singly degenerate B_{2g} and B_{1u} states, removal of the contributions from A_g phonons would reduce the coupling to zero. The strongest coupling, both with and without the A_g contributions, is due to the doublet electronic states which are also the dominant component of the large peak in the DOS at the Fermi energy in our calculations.

TABLE I. Electron-phonon coupling for the D_{6h} C_{36} molecule. States within 1 eV of the Fermi level are considered and the corresponding phonons which contribute to the electron-phonon interaction potential V_{ep} [see Eq. (1)] are listed. For each state, we list calculated values of V_{ep} (meV) for the given phonon modes. For comparison, the last row shows the same quantities calculated for A_3C_{60} with previous LDA results listed in parentheses.

Electronic states	Phonons coupled	V_{ep} (meV)
E_{2g}	A_{1g}	32
	E_{2g}	154
B_{2g}	A_{1g}	136
B_{1u}	A_{1g}	126
E_{1g}	A_{1g}	39
	E_{2g}	120
$T_{1u}(C_{60})$	A_g	8
	H_g	63 (52 [9], 56 [10], 68 [11], 49 [12])

We have analyzed each vibrational mode that gives a nonzero contribution to V_{ep}. Interestingly, the largest contributions to both singlet states involve one phonon which displaces the atoms along the direction of the covalent bonds between the molecules. In contrast, most of the contributions to V_{ep} from the conduction band doublet state involve motions of atoms in the top and middle layers of sixfold rings, which are not involved in intermolecular bonding. This observation is reinforced by the fact which is cited above that the two singlet states near E_F are greatly shifted upon formation of the solid whereas the doublets remain close to their original positions. It is likely, therefore, that coupling to the doublets will not cause serious deformation of the crystal and hence a structural transformation is not probable.

The strength of the electron-phonon interaction potential plays a crucial role in determining the superconducting transition temperature. Thus, our results imply that T_c in solid C_{36} can be significantly different than in solid C_{60}. The evaluation of T_c also requires knowledge of $N(0)$ and μ^*, which describes the Coulomb electron-electron repulsion. As we have shown, $N(0)$ for the solid C_{36} considered in this Letter is expected to be comparable to that of doped C_{60}. Very recent experimental evidence suggests that μ^* is about 0.25 for A_3C_{60} compounds [29]. We may expect μ^* for C_{36} to be close to this value since the range and width of narrow subbands near the Fermi level and typical phonon energies are similar. However, due to the sensitivity of T_c to μ^* and the fact that μ^* is not known for C_{36}, only a very qualitative comparison of T_c can be made here. As an example, if we choose the same $N(0)$ and μ^* for C_{60} and C_{36}, such that $T_c = 18$ K for C_{60}, then a solution of the Eliashburg equations yields T_c (C_{36}) $\approx 6T_c$ (C_{60}).

In summary, we have carried out *ab initio* pseudopotential density functional calculations for molecular and solid C_{36}. We suggest the possibility of forming a periodic structure using the C_{36} of D_{6h} symmetry and that this crystal is likely to form covalent bonds between the molecules. We analyze the electron-phonon interaction potentials for the four different electronic states near E_F and find that they are greatly enhanced compared to C_{60} for the two doubly degenerate states. The present work suggests that C_{36} fullerenes are excellent candidates for new superconducting solids. Finally, we mention that substitutional doping has also been considered and preliminary results for $C_{24}N_{12}$ solids look promising for further enhancement of both V_{ep} and $N(0)$.

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Note added.—Recently Piskoti *et al.* have successfully synthesized crystals made of the D_{6h} C_{36} structure [30].

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