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$_3$C$_{60}$ 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 $T_c$, although we note that the difference between the rhombohedral and hcp structures is in the second nearest neighbor [24]. In order to lessen computational demands, our calculations show that the rhombohedral lattice since it is small yet 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 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 corranulene-like 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 0.03 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.

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 $98.4^\circ$. The surface of constant charge density shows covalent-like 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 × 3 × 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\textsubscript{36} molecules bind together covalently with a distance of 1.56 Å between the closest atoms of neighboring molecules. Hence, this rhombohedral C\textsubscript{36} solid will not be a van der Waals crystal but rather one where the fullerenes polymerize, similar to what is observed for A\textsubscript{1}C\textsubscript{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\textsubscript{36} must touch, leading to more reactive sites than in C\textsubscript{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\textsubscript{60}; the difference can be attributed to the extra covalent-like bonding in the C\textsubscript{36} solid. The binding energy per C\textsubscript{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\textsubscript{60}.

Figure 2 shows the density of states (DOS) per eV per C\textsubscript{36} per spin, which has been calculated using a 4 × 4 × 4 unshifted k-points grid in the Brillouin zone. Within the LDA, undoped rhombohedral C\textsubscript{36} is metallic with a half-filled conduction band. The Fermi level E\textsubscript{F} falls within a DOS peak, with a value comparable to that of the doped C\textsubscript{60} superconducting materials (e.g., −6−14 states per molecule per eV per spin [1]). A closer look at the DOS reveals that, unlike the case of C\textsubscript{60}, the ordering of the electronic levels near E\textsubscript{F} is changed compared to the isolated C\textsubscript{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\textsubscript{60}, these states are re-ordered in solid C\textsubscript{36} so that the conduction band arises from the broadened doublet states (E\textsubscript{1g} and E\textsubscript{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\textsubscript{60} fullerene is thought to be responsible [8,9] for the substantial increase in T\textsubscript{c} in its solid phase compared to intercalated graphite. Since C\textsubscript{36} is even more curved than C\textsubscript{60}, this argument is suggestive of even higher transition temperatures in C\textsubscript{36} based solids. To explore this possibility, we have carried out state of the art calculations of the electron-phonon interaction potential, V\textsubscript{ep}, which is used in the definition of the coupling parameter \( \lambda = N(0)V_{ep} \), where N(0) is the DOS at E\textsubscript{F}.

One can extract V\textsubscript{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\textsubscript{ep}. In the case of solid C\textsubscript{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\textsubscript{36} crystal is mostly molecular-like which allows us to use the procedure described above for the calculation of V\textsubscript{ep}. Since the states of the isolated C\textsubscript{36} molecule rearrange in the crystal, we evaluate V\textsubscript{ep} for the four molecular states which are nearest in energy to E\textsubscript{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, $\epsilon_{\alpha}$, with normalization $\epsilon_{\alpha} \cdot \epsilon_{\beta} = \delta_{\alpha\beta}$ which means that we have to use the DOS per unit cell in the expression for $\lambda$. Using the approach outlined in the preceding paragraph, one can write

$$V_{ep} = \sum_{\alpha} \frac{1}{M} \frac{1}{g^2} \sum_{i,j=1}^{g} |\langle i | \epsilon_{\alpha} \cdot \nabla | j \rangle|^2,$$

(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 $\langle i | \epsilon_{\alpha} \cdot \nabla | j \rangle$ 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.

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 $\mu^*$, 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 $\mu^*$ is about 0.25 for $A_3C_{60}$ compounds [29]. We may expect $\mu^*$ 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 $\mu^*$ and the fact that $\mu^*$ 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 $\mu^*$ for $C_{60}$ and $C_{36}$, such that $T_c = 18$ K for $C_{60}$, then a solution of the Eliashberg equations yields $T_c (C_{36}) = 6 T_c (C_{60})$.

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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### Table I

<table>
<thead>
<tr>
<th>Electronic states</th>
<th>Phonons coupled</th>
<th>$V_{ep}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{2g}$</td>
<td>$A_{1g}$</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>$E_{2g}$</td>
<td>154</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>$A_{1g}$</td>
<td>136</td>
</tr>
<tr>
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<td>126</td>
</tr>
<tr>
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<td>$E_{2g}$</td>
<td>120</td>
</tr>
<tr>
<td>$T_{1u}(C_{60})$</td>
<td>$A_g$</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>$H_g$</td>
<td>63 (52 [9], 56 [10], 68 [11], 49 [12])</td>
</tr>
</tbody>
</table>
supercomputer. This work was supported by National Science Foundation Grant No. DMR-9520554 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Computational resources have been provided by NCSA and by NERSC. One of us (M.C.), acknowledges the support of the Natural Sciences and Engineering Research Council of Canada.

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