# Ground State and Phase Transitions in Solid $C_{60}$

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A simple model is developed to describe the intermolecular interactions in solid $C_{60}$. The model predicts correctly the observed ground-state structure $Pa\bar{3}$ and the first-order transition to the high-temperature fcc phase. The calculated transition temperature $T_c \sim 270$ K and its pressure dependence $dT_c/dP = 11.5$ K/kbar agree very well with recent experiments. Below $T_c$, there exist nearly degenerate orientations which are separated by potential barriers of order $\sim 300$ meV, leading to a glassy behavior with $T_g \sim 90$–130 K. It is suggested that similar orientational disorder exists in $K_3C_{60}$ and other fullerides.

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The recent discoveries of an efficient synthesis [1] of $C_{60}$ and superconductivity in $K_3C_{60}$ and $Rb_3C_{60}$ [2] have generated great interest in the structural and electronic properties of these materials. It is known that at room temperature $C_{60}$ molecules are centered at fcc Bravais lattice sites in both solid $C_{60}$ and $K_3C_{60}$ [3]. Recently it was reported [4] that solid $C_{60}$ undergoes a structural phase transition around 250 K from fcc to the simple cubic $Pa\bar{3}$ structure at low temperature. Both x-ray and NMR measurements [5] indicate that this transition is related to the orientational order of the $C_{60}$ molecules.

We have developed a model to study the basic structural properties of solid $C_{60}$. The model consists of two distinct types of intermolecular interactions. The dominant one is the van der Waals–type interactions between carbon atoms on different $C_{60}$ molecules. A secondary short-range Coulomb interaction is modeled by a small charge transfer between the two types of bonds in the $C_{60}$ molecule. In contrast to early calculations [6] which include the van der Waals interactions only, our model predicts correctly the observed cubic ground-state structure $Pa\bar{3}$. Many structural properties calculated, such as the compressibility, cohesive energy, and specific heat, are in good agreement with experiments [7].

Most importantly, the model enables us to examine the possible structural phase transitions and orientational order in bulk $C_{60}$. In this Letter we describe our model and summarize some of our basic results which include the following: (1) The orientationally ordered ground state is simple cubic with symmetry $Pa\bar{3}$ as observed in experiments [8]. (2) At $T_c$ the structure undergoes a first-order transition from $Pa\bar{3}$ to the high-temperature fcc phase where each molecule can freely rotate. The estimated transition temperature is $T_c \sim 270$ K, in agreement with experiments [4,9]. (3) The pressure dependence of the $T_c$ is calculated to be $dT_c/dP = 11.5$ K/kbar which agrees very well with the observed values of 11.7 and 10.4 K/kbar [10]. (4) Below $T_c$, there are many nearly degenerate orientations for each $C_{60}$ which are separated by potential barriers of order $\sim 300$ meV. This leads to novel frequency-dependent relaxation dynamics. (5) We predict that around $T_g \sim 90$–130 K the system undergoes a glassy transition when the equilibrium relaxation time exceeds the laboratory time scale. This explains the existence of disorder at low temperature as observed in the neutron-scattering experiments [9,11]. (6) It is suggested that similar disorder exists in fullerides such as $K_3C_{60}$ and $Rb_3C_{60}$.

*The intermolecular interactions and the ground state.*— As a result of the strong intra-$C_{60}$ covalent bonds one expects that the structural properties of bulk $C_{60}$ at low temperature are dominated by the weak inter-$C_{60}$ interactions. This is supported by the fact that the internal molecular structure is unchanged in the solid state. Since the minimum distance between two C atoms on different $C_{60}$ molecules (3 Å) is much larger than the covalent bond length, the interaction is primarily van der Waals in nature and can be described by the Lennard-Jones potential. As the minimum distance is comparable to the interlayer spacing in graphite (3.5 Å), it is reasonable to assume that the van der Waals interaction is similar to that in graphite. There are two parameters in the standard Lennard-Jones potential:

$$U(R) = 4\epsilon[(\sigma/R)^{12} - (\sigma/R)^6] . \tag{1}$$

In the case of graphite it is easy to see that lattice constant $c$ and the modulus of elasticity $c_{33}$ are solely determined by the above potential. From the well-documented graphite data [12], $c = 6.708$ Å and $c_{33} = 0.408 \times 10^{12}$ dyn/cm$^2$, it is found that $\epsilon = 2.964$ meV and $\sigma = 3.407$ Å.

If Eq. (1) is the only interaction between two $C_{60}$ molecules, then the ground state is found to be orthorhombic [6], in contradiction to the observed simple cubic structure $Pa\bar{3}$. On the other hand, the cohesive energy calculated is in fair agreement with experiment. This demonstrates that there exists a secondary interaction which makes the $Pa\bar{3}$ structure more stable. Indeed there is one crucial difference between a sheet of graphite and the $C_{60}$ molecule—the former contains only one type of covalent bond while there are two in the latter. Because of the differences in the bond length in $C_{60}$, 1.45 Å for "single" bonds and 1.40 Å for "double" bonds, one expects that there will be a deficiency of electrons in the single bonds and an excess in the double bonds. Such a charge transfer will naturally lead to short-ranged intermolecular Coulomb interactions. (Because the $C_{60}$ molecule is charge neutral and has a high symmetry, the interaction decays as $1/R^{13}$ at long distance.) This interaction will favor a nearest-neighbor configuration in which a pentagon (consisting of five single bonds) of a $C_{60}$ molecule faces an oppositely charged double bond of the other molecule. Indeed this has been found in experiments [8].

To model the secondary interaction we introduce an effective charge $q$ on single bonds (by the charge neutrality the effective charge on double bonds is $-2q$). Thus the total interaction between two $C_{60}$ molecules is

$$V_{12}=\sum_{i,j=1}^{60} 4\epsilon\left[\left(\frac{\sigma}{|\mathbf{r}_{1i}-\mathbf{r}_{2j}|}\right)^{12}-\left(\frac{\sigma}{|\mathbf{r}_{1i}-\mathbf{r}_{2j}|}\right)^{6}\right]+\sum_{m,n=1}^{90}\frac{q_m q_n}{|\mathbf{b}_{1m}-\mathbf{b}_{2n}|}, \qquad (2)$$

where $\mathbf{r}_{1i,2j}$ are coordinates of C atoms, $\mathbf{b}_{1m,2n}$ are coordinates of bond centers, and $q_{m,n}$ are the effective bond charges. The above interaction not only depends on the relative distance between the two molecules, but also on the orientations of two molecules, thus giving rise to interesting orientational dynamics in solid $C_{60}$.

Using the above interaction a search for the ground state was carried out by minimizing the total energy using the steepest descent method with four independent $C_{60}$ per unit cell. It is found that for $q > 0.21e$, where $e$ is the electron charge, the lowest energy state is always cubic with the $Pa\bar{3}$ symmetry. The ground-state orientation is described by rotating four molecules through the same angle $\phi=21.3°$ (clockwise) but about different $\langle 111\rangle$ axes: the molecule at (0,0,0) about [111], that at $(0,\frac{1}{2},\frac{1}{2})$ about $[\bar{1}1\bar{1}]$, that at $(\frac{1}{2},0,\frac{1}{2})$ about $[\bar{1}\bar{1}1]$, and that at $(\frac{1}{2},\frac{1}{2},0)$ about $[1\bar{1}\bar{1}]$ [8]. These rotations result in twelve identical nearest neighbors for each $C_{60}$ with six pentagons almost directly facing the double bonds of neighboring molecules, thus maximizing the short-range Coulomb interactions. Experimentally the rotational angle was found to be 22° and 26° [8], in good agreement with our calculation.

Since the only free parameter in our model is the effective charge $q$, we fixed it by fitting the low-temperature lattice constant. From $a=14.041$ Å [9] one obtains $q=0.27e$, which is reasonable as one expects that the charge transfer should be a fraction of a single electron charge. Once the effective charge is known, the intermolecular interactions, and hence the low-temperature structural properties, are completely determined. Elsewhere we summarize elastic properties, phonon and libron spectra, and specific heat [7]. These results are in close agreement with experiments where data are available. The calculated cohesive energy is $-1.990$ eV/$C_{60}$, of which 90% comes from the Lennard-Jones interaction and only 10% is due to the Coulomb part.

*The sc-fcc first-order transition.*— As the temperature increases, $C_{60}$ molecules can be thermally activated into other orientations. Therefore above a certain temperature $T_c$ one expects that they can rotate freely and the average structure will be fcc. Indeed at room temperature this is the observed experimental structure.

To estimate the transition temperature we employ a mean-field argument by calculating the free energies. For the fcc phase we approximate each $C_{60}$ as a three-dimensional free rotor. The free energy is the sum of the static energy $E_{\text{fcc}}$ and the free energy of three-dimensional rotors at temperature $T$, $F_{\text{fcc}}(T)=N[E_{\text{fcc}}-k_BT\times\ln 8\pi^2(Ik_BT/2\pi\hbar^2)^{3/2}]$, where $I=1.0\times10^{-43}$ kgm$^2$ is the moment of inertia for the $C_{60}$ molecule. The static energy $E_{\text{fcc}}$ is calculated by averaging over random configurations. In the $Pa\bar{3}$ phase each molecule vibrates around its optimal orientation. So, the free energy is the sum of the static energy $E_{Pa\bar{3}}$ and that of three-dimensional harmonic oscillators, $F_{Pa\bar{3}}(T)=N[E_{Pa\bar{3}}+3k_BT\ln(1-e^{-\hbar\omega_0/k_BT})]$, where $\omega_0=1.86\times10^{12}$ s$^{-1}$ is the average frequency of librons [7]. The transition temperature is identified as the point where the two free energies are equal. Using the lattice constant of $a=14.16$ Å [9] we find $E_{\text{fcc}}=-1.772$ eV/$C_{60}$ and $E_{Pa\bar{3}}=-1.968$ eV/$C_{60}$, from which we obtain a first-order transition at $T_c\sim270$ K. The change of entropy at the transition temperature is estimated to be $\Delta S\sim6R$ from the calculated $T_c$. Experimentally it is found that there is a first-order transition at 260 K [9]. The measured entropy discontinuity ranges from $2.1R$ [4] to $3.7R$ [13]. We expect that our mean-field estimation of the entropy discontinuity is very crude; a Monte Carlo study [14] is being carried out to calculate thermodynamic properties near $T_c$.

Using the above criteria we also calculated the pressure dependence of the transition temperature. Elsewhere [7]

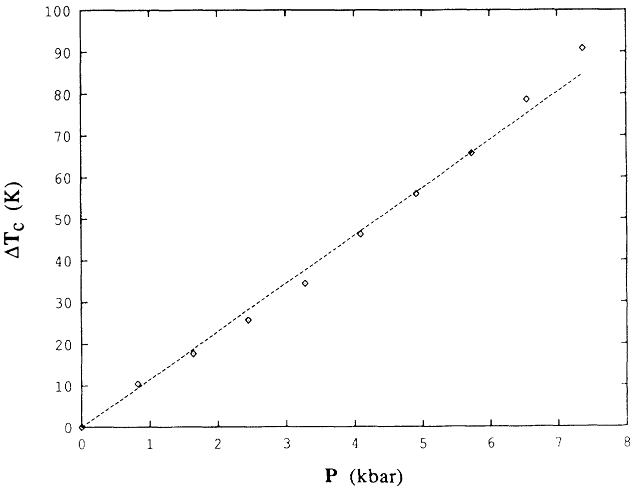

FIG. 1. The increment of the first-order transition temperature $T_c$ as a function of the pressure. The calculated $T_c$ at zero pressure is 270 K. A linear fitting through the calculated points gives $dT_c/dP=11.5\pm0.7$ K/kbar. This is in good agreement with recent experimental results of 11.7 and 10.4 K/kbar [10].

we have calculated the compressibility of the ground state to be $K_0=5.175$ Mbar$^{-1}$ which leads to $da_0/dP=0.024$ Å/kbar. Assuming that the only effect of the pressure is to change the lattice constant we calculated the static energy $E_{Pa\bar{3}}$ and $E_{\mathrm{fcc}}$ as functions of pressure from which the transition temperature is obtained. Figure 1 shows the calculated increment of $T_c$ as a function of the pressure. The linear fitting gives a slope of $dT_c/dP=11.5 \pm 0.7$ K/kbar. This result agrees very well with recent experimental results of 11.7 and 10.4 K/kbar [10].

*The glassy transition at low temperature.*— As described in the previous section, in the ideal ground-state structure each $C_{60}$ molecule has a unique orientation. However, there are many local minima with energy close to that of the ground state. These local minima are separated by large potential barriers of 300 meV. An example is shown in Fig. 2 where the potential energy for the $C_{60}$ at (0,0,0) is shown as a function of the rotation angle along three high-symmetry axes. As one can see there are many local minima; particularly a rotation of 60° along the threefold axis leads to a deep local minimum. Near $T_c$ one expects there will be a thermal distribution of orientations among different local minima, achieved by thermal activation of molecules from one local minimum to another. As temperature decreases, the time needed to reach equilibrium increases exponentially, similar to what occurs in the orientational glasses such as $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ [15]. Thus we expect that at a temperature for which the equilibrium time exceeds the experimental time scale, the system freezes with a finite amount of disorder which persists down to zero temperature. This explains the neutron-scattering results which indicate that even at 14 K there is still about 20%–30% of disorder [9,11].

The freezing temperature $T_g$ can be roughly estimated by considering the transition rate $1/\tau$ for a molecule to be thermally activated between local minima,

$$1/\tau = \nu e^{-E_b/k_BT}, \tag{3}$$

where $\nu \sim 10^{12}$ Hz is the libration frequency and $E_b \sim 300$ meV is the typical potential barrier. $\tau$ should serve as a time scale needed for the system to reach equilibrium. From Eq. (3) one concludes that $\tau$ changes from 1 s to 1 day between 130 and 90 K. Therefore we expect that within this temperature range the system undergoes a glassy transition below which disorder becomes frozen. The amount of disorder will depend on the experimental details such as the cooling rate.

Equation (3) has several other important implications which can be directly confirmed by finite-frequency probes. One example is the motion-narrowing effect in NMR experiments which is expected to disappear when $1/\tau$ is below the chemical-shift-anisotropy (CSA) width. Indeed the NMR results of Tycko *et al.* [16] indicate that for a CSA width of 18.2 kHz the line broadens below 190 K and develops a powder pattern at lower temperature. This is in fair agreement with the 200 K calculated from Eq. (3). They also concluded that the thermal activation energy is around 260 meV below $T_c$, again close to the values we calculated. The glassy dynamics can be probed by other experiments such as sound attenuation, microwave absorption, and thermal conductivity. In particular the characteristic temperature will depend on probe frequency. Such studies are essential to fully understand the low-temperature orientational dynamics.

Finally, we comment on the existence of similar disorder in doped fullerides. For the metallic $K_3C_{60}$ it has been shown that at room temperature the structure is fcc with $C_{60}$ centered on the fcc Bravais lattice site and three K occupying the tetrahedral and octahedral interstitial sites [3]. It is also known that there are only two possible orientations for each molecule, corresponding to two possible ways of lining up the three orthogonal twofold axes of the icosahedron with cubic lattice axes. At high temperature, one expects that each $C_{60}$ molecule can randomly flip between the two orientations. Because of the presence of ionic charge, one expects that the potential barrier between the two orientations is substantially larger than that in pure $C_{60}$. Hence the freezing temperature could be higher than that estimated for the bulk $C_{60}$. Whether it is higher than the characteristic temperature when K ions start to be mobile is an interesting question. At the moment, we are not aware of any experiments which probe this orientational disorder. It is expected that if such a glassy transition exists, it could have a strong effect on the normal-state transport properties.

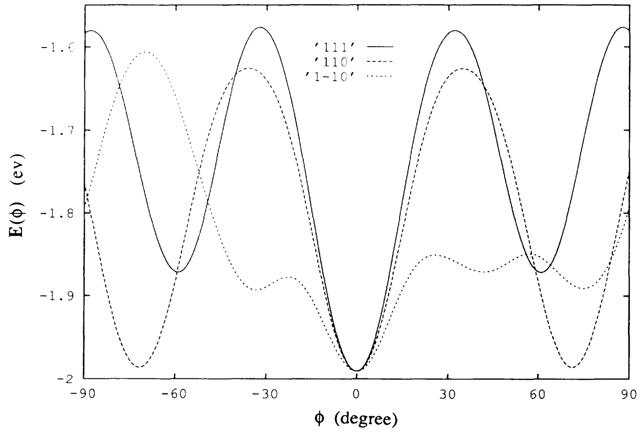

FIG. 2. The potential energy for the $C_{60}$ sitting at (0,0,0) as a function of rotation angle away from its equilibrium orientations. "111," "110," and "1-10" correspond, respectively, to threefold, fivefold, and twofold rotation axes of the molecule.

In conclusion, we have constructed a model for the intermolecular interactions in solid $C_{60}$. The basic structural properties calculated are in good agreement with experiments. It is shown that around $T_c \sim 270$ K the structure undergoes a first-order transition from the high-temperature fcc phase to the ordered $Pa\bar{3}$ structure. The pressure dependence of the transition temperature is calculated to be $dT_c/dP = 11.5$ K/kbar which agrees very well with recent experiments. We predict that between 90 and 130 K the system should undergo a glassy transition below which there is a finite amount of frozen disorder. This is due to the existence of many local minima which are separated by potential barriers of order 300 meV. The glassy behavior should manifest interesting frequency-dependent relaxation dynamics [17]. Finally, we expect that similar disorder exists in $K_3C_{60}$ and other fullerides.

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[17] After we finished the manuscript we learned of recent experiments by X. Shi *et al.* on sound attenuation (to be published) and by R. Yu *et al.* on thermal conductivity (private communication). Their results indicate that there is a frequency-dependent glassy behavior at low temperature, in agreement with our predictions.