

## Ground-state structural and dynamical properties of solid $C_{60}$ from an empirical intermolecular potential

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(Received 23 January 1992)

A simple intermolecular potential is constructed to describe solid  $C_{60}$ . The structural and elastic properties are calculated and show good agreement with available experimental results. Phonon-dispersion curves and density of states are predicted. The librational modes are found to be between 10 and 20  $\text{cm}^{-1}$  and the highest vibrational mode is at 45  $\text{cm}^{-1}$ . The phonon density of states is used to calculate the specific heat, which agrees reasonably well with experiment.

Following the recent success in generating macroscopic quantities of  $C_{60}$  molecules,<sup>1</sup> there has been intense interest and activity in studying various properties of solid  $C_{60}$ . The structure of solid  $C_{60}$  at room temperature has been determined to be face-centered-cubic<sup>2</sup> (fcc), with  $C_{60}$  molecules almost freely rotating, and the ground-state structure to be simple cubic<sup>3,4</sup> (sc, with space group  $Pa3$ ). Furthermore, an orientational order-disorder phase transition has been observed.<sup>2</sup> Many theoretical, first-principles investigations have been carried out,<sup>5-7</sup> but the ground-state structure is assumed to be fcc instead of sc in these studies. We have constructed an empirical classical potential for intermolecular interactions which takes into account the features that stabilize the observed ground state. In a separate paper we show our potential predicts the phase transition to the rotating phase accurately.<sup>8</sup> Here we show that the same potential describes

well the structural and elastic properties. The intramolecular phonon modes have been studied both experimentally<sup>9</sup> and theoretically.<sup>10,11</sup> With the use of our classical potential, we are able to predict the vibrational and librational phonon modes and specific heat of solid  $C_{60}$  at low temperatures.

TABLE I. Structural and elastic properties of solid  $C_{60}$  at  $T=0$  K.

	Present theory	Experiment
Cohesive energy (eV)	1.988	1.739(56) <sup>a</sup>
Lattice constant ( $\text{\AA}$ )	14.049	14.05, <sup>b</sup> 14.041 <sup>c</sup>
Angle $\phi$ (deg)	21.22	26, <sup>b</sup> 22 <sup>c</sup>
Bulk modulus $B_0$ (Mbar)	0.1932	0.181(18), <sup>d</sup> 0.143(20) <sup>e</sup>
Compressibility $K_0$ (Mbar <sup>-1</sup> )	5.175	5.52(55), <sup>d</sup> 7(1) <sup>e</sup>
$dB_0/dP$	18.2	5.7(6) <sup>d</sup>
$c_{11}$ (Mbar)	0.2986	
$c_{12}$ (Mbar)	0.1405	
$c_{44}$ (Mbar)	0.1590	

<sup>a</sup>Reference 14, at  $T=707$  K (above the phase transition).

<sup>b</sup>Reference 3, at  $T=11$  K.

<sup>c</sup>Reference 4, at  $T=5$  K.

<sup>d</sup>Reference 13, at room temperature (above the phase transition).

<sup>e</sup>Reference 12, at room temperature (above the phase transition).

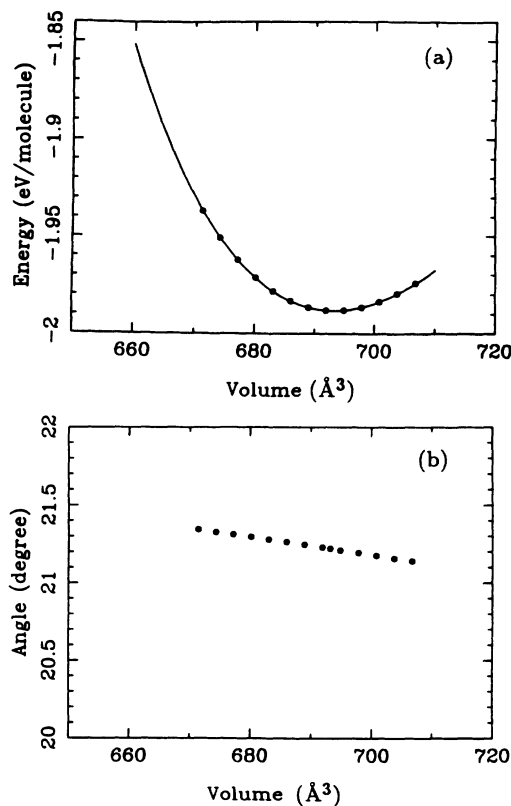


FIG. 1. (a) Equation of state of solid  $C_{60}$  at  $T=0$  K. The solid line is the result of a least square fit with the Murnaghan equation of state. (b) The angle  $\phi$  (the only degree of freedom in space group  $Pa3$ , see text) as a function of volume.

Our intermolecular potential is of the following form:<sup>8</sup>

$$V(I,J) = 4\epsilon \sum_{i,j} \left[ \left( \frac{\sigma}{r_{ij}^{IJ}} \right)^{12} - \left( \frac{\sigma}{r_{ij}^{IJ}} \right)^6 \right] + \sum_{l,m} \frac{q_l q_m}{b_{lm}^{IJ}}, \quad (1)$$

where  $I$  and  $J$  denote two molecules,  $r_{ij}^{IJ}$  is the distance between the  $i$ th atom in molecule  $I$  and the  $j$ th atom in molecule  $J$ , and  $b_{lm}^{IJ}$  is the distance between the bond centers of the  $l$ th bond in molecule  $I$  and the  $m$ th bond in molecule  $J$ . The first part of the potential is a Lennard-Jones (LJ) potential between the carbon atoms in different  $C_{60}$  molecules, and the second part is a Coulomb interaction which arises from a net charge transfer between the two types of bonds in a  $C_{60}$  molecule. This potential has been employed to study phase transitions in solid  $C_{60}$  successfully.<sup>8</sup>

Using the potential of Eq. (1), we can easily calculate various properties of solid  $C_{60}$  at  $T=0$  K. In Ref. 8, Lu, Li, and Martin showed that at  $T=0$  K, solid  $C_{60}$  is in a

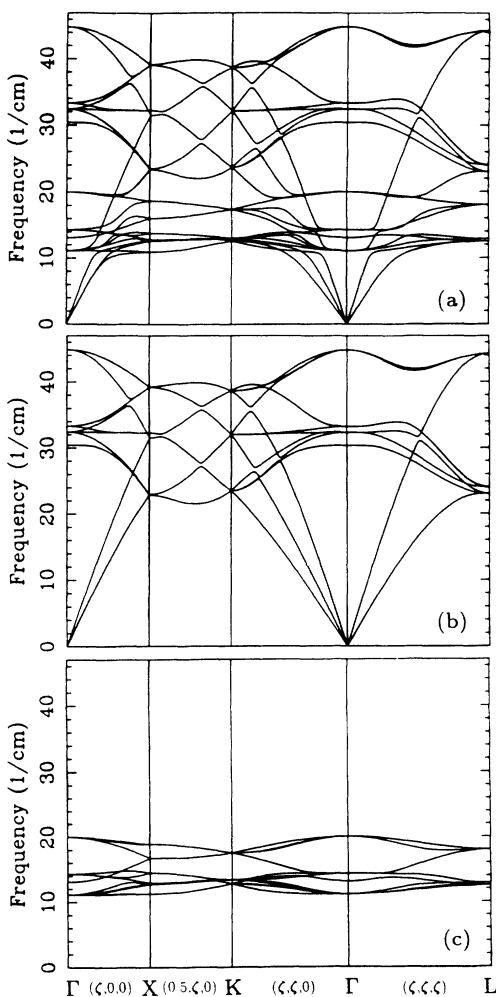


FIG. 2. (a) Phonon-dispersion curves along some high-symmetry directions. (b) and (c) are the vibrational and librational modes, respectively, when the coupling between them is turned off.

partly ordered glassy state, but here we concentrate on the ideal ground state. The equation of state is shown in Fig. 1(a), and the structural and elastic properties are listed in Table I. The calculated compressibility and bulk modulus are in good agreement with experimental results.<sup>12,13</sup> The calculated pressure derivative of the bulk modulus at  $T=0$  K is, however, much larger than the experimental result at room temperature, probably because of the phase transition and the volume change due to thermal expansion. The heat of sublimation has only been measured<sup>14</sup> at high temperature (707 K) and should not be compared directly with our  $T=0$  K cohesive energy because of the first-order phase transition in between. Nevertheless, the calculated cohesive energy seems reasonable to be slightly larger than the high-temperature heat of sublimation.

In the ground-state structure of solid  $C_{60}$  with space group  $Pa\bar{3}$ , there is only one free parameter, the angle  $\phi$  that each molecule rotates,<sup>3,4</sup> if the volume is given. Figure 1(b) shows this angle as a function of volume. Remarkably,  $\phi$  is almost a constant. This is not surprising because  $\phi$  is determined by the energetically favored relative orientation of two neighboring molecules, i.e., a negatively charged double bond in one molecule facing a positively charged pentagon in the other. This relative orientation does not depend on the volume.

The phonon-dispersion curves along some symmetry lines in the first Brillouin zone are shown in Fig. 2(a). Since there are four  $C_{60}$  molecules in a unit cell and each molecule has six degrees of freedom (three translational and three rotational), there are totally 24 branches of dispersion curves. It is not difficult to tell the vibrational modes from the librational modes; there is, however, coupling between them. Figures 2(b) and 2(c) show the vibrational and librational modes, respectively, when the coupling between them is turned off. If Figs. 2(b) and 2(c) are put on top of each other, the curves are very similar to those in Fig. 2(a), except where some of the vibrational and librational curves cross, indicating that the coupling between them is weak.

The phonon density of states (DOS) is shown in Fig. 3. The three peaks between 10 and 20  $\text{cm}^{-1}$  correspond to

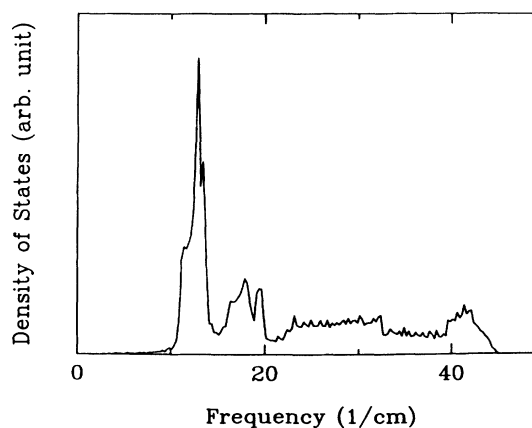


FIG. 3. Phonon density of states.

the librational modes. The highest vibrational frequency is  $45 \text{ cm}^{-1}$ . Neutron-scattering experiments<sup>15</sup> found that the librational frequency is around  $2.8 \text{ meV}$ , or  $23 \text{ cm}^{-1}$ , slightly higher than our calculated result. The specific heat is calculated using our phonon DOS and the intramolecular phonon modes of a free molecule given by other authors,<sup>16</sup> assuming that the intramolecular vibrational modes do not differ appreciably between the solid and a free molecule. Figure 4 compares our calculated specific heat  $C_v$  with experimental  $C_p$  (Ref. 17), and the agreement is very good except at the peak near the phase transition. The difference between  $C_v$  and  $C_p$  is expected to be small in a solid at low temperature, thus this comparison is valid. The contribution from the intermolecular phonon modes saturates at about 30 K, and the intramolecular phonons start to contribute at about 60 K. At very low temperature, our specific heat is higher than the recently measured results,<sup>18</sup> reflecting the fact that our librational frequency is higher than experiment.

In summary, we have constructed a classical intermolecular potential for  $\text{C}_{60}$ . The ground state structural and elastic properties calculated using this potential are in agreement with experimental results. Intermolecular phonon-dispersion curves and density of states have been

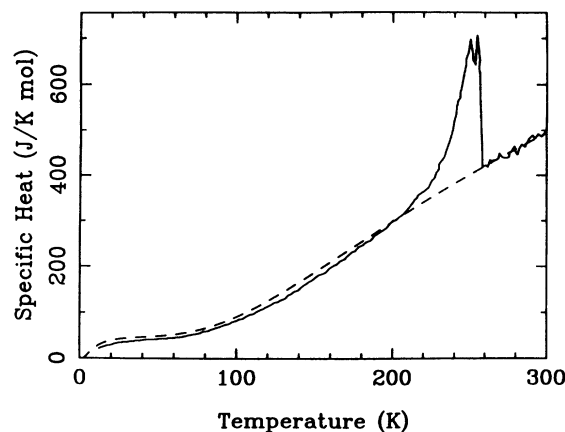


FIG. 4. Calculated specific heat  $C_v$  (dashed line) compared with experimental  $C_p$  (solid line).

predicted, and the calculated specific heat agrees with experiment reasonably well.

This work was supported by the National Science Foundation (No. NMR 89-20538) and the Department of Energy (No. DEFG02-91ER45439).

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