Calculation of static, dynamic, and thermodynamic properties of solid C_{60}

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Using a simple intermolecular potential we study a large number of properties of solid C_{60} in its sc and fcc phases. By establishing an equation of state for the cell parameter $a(P,T)$ we are able to calculate the behavior of both phases as a function of temperature and pressure in a unified, consistent framework.

Recently, numerous theoretical and experimental papers dealing with properties of solid C_{60} that depend essentially on its intermolecular interactions have appeared in the literature. Quite a few calculations address the order-disorder phase transition,[1–4] and many others address specific experimental results.[5–9] Here we present a calculation, based on a simple intermolecular potential, which deals with all relevant experiments (known to us) on both the ordered and the disordered phases in a unified, consistent way. These properties include the following: crystal structure, partial orientational disorder, thermal expansion, heat of sublimation, bulk modulus, specific heat, speed of sound, dynamical properties, critical temperature of the phase transition and discontinuity in cell parameter and speed of sound associated with it, transition heat, and changes in these properties induced by pressure.

Our model consists of atom-atom interactions of the Buckingham type between C nuclei sites, with parameters fitted by Pertsin and Kitaigorodskii[10] for hydrocarbon molecular crystals, and electrostatic interactions. These are represented by 30 charges $-q$ located at the double bonds and 12 charges $5/2q$ at the centers of the pentagonal faces. A previous study of electrostatic interactions[11] shows that this choice of interaction sites is as suitable as (and more economical than) that of 90 charges on the simple and double bonds, previously used,[8] and better than another one locating charges in angular positions of the C nuclei, which yields a wrong minimum energy structure.[4] The only free parameter in our model was chosen as $q=0.25e$, for reasons given below. The lengths of the double and single bonds were taken as 1.40 and 1.44 Å,[12,13] respectively.

At $T<260$ K crystalline C_{60} is simple cubic (sc) $Pa\bar{3}$,[13–15] and shows partial disorder in the molecular orientation characterized by the angle Φ, defined as the counterlockwise rotation of the origin molecule about the crystal [111] direction, starting from the standard orientation in which three twofold molecular axes coincide with the crystal axes. In the equilibrium structure at low temperature $\Phi=98°$; interaction sites at the nuclei positions yield the lowest minimum at $\Phi\sim48°$ and a secondary one at $\sim97°$.[11,16] Electrostatic interactions produced by charges located on other sites may invert the relative depths of the minima; in our case, we need $q>0.23e$. On the other hand, the orientational disorder observed with different techniques,[14,15,17] which partially remains at low temperatures, requires the two minima to be separated by potential barriers of ~6–7 K cal/mol, with energy differences $\Delta E\sim0.2$ K cal/mol. In our model, these conditions are met for $q<0.28e$. Taking $q=0.25e$ our model correctly predicts a minimum energy $Pa\bar{3}$ structure, with $a_{\min}=13.92$ Å, about 0.7% lower than the cell parameter observed at 5 K,[13] and $\Phi=97°$. When a single molecule is rotated, secondary minima at $97\pm60°$, separated by barriers of 6.5 K cal/mol with $\Delta E=1.5$ K cal/mol appear. If all molecules in the crystal are rotated preserving the crystal symmetry, we find a secondary minimum at about $\Phi=49°$, with $\Delta E=0.3$ K cal/mol and barriers of 3.0 K cal/mol. These situations correspond to extreme cases of individual molecules bouncing between different positions and the existence of domains. The calculated cohesion energy is $E_{sc}=-41.9$ K cal/mol, with 92% due to atom-atom interactions.

The model predicts that for the cell parameter a in the range $a=a_{\min}\pm0.4$ Å, the positions of the minima are nearly independent of a. This fact allows a simple, self-consistent description of the properties under consideration as a function of temperature and pressure, enabling us to establish numerically an equation of state $a=a(P,T)$. To do so, we have calculated E_{sc}, the vibrational density of states (DOS) of the sc crystal in the quasiharmonic and rigid molecule approximations, and the vibrational contribution to the free energy F_{sc}, for a in the range $a_{\min}\pm0.4$ Å, and $T<400$ K, at zero pressure. Minimizing $G_{sc}(T,P=0)=E_{sc}(a)+F_{sc}(T,a)$, we obtain $a(T)$, shown in Fig. 1. The calculated thermal ex-

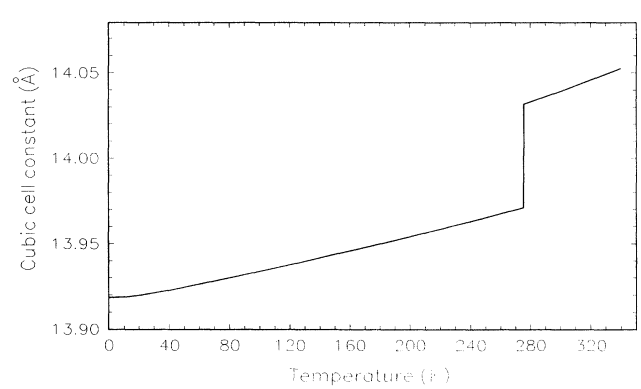

FIG. 1. Cell parameter $a(T)$ of the sc and fcc phases.

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pansion in the range 0–250 K, 0.048 Å, compares well with the experimental value 0.055 Å.[14] Figure 2 shows the DOS at $T=0$. The results are qualitively similar to those found by Cheng and Klein[2] with a molecular-dynamics method, and very recently by Li, Lu, and Martin[9] with a 90 charge model, although our low-frequency peak, due to librational motions, is centered at ~ 17 cm^{-1}, compared to the 23 cm^{-1} observed by neutron scattering,[18] and to the 20–21 cm^{-1} (Ref. 6) estimated from specific heat measurements, whereas the calculations in Refs. 2 and 9 give 11 and 13 cm^{-1}, respectively. The calculated optical frequencies at $T=0$, in cm^{-1} are $57.6(F_u)$; $42.6(E_u)$; $41.6(F_u)$; $39.5(A_u)$; $26.1(F_g)$; $18.9(F_g)$; $16.2(A_g)$; $14.3(E_g)$; $14.1(F_g)$. Far-infrared spectra[19] show peaks at 58.5, 41, 37, 21.6, 17.7, 12.8, and 8.5 cm^{1}; allowing for the infrared activation of modes due to impurities and/or orientational disorder, the agreement with our calculations is excellent. The optical frequencies calculated by Li, Lu, and Martin[9] are about 30% lower in the average, indicating that their potential parameters are much too soft.

Figure 3 shows observed and calculated values of C_v/T vs T in the range 0–20 K; the agreement is qualitatively correct: the early rising of the calculated curve is due to the somewhat too low value of the librational peak. It should be noted that this is a very revealing way to present the results: a C_v vs T plot in the range 0–400 K does not show these details.[9] Figure 4 shows the longitudinal and transverse speeds of sound, v_l and v_t, for the

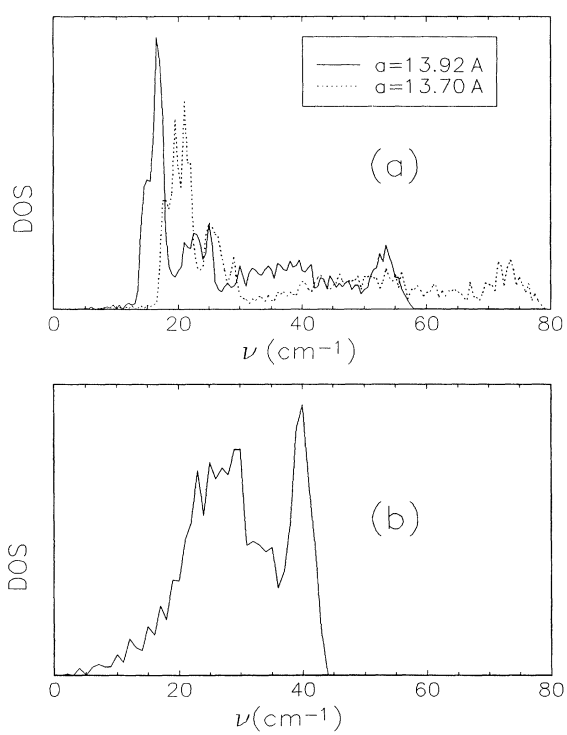

FIG. 2. Vibrational densities of states of (a) the sc phase for $a(T=0,P=0)$ and $a(T=0,P=1.1$ GPa), and (b) the fcc phase for $a(T=280$ K, $P=0)$.

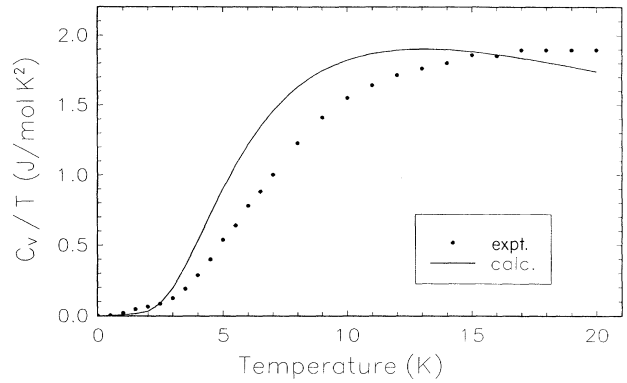

FIG. 3. C_v/T vs T for the sc phase at low temperatures.

[111] and [100] directions. In all cases $\Delta v/v_0$, the variation of v with respect to v at $T=0$ in the range 0–250 K, is $\sim 8\%$, lower than the observed 13%.[20] The absolute values are consistent with those estimated using a Debye approximation[6] and, in the average, obey Cauchy's criterion.

At 260 K crystalline C_{60} undergoes a first-order phase transition to a fcc structure of quasifree rotors, with uncorrelated rotational diffusion.[19,21] With a mean-field argument, used before,[8] we have calculated the transition temperature T_c and the changes in volume, entropy, etc. associated with it. Assuming spherical, freely rotating molecules, we average the interaction energy of neighboring molecules over relative orientations in the range $13.6<a<14.4$ Å. It should be noted that electrostatic interactions do not contribute to this average. With the effective potential thus obtained we calculate E_{fcc}, the DOS of the accoustic modes [shown in Fig. 2(b)] and their contribution to F_{fcc}. Minimizing the free energy $G_{fcc}(T,P=0)=E_{fcc}(a)+F_{fcc}(a,T)+F_{rot}(T)$, where $F_{rot}(T)$ is the classical contribution of free rotators, we obtain $a(T)$ in the fcc phase (Fig. 1). The crossing of the functions $G_{sc}(T,P=0)$ and $G_{fcc}(T,P=0)$ occurs at $T_c\sim 275$ K. The discontinuities in the cell parameter, 0.059 Å (Fig. 1), and in the entropy, $2.4R$, are in good

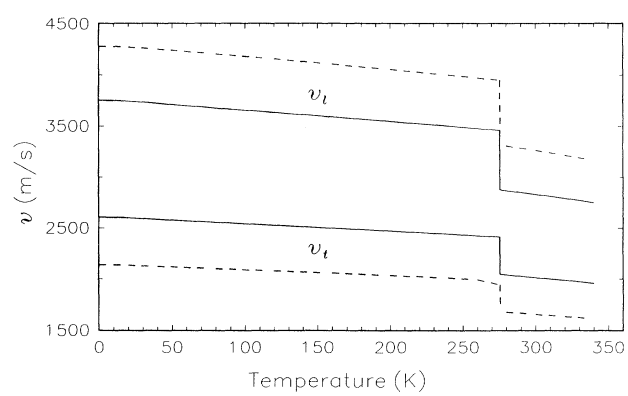

FIG. 4. Longitudinal and transverse sound velocities of the sc and fcc phases in the [111] (dashed lines) and [100] (full lines) directions.

agreement with the experimental values 0.049 Å (Ref. 14) and $2.1R$.[22] The discontinuities in the speed of sound (Fig. 4), however, are in excess of the experimental value of 4%.[20]

Pressure effects may be introduced simply by adding to the free-energy expression a PV term. Minimizing this function, we have calculated $a(T,P)$ and the properties discussed above as a function of temperature and pressure for both phases. In particular, the model predicts changes of T_c with pressure of 70 K/GPa, decreasing with pressure, compared with 100 K/GPa found experimentally in the range 0–1 GPa.[22] The calculated critical pressure at room temperature is $P_c = 0.4$ GPa, in coincidence with the observed value;[23] therefore all high-pressure experiments should be interpreted in terms of the sc phase. In particular, the cell contraction from $P=0$ to 1.2 GPa, reported in Ref. 24 to be 0.4 Å, includes the discontinuity due to the phase transition, ~0.05 Å; our calculation yields 0.33 Å. Two values for the bulk modulus at room temperature have been reported: $B=18.1$ GPa (Ref. 24) and $B=14.5$ GPa;[25] our calculated value is ~13 GPa. In Fig. 5 we show measurements of $\Delta V/V_0$ vs P,[24] and compare them with our results on the sc phase.

All the calculations on the sc phase presented here were performed assuming a perfect crystal in the equilibrium position $\Phi=97°$. Calculations using $\Phi=48°$ do not dramatically alter the results. However, it should be noted that as the cell contracts, atom-atom interactions get stiffer faster than the electrostatic ones, and therefore the relative depth of the two minima changes. With our model, $\Delta E=0$ for $P\sim0.6$ GPa at room temperature; since at the same time the barrier height increases considerably, it is clear that populations of the minima at low temperature and high pressure will strongly depend on the order in which the samples are cooled down and compressed. Experiments along this line would certainly reveal further details of the intermolecular interactions in solid fullerites.

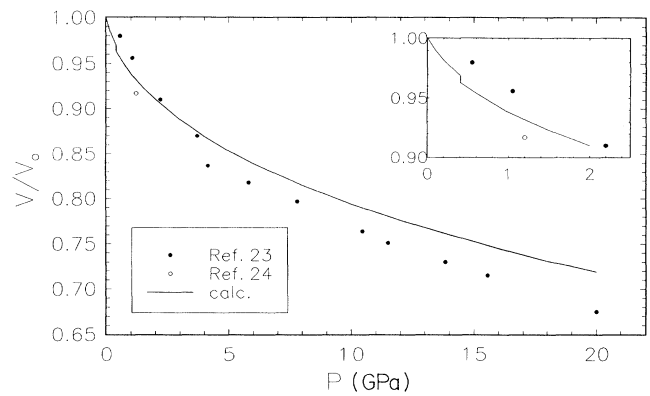

FIG. 5. Fractional change in volume of the sc phase as a function of pressure. The pressure induced fcc-sc transition is shown in the inset.

[1]A. Cheng and M. L. Klein, J. Phys. Chem. **95**, 6750 (1991).
[2]A. Cheng and M. L. Klein, Phys. Rev. B **45**, 1889 (1992).
[3]K. H. Michel, J. R. D. Copley, and D. A. Neumann, Phys. Rev. Lett. **68**, 2929 (1992).
[4]M. Sprik, A. Cheng, and M. L. Klein, J. Phys. Chem. **96**, 2027 (1992).
[5]Y. Guo, N. Karasawa, and W. A. Goddard III, Nature **351**, 464 (1991).
[6]W. P. Beyermann, M. F. Hundley, and J. D. Thompson, Phys. Rev. Lett. **68**, 2046 (1992).
[7]R. C. Yu, N. Tea, N. B. Salamon, D. Lorentz, and R. Malhotra, Phys. Rev. Lett. **68**, 2050 (1992).
[8]J. P. Lu, X.-P. Li, and R. M. Martin, Phys. Rev. Lett. **68**, 1551 (1992).
[9]X.-P. Li, J. P. Lu, and R. M. Martin, Phys. Rev. B **46**, 4301 (1992).
[10]A. J. Pertsin and A. I. Kitaigorodskii, *The Atom-Atom Potential Method* (Springer-Verlag, Berlin, 1987).
[11]E. Burgos, E. Halac, and H. Bonadeo, Phys. Rev. B **47**, 7542 (1993).
[12]J. M. Hawkins *et al.*, Science **252**, 312 (1991).
[13]W. I. F. David, R. M. Ibberson, J. C. Mathewman, K. Prassides, T. S. J. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, and R. M. Walton, Nature **353**, 147 (1991).
[14]W. I. F. David, R. M. Iberson, T. J. S. Dennis, J. P. Hare, and K. Prassides, Europhys. Lett. **18**, 219 (1992).
[15]R. Moret, P. A. Albouy, V. Agafonov, R. Ceolin, D. Andre, A. Dworkin, H. Szwarc, C. Fabre, A. Rassat, A. Zahab, and P. Bernier, J. Phys. I **2**, 551 (1992).
[16]Z. Gamba and M. L. Klein, in *Condensed Matter Theories,* edited by L. Blum and F. B. Falik (Plenum, New York, in press).
[17]R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991).
[18]D. A Neumann, J. R. D. Copley, W. A. Kamitakahara, J. J. Rush, R. L. Cappelletti, N. Coustel, J. P. McCauley, Jr., J. E. Fischer, A. B. Smith III, K. M. Creegan, and D. M. Cox, J. Chem. Phys. **96**, 8631 (1992).
[19]S. Huant, J. B. Robert, G. Chouteau, P. Bernier, C. Fabre, and A. Passat, Phys. Rev. Lett. **69**, 2662 (1992).
[20]X. D. Shi, A. R. Kortan, J. M. Williams, A. M. Kini, B. M. Savall, and P. M. Chaikin, Phys. Rev. Lett. **68**, 827 (1992).
[21]D. A. Neumann, J. R. D. Copley, R. L. Cappelletti, W. A. Kamitakahara, R. M. Lindstrom, K. M. Creegan, D. M. Cox, W. J. Romanow, N. Coustel, J. P. McCauley, Jr., N. C. Maliszewskyj, J. E. Fischer, and A. B. Smith III, Phys. Rev. Lett. **67**, 3808 (1991).
[22]P. A. Heiney, J. E. Fischer, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, A. B. Smith III, and D. E. Cox, Phys. Rev. Lett. **66**, 2911 (1991).
[23]G. A. Samara, J. E. Schirber, B. Morosin, L. V. Hansen, D. Loy, and A. P. Sylwester, Phys. Lett. **67**, 3136 (1991).
[24]S. J. Duclos, K. Brister, R. C. Haddon, A. R. Kortan, and F. A. Thiel, Nature **351**, 380 (1991).
[25]J. E. Fischer, P. A. Heiney, A. R. McGhie, W. J. Romanow, A. M. Denenstein, J. P. McCauley, and A. B. Smith III, Science **252**, 1288 (1991).