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Extended Mie-Grüneisen theory applied to C_{60} in the disordered fcc phase

L. A. Girifalco
Department of Materials Science, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272

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The large difference between the interatomic forces within a C_{60} molecule and the intermolecular forces allows the intermolecular contributions to thermodynamic properties to be treated by a simple pairwise central force theory when the molecules are freely rotating. This circumstance was utilized to compute the intermolecular contribution to the properties of the disordered phase. The anharmonicity was treated by an extension of Mie-Grüneisen theory in which the Grüneisen constant was replaced by a Grüneisen parameter calculated as a function of volume from the intermolecular potential. The equation of state, compressibility, and coefficient of thermal expansion, as well as the ratio of the constant pressure to constant-volume heat capacity were computed in the quasiharmonic approximation using the calculated Grüneisen parameter. The agreement with experiment was satisfactory on all counts.

I. INTRODUCTION

The harmonic approximation for thermal vibrations in solids cannot account for the thermal expansion or for the temperature dependences of the equation of state and compressibility. A formal representation of these anharmonic properties is embodied in the Mie-Grüneisen theory by assuming that at every temperature the harmonic approximation is adequate, but that the magnitude of the vibration frequencies varies with the crystal volume.[1] This dependence is represented by the Grüneisen parameter γ which is defined by

$$\gamma = -\frac{d\ln\nu_j}{d\ln V}, \tag{1}$$

where V is the volume and ν_j are the normal-mode frequencies.

This is the quasiharmonic approximation. It only partially accounts for the vibrational anharmonicity since it still uses the harmonic oscillator energy levels in the crystal partition function. γ is normally taken to be a constant that is independent of volume and is the same for all the normal-mode vibrations ν_j, although it is well recognized that the variation of frequency with volume is different for different modes. γ is usually calculated from experimental thermodynamic data and the Mie-Grüneisen approach is thus almost completely empirical.

In this paper, it is pointed out that if the crystal energy is known as a function of lattice parameter, the Grüneisen parameter can be calculated explicitly as a function of volume. This is particularly simple for crystals in which the pair-wise central force approximation is valid. The Mie-Grüneisen approach can then be extended in the sense that the Grüneisen parameter is obtained from the crystal energy rather than from empirical thermodynamic data, and it is not necessarily independent of volume.

An interesting application of this method is to the face-centered-cubic phase of C_{60}. In the molecule, the atoms are held together by strong chemical bonds while the interactions among these molecules in the fcc solid arise primarily from van der Waals-type forces and are much weaker. To a good approximation therefore, the thermal properties of fcc C_{60} can be treated as the sum of those resulting from intermolecular vibrations and those arising from intramolecular vibrations. In addition, there are molecular rotational and librational modes. However, these modes are completely excited in the fcc phase and for purposes of computing the thermal expansion and compressibility the molecules can be thought of as freely rotating with a negligible contribution to these quantities. These modes certainly contribute to the heat capacity but not to the ratio of the heat capacity at constant pressure to that at constant volume, which is determined by the thermal expansion and compressibility. In computing the anharmonic crystal properties, therefore, it is sufficient to consider only the intermolecular vibrational modes.

An intermolecular potential is known[2] that treats the C_{60} molecule as a "pseudoatom" by computing a spherically averaged intermolecular potential. This has had some success in the computation of molecular properties of fcc C_{60}. Using this potential, it is possible to get γ as a function of volume and to then compute the intermolecular contributions to the equation of state, the thermal expansion, and the temperature dependence of the compressibility. For pressures that are not too high, the intramolecular contributions should be quite small. Calculations of the intermolecular contributions are reported in this paper.

The difference between the heat capacities at constant volume and constant pressure is also an anharmonic effect. The measured heat capacity, however, has impor-

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tant contributions from both the inter- and intramolecular vibrations. In fact, because there are 180 degrees of freedom per molecule and only three vibrational and three rotational modes, the intramolecular contribution dominates the heat capacity except at low temperatures. It is nevertheless of interest to examine the intermolecular contribution.

II. THEORY OF ANHARMONIC THERMODYNAMIC PROPERTIES

Starting with the harmonic crystal expression for the Helmholtz free energy and the standard thermodynamic relations for its connection to the pressure P, volume coefficient of thermal expansion α, and compressibility κ, and using (1) for the derivatives of the frequencies with respect to volume, gives

$$P=-\left[\frac{\partial U_0}{\partial V}\right]_T-\left[\frac{\partial E_{\text{zp}}}{\partial V}\right]_T+\frac{\gamma}{V}E_{\text{th}}\ , \tag{2}$$

$$\frac{1}{\kappa}=V\left[\frac{\partial^2 U_0}{\partial V^2}\right]_T+V\left[\frac{\partial^2 E_{\text{zp}}}{\partial V^2}\right]_T+\frac{\gamma^2+\gamma}{V}E_{\text{th}}-\frac{\gamma^2 C_v T}{V}-\frac{d\gamma}{dV}E_{\text{th}}\ , \tag{3}$$

$$\frac{\alpha}{\kappa}=\frac{\gamma C_v}{V}\ , \tag{4}$$

$$\frac{C_p}{C_v}=1+\gamma\alpha T\ . \tag{5}$$

U_0 is the energy of the crystal when all atoms are at their mean equilibrium positions, E_{zp} is the zero-point vibrational energy, and E_{th} is the thermal energy defined by $E_{\text{th}}=U-U_0-U_{\text{zp}}$, U being the total energy. C_v is the heat capacity at constant volume and T is the absolute temperature. It must be stressed that the heat capacity and thermal energy do not include the contributions from the intramolecular vibrations so that the high-temperature limits of these quantities are $3k$ and $3kT$ *per molecule,* respectively.

Within the expected accuracy of the theory, the Debye theory can be used to compute the vibrational contributions to the above equations. The current work is restricted to temperatures above 300 K so that, since the Debye temperature, Θ_D, of fcc C_{60} is 73 K, the thermal energy and the heat capacity are given by the classical results of $3NkT$ and $3Nk$, respectively, k being Boltzmann's constant and N being the number of molecules. From Debye-Grüneisen theory, the zero-point energy and its derivatives are given by

$$E_{\text{zp}}=\frac{9}{8}Nk\Theta_D\ , \tag{6}$$

$$\frac{dE_{\text{zp}}}{dV}=-\frac{9\gamma}{8V}Nk\Theta_D\ , \tag{7}$$

$$\frac{d^2E_{\text{zp}}}{dV^2}=\left[\frac{\gamma^2+\gamma}{V^2}-\frac{d\gamma}{VdV}\right]\frac{9}{8}Nk\Theta_D\ . \tag{8}$$

In the usual Mie-Grüneisen theory, the derivative of the Grüneisen parameter with respect to volume does not appear because it is assumed to be zero. Also, the Grüneisen parameter is normally obtained from Eq. (4) using experimentally determined values of the heat capacity, the compressibility, and the coefficient of volume expansion. Here, however, we compute the Grüneisen parameter by assuming that the vibration frequencies are proportional to the square root of the second derivative of the intermolecular potential.

III. INTERMOLECULAR POTENTIAL AND GRÜNEISEN PARAMETER

The potential energy of interaction between two freely rotating C_{60} molecules has been approximated by treating each molecule as if it were a sphere with a surface consisting of a uniform density of carbon atoms. The equation for this potential is[2]

$$\phi(r)=\alpha\left[\frac{1}{s(s-1)^3}+\frac{1}{s(s+1)^3}-\frac{2}{s^4}\right]+\beta\left[\frac{1}{s(s-1)^9}+\frac{1}{s(s+1)^9}-\frac{2}{s^{10}}\right]\ . \tag{9}$$

r is the distance between the centers of the two C_{60} molecules and $s=r/2a$, a being the radius of a C_{60} molecule. The attractive and repulsive constants were obtained by fitting the potential to the heat of sublimation and the lattice constant of C_{60}. They have the values $\alpha=74.94\times10^{-15}$ erg and $\beta=135.95\times10^{-18}$ erg and $2a=7.1\times10^{-8}$ cm.

In the harmonic approximation, the normal-mode frequencies are determined by the second derivative of the static crystal energy as a function of atomic displacement. In keeping with the Grüneisen approach, we assume this to also be true in the quasiharmonic approximation. For C_{60}, the intermolecular potential has a very short range and the bulk of the crystal energy is accounted for by nearest-neighbor interactions. Accordingly, we assume that the frequencies are proportional to the square root of the second derivative of the interaction potential, evaluated at the nearest-neighbor intermolecular spacing λ. From Eq. (1) the Grüneisen parameter is then given by

$$\gamma=-\frac{d\ln\phi^{(2)}}{6d\ln\lambda}=-\frac{\lambda\phi^{(3)}}{6\phi^{(2)}}\ , \tag{10}$$

$\phi^{(2)}$ and $\phi^{(3)}$ being the second and third derivatives of $\phi(r)$ evaluated at λ. Equation (10) shows that the Grüneisen parameter is not a constant even in the nearest-neighbor quasiharmonic approximation. The derivatives of $\phi(r)$ are readily evaluated from (9) so that the Grüneisen parameter can be obtained as a function of nearest-neighbor distance and therefore of volume.

IV. RESULTS AND COMPARISON WITH EXPERIMENT: GRÜNEISEN PARAMETER

The Grüneisen parameter was computed analytically by obtaining the second and third derivatives from Eq. (9)

to put into Eq. (10). Figure 1 displays the Grüneisen parameter as a function of V/V_0, V_0 being the volume at zero pressure, and shows that γ is not constant. At zero pressure, $\gamma = 9.15$. This is high compared to Grüneisen parameters for metals and reflects the facts that the thermal expansion is high and that our γ refers only to intermolecular interactions.

Some inferences concerning experimentally obtained Grüneisen parameters can now be drawn. Because the inter- and intramolecular modes arise from very different kinds of forces, the Grüneisen method can be applied to each set of modes separately but not to both sets simultaneously. Lundin *et al.*[3] measured a constant pressure heat capacity of 0.73 J/g K at room temperature and derive a Grüneisen parameter of 1.4. But this is not very informative since the major contributions to the thermal expansion and to the compressibility are from the intermolecular vibrations, while the major contribution to the heat capacity is from the intramolecular modes. There are, of course, three different Grüneisen parameters, one each for intramolecular vibrational, librational, and intermolecular vibrational modes. The experimental data used in the calculation of the Grüneisen parameter must first be separated into these contributions. Sundqvist[4] amended the calculation of the Grüneisen constant to take this into account and obtained a value of 9.8 at zero pressure (for the Grüneisen parameter corresponding to the intermolecular vibrations).

Calculations of the Grüneisen parameters from experimental data for the ordered phase (200 K and below) have recently been performed by White *et al.*[5] in three ways corresponding to including all, vibrational and librational, and vibrational only modes. The calculation using only the vibrational modes gave a Grüneisen parameter of 10 at 200 K for the sc phase, which is close to our value for the fcc phase. The excellent agreement of the experimental values with our theory is probably fortuitous since the experimental values were computed using compressibilities that were much larger than that in the theory.

V. RESULTS AND COMPARISON WITH EXPERIMENT: THERMODYNAMIC PROPERTIES

With the computed values of $\gamma(V)$, the equation of state is readily obtained from Eq. (2) using the classical values for the thermal energy and the Debye-Grüneisen value for the zero-point energy contribution. A value of $\theta_D = 73$ K was used (this differs from the value previously reported by a factor of π which was inadvertently left out of the previous calculation[2]). This value of the Debye temperature was obtained from a simple lattice-dynamics calculation using the potential of Eq. (9) and is therefore consistent with our other calculations. The derivative of the energy of the static lattice was obtained by computing U_0 from a lattice sum of the intermolecular potential out to fifth-nearest neighbors and then differentiating. The results are shown in Fig. 2. As expected, the static term dominates at high pressures, but the vibrational terms become important at low pressures because, while the vibrational terms vary slowly with volume, the static term is very small at zero pressure. A point to note is that when the thermal contributions are taken into account, the equilibrium nearest-neighbor distance is computed to be 10.09 Å instead of the static lattice value of 10.05 Å. It would be interesting to recompute the intermolecular

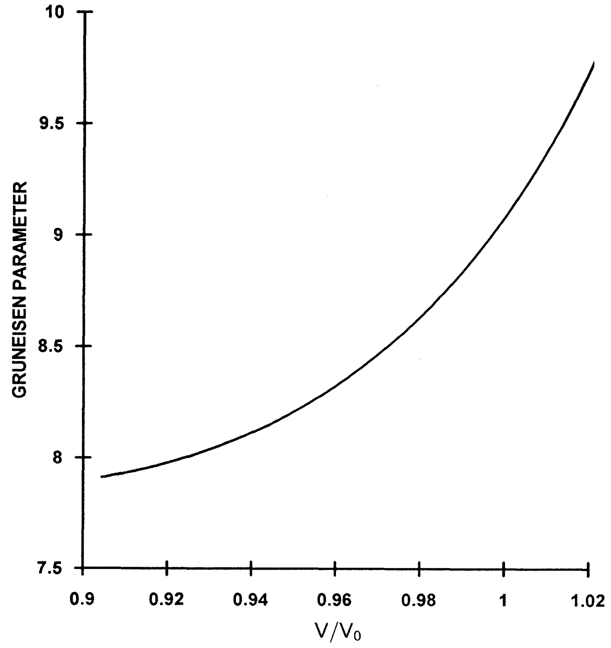

FIG. 1. Calculated Grüneisen parameter as a function of volume.

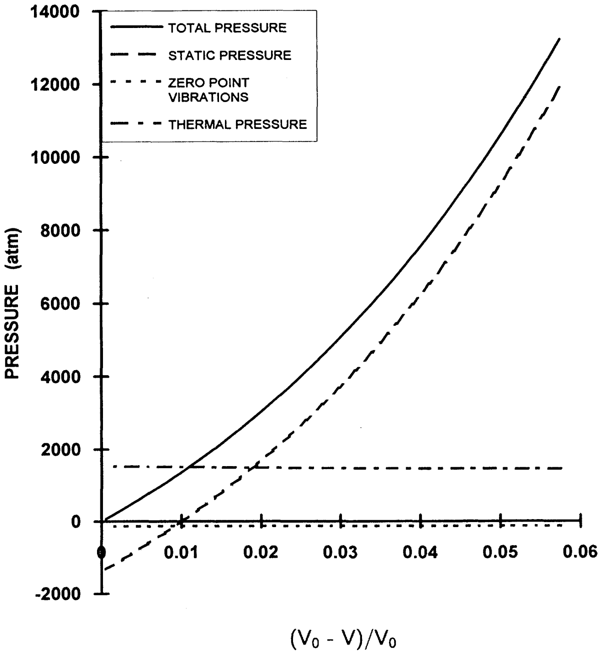

FIG. 2. Calculated equation of state for fcc C_{60} at 300 K.

potential function from the requirement that the total energy is minimized instead of just the static energy, but the experimental data are not accurate enough to make this a meaningful calculation.

A comparison of the calculated P-V relation to the data of Ludwig *et al.*[6] at 336 K is shown in Fig. 3. Their measurements spanned the rotationally disordered fcc phase and the ordered sc phase and only their low-pressure results are included in Fig. 3. The calculated curve is an estimate of the P-V relation for an fcc phase that is fictitious above several thousand atmospheres. The agreement between theory and experiment is excellent in the pressure range corresponding to the fcc phase.

The calculated compressibility at 300 K and zero pressure is shown as a function of temperature in Fig. 4 and is approximately linear from room temperature to 1500 K. The calculated bulk modulus at absolute zero is 1.55×10^{11} dyn/cm^2 whereas an earlier calculation[2] gave 1.58×10^{11} dyn/cm^2. The difference between the two results is the result of the greater accuracy of the present calculation which took more neighbors into account. At 300 K the bulk modulus is 1.193×10^{11} dyn/cm^2. The calculated compressibility at 300 K is 8.373×10^{-12} cm^2/dyn.

The relatively large variation with temperature shown in Fig. 4 is the result of the large value of the Grüneisen parameter. The direct contribution of the vibrational terms to this variation is less than 2% but the thermal expansion of the lattice has a large effect on the second derivative of the static lattice energy and this is responsible for the large temperature effect.

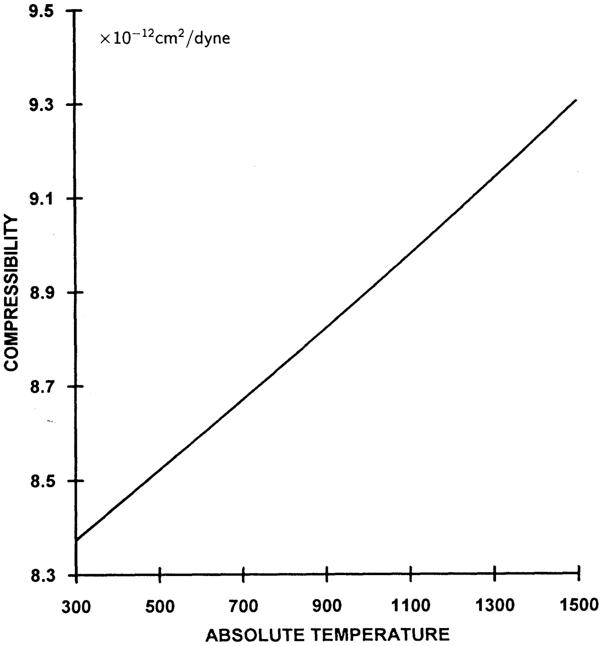

FIG. 4. Calculated compressibility as a function of temperature for C_{60}.

A recent calculation of the compressibility by Burgos, Halac, and Bonadeo[9] yielded a room-temperature compressibility of 7.6×10^{-12} cm^2/dyn for the fcc phase. They used a Buckingham-type potential plus electrostatic interactions placed at double bonds and at the centers or pentagon faces. However, their calculation of the compressibility of the fcc rotating phase was based on a spherical average of the Buckingham potential alone. The electrostatic contribution to the spherical average is therefore zero and their method is directly comparable to ours. The agreement with our calculation is remarkably close considering that they did not obtain the parameters in the potential by fitting them to C_{60} data, but used parameters obtained for molecular hydrocarbon crystals. La Rocca[10] computed the compressibility of the fcc phase using a density-functional statistical method and obtained a value of 8.33×10^{-12} dyn/cm^2, in excellent agreement with the present results.

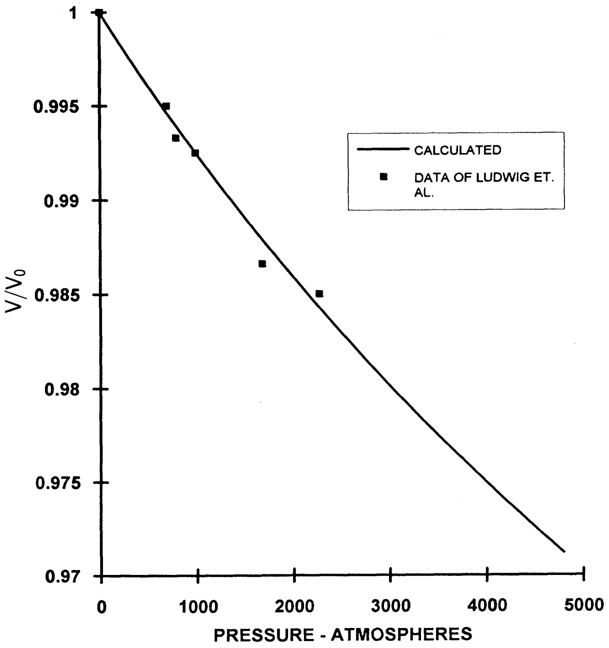

FIG. 3. Volume vs pressure for fcc C_{60}.

Lu, Li, and Martin[11] computed a compressibility of 5.18×10^{-12} dyn/cm^2 for the ground state of C_{60} using Lennard-Jones potentials centered on each carbon atom plus electrostatic contributions. While not directly comparable to our work, their result is surprisingly close to ours. A comparison to the available data and theory is shown in Table I.

The result of Fischer *et al.*[12] is close to our value. However, their compressibility was computed from just one data point at a high pressure and is therefore an average over a large range of pressure and over the ordered as well as the disordered phases of C_{60}. This measurement is therefore not directly comparable to the present model and the agreement is fortuitous.

The agreement between the calculations and the value of Duclos *et al.*[13] is good, but their result was an extrapo-

TABLE I. Experimental and calculated compressibility of C_{60} in units of 10^{-12} cm^2/dyn.

Reference	Experimental	Theoretical
6	7.46	
7	8.3	
8	14.7	
13	5.5	
12	7	
9		7.6
10		8.33
11		5.18
Present work		8.373

lation from the sc phase. The theory agrees best with the neutron-diffraction results of Schirber *et al.*[7] and differs by about 12% from the x-ray-diffraction results of Ludwig *et al.*[6]

The calculations state that C_{60} is harder than indicated by the results of Lundin and Sundqvist. In fact, their experiments yield compressibilities that are significantly greater than those of other work or of the present calculations.

The errors in the theory of the compressibility can arise from the following sources:

(1) Calculation of the thermal contribution to the bulk modulus;

(2) The functional form of the C-C interaction potential;

(3) The constants in the interaction potential;

(4) The use of spherical averages over the surface of interacting molecules.

The thermal contribution amounts to less than 10% and cannot be in error enough to matter. It is true that the functional form of the carbon-carbon potential is empirical, but only its values near the equilibrium lattice constant are relevant to the calculation and these are determined by well-known experimental data. The same consideration holds for possible errors in the constants of the interaction potential. Also, the carbon-carbon potential function is of the same form as for graphite and has constants with similar values. The fact that the same kind of calculation gives quite good results for graphite indicates that the results for C_{60} should be equally reliable. The approximation of spherical averaging which was used to derive the potential given by Eq. (13) might be suspect, but a recent calculation of graphite properties using a similar continuum approximation[14] yields results that are very close to those computed on the basis of the correct distribution of discrete atoms.[15] Another calculation that shows the utility of the spherically averaged approximation has been carried out by Rey, Gallego, and Alonso.[16] These authors performed a molecular-dynamics study on the stability of C_{60} clusters using the spherically averaged potential and found that clusters containing 7, 13, 18, and 22 molecules were particularly stable. This compared well with the results of Martin *et al.*[17] who found abundance peaks in mass spectroscopy experiments at cluster sizes of 7, 13, 19, and 23. Also, the measured compressibility of graphite is 2.7×10^{-12} cm^2/dyn.[18] Since practically all the volume change is the result of compression in the *c* direction, this number must be multiplied by three for comparison to the compressibility of C_{60}. The resulting 8.1×10^{-12} dyn/cm^2 is close to our calculated value and lends further support to the validity of the calculation, provided that the assumption of complete rotational disorder is valid. These theoretical considerations, along with the reasonable agreement of the theory with experiment, indicate that our spherically averaged potential is adequate for the fcc phase.

The calculated thermal-expansion coefficient is shown in Fig. 5. The rather large increase by 1/6th from room temperature to 1500 K is again the result of a large Grüneisen parameter. A comparison with experiment is shown in Fig. 6 in which the calculated lattice parameter of fcc C_{60} is shown along with the data from Fischer and Heiney.[19] The experimental value of 1.63×10^{-5} for the linear coefficient of thermal expansion is in satisfactory agreement with the calculated value of 1.44×10^{-5}.

The agreement of the calculated thermal-expansion coefficient with experiment, the similarity in both theoretical and experimental results for graphite and the success of other calculations based on continuum averaging of the potential makes the results of Lundin and Sundqvist hard to understand. It is true that even at room temperature and zero pressure the degree of orientational order amounts to 16% (Refs. 20 and 21) and that this increases with increasing pressure. The calculated compressibility and equation of state is for a fully disordered system, which is not realized under the conditions

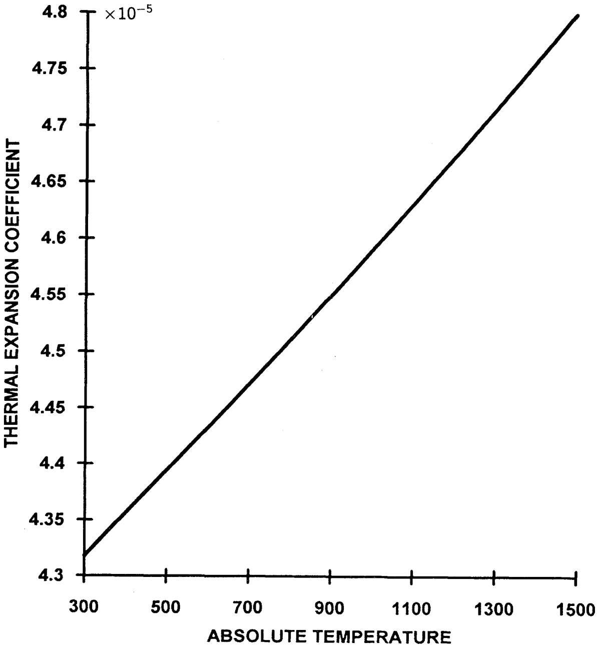

FIG. 5. Calculated thermal expansion coefficient for C_{60} as a function of temperature.

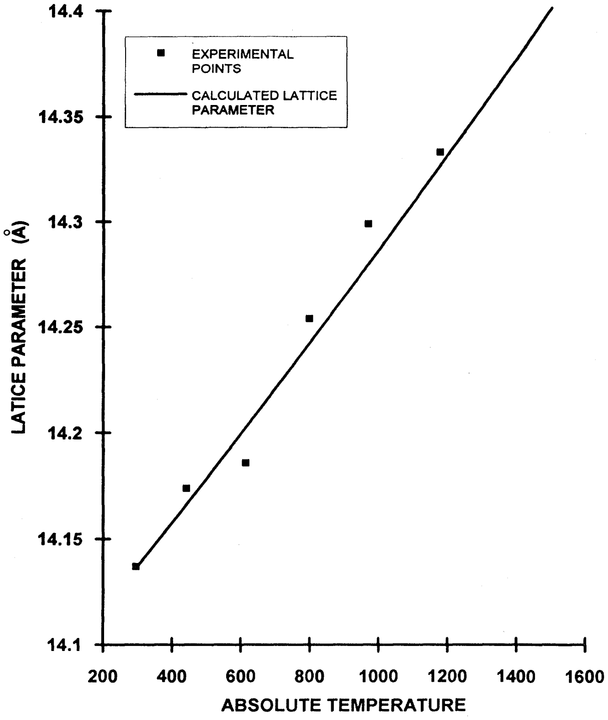

FIG. 6. Lattice parameter for C_{60} as a function of temperature.

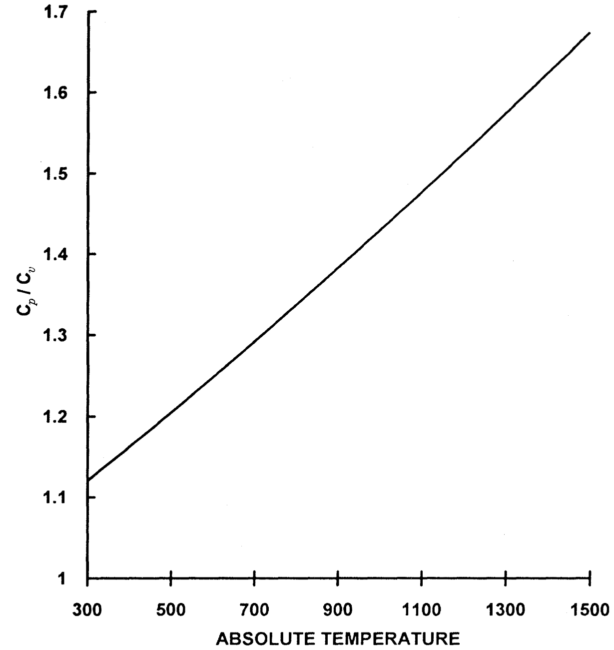

FIG. 7. Ratio of constant pressure to constant-volume heat capacity of C_{60}.

of the measurements of Lundin and Sundqvist. But if adjacent molecules are rotationally ordered, there are two sources of error in the present calculations. The first is that the use of spherically averaged potentials is incorrect; the second is that the form of the potential may need to be modified to include an effect arising from the interactions of the localized orbitals on the molecules. The thermal-expansion measurements, on the other hand, more closely correspond to the model calculations since they extend to high temperatures and the degree of rotational order should decrease with increasing temperature. The angular variation of the potential could be quite large. A collection of data from several sources gives an activation energy of rotation of 0.3 eV,[19] which is approximately equal to the well depth of the spherically averaged potential. This potential can therefore be in serious error when applied to an orientationally ordered phase.

However, Lundin and Sundqvist report a compressibility for the ordered phase that differs by less than 20% from that of the disordered phase. This is not consistent with a factor of 2 difference between the potentials in the two phases. Both the theoretical analysis and the experimental diffraction results lead to the conclusion that the lower values of the compressibility are to be preferred.

The calculated ratio of the constant pressure to constant-volume heat capacity for the intermolecular vibrational modes is shown in Fig. 7. Again, the anharmonic effect is large. Even at room temperature the two heat capacities differ by 11% and this approaches 70% at high temperatures. This is the direct result of the large value of the Grüneisen parameter computed from the intermolecular C_{60} potential. This potential is quite narrow so that a small change in crystal volume yields a large change in vibration frequencies thereby giving a large Grüneisen parameter. These results were used to subtract out the intermolecular contribution to measured values of the heat capacity. It was found that at room temperature the intramolecular contribution was 20 times that from the intermolecular vibrations.

VI. CONCLUSIONS

The intermolecular contribution to the thermodynamic properties of C_{60} in the disordered C_{60} phase can be computed from a model potential which assumes that the molecules interact according to a potential obtained from an average over spherical surfaces of a Lennard-Jones potential between individual carbon atoms on different molecules. The potential permits the Grüneisen parameter to be computed as a function of volume so that the anharmonic thermodynamic properties can be obtained from standard statistical mechanics within the quasiharmonic approximation. The calculations are compatible with experiment and a number of theoretical considerations indicate that the calculations are valid for the disordered fcc phase.

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