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Thermodynamic model of the ordering transition in solid C₆₀

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A thermodynamic model of the rotational phase transition in solid C₆₀ is presented. The phase transition which appears at 257 K is a first-order phase transition in which a competition occurs between entropy gain by rotation and energy gain by intermolecular attraction. The anomaly in the specific heat, and the entropy and enthalpy changes observed at the critical temperature are well reproduced in the present numerical results.

I. INTRODUCTION

Fullerene C₆₀ has attracted much interest in many fields of science as a new form of carbon; it is an aromatic molecule with high symmetry.¹⁻³ Solid C₆₀ has a face-centered-cubic (fcc) crystal structure above $T_c=257$ K, and below T_c the solid fcc phase is transformed into a simple cubic structure (sc) or $Pa\bar{3}$ symmetry.⁴ The first order orientational phase transition has been investigated by many experimental techniques such as x-ray diffraction,⁴ nuclear magnetic resonance (NMR),⁵⁻⁷ specific-heat measurements,⁸⁻¹⁰ Raman spectroscopy,¹¹⁻¹³ inelastic neutron scattering,¹⁴⁻¹⁷ electron diffraction,¹⁸ and other transport experiments. These experiments show that below 257 K, each C₆₀ molecule rotates in a discrete rotation about a specific threefold (C_3) axis in a single $\langle 111 \rangle$ direction. In the low temperature sc phase, each of the four molecules in a unit cell has a different $\langle 111 \rangle$ direction, though the center of mass of each molecule is the same as that for the fcc phase. In the high-temperature fcc phase, the threefold axes rotate freely and all four molecules are equivalent. However, the temperature dependence of the ¹³C NMR spin correlation time, τ , which is obtained from the spin-lattice relaxation time, T_1 , shows that for phases both below and above T_c the rotations exhibit an activation-type behavior in which the diffusion constant D is given by $D = D_0 \exp(-T_A/T)$.¹⁹ Here the T_A 's are activation temperatures for discrete rotation below T_c ($T_A^{\text{dis}} = 2100 \pm 600$ K) and for rotational motion above T_c ($T_A^{\text{rot}} = 695 \pm 45$ K).¹⁹ Even above T_c the activated motion shows that the molecule jumps from one local potential minimum to another. Neutron inelastic and Raman scattering experiments show that the librational motion around a local potential minimum has a broad peak at about 2.4 meV, which decreases with increasing temperature.¹⁷ Thus the specific heat due to the libra-

tional motion saturates at about 30 K (Ref. 20) (Dulong-Petit law), above which the librational motion can be considered classically. Because of the order of magnitude difference in thermal energy, the anomaly in the specific heat just below T_c does not come from the specific heat associated with the librational motion.

Using an intermolecular model potential, many theoretical calculations have been reported such as the molecular dynamics of discrete rotation in C₆₀,^{21,22} calculation of the librational and intermolecular vibrational dispersion relations,^{20,23} and Landau theory.²⁴ However, to our knowledge, no published model predicts the characteristics of the anomaly of the specific heat at the first order phase transition at 257 K.

In the present paper we consider a simple but realistic model²⁵ for the discrete rotation of C₆₀ molecules to describe the phase transition. In Sec. II the model is described and in Sec. III the calculated thermodynamic properties near T_c are presented and discussed. In Sec. IV a summary of this paper is given.

II. MODEL

The model that we consider consists of three states: (a) the freezing of any discrete rotation, (b) discrete rotation with three positions per molecule for rotation about the threefold axis, and (c) discrete rotation not only about the threefold axis but also about a fivefold (C_5) axis, thus yielding a total of 90 positions.

In a C₆₀ molecule, there are 10 C_3 axes, and 6 C_5 axes. If a C_3 axis is frozen in the $(1, 1, 1)$ direction in the low temperature simple cubic phase, then the only possible discrete rotation is about the C_3 axis in which there are three potential minima. When we also consider 30 symmetry operations about 6 C_5 axes at high temperature, all C_3 axes permute with each other and thus we will

have 90 potential minima. Here we have three absolute potential minima and six local minima per C_3 axis.²³ We did not consider the rotation about 20 C_2 axes because the rotation angle 180° is large and the potential barrier for this rotation would be expected to be high.

All motions which are relevant to the phase transition are the hopping between local potential minima below and above the phase transition. Actually the nuclear magnetic resonance experiment¹⁹ shows an activation-type temperature dependence of the spin correlation time τ with two different activation energies of 2100 K and 700 K for the lower and higher temperature phases, respectively, which we assigned to the discrete rotation about the C_3 and C_5 axes, respectively. This assignment is reasonable in light of the potential calculations in which the authors show that some local minima whose depths are $\sim 0.1 - 0.2$ eV.²³

In states (b) and (c), there are 3 and 90 equivalent sites, respectively, which correspond to the potential minima for the discrete rotation. When we assume N_1 , N_2 , and N_3 molecules of a total of N molecules are in (a), (b), and (c) states at a given temperature, the total number of states, W , is given by

$$W = \frac{N!}{N_1!N_2!N_3!} 3^{N_2} 90^{N_3}. \quad (1)$$

Using the Stirling formula, $\log_{10} N! \sim N \log_{10} N - N$, we calculate the entropy, S , which is given by

$$\begin{aligned} S &= k_B \log_{10} W \\ &= -Nk_B (X_1 \log_{10} X_1 + X_2 \log_{10} X_2 + X_3 \log_{10} X_3) \\ &\quad + Nk_B (X_2 \log_{10} 3 + X_3 \log_{10} 90), \end{aligned} \quad (2)$$

where

$$N = \sum_{i=1}^3 N_i, \quad X_i = N_i/N, \quad \text{and} \quad \sum_{i=1}^3 X_i = 1. \quad (3)$$

The internal energy E consists of two parts as follows:

$$E = -NJ_a X_1 - \frac{NzJ_b}{2} (X_1 + X_2)^2, \quad (4)$$

in which $J_a (> 0)$ stands for the energy gained from freezing the motion for the (a) states, and $J_b (> 0)$ and $z = 12$ are the intermolecular attractive interaction and the number of the nearest neighbor molecules, respectively. Here we assume that the attractive interaction acts only when two molecules in (a) or (b) states are nearest neighbors.

In the thermal equilibrium state, we can minimize the free energy, $F = E - TS$, with respect to X_1 and X_2 keeping the temperature fixed and the condition that $X_1 + X_2 + X_3 = 1$. Eliminating X_2 and X_3 , we obtain a self-consistent equation for X_1 ,

$$X_1 = \frac{1}{\alpha + \beta\gamma(X_1)}, \quad (5)$$

where the dimensionless parameters α , β , and the function γ which depends on X_1 are expressed as

$$\begin{aligned} \alpha &= 1 + 3 \exp\left(-\frac{T_a}{T}\right) \quad (T_a = J_a/k_B), \\ \beta &= 90 \exp\left(-\frac{T_a}{T}\right), \\ \gamma(X_1) &= \exp\left(-\frac{T_b}{T} \alpha X_1\right) \quad (T_b = zJ_b/k_B). \end{aligned} \quad (6)$$

Because of the simple model that we use, there is only one solution of Eq. (5) at any temperature. Thus the thermal equilibrium value of X_1 is easily obtained numerically. The corresponding values of X_2 and X_3 are given as follows:

$$X_2 = (\alpha - 1)X_1 \quad \text{and} \quad X_3 = 1 - X_2 - X_1. \quad (7)$$

In Fig. 1, the temperature dependences of X_1 , X_2 , and X_3 are plotted by dotted, dashed, and solid lines, respectively, as a function of T/T_b with a fixed ratio of $T_a/T_b = 1/3$. The choice of this ratio is motivated by the observed ratio of the two phase transition temperatures, 87 K/257 K being close to 1/3. From Fig. 1, X_1 , the probability that a molecule is frozen, decreases monotonically in the range $0.05 < T/T_b < 0.21$ and at $T/T_b = 0.21$ there is a discontinuous change in many properties, characteristic of a first order transition. Hereafter we denote this temperature by $T_c = 0.21T_b$. The onset value denoted by $T_0/T_b = 0.05$ is defined by the temperature where X_1 becomes 0.99. It is clear from Eq. (7) that the increase of X_2 (or the decrease of X_1) starts from $T = 0$ where $X_1 \sim 1.0$. Thus we need the above definition.

In Fig. 2, the onset temperature normalized by T_b , T_0/T_b (dotted line), the critical temperature normalized by T_b , T_c/T_b (solid line), and the change of X_1 at T_c , ΔX_1 (dashed line), are plotted as a function of T_a/T_b . From the figure, the onset temperature is seen to be propor-

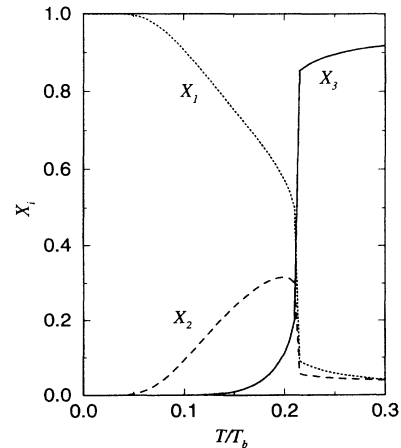


FIG. 1. Temperature dependence of X_1 (dotted line), X_2 (dashed line), and X_3 (solid line) plotted as a function of T/T_b .

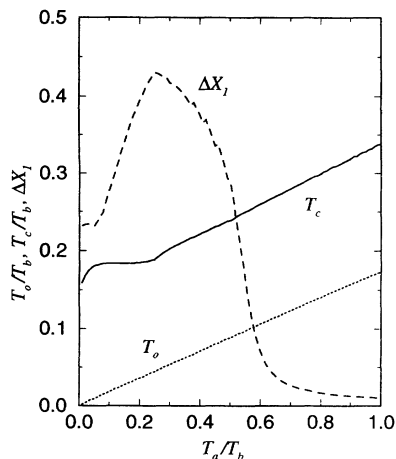


FIG. 2. The onset temperature of decreasing X_1 normalized by T_b , T_0/T_b (dotted line), the critical temperature normalized by T_b , T_c/T_b (solid line), and the change of X_1 at T_c , ΔX_1 (dashed line) are plotted as a function of T_a/T_b .

tional to T_a . As for the transition temperature T_c , there is no significant dependence of T_c on T_a for $T_a/T_b \leq 0.3$ and then for higher values of T_a/T_b , a linear dependence on T_a for $T_a/T_b \geq 0.3$. The discontinuous change of X_1 at T_c is observed for $T_a/T_b \leq 0.6$ with a maximum at $T_a/T_b \sim 0.25$. For $T_a/T_b \geq 0.6$ there is no significant discontinuous change in ΔX_1 but rather a continuous change occurs. For the case of $T_a/T_b \sim 0.0$, there is no difference in the internal energy between X_1 and X_2 and we do not consider this unphysical case further. As shown in Fig. 2, our model is applicable for a wide region of T_a/T_b from 0.1 to 0.6. Hereafter, we consider only case $T_a/T_b = 1/3$ which gives the best results in comparison to experimental data for solid C_{60} .

III. THERMODYNAMIC PROPERTIES AND DISCUSSION

Using the self-consistent solution of X_1 discussed above, we calculate the entropy, free energy, internal energy, and specific heat as a function of the normalized temperature T/T_b .

A. Entropy

In Fig. 3, the entropy S normalized by Nk_B is plotted as a function of T/T_b by putting the solutions of Eqs. (5) and (7) into Eq. (2). The entropy increase associated with the transition from the frozen state to the discrete-rotation states occurs from $0.05T_b$ all the way to the discontinuity at T_c . Above T_c the entropy S saturates to the value of $\sim Nk_B \ln 90 = 4.5Nk_B$ or $37.4 \text{ J/K}^{-1} \text{ mol}^{-1}$. The entropy change at T_c in the present calculation is $2.30Nk_B$ or $19.1 \text{ J/K}^{-1} \text{ mol}^{-1}$. The experimental specific heat results⁹ show a discontinuity of $\sim 30 \text{ J/K}^{-1} \text{ mol}^{-1}$ between the above two values of 19.1 and $37.4 \text{ J/K}^{-1} \text{ mol}^{-1}$. The basic idea behind the

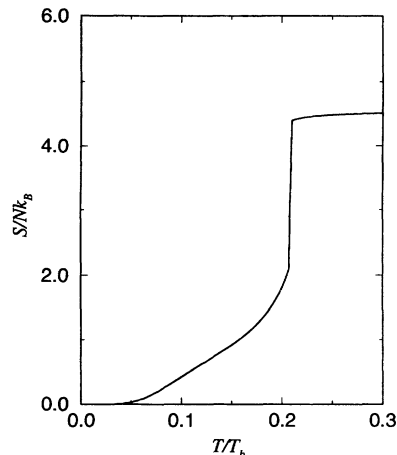


FIG. 3. Temperature dependence of the entropy S/Nk_B in dimensionless units.

entropy change at T_c is the increase in the number of equivalent states from 3 to 90 and the corresponding entropy difference $\Delta S = Nk_B \ln 30 = 28.3 \text{ J/K}^{-1} \text{ mol}^{-1}$, in very good agreement with the experimental results.

B. Free energy

In Fig. 4, the free energy F (dotted line) and the internal energy E (solid line) normalized by $Nk_B T_b$ are plotted by putting the solution of Eqs. (5) and (7) into F and E . The free energy is continuous for the whole temperature range but has a kink at $T = T_c$ (see Fig. 4) corresponding to the discontinuous change of X_1 as shown in Fig. 1. With increasing T , the internal energy increases from the lower temperature range, reflecting that the energy gain associated with the freezing molecules,

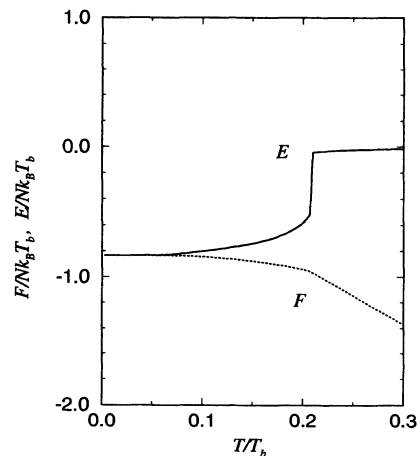


FIG. 4. Temperature dependence of the free energy $F/Nk_B T_b$ (dotted line) and the internal energy $E/Nk_B T_b$ (solid line) in dimensionless units. A discontinuity in the derivative of E is seen at T_c . The derivative of F with respect to T is not continuous at T_c , which appears as a kink in the figure.

J_a , is decreasing. At $T = T_c$ there is a discontinuity of E through loss of the intermolecular interaction, J_b , by an order-disorder transition. As mentioned above, the internal energy from the librational motion is not considered here. Since the specific heat for 24 librational modes is expected to be saturated to $12R$ ($R = Nk_B$) above $T = 30$ K, the internal energy from the librational motion is $12RT$ which does not depend on X_1 and thus can be excluded from the model. Since we do not consider the effects of pressure in the thermodynamic model, we can compare the present discontinuity in the internal energy with the discontinuity in the enthalpy. The present calculated result of the enthalpy change, $\Delta H = \Delta E$, at $T = T_c$ is $0.475Nk_B T_b$. If we use $T_b = 1224$ K so as to reproduce the critical temperature $T_c = 0.21T_b = 257$ K, we obtain $\Delta H = 4829 \text{ J mol}^{-1} = 6.71 \text{ J g}^{-1}$ which is comparable to the results of the differential scanning calorimetry experimental value⁴ of $\Delta H = 5.9 \text{ J g}^{-1}$. Thus both T_c and ΔE can be explained consistently with the same parameter of $T_b = J_b/k_B = 1224$ K.

C. Specific heat

The specific heat C_v is calculated by

$$C_v = \frac{dE}{dT} = - \left(N J_a + \frac{N z J_b \alpha^2}{2} X_1 \right) \frac{dX_1}{dT} - \frac{N z J_b \alpha}{2} X_1^2 \frac{d\alpha}{dT}, \quad (8)$$

where we use the fact that

$$X_1 + X_2 = \alpha X_1, \quad (9)$$

and we calculate $\frac{dX_1}{dT}$ by differentiating Eq. (5) with respect to T . In Fig. 5, we show the specific heat C_v/Nk_B as a function of T/T_b .

The specific heat in Fig. 5 increases starting from $T/T_b = 0.04$. Since the definitions of onset for the specific

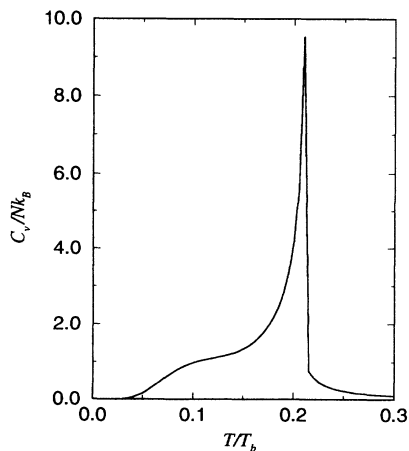


FIG. 5. Temperature dependence of the specific heat C_v/Nk_B in dimensionless units.

heat and decreasing X_1 are different, the small difference of $T/T_b = 0.04$ and $T_0/T_b = 0.05$ in the previous section is not meaningful. The specific heat in the figure saturates at about $\Delta C_v \sim 1.0Nk_B = 8.3 \text{ J/K}^{-1} \text{ mol}^{-1}$ starting at $T/T_b \simeq 0.1$, and has a sharp peak below T_c and then decreases to zero for $T > T_c$. The excess heat capacity which is obtained by subtracting the contribution of the librational and vibrational motions from C_v is quite similar to the experimental results.⁸⁻¹⁰ It is noted that the peak value of C_v near T_c does not have an important physical meaning since the calculation uses discrete points for specifying T . Thus the peak would show a larger value if we take values of T closer to T_c . On the other hand, the excess specific heat at $T/T_b = 0.1$ may be compared to the glassy transition observed at 87 K in which a jump in C_v of $\Delta C_v = 7 \text{ J/K}^{-1} \text{ mol}^{-1}$ was reported,⁹ in satisfactory agreement with our calculated result of $8.3 \text{ J/K}^{-1} \text{ mol}^{-1}$. This excess heat capacity at $T/T_b = 0.1$ may be identified as a Schottky type specific heat anomaly.

D. Discussion

In Table I, we compare the experimental data with theory. In spite of the simple picture of the phase transition described by the present model, good agreement between the model and the experimental data is achieved.

The temperature dependence of the order parameter X_1 may be compared with that of an x-ray diffraction spot such as (4,5,1) (Ref. 26) and (4,5,0) (Ref. 4) which are forbidden in the fcc structure. The (4,5,1) [or (4,5,0)] peak intensity decreases from its value at very low temperature and experiences a discontinuous jump of about half of its intensity at $T = 255$ K.²⁶ The T dependence of this x-ray peak is similar to that for X_1 shown in Fig. 1. We also compare these values in Table I.

A discontinuity in the order parameter is observed, too, in the low-energy region of the Raman spectrum ($\sim 30 \text{ cm}^{-1}$).²⁷ The observed temperature dependence of the libron intensity and the uncorrelated Lorentzian scattering intensity are similar to the temperature dependence of X_2 and X_3 , respectively.

The present model does not consider any change in the free energy associated with the lattice constant jump at T_c observed by x-ray and neutron experiments⁴ in the vicinity of T_c . According to the discontinuous change from discrete rotation to relatively free motion, the lat-

TABLE I. Thermodynamic quantities of the phase transition of solid C_{60} .

| | Model | Expt. | |
|---|------------------|----------------------|-----------------------|
| ΔH (J g^{-1}) | 6.7 ^a | 5.9 ^b | at $T = 255$ K |
| ΔS ($\text{J K}^{-1} \text{ mol}^{-1}$) | 19.1 | 30.0 ^c | at $T = 255$ K |
| ΔC_v (J g^{-1}) | 8.3 | 7 ^c | at $T = 70 \sim 90$ K |
| ΔX_1 | 0.41 | 0.4–0.5 ^d | at $T = 255$ K |

^a When we use $T_b = 1214$ K.

^b Reference 4.

^c Reference 9.

^d Intensity of fcc forbidden x-ray peaks (4,5,0) and (4,5,1) (Refs. 4 and 26).

tice should be expanded by being free from very weak van der Waals interaction and from weak Coulomb interactions between electron-rich double-bond regions on one molecule and electron poor pentagon regions on the adjacent molecule. This effect may be included in J_b if J_b is a function of the lattice constant. Weak hysteresis effects near T_c are characteristic of a first-order transition in which there is a local maximum in the free energy between two local minima as a function of order parameter. Though the two local minima have equal energy, hysteresis appears at $T = T_c$, because the order parameter cannot jump from one minimum to another. To account for this situation requires higher order terms in the order parameter in the free energy,²³ and such terms are not considered in the present model. It is noted that the discontinuous jump in X_1 in the present model corresponds to a smooth change from one minimum to the other. Such higher order terms could appear when J_a and J_b depend on X_i or when we consider a more realistic model beyond the mean field model. The important point to be stressed is the basic picture of the phase transition as the competition between entropy gain by rotation and energy gain by intermolecular attraction.

The present model does not explain the anomalies observed in a number of experiments at 165 K.¹⁸ This anomaly may have something to do with alignment of the double-bond with pentagons in preference to hexagons below 165 K and little preference between them above 165 K. This phenomena is referred to as merohedral disorder. Some structural studies have suggested a doubled lattice constant for C_{60} in the low temperature phase.¹⁸ In order to explain such an effect, at least next-nearest-neighbor interactions must be considered. Another important point that we should mention is the glassy phase transition which is not included clearly in the present model though we can explain the excess specific heat associated with such a transition. Because of the cubic symmetry of the solid, the relative orientations of the C_{60}

pentagons on one ball relative to its 12 nearest neighbors is prescribed. This restriction makes it impossible for the 12 pentagonal faces to line up perfectly with double bonds on adjacent molecules. Thus an intrinsic residual disorder must remain at low temperature, which is described by fluctuations in the order parameter. Thus a more realistic model is necessary for explaining the relaxation process in detail.

IV. CONCLUSION

In summary, we propose a simple but realistic statistical model for the phase transition of solid C_{60} in which the molecules can have any of three possible states: (a) a frozen state, (b) a three-state discrete rotation about a single axis, or (c) a 90 state associated with 90 rotations about both threefold and fivefold axes. The order-disorder transition from (b) to (c) is modeled by a first order phase transition in which discontinuous jumps of the order parameter, the internal energy, and the entropy at T_c are well reproduced by fitting the energy parameters J_a and J_b (or T_a and T_b) so as to obtain the transition temperature T_c . The temperature dependence of the specific heat, the order parameter, and the increase in specific heat at ~ 80 K are in good agreement with experimental data.

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