

Pressure-Induced Ordering in Adamantane: A Monte Carlo Simulation Study

N. Arul Murugan and S. Yashonath*,†

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India 560 012

Received: June 29, 2004; In Final Form: October 4, 2004

Isothermal–isobaric ensemble Monte Carlo simulation of adamantane has been carried out with a variable shape simulation cell. The low-temperature crystalline phase and the room-temperature plastic crystalline phases have been studied employing the modified Williams potential. We show that at room temperature, the plastic crystalline phase transforms to the crystalline phase on increase in pressure. Further, we show that this is the same phase as the low-temperature ordered tetragonal phase of adamantane. The high-pressure ordered phase appears to be characterized by a slightly larger shift of the first peak toward a lower value of r in C–C, C–H, and H–H radial distribution functions as compared to the low-temperature tetragonal phase. The coexistence curve between the crystalline and plastic crystalline phase has been obtained approximately up to a pressure of 4 GPa.

1. Introduction

Adamantane, C₁₀H₁₆, is a highly symmetric globular molecule. The molecular structure of adamantane consists of four CH groups at the corners of a tetrahedron and six CH₂ groups interconnecting these four CH groups. The structure consists of three cyclic rings each with six carbon atoms, made up of three alternating CH and CH₂ groups. At atmospheric pressure and low temperatures, adamantane exists in an ordered crystalline tetragonal phase with space group $P4_21c$.^{1,2} This phase undergoes a transition to a cubic phase³ (space group $Fm3m$) at 208.62 K, an orientationally disordered phase.

Experimental investigations of adamantane exist for both the crystalline and plastic crystalline phases. Calorimetric, infrared, differential thermal analysis (DTA), and NMR studies have been reported.^{4–7} Studies by Chang and Westrum⁸ show that the molar enthalpies (molar entropies) of transition for adamantane for the crystal to the plastic crystal phase and the plastic crystal to the liquid phase are 3.38 kJ/mol (16.2 J/(mol K)) and 13.8 kJ/mol (25.4 J/(mol K)), respectively. Kabo et al.⁴ have looked at the relationship of the thermodynamic data to the orientational disorder as a function of temperature. Salman et al.⁶ have measured the C–H infrared frequency shifts in the two phases of adamantane. Corn et al.⁵ have looked at the orientational dynamics by IR spectroscopy.

There have been previous attempts to investigate properties of adamantane by computer simulation. The crystal to plastic crystal transition has been investigated as a function of temperature by a number of groups.^{9–11} These studies look at the orientational ordering as a function of temperature. Yashonath and Rao⁹ and Ciccotti et al.¹⁰ and Trew et al.¹¹ have investigated the orientationally disordered plastic crystal phase. More recently, Greig and Pawley¹² have investigated the transition from the crystalline to the plastic crystalline phase as a function of temperature. They also simulated the reverse transition as a function of temperature.

Ito¹³ has carried out X-ray diffraction measurements on adamantane up to 0.8 GPa under hydrostatic pressure. They find

that the room-temperature orientationally disordered phase undergoes a transition to an ordered tetragonal phase between 0.4 and 0.5 GPa. Further, they report that this phase is the same as the low-temperature ordered crystalline phase of adamantane at atmospheric pressure. Vijayakumar et al.^{14–16} have obtained volume and lattice parameters of adamantane as a function of pressure. Further, they report Raman studies under extremely high pressures (up to 26 GPa) which suggest that the molecular geometry undergoes distortion leading to a lowering of symmetry.^{14–16}

In the present work, we simulate the transition between the crystalline and the orientationally disordered phase as a function of pressure and temperature. It is shown that a moderate increase in pressure leads to a change from an orientationally disordered plastic crystalline phase to the crystalline phase. Further, we show that this phase is identical to that obtained by cooling. This is in excellent agreement with the X-ray diffraction studies of Ito¹³ as a function of pressure. We have also computed the coexistence curve between the crystalline and plastic crystalline regions of the phase diagram.

2. Methods

2.1. Intermolecular Potential. We employ the intermolecular potential of Greig and Pawley. This is the potential originally proposed by Williams¹⁷ but subsequently modified by Greig and Pawley¹² to reproduce the properties of adamantane. It has one site located on each of the carbon and hydrogen atoms. The site–site interaction is of the 6-exp form.

$$\phi(r) = -\frac{A}{r^6} + B \exp(-Cr) \quad (1)$$

The parameters A , B , and C are listed in Table 1. There are no charges on any of the atoms. There are in all 26 sites ($N_a = 26$). We chose this potential as it is the most recent potential employed to simulate adamantane. This potential predicts the transition temperature from the crystalline to the plastic crystalline phase to be around 400 K which may be compared to the experimental value of 208.62 K. Although it is possible to scale the potential and thereby obtain the correct transition temper-

† Also at the Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore, India.

TABLE 1: Potential Parameters for Adamantane

type	A, kJ/mol Å ⁶	B, kJ/mol	C, Å ⁻¹
C–C	2374.42	359824.00	3.60
C–H	522.67	38492.80	3.67
H–H	113.93	11715.2	3.74

ature, we have retained the original potential parameters to enable comparison with the previous results of Greig and Pawley.¹²

We have also carried out calculations on adamantane incorporating internal degrees of freedom such as bond bending terms and so forth. The variation of lattice parameters with pressure up to 26 GPa (not shown) for both the rigid and the flexible molecule indicated that the variation in the lattice parameters for the rigid case is almost similar to the flexible molecule case at least up to 5 GPa. As our study here is restricted to 4 GPa, we employ a rigid molecule in the present study. The potential of Williams includes all the important contributions to the energy that are required to investigate the crystal to plastic crystal transition over this pressure range. All previous simulations of crystal to plastic crystal transitions of many different molecules such as nitrogen, methane, neopentane, and so forth have employed only an intermolecular potential term¹⁸ and no intramolecular terms.

2.2. NPT Monte Carlo Simulations. All simulations have been carried out in the isothermal–isobaric ensemble with a variable shape simulation¹⁹ cell using the Metropolis algorithm²⁰ within the Monte Carlo (MC) method. The method employed here uses only six variables²¹ to represent the simulation cell for the **h** matrix instead of the usual nine originally proposed.¹⁹ Here, the **h** matrix is the matrix used to represent the simulation cell. The **h** matrix is made up of the three column vectors which are also the cell vectors: **h** = {**a**, **b**, **c**} where **a**, **b**, and **c** are the three vectors defining the simulation cell. Note that cell vector **a** is now restricted to lie along the *x*-axis and **b** to the *xy*-plane thereby²¹ reducing the degrees of freedom from 9 to 6. The advantage of giving only 6 degrees of freedom for the cell is that it not only prevents the rotation of the cell observed in polyatomic systems by Nose and Klein^{22,23} and us²¹ but also reduces the total number of variables in the simulation.

3. Computational Details

3.1. Temperature Variation. Three different sets of runs have been carried out at specified pressure and temperature. In one set of runs, set I, simulations have been carried out at 188, 298, 310, 320, 350, 380, 410, 420, 450, and 500 K temperatures and a pressure of 1 atm. For the 188 K run, we employed the configuration given by the experimental low-temperature crystalline phase as the starting configuration. At higher temperatures, the final configuration obtained from the previous lower temperature run was used as the starting configuration. Thus, set I runs attempt to study the crystalline to plastic crystalline phase change with temperature.

3.2. Pressure Variation. In a second set of simulations, termed set II, runs have been carried out at a fixed temperature of 450 K and different pressures. Initially, simulation was carried out at 1 atm (and 450 K). The pressure was then increased in steps of 0.1 GPa up to 1.3 GPa. The simulation was then carried out at 1.5 GPa. Beyond 1.5 GPa, pressure was increased in steps of 0.5 GPa until a pressure of 4 GPa was reached. The configuration at the previous value of pressure was used for the calculation at the next higher pressure. The starting phase for the run at 450 K and 1 atm is the plastic crystalline phase obtained from the set I run at 450 K and 1 atm. The set II runs

attempt to investigate the transition from the plastic crystalline phase to the crystalline phase with gradual increase in pressure. This, therefore, attempts to look at the transition from the orientationally disordered to the ordered crystalline phase that was observed by Ito.¹³

3.3. Coexistence Curves. Set III runs are carried out at various temperatures keeping the pressure fixed except for a single pressure-varying run at 800 K. These runs are meant to compute the coexistence curve between the crystalline and plastic crystalline phases.

Variable shape simulation cell Monte Carlo calculations in isothermal–isobaric ensemble have been carried out for the low-temperature tetragonal crystallographic structure and the high-temperature cubic phase. The initial configuration for our calculations was the one given by Amoureux and Foulon.² This structure (space group *P*4₂*c*) has two molecules per unit cell, and the cell parameters are *a* = 6.639 Å and *c* = 8.918 Å at 188 K. For the three sets of calculations, namely, sets I–III, we have taken *N* = 128 molecules from 4 × 4 × 4 unit cells. The molecules are considered to be rigid with just 6 degrees of freedom.

A center of mass–center of mass (com–com) radius of 12.5 Å has been employed as a cutoff. Each MC move consists of a single attempt on each of the *N* molecules once^{24,25} to translationally displace the molecular center of mass followed by a rotation of the molecule as a whole through an axis chosen randomly and rotated by a random angle (with a maximum chosen so as to obtain about 40% acceptance probability). A MC move also consists of an attempt to modify the cell vectors defining the simulation cell.²¹ We have carried out simulations for a total of 23000 MC moves (or 2.9 × 10⁶ steps) which include 3000 MC moves (or 3.84 × 10⁵ steps) for equilibration. Relatively shorter runs (9000 MC moves) have been employed for high pressure (>1 GPa) calculations since the fluctuations are smaller. We found that the average values of the properties reported with these shorter runs were the same as those obtained from the longer runs. After the equilibration, various average structural quantities such as cell parameters, volume, and radial distribution functions were calculated. The starting configuration for obtaining the partial phase diagram is the experimental crystalline phase.² The pressure is usually kept constant and the temperature is varied till the transition from the crystalline to plastic crystalline phase is observed (except for the 800 K run where pressure was varied).

4. Results and Discussion

4.1. High-Temperature Plastic Crystalline Phase. Simulation was carried out at 188 K and 1 atm pressure starting with the experimentally reported structure by Amoureux and Foulon.² Temperature was then increased in steps keeping the pressure constant. Figure 1 shows the variation of the lattice parameters with temperature. There is significant change in *a*, *b*, and *c* on increasing the temperature beyond 300 K. Figure 1 also shows the variation of volume of the unit cell as a function of temperature. Here the volume has been scaled by *V*₀ where *V*₀ is the volume of the unit cell at 188 K and 1 atm obtained from the calculation. A significant change in the volume occurs around 300 K, suggesting the possibility of the ordered phase transforming to a disordered phase. The error bars in volume at 1 atm are ±0.05% and ±0.09% at 188 and 310 K, respectively. The three angles α, β, and γ were close to 90° and did not show any significant variation with temperature.

The com–com, C–C, C–H, and H–H radial distribution functions (rdf's) for various temperatures are plotted in Figure

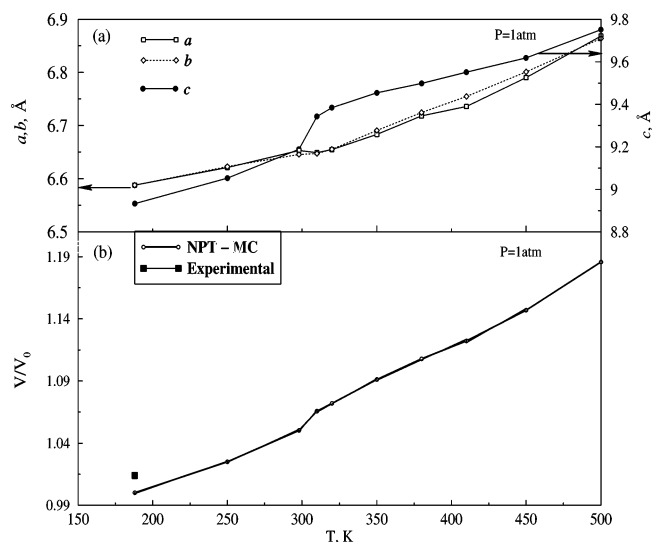


Figure 1. (a) Variation of cell parameters a , b , and c as a function of temperature, at 1 atm pressure. (b) V/V_0 at temperatures of 188, 298, 310, 320, 350, 380, 410, 420, 450, and 500 K at 1 atm pressure. V_0 is the volume at 188 K and 1 atm. The error bars in volume at 188, 298, 310, and 450 K are $\pm 0.05\%$, $\pm 0.09\%$, $\pm 0.09\%$, and $\pm 0.13\%$, respectively.

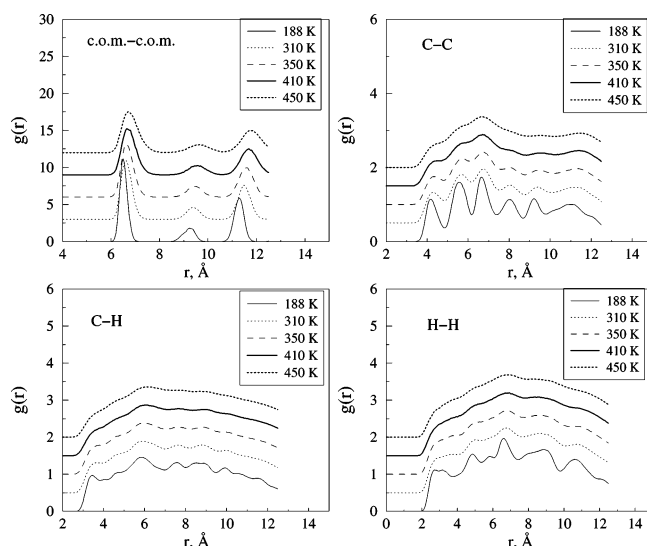


Figure 2. The com-com, C-C, C-H, and H-H rdf's at one atmospheric pressure.

2. Here we define center of mass as the mass-weighted molecular center. For undistorted adamantane, this will coincide with the center of the tetrahedron formed by the tertiary carbons. At 188 K, the rdf's show well-defined peaks suggesting the presence of orientational order in the crystal. By 298 or 310 K, there is significant loss of fine structure particularly in C-C and H-H rdf's. There is complete loss of structure by 410 K. In contrast to these, the com-com rdf shows only a broadening of the peaks with increase in temperature, suggesting loss of orientational order and transformation to a plastic crystalline phase.

The adamantane molecule has four C_3 axes directed from center of mass to the carbon of the four CH groups and six C_2 axes from center of mass to the six CH_2 groups. In the crystal lattice of the ordered low-temperature phase, the alignments of C_3 axes with $[111]$ directions give rise to two distinct orientations. In one sublattice, the C_3 axes are along the $[111]$, $[\bar{1}\bar{1}\bar{1}]$, $[\bar{1}\bar{1}1]$, or $[1\bar{1}\bar{1}]$ directions (the up-spin orientation), and in the other sublattice the adamantane molecules are such that the C_3

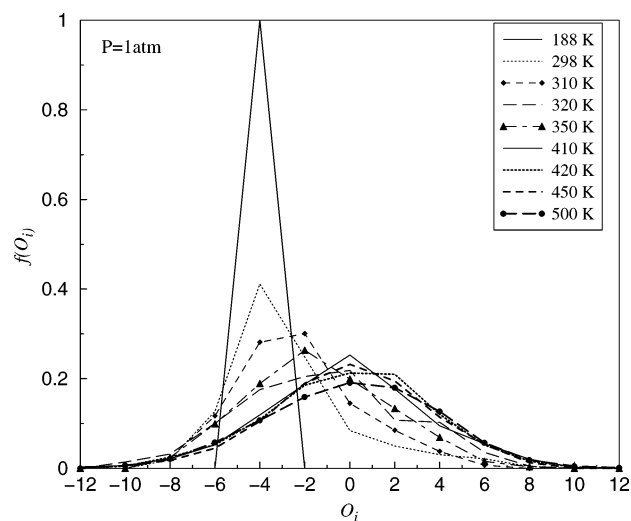


Figure 3. Orientational correlation function (O_i) at various temperatures at 1 atm pressure in set I runs.

axes are along the inverse directions $[\bar{1}\bar{1}\bar{1}]$, $[11\bar{1}]$, $[1\bar{1}1]$, or $[\bar{1}11]$ (termed the down-spin orientation). However, at any given time the C_3 axes of the molecules are never precisely oriented along the crystallographic $[111]$ directions. Instead, the four C_3 axes make a certain nonzero angle with the two sets of these four directions. Thus, Greig and Pawley computed all the angles and found the smallest angle with either the up or the down set of crystallographic axes. Thus, they mapped an infinite number of possible orientations of adamantane to either an up (spin +1) or down (spin -1) orientation of an Ising model, depending on whether the smallest angle was with the up or the down set of crystallographic axes. A measure of ordering in the crystal lattice is given by O_i where

$$O_i = \sum_{j=1}^{12} s_i s_j \quad s_i, s_j = \pm 1 \quad (2)$$

Figure 3 shows the variation of $f(O_i)$ with temperature. Up to 320 K, the peak of the distribution is seen at a value of $O_i = -4$ corresponding to eight neighbors with -1 spin and the remaining four having +1 spin. By 400 K, it is seen that the peak in the distribution shifts to $O_i = 0$, suggesting an orientationally disordered phase. The rdf's, $f(O_i)$, and V/V_0 suggest that the transition to the orientationally disordered phase occurs between 300 and 400 K. Experimentally, the transition from an ordered to a disordered phase occurs at 208.62 K. Previous studies on adamantane by Greig and Pawley¹² employing the modified intermolecular potential of Williams reported a transition temperature between 380 and 420 K. The difference in the transition temperature between the simulation and the experiment is due to the stronger intermolecular attraction between the adamantane molecules arising from the larger depth of the potential (see eq 1) of Williams. Previous studies by us on liquid and solid benzene using the potential of Williams also suggested a somewhat large intermolecular attraction.²⁶ In general, there appears to be an overestimation of the attractive interaction in the Williams potential. A consequence of this is that while it predicts the structural data correctly, the transition temperatures are often incorrectly reproduced. Another consequence is that molecular dynamics simulations using the Williams potential are expected to exhibit slower dynamics than real systems. This could lead to the higher transition temperature (around 400 K) observed by Greig and Pawley as compared to

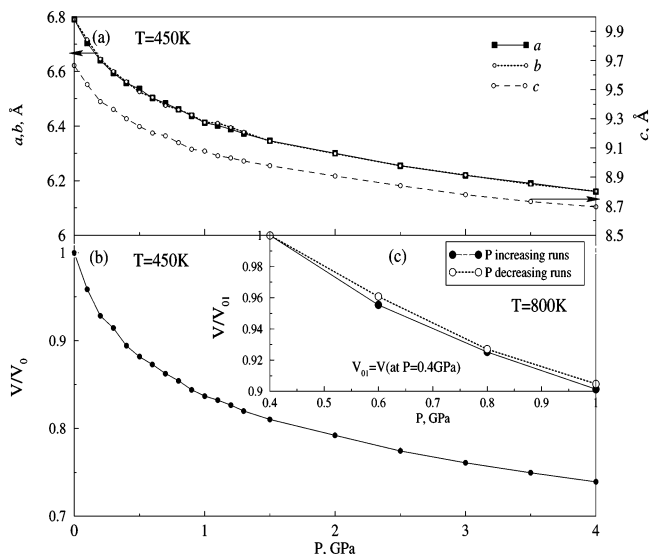


Figure 4. (a) Variation of cell parameters a , b , and c at various pressures and at a temperature of 450 K. (b) V/V_0 at pressures between 1 atm to 4 GPa, at 450 K where V_0 is the volume at 1 atm and 450 K. The error bars in volume have been shown at 1 and 2.5 GPa and are $\pm 0.09\%$ and $\pm 0.07\%$, respectively. (c) Inset shows the hysteresis observed during pressure increasing and decreasing runs. Volume has been scaled with V_{01} the volume of the unit cell at 0.4 GPa and 800 K.

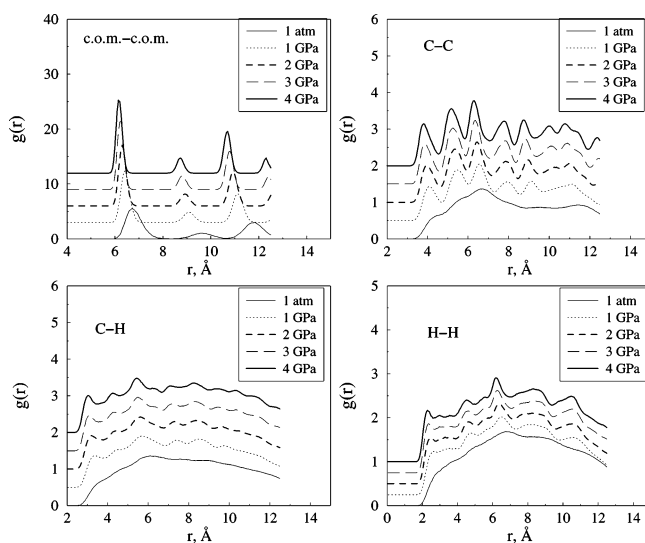


Figure 5. The com-com, C-C, C-H, and H-H rdf's at a temperature of 450 K and as pressure is increased from 1 to 4 GPa.

the 300 K observed in our MC simulations where equilibration is not a problem.

4.2. Pressure-Induced Transition from Disordered to Ordered Phase. Figure 4 shows a plot V/V_0 and lattice parameters at various pressures for $T = 450$ K. Here V is the volume of the unit cell at any given pressure and V_0 is the unit cell volume at 450 K and 1 atm obtained from the calculation. The error bars in volume at 450 K and 1 atm pressure are $\pm 0.07\%$ and $\pm 0.09\%$ at 1 and 2.5 GPa, respectively. The error bar in the lattice parameters is in the range of 2–3%. These were estimated using the method of Wood.^{27–29} Note the significant change in a , b , and c on going from 0.0001 to 1 GPa, suggesting the possibility of a structural transition. The cell angles α , β , and γ remained close to 90° and did not show any significant variation with pressure.

Figure 5 shows the variation in com-com, C-C, C-H, and H-H rdf's at 450 K and at pressures of 0.0001, 1, 2, 3, and 4 GPa. The appearance of well-defined structure in rdf's at and

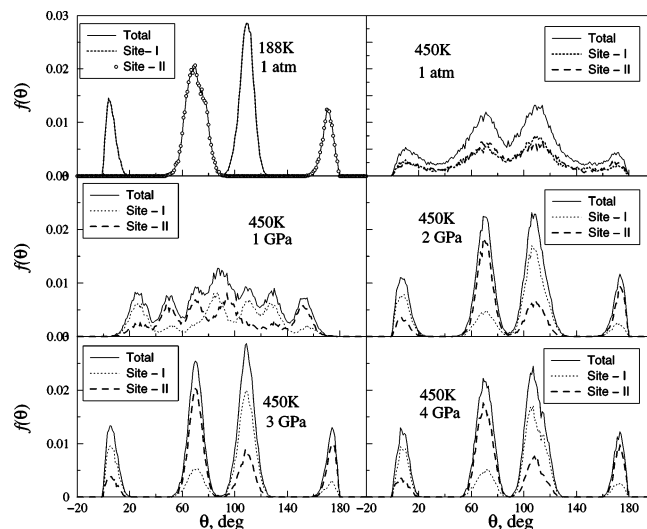


Figure 6. Angle distribution function at 1 atm, 188 K (crystalline); 1 atm, 450 K (plastic crystalline); 1 GPa, 450 K (crystalline); 2 GPa, 450 K; 3 GPa, 450 K; and 4 GPa, 450 K.

above 1 GPa suggests that the orientationally disordered phase has transformed to an ordered phase. $\langle O_i \rangle$ gives only an average estimate of the orientation without giving a detailed picture of the orientational order. We have therefore characterized the orientational ordering through a calculation of the distribution of the angle that C_3 axes make with the family of $[111]$ directions. Figure 6 shows this for pressure increasing runs at different pressures. Two separate distributions corresponding to molecules located in two sublattices are shown. In one sublattice, the distribution is seen to have maxima near 0° and 120° . In the other, they are near 60° and 180° . These two correspond to the spin up and down configurations of Greig and Pawley. With increasing pressure, especially at 3 and 4 GPa, it is seen that the molecules located on sublattice 1 are predominantly oriented with maxima near 0° and 120° . Fewer molecules in sublattice 1 have their C_3 axes making an angle of 60° and 180° . Molecules on sublattice 2 are predominantly those with their C_3 axes at 60° or 180° , but a small fraction exist where these angles are 0° or 120° . These fractions are 0.1557 and 0.1097 for sublattice 1 and sublattice 2, respectively.

Figure 7 shows the various rdf's at 188 K and 1 atm. This is the orientationally ordered crystalline phase. The rdf's of the phase at 4 GPa and 450 K obtained here are also shown after scaling the abscissa by $\zeta = (V_T/V_P)^{1/3}$ where V_T and V_P are the simulation cell volumes of the phases at 188 K, 1 atm and 450 K, 4 GPa. The difference curve showing the deviation between them is also plotted. The good agreement between the features of the four rdf's suggests that the two phases are essentially the same. These results are in good agreement with those of Ito.¹³ X-ray diffraction measurements at room temperature on the structure of adamantane by Ito up to 0.8 GPa of hydrostatic pressure suggest that adamantane undergoes a transition from the plastic crystalline phase to another phase in the region of pressure between 0.4 and 0.5 GPa. Based on the observed spacings and intensities, they concluded that this new phase has the same structure as the phase of adamantane at low temperature and atmospheric pressure, the well-known tetragonal phase with space group $P4_2/c$.^{1,2} Our simulations also suggest that the high-pressure phase has a structure similar to that of the low-temperature tetragonal phase, in excellent agreement with the findings of Ito.¹³

Note that C-C, C-H, and H-H rdf's show little deviation except near the first peak. This arises from the nonuniform

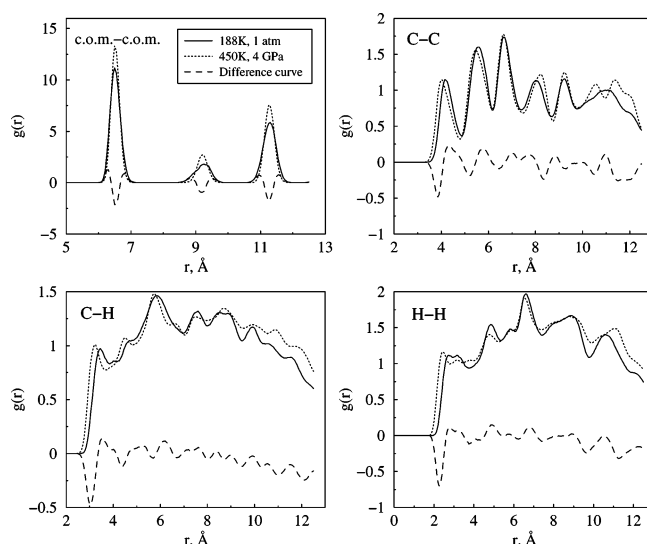


Figure 7. The com-com, C-C, C-H, and H-H rdf's at 188 K, 1 atm and 450 K, 4 GPa and the difference curve. For the phase at 450 K, 4 GPa, the abscissa of all the rdf's is scaled by a factor of 1.0555 which is $(V_T/V_P)^{1/3}$ where V_T and V_P are the unit cell volumes of the phases at 188 K, 1 atm and 450 K, 4 GPa, respectively.

shifting of the peaks in the rdf's on increase in pressure; it appears that the first peak of the high-pressure phase exhibits a greater shift to lower values of r than the other peaks. In contrast, the other peaks shift to lower values of r in proportion to the density ratio given by ζ . In the case of the com-com rdf, the nonzero difference seen near the first three peaks arises from the difference in the width of the peaks: the high-pressure phase generally has a lower width than the low-temperature phase.

Figure 8 displays snapshots of molecular orientations of adamantane, shown as tetrahedra by joining all tertiary carbons at (188 K, 1 atm), (450 K, 1 atm), and (450 K, 1 GPa). At 188 K and 1 atm, we see the well-ordered crystalline phase. At 450 K and 1 atm, the plastic crystalline phase has little orientational order. On increasing the pressure to 1 GPa, the adamantane molecules are orientationally ordered. To obtain an insight into the reasons for the transition, U_{inter} as a function of pressure up to 4 GPa is plotted in Figure 9. Here,

$$U_{\text{inter}} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^{N_a} \sum_{l=1}^{N_a} \phi(r_{ij}^{kl}(r)) \quad (3)$$

which is the intermolecular interaction energy. Here i and j refer to the molecules and indices k and l refer to the atoms within the molecule of adamantane. It is evident from Figure 9 that U_{inter} exhibits a minimum in the pressure range of 0.6–0.8 GPa. In terms of magnitude, U_{inter} is maximum at around these pressures. This suggests that the transition from the plastic crystalline phase to the crystalline phase is likely to occur in this pressure range. This is in agreement with the 0.4–0.5 GPa reported by Ito¹³ and the value of around 0.5 GPa reported by Vijayakumar.^{14–16}

4.3. Coexistence Curve: Crystal-Plastic Crystal Transition. Extensive simulations have been carried out by us to locate the temperature of transition at various pressures. These runs are carried out at a fixed pressure and temperature in the isothermal-isobaric ensemble (N, P, T). The runs are performed at different temperatures starting with the final configuration of the previous low temperature of the same pressure. The lowest temperature run employed the structure of the low-temperature orientationally ordered crystalline phase. Figure 10 summarizes

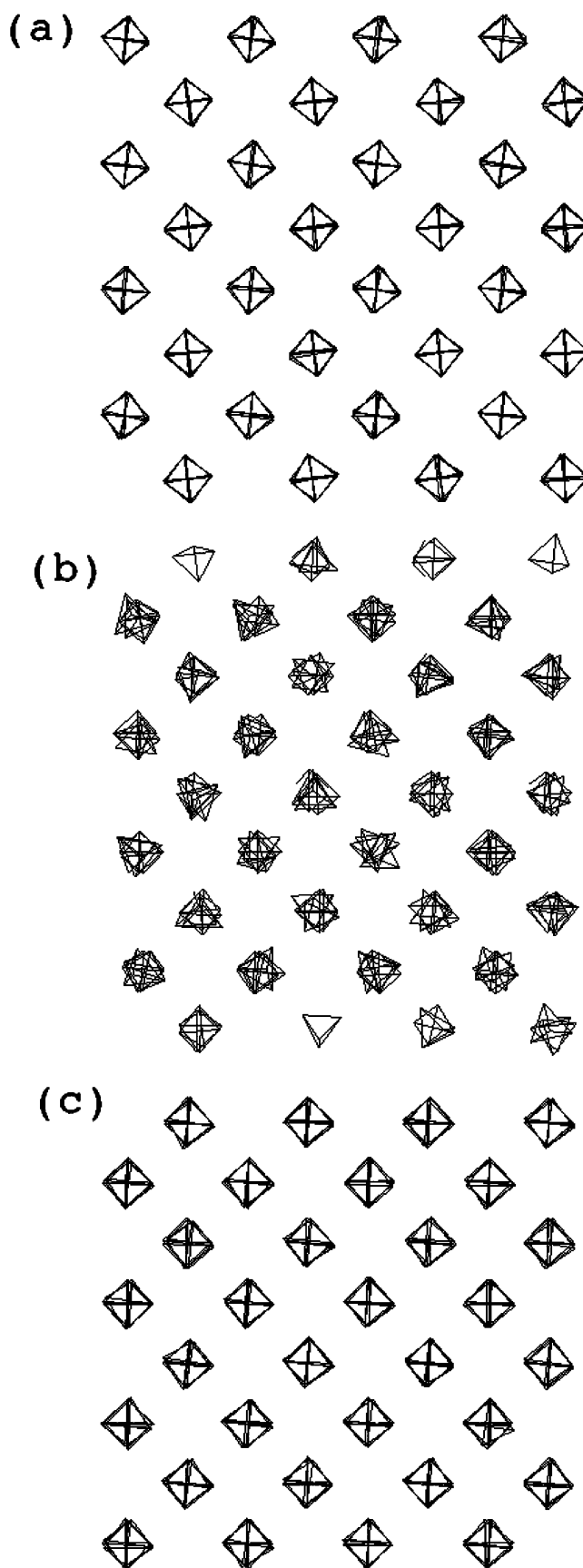


Figure 8. Snapshots of the simulated structure along crystallographic c axes at (a) 1 atm, 188 K (crystalline); (b) 1 atm, 450 K (plastic crystalline); and (c) 4 GPa, 450 K (crystalline).

the findings of these runs. Open circles and squares indicate the orientationally ordered crystalline phase, and filled circles

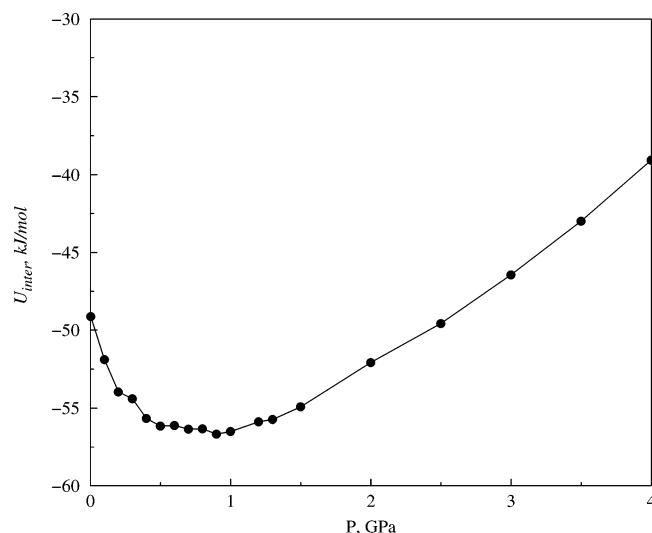


Figure 9. U_{inter} as a function of pressure at 450 K.

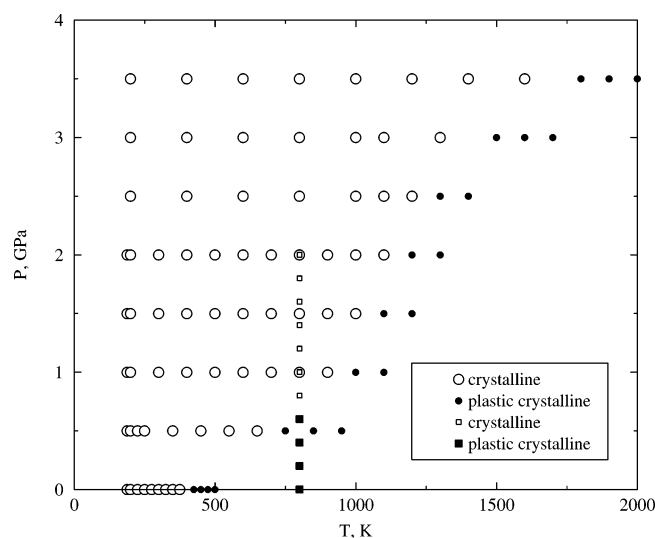


Figure 10. Coexistence curve between the crystalline and the plastic crystalline phases in the temperature range (0–2000 K) and 0–4 GPa. Open and closed circles correspond to the temperature increasing simulations, and open and closed squares correspond to the pressure decreasing simulations.

and squares the orientationally disordered phase. While circles (open and filled) correspond to temperature increasing runs, the squares (both open and filled) are for pressure-induced transition. The latter correspond to a pressure decreasing run starting with the orientationally ordered configuration at (800 K, 2 GPa) and a pressure step of $\Delta P = -0.2$ GPa. It is seen that when the pressure is reduced below 0.6 GPa, the crystalline phase transforms to a plastic crystalline phase.

The transition temperature obtained from the temperature increasing runs is in excellent agreement with that from the pressure decreasing run. This consistency between the temperature increasing and pressure decreasing runs suggests that the transition temperatures from these runs are probably reliable. In other words, the coexistence curve reported in Figure 10 is correct for the modified Williams potential. However, in view of the deficiencies in the Williams potential discussed earlier, the phase diagram may not show good agreement with the experimentally derived phase diagram. It is expected that the curve will shift to lower temperatures. However, the trends are likely to be similar. It is difficult to comment on the slope of

this curve in the P – T plane without a knowledge of experimental isothermal compressibility and thermal expansivity.

4.4. Conclusions. We find that the orientationally disordered phase changes to an ordered crystalline phase on increase in pressure between 0.6 and 0.8 GPa. We have shown that this new phase is the same as the low-temperature ordered tetragonal phase reported by Amoureux and Foulon² in 1987. Orientational order has been characterized in terms of the angle between the C_3 axes and the [111] directions. Previously, simulation methods have been employed successfully in simulating the transition from ordered to disordered phase but not from disordered to ordered phase as reported in the present study. The magnitude of the contribution of U_{inter} with pressure is maximum near 0.6 GPa, which seems to be responsible for the transition to the ordered phase. The variation in U_{inter} is smooth, suggesting that this is not a first-order transition. The decrease in entropy appears to be more than compensated by the increase in magnitude of U_{inter} . The results are in excellent agreement with the X-ray diffraction measurements of Ito¹³ and also of Vijayakumar et al.^{14–16} who report the existence of a transition around 0.5 GPa. A comparison of the low-temperature ordered phase and the high-pressure ordered phase suggests that the first peak in C–C, C–H, and H–H rdf's appears at a slightly lower value of r in the latter.

The coexistence curve between the orientationally ordered phase and the plastic crystalline phase has been obtained for the first time by extensive simulations at different temperatures, at a fixed pressure. A single pressure decreasing run was carried out to obtain the transition pressure and temperature. These transition pressure and temperature results agree with those of temperature increasing runs (see Figure 10). The Williams potential, in general, predicts a higher transition temperature. This is due to a stronger intermolecular attraction. Such stronger attractions seen here are in agreement with previous work on benzene using the Williams potential.²⁶ As a result, the dynamics is generally incorrectly predicted by the Williams potential.

Presently, simulations of solid adamantane at high pressures (up to 26 GPa) are in progress where distortion of the molecular geometry of adamantane has been observed.

Acknowledgment. The authors thank the Department of Science & Technology, New Delhi and BRNS (DAE), Mumbai for financial support and JNCASR, Jakkur, for support to N.A.M.

References and Notes

- (1) Donohue, J.; Goodman, S. H. *Acta Crystallogr.* **1967**, 22, 353.
- (2) Amoureux, J. P.; Foulon, M. *Acta Crystallogr.* **1987**, B43, 470.
- (3) Amoureux, J. P.; Bee, M.; Damien, J. C. *Acta Crystallogr.* **1980**, B36, 2633.
- (4) Kabo, G. J.; Blokhin, A. V.; Charapennikau, M. B.; Kabo, A. G.; Sevrak, V. M. *Thermochim. Acta* **2000**, 145, 125.
- (5) Corn, R. M.; Shannon, V. L.; Snyder, R. G.; Strauss, H. L. *J. Chem. Phys.* **1984**, 81, 5231.
- (6) Salman, S. R.; Said, E. Z.; Abas, K. F. *Thermochim. Acta* **1987**, 111, 21.
- (7) Graham, J. D.; Choi, J. K. *J. Chem. Phys.* **1975**, 62, 2509.
- (8) Chang, S.-S.; Westrum, E. F. *J. Phys. Chem.* **1960**, 64, 1547.
- (9) Yashonath, S.; Rao, C. N. R. *J. Phys. Chem.* **1986**, 90, 2552.
- (10) Ciccotti, G.; Ferrario, M.; Memeo, E.; Meyer, M. *Phys. Rev. Lett.* **1987**, 59, 2574.
- (11) Trew, A. S.; Pawley, G. S. *Can. J. Chem. Phys.* **1988**, 66, 1018.
- (12) Greig, D. W.; Pawley, G. S. *Mol. Phys.* **1996**, 89, 677.
- (13) Ito, T. *Acta Crystallogr.* **1973**, B29, 364.
- (14) Rao, R.; Sakuntala, T.; Deb, S. K.; Roy, A. P.; Vijayakumar, V.; Godwal, B. K.; Sikka, S. K. *J. Chem. Phys.* **2000**, 112, 6739.
- (15) Vijayakumar, V.; Garg, A. B.; Godwal, B. K.; Sikka, S. K. *Chem. Phys. Lett.* **2000**, 330, 275.
- (16) Vijayakumar, V.; Garg, A. B.; Godwal, B. K.; Sikka, S. K. *J. Phys.: Condens. Matter* **2001**, 13, 1961.
- (17) Williams, D. E. *J. Chem. Phys.* **1967**, 47, 4680.

- (18) Rao, C. N. R.; Yashonath, S. *J. Solid State Chem.* **1987**, 68, 192.
- (19) Parrinello, M.; Rahman, A. *Phys. Rev. Lett.* **1980**, 45, 1196.
- (20) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, 21, 1087.
- (21) Yashonath, S.; Rao, C. N. R. *Chem. Phys. Lett.* **1985**, 119, 22.
- (22) Nose, S.; Klein, M. L. *Mol. Phys.* **1983**, 50, 1055.
- (23) Nose, S.; Klein, M. L. *J. Chem. Phys.* **1983**, 78, 6928.
- (24) Normand, J.-M. *A Lie Group: Rotations in Quantum Mechanics*; North-Holland: Amsterdam, 1980.
- (25) Allen, M. P.; Tildesley, T. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.
- (26) Yashonath, S.; Price, S. L.; McDonald, I. R. *Mol. Phys.* **1988**, 64, 361.
- (27) Wood, W. W. *Physics of Simple Liquids*; Temperley, H. N. V., Rowlinson, J. S., Rushbrooke, G. S., Eds.; North-Holland: Amsterdam, 1968.
- (28) Chitra, R. Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1998.
- (29) Chitra, R.; Yashonath, S. *J. Phys. Chem.* **1997**, B101, 5437.