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DOI

[10.1063/1.473940](https://doi.org/10.1063/1.473940)

Publication date

1997

Published in

Journal of Chemical Physics

[Link to publication](#)

Citation for published version (APA):

Mulder, A., Michels, J. P. J., & Schouten, J. A. (1997). Monte Carlo simulations of the gamma-beta, alpha-gamma and alpha-beta phase transitions of nitrogen. *Journal of Chemical Physics*, 106, 8806. <https://doi.org/10.1063/1.473940>

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Monte Carlo simulations of the γ - β , α - γ , and α - β phase transitions of nitrogen

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(Received 31 October 1996; accepted 28 February 1997)

We have performed Monte Carlo simulations in order to determine the γ - β , α - γ , and the α - β phase transition lines of nitrogen with a recently developed nitrogen-nitrogen potential, and to examine the driving forces for these transitions. We have shown that it is possible to obtain the α - γ phase transition line by starting, at higher temperature, with the hexagonal representation of the disordered fcc structure. The transition line was found about 0.4 GPa higher than the experimental line. The orientational order-disorder behavior of the γ - β and the α - β phase transitions could be observed, but the structural changes, fcc-hcp, did not occur, probably due to a potential barrier. It is also possible that the potential model causes the fcc structure to be stable with respect to the hcp structure. The orientational entropy of the various phases has been compared qualitatively by introducing the orientational order parameters. It is suggested that a small difference in translational entropy, due to a difference in the c/a ratio, stabilizes the hcp structure (β phase) with respect to the fcc structure at zero pressure. In contrast with previous work, our simulations reveal that not all the layers of the ordered hcp structure at low temperature have the same orientational order. This might be the reason that the ordered fcc structure is stable at low temperature. © 1997 American Institute of Physics. [S0021-9606(97)51121-4]

I. INTRODUCTION

In a previous article¹ we developed a nitrogen-nitrogen potential, which is an improvement on the so-called Etters potential,² by performing Monte Carlo simulations. The improvement was made with respect to the stability of the solid phases of nitrogen (α , β , γ , δ , and ϵ). Although, the α , β , and δ -phase could be simulated³ with the original potential, it failed to describe the γ and ϵ -phase correctly. The addition of an anisotropic energy term to the Etters potential did stabilize the γ and ϵ -phase, next to the α , β , and δ -phase, where the stability of the phases was examined only at one state point. In this work we will examine the γ - β , α - γ , and α - β transitions, discuss the driving force of these transitions, and determine the phase transition lines in the model system with this new nitrogen-nitrogen potential.

The α -phase ($Pa3$) (Refs. 4–8) is a fcc structure with orientationally ordered molecules. The structure can be represented in a cubic and hexagonal way. In the cubic representation, the centers of mass are located at the corners of the cube and in the middle of the faces; the molecules are aligned in the direction of the four body diagonals. The centers of mass of the hexagonal representation are located on a hexagonal lattice in layers with an $ABCABC\dots$ sequence. Within one layer, the molecules are aligned in a so-called pinwheel structure; one molecule being the pin and the neighbor molecules forming the wheel. The pin molecules are aligned along the c axis and the wheel molecules align at an angle of 20° alternating above and below the plane and at an angle of 60° in the plane with respect to each other. In Fig. 1 the ordering of the molecules within one layer is shown and the position of the pin molecules of the layer underneath and above is indicated. Whereas the α -phase is

an ordered fcc structure, the β -phase ($P6_3/mmc$) (Refs. 3, 4, 6, 7, 9–19) is a disordered hcp structure with an almost ideal c/a ratio. The centers of mass are located on a hexagonal lattice, as with the α -phase, but the layers are stacked in an $ABABAB\dots$ sequence instead of an $ABCABC\dots$ sequence. The character of the orientational disorder has been the subject of various studies. The first studies^{6,11} suggested that the molecules are freely precessing around the crystal c axis with an angle of approximately 56° or that the molecules are orientationally distributed randomly among 24 equivalent positions of the $P6_3/mmc$ space group. More recent experiments^{9,10} suggested that the molecules are randomly oriented. Calculations^{15,16} and computer simulations^{3,19,20} demonstrated that the orientational behavior of the molecules is highly dynamical, although there are slightly preferred orientations. The *ab initio* calculations by van der Avoird *et al.*¹⁷ suggest that the molecules jump rapidly between six orientationally localized states.

The tetragonal γ -phase ($P4_2/mnm$) (Refs. 7, 21) is just like the α -phase, orientationally ordered; the molecular axis make an angle of 90° with the c axis, are parallel to each other within the ab plane and perpendicular between the ab planes.

The experimentally determined α - β , γ - β , and α - γ phase transition lines^{7,22,23} are shown by the dashed lines in Fig. 8(a). Kuchta *et al.*²⁰ have performed Monte Carlo simulations to study the α - β phase transition at zero pressure using the original Etters potential. Although in principle the method of simulation allows the transition, the failure to detect the α - β transition is ascribed to a large potential barrier between the fcc and hcp phases, due to the reconstruction of

FIG. 1. The ab plane of the hexagonal representation of the α -phase; the unit cells are indicated by the dashed lines, the cross indicates the pin of the plane above, and the star the pin of the plane below.

the layer sequence, which is required to realize this transition.

Raich *et al.*²⁴ and Kobashi *et al.*²⁵ have examined the α - γ transition only at zero Kelvin by calculation of the crystal energy of both phases. The transition pressure was found at 0.43 GPa and 0.40 GPa, respectively, whereas the experimental value²² near 0 K is 0.39 GPa. However, the parameters of the potential used in these calculations are optimized with respect to experimental data, including p - V measurements, of both phases. Kobashi *et al.*²⁵ used different nitrogen quadrupole moments for the α and γ -phase.

No simulations have been performed for the γ - β phase transition, because until recently no potential was available, which could be used to simulate the γ -phase of nitrogen.

In this work we will present the results of the simulations of the γ - β , α - γ , but also the α - β phase transitions by making use of the new, improved potential.

II. METHOD

We have performed Monte Carlo simulations with an (N, P, T) ensemble. The simulation method should allow the transformation from one phase to another, and to achieve this, a deformable simulation cell was used; the angles and lengths of the cell are allowed to change during the simulation. In principle, each phase transition which can be described by one or more of these changes, can be studied with this method. However, it is possible that the transition will not occur, because of a potential barrier corresponding to the deformation of the cell or the possible changes in lattice positions. The new site-site potential and the Monte Carlo procedure have been described extensively in a previous article.¹

The number of unit cells was chosen in such a way, that the dimensions of the box lengths were larger than two times

FIG. 2. The c/a ratio of the γ -phase (dots), and the c/a ratio (down triangles), b/a ratio (up triangles), and box angle α (diamond) of the β -phase, as a function of temperature.

the cut off range, 9.0 Å, of the potential. The unit cell of the γ -phase contained two molecules, and the simulation cell was made up of six unit cells in the a and b directions and four in the c direction, resulting into a total of 288 molecules. At the start of the simulations the molecules were given an orientation corresponding to the experimental crystal structure.

The unit cell of the β -phase (disordered hcp) was taken rectangular and contained four molecules. The simulation cell was made up of six unit cells for the a direction, and four unit cells for the b and c directions, resulting into a total of 384 molecules. The molecules were given a random orientation.

The cubic unit cell of the α -phase contained four molecules, and the simulation cell was made up of four unit cells in each direction, resulting into a total of 256 molecules. The molecules were given an orientation corresponding to the cubic, experimental crystal structure. The unit cell of the hexagonal representation was taken rectangular, as the unit cell of the β -phase, and contained six molecules. The simulation cell was made up of six unit cells for the a direction, four for the b direction, and two for the c direction, resulting into a total of 288 molecules. Note that in this way two ABC layers (fcc) were generated in order to create the possibility to get three AB layers (hcp) during the simulations. The molecules were given an orientation corresponding to the experimental crystal structure of the hexagonal representation (Fig. 1).

As a standard, the thermodynamic averages were calculated over 7000 Monte Carlo steps (MCS), after 3000 MCS in which the system could go to equilibrium. The orientational behavior of the molecules was examined by recording the orientation distribution functions (ODF), in polar coordinates φ and $\cos \theta$, during the second part of the calculation.

FIG. 3. The φ distribution of the ODF of the hcp and fcc structures at several temperatures at 1.0 GPa and zero pressure.

III. RESULTS

A. The γ - β transition

We have examined the γ - β phase transition [Fig. 8(a)] at 1.0 GPa. The simulations are performed at 10, 20, 30, 40 K, and from 50 to 90 K in steps of 2 K. The cooling run performed with the β -phase structure as well as the heating run with the γ -phase structure, show a jump in energy, volume and enthalpy. Both the γ and the β -phase undergo a phase transition, which involves a change in structure and orientational order. The transition of the β -phase is accompanied by a change in the c/a ratio from 1.621 to 1.547, the b/a ratio from 1.731 to 1.689, and the box angle α from 90° to 93° (Fig. 2); the molecules align at ($\varphi \approx +38^\circ$, $\theta \approx 65^\circ$) and ($\varphi \approx -38^\circ$, $\theta \approx 65^\circ$). This ordered structure is not the

γ -phase structure, but closely related, and shall be denoted as γ^{hcp} . The ODF at several temperatures of the β as well as the γ^{hcp} -phase at 1.0 GPa, are shown in Fig. 3(a). The transition of the γ -phase is accompanied by a change in the c/a ratio from about 1.31 to 1.41 (Fig. 2), and the molecules, which are aligned at $\varphi = \pm 45^\circ$ and $\theta = \pm 54.7^\circ$ in the γ -phase, become orientationally disordered. This disordered structure is not the hcp structure of the β -phase, but it appears to be a *rectangular* representation of the disordered fcc structure (Fig. 4). The disorder of the fcc as well as the hcp (β -phase) structure at high temperature is highly dynamical, with only weakly preferred orientations, which correspond to the orientations of the pinwheel structure.

Additional calculations near the transition with 100.000

FIG. 4. The rectangular representation of the fcc structure, the dashed lines indicate the ab plane of the hexagonal representation of the fcc structure ($b = \sqrt{3}$).

MCS revealed that both transitions are reversible, although the β -phase showed a small metastability range. The disordered fcc- γ transition occurred between 57 and 58 K, and the γ^{hcp} - β transition between 51 and 53 K. Experimentally the γ - β phase transition occurs at about 68 K.⁷

The γ - β phase transition did not occur, although the method allows the transition. The transition can be thought of as taking place in two parts; first the structural and orientational changes, discussed above, which transforms the γ -phase into the disordered fcc, second the shift of layers of molecules, which transforms the disordered fcc to the disordered hcp structure (β -phase). Whereas the first part could be achieved, the shift of the layers did not occur. Because the disordered hcp as well as the disordered fcc structure could be simulated within the same high temperature region, the fcc-hcp transition apparently involves a potential barrier, which is too large to overcome. It is difficult to determine by simulations which one is the metastable structure. The relative stability of hcp and fcc structures is a well-known problem.^{26,27}

In case of the *ordered* structures, the γ^{hcp} structure is probably metastable with respect to the γ -phase, because the enthalpy of the γ -phase is lower by 5–9 K in the range from 0 to 40 K. We do not expect that the difference in configurational entropy of the ordered structures will overcome this enthalpy difference.

The calculations of this work reveal equal enthalpies for both *disordered* structures. The orientational order parameter is introduced, providing a quantitative way to describe the orientational behavior of the molecules, and a tool for measuring the rotational entropy. The structures exhibit the same, weakly preferred orientations of the pinwheel structure. The order parameter of the φ -coordinate, based on the orientations of the pinwheel structure, can be defined as

FIG. 5. The c/a ratio (dots), b/a ratio (down triangles), and box angle α (up triangle) of the fcc structure as a function of temperature.

$$O_{\varphi}^{\text{hex}} = \cos[6(\varphi - 30^{\circ})] \quad (1)$$

which is unity at the $\varphi = -30^{\circ}$, 30° , and 90° preferential orientations. Because the order parameters are defined within the *hexagonal* representation of the hcp and fcc structure, additional simulations have been performed on the disordered fcc structure in the *hexagonal* representation, while decreasing the temperature. The simulation cell of this structure has been taken the same as that of the hexagonal representation of the α -phase, but the molecules were given a random orientation. Likewise, it is interesting to know if the disordered fcc structure in the *hexagonal* representation will transform to the γ -phase during the simulations.

Simulations were performed from 82 to 50 K in steps of 2 K and at 50, 40, 30, 20, and 10 K with 10.000 MCS, and at 57 and 56 K with 100.000 MCS. The energy and volume of the cooling run with the hexagonal fcc structure are identical to the values of the previous heating run with the γ -phase structure. The hexagonal fcc structure undergoes a transition at 56 K; the structure becomes orientational ordered, and the b/a and c/a ratios, and the box angle α change from about 2.45° , 1.73° , and 90.0° to about 2.40° , 1.65° , and 93.9° (Fig. 5), which indeed corresponds to the γ -phase structure. In this representation, the molecules of the γ -phase align along two different directions, ($\varphi = 30^{\circ}$, $\theta = 54.7^{\circ}$) and ($\varphi = -30^{\circ}$, $\theta = 125.3^{\circ}$). The ODF at several temperatures of the γ as well as the disordered fcc structure at 1.0 GPa, are shown in Fig. 3(b).

The order parameters of the fcc and hcp structures are equal in the temperature region where both structures are orientationally disordered. Clearly, the disorder of both structures is the same, and the rotational entropy will likely be almost equal. However, the c/a ratio (Figs. 2 and 5) of both phases could indicate that the *translational* entropies are different. The c/a ratio of the fcc structure is equal to the ideal value of $\sqrt{6} \approx 2.45$, whereas the c/a ratio of the hcp structure is slightly less than the ideal value of $\frac{2}{3}\sqrt{6} \approx 1.63$,

FIG. 6. The orientational order parameter as function of the temperature of the fcc structure in the hexagonal representation (up triangle), and the hcp structure (down triangle). The 40–80 K region is enlarged for the disordered fcc and hcp structure.

suggesting less translational freedom. As a result the volume of the fcc structure is larger than the volume of the hcp structure, which could indicate a larger *translational* entropy. These results would suggest that, in the case of these simulations, the disordered hcp structure (β -phase) is metastable with respect to the disordered fcc structure at 1.0 GPa. This is in contradiction with experiment.

B. The α - β transition

The calculations of the α - β phase transition [Fig. 8(a)] have been performed at zero pressure, in order to compare the results obtained with the new potential with those of Kuchta *et al.*²⁰

A cooling run has been performed with the disordered hcp (β -phase) as well as the disordered fcc structure from 70 K to 10 K. The cooling run of both phases show an energy and volume jump. Whereas the transition of the γ and β -phase simulated at 1.0 GPa involves structural *and* orientational changes, the transition of the α and the β -phase at zero pressure are caused only by an orientational order-disorder transition. The ODF are given in Figs. 3(c) and 3(d). Again, additional calculations reveal that both transitions are reversible. As with the γ - β transition, the α - β phase transition did not occur. Apparently, also at zero pressure the potential barrier of the fcc-hcp transition is too large to overcome.

Figure 6 shows the order parameters, as defined in the previous section, as a function of temperature; for both structures the orientational order changes at the transition. The order parameter of the α -phase goes to $\frac{3}{4}$ in the zero temperature limit, because the pin molecules contribute to the order parameter. The order parameter of the ordered hcp structure is lower than that of the fcc structure, although the orientations correspond to the pinwheel ordering [Fig. 3(b)]. This is caused by the stacking of the layers of the hcp structure. A

FIG. 7. The c/a ratio of the hcp and fcc phases as a function of temperature.

calculation with a simulation cell of six layers (three unit cells in the c direction, $N=288$) performed at 10 K, revealed that not all layers exhibit the same orientational order; two layers with pinwheel ordering ($O_{\varphi}^{\text{hcp}}=0.49$) are alternated with one layer with a different ordering ($O_{\varphi}^{\text{hcp}}=0.09$). Kuchta *et al.*²⁰ observed a pinwheel ordering in *each* plane, but only at *short range*. Both the intermolecular potential as well as the number of unit cells used in their calculations can cause this difference. To preserve the pinwheel ordering, the boundary conditions require an even number of rectangular hcp unit cells in the a and b directions.

This stacking of the layers also causes the energy to be about 30 K higher. Therefore, it is likely that the ordered hcp structure is metastable with respect to the ordered fcc structure, although the rotational entropy of the hcp structure will be slightly higher.

As with the calculations at 1.0 GPa, at high temperature the orientational disorder of both structures is highly dynamical, with only weakly preferred orientations, which correspond with the pinwheel ordering. The order parameters (Fig. 6) indicate equal rotational entropies. The energy of the disordered fcc is slightly lower than that of the disordered hcp. The c/a ratio (Fig. 7) of the fcc structure has the ideal value, whereas the disordered hcp structure has a ratio, which is slightly higher than the ideal value. This higher value suggests more *translational* entropy, and results in a larger volume. This difference in translational entropy could overcome the very small difference in energy, and stabilizes the hcp structure (β -phase) with respect to the fcc structure.

C. The α - γ transition

The α - γ phase transition [Fig. 8(a)] has been examined in three different ways. First, the stability of the α and the γ -phase was examined along an isotherm, because the experimentally determined α - γ phase transition line²² is only slightly dependent on pressure. Second, the transition pressure at zero temperature was determined by calculation of

FIG. 8. The phase diagram of nitrogen; (a) the experimental lines; (b) the fcc $\rightarrow\alpha$ (up triangles) and fcc $\rightarrow\gamma$ (down triangles) transitions, and the $\alpha\rightarrow\gamma$ (star) transition at zero temperature; (c) the $\gamma\rightarrow\alpha$ (solid squares), the $\gamma\rightarrow$ fcc (diamonds), and the $\alpha\rightarrow$ fcc (dots) transitions.

the enthalpies of both phases. Third, the fcc- α , fcc- γ , and $\gamma\rightarrow\alpha$ transitions were examined at various pressures and temperatures.

The calculations were performed at 10 K, where the contribution of the entropy to the free energy is small, because of the low temperature and because both phases are orientationally ordered. Starting at zero pressure, the α -phase was simulated with the cubic simulation cell up to 1.0 GPa in steps of 0.05 GPa. The γ -phase was simulated with the rectangular simulation cell, starting from 1.0 GPa down to zero pressure in steps of 0.05 GPa. The $\alpha\rightarrow\gamma$ phase transition was not observed within the $0\leq p\leq 1.0$ GPa region; both structures remained stable and no jump in energy or volume could be detected. At zero pressure the enthalpy of the α -phase structure is lower than the enthalpy of the γ -phase structure, but between 0.85 and 0.90 GPa the difference in enthalpy becomes zero. Therefore, we expect the $\alpha\rightarrow\gamma$ phase transition to occur between 0.85 and 0.9 GPa. The phase transition was not detected, probably because the cubic simulation cell of the α -phase and the rectangular cell of the γ -phase could not transform into one another.

Whereas at zero temperature, the energy of the α -phase could be calculated directly given the volume, the energy of the γ -phase was minimized with respect to the c/a ratio. The interactions within a range of 50 Å were taken into account. A third order polynomial was fitted through the data points, and the pressure and enthalpy could be calculated. The enthalpy of the α and γ -phase are equal at $p=0.855(1)$ GPa with $\Delta V=0.328$ cm³/mol. These values are higher than the experimental values;²² $p=0.39$ GPa and $\Delta V=0.165$ cm³/mol. We have also calculated the $\alpha\rightarrow\gamma$ transition at zero temperature without the anisotropic energy term, the original Etters potential. The α -phase remained stable up to $p=3.12(1)$ GPa. The zero temperature values obtained by Raich *et al.*²⁴ and Kobashi *et al.*²⁵ are close to the experimental values, but the parameters of the nitrogen potentials used in these calculations have been optimized with respect

to experimental data of the α and the γ -phase, and are different for both phases.

In the previous sections, we have found that the disordered fcc structure transformed at zero pressure to the ordered fcc structure, the α -phase, but at 1.0 GPa to the γ -phase structure. Therefore, additional simulations have been performed while cooling down the disordered fcc structure with the hexagonal simulation cell, in steps of 2 K at various pressures. Depending upon the pressure, the hexagonal fcc structure will transform to the α -phase structure or the γ -phase structure. The transition temperature of the fcc $\rightarrow\alpha$ and the fcc $\rightarrow\gamma$ transitions at various pressures are presented in Table I and Fig. 8(b). Whereas between 0 and 0.8 GPa the disordered fcc structure transforms to the α -phase, at 0.9 it transforms to the γ -phase. These results indicate that the $\alpha\rightarrow\gamma$ phase transition at $T=53(1)$ K occurs between 0.8 and 0.9 GPa.

Finally, simulations have been performed in steps of 2 K to investigate the stability of the α and the γ -phase in the region $0\leq p\leq 1.2$ GPa, with the hexagonal simulation cell for both structures. The $\gamma\rightarrow\alpha$, $\alpha\rightarrow$ fcc, and $\gamma\rightarrow$ fcc transition temperatures are presented in Table I and Fig. 8(c). It is

TABLE I. Transition temperatures obtained from simulations with the hexagonal simulation cell of the fcc, α -phase, and γ -phase structure.

Pressure (GPa)	$T_{\text{fcc}\rightarrow\alpha}$ (K)	$T_{\text{fcc}\rightarrow\gamma}$ (K)	$T_{\alpha\rightarrow\text{fcc}}$ (K)	$T_{\gamma\rightarrow\text{fcc}}$ (K)	$T_{\gamma\rightarrow\alpha}$ (K)
0.0	42.5(5)		43.5(5)		
0.1	47(1)		49(1)		11(1)
0.3	49(1)		53(1)		27(1)
0.6	51(1)		58(1)		47(1)
0.7	51(1)		59(1)	52.5(5)	
0.8	53(1)		61(1)	53(1)	
0.9		53(1)	61(1)	57(1)	
1.0		56.5(5)	63(1)	57.5(5)	
1.2			65(1)	63(1)	

shown that it is indeed possible to simulate the $\gamma \rightarrow \alpha$ phase transition. However, the previous calculations of this section show that at this transition the γ -phase is metastable. This holds also for the simulations performed at 0.7 and 0.8 GPa, where the γ -phase structure transforms to the disordered fcc structure. The α -phase continued to exist in the whole region, also above 0.8 GPa, where it is metastable; the $\alpha \rightarrow \gamma$ transition did not occur.

The zero temperature calculations and the simulations with the disordered fcc structure, indicate that the α - γ phase transition line is nearly horizontal, in agreement with experiment, and will be between 0.8 and 0.9 GPa, which is about 0.4 GPa higher than the experimental transition line.²² The zero temperature calculations revealed that the energy of the α -phase is lower than that of the γ -phase, and that the difference is increasing with pressure. The α - γ phase transition is not caused by the energy, but by the larger compressibility of the γ -phase.

IV. CONCLUSION AND DISCUSSION

Although in principle, the simulation method allows the occurrence of the transitions between the α , β , and γ phases of nitrogen, in practice the transitions did not happen due to potential barriers. However, we have shown that it is still possible to obtain the α - γ phase transition line by starting, at high temperature, with the hexagonal representation of the disordered fcc structure.

Depending on the pressure the disordered fcc structure transformed to the α or to the γ -phase structure. The transition pressure obtained this way in combination with the zero temperature calculations resulted in a nearly horizontal transition line, which is about 0.4 GPa higher than the experimental phase transition line.²² The investigation of the α - γ phase transition revealed that the α -phase as well as the γ -phase showed large metastability; only the γ to α -phase transition occurred, under the condition that the simulation cell obtained from the fcc structure in the hexagonal representation was used for both structures.

The ordered structure of both the γ and the α -phase transformed to the disordered fcc structure. The disordered hcp structure of the β -phase transformed to an ordered hcp structure at zero pressure, and to a structure which is closely related to the γ -phase, at 1.0 GPa. All transitions were found to be reversible. Both ordered structures obtained from the disordered fcc structure, the α and γ -phase structures, exhibit a lower enthalpy than the ordered structures obtained with the hcp structure. On the basis of the simulations, we expect them to be stable, in agreement with experiment.

The α - β phase transition involves an order-disorder and a fcc-hcp transition. Although the order-disorder transition could be simulated, the fcc-hcp transition did not occur. The same holds for the γ - β phase transition; the order-disorder transition was observed, but the rearrangement of the layers did not occur. There are two possible explanations. First, because both disordered phases could be simulated within the same temperature region, the reconstruction of the layer sequence, required for the fcc-hcp transition, involves

a potential barrier which is too large to overcome. Besides, it is possible that the potential causes the fcc structure to be stable with respect to the hcp structure.

Although we cannot discriminate between the stable and metastable phase, because the entropies can not be calculated with this method, there are two striking features. First, whereas the enthalpy (energy) of the disordered fcc structure is lower than that of the disordered hcp structure at zero pressure, it becomes equal at 1.0 GPa. Next to this, the c/a ratio of the hcp structure changes from slightly higher than the ideal value at zero pressure, to slightly lower at 1.0 GPa. This is reflected in a larger volume of the hcp structure compared to that of the fcc structure at zero pressure, and vice versa at 1.0 GPa. Although the rotational entropies of the disordered structures, indicated by the orientational order parameters, are about equal at both pressures, the difference in volume might indicate a difference in configurational entropy. It is possible that the potential and the conditions of the simulations cause the disordered hcp structure to be stable at low pressure, and the disordered fcc structure at high pressure. The calculation of the free energy can give a decisive answer on the stability of the disordered as well as the ordered structures.

Whereas the α - β , and γ - β transitions are order-disorder transitions, and are driven by the rotational entropy, in the course of which nature apparently prefers the disordered hcp structure, the α - γ transition is caused by the larger compressibility of the γ -phase.

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