Computer-simulation study of high-temperature phase stability in iron

Yu. N. Osetsky

Russian Research Center 'Kurchatov Institute,'' Kurchatov sq.1, 123182 Moscow, Russia and Departament de Matemàtica Aplicada III, Universitat Politècnica de Catalunya, Gran Capitán, s/n, E-08034 Barcelona, Spain

A. Serra

Departament de Matemàtica Aplicada III, Universitat Poliècnica de Catalunya, Gran Capitán, s/n, E-08034 Barcelona, Spain (Received 4 March 1996; revised manuscript received 19 May 1997)

A pair-potential model describing interatomic interactions in γ - and δ -iron based on the generalized pseudopotential theory is presented. This potential describes the temperature-dependent stability of different phases and simulates forward and reverse transformations. This, together with the results obtained in the calculation of the thermal expansion, the Gruneisen parameter, and the temperature dependence of the mean-square displacements, for both the fcc and bcc phases, show the reliability of the potential for describing temperaturedependent properties. The stability of fcc and bcc phases has been studied by molecular dynamics. It was found that γ -Fe is unstable for temperatures higher than 1820 K and δ -Fe is unstable for temperatures lower than 1400 K and higher than 1950 K. In perfect crystallites, when Parinello-Rahman and Nose mechanics are applied, these instabilities lead to the fcc \rightarrow bcc transformation via Bain distortions and to the bcc \rightarrow fcc transformation via a Burgers mechanism. The estimated phase-transformation temperature is about 1610 K, which is in good agreement with the experiments. The important role of the vibrational energy in the phase stability has been concluded. The melting temperature of the bcc-Fe was estimated as ≈ 1880 K which is about 70 K higher than the experimental one. [S0163-1829(98)03002-1]

I. INTRODUCTION

The phase stability and phase transformations (PT's) of metals and alloys play an important role in their manufacture and behavior at working conditions. There are a lot of works devoted to this problem and several phenomenological models have been reported. Any phenomenological model of PT is based on a particular atomic-level mechanism of transformation from one lattice type to the other. Two mechanisms have been suggested for the bcc \leftrightarrow fcc transformations. Bain¹ proposed that an fcc-bcc transformation is the appropriate axial deformation alone. Thus, the original fcc crystal expands along [100] and [010] by about $\approx 11\%$ and contracts along [001] by $\approx 21\%$, so that these axes transform to [110], [110], and [001] in the bcc crystal. This mechanism is used in many theoretical models of martensitic PT for different metals including Fe (see, for example, a discussion in Ref. 2). Burgers³ suggested a mechanism for the hcp \rightarrow bcc transformation in Zr that can be applied to the bcc⇔fcc transformation as well. According to this mechanism the original (011), (011), and (100) planes of a bcc crystal transform to the (111), (112), and (110), respectively, of the fcc crystal. During this transformation the original bcc crystal oriented along [100], [011], and [011] is deformed ≈ -12 , ≈ 2 , and ≈ 8 %, respectively. The Burgers transformation is more complex than the Bain distortions because it demands shifts of some atomic planes and lines. This mechanism was also used in many models of PT in metals.⁴

Although the above mechanisms for lattice transformations are widely used, the kinetics of the structural transformations (both diffusional and diffusionless or martensitic) is still not understood at the atomic level. At present, the experimental methods are not able to follow such fast processes at the atomic level and perhaps only computer simulation methods can help in the understanding of the atomic scale details of phase transformations. However, the number of computer simulation works devoted to the study of PT mechanisms is rather small because of the lack of suitable potentials. In fact, it is difficult to find a single interatomic potential able to describe the stability of different phases for different temperatures.

Actually, the main part of these works deals with the lattice reconstruction under pressure (see, for example, Ref. 5), while the literature on the modeling of the temperatureinduced transformations is quite scarce. We found only a few works devoted to the fcc \leftrightarrow bcc phase transformation,^{6–9} but, among them, no one reported the simulation of forward and reverse transformations with the same potential.

One of the aims of this paper is to create a potential able to meet the above-mentioned requirements, i.e., to describe the temperature-dependent stability of different phases and to simulate forward and reverse transformations. The other objective is to study the applicability of different techniques related to the molecular-dynamic (MD) simulation of phase transformations and phase stability.

The metal chosen for this study is iron. It is well known that at low temperatures iron has a bcc structure of ferromagnetic character (α -Fe) that changes to a paramagnetic fcc structure (γ -Fe) at about 1430 K. At 1610 K it changes again to a bcc paramagnetic structure (δ -Fe) up to the melting point at 1811 K.

Provided that magnetic transformations are out of the scope of this paper we have studied the changes in structure at high temperature, where the magnetic contribution to the structural stability may be considered negligible. Therefore, we focused the work on the $\gamma \leftrightarrow \delta$ stability and melting.

755

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II. INTERATOMIC POTENTIAL

A. Construction

As in our previous works^{9,10} we constructed the effective potential for the Fe-Fe interaction within the pair approximation of the generalized pseudopotential theory by Moriarty^{11,12}

$$\phi(r) = V_{\rm sc}(r) + V_d(r) + V_{ol}(r).$$
(1)

The first term of Eq. (1) is the screened Coulomb interaction which in the second-order pseudopotential theory has the form:

$$V_{\rm sc}(r) = \frac{Z^2 e^2}{r} - \frac{\Omega^2}{8\pi^3 e^2 r} \int_0^\infty q^3 V^2(q) \left(1 - \frac{1}{\epsilon(q)}\right) \sin(qr) dq,$$
(2)

where Z is the effective valence, $\epsilon(q)$ is the dielectric function, and V(q) is the Fourier transform of the pseudopotential. Here we used the approximation of Geldart-Taylor¹³ for $\epsilon(q)$ and the local pseudopotential of Heine-Animalu in the form¹⁴

$$V(q) = -\frac{4\pi Z e^2}{\Omega q^2} \left[\cos(qR_s) + U_s \left(\frac{\sin(qR_s)}{qR_s} - \cos(qR_s) \right) \right] \\ \times \exp\left(-\frac{\gamma q^4}{16k_F^4} \right), \tag{3}$$

where $k_F = (3\pi^2 z/16\Omega)^{1/2}$ is the Fermi momentum of the metal at T = 0 K and R_s , U_s , and γ are fitting parameters.

The second term in Eq. (1) describes the volumedependent *d*-electron interactions and consists of secondand fourth-order contributions according to¹²

$$V_d(r) = C_2 \left(\frac{r_0}{r}\right)^{4p} - C_1 \left(\frac{r_0}{r}\right)^{2p}, \tag{4}$$

where C_1 and C_2 are material-related parameters which mainly depend on the *d*-band filling and width, r_0 is taken as $1.8R_{\rm WS}$ and $R_{\rm WS}$ is the Wigner-Seitz radius. For transition metals the canonical *d*-band calculation gives p=5 and we used this value for Zr, Fe, and Cu.^{9,10,15} However, Moriarty¹² showed that in the case of Mo the choice p=4 gives a better agreement with the corresponding first-principles calculations. In the present work we chose p=4.5 for the Fe potential which is an intermediate value between that for the halffilled *d*-zone metals as Mo and the filled ones as Cu.

The third term in Eq. (1) is a short-ranged overlapping potential containing the electrostatic and exchangecorrelation contributions. It is described by a Born-Mayer potential:

$$V_{ol}(r) = A \exp(-Br), \tag{5}$$



FIG. 1. Effective pair interatomic potential for fcc-Fe.

where A and B are the model parameters.

The detailed description of the calculations of the total energy, pressure, elastic constants, phonon spectra, and other properties can be found in Ref. 16. Applying the formalism described in Ref. 9 we fitted the potential to the equilibrium lattice parameter, the shear modulus, and some points of the phonon-dispersion curves in γ -Fe extrapolated to zero temperature.

For long-range potentials the cutoff radius r_c is another important parameter. We chose $r_c = 2.07a_0$ (a_0 is the lattice parameter for fcc-Fe at 0 K). With this cutoff radius we obtained a good convergence of lattice properties such as vacancy formation and stacking fault energy. The potential is plotted in Fig. 1 and the parameters are presented in Table I.

We checked the potential by calculating different static properties of the γ - and δ -Fe model at T=0 K and for the atomic volumes Ω_{γ} and Ω_{δ} , corresponding to the experimental temperatures for the $\alpha \rightarrow \gamma$ transformation (1430 K) as well as for the estimated temperature for the $\gamma \rightarrow \delta$ transformation (1610 K). The results of the elastic constants, unrelaxed vacancy formation energy, and stacking fault energy are presented in Table II. The phonon-dispersion curves for both structures were calculated within the quasiharmonic approximation for the same atomic volumes Ω_{γ} and Ω_{δ} . The results are presented in Figs. 2 and 3. We did not find any data for the phonon dispersion in δ -Fe, but the data calculated for γ -Fe at T = 1430 K are in good agreement with the experimental results.¹⁷ Besides, we calculated the P-V dependence for fcc-Fe which is in good agreement with that obtained by using the universal equation of state.¹⁸

According to the accepted classification, the potential obtained is nonequilibrium. This means that the structural pressure is not equal to zero and the electronic contribution has to be added for the total pressure to be zero. Strictly speaking

TABLE I. Parameters for Fe potentials. Equilibrium atomic volumes are in $Å^3$, the other parameters are in atomic units.

Metal	Ω_0	Ζ	R_s	U_s	γ	C_1	C_2	Α	В
Fe	11.86	1.60	0.90	- 1.50	0.06	0.0150	0.0010	701	2.30

TABLE II. Lattice parameters *a* (in Å), elastic constants *B*, $C' = (C_{11} - C_{12})/2$, C_{44} (in GPa), unrelaxed vacancy formation energy E_v^f (in eV), and stacking fault energy γ (in mJ/m²) in fcc and bcc iron phases for different atomic volumes Ω (in Å³). Ω_{γ} = 13.18 for fcc-Fe corresponds to T = 1430 K, $\Omega_{\delta} = 13.37$ for bcc-Fe corresponds to T = 1610 K (estimated phase transformation temperature). Elastic constants in γ -Fe for T = 1428 K are taken from Ref. 33.

	В	<i>C'</i>	C_{44}	E_n^f	γ
				U	,
fcc: $\Omega_0 = 11.86$,	$a_0 = 3.62$				
Present calc.	198	23.4	141	2.12	110
fcc: $\Omega_{\gamma} = 13.18$,	a=3.75				
Present calc.	113	16.1	89	1.19	72
Experiment	133	16	77		
bcc: $\Omega_0 = 11.83$,	$a_0 = 2.87$				
Present calc.	271	23.2	210	2.15	
bcc: $\Omega_{\delta} = 13.37$,	a = 2.99				
Present calc.	141	11.5	122	1.09	

this potential describes the atomic interactions under constant volume and zero temperature. We used this potential to calculate the Gruneisen parameter (Sec. III B).

B. Adaptation to MD simulations

To use the potential in MD simulations under nonzero constant temperature and constant volume conditions it should be recalculated for the equilibrium atomic volume corresponding to the desired temperature so that the total pressure would be zero. (See the Appendix in Ref. 9.) Using this technique it is possible to simulate the evolution of a system at constant volume. When a property is simulated along a range of temperatures, the volume changes (together with the potential) from temperature to temperature,⁹ although it is kept constant for every temperature. This kind of simulation is denoted as *semiconstant volume simulation* hereafter. We applied this method to calcu-



FIG. 2. Phonon-dispersion curves for fcc-Fe calculated in the quasiharmonic approximation for T=0 (dashed lines) and T = 1430 K (solid lines). Experimental data for T=1428 K were taken from Ref. 17.



FIG. 3. Phonon-dispersion curves for bcc-Fe calculated in the quasiharmonic approximation for T=0 (dashed lines) and T = 1610 K (solid lines).

the thermal expansion and the mean-square late displacements (Sec. III C). However, for the simulation of processes from nonequilibrium to equilibrium states (phase transformations) at nonconstant volume conditions one should change the potential every time step according to the instantaneous pressure, temperature, and volume. In practice, it is not possible to include the change of potential in the molecular-dynamics scheme and we have used an approximation, controlling a posteriori the error introduced in the results. The method used, Parinello-Rahman-Nose (PRN),^{19,20} keep constant the temperature and pressure. This formalism was used in the simulation of both melting and bcc⇔fcc phase transformations (Secs. III D and III F). For example, in the case of melting simulated with PRN, the inaccuracy was proved to be small provided the typical change in volume was found to be $\delta V \approx 0.9 - 1.0$ % and the changing in the electronic contributions of the total pressure for this value of δV was $\Delta P_e \approx 1.5$ Kbar ($\delta P_e \approx 1\%$). For middle temperatures (about 1500–1800 K) this leads to a temperature deviation $\Delta T \approx 30-60$ K ($\delta T \approx 2-3$ %).

C. Remarks

The most notable feature of the potential used here is that the volume- and structure-dependent parts were calculated separately. We ignored the details on the nature of the cohesive energy which were included in the volume-dependent part of the energy that is supposed to be constant for a given atomic volume. As a result, we obtained an effective interatomic potential formed by a pure volume-dependent term, which describes the larger part of the cohesive energy, and a relatively weak long-ranged oscillatory term which is responsible for the structural-dependent metallic character of the interactions. Provided the potential satisfies the P-V dependence given by the universal equation of state, it describes correctly the general tendency of the volume dependence of the cohesive energy.

Although the model has eight fitting parameters, the possible choice of their values is quite restricted (see, for example, Ref. 9). Thus, we cannot reach a good agreement for



FIG. 4. Enthalpy differences between bcc and fcc lattices. The regions where fcc and bcc structures are dynamically stable are indicated.

the bulk modulus at high temperature and for the thermal expansion. In addition to the simplicity of the model, there are several reasons for these discrepancies. For example, it is very difficult, in practice, to fit properties which are related to nonzero temperatures because every step of the fitting implies a fit-back using a set of MD simulations to calculate thermal expansion, elastic moduli, phonon spectra, etc. Therefore, we limited our fitting to some properties extrapolated to T=0 K which were calculated within the quasiharmonic approximation and taking only into account changes in the atomic volume but not other contributions related to the anharmonic behavior at high temperatures.

We should underline that the obtained potential is more anharmonic than the image of Fe suggested by the experimental data. Actually the calculated values of Gruneisen parameters and thermal expantion are rather high. However it is a problem to compare the equivalent properties of γ and δ Fe because of the lack of experimental results. Moreover, the macroscopic experimental data cannot be straightforwardly compared with the simulation results for microscopic perfect crystallites.

Summarizing, this potential can be described as an effective potential able to simulate the general behavior of phase stability and some properties close to the γ and δ Fe.

III. RESULTS

A. Phase stability at 0 K

We studied the phase stability of fcc and bcc structures at 0 K by calculating the enthalpy difference $\Delta H_{\text{bcc-fcc}}$ for different atomic volumes. Figure 4 shows that, in the range from $0.8\Omega_0$ to $1.3\Omega_0$ (Ω_0 is the fcc equilibrium atomic volume given by the potential), the fcc structure is favored although there is a perceptible drop in the enthalpy difference near $1.1\Omega_0$. We include in the figure the ranges of volumes where each structure is dynamically stable, they were deduced from the study by molecular dynamics and PRN techniques of the phase stability at different temperatures (see Sec. III F).



FIG. 5. Thermal expansion of the fcc- and bcc-Fe. The linear approximation at low temperature is shown.

B. Gruneisen parameter

A special case where the potential describing the atomic interactions under constant volume conditions can be used in MD simulations at $T \neq 0$ is the calculation of the Gruneisen parameter (γ_G) that can be determined as follows:

$$\gamma_G = V \left(\frac{dP}{dE}\right)_{V=\text{const}} = \frac{V}{3Nk_B} \left(\frac{dP}{dT}\right)_{V=\text{const}},\tag{6}$$

where *N* is the number of atoms in the simulated system and k_B is the Boltzmann constant. We obtained γ_G by calculating the dependence of the pressure versus temperature, P(T), for both structures. These dependences were calculated for crystallites made up of 1400–1500 mobile atoms with the usual periodic boundary conditions and constant volume during 15–60 ps depending on the temperature. We found that P(T) is linear with high accuracy within 200 and 2000 K for both bcc and fcc structures. The resulting parameters were $\gamma_G = 1.98$ for fcc and $\gamma_G = 1.96$ for bcc. We have not found the experimental values of γ_G for γ -Fe and δ -Fe but our results are close to those for Ni $\gamma_G = 1.9$ (Ref. 21) and α -Fe $\gamma_G = 1.7$.²²

C. Thermal expansion and mean-square displacements (MSD)

The thermal expansion of the γ - and δ -Fe were studied in crystallites containing 1400–1500 mobile atoms under zero total pressure conditions⁹ by MD (semiconstant volume simulation). The simulation was carried out during 20–80 ps depending on the temperature. The results of the thermal expansion for both structures are presented in Fig. 5. In the low-temperature region the equilibrium lattice parameter a(T) shows a linear dependence of the temperature. However, for $T \ge 1200$ K there is a noticeable deviation from linearity. Using the linear part of a(T) we estimated the thermal-expansion coefficients for γ - and δ -Fe at low temperature— $\gamma_{\gamma} = 2.2 \times 10^{-5}$ K⁻¹ and $\gamma_{\delta} = 2.0 \times 10^{-5}$ K⁻¹. Since we do not know the experimental data for γ - and δ -Fe, we have chosen for comparison Ni $[\gamma_{\text{Ni}}=1.5 \times 10^{-5}$ K⁻¹ (Ref. 23)] and bcc α -Fe $[\gamma_{\alpha-\text{Fe}}=1.2 \times 10^{-5}$ K⁻¹ (Ref. 24)] as



FIG. 6. Mean-square displacements versus temperature for fcc- (\bigcirc) and bcc-Fe (\triangle) obtained in semiconstant volume (solid lines) and in constant volume (dashed lines) simulations.

being the closest metals for many other properties. It seems that the calculated values are too high, emphasizing the anharmonicity of the potential. However, it should be noticed the difficulties in comparing directly the experimental data obtained for polycrystals with different kind of defects (such as grain boundaries, impurities, etc.) with the data calculated for a microscopic perfect crystallite. Using the same crystallites and zero total pressure conditions we calculated the MSD as a function of temperature in bcc and fcc Fe. The results are plotted in Fig. 6. One can see that the MSD's in the bcc phase are higher than in the fcc one and both curves strongly deviate from linearity at high temperatures. For comparison we include in Fig. 6 the data obtained for constant volume conditions which were obtained in the calculation of the Gruneisen parameter (Sec. III B).

In general one can see that the anharmonic effects in the present model for Fe are quite strong as reflected by the large thermal-expansion coefficients and Gruneisen parameters as well as by the behavior of the MSD at high temperatures.

D. Melting of bcc-Fe

The bcc-Fe melting was studied using two different methods. The former was a semiconstant volume simulation using periodic boundary conditions. The second (PRN) was a simulation at constant temperature and pressure.

An important difficulty for the simulation of melting is the large difference (several orders of magnitude) between the duration of real processes and the interval that is possible to simulate. Therefore, the crystal should be overheated by $\Delta T_m = T_{inst} - T_{melt}$ to reach the desired instability (T_{inst} is the simulated temperature when one obtain instability of the crystallite and T_{melt} is the real melting temperature). It is clear that, the larger the simulated time, the smaller the value of ΔT_m , and therefore, the more correct melting temperature can be obtained. In the present study we were more interested in the qualitative aspects of phase stability than in the accurate value of T_{melt} . Thus, we limited our simulation to a time interval of about 100–120 ps ($\approx 2.0 \times 10^5$ time steps), assuming that the temperature for which the lattice becomes unstable is larger than T_{melt} .



FIG. 7. Mean-square displacements (a) and mean crystallite temperature (b) versus time during a semiconstant volume simulation of the bcc-Fe melting.

Using semiconstant volume conditions the critical temperature for the bcc-Fe instability was $T_{inst} \approx 1950$ K. For this temperature we observed melting after about 65 ps. After melting we detected a decreasing of the crystallite temperature up to \approx 1880 K. The temporal behavior of the MSD and temperature obtained in this simulation are shown in Fig. 7. At 33 ps we observed a local "melting" when few Frenkel pairs were formed and their migration led to an increase of the MSD. However, they annihilated soon and the final melting happened ≈ 32 ps later. After that, the increase of the MSD with time was almost linear, as corresponds to a diffusion process in melted Fe. The decrease of the temperature during melting is related to the increase in the potential energy of the system when it changes from solid to liquid. Provided that, when the whole simulated crystallite has melted, the temperature should be $\geq T_{\text{melt}}$, we may estimate the highest limit of the melting temperature as $T_{\text{melt}} \approx 1880$ K. Considering that we simulated the melting of a perfect crystallite and the existence of lattice defects should decrease the melting temperature,^{25,26} our estimation compares well with the experimental value $T_{melt}^{exp} = 1811$ K.

For PRN conditions we obtained that the simulation time before melting of bcc-Fe depends on both the effective mass A_T of the Nose thermostat and the effective crystallite mass A_c in the Parinello-Rahman simulation. In the present work we have studied only the effect of A_T and we used A_c = const=0.1 M_c (M_c is the physical mass of the crystallite).

Thus, we found for $T_{inst} \approx 1950$ K and for a high value of $A_T = 10$ ps² that melting starts at ≈ 50 ps, therefore earlier than for the simulation at semiconstant volume conditions. Before melting, a PRN simulation with such a great A_T value is close to the pure PR conditions provided that the tempera-



FIG. 8. Mean-square displacements (a) and mean crystallite volume (b) versus time during a constant pressure and constant temperature simulation of the bcc-Fe melting under temperature T = 1950 K.

ture and volume oscillations are small. However, after melting we observed large temperature fluctuations as response of a Nose system with high A_T to the fast decreasing of temperature after melting. Consequently, a highly distorted system appears which is difficult to analyze. For a lower value $A_T = 2 \text{ ps}^2$, the temperature oscillations after the phase transformation are small enough for the analysis of the structure to be feasible. In this case we found that melting occurs after ≈ 110 ps which is greater than the time required in the above simulations. In Fig. 8 we present the evolution with time of both the MSD and the volume of the crystallite for this case. Like in Fig. 7 there is one attempt to melt at \approx 50 ps and after this time there are large volume fluctuations until the system becomes completely melted. We estimate that the change of volume in the melting process is $\delta V \approx 0.9\%$. For $A_T = 0.5 \text{ ps}^2$ and the same temperature we did not observe melting during a simulation of 300 ps, although we observed few attempts similar to those presented in Figs. 7 and 8.

In general, we could observe that melting becomes faster using the PR technique, at least for the A_c that we used, while the Nose thermostat increases the time required for melting.

E. Lindermann criterion for melting

The MSD data obtained in Sec. III C and the melting temperature estimated in Sec. III D have been analyzed according to the Lindermann criterion for melting.²⁷ The Lindermann law can be written as

$$\langle R^2(T_{\text{melt}}) \rangle = \delta^2 \cdot d^2,$$
 (7)



FIG. 9. Temporal evolution of the crystallite sides during the fcc \rightarrow bcc phase transformations following the Bain mechanism.

where $\langle R^2(T_{\text{melt}}) \rangle$ is the MSD at melting temperature, *d* is the nearest-neighbor distance, and δ is a parameter. Both theoretical and experimental estimations of δ for bcc metals provides a value of the order of 0.1,^{28,29} whereas the result of the simulation of melting in bcc-Zr is $\delta \approx 0.11$.³⁰ The analysis of our MSD results for the estimated melting temperature $T_{\text{melt}}=1880$ K and using ordinary periodic boundary conditions gives $\delta=0.12$ which is close to the above estimations. Moreover, the value of δ should be slightly smaller for the real melting temperature T_{melt} .

F. Simulation of the bcc⇔fcc transformation

The procedure for the simulation of the bcc \leftrightarrow fcc transformations was as follows. The crystallite was heated up to the chosen temperature and it was thermalized during ≈ 0.5 ps under the usual periodic boundary conditions. After, the system was allowed to evolute under PRN conditions. The time steps used were in the range of $(0.1-1.0) \times 10^{-15}$ s depending on the temperature. The values of A_c in Parinello-Rahman and A_T in Nose techniques were $0.1M_c$ and 0.1 ps², respectively.

We modeled γ -Fe in crystallites oriented along [100], [010], and [001] axes and containing $N_a = 256$ to 1372 mobile atoms. It was found that the fcc structure is unstable for temperatures $T \ge 1820$ K and transforms to bcc following Bain distortions. The temporal evolution of the edges of the parallelopipedic crystallite of $N_a = 500$ atoms at T = 1820 K is presented in Fig. 9. It should be noted that the 90° angles between sides show deviations within a range of $\pm 1^{\circ}$. As a result of this transformation we obtained a perfect bcc crystallite. We found that the limit for the PT temperature depends on the size of crystallites. Thus crystallites of N_a = 256–500 atoms transformed at T=1820 K, while the crystallite of $N_a = 1372$ atoms only transformed at T \geq 1900 K. We simulated the fcc \rightarrow bcc transformation at temperatures up to 2000 K during \approx 50 ps and we did not observe the melting of the secondary bcc lattice. We attribute this result to the small value of $A_T = 0.1 \text{ ps}^2$ used in these simulations. We want to point out that the results in Fig. 4 show that the fcc structure is more favorable at T=0. There-



FIG. 10. Temporal evolution of the crystallite sides during the $bcc \rightarrow fcc$ transformation following the Burgers mechanism.

fore, the paramagnetic bcc structure is only stable at high temperatures when the vibrational energy can contribute significantly to its stability.

The δ -Fe was modeled in crystallites oriented along [100], [011], and [011] axes and containing $N_a = 384 - 1296$ mobile atoms. We found that the highest temperature at which the crystallite of $N_a = 384$ atoms was transformed was T = 1400 K. As for γ -Fe, the temperature at which the instability appears depends on the size of the crystallite (the bigger the crystallite, the lower the temperature). As an example of bcc->fcc transformation, we present in Fig. 10 the temporal evolution of the edges of a crystallite of $N_a = 700$ at a T = 1123 K. The transformation follows the Burgers mechanism and the final structure depends on temperature, size, and the effective crystallite mass in the Parinello-Rahman method. In general, the transformed crystallite contains twins and stacking faults and the angle between the original [011] and [011] axes takes values from 83° to 94°. We can estimate the temperature for the $\gamma \rightarrow \delta$ phase transformation as the mean between the maximum temperature for bcc->fcc transformation ($T_{bcc \rightarrow fcc}$ =1400 K) and the minimum temperature for fcc \rightarrow bcc transformation ($T_{fcc \rightarrow bcc}$ =1820 K). The result $T \approx 1610$ K compares reasonably with the experimental one $(T_{\gamma \to \delta}^{\exp} = 1667 \text{ K}).$

IV. DISCUSSION

A. Effects of the simulation model on the results

As described in Sec. III, different techniques were used in this study according to the specific characteristics of the processes. For instance, a constant volume simulation is suitable for the study of melting (see Sec. III D) provided the volume fluctuations necessary for the initiation of melting, that are related to the Frenkel pair formation, are rather small. However, other phase transformations studied here demand much bigger fluctuations that cannot be reached if the volume is kept constant. Then, other techniques, such as Parinello-Rahman (PR) and Nose, are required although its application demands the introduction of two extra parameters, A_c and A_T .

For temperature-induced transformations, the PR technique can be used successfully in the simulation of the system before the transformation. But, once the transformation starts, large volume and temperature fluctuations appear and the time required to restore the equilibrium necessary for the analysis of the transformed crystallite can be very large. Therefore, to keep the temperature constant and to have a mechanism for damping the fluctuations after the phase transformation we have used the Nose thermostat.

It is accepted, and has been confirmed in previous studies,^{9,19} that the effective crystallite mass A_c do not affect the stability of phases but can affect to the time required for the transformation process. Thus we chose a fixed value as explained in Sec. III F. The effective mass A_T of the Nose thermostat affects the value of the temperature fluctuations and the time of its relaxation. To investigate the influence of such a parameter we have simulated a melting process by two different methods as explained in Sec. III D.

Our tentative interpretation of the effect of A_T is as follows. A system under Parinello-Rahman conditions is isoenthalpic. Hence, there is a correlation between the volume and temperature fluctuations: when the volume increases the temperature decreases and vice versa. Moreover, there is a clear relationship between the amplitudes of the volume and temperature fluctuations. When a Nose thermostat is introduced it influences the temperature fluctuations, so that it affects the volume fluctuations, which, in turn, modify the probability of the system to reach the new phase. In general, we expect a stabilization effect due to the modification of phonons introduced by the Nose thermostat. When the simulated system is close to the equilibrium a high value of A_T can be used. In this case the periods of Nose temperature fluctuations are much greater than those of the Parinello-Rahman volume/temperature fluctuations and the stabilization effect should be small. However, when the simulated system is far from equilibrium (simulation of phase transformations) the value of A_T has to be reduced in order to avoid large temperature fluctuations, but in this case the stabilization effect of the Nose thermostat increases. The above results confirm that the interval of time required for the phase transformation increases and it can even change the limit temperature for transformation. We relate the great difference between the lowest temperature for the fcc→bcc transformation and the highest temperature for bcc->fcc transformation (Sec. III F) to the small value of A_T $=0.1 \text{ ps}^2$ used. Therefore, because of the stabilization effect of the Nose thermostat we should impose large overcools on the bcc lattice and overheats on the fcc lattice in order to get the corresponding transformations.

B. The mechanisms of $bcc \leftrightarrow fcc$ transformations

The analysis of the kinetics of the simulated transformations shows that the forward and reverse transformations occur following different mechanisms. In the bcc \rightarrow fcc Burgers transformation there is a stage of nucleation of an fcc embryo that grows anisotropically, whereas the fcc \rightarrow bcc Bain transformation happen at the same time in the whole crystallite without the creation of embryos.

1. The Burgers mechanisms of the $bcc \rightarrow fcc$ transformations

The nucleation of embryos was clearly observed in big crystallites. The fcc embryo has a lenticular shape with $(111)_{fcc}$ habit plane and it grows faster in the habit plane than in the perpendicular directions. As a result of such a transformation we normally observed a number of twins and stacking faults. A minimum of two twins have to be formed due to the periodic boundary conditions when the fccembryo growing in a $\langle 111 \rangle_{fcc}$ direction meets its image. Other twins and stacking faults can be created during the transformation depending on the size of the crystallite and the temperature. Similar features were observed in the modeling of the bcc \rightarrow fcc transformation in Cu.⁹

For the nucleation stage it is necessary to have local volume fluctuations. Once an embryo of the new fcc phase is nucleated it can grow if either the model crystallite is big enough or there are geometrical conditions that accommodate the resulting deformations. In this work we introduce these geometrical conditions through the Parinello-Rahman method although in some special cases the Burgers mechanism can be simulated without it. This is the case studied in Ref. 31 where the bcc \rightarrow fcc transformation of a coherent Cu precipitate in a bcc-Fe matrix was simulated. We observed the nucleation and growth of two fcc embryos of different orientations inside a spherical precipitate of ≈ 18000 Cu atoms. The nucleation of embryos was enhanced by the vacancies previously trapped inside the precipitate, and the different orientation of embryos allowed the compensation of the deformations created during the transformation.

2. The Bain mechanisms of the $fcc \rightarrow bcc$ transformations

Another qualitative picture was observed during the fcc-bcc transformations. In this case the whole crystallite transforms at the same time resulting in a perfect bcc structure. We found a correlation between the size of crystallite and the time necessary for the transformation, the larger the crystallite the longer the time we have to simulate before the transformation starts. This time is related to the appearance of *large* enough fluctuations in volume, which are allowed in our simulation by the PR conditions, and permit the transformation to start. As in the case of $bcc \rightarrow fcc$ transformation, it was found that the larger the crystallite the higher overheating and the longer time we have to apply. However unlike the bcc->fcc case we could not simulate Bain transformations in crystallites larger than ≈ 3000 mobile atoms. For this system we observed only volume fluctuations up to $\pm 5\%$. The reason is that, unlike in Burgers mechanism, no embryos were ever created to trigger the mechanism in large systems. Bearing in mind the large deformations that are related to the Bain mechanism, we suspect that the transformation observed in the present work is an artifact of the application of Parinello-Rahman conditions to a microscopic perfect system. The lack of embryos can be attributed to the difficulties to accommodate an embryo transformed via Bain mechanism in an fcc untransformed lattice. In other words, the Bain mechanism is the easiest way to go from an fcc lattice to a bcc one if no boundaries constrict the deformation of the crystal and the whole system can transform at the same time without the need of an embryo.

In previous simulations we found some evidence that other fcc \rightarrow bcc transformation mechanisms can exist. So, the fcc \rightarrow bcc transformation was studied using a similar potential for α -Fe and PRN technique in Ref. 9. It was found that the fcc \rightarrow bcc transformation can follow two mechanisms depending on the conditions. One of them was a Bain deformation but the other was a deformation close to that of the Burgers mechanism together with a rotation of the crystallite.

Thus, reliable conclusions on the phase stability can be obtained from the simulations made in this work. However, to study the phase-transformation mechanisms, the applied methods should be modified to consider lattice defects and the interactions of the new growing phase with the untransformed matrix. Moreover, the above transformations happen at high temperature and the diffusional contribution to the transformation can be significant.

C. The dependence of the phase stability with the temperature

In Sec. III A it was found that the entalpy difference between bcc and fcc structures calculated at T=0 indicates that the fcc structure is stable in a wide range of volumes, while the molecular-dynamic simulations in Sec. III F indicate that the fcc structure is unstable at temperatures higher than \approx 1820 K. Therefore there is a temperature-dependent contribution to the bcc-phase stability which should be significant in order to provide a fcc→bcc transformation in a reasonable simulation time. We attribute this result to the contribution of the vibrational energy into the fcc-bcc phase stability. The full free-energy calculation within such a model is rather complicated and we did not do it. However, we think that the MD results obtained are the evidence that this model describes qualitatively the general temperature behavior of the vibrational spectra in both phases. Therefore, a feature of the potential used is that in order to describe the dependence of the stability of fcc and bcc phases with the temperature, it is not necessary to have two minima on the potential energy hypersurface as it is usually expected.^{7,32}

V. SUMMARY

A pair potential describing interactions in the γ - and δ iron is presented. The potential is based on the generalized pseudopotential theory and fitted to the lattice parameters, phonon data and the elastic constants of γ -iron.

This potential describes the atomic interactions under constant volume conditions and zero temperature, but its applicability has been extended to more general cases including MD simulations under nonzero constant temperature and constant volume.

For the simulation of the evolution *from nonequilibrium* to equilibrium states (phase transformations), where the potential should be changed at every time step according to the instantaneous conditions of pressure, temperature, and volume, only approximate methods could be used controlling *a posteriori* the error introduced in the results. The methods used keep constant either the volume (usual periodic boundary conditions) or the temperature and pressure (Parinello-Rahman-Nose). In the last case the effect of the effective thermostat mass in the Nose mechanics to the melting process has been studied. It was found that small values of A_T lead to the stabilization of the lattice.

Some properties of fcc- (γ) Fe and bcc- (δ) Fe has been studied. The thermal expansion, Gruneisen parameters, and mean-square displacements show a high level of anharmonicity of the potential.

It was found that fcc-Fe is unstable for T > 1820 K. At

these temperatures the bcc structure is more stable despite that the enthalpy at 0 K is higher than that of the fcc structure. This fact emphasizes the important role of the vibrational energy in the phase stability. bcc-Fe is unstable at temperatures below 1400 K and above 1950 K. The estimated temperature for bcc \leftrightarrow fcc transformation is ≈ 1610 K which is in coincidence with the experimental value ($T_{\gamma \to \delta}^{exp}$ = 1667 K). The estimated melting temperature for a perfect crystallite was found to be ≈ 1880 K and is nastisfactory agreement with the experimental value ($T_{melt}^{exp}=1811$ K).

In our simulation the $bcc \rightarrow fcc$ transformation was produced via Burgers mechanism through the creation and growth of fcc embryos. In the fcc \rightarrow bcc transformation the whole crystallite was transformed at the same time by a Bain deformation without the creation of bcc embryos. We think

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that the Burgers mechanism is physically feasible whereas the Bain transformation is unlikely to happen in a real system and it can be an artifact of the computational model, in particular of the Parinello-Rahman conditions.

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