Melting of Fe and Fe$_{0.9375}$Si$_{0.0625}$ at Earth's core pressures studied using *ab initio* molecular dynamics

Anatoly B. Belonoshko,[1,2] Anders Rosengren,[2] Leonid Burakovsky,[3] Dean L. Preston,[4] and Börje Johansson[1,5]

[1]*Department of Materials Science and Engineering, Applied Materials Physics, The Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

[2]*Department of Theoretical Physics, Condensed Matter Theory, AlbaNova University Center, The Royal Institute of Technology, SE-106 91 Stockholm, Sweden*

[3]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

[4]*Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

[5]*Department of Physics, Condensed Matter Theory Group, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden*

The issue of melting of pure iron and iron alloyed with lighter elements at high pressure is critical to the physics of the Earth. The iron melting curve in the relevant pressure range between 3 and 4 Mbar is reasonably well established from the theoretical point of view. However, so far no one attempted a direct atomistic simulation of iron alloyed with light elements. We investigate here the impact of alloying the body-centered cubic (*bcc*) Fe with Si. We simulate melting of the bcc Fe and Fe$_{0.9375}$Si$_{0.0625}$ alloy by *ab initio* molecular dynamics. The addition of light elements to the hexagonal-close-packed (*hcp*) iron is known to depress its melting temperature (T_m). We obtain, in marked contrast, that alloying of bcc Fe with Si does not lead to T_m depression; on the contrary, the T_m slightly increases. This suggests that if Si is a typical impurity in the Earth's inner core, then the stable phase in the core is bcc rather than hcp.

The iron phase diagram is the key to understanding the deep interior of the Earth. The crystal structure of iron controls the heat balance, seismic properties (anisotropy), and the inner core (IC) dynamics. At ambient temperatures (T) hcp iron is stable at pressures (P) from ∼14 GPa to at least 300 GPa.[1] The hcp phase is also stable at P's just above 1 Mbar up to T's of 3400 K.[2] On the basis of these observations it is generally assumed that iron in the IC is in the hcp phase. The (ambient) elastic anisotropy of hcp Fe has been offered as an explanation for the measured difference (3–4 %) between north-south and equatorial seismic wave velocities.[3] Several groups have calculated the melting curve of pure hcp Fe to IC P's.[4–7]

There are, however, several compelling reasons to question the assumption that IC iron is hcp. In 1986 Brown and McQueen (BM) (Ref. 8) obtained shock wave Hugoniot data on iron that indicated another high-PT phase between hcp and liquid. The BM result was subsequently explained by the high-PT stabilization of the bcc phase;[9] and in 2001, on the basis of new Hugoniot data, Brown also concluded that there is another, likely bcc, phase.[10] In 2004 the BM experiment was challenged by Nguyen and Holmes.[11] A number of properties of the IC have been explained by assuming a bcc structure.[12–14] The anisotropy of the IC, previously thought to be strong evidence for the hcp phase, was recently explained within the bcc paradigm.[13] *Ab initio* simulations show that the hcp phase becomes increasingly isotropic with increasing T,[14,15] while the bcc phase remains highly anisotropic.[14] Thus, the observed IC anisotropy[16] is in fact only consistent with the bcc phase.[14]

The relative stabilities of the hcp and the bcc phases can be ascertained by comparing their melting T_m: a higher T_m at a given P implies a greater stability. Belonoshko *et al.*[15] carried out classical molecular-dynamics (MD) calculations

of the hcp and the bcc Fe T_m's at 323.5 GPa using an embedded atom method (EAM) potential fitted to the results of projector-augmented wave (PAW) calculations of iron energies. The model was created by Alfé *et al.*[17] as a fine tuning of the model developed by Belonoshko *et al.*[6] According to the "tuned" model the T_m of the hcp phase is 6300 K, while that of the bcc phase is 6600 K; hence, bcc is the more stable phase at IC P's. However, according to independent PAW calculations of free energies by Vočadlo *et al.*,[18] the opposite holds: hcp Fe is marginally (30–60 meV per atom) more stable than bcc. Thus EAM MD results and PAW free-energy calculations of the hcp-bcc stability in the IC are inconsistent. We need to mention here that precise calculations of temperature-induced solid-solid transitions might require millions of atoms.[19] Because the PAW calculations are performed for much smaller systems, it is possible that calculations for a much larger number of atoms would lead to results consistent with the EAM MD. The overall conclusion is that at present the question of the bcc and hcp relative stability might be beyond the present level of computational possibilities.

The inner core is lighter than the computed density of iron at the same PT conditions. To match the IC density, iron has to be alloyed with some light elements. Impurities in the inner core could have profound effects on its phase stability. Vočadlo *et al.*[18] found that the addition of a few mole percent Si or S in the core would stabilize the bcc structure, a result which is consistent with the earlier experimental finding that the addition of Si vastly expands the bcc stability field.[20] More recent calculations indicate that the addition of Si to hcp Fe lowers the T_m, that is, it increases its free energy.[21]

Here we obtain analogous results for both pure bcc iron and bcc iron alloyed with Si in order to compare their T_m's and find out the impact of Si on the bcc phase stability within

the same *ab initio* PAW description. The phase with the higher T_m is the more stable phase.

To compute the energies and forces needed for MD simulations, we applied the PAW method (as implemented in VASP)[22] based on density-functional theory within the generalized gradient approximation using the Perdew-Wang parametrization.[23] The calculations were performed with a cutoff energy of 27 Ry, treating the $3p$, $3d$, and $4s$ orbitals of Fe and the $3s$ and $3p$ orbitals of Si as valence states. This is different from the studies where only six electrons were treated as valence electrons, while sp electrons were described by a repulsive potential.[5,17,18,21] The methodology of the present calculations is essentially the same as in our recent work on the dynamical stability of the phases of iron.[24]

We performed a series of MD runs for both pure bcc Fe and bcc Fe alloyed with Si. We chose two volumes, 7.21 and 7.0 Å³/atom, corresponding to IC P's of ~ 3.0 and ~ 3.5 Mbar. Supercells of 128 atoms (obtained as the $4 \times 4 \times 4$ multiplication of the bcc unit cell with two atoms along a, b, and c crystallographic axes) were simulated. The initial configuration of the $Fe_{120}Si_8$ alloy was formed by randomly substituting an Fe atom in each of the eight octants of the computational cell. This Si concentration was chosen to match the density of the IC (Ref. 25) as obtained from our recently developed equation of state for bcc iron.[26] Starting from these configurations at a number of initial T's, we performed *ab initio* MD runs of 20 000 time steps with a time step of 0.5 fs. We used the recently developed Z method[27,28] to ensure that every simulation gave the true T_m rather than T of a superheated solid.

Computed points are shown in Fig. 1 for the volume of 7.0 Å³/atom. The points clearly fall into two sets. The point set at lower (higher) P's corresponds to solid (liquid) states at the ends of the MD runs. The initial T increment was chosen to be just 250 K in the vicinity of the melting transition in order to bound the T_m as tightly as possible. The inset in Fig. 1 shows the performance of the Z method for Cu. The thick melting curve for Cu was obtained by the well-established two-phase method[29] for exactly the same model.[30] The Z-shaped isochore gives the melting temperature identical with the two-phase method. Similar results are obtained for other materials.[27,28] Therefore, similar performance of the Z method can be expected for Fe. Figure 2 shows the P (upper panel) and the T (lower panel) time evolutions during the simulation where melting occurs around 10 000 time steps. Pressure increases (upper panel) as should be expected in the liquid and temperature decreases (lower panel) because the thermal energy is spent to increase the potential energy on liquid transition. Figure 3 illustrates the change in the radial distribution function (RDF) characteristic of melting. One can see that on melting the first peak, and particularly the second peak, becomes lower that points to the loss of the long-range order and a more homogeneous distribution of atoms in the liquid. Figure 4 shows the points we computed for pure and Si-alloyed bcc Fe. It is important to place these points within the context of existing data on the iron phase diagram. First, we note that our two melting points for pure bcc Fe (filled circles) are about 300 K above, but still consistent (overlapping error bars) with the bcc T_m's computed from an EAM model (thin curve).[15,17] Also, our
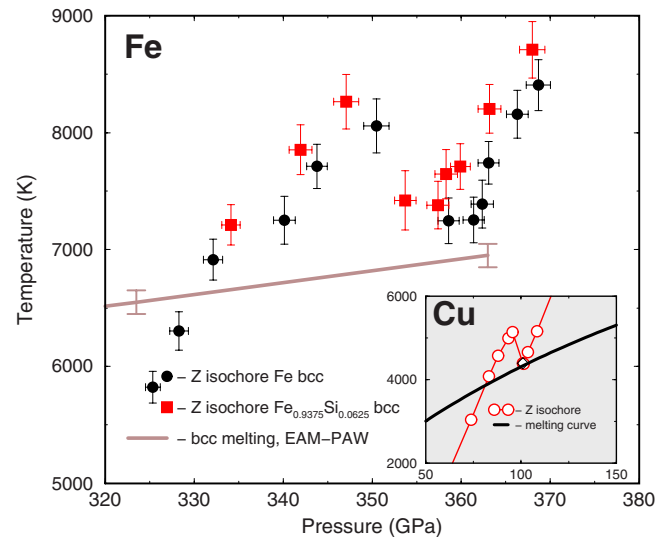

FIG. 1. (Color online) Temperature versus pressure for pure bcc iron (filled circles) and $Fe_{0.9375}Si_{0.0625}$ (squares) at a constant volume of 7.0 Å³/atom. The melting curve of pure bcc iron (Ref. 15) is shown for comparison. The lower corner of the Z-shaped isochore (see also the inset) is located at the melting temperature along the isochore. The inset illustrates the precision of the Z method (Ref. 27) for computing melting temperatures in Cu. The thick curve in the inset is computed with the two-phase method (Ref. 29), while the curve with open circles is computed by the Z method. The melting temperatures are identical.

obtained bcc points and the EAM T_m's for bcc both lie above the melting curve for pure hcp iron (thick curve).[5] We find that the addition of 6% Si increases the bcc T_m's (filled squares) by approximately 200 K; however, the same concentration of Si reduces T_m of hcp iron (inverted triangle) by about 500 K at 3.3 Mbar,[21] which is P of the inner-outer core
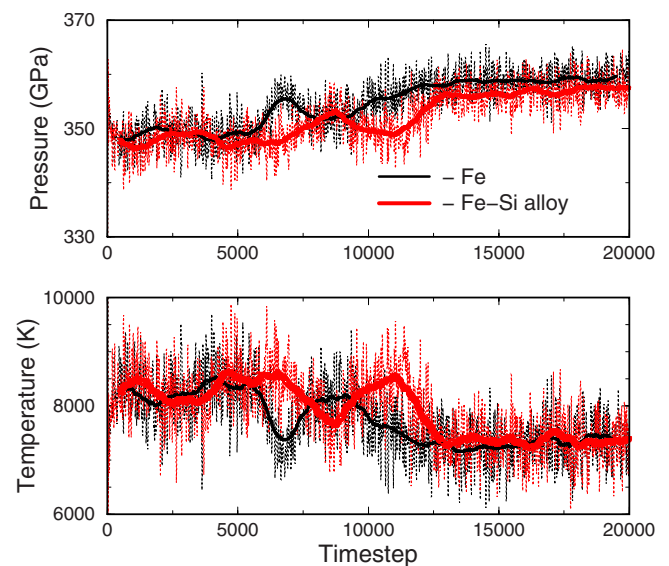

FIG. 2. (Color online) Time evolution of P (upper) and T (bottom) during an MD run where the melting transition occurs. Thin (Fe) and thick ($Fe_{0.9375}Si_{0.0625}$) curves show time dependence of the averages running over 500 time steps. The dotted lines show the raw MD data.
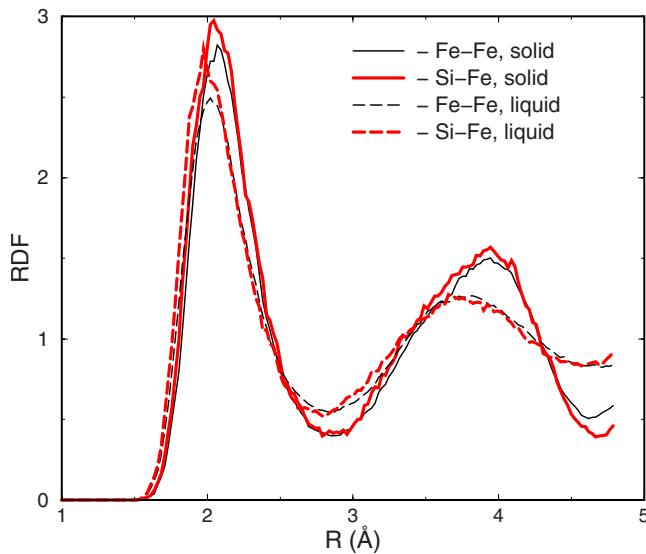
FIG. 3. (Color online) Comparison of RDF for liquid (dashed curves) and solid (continuous curves) pure bcc iron (thin curves) and Si-alloyed iron (thick curves). The Si-Fe RDF is more structured; that points to the Si-Fe bond being stronger than the Fe-Fe bond.
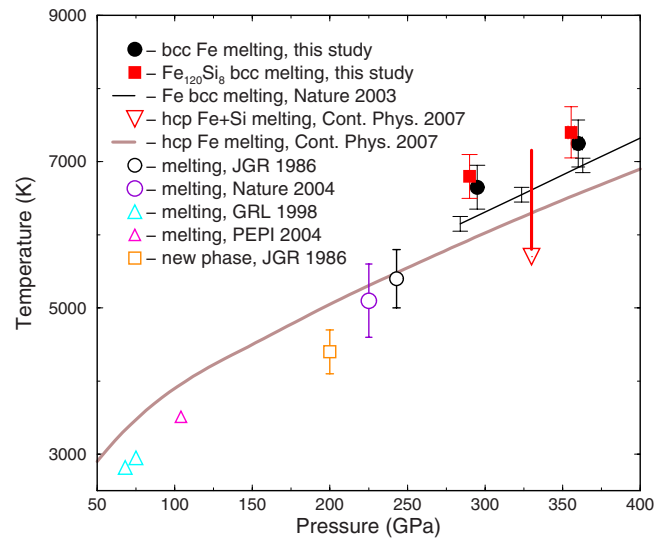

FIG. 4. (Color online) Iron phase diagram. Computed in this paper melting points for pure bcc Fe (black circles) and the Fe-Si alloy (squares) are shown along with earlier data on the iron phase diagram.

boundary. The difference is shown by the thick vertical bar in Fig. 4. The reason for the contrary response of the bcc and the hcp lattices to alloying with Si lies in the nature of the Fe-Si bond.[31] At low P's the bond is formed with coordination 7 for both Fe and Si (low-P FeSi is in the seven-coordinated ε phase), but at Mbar P's the coordination for both Fe and Si increases to eight (at high P FeSi assumes the eight-coordinated CsCl structure, the analog of bcc for a binary system). The bonding between Si and Fe atoms in the bcc structure is actually stronger than that between Fe atoms themselves; this is clear from the higher and narrower peak of the Si-Fe RDF compared to that of the Fe-Fe RDF (Fig. 3) (even though Si is lighter than Fe and, if not the stronger bonding, one should expect the opposite relation). Therefore, Si stabilizes bcc Fe, in agreement with observations.[20] In the case of hcp Fe with coordination 12, the Fe-Si bond does not form, and Si atoms act like point defects (impurities) which depress the melting point of the hcp Fe.

The generally accepted T_m of iron is about 6000 K at the inner-outer core boundary;[32] this estimate is based on the harmonic approximation for thermal pressure in hcp. The calculation of T_m^{hcp} by Alfé *et al.*[21] (thick curve in Fig. 4) gives the IC boundary T as approximately 6300 K. Straight line fits to our pure bcc and 6% Si T_m's, each with a slope of 10 K/GPa (equal to the slope of the EAM melting line in Fig. 4), give IC boundary T_m's of 7000 and 7200 K. The lower estimate within the error bars is on the level of 6800–7000 K. We note that the density of our sample of Fe$_{120}$Si$_8$ is 12.834 g/cm^3 at ~334 GPa and 7100 ± 100 K, and this closely matches the preliminary Earth model[25] density of 12.825 g/cm^3 at 335.3 GPa.

In conclusion, we have shown that iron, alloyed with Si, is likely to be stable in the bcc phase at the high pressures of the IC. Melting temperatures of bcc Fe, alloyed with Si are in the range of 7000 K and higher in the IC pressure range (3.35–3.65 Mbar).

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