Instability of the body-centered tetragonal phase of iron under extreme conditions

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The influence of the tetragonal and orthorhombic axial distortions on the body-centered cubic (*bcc*) phase of Fe at extreme conditions has been studied by means of first-principles calculations. We unambigiously demonstrate that the energy minimum corresponding to the body-centered tetragonal (bct) ($c/a \approx 0.9$) structure, previously found in Fe upon the axial tetragonal distortion of the bcc phase along the Bain's path under compression at zero temperature, is an artifact of the structural constraint. When the bcc structure is examined using the orthorhombic distortion involving the tetragonal distortion as a particular case, the bct ($c/a \approx 0.9$) structural framework represents a saddle point between two mirrored face-centered cubic minima rather than a local minimum. Therefore we conclude that there is no ground to emphasize on possible thermal stabilization of the bct structure with a particular c/a ratio apart from the whole family of structures obtained by tetragonal, orthorhombic, or another type of axial distortions.

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Iron is the dominant component of the Earth's inner core (IC).[1] Its structural and physical properties at extreme pressure (P) and temperature (T) conditions are the key issue for understanding of the composition, structure, and evolution of the earth. Although Fe has been a subject of extensive research for the last several decades,[1–18] the nature of the stable phase at extreme conditions of the Earth's IC [P =330–360 GPa (Refs. 3 and 4) and T=4000–8000 K (Refs. 5 and 6)] is still controversial. At low temperature in the pressure range of the Earth's IC iron adopts the hexagonal close-packed (hcp) structure (ε-Fe).[7,8] However, shock-wave experiments by Brown and McQueen[9,10] indicate a post-hcp solid-solid phase transformation at pressures between 200 and 40 GPa and temperature between 4600 and 5100 K. Most recent studies ascribe this solid-solid phase transition to the development of the body-centered cubic (bcc) phase[6,11–13] or the face-centered cubic (fcc) phase.[14]

Besides the latter phases, a body-centered tetragonal (bct) ($c/a \approx 0.9$) phase is also extensively discussed as a possible alternative candidate.[15,16,18] When performing tetragonal distortion of the bcc structure along the prominent Bain's path at high pressure and T=0 K the energy curve displays a double well with a deeper minimum at $c/a=\sqrt{2}$, corresponding to the fcc structure and another shallow minimum corresponding to the above mentioned bct structure with $c/a \approx 0.9$. The bcc phase ($c/a=1$) is situated in a local energy maximum separating these two minima.[15,18] Both the nonmagnetic bcc and bct ($c/a \approx 0.9$) phases are dynamically unstable at low temperature at the earth's IC pressure.[6,13,18] The bcc phase can be stabilized by entropic effects at very high temperature.[6,13] Thereupon, as the bct ($c/a \approx 0.9$) phase of Fe is lower in energy than the bcc-Fe at pressures relevant to the earth's IC, one may expect that in light of the thermal stabilization the bct ($c/a \approx 0.9$) phase at the earth's IC conditions may become more stable than the bcc phase.

The energy double well for Fe upon the monoaxial distortion is not unique. Such a remarkable feature occurs for many dynamically unstable structures of other systems. For instance, at ambient conditions Mo, an element of the neighboring to Fe in the periodic table, stabilizes in the bcc structure and its fcc structure is dynamically unstable.[19] The total energy of Mo as a function of the tetragonal distortion exhibits a double-well behavior with a global minimum at the bcc structure, a local maximum at the fcc structure, and a shallow minimum at a bct structure with a c/a ratio $>\sqrt{2}$. More examples of similar characteristic energy double-well behavior of elemental materials are given in Ref. 20. The energy double-well behavior occurs also in dynamically stable phases.[21–26] However, as we show below, the second shallow minimum could be an artifact due to a symmetry constraint since the distortion is restricted to monoaxial. In particular, it is known that for In and high-pressure Ga the tetragonal distortion of the bct structure results in the appearance of an energy double well.[21,23,24] However, when the bct-In and bct-Ga are examined using a more general orthorhombic distortions, containing the tetragonal one as a particular case, then the second energy minimum appears to be a saddle point between two mirrored minima, corresponding to the most stable structure. Nevertheless, in the case of In under compression, the bct phase, which corresponds to the saddle point, first develops into the real second local minimum and then becomes more stable than the ground-state bct phase between 45 and 90 GPa.[23,22]

The interest in the bct ($c/a \approx 0.9$) phase of Fe stems from the suggested thermal stabilization of the body-centered structural arrangement.[6] Traditionally the bcc and fcc phases are connected via tetragonal distortions along the prominent Bain's path, which is just one of 21 known options. But this bct minimum may disappear when the energy landscape is considered with respect to a more general orthorhombic distortion. Actually such an option has never been considered before, which convinced us of the necessity to address this

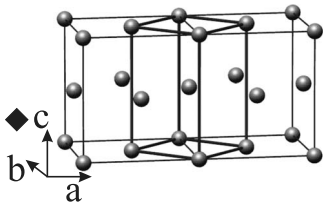

FIG. 1. Structural relation between the face-centered and body-centered crystal structures.

issue here. To analyze the relevance of the bct ($c/a \approx 0.9$) phase of Fe we performed a series of first-principles calculations of the enthalpies for body-centered Fe with tetragonal and orthorhombic distortions under ultrahigh pressure relevant to the earth's IC conditions.

The total-energy calculations were performed in the framework of the frozen core all-electron projector augmented wave (PAW) method,[27] as implemented in the program VASP.[28] The energy cutoff was set equal to 500 eV. Exchange and correlation effects were included within the generalized gradient approximation (GGA).[29] The semicore $3p$ states of Fe were treated as valence. The integration over the Brillouin zone (BZ) was performed on a grid of special k points determined according to the Monkhorst-Pack scheme.[30] Energy differences between the body-centered cubic, tetragonal, and orthorhombic structural arrangements require special care. Therefore we used about 3600 and 8000 irreducible k points in the BZ for the bct and body-centered orthorombic (bco) structures, respectively. The total-energy calculations were done with the linear tetrahedron method with Blöchl's correction.[31] The total energies were converged to within 0.5 meV per atom. The enthalpies of all structural arrangements were obtained by accurate numerical fitting of the total energy curves.

The relation between the *body-centered* and *face-centered* structural arrangements is depicted in Fig. 1. When the c lattice constant differs from the a and b lattice constants the bcc structure becomes bct and can be transformed into the fcc structure via the Bain's path, i.e., by varying the c/a ratio. Figure 2 shows the change in the enthalpy upon the tetragonal distortion of the bcc structure along the Bain's path. In our study we kept average external pressure corresponding to 320 GPa at zero temperature in all the structures. There are two minima, corresponding to the fcc and bct structures, which are separated by a maximum, corresponding to the bcc structure. Actually upon increasing the c/a ratio the bcc structure transforms continuously into the fcc structure. The shallow minimum corresponds to the bct structure with the c/a ratio of about 0.9. The energy difference between the bct ($c/a \approx 0.9$) and bcc structures is about 45 meV per atom. Our results agree with the results of previous studies.[15,18] We, however, notice that the c/a ratio in our calculations slightly differs from that in Refs. 15 and 18. We also notice that our calculations are more accurate both with respect to the method applied and the number of k points used for the energy integration over the BZ.

Furthermore we study the effect of the orthorhombic distortions on the enthalpy of the bcc-Fe at the same conditions. In Fig. 3 we show energy contour $H(c/a, b/a)$ obtained in

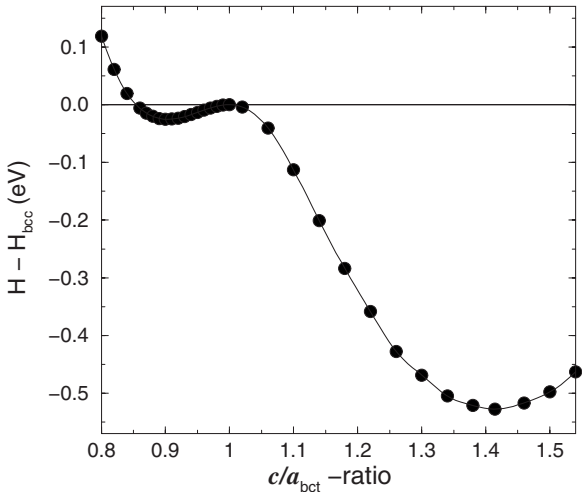

FIG. 2. Enthalpy difference $H-H_{\mathrm{bcc}}$ of the bct structural arrangements of Fe as a function of c/a ratio along the Bain's path at 330 GPa and 0 K. $c/a=\sqrt{2}$ corresponds to the fcc and $c/a=1.0$ to the bcc structure.

our calculations. The bcc structure corresponds to $b/a=c/a=1$. The bct structures ($a=b\neq c$) require that two lattice constants are chosen equal and the third one is longer for bct with $c/a>1$ and shorter for bct with $c/a<1$. Since the orthorhombic representation allows one to choose the third axis along any of the three directions a, b, or c, then, accordingly, the bct structures can be obtained in three ways: ($b/a=1$, $c/a\neq 1$), ($c/a=1$, $b/a\neq 1$), and ($b/c=1$, $a\neq 1$, i.e., $b/a=c/a\neq 1$). Consequently the bct structures are situated along the dotted-dashed, solid, and diagonal dashed lines in Fig. 3. The fcc structure can be obtained by a monoaxial tetragonal distortion of either c/a, or b/a, or simultaneously c/a and b/a to $\sqrt{2}$. We observe three minima [points ($c/a=\sqrt{2}$, $b/a=1$), ($c/a=1$, $b/a=\sqrt{2}$), and ($c/a=b/a$

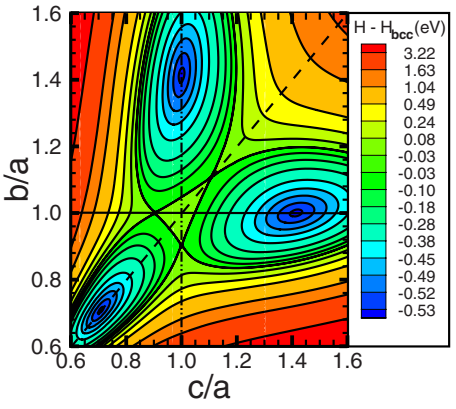

FIG. 3. (Color online) Enthalpy difference $H-H_{\mathrm{bcc}}$ of the body-centered orthorhombic (bco) structural arrangements of Fe as a function of c/a and b/a at 330 GPa and zero temperature. Notice that the point ($b/a=c/a=1$) corresponds to the bcc structure; the lines ($b/a=1$, $c/a\neq 1$), ($b/a\neq 1$, $c/a=1$), and ($b/a=c/a\neq 1$) correspond to the bct structures; the points ($b/a=1$, $c/a=\sqrt{2}$), ($b/a=\sqrt{2}$, $c/a=1$), and ($b/a=c/a=1/\sqrt{2}\approx 0.7071$) correspond to the fcc phase; the points ($b/a=1$, $c/a\approx 0.9$), ($b/a\approx 0.9$, $c/a=1$), and ($b/a=c/a\approx 1.11$) correspond to bct ($c/a\approx 0.9$) phase.

$=1/\sqrt{2}\approx 0.7071)]$ corresponding to the fcc phase. These three mirrored minima are separated by barriers corresponding to the bct structure with $c/a\approx 0.9$. In agreement with Fig. 2 the enthalpy of the bct structure ($c/a\approx 0.9$) is lower than that of the bcc phase. However, the local minimum at bct ($c/a\approx 0.9$), seen in Fig. 2, becomes a saddle point, which separates two fcc minima, when the orthorhombic distortions are considered (cf. Fig. 3).

As follows from the analysis by *ab initio* molecular dynamics (AIMD) in Ref. 18 the application of the tetragonal distortions to the bcc structure leads to dynamical destabilization of the crystal structure. In particular, the bct ($c/a\approx 0.9$) structure was found to be dynamically unstable. Therefore the free energy of the bct ($c/a\approx 0.9$) phase cannot be physically determined either by static phonon calculations within the harmonic approximation or by molecular-dynamics simulations, which take into account anharmonic effects.

In conclusion we have shown that the energy minimum attributed to the bct structure, which was previously found in Fe upon the monoaxial tetragonal distortion of the bcc phase along the Bain's path under compression at zero temperature, is actually an artifact of the structural constraint. When the bcc structure is examined using the orthorhombic distortion with the tetragonal distortion as a particular case, the bct structural framework represents a saddle point between two mirrored fcc minima. Therefore we conclude that there is no ground to emphasize on possible thermal stabilization of the bct structure with a particular c/a ratio apart from the whole family of structures obtained by tetragonal, orthorhombic, or another type of axial distortion.

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