Stability of body-centered cubic iron–magnesium alloys in the Earth's inner core

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The composition and the structure of the Earth's solid inner core are still unknown. Iron is accepted to be the main component of the core. Lately, the body-centered cubic (bcc) phase of iron was suggested to be present in the inner core, although its stability at core conditions is still in discussion. The higher density of pure iron compared with that of the Earth's core indicates the presence of light element(s) in this region, which could be responsible for the stability of the bcc phase. However, so far, none of the proposed composition models were in full agreement with seismic observations. The solubility of magnesium in hexagonal Fe has been found to increase significantly with increasing pressure, suggesting that Mg can also be an important element in the core. Here, we report a first-principles density functional study of bcc Fe–Mg alloys at core pressures and temperatures. We show that at core conditions, 5–10 atomic percent Mg stabilizes the bcc Fe both dynamically and thermodynamically. Our calculated density, elastic moduli, and sound velocities of bcc Fe–Mg alloys are consistent with those obtained from seismology, indicating that the bcc-structured Fe–Mg alloy is a possible model for the Earth's inner core.

ab initio calculations | high pressure

Recently, intensive research efforts have been devoted to determine the composition of the Earth's solid inner core. Its main component, iron, has been proposed to be present in body-centered cubic (bcc) structure (1–5), although the stability of this phase of iron is still in discussion (6, 7). Silicon (6, 8, 9), sulfur (6), and nickel (10) have been considered as alloying elements in bcc-structured iron at core conditions. Composition models containing these elements succeeded in reproducing the density deficit (11) of the inner core. However, none of them was reported to show agreement in other physical properties (12) of the core. On the other hand, it has been demonstrated (13) that Mg alloying not only decreases the density of the hexagonal close-packed (hcp) phase of iron, but also changes its elastic properties (bulk modulus, shear modulus, and longitudinal and transverse sound velocities) in such a way that the differences relative to those predicted by the Preliminary Reference Earth Model (12) (PREM) decrease. However, the partition of Mg into the inner core has always been debated (13), and its presence in the core has often been precluded. This orthodox bias has been supported by two main arguments. First, because of the consistency between the relative amount of Mg in the Earth's mantle and in the chondritic models, the occurrence of Mg in the core is thought to be unlikely (14). Second, based on oxygen fugacity (15) at mantle conditions, it is believed that metallic Mg in the core would require extremely reducing conditions. But there are also counterarguments: the increasing solubility of Mg in Fe with increasing pressure (16), the rapidly increasing oxygen fugacity for Mg with increasing temperature (15), or the unknown ionic character of metal oxides at core conditions. Therefore, currently, the occurrence of Mg at inner-core conditions cannot be completely ruled out. Here, without examining the partition of Mg into the core, we demonstrate that the physical properties of bcc Fe–Mg alloys containing 5–10 atomic percent (at %) Mg in fact reproduce those given in the PREM (12), suggesting that Mg

can be the bcc Fe stabilizing light element in the Earth's solid core.

Results and Discussion

At core pressures (329–364 GPa) and zero temperature, the calculated tetragonal shear modulus $C' = (C_{11} - C_{12})/2$ of bcc Fe is negative, and thus, this phase is dynamically unstable. With increasing temperature, C' increases but remains negative even at core temperatures (11), i.e., between 5,000 and 8,000 K. We calculate $C'_{\text{Fe}} = -113$ GPa at 5,000 K and 355 GPa, and $C'_{\text{Fe}} = -14$ GPa at 8,000 K and 367 GPa. We find that small amount of magnesium addition stabilizes dynamically the bcc phase of Fe–Mg alloys. At the lowest core temperature ($\approx 5,000$ K), we obtain $C'(\text{Fe}_{0.91}\text{Mg}_{0.09}) = 6.4$ GPa at 355 GPa. However, at higher temperature, i.e., closer to the center of the core, significantly less Mg is sufficient for dynamical stability. For instance, at 7,000 K already 5 at % Mg addition leads to positive C' for the bcc phase.

To study the thermodynamic stability, we compare the Gibbs energies (G) calculated for the bcc and hcp phases as a function of temperature and pressure. For pure Fe, we obtain $\Delta G = G_{\text{bcc}} - G_{\text{hcp}} = 43.2$ mRy at zero temperature and 330 GPa. Taking into account the electronic temperature, the bcc–hcp energy difference changes to 27.6 mRy at 5,000 K and 23.5 mRy at 6,000 K. This finding confirms the strong stabilization effect of temperature on the bcc phase of Fe, which is in agreement with other theoretical results (6). Adding 10 at % Mg to Fe decreases the zero temperature ΔG from 43.2 mRy to 24.6 mRy. Therefore, in addition to its dynamical stabilization effect, Mg is also found to have a large impact on the thermodynamic stability of the bcc phase. The calculated Gibbs energies show that at 5,000 K and 325 GPa, the bcc phase of $\text{Fe}_{0.9}\text{Mg}_{0.1}$ is by 26.3 mRy more stable than the hcp phase. We emphasize that the thermodynamic stabilization effect of Mg on bcc Fe is significantly larger than that calculated for Ni (10).

In the following, we examine the physical properties of bcc Fe–Mg alloys. The calculated density of the bcc $\text{Fe}_{0.91}\text{Mg}_{0.09}$ alloy is 13.17 g/cm³ at 5,000 K and 350 GPa, which shows an excellent agreement with the corresponding core density (12), the deviation being 1.6%. The present density is smaller than 13.58 g/cm³ obtained from ab initio molecular dynamics simulations (4) for pure bcc iron at 356.7 GPa. In Fig. 1, we compare the shear (G) and bulk (B) moduli, as well as compressional (v_p) and shear (v_s) wave velocities of $\text{Fe}_{0.91}\text{Mg}_{0.09}$ at 5,000 and 7,000 K, and those of $\text{Fe}_{0.95}\text{Mg}_{0.05}$ at 7,000 K with the PREM data. The shear modulus of $\text{Fe}_{0.91}\text{Mg}_{0.09}$ at 5,000 K is in very good agreement with the seismic data, the deviation being $\sim 7.8\%$ at 353 GPa (Fig. 1 Upper). The figure also demonstrates that G increases with increasing temperature at constant Mg content. However, at higher temperatures smaller amount of Mg can

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the bcc-structured Fe–Mg alloy is a strong candidate model for the Earth's inner core.

Methods

The present ab initio calculations are based on the density functional theory (17) using the generalized gradient approximation (GGA) (18) for the exchange-correlation functional. The Kohn–Sham equations were solved by using the exact muffin-tin orbitals method (19–21). The substitutional disorder of the Mg atoms was taken into account using the coherent potential approximation (CPA) (22, 23) as implemented in the EMTO-CPA method (24). This scheme was proved to be an accurate approach in the theoretical description of the disordered solid solutions (24–26). Nonmagnetic density functional calculations were performed, because bcc Fe and Fe–Mg alloys are nonmagnetic at inner-core conditions.* The two cubic shear constants, $C' =$

$(C_{11} - C_{12})/2$ and C_{44} , were obtained from volume-conserving orthorhombic and monoclinic distortions (29), respectively. At each volume V , the total energy was computed for six different orthorhombic and monoclinic distortions ($\delta_{\text{ort/mon}} = 0.00, 0.01, \dots, 0.05$). The bulk modulus was determined from an exponential Morse-type function (30) fitted to the total energies of the nondistorted bcc structure ($\delta = 0$) calculated for 10 different volumes. Finally, C_{11} and C_{12} were separated by using C' and the cubic bulk modulus $B = (C_{11} + 2C_{12})/3$. The temperature dependence of the elastic constants was calculated for $T = 5,000\text{--}8,000$ K as described in ref. 31. The Hashin–Shtrikman averages (32) were applied to calculate the shear moduli and the sound velocities. We used the Debye model to account for the lattice vibration effects in the Gibbs energy. In the self-consistent calculations, the one-electron equations were treated within the scalar relativistic and soft core approximations. The Green's function was calculated for 16 energy points. In the basis set s, p, d , and f orbitals were included. In the case of the strained bcc structures 22,000 k-points were used in the monoclinic Brillouin zones.

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*At low temperature the calculated ferromagnetic moment on Fe gradually diminishes and disappears at pressures above ≈ 270 GPa. The high-temperature paramagnetic phase was modeled by using the disordered local magnetic moment (DLM) approach. The DLM was shown to accurately describe the effect of loss of the net magnetic moment above the transition temperature (27). Our calculated DLM moments rapidly vanish with pressure and become zero already at ≈ 10 GPa. Furthermore, in bcc Fe spin fluctuations were also found to diminish the local magnetic moments in the paramagnetic phase (28).

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