MINERAL PHYSICS OF EARTH CORE: IRON ALLOYS AT EXTREME CONDITION

LEONID DUBROVINSKY*[1], JUNG-FU LIN[2],
NATALIA DUBROVINSKAIA[3]
[1]Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany, [2]Department of Geological Sciences, Jackson School of Geosciences, the University of Texas at Austin, USA, [3]Mineralphysik, Institut für Geowissenschaftent, Universität Heidelberg, D-69120 Heidelberg, Germany and Lehrstuhl für Kristallographie, Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

Abstract Mineral physics and high-pressure crystallography research provide crucial information on the enigmatic properties of the Earth's interior and is motivating multidisciplinary efforts to re-evaluate our understanding of the past and current states of the planet. We discuss the structures, melting temperatures, sound velocities of the dominant core-forming iron–nickel-light element alloys, as well as seismic anisotropy, thermal and chemical states of the Earth core in view of structural studies of iron-based alloys at multimegabar pressure range.

Keywords: Earth core, iron alloys, high pressure

1. Introduction

The Earth's core is the most remote region on our planet (Figure 1). The boundary of the core is at about 2,900 km in depth. Not only do we not have samples from the core, we do not even expect to get any. To date, the most direct observations of the core have come from seismological studies using remote-sensing techniques. Due to the complex internal structure of the Earth, seismic investigations require extensive data coverage and appropriate

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[*] E-mail: Leonid.Dubrovinsky@uni-bayreuth.de

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models. Decoding geochemical signature of the core carried by mantle plumes faces similar challenges. Experimental and computational simulations have been hindered by the necessity to approach pressures over 140 GPa and temperatures above 3,000 K, prevalent in the core. For these reasons, many fundamental issues concerning the Earth's core remain controversial and poorly understood.

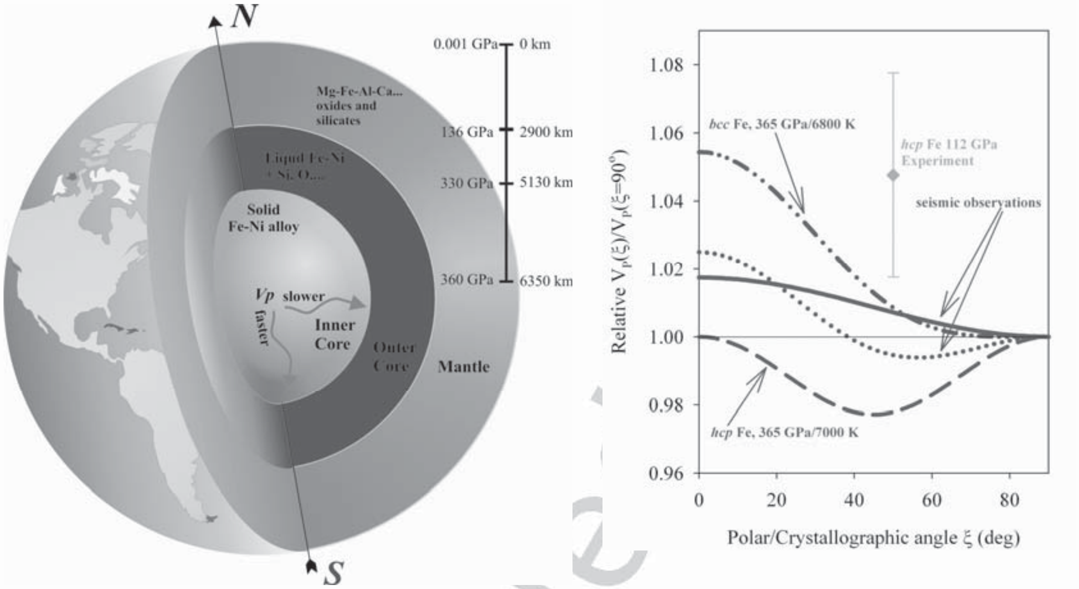

Figure 1. A cutaway of the Earth's interior (left) reveals seismic anisotropy of the inner core (right). Representative elastic anisotropies of single-crystal hcp dashed line) and bcc (solid line) iron from theory (*Belonoshko et al.*, 2008), prefer-oriented hcp iron from static experiments at 112 GPa (diamond) (*Antonangeli et al.*, 2004), and seismic observations in the inner core are shown for comparison.

Despite all these difficulties, the Earth's core is in focus of the highest research interest due to development of experimental and computational methods, as well as steady improvement in observational techniques. Recent studies reveal a number of unusual and enigmatic phenomena related to the core properties and dynamics. Among them is the discovery of the inner core anisotropy, *i.e.*, seismic waves travel faster along the Earth's polar axis than in the equatorial direction. There is also evidence for differential rotation between the inner core and the rest of the Earth and fine–scale heterogeneity. Earth's magnetic field strongly links to the core dynamics. Acceleration of the movement of magnetic poles over the last 150 years is a clear manifestation of the importance of understanding of the Earth core properties for human society.

2. Composition of the Earth's Core

Composition of the Earth's core is a geochemical parameter crucial for understanding the evolution and current dynamics of our planet. Since the discovery of the Earth's core about a century ago, the idea of iron being the dominant component of the core gained firm support from cosmochemical and geochemical observations, seismic data, theory of geomagnetism, and high-pressure studies. Cosmochemical data and studies of iron meteorites give evidence that the Earth's core contains significant (5–15%) amounts of nickel. Already in the early 1950s it was recognized that the outer core is less dense than iron or an iron–nickel alloy at corresponding conditions. Current estimates for the density deficit relative to solid iron vary between 6% and 10% for the outer core and 2–5% for inner core (*Dubrovinsky et al.*, 2000, 2007; *Dewale et al.*, 2006). Uncertainties are in part related to the experimental difficulties in measurements of the properties of iron (or iron–nickel alloys) at multimegabar pressure range and high temperatures, but the fundamental problem is the absence of a universal pressure scale that has led to significant discrepancies in the inter-laboratory studies (see, for example, *Dubrovinsky et al.*, 2007). Nevertheless, the core is expected to contain other element(s) apart from iron and nickel. In order to be considered as an important component of Earth's outer core, an element lighter than iron must be geochemically abundant, alloying readily with iron, and partitioning preferably to liquid rather than to a solid iron phase. These constraints have resulted in S, O, Si, C, and H being the preferred candidates, but practically all geochemically abundant elements which are lighter than iron were suggested and have their proponents. Additional constrains come up from the analysis of elements depletion in the mantle (*e.g.* how much of a certain element was available to be incorporated into the bulk core in the past (on stage of the Earth differentiation) and at present), the comparison of physical properties (density, compressibility, sound velocities, *etc.*) of Fe–(Ni)-light element compounds with corresponding properties of the core, the observation of the partitioning of elements at the core–mantle and inner-outer core boundaries. Available information suggests that none of elements alone could satisfy all constrains simultaneously. Studies of elements solubility in molten iron in laser-heated diamond anvil cells at megabar pressure range and temperatures in excess of 3,000 K by means of analytical transmission electron microscopy (*Takafuji et al.*, 2005) and measurements of compressional sound velocities in light element alloys of iron at high-pressure by inelastic X-ray scattering (*Badro et al.*, 2007) gave consistent results. The preferred model derived form these experimental works is the outer core containing about 5.3 wt.% oxygen and 2.8 wt.% silicon, and the inner core with about 2.3 wt.% silicon. Note that these conclusions depend on the structure of the iron–nickel-light element(s) alloys at core conditions and on the assumed temperature of the Earth's core.

3. Melting of Iron and Temperature of the Earth' Core

One of the major uncertainties in the modern geophysics is temperature of the Earth's core. This is a basic parameter, essential for modeling thermal budget and dynamics of the planet, including such surface processes as volcanism and tectonics. There is no way to obtain temperature distribution in the Earth core from direct observations. However, temperature of solidification of the core material at inner-outer core boundary (ICB, ~330 GPa) could provide a good estimate of temperature at the depth of ~5,100 km, and melting temperature of core-forming material would give low bound of the temperature at core–mantle boundary (CMB, depth ~2,900 km and pressure ~136 GPa). Assuming that iron is the main component of the Earth's core, necessary information could be extracted from an experimentally measured melting curve of iron at multimegabar pressures (Figure 2). At ICB conditions the only experiments possible at the moment are those based on shock waves (see, for example, *Nguyen and Holmes*, 2004). In these experiments temperature estimations are difficult and require significant assumptions. Studies in laser-heated diamond anvil cells (DACs) could be

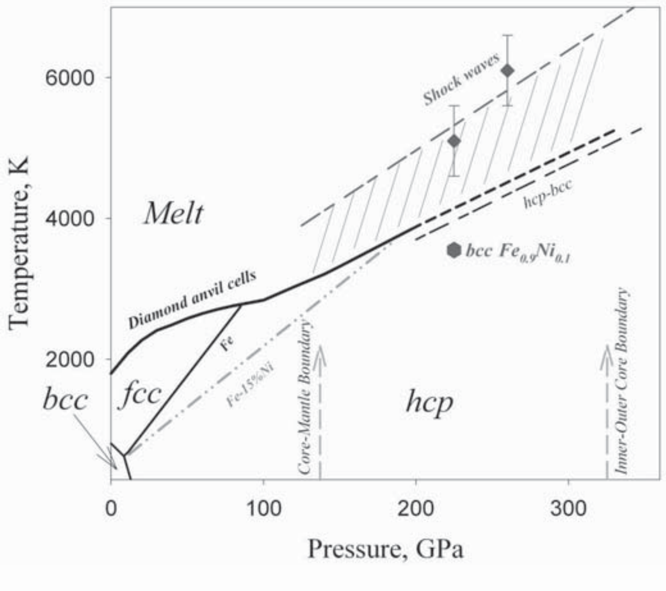

Figure 2. Representative phase diagram of iron and iron–nickel alloys at high pressures and temperatures. hcp iron is stable over a wide range of pressures and temperatures, while bcc iron is predicted to exist in the inner core (dashed line) and a bcc $Fe_{0.9}Ni_{0.1}$ alloy is experimentally observed at 225 GPa and 3,400 K (hexagon). Melting curves of iron from shockwave measured (diamonds) are much higher than static diamond cell results (dashed line). Shaded area: current survey of the melting temperatures of iron at core pressures.

extended to over 200 GPa, but a detection of the melting event in DACs is not easy and even at a moderate pressure below 100 GPa there is no unambiguous consensus. Currently the difference between the shock wave and DAC results on iron melting at ICB is more than 1,000 K (Figure 2) with different theoretical calculations supporting either of the estimates (*e.g. Alfè et al.*, 2003; *Belonoshko et al.*, 2003). The effect of light elements on melting temperature and sub-solidus relations in iron-based alloys at Earth's core conditions adds further uncertainties in guessing temperature of the Earth's core.

4. Structure of Iron and Iron-Based Alloys in the Earth's Inner Core

Iron has been reported to have several phases based on x-ray diffraction at high pressure and temperature, *i.e.*, α and δ, body-centered-cubic (*bcc*); γ, face-centered-cubic (*fcc*); ε, hexagonal closed-packed (*hcp*); β, double-hcp phase (*dhcp*) or orthorhombic phase. The α-, δ-, and γ-phases at lower pressures are well established and broadly accepted. The ε-phase has been proved to be a dominant phase in a wide pressure–temperature range approaching the Earth's core conditions. The β-phase, observed at pressures above 30 GPa and high temperature, is probably metastable, or stabilizes due to contaminations.

While studying of pure iron at multimegabar pressures draw considerable attention and have provided rich experimental data, the knowledge of the behavior and properties of Fe–Ni alloys at conditions of the Earth's core is still limited. At ambient pressure iron–nickel alloys with up to 25 at% of Ni have the *bcc* structure, while higher nickel contents promote crystallization of the *fcc*-structured phase (Figure 2). Compression of *bcc*-structured alloys at ambient temperature results in their transformation to the *hcp*-phase at pressures between 7 and 14 GPa (depending on composition and conditions of experiments). Like in case of pure iron, no further transformations were observed up to a pressure of ~300 GPa on compression of the Fe–Ni alloys with up to 20 at% Ni. However, the presence of nickel significantly affects phase relations in the Fe–Ni system at high temperatures and pressures. While the slope of the *hcp–fcc* phase boundary for pure iron is 35–40 K/GPa, there are indications that the phase boundaries of Fe-Ni alloys with 10 to 30% Ni might have much lower slopes (15–25 K/GPa). Simple extrapolation of experimental results (Figure 2) for Fe with 10–20 wt.% Ni suggests that the stable phase at the inner core conditions is either hexagonal close packed, or a mixture of *hcp* and *fcc* phases (*Lin et al.*, 2002; *Mao et al.*, 2006; *Dubrovinsky et al.*, 2007).

Unlike experiments, theoretical calculations do not require extrapolation in modeling the state and properties of iron and iron-based alloys at conditions of the Earth's core and suggest that at sufficiently high pressures (above 100 GPa) and temperatures close to the melting point iron transforms into *bcc* structured phase (*Belonoshko et al.*, 2003). Although for pure iron this prediction has not been confirmed yet, the *hcp–bcc* transformation of the $Fe_{0.9}Ni_{0.1}$ alloy was observed at pressures above 225 GPa and temperatures over 3,400 K (*Dubrovinsky et al.*, 2007). Moreover, both experimental (*Lin et al.*, 2003) and theoretical (*Vocadlo et al.*, 2003) works point out towards stabilization of the *bcc*-structured phase due to the elements (particularly, silicon) important for the Earth's inner core chemistry.

If *bcc*-structured phase is indeed dominant in the Earth's inner core, it could help to clarify at least one of its enigmatic properties – elastic anisotropy (Figure 1b). Preferred orientation of crystals of the *hcp*-structured iron-based alloy could, in principle, explain why sound waves propagate faster along Earth's spin axis than in the equatorial plane. However, elastic anisotropy of *hcp* iron rapidly decreases with increasing temperature. In contrast, according to molecular dynamic simulations (*Belonoshko et al.*, 2008) cubic *bcc* iron is extremely anisotropic and can account for 12% of the seismic wave anisotropy sufficient for explanation of anisotropy of the inner core. Simulations reveal also that abundant grain boundaries and defects formed in *bcc* iron at high temperatures could lead to drastic decrease of the shear modulus and shear wave velocity, as compared to those estimates obtained from the averaged single-crystal values, thus providing possible explanation of low rigidity of the Earth's inner core.

5. Conclusions

The emerging picture of the Earth's core shows that it as a very dynamic region. Functioning of the geodynamo requires the outer core liquid with small enough viscosity to permit fluid motion with typical velocities of 20 km/year. Intensive convection in the outer core is powered by secular cooling which results in solidification at the inner core boundary and growth of the inner core. Preferential fractionation of elements during crystallization of the inner core changes composition, density, and chemical activity of outer core. Continuous changes of the outer core provoke its continuous reactions with the mantle and induce small-scale dynamic processes at the core–mantle boundary. Mineral physics plays a key role in providing data about the state and properties of the materials at conditions of the Earth's core. The main challenge of the studies of mineralogy of the Earth's core is to find a common ground for explanation of different, sometimes seemingly unconnected or controversial, properties – the chemical and phase composition, temperature and the heat flow, nature of the dynamics and geomagnetism, convection and elasticity.

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