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# Thermodynamic properties of Fe-S alloys from molecular dynamics modeling: Implications for the lunar fluid core

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ABSTRACT

Density and sound velocity of Fe-S liquids for the P-T parameters of the lunar core have not been constrained well. From the analysis of seismic wave travel time, Weber et al. (2011) proposed that the lunar core is composed of iron alloyed with ⩽6 wt% of light elements, such as S. A controversial issue in models of planetary core composition concerns whether Fe-S liquids under high pressure – temperature conditions provide sound velocity and density data, which match the seismic model. Here we report the results of molecular dynamics (MD) simulations of iron-sulfur alloys based on Embedded Atom Model (EAM). The results of calculations include caloric, thermal and elastic properties of Fe-S alloys at concentrations of sulfur 0–18 at.%, temperatures up to 2500 K and pressures up to 14 GPa. The effect of sulfur on the elastic properties of Fe-rich melts is most evident in the notably decreased density with added S content. In the MD simulation, the density and bulk modulus $K_T$ of liquid Fe-S decrease with increasing sulfur content, while the bulk modulus $K_S$ decreases as a whole but has some fluctuations with increasing sulfur content. The sound velocity increases with increasing pressure, but depends weakly on temperature and the concentration of sulfur. For a fluid Fe-S core of the Moon (~5 GPa/2000 K) with 6–16 at.% S (3.5–10 wt%), the sound velocity and density may be estimated at the level of 4000 m $s^{-1}$ and 6.25–7.0 g $cm^{-3}$. Comparison of thermodynamic calculations with the results of interpretation of seismic observations shows good agreement of *P*-wave velocities in the liquid outer core, while the core density does not match the seismic models. At such concentrations of sulfur and a density by 20–35% higher than the model seismic density, a radius for the fluid outer core should be less than about 330 km found by Weber et al. because at the specified mass and moment of inertia values of the Moon an increase of the core density leads to a decrease of the core radius. These results are important for modeling the current state and composition of the lunar core and can be applied to models of large satellites' core properties.



## 1. Introduction

A particular place in the physics of the Moon belongs to the study of the lunar core and adjacent area within a radius of about 500 km at the boundary between the solid mantle and the liquid or partially molten core, and with a low velocity and viscosity layer in the lowermost part of the mantle (Williams et al., 2001, 2014; Weber et al., 2011; Harada et al., 2014; Khan et al., 2014; Raevskiy et al., 2015). The study of the central area is important for understanding the thermal regime, history of lunar dynamo, origin, and evolution of the Moon (Galimov, 2004; Weiss and Tikoo, 2014; Laneuville et al., 2014; Hartmann, 2014).

The seismic properties and electrical conductivity data (Nakamura, 1983; Lognonné and Johnson, 2007; Khan et al., 2013) show that the lunar mantle is rigid to depths of ~1200 km where the temperature distribution must be below the solidus temperature (Kuskov et al., 2014). Since the Apollo experiment did not give direct information about the presence of the core, the composition, state, thermo-physical properties and size of the lunar core remain uncertain to the large extent. Despite determining the real size of the lunar core is a difficult task, Garcia et al. (2011, G11) and Weber et al. (2011, W11) first provide seismic evidence for the existence of a small and partially molten lunar core of pure Fe or Fe-S (the alloying element is not really known) <400 km in radius. Non-seismic evidence for a fluid state of the outer core

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comes from moment of inertia, magnetic induction, lunar laser ranging and GRAIL data analyses (Williams et al., 2001, 2014; Hood et al., 1999; Shimizu et al., 2013; Matsumoto et al., 2015).

The Earth's core may contain a considerable amount of one or more light elements such as Si, O, S, C, H (e.g., Kuskov and Khitarov, 1982; Alfè et al., 2002a,b; Hirose et al., 2013; Belashchenko, 2014; Badro et al., 2014; Umemoto et al., 2014; Saxena and Hrubiak, 2014; Umemoto and Hirose, 2015; Litasov and Shatskiy, 2016). Quantitative estimation of the high *P-T* thermodynamic properties of solid and liquid iron alloys remains a key problem in geophysics.

Fe-S core composition is usually taken for planetary bodies, smaller in sizes than the Earth. Cosmochemical data (Lewis, 1997; Lodders, 2003) indicate that sulfur condensed at 700 K in the form of FeS (pyrrhotite or troilite – the common minerals in meteorites). Sulfur represents one of the major trace elements that make up metallic cores of the parent bodies of meteorites, as well as terrestrial planets and large satellites (Kuskov and Kronrod, 2000, 2001; Balog et al., 2003; Hauck et al., 2006; Rivoldini et al., 2011; Kronrod and Kuskov, 2011; Saxena and Hrubiak, 2014; Rai and van Westrenen, 2014). In addition, sulfur is a leading candidate as an important light element in the lunar core (Nishida et al., 2013; Jing et al., 2014; Belashchenko and Kuskov, 2015).

Thermodynamics of Fe and Fe-S at high pressures fairly well studied (Alfè and Gillan, 1998; Belonoshko et al., 2000; Vočadlo et al., 2003a; Komabayashi and Fei, 2010; Tsujino et al., 2013; Belashchenko, 2014; Ichikawa et al., 2014; Dorogokupets et al., 2014). Melting relations and thermodynamic properties of the Fe and Fe-S systems are of great significance under *P-T* conditions of the Moon for understanding the outer / inner core compositions and crystallization mechanism of the inner core. Measurements of the physical-chemical properties of iron and iron-alloys under the conditions in the center of large satellites (5–10 GPa, ~1800–2000 K), which are critical for discussions of the liquid outer core properties, appeared relatively recently and still remain extremely limited. Density measurements of liquid Fe–S were carried out under static high-pressure conditions (Sanloup et al., 2000; Balog et al., 2003; Nishida et al., 2008; Chen et al., 2014). Sound velocity measurements were carried out using the ultrasonic methods (Nasch et al., 1994, 1997; Nishida et al., 2013; Jing et al., 2014). Antonangeli et al. (2015) using inelastic X-ray scattering combined with X-ray diffraction measured density and sound velocity of bcc and fcc iron.

This study is motivated by the availability of new models of the seismic structure of the lunar core and deep interior based on both *P* and *S* wave velocity models (Garcia et al., 2011; Weber et al., 2011). Both models are based on the re-analyses of the Apollo seismic data. Despite the resolution of seismic sources is insufficient for reliably identifying the core structure, Garcia et al. and Weber et al. have for the first time estimated the radius of the core by seismic methods.

We have investigated the thermodynamic properties of the binary Fe-S alloys by a method of molecular dynamics (MD) in implications for the lunar fluid core. Quantitative estimation of the thermodynamic properties of iron-sulfur alloys (internal energy, density, thermal expansion, bulk moduli, sound velocity, adiabatic gradient, etc.) at concentrations of sulfur 0–18 at.%, temperatures up to 2500 K and pressures up to 14 GPa is based on Embedded Atom Model (EAM), which is a good description of the system Fe-S in a wide range of temperatures and pressure (Belashchenko, 2014; Belashchenko and Kuskov, 2015). The results of molecular dynamics simulations of the density and sound velocity of Fe-S liquids can then be compared to geophysical observations for the Moon to provide constraints on the composition and properties of planetary cores.

## 2. Method

In the simulation of physical-chemical properties of iron and iron alloys various computer approaches have been used. Among the main theoretical approaches is the method of molecular dynamics (Belonoshko and Ahuja, 1997; Belonoshko et al., 2000; Alfè et al., 2000, 2002a,b; Vočadlo et al., 2000, 2003a,b; Belashchenko, 2006, 2013; Koči et al., 2007; Umemoto et al., 2014; Ichikawa et al., 2014; Umemoto and Hirose, 2015; Zhang et al., 2015).

The technical details employed in our calculations have been reported extensively in previous papers (Belashchenko, 2006, 2013, 2014), so we give only a brief summary here. Properties of the Fe–S system at pressures up to 360 GPa have been studied in detail by MD simulations (Belashchenko et al., 2007; Belashchenko and Ostrovski, 2011). On this basis, the temperature and the concentration of sulfur in the Earth's outer (11–12 at.%) and inner (5 at.%) core were estimated; the deviation from the PREM sound velocity is 5–10% (Belashchenko, 2014).

Models of pure iron and/or Fe-S alloys with 2000 atoms in the basic cube with periodic boundary conditions were modeled by EAM. The EAM potential for pure iron (Mendelev et al., 2003) has been refined (Belashchenko, 2006, 2014). The parameters of potentials for pairs 1–2 and 2–2 were specified taking into account the variations in the potential in the Fe–S system for pair 1–1 (Belashchenko and Ostrovski, 2011), resulting in a good agreement with experiments on the density and the heat of formation of melts at concentrations up to 14–18 at.% S (Belashchenko, 2014). At a higher sulfur content, the nature of the chemical bond is changing, so another potential is needed.

Preliminarily, in the Fe–S system by means of multiple rearrangements of atoms we modeled the bcc lattice with a random position of numbers of particles in the basic cube, which is used to create models with a given atom concentration of the second component (sulfur). The Verlet algorithm and EAM potential are applied in the model. We attained the thermodynamic equilibrium repeating the required number of runs with the length of 20,000 time steps in the isobaric-isothermal NpT ensemble. The time interval in the MD runs was $\Delta t = 0.005 t_0$, where $t_0 = 7.608 \cdot 10^{-14}$ s is the internal time unit; thus we performed calculations with simulation time of 7.6 ps. The phase state of the system was traced by the mean square of particle displacements at the run length and by the maximum value of the structural factor of the model.

The displacements were summarized for each particle at each time step from the initial position at the beginning of the MD run to the end position (excluding changes, associated with periodic boundary conditions). These displacements were used for the calculating the mean square displacement of the particles in the modeling process. In the case of solid phase the mean square displacement usually does not exceed 1 Å$^2$, and after melting it behaved in accordance with normal diffusion kinetics and increased approximately linearly with time. The structural factor $S(\mathbf{q})$ is expressed as (Belashchenko and Ostrovski, 2011)

$$S(\mathbf{q}) = \frac{1}{N}\left|\sum_j e - i\mathbf{q}\mathbf{R}j\right|^2,$$

where N is the number of particles, $\mathbf{q}$ – the scattering vector, $\mathbf{R}_j$ – the radius vector of the particles, and the sum is taken over all the particles of the component. If the particles form an almost ideal lattice, the factor $S(\mathbf{q})$ should be close to N in the directions of the reciprocal lattice vectors and to zero in other directions. Upon melting the model, the maximum values $S(\mathbf{q})$ decrease sharply to about 20. Since we considered liquid and amorphous models, the existence of isotropic properties was supposed. Therefore, the basic