Superionic hcp-Fe alloys and their seismic velocities in Earth’s inner core

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Physical Sciences - Article

Keywords: Earth’s inner core, hcp-Fe alloys, superionic

DOI: https://doi.org/10.21203/rs.3.rs-108794/v1

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Abstract

Earth's inner core (IC) is less dense than pure iron, indicating the existence of light elements within it\(^1\). Si, S, C, O, and H have been suggested to be the candidates\(^2,3\), and the properties of Fe-light-element alloys were studied to constrain the IC composition\(^4-19\). Light elements have a significant influence on seismic velocities\(^4-13\), melting temperatures\(^15-17\), and thermal conductivities of Fe-alloys\(^18,19\). However, the state of the light elements in the IC is rarely considered. Using \textit{ab initio} molecular dynamics (AIMD) simulations, we found that H, O, and C in hexagonal close-packed (hcp) Fe transform to a superionic state under IC conditions, showing high diffusion coefficients like liquid. It suggests the IC can be in superionic state rather than normal solid state. The liquid-like light elements lead to a significant reduction in the seismic velocities approaching the seismological observation of the IC\(^20,21\). The significant decrease in shear wave velocity (\(V_S\)) gives an explanation on the soft IC\(^21\). In addition, the light-element convection in the IC has potential influence on the IC seismological structure and magnetic field.

Full Text

Earth's inner core (IC), the central part of our planet, was formed and grown because of the solidification of liquid Fe alloys in the outer core. Seismological observations suggest that the structure of the IC is very complicated and difficult to understand. An unresolved problem is that the IC is soft with a low shear-wave velocity (\(V_S = \sim 3.6 \text{ km/s}\))\(^20,21\), which cannot be matched by sound velocities in Fe and Fe alloys\(^8-13\). Theoretical prediction suggests that the premelting effect of Fe and Fe alloys can lead to strong nonlinear shear weakening at high temperatures\(^22-24\). However, a temperature close to the melting temperature with a small gradient is required. Alternatively, some fractions of melts need to be considered\(^25\), but the mechanism of the stable presence of the melting fraction since the formation of the IC is unclear. Another long-standing controversy is the reason for the anisotropic seismic velocity structure. Generally, the compression wave velocities in the polar direction are \(~3\%\) larger than those in the equatorial direction in the IC\(^26\). This phenomenon is explained by the preferred orientation of hexagonal close-packed (hcp) Fe lattices with \textless 001\textgreater directions\(^27\) or body-centre-cubic (bcc) Fe lattices with \textless 111\textgreater directions\(^28\) along the spin axis. Moreover, earthquake doublets show that seismic waves present different travel times in the IC over the past few decades. This suggests that the IC structure changes with time, which is attributed to the super-rotation or oscillation of the IC\(^29-31\). Investigations on the seismic properties of Fe and Fe alloys have improved the understanding of the IC structure. However, direct experimental measurements under the IC conditions are extremely challenging, while AIMD simulations have increased the knowledge on the properties of Fe alloys\(^13,22-24,27,28\).

H, O, and C are, respectively, the first, second, and fourth abundant elements in our solar system\(^32\). They are also critical volatiles presenting in Earth's interior since its formation. In addition, they can be brought down to the core through mantle convection. In our simulations, H, O, and C atoms were placed at the interstitial sites of hcp-Fe to verify light-element effects on the properties of Fe alloys. AIMD simulations
were carried out at high \( P-T \) on \( \text{FeH}_{0.25}, \text{FeO}_{0.0625}, \) and \( \text{FeC}_{0.0625} \) structures, which contained 0.45, 1.75, and 1.33 wt. % of light elements, respectively. The structures were constructed based on previous experimental studies, and the details are provided in the supplementary information S1. Solid-superionic-liquid phase transitions with increasing temperature are obtained and shown in Fig. 1. At low temperatures, light elements in hcp-Fe undergo small mean-square displacements (MSDs) and simply vibrate about their lattice positions demonstrating that the material is an ordinary solid. At temperatures above 3000 K, the light elements become highly diffusive like liquid as the MSDs increase monotonically during the simulation last over 100 ps indicating a superionic state (Supplementary Fig. 2). A further increase in temperature leads to the melting of the lattice. The melting temperatures of these structures were estimated using the two-phase method to exclude the superheating state in the calculations (Supplementary Information S2)\(^{33}\). The estimated melting temperatures of \( \text{FeH}_{0.25}, \text{FeO}_{0.0625}, \) and \( \text{FeC}_{0.0625} \) are approximately 5770 (± 200), 5595 (± 200), and 5413 (± 200) K at \( \sim 330 \) GPa, which are about 500-800 K lower than that of the pure hcp-Fe at the pressure of the inner core boundary (ICB)\(^{33,34}\) (Supplementary Fig. 5).

Superionic state is an intermediate state between solid and liquid. Superionic ice has been widely investigated and is suggested to exist in the interior of ice giants such as Neptune and Uranus\(^{35-39}\). Liquid-like protons in superionic ice may have a significant influence on the magnetic field of these exoplanets\(^{39}\). In this study, it is shown that Fe alloys (H, O, and C) also transform to the superionic state under the IC conditions. In this case, H, O, and C behave like liquid diffusing within the hcp-Fe lattice. The diffusion coefficients of H, O, and C in solid and liquid iron were calculated (Fig. 2). The diffusion coefficients increase dramatically with temperature, while the effect of pressure is insignificant. Intriguingly, the diffusion coefficients of H, O, and C in solid and liquid Fe alloys are nearly identical under the ICB conditions. Although a significant phase transition from liquid to solid in Fe takes place at ICB, some light elements such as H, O, and C still maintain high mobility as fluids in the IC. Therefore, Earth's IC may be composed of solid-like iron and liquid-like light elements, and the convection of light elements continues in it.

The electric conductivities of Fe alloys are very important in understanding the energy budget of geodynamo and the heat flux of Earth's core\(^{18,19}\). For superionic Fe alloys, the electric conductivity is composed of ionic conductivity and electronic conductivity. The ionic conductivities were calculated by Nernst-Einstein equation, and the values are in the range \( 10^{-2} - 10^{3} \) S m\(^{-1}\) (Supplementary Fig. 7). We also estimated the electronic conductivities using the combination of density functional theory with dynamical mean field theory (DFT+DMFT) method (Supplementary Information S4). Although the presence of light elements decreases the electronic conductivity of pure Fe, it is still over 2-3 orders of magnitude higher than the ionic conductivity, and therefore the conductivity contribution due to the ionic diffusion is negligible.

The liquid-like light elements in the Fe lattice also affect the seismic velocities. AIMD simulations with the NVT ensemble were conducted on \( \text{FeH}_{0.25}, \text{FeO}_{0.0625}, \) and \( \text{FeC}_{0.0625} \) at 2000–6000 K and 360 GPa. In
order to exclude the effect of the superheating state, the simulation temperatures are lower than the predicted melting temperatures. The structures and cell parameters were carefully determined to maintain hydrostatic stress. The independent elastic constants for $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, and $C_{44}$ were calculated by distorting the equilibrium structure and solving the stress-strain relations (Supplementary information S5). The compression ($V_P$) and shear ($V_S$) wave velocities of these structures at high $P-T$ were deduced from the elastic constants and are plotted in Fig. 3. The $V_P$ of the alloys decrease almost linearly with temperature, while $V_S$ show an accelerated decline upon the solid-superionic transition (Fig. 3c). It suggests that the diffusion of light elements may introduce anharmonic vibration in the lattice resulting in significant effect on $V_S$. Owing to this effect, a small amount of diffusive light elements lead to a decrease in seismic velocities and densities approaching the geophysical observations at the IC conditions. H, O, and C superionic light elements have different effects on seismic velocities and densities. A content of 0.45 wt. % superionic H in hcp-Fe causes the expected decrease in density. The density of FeH$_{0.25}$ at 6000 K is 13.12 g/cm$^3$, which is very close to that of the Preliminary Reference Earth Model (PREM), while the presence of superionic O and C elements has an inconspicuous effect on the density. On the other hand, the $V_S$ of FeO$_{0.0625}$ and FeC$_{0.0625}$ is lower than that of FeH$_{0.25}$ at approximately 5500 K. Although the $V_S$ of the Fe alloys are slight higher than that of the PREM, they may be further reduced considering the presence of nickel$^8$. Poisson's ratio is also an important probe to constrain the composition and structure of the IC. The presence of superionic light elements also increases Poisson's ratio to 0.41 for H, and 0.43 for C and O, which is quite close to that of the PREM (Supplementary Table 1 and Supplementary Fig. 9). Therefore, the superionic Fe alloys at 5500–6000 K show quite similar seismic characteristics as that of the IC. Previous theoretical simulations show a decrease in $V_P$ and $V_S$ of Fe and Fe alloys with increasing temperature because of the premelting effect$^{22-24}$. However, the calculated velocities can be consistent with the PREM at approximately 7200 K for Fe and 6700 K for Fe-Si-C alloy$^{22,24}$, which are higher than the most computationally and experimentally predicted temperatures of IC$^{15-19}$. Here we provide a new mechanism by which highly diffusive light elements bring strong anharmonic vibration to Fe alloys and lead to significant reductions of $V_P$ and $V_S$ close to the PREM model at 5500–6000 K. Elastic softening caused by its superionic effect was also reported in Li$_2$O when it is used as a nuclear fusion material at high temperatures$^{40}$.

Seismologic observations suggest that Earth's core is composed of the liquid outer core with $V_S$ equal to zero, and the solid inner core with $V_S$ equal to $\sim$3.6 km/s. At the ICB, solidification of the IC generates latent heat and leads to the separation and buoyancy of light-element phases, which promote the convection flows of the outer core, producing and powering the geomagnetic field (black dashed arrows in Fig. 4). Based on our simulations, some light elements such as H, O, and C can present in the IC in the superionic state. Owing to the high diffusion coefficients, light elements continue their circulation in the IC (red dashed arrows in Fig. 4). In this case, the IC is not conventionally known normal solid Fe alloy, but a mixture of solid Fe and light-element fluids. The convection of the ionic light elements may generate magnetic field in the IC. However, quantitative modelling is needed to study if this magnetic field is sufficient to influence Earth's magnetic field.
The liquid-like light elements also bring significant influence on the elastic properties of the IC, and the long-standing seismic puzzles in the IC, as mentioned above, can be rationalized within the superionic IC model. First, the liquid-like light elements have a profound effect on the seismic velocities, presenting the $V_S$ quite close to that of the PREM at 5500–6000 K, which explains why the IC is quite soft. In addition, superionic Fe alloys show 8–11 % lower Vp than that of pure Fe. If the distribution of superionic light elements in the IC is inhomogeneous with a higher concentration in the equatorial direction than in the polar direction, seismic velocities along the equatorial direction will be lower, which gives a simple reason for the anisotropic seismological structure. Also, the enrichment of liquid-like light elements may enhance seismic wave attenuation, which has been widely observed in the IC\textsuperscript{21}. Moreover, the light-elements convection changes the distribution of light element in the IC leading to the evolution of the seismological structure with time. This phenomenon may provide an alternative interpretation of the differential travel time of similar earthquakes\textsuperscript{29-31}. Generally, the seismic properties of superionic Fe alloys are consistent with the seismology characteristics of the IC.

Suggested by some geodynamo models, geomagenetic field also has influence on the IC\textsuperscript{41,42}. In this case, the diffusion of ionic light element can be affected by the inner-core magnetic field under Lorentz force, and the convection and distribution of light elements may related with geometry and strength of the magnetic field. Besides, both seismic velocity in the IC and the geomagnetic field show observable change in last few decades\textsuperscript{29-31}. Then, it is important to study if there is a certain relation between the inner core seismic structure and geomagnetic field, which might be a clue for understanding the structure and evolution of the IC.

**Method**

The calculations were performed using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and projector augmented wave (PAW) method\textsuperscript{43} as implemented in the Vienna Ab Initio Simulator Package (VASP)\textsuperscript{44}. A plane wave representation for the wave function with a cutoff energy of 800 eV was adopted. In AIMD simulations, the cutoff energy was set to 400 eV with Γ point for k-space sampling. AIMD simulations within canonical ensemble (NVT) were conducted to study the solid-superionic-liquid phase transition and diffusion coefficients of superionic light elements. The simulations lasted ~10-100 ps at temperatures from ~2000 to ~7000 K and pressure from ~250 to ~400 GPa with a time step of 1fs. The two-phase method\textsuperscript{33} was adopted to predict the melting temperatures for FeH\textsubscript{0.25}, FeO\textsubscript{0.0625} and FeC\textsubscript{0.0625}. The simulations within NVE ensemble were conducted on the solid-liquid coexistence system containing 256 Fe atoms and 64, 16, and 16 of H, O, and C atoms, respectively (Supplementary Information S2). Our calculations on ionic transport and elastic properties of superionic phases were constrained at the temperatures below the melting temperature. Structures for Fe-hcp with C, H and O atoms at the interstitial sites of $4 \times 4 \times 2$ supercells at 2000–6000 K and 360 GPa were constructed to investigate elastic properties. We determined the equilibrium volumes and cell parameters at different temperatures by conducting a grid of NVT ensemble simulations over volumes and temperatures using a Nosé thermostat\textsuperscript{45}. For each equilibrium structure, a 10,000 time-steps (10 ps)
simulation was conducted to check for sure that the stress field is hydrostatic. The elastic constant $C_{ij}$ was calculated by distorting the equilibrium structure and solving the stress-strain relations. Details for the calculation methods and convergence tests with large supercells and long simulation time are provided in Supplementary Information.

**Declarations**

**Data availability**

The data that support this study are available from the corresponding author upon reasonable request.

**Acknowledgments:**

This study was supported by the Strategic Priority Research Program (B) of the Chinese Academy of Sciences (XDB 18010401). We acknowledge the support of the National Natural Science Foundation of China (41774101) and the Youth Innovation Promotion Association of CAS (2020394).

**Author contributions:**

Y.H. and S.S. contributed equally to this work, conducted the calculations, analysed the data, and wrote the manuscript. Y.H., D.Y.K., and H.K.M initiated and designed the project. S.S. performed simulations on elastic properties. B.G.J. performed electronic conductivity calculations. All authors discussed the data analysis and interpretation and commented on the manuscript.

**Competing interests**

The authors declare no competing interest.

**References**

1. Birch, F. Elasticity and constitution of the Earth's interior. J. Geophys. Res. **57**, 227–286 (1952).
2. Poirier, J. P. & Shankland, T. J. Dislocation melting of iron and temperature of the inner core boundary, revisited. Geophys. J. Int. **115**, 147–51 (1993).
3. Li, J. & Fei, Y. Experimental constraints on core composition. In Treatise on Geochemistry, Vol. 2: The Mantle and Core, ed. RW Carlson, Amsterdam: Elsevier pp. 1–31 (2007).
4. Li, J., Fei, Y., Mao, H. K., Hirose, K. & Shieh, S. R. Sulfur in the Earth's inner core. Earth Planet. Sci. Lett. **193**, 509–14 (2001).
5. Badro, J. et al. Effect of light elements on the sound velocity of solid iron: implications for the composition of Earth's core. Earth Planet. Sci. Lett. **254**, 233–38 (2007).
6. Mao, Z. et al. Sound velocities of Fe and Fe-Si alloy in the Earth's core. Proc. Natl. Acad. Sci. USA **109**, 10239–44 (2012).
7. Lin, J. F., Heinz, D. L., Campbell, A. J., Devine, J. M. & Shen, G. Y. Iron-silicon alloy in Earth's core? Science 295, 313–15 (2002).

8. Lin, J. F. et al. Sound velocities of iron-nickel and iron-silicon alloys at high pressures. Geophys. Res. Lett. 30, 2112 (2003).

9. Antonangeli, D. et al. Composition of the Earth's inner core from high-pressure sound velocity measurements in Fe-Ni-Si alloys. Earth Planet. Sci. Lett. 295, 292–96 (2010).

10. Chen, B. et al., Hidden carbon in Earth's inner core revealed by shear softening in dense Fe$_2$C$_3$. Proc. Natl. Acad. Sci. USA 111, 17755–58 (2014).

11. Prescher, C. et al. High Poisson's ratio of Earth's inner core explained by carbon alloying. Nat. Geo. 8, 220 (2015).

12. Shibazaki, Y. et al. Sound velocity measurements in dhcp-FeH up to 70 GPa with inelastic X-ray scattering: Implications for the composition of the Earth's core. Earth Planet. Sci. Lett. 313-314, 79–85 (2012).

13. Caracas, R. The influence of hydrogen on the seismic properties of solid iron. Geophys. Res. Lett. 42, 3780–3785 (2015).

14. Alfè, D., Gillan, M. J. & Price, G. D. Composition and temperature of the Earth's core constrained by combining ab initio calculations and seismic data. Earth Planet. Sci. Lett. 195, 91–98 (2002).

15. Terasaki, H. et al. Liquidus and solidus temperatures of a Fe-O-S alloy up to the pressures of the outer core: implication for the thermal structure of the Earth's core. Earth Planet. Sci. Lett. 304, 559–64 (2011).

16. Morard, G. et al. Fe–FeO and Fe–Fe3C melting relations at Earth's core–mantle boundary conditions: Implications for a volatile-rich or oxygen-rich core. Earth Planet. Sci. Lett. 473, 94-103 (2017).

17. Mashino, I., Miozzi, F., Hirose K., Morard, G. & Sinmyo, R. Melting experiments on the Fe–C binary system up to 255 GPa: Constraints on the carbon content in the Earth's core. 515, 135–144 (2019).

18. Pozzo, M., Davies, C., Gubbins, D. & Alfè D. Thermal and electrical conductivity of iron at Earth's core conditions. Nature 485, 355, (2012).

19. de Koker, N., Steinle-Neumann, G. & Vlcek, V. Electrical resistivity and thermal conductivity of liquid Fe alloys at high P and T, and heat flux in Earth's core. Proc. Natl. Acad. Sci. USA 109, 4070–73 (2012).

20. Dziewonski, A. M. & Anderson, D. L. Preliminary reference Earth model. Phys. Earth Planet. Inter. 25, 297–356 (1981).

21. Tkalčič, H. & Pham, T.-S. Shear properties of Earth's inner core constrained by a detection of J waves in global correlation wavefield Science 362, 329 (2018).

22. Martorell, B., Vočadlo, L., Brodholt, J. & Wood, I. G. Strong Premelting Effect in the Elastic Properties of hcp-Fe Under Inner-Core Conditions. Science 342, 466 (2013).

23. Martorell, B., Wood, I.G., Brodholt, J., & Vočadlo, L., The elastic properties of hcp-Fe1-xSix at Earth's inner-core conditions. Earth Planet. Sci. Lett. 451, 89–96 (2016).
24. Li, Y., Vočadlo, L. & Brodholt J. B. The elastic properties of hcp-Fe alloys under the conditions of the Earth's inner core. Earth Planet. Sci. Lett. 493, 118 (2018).

25. Singh, S. C., Taylor, M. A. J. & Montagner, J. P. On the Presence of Liquid in Earth's Inner Core. Science 287, 2471 (2000).

26. Creager, K. C. Anisotropy of the inner core from differential travel times of the phases PKP and PKIKP. Nature 356, 309 (1992).

27. Steinle-Neumann, G., Stixrude, L., Cohen, R. E. & Gülseren O. Elasticity of iron at the temperature of the Earth's inner core. Nature 413, 57 (2001).

28. Belonoshko, A. B., Skorodumova, N. V., Rosengren, A. & Johansson, B. Elastic Anisotropy of Earth's Inner Core. Science 319, 797 (2008).

29. Song, X. & Richards, P. Seismological evidence for differential rotation of the Earth's inner core. Nature 382, 221–24 (1996).

30. Su, W. J., Dziewonski, A. M. & Jeanloz, R. Planet within a planet: rotation of the inner core of Earth. Science 274, 1883–87 (1996).

31. Tkáčíč, Young, M., Bodin, T., Ngo, S. & Sambridge, M. The shuffling rotation of the Earth's inner core revealed by earthquake doublets. Nat. Geosci. 6, 497–502 (2013).

32. Lodders, K. Solar system abundances and condensation temperatures of the elements. Astrophys. J 591, 1220-1247 (2003).

33. Alfè, D. Temperature of the inner-core boundary of the Earth: Melting of iron at high pressure from first-principles coexistence simulations. Phys. Rev. B 79 060101 (2009).

34. Anzellini, S., Dewaele, A., Mezouar, M., Loubeyre, P. & Morard, G. Melting of Iron at Earth's Inner Core Boundary Based on Fast X-ray Diffraction. Science 340, 464–466 (2013).

35. Cavazzoni, C. et al. Superionic and metallic states of water and ammonia at giant planet conditions. Science 283, 44–46 (1999).

36. Goldman, N., Fried, L. E., Kuo, I.-F. W. & Mundy, C. J. Bonding in the Superionic Phase of Water. Phys. Rev. Lett. 94, 217801 (2015).

37. Hernandez, J.-A. & Caracas, R. Superionic-Superionic Phase Transitions in Body-Centered Cubic H2O ice. Phys. Rev. Lett. 117, 135503 (2016).

38. Millot, M. et al. Nanosecond X-ray diffraction of shock-compressed superionic water ice. Nature 569, 251 (2019).

39. Millot, M. et al. Experimental evidence for superionic water ice using shock compression. Nat. Phys. 14, 297–302 (2018).

40. Hull, S., Farley, T. W. D., Hayes, W. & Hutchings, M. T. The elastic properties of lithium oxide and their variation with temperature. J. Nucl. Mater. 160, 125-134 (1988).

41. Glatzmaier, G. A. & Roberts, P. H. Rotation and Magnetism of Earth's Inner Core. Science 274, 1887-1891 (1996).
42. Wicht J. Inner-core conductivity in numerical dynamo simulations. Earth Planet. Inter. 132, 281-302 (2002).

43. Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B 50, 17953–17979 (1994).

44. Kresse, G. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 54, 11169–11186 (1996).

45. Nosé, S. A unified formulation of the constant temperature molecular dynamics methods. J. Chem. Phys. 81, 511 (1984).