Peer Review File

Manuscript Title: Superionic iron alloys and their seismic velocities in Earth's inner core

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1:

The manuscript presents an interesting idea about the possibility of ionic diffusion of light impurities in the solid inner core, and how this process would affect convection, ionic conductivity and the generation of the Earth's magnetic field. This would be an exciting and interesting contribution, however, I have some reservations about the results, as I explain below.

The authors used the method of ab-initio molecular dynamics to look at diffusion, and to compute the melting properties of several Fe-X mixtures. I will discuss these in turns.

1) Diffusion. The authors report the behaviour of the mean square displacement (MSD) of Fe and several impurities X in their simulations, and show that although the MSD of Fe is constant, showing that Fe atoms do not diffuse, those of the various impurities X show a linear behaviour with time, indicative of ionic diffusion. This is interesting, but this diffusion is only possible if the impurities sit in interstitial sites. Have the authors computed the relative stability of these solid solutions compared with X atoms in substitutional sites? Without proof of thermodynamic stability this behaviour is irrelevant.

2) Melting. The authors report on calculation of melting temperatures of various mixtures using the Z method. Here I need to split my comments into two subsections: i) the Z method itself and ii) melting of mixtures.

2.1) The Z method is based on the idea that by simulating a solid at constant volume at increasingly higher temperatures, at some point one reaches the overheating limit and the system melts. Latent heat of melting cause the temperature to decrease and one is left with a liquid which is, supposedly, at the melting temperature. Homogeneous melting is a random process, which has been shown to be described well by an exponential time distribution (see J. Chem. Phys. 135 024102 (2011)). The average waiting time, tav, that one is expected to wait to observe a melting event is inversely proportional to the amount of excess overheating.
This means that it is impossible to observe melting at exactly the superheating limit, as in this case the waiting time is infinite and one would never see a melting event. However, it is possible to perform a series of ensemble simulations, and by gathering statistics on the time distribution of the melting events one can obtain the dependence of tav on the amount of excess heating, and extrapolating that to zero excess heating. A complete analysis requires hundreds of simulations, with simulation times of the order of nanoseconds. If one performs a single simulation, as the authors did, there is no information whatsoever on the waiting time, and it is impossible to gauge the amount of overheating.
All one can say is what would be the amount of excess overheating if one wanted to observe, on average, a melting event during the 10ps simulation that the authors can afford. Note that this would be a very crude estimate, such as measuring the half-life of a radioactive substance by observing a single radioactive decay event. However, if one insisted of wanting to do this anyway, based on previous analysis (see JCP paper mentioned above) I would expect that to have any chance of observing a homogeneous event within 10 ps one would have to have thousands of degree of excess heating, resulting in a similar overestimate of the melting temperature.

2.2) Melting of a mixture is not the same as melting a pure substance. In particular, the melting temperature is affected by partitioning of the solute between liquid and solid and the excess

entropy created in the process. In addition to all my reservations regarding the Z method, as detailed above, this approach makes it impossible for the system to access this excess entropy.

****
Referee #2:

In the manuscript on possible superionic Fe alloys in the Earth's inner core, He and co-workers employ first-principles calculation to address a very peculiar state of matter - the supersonic solids - and to show its potential presence in the Earth's inner core. In superionic solids one atomic species, typically a small light atom, decouples from the vibration of the lattice and start to freely diffuse behaving in practice like a fluid flowing inside a fixed solid lattice. These solids show higher conductivity and lower elastic constants than their solid counterparts. I think that study of He and co-workers is interesting because they found for the first time, at my best knowledge, the potential presence of such a solid inside the Earth.

I think there are some major aspects of this work that need to be clarified before this work can be considered.

The simulations, specially for O and C look too short. The kink in MSD at large times is an indication that something is not yet fully converged. I suggest the authors run longer simulations for these elements. Alternatively problems can arise from the reduced sampling due to small simulation cells. As the number of simulation points is rather limited I think the authors could the diffusion simulations with the large supercells.

The predicted core temperature are unreliable as the concentration in light elements changes with depth. Moreover at the OC/IC boundary the difference in partitioning of the light elements changes the concentration, and thus the melting T itself. Such a diagram can be drawn only if partitioning is taken into account.

The discussion on electrical conductivity should be completely revised. In a metallic system the electrical conductivity comes in 90% from the electrons. These are completely neglected in this study when reported conductivity. The fact itself that the alloys are superionic suggest the ionic conductivity is important. However this is now supersonic water or ammonia. Th electronic part will still remain important. How much? We don't know and I think this is a very important and interesting question that needs an answer and should address here. Or completely discarded.

There are also a whole list of more minor modifications to be done:

line 5: "the IC has potential affection on its seismological structure"

line 6: "magnetic fields with an in-depth influence"

line 76: "The melting temperatures of these structures were strictly predicted using the Z method" The Z method is at least highly dependent on the size of the system, and it is not yet fully clear that it is reliable. While comparison to previous results seem to point into the right direction, I think it should be used with a lot of care. I think w are a far shot away from this being "strict".

line 87: References 34-36. Maillot et al. only "confirmed" the theoretical predictions. The theoretical works of Goldman et al. (Phys. Rev. Let.. 2005) and Hernandez and Caracas (Phys Rev Lett, 2016) on the supersonic ice should be cited here.

ref. 36: Cavvazzoni et al. predicted and analysed first the influence of the superionic phase on the interior of giant planets
line 96: "light elements such as H, O, and C can penetrate across the ICB" the light elements do not "penetrate" in the inner core but they can be incorporated in the hcp structure based on

partitioning and free energy

lines 144-145: "Based on our simulations, some light elements such as H, O, and C can diffuse into the IC in the superionic state." Again it is not that because diffusion happens that these light elements actually go into the inner core. It is the chemical potential that determines the solubility and the partitioning. This needs to be revised.

lines 146-148: "Motivated by the geomagnetic field" well .. not rally. as the field is generated in the outer core it should not influence and less induce the convection and diffusion in the inner core

lines 159-160: "the convection of light elements leads to the evolution of the seismological structure with a significant influence on the change of seismic velocities with time." This statement deserves to be discussed and analysed at length. Fist of all the diffusion coefficients, even if high, are not enough to influence the pattern of seismic velocities over observable time. What is the diffusion length of the light elements

lines 165-166: "The diffusion of light elements greatly enhance the ionic conductivity of the IC" We do not care about it! It is so small, just as the authors themselves say on the net line, that it doesn't matter. The authors should rather focus on the other properties and remove this part completely. Or determine properly the conductivity of the superionic phase

lines 168-171: "This study shows that a magnetic 170 field can be generated by the light element convection in the IC," This part is easy not convincing. There is no clear estimations of the intensity of these currents, the difference with respect to electronic conductivity, and even less so a clear discussion about the magnetic fields that can be generated from this diffusion.

line 172: "These results may offer a clue on the geodynamo simulations" Again this is a general and unconvincing statement that sounds more like the authors are trying to find some sort of important effort stemming out of these numbers

lines 175-177: "some light elements may exist in the IC in superionic state with influence on the seismic wave velocities and the mangeneitc field, indicating a potential connection between these two critical geophysical parameters in the IC." Same observation as above, vague and unconvincing.

Author Rebuttals to Initial Comments:

Referee #1:

The manuscript presents an interesting idea about the possibility of ionic diffusion of light impurities in the solid inner core, and how this process would affect convection, ionic conductivity and the generation of the Earth's magnetic field. This would be an exciting and interesting contribution, however, I have some reservations about the results, as I explain below.

[Authors]: We are grateful for the recognition of the importance of our work.

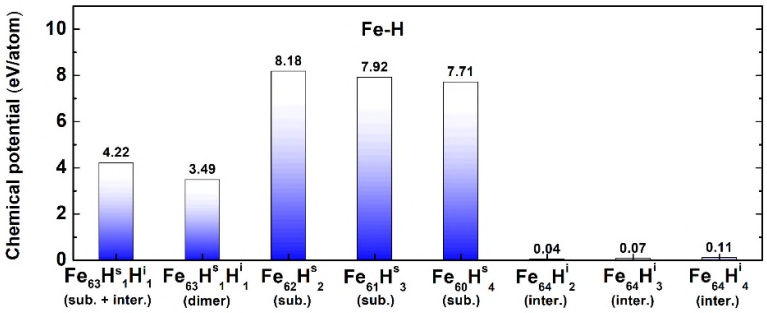
The authors used the method of ab-initio molecular dynamics to look at diffusion, and to

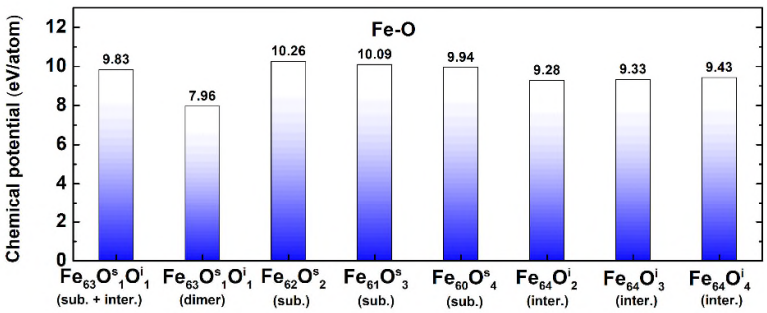
compute the melting properties of several Fe-X mixtures. I will discuss these in turns.

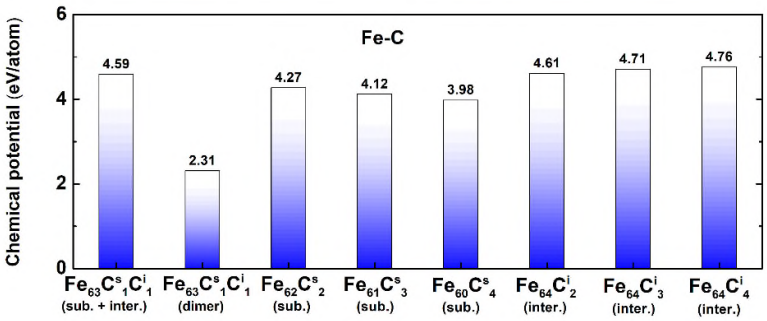
1) Diffusion. The authors report the behaviour of the mean square displacement (MSD) of Fe and several impurities X in their simulations, and show that although the MSD of Fe is constant, showing that Fe atoms do not diffuse, those of the various impurities X show a linear behaviour with time, indicative of ionic diffusion. This is interesting, but this diffusion is only possible if the impurities sit in interstitial sites. Have the authors computed the relative stability of these solid solutions compared with X atoms in substitutional sites? Without proof of thermodynamic stability this behaviour is irrelevant.

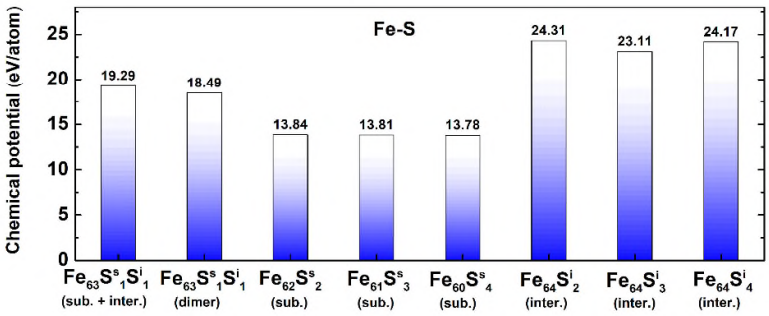
[Authors]: This is a very good question. Follow your suggestions, we calculated enthalpies of Fe-X (X= H, C, O, S and Si) with X at interstitial and/or substitutional sites (**Fig. 1**). We found that H at interstitial site is energetically much more favorable, which is consistent with previous experimental and computational results [Tagawa et al., 2016; Caracas 2015], while substitutional structure is more stable for Fe-S and Fe-Si alloys. We also check the structural stability of Fe-H, Fe-S and Fe-Si by performing AIMD simulations at high *P*-*T*, and found the substitutional structure of Fe-H, and the interstitial structure of Fe-S and Fe-Si alloys are not stable at the inner core conditions.

For C and O, the dimer structure (coexisting of both substitutional and interstitial defects) is the most stable structure at 0 K. However, quasiharmonic approximation (QHA) study on Fe-C alloys [Li et al., 2019] suggests C at substitutional site is slightly more stable than the dimer structure at 6500 K and 360 GPa. Nevertheless, the interstitial defects for C and O may still exist in Earth's inner core due to the small free energy difference and complicated thermodynamic conditions in Earth's inner core with different pressures, temperatures, compositions. Thus, it is still valuable to study the influence of C and O interstitial defects on the elastic properties of Fe alloys and compare with geophysical observations. Here we also confirmed the elastic stability of interstitial Fe-H, Fe-O and Fe-C structures at 360 GPa and 3000-6000 K.









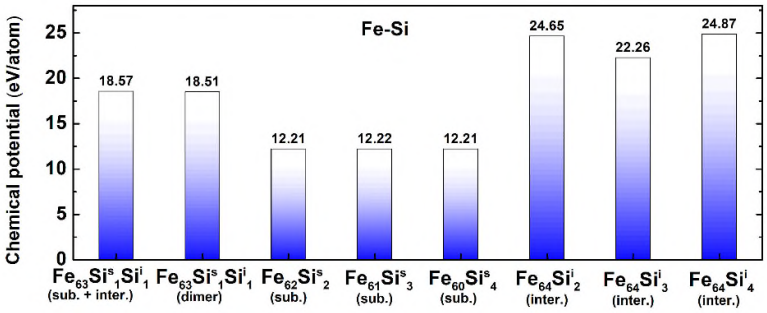


Fig. 1 Calculated chemical potentials of X (X = H, O, C, S, and Si) in hcp-Fe with different configurations at 360 GPa and 0 K.

2) Melting. The authors report on calculation of melting temperatures of various mixtures using the Z method. Here I need to split my comments into two subsections: i) the Z method itself and ii) melting of mixtures.

2.1) The Z method is based on the idea that by simulating a solid at constant volume at increasingly higher temperatures, at some point one reaches the overheating limit and the system melts. Latent heat of melting cause the temperature to decrease and one is left with a liquid which is, supposedly, at the melting temperature. Homogeneous melting is a random process, which has been shown to be described well by an exponential time distribution (see J. Chem. Phys. 135 024102 (2011)). The average waiting time, tav, that one is expected to wait to observe a melting event is inversely proportional to the amount of excess overheating.

This means that it is impossible to observe melting at exactly the superheating limit, as in this case the waiting time is infinite and one would never see a melting event. However, it is possible to perform a series of ensemble simulations, and by gathering statistics on the time distribution of the melting events one can obtain the dependence of tav on the amount of excess heating, and extrapolating that to zero excess heating. A complete analysis requires hundreds of simulations, with simulation times of the order of nanoseconds. If one performs a single simulation, as the authors did, there is no information whatsoever on the waiting time, and it is impossible to gauge the amount of overheating.

All one can say is what would be the amount of excess overheating if one wanted to observe, on average, a melting event during the 10ps simulation that the authors can afford. Note that this would be a very crude estimate, such as measuring the half-life of a radioactive substance by observing a single radioactive decay event. However, if one insisted of wanting to do this anyway, based on previous analysis (see JCP paper mentioned above) I would expect that to

have any chance of observing a homogeneous event within 10 ps one would have to have thousands of degree of excess heating, resulting in a similar overestimate of the melting temperature.

2.2) Melting of a mixture is not the same as melting a pure substance. In particular, the melting temperature is affected by partitioning of the solute between liquid and solid and the excess entropy created in the process. In addition to all my reservations regarding the Z method, as detailed above, this approach makes it impossible for the system to access this excess entropy.

[Authors]: Thanks for the detail suggestions and explanations. Although Z method has been used in different systems, it is right that the effect of light-element partition cannot be accounted in the one-phase simulations under NVE ensemble. Therefore, we used the solid-liquid coexistence method (two-phase method) to estimate the melting temperature of Fe-H, Fe-O and Fe-C systems in the section Supplementary S2. In our simulations, we observed the inter-diffusion of the light elements between the solid and the liquid phase, and the melting temperatures are approximately 5770 (± 200), 5595 (± 200), and 5413 (± 200) K at ~330 GPa (**Fig. 2**). We also estimated the melting temperature on the data of previous experimental results (**Fig. 3**). They are in agreement with our two-phase simulation results. Thus, it is reasonable to calculate the elastic properties of $FeH_{0.25}$ at temperatures below 6000 K, and $FeO_{0.0625}$ and $FeC_{0.0625}$ at temperatures below 5500 K at 360 GPa.

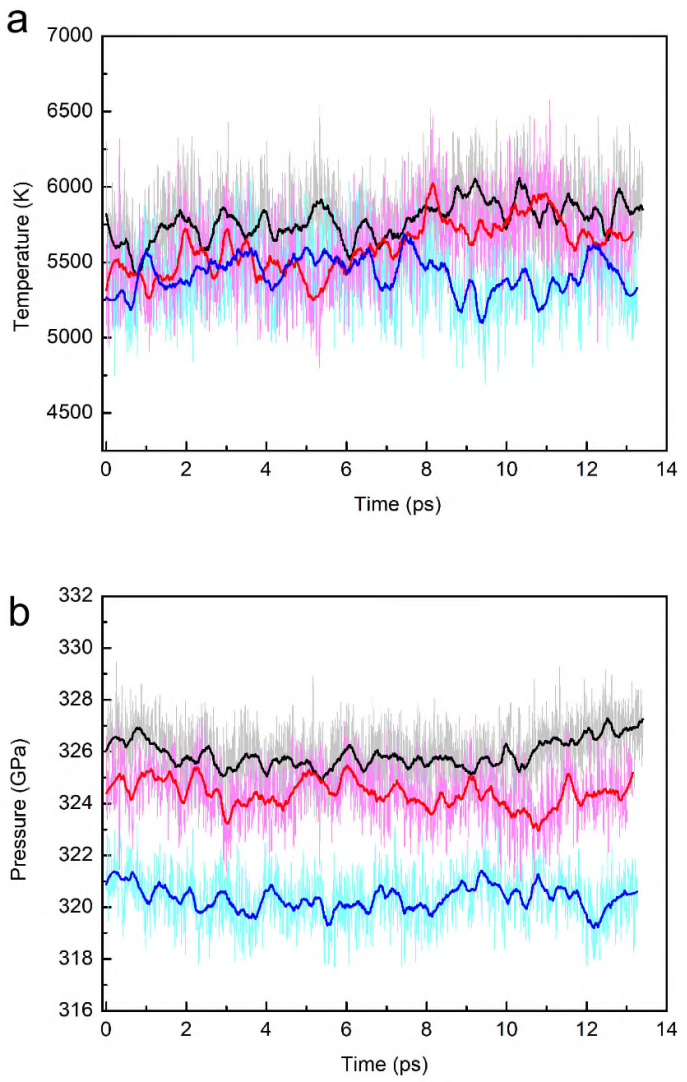
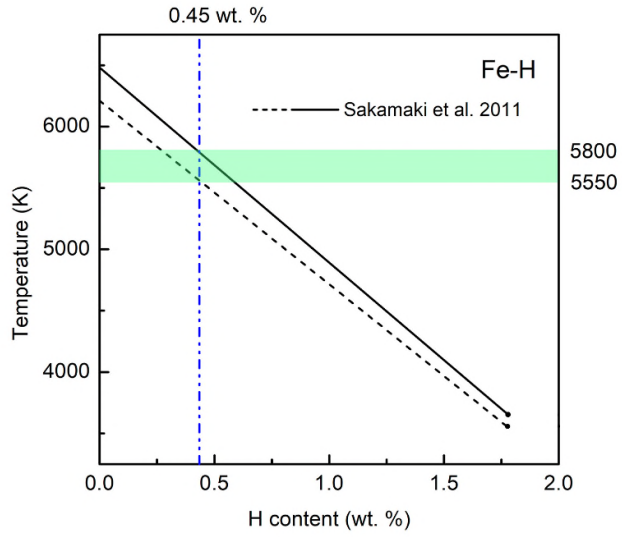
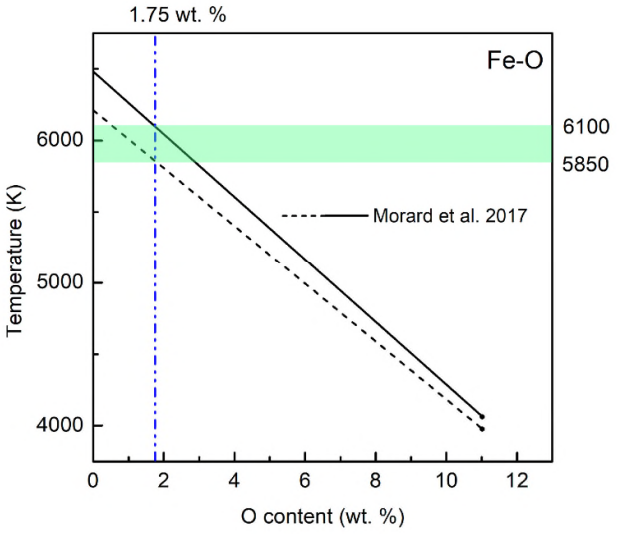


Fig. 2 The evolution of temperature and pressure with respect to simulation time in the two-phase coexisting systems for Fe-H, Fe-O and Fe-C alloys. a. temperatures and, b. pressures of AIMD simulations on Fe-H, Fe-O and Fe-C alloys are shown with light grey, pink and cyan curves, and the averaged data over a 0.5 ps period are shown with thick black, red, and blue curves.





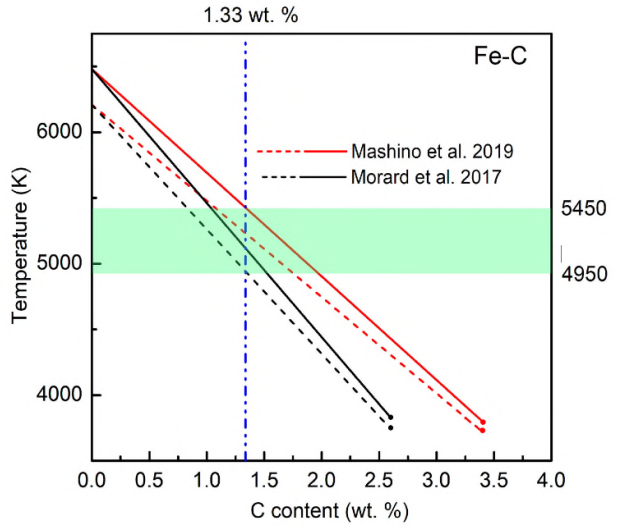


Fig. 3 Estimated melting temperatures of Fe-H, Fe-O, and Fe-C alloys with different light element content at 330 and 360 GPa. The melting temperatures are estimated from the extrapolated melting curves of Fe-H, Fe-O, and Fe-C systems measured by high pressure experiments[12,14,37]. The solid and dash lines represent the melting temperatures at 360 and 330 GPa. The dot-dash lines exhibit the light element content in our simulation modes, with corresponding melting temperatures shown by green regions.

****

Referee #2:

In the manuscript on possible superionic Fe alloys in the Earth's inner core, He and co-workers employ first-principles calculation to address a very peculiar state of matter - the supersonic solids - and to show its potential presence in the Earth's inner core. In superionic solids one atomic species, typically a small light atom, decouples from the vibration of the lattice and start to freely diffuse behaving in practice like a fluid flowing inside a fixed solid lattice. These solids show higher conductivity and lower elastic constants than their solid counterparts. I think that study of He and co-workers is interesting because they found for the first time, at my best knowledge, the potential presence of such a solid inside the Earth.

[Authors]: We are grateful for the recognition of our work. We agree with you that the superionic behavior on elastic property is very important in understanding the anomaly low Vs in the inner core.

I think there are some major aspects of this work that need to be clarified before this work can be considered.

The simulations, specially for O and C look too short. The kink in MSD at large times is an indication that something is not yet fully converged. I suggest the authors run longer simulations for these elements. Alternatively problems can arise from the reduced sampling due to small simulation cells. As the number of simulation points is rather limited I think the authors could the diffusion simulations with the large supercells.

[Authors]: We appreciate for the excellent suggestion. Following it, we conducted much

longer time (over 100 ps) and larger supercell (over 200 atoms) simulations at 5000-6000 K and 360 GPa. Superionicity of Fe-H, Fe-C, and Fe-O alloys is quite clear in the new simulations, and the MSDs are also fully converged. We also calculated the diffusion coefficients and ionic conductivities based on our new simulations. Our new results are consistent with our previous simulation ones, exhibiting enough convergence. The details for these simulations are shown in Supplementary Fig. 2, Fig. 7, and Fig. 11. The detailed method and comparison are shown in Supplementary S6.

The predicted core temperature are unreliable as the concentration in light elements changes with depth. Moreover at the OC/IC boundary the difference in partitioning of the light elements changes the concentration, and thus the melting T itself. Such a diagram can be drawn only if partitioning is taken into account.

[Authors]: It is a good suggestion. As criticized by the Referee, the prediction of the outer core temperature profile can give a misleading information while it is not critical part of this manuscript. Following the suggestion, we removed this part from the supplementary information.

The discussion on electrical conductivity should be completely revised. In a metallic system the electrical conductivity comes in 90% from the electrons. These are completely neglected in this study when reported conductivity. The fact itself that the alloys are superionic suggest the ionic conductivity is important. However this is now supersonic water or ammonia. Th electronic part will still remain important. How much? We don’ t know and I think this is a very important and interesting question that needs an answer and should address here. Or completely discarded.

[Authors]: Thanks for the very good suggestion. Actually, we mentioned the difference of ionic and electronic conductivity in our original manuscript: “*The diffusion of light elements*

greatly enhance the ionic conductivity of the IC to a magnitude of 10^2–10^3 S m^{-1} (Supplementary Fig. 5). Although the ionic conductivity is much lower than that of the electronic conductivity of Fe alloys with negligible affection on the total conductivity…"
Follow you suggestion, we calculated the electronic conductivities at inner core conditions by using the combination of density functional theory with dynamical mean field theory (DFT+DMFT) as implemented in the WIEN2k+eDMFT package (http://hauleweb.rutgers.edu/tutorials/). We used the volume obtained from AIMD calculation at ~6000 K in DFT+DMFT calculation to include the volume expansion effect on the electrical conductivity. The DFT+DMFT method has also be used to predict the electronic conductivity of pure iron [Xu et al. PRL 2018]. It is found that the electronic conductivities of Fe-X (X= C, H, O) alloys is lower than pure iron. But they are still over 2-3 order of magnitude higher than the ionic conductivity (Fig. 4). Thus, the contribution of ionic conductivity is negligible. We added calculated results of electronic conductivity in the Supplementary Information S4 and the following discussion in our main text:

"*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 the 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 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.*"

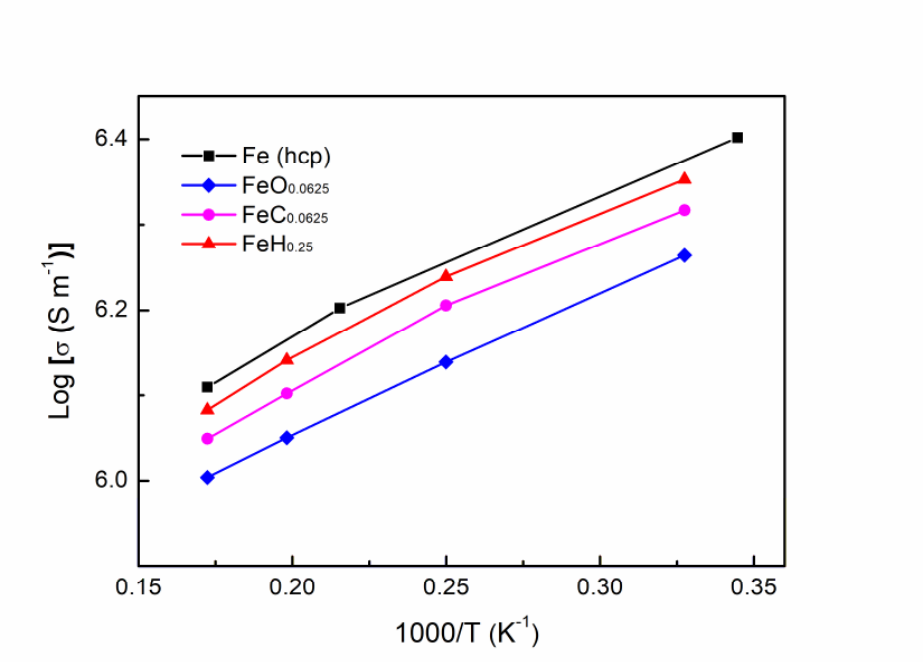


Fig. 4 Electronic conductivity of Fe and Fe alloys at 360 GPa with increasing temperature. The electronic conductivities of Fe, $FeH_{0.25}$, $FeO_{0.0625}$, and $FeC_{0.0625}$ calculated by DFT + DMFT method are shown by black, blue, red, and magenta symbols.

There are also a whole list of more minor modifications to be done:

line 5: "the IC has potential affection on its seismological structure "

[Authors]: Thanks, we revise it to "*The light-element convection in the IC also has potential influence on the IC seismological texture and geomagnetic field.*"

line 6: "magnetic fields with an in-depth influence"

[Authors]: Thanks, following you suggestion, we remove this sentence.

line 76: "The melting temperatures of these structures were strictly predicted using the Z method" The Z method is at least highly dependent on the size of the system, and it is not yet fully clear that it is reliable. While comparison to previous results seem to point into the

right direction, I think it should be used with a lot of care. I think w are a far shot away from this being “strict”.

[Authors]: Thanks for the good suggestion. We have changed the “strictly predicted” to “estimated”

line 87: References 34-36. Maillot et al. only “confirmed” the theoretical predictions. The theoretical works of Goldman et al. (Phys. Rev. Let.. 2005) and Hernandez and Caracas (Phys Rev Lett, 2016) on the supersonic ice should be cited here.

ref. 36: Cavvazzoni et al. predicted and analysed first the influence of the superionic phase on the interior of giant planets

[Authors]: Thanks for the good suggestion. We sited these references in lines 83-84 of the main text:

Superionic ice has been widely investigated and is suggested to exist in the interior of ice giants such as Neptune and Uranus[35-39].

line 96: “light elements such as H, O, and C can penetrate across the ICB” the light elements do not “penetrate” in the inner core but they can be incorporated in the hcp structure based on partitioning and free energy

[Authors]: Thanks for the comments. We revise this sentence as below:

“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.”

lines 144-145: “Based on our simulations, some light elements such as H, O, and C can diffuse into the IC in the superionic state.” Again it is not that because diffusion happens that these light elements actually go into the inner core. It is the chemical potential that determines the solubility and the partitioning. This needs to be revised.

[Authors]: Thanks for the comments. We revised this sentence into “Based on our

simulations, some light elements such as H, O, and C can present in the IC in the superionic state."

lines 146-148: "Motivated by the geomagnetic field" well .. not rally. as the field is generated in the outer core it should not influence and less induce the convection and diffusion in the inner core

[Authors]: It is a good question. Geomagnetic field is generated in the outer core due to the convection of outer core fluids. Based on some geodynamo simulations, geomagnetic field can present in the inner core with influence on the inner core rotation [Glatzmaier & Roberts 1996 Science] and lattice orientation of iron crystalline resulting in the inner core anisotropic structure [Karato 1999 Nature; Buffett & Bloxham 2000 GRL]. Thus, it is reasonable to consider the influence of the inner-core magnetic field on the diffusive ionic light element. We added related background and implication in the manuscript as below:

"*Suggested by some geodynamo models, geomagenetic field also has influence on the IC*[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 dacades*[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.*"

lines 159-160: "the convection of light elements leads to the evolution of the seismological structure with a significant influence on the change of seismic velocities with time." This statement deserves to be discussed and analysed at length. Fist of all the diffusion coefficients, even if high, are not enough to influence the pattern of seismic velocities over observable time. What is the diffusion length of the light elements

[Authors]: Thanks for the very good suggestion. In this study, we show that the light elements are highly diffusive in hcp-Fe, and the change of these light element concentration

can lead to significant change in seismic velocity. Thus, the seismic texture of the IC will change with the distribution of light element in the convection. Therefore, it is appropriate to say that seismic structure may change with time due to this effect. Your question is whether the diffusion length of this light-element is sufficient to change the structure over observable time, so the important issue here is diffusion length over the time of doublet earthquake (decades). The diffusion length (L) can be deduced by:

$$L = 2\sqrt{Dt}$$

where D is the diffusion coefficient, t is the time. Then we estimated the diffusion length of $FeH_{0.25}$ at 6000 K and 360 GPa. The diffusion coefficient is about 10^{-7} m^2/s, and the length of the diffusion for 10 years is about 40 m. However, this estimation ignore the influence of electromagnetic field in the inner core. It is reported that under the act of electromagnetic field ionic diffusion can be very anisotropic with one order of magnitude higher velocity in some directions [Ramirez 1997 PRB; Majewski 2010 JACS]. Thus the diffusion length can be much higher and anisotropic at the inner core condition, which can be sufficient to influence the seismic structure of IC within the period of doublet earthquakes [Belonoshko 2019 Nat. Comm.]. We think you are right that it can be a good subject to study the time-scale on the seismic texture evolution in the IC. However, consideration the complicated situation in IC due to the presence electromagnetic field, a specific and quantitative analyze may not be straightforward.

lines 165-166: "The diffusion of light elements greatly enhance the ionic conductivity of the IC" We do not care about it! It is so small, just as the authors themselves say on the net line, that it doesn't matter. The authors should rather focus on the other properties and remove this part completely. Or determine properly the conductivity of the superionic phase

[Authors]: Thanks for the valuable suggestion. As we replied previously, we used DFT+DMFT method to predict the electronic conductivity of these Fe alloys. The total conductivities are about 10^6 S/m at the inner core conditions.

lines 168-171: "This study shows that a magnetic 170 field can be generated by the light element convection in the IC," This part is easy not convincing. There is no clear

estimations of the intensity of these currents, the difference with respect to electronic conductivity, and even less so a clear discussion about the magnetic fields that can be generated from this diffusion.

[Authors]: Thanks for the suggestion. Here we want to express the idea that electric current of light element convection can generate magnetic field. As a result, rather than the outer core, magnetic field can also be generated in the inner core. It is no doubt that magnetic fields can be generated by currents. Regarding the intensity of current and magnetic field, we agree that it is worth to be investigated. But the main motivation of light element convection is not clear here. It may be driven by the concentration gradient, thermal convection, and/or magnetic field. Thus the intensity of the magnetic field generated by inner core convection should be investigated in conjunction with geodynamo model, which is beyond our capability. In this case, we mentioned that "*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 the Earth's magnetic field.*"

line 172: "These results may offer a clue on the geodynamo simulations" Again this is a general and unconvincing statement that sounds more like the authors are trying to find some sort of important effort stemming out of these numbers

[Authors]: Thanks for the suggestion. As the density of the current and magnetic field were not calculated here, the influence on geodynamo is uncertain. Thus, we removed this part, and state that "*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 the Earth's magnetic field.*"

lines 175-177: "some light elements may exist in the IC in superionic state with influence on the seismic wave velocities and the mangeneitc field, indicating a potential connection between these two critical geophysical parameters in the IC." Same observation as above, vague and unconvincing.

[Authors]: Thanks for the comment. We need to clarify our idea on the connection between inner-core seismic and the geomagnetic field. First, in this study, we show some light elements in IC can be highly diffusive and these light elements has influence on the seismic velocity. Second, as we mentioned above, the movement and distribution of these ionic light elements can be affected by the inner-core geomagnetic field. Therefore, we raise the question if there is certain connection between geomagnetic field and seismic structure of the IC. Indeed, more studies such as seismic anisotropic of Fe alloys and geophysical observations are needed to better understand this possible connection. However, we think it is still important to raise this question here, which may inspire some new ideas or observations of other researchers to settle this question. This question is certainly very important for our understanding on the texture and history of the IC. We improved our statement on this issue as below.

"*Suggested by some geodynamo models, geomagenetic field also has influence on the IC*[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 dacades*[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.*"

Reviewer Reports on the First Revision:

Referee #1:

The authors have tried to address my point about the thermodynamic stability of the interstitial site, and provided enthalpy calculations that actually show that for C this site is not stable compared to the substitutional site. Of course enthalpy is not enough to judge stability at T>0, especially at core temperatures, and they refer to previous work (Li et al.) who evaluated the stability of the interstitial site using quasi harmonic calculations, and found that also at high T the substitutional site is the most stable. However, the authors argue that the free energy difference between the interstitial and the substitutional site is not huge, and so it is possible that some C could be found in interstitial sites. It should be pointed out that anharmonicity could play an important role here (not investigated by Li et al.), and could tilt the balance towards the substitutional site even further, because of the weaker interaction between C and its surroundings in this site.

However, although I am prepared to accept the argument of the thermodynamic competition of the interstitial site, I note that this is not discussed in the paper. The main article works on the 'given' than the site is interstitial, which in my view is misleading. I appreciate that this is discussed somewhat in the supplementary information, but this is a very important disclaimer that in my view should be highlighted with flashing lights in the main body of the paper.

The paper should say something along the lines 'although we appreciate that the interstitial site is thermodynamically less stable than the substitutional site (for which no super-ionicity behaviour is observed), we suggest (based on previous approximate free energy calculations) that at core temperatures it will compete with the substitutional site, and so some of C in the core could be found in this site. The super-ion behaviour discussed in this paper only applies to C in this interstitial site.'

I note that the authors have accepted that the Z method cannot be used for mixtures, although they still point out that 'it has been used for different systems', which makes me think that they did not appreciate the points I made in my previous review. They have now addressed the melting behaviour of the system using the coexistence approach, which is fine in principles, but it requires large systems and very long simulations. The authors have hardly shown convergence of the results w.r.t. size and length of the simulations, however, these mixture melting temperatures have been addressed in the past, and I think the values quoted by the authors are in line with those previous results.

****
Referee #2:

In the revised manuscript on supersonic hcp-Fe alloys in the Earth's inner core, He and co-authors try to address all the comments and suggestions of both reviewers.

In particular I appreciate that they use a different method - the two-phase method - to estimate the melting temperature. This still has important limitations, notably related to the fact that the melting is incongruent. However, it seems that the impurity atoms have the time to migrate between the two, liquid and solid, phases. Moreover the use of this method to estimate the coexistence temperature helps situating the Fe-X systems inside their liquidus - solidus loops. Consequently the relevant conditions for rest of the simulations must be below this coexistence regions, if one wants to sample only the solid phases.

Concerning the conductivity, the supersonic contribution is considerably smaller than the electronic one, and it is very nice that the authors could perform further simulations to confirm it, and actually put a number on it.

I think the rest of the comments have been generally well addressed, more geophysical implications added (like the influence of the magnetic field), and the references reflect better now the previous literature.

As such I do not see any major impediment that could prevent the paper to be published.

Author Rebuttals to First Revision:

Referee #1:

The authors have tried to address my point about the thermodynamic stability of the interstitial site, and provided enthalpy calculations that actually show that for C this site is not stable compared to the substitutional site. Of course enthalpy is not enough to judge stability at T>0, especially at core temperatures, and they refer to previous work (Li et al.) who evaluated the stability of the interstitial site using quasi harmonic calculations, and found that also at high T the substitutional site is the most stable. However, the authors argue that the free energy difference between the interstitial and the substitutional site is not huge, and so it

is possible that some C could be found in interstitial sites. It should be pointed out that anharmonicity could play an important role here (not investigated by Li et al.), and could tilt the balance towards the substitutional site even further, because of the weaker interaction between C and its surroundings in this site.

[Authors]: Thank you very much for the specific discussion on the free energy of C defect in hcp-Fe. A recent study shows that the interstitial C is more stable at pressure lower than 350 GPa, and they propose that the high temperature correction with QHA method does not significantly change the relative stability of C defects (Pamato et al., 2020 JGR). We also conducted QHA calculations to check their results and find that the interstitial C is more stable at 340 GPa and temperatures up to 6000 K (Supplementary Fig. 2). In this case, both interstitial and substiutional C can exist in hcp-Fe at inner core conditions (~330 < P < ~350 GPa: interstitial C is more stable; ~350 < P < ~360 GPa: substitutional C is more stable). We agree with you that the anharmonic effect should be considered to evaluate the relative stability of C defects more strictly. Especially, the diffusion of these interstitial defects contributes extra entropy to the system (Millot et al., 2019 Nature; Klarbring and Simak, 2018 PRL), resulting in lower Gibbs free energy and further stabilize the supersonic structure at high temperature. However, a specific and quantitative analyze may not be straightforward.

However, although I am prepared to accept the argument of the thermodynamic competition of the interstitial site, I note that this is not discussed in the paper. The main article works on the 'given' than the site is interstitial, which in my view is misleading. I appreciate that this is discussed somewhat in the supplementary information, but this is a very important disclaimer that in my view should be highlighted with flashing lights in the main body of the paper. The paper should say something along the lines 'although we appreciate that the interstitial site is thermodynamically less stable than the substitutional site (for which no super-ionicity behaviour is observed), we suggest (based on previous approximate free energy calculations) that at core temperatures it will compete with the substitutional site, and so some of C in the core could be found in this site. The super-ion behaviour discussed in this paper only applies to C in this interstitial site.'

[Authors]: We appreciate for the specific suggestion. Due to our new QHA calculations and the result of the recent study (Pamato et al., 2020 JGR), our understanding on the stability of interstitial C has been improved. According to your suggestion, we added following discussion in the main text to clarify the stability of interstitial defects. “In hcp-Fe, H and O prefers to take interstitial site under the inner core conditions (Supplementary Information S1). For C, recent studies show that interstitial C is more stable than substitutional C below ~350 GPa, and substitutional structure is stabilized above ~350 GPa suggesting the coexistence of interstitial and substitutional C in hcp-Fe under inner core conditions (Li et al., 2018 & Pamato et al., 2020).”

Furthermore, we added more detailed discussions in the supplementary information “We also conducted AIMD simulations on substitution H model ($Fe_{60}H_4$) at 360 GPa and 5000 K, and find the obvious diffusion of Fe atoms suggesting this structure is not stable (Supplementary Fig. 2a). As the incorporation of interstitial H leads to very small increase in chemical potential compared with other defects and Earth’s core is suggested as a large hydrogen reservoir (Li et al., Nat. Geosci. 2020), hydrogen may be the dominant interstitial defect in the IC.

On the other hand, substitutional structures are more stable for Fe-S and Fe-Si alloys. For C and O, the dimer structure is the most stable one indicating the coexisting of both substitutional and interstitial defects. Li et al. (JGR, 2019) investigated the stability of Fe-C alloys at high temperature by quasiharmonic approximation (QHA) method, and they found the stability of the dimer structure is weakened and its relative free energy is slightly higher than that of the substitutional structure at 6500 K. A recent study from the same group suggests that the interstitial C becomes thermodynamically more stable than substitutional C at pressures below ~350 GPa (Pamato et al., 2020). The stability of interstitial C in hcp-Fe at 340 GPa is further confirmed by QHA calculations, and O is also more stable at interstitial site at 360 GPa and temperatures up to 6000 K (Supplementary Fig. 2). Generally, H and O is thermodynamically stable at interstitial site in hcp-Fe under the IC conditions. The substitutional C is more stable than interstitial C at pressure above ~350 GPa indicating the coexistence of interstitial and substitutional C in hcp-Fe under inner core conditions. It is worth noting that extra entropy contributed by the highly diffusive light elements at interstitial sites, which is not considered in QHA calculations, may further stabilize the superionic structure at high temperature (Millot et al., 2019 Nature; Klarbring and Simak,

2018 PRL).” Once again we appreciate for your suggestion. These revised data clarify the stability of interstitial defects in hcp-Fe, which is important for the superionic state and its implication for the inner core.

I note that the authors have accepted that the Z method cannot be used for mixtures, although they still point out that 'it has been used for different systems', which makes me think that they did not appreciate the points I made in my previous review. They have now addressed the melting behaviour of the system using the coexistence approach, which is fine in principles, but it requires large systems and very long simulations. The authors have hardly shown convergence of the results w.r.t. size and length of the simulations, however, these mixture melting temperatures have been addressed in the past, and I think the values quoted by the authors are in line with those previous results.

[Authors]: We do appreciate your suggestion that the Z method is not suitable for the mixture. In the revision, we removed the discussion and references related with Z method in the main text and supplementary information.

Referee #2:

In the revised manuscript on supersonic hcp-Fe alloys in the Earth’s inner core, He and co-authors try to address all the comments and suggestions of both reviewers.

In particular I appreciate that they use a different method - the two-phase method - to estimate the melting temperature. This still has important limitations, notably related to the fact that the melting is incongruent. However, it seems that the impurity atoms have the time to migrate between the two, liquid and solid, phases. Moreover the use of this method to estimate the coexistence temperature helps situating the Fe-X systems inside their liquidus - solidus loops. Consequently the relevant conditions for rest of the simulations must be below this coexistence regions, if one wants to sample only the solid phases.

Concerning the conductivity, the supersonic contribution is considerably smaller than the electronic one, and it is very nice that the authors could perform further simulations to confirm it, and actually put a number on it.

I think the rest of the comments have been generally well addressed, more geophysical implications added (like the influence of the magnetic field), and the references reflect better now the previous literature.

As such I do not see any major impediment that could prevent the paper to be published.

[Authors]: We are grateful for the recognition and your valuable suggestion for publication.

Reviewer Reports on the Second Revision:

Referee #1:

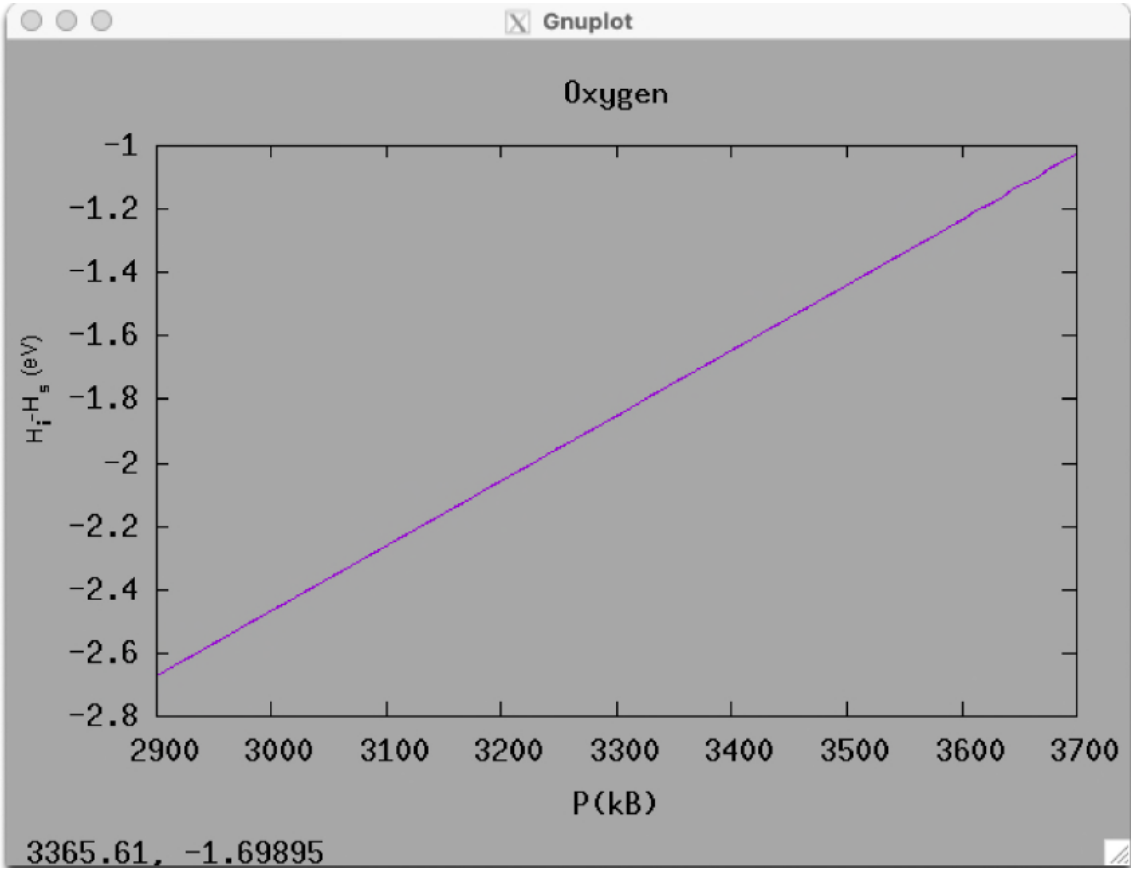
The authors have provided new evidence on the stability of the interstitial site compared to the substitutional site. I have myself repeated some of the calculations, and indeed I do find that the interstitial site is more stable, albeit with a strong pressure dependence. I am attaching two figures showing the enthalpy difference between the two sites, as function of pressure.
For oxygen at 360 GPa the relative stability of the interstitial site is about 1.2 eV, which is about half of what reported by the authors, but still large enough to justify the stability of this site. For carbon the stability at 340 GPa is about 0.6 eV, which is very close to the number reported by the

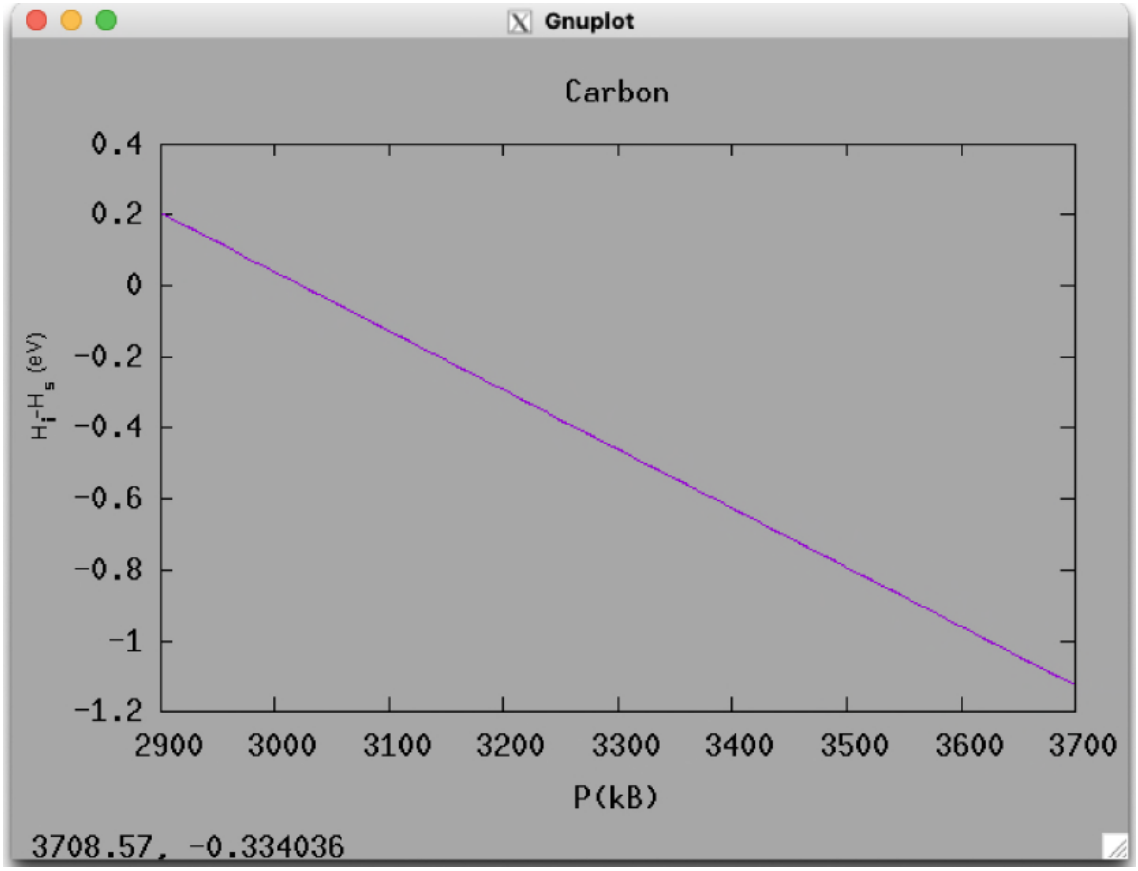
authors. I have not looked at the stability as a function of temperature, as this would go well beyond the scope of this review (it would imply an order of magnitude more expensive calculations), but I have no reason to doubt the temperature dependence found by the authors.

I have also repeated molecular dynamics simulations, and indeed found that in the interstitial site both oxygen and carbon are mobile, which supports the diffusion mechanism found by the authors.

I don’t usually repeat calculations when refereeing a paper, at least not on a regular basis, but I was very intrigued by these results and this is why I did it this time. I am now persuaded that the author's argument is valid, and indeed and in interesting and important result, so I would like to recommend publication of these results.

Dario Alfe





Author Rebuttals to Second Revision:

Referee #1:

The authors have provided new evidence on the stability of the interstitial site compared to the substitutional site. I have myself repeated some of the calculations, and indeed I do find that the interstitial site is more stable, albeit with a strong pressure dependence. I am attaching two figures showing the enthalpy difference between the two sites, as function of pressure.

For oxygen at 360 GPa the relative stability of the interstitial site is about 1.2 eV, which is about half of what reported by the authors, but still large enough to justify the stability of this site. For carbon the stability at 340 GPa is about 0.6 eV, which is very close to the number reported by the authors. I have not looked at the stability as a function of temperature, as this would go well beyond the scope of this review (it would imply an order of magnitude more

expensive calculations), but I have no reason to doubt the temperature dependence found by the authors.

I have also repeated molecular dynamics simulations, and indeed found that in the interstitial site both oxygen and carbon are mobile, which supports the diffusion mechanism found by the authors.

I don’t usually repeat calculations when refereeing a paper, at least not on a regular basis, but I was very intrigued by these results and this is why I did it this time. I am now persuaded that the author's argument is valid, and indeed and in interesting and important result, so I would like to recommend publication of these results.

[Authors]: We are grateful for your valuable and positive comment.