A deep Aurum reservoir: Stable compounds of two bulk-immiscible metals under pressure

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The Earth’s crust is known to be depleted of gold, among other slightly heavy noble metals transported by magma from the Earth’s mantle to the crust. The bulk silicate Earth (BSE) model also suggests significant depletion of Au in the silicate mantle itself, which cannot be explained by the amount of Au in the mantle’s magma. This implies that Au could remain in the lower mantle and form stable compounds, especially with iron, which is the predominant element within the core. While Fe does not form binary compounds or a bulk alloy with Au under ambient conditions, it may do so at the elevated pressures found in the Earth’s interior. Here, using density-functional methods, we investigated the possibility of identifying stable, binary Fe-Au compounds at pressures up to 210 GPa. We found three such Fe-Au compounds, which are stabilized by pressure and notable electron transfer, including an orthorhombic AuFe$_3$ phase that is ferromagnetic in nature with Au possessing a significant magnetic moment. While our results suggest that thermal conduction due to the conductivities and the heat flux from the Fe-Au compounds could be an energy source to power the Earth’s geodynamo, they also point towards changes in Au’s chemical properties, as it can exist as either an anion or cation under pressure. In addition, the sound velocity and the density predicted for the various Fe-Au compounds suggest that they could shed light on the composition of the core-mantle boundary and the Earth’s boundary, while demonstrating how the presence of trace amounts of Au could influence agreement with seismic data.

Significance Statement

We have demonstrated that gold (Au), a noble and precious metal, can react with hexagonal close packed iron (Fe) to form stable intermetallic compounds under sufficient compression. We also demonstrated that Au, which is diamagnetic at ambient pressure, could attain a magnetic moment in compound form when compressed to the pressures found in the Earth’s interior. The Fe-Au compounds show significant lattice thermal conductivity and their sound velocities have better agreement with seismic data relative to some other available binary models of the Earth’s core. Our results suggest that the Earth’s core could hold more Au than previously thought.

Of these elements, Au is of particular interest because of its economic value, inertness, and the remarkable stability of its crystal structure over a wide range of pressures traversing that of the Earth’s core. In addition to depletion of Au from the Earth’s crust, the bulk silicate Earth (BSE) model also suggests significant depletion of Au from the silicate mantle, which cannot be explained by the amount of Au in the mantle’s magma. Since Au is heavy and less volatile than Cr, V, and Mn, it could not have evaporated into space. However, it is challenging to propose a likely form for Au in the neighborhood of the core-mantle boundary (CMB) without violating various constraints imposed in seismological models.

Meanwhile, seismological studies indicate a 2-5% density deficit for the Earth’s solid inner core, proposing that the core is not a ‘bank’ of pure Fe after all. The core must, therefore, be home to some lighter siderophile elements, such as H, C, Si, S, and K. Additionally, experiments at elevated temperatures and pressures, combined with theoretical studies, suggest the reactivity of the noble gases Xe and Ar with Ni and Fe. The stability of the resulting compounds was attributed to pressure-induced energy raising of the valence p-shell states of the noble gas, allowing charge transfer to the partially filled 3d or 4s states of the transition metal. However, none of these studies could exhaustively explain the mass and density deficit in the Earth’s core from the preliminary reference Earth model (PREM). This means that slightly heavy (siderophile) metals depleted in the Earth’s crust could have found their way into the core, where they form stable compounds. Thus, knowing the form(s) in which Au could exist when subject to the thermodynamic

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conditions present within the core may help provide a solution to the problem of depleted Au.

It is well known that the Earth’s core is predominantly composed of Fe (4, 15, 19). Thus, a natural line of thought would be that Au, which was drawn towards and into the core, may have formed a bimetallic compound with Fe. However, under ambient conditions, the magnetic metals (Fe, Co, and Ni) do not form compounds or bulk alloys with many heavier metals, including Au. This is primarily because of the size mismatch between the constituent atoms, coupled with little or no solid solubility (25, 26). If a stable, binary Fe-Au compound is demonstrated to form under high pressures, transversing that of the Earth’s interior, we can then begin to search for Au in this form within the mantle and core.

To this end, we explore the Fe-Au potential energy surface from ambient to high pressure using density-functional theory (DFT). Interesting physics plays out under pressure and, as such, ushers in new chemistry (27). This is exemplified by the predicted formation of stable intermetallic compounds of Fe and Au under high pressure, reported here for the first time. Analysis of the electron density (28) reveals an unusual charge transfer between Au and Fe. Using a combination of DFT and the Boltzmann transport equation, we also predict the phonon-assisted thermal conductivity of the Fe-Au compounds at thermodynamic conditions relevant to the lower mantle (near the CMB) and the outer core. This work contributes to our understanding of the Earth’s lower mantle and the outer core, revealing how it is able to keep such a noble metal as Au mixed with Fe without decomposition into its elemental form.

RESULTS

Phase stability and stable crystal structures of Fe-Au. We systematically searched for stable structures of the binary compounds Fe$_x$Au$_y$ ($x, y \in \{1 \ldots 4\}$) with cells containing 1-4 structural formula units at 0 K temperature and pressures ranging from 0-200 GPa. Spin-polarized calculations were carried out on the lowest-energy structures for all stoichiometries explored and the nonmagnetic configurations were found to be the most energetically favorable, with an exception observed for the AuFe$_4$ stoichiometry at 140 GPa.

The convex hull calculated at various search pressures shows that Au and Fe do not form any stable binary compounds at ambient conditions up to 140 GPa (Fig. 1). At this pressure, an orthorhombic AuFe$_4$ phase (space group Cmcn) becomes thermodynamically stable relative to elemental fcc-Au and hcp-Fe (see Fig. 1a) and, as such, should be synthetizable.

Furthermore, at 200 GPa, AuFe$_4$ crystallizes into a tetragonal cell with space group I4/m. An orthorhombic AuFe$_3$ phase (space group Pmmn) that is metastable with respect to the tetragonal I4/m-AuFe$_4$ was also uncovered (see Fig. 1b). Inclusion of the free-energy contribution from lattice vibrations at 0 K (zero-point energy, ZPE) did not change the formation pressure, destabilize stable phases, nor stabilize other phases that were not initially energetically favorable. However, the magnitude of the formation enthalpy (enthalpy being $U+pV$) for the stable phases were slightly changed (Fig. S1).

The calculated equations of states (EOS) for the predicted structures reveal that the Cmcn-AuFe$_4$ has a stability pressure range of 120-160 GPa (Fig. 1c) and, as such, will decompose below 120 GPa and above 160 GPa. This explains why our structure searches at 100 GPa and 200 GPa could not find this structure. On the other hand, the I4/m-AuFe$_4$ and Pmmn-AuFe$_3$ phases are thermodynamically stable from 184 and 189 GPa, respectively, up to at least 210 GPa (Fig. 1d).

Structural geometry of Fe-Au phases. The structural parameters of the thermodynamically stable phases of the Fe$_x$Au$_y$ compounds are presented in Table 1 and the unit-cell ge-

### Table 1. Structural parameters (and Bader atomic charges) of various predicted Fe-Au phases at 0 K

| System   | P (GPa) | SG    | Lattice parameter          | Element | Wyc. site | Atomic coordinate (fractional) | Bader charge/atom |
|----------|---------|-------|---------------------------|---------|-----------|---------------------------------|-------------------|
| AuFe$_4$ | 140     | Cmcn  | $a = 12.12 \text{ Å, } b = 4.00 \text{ Å, } c = 3.69 \text{ Å}$ | Au      | 4c        | 0.000, 0.796, 0.750              | 0.34              |
|          |         |       |                           | Fe      | 8g        | 0.883, 0.325, 0.750              | 0.33 / 0.37       |
|          |         |       |                           | Fe      | 8g        | 0.705, 0.333, 0.750              | -0.51 / -0.53     |
| AuFe$_4$ | 200     | I4/m  | $a = 10.00 \text{ Å, } c = 10.01 \text{ Å}$ | Au      | 2b        | 0.000, 0.000, 0.500              | 0.40              |
|          |         |       |                           | Fe      | 8h        | 0.091, 0.690, 0.000              | -1.10             |
| AuFe$_3$ | 200     | Pmmn  | $a = 2.35 \text{ Å, } b = 2.95 \text{ Å, } c = 9.86 \text{ Å}$ | Au      | 2b        | 0.000, 0.500, 0.585              | -0.26             |
|          |         |       |                           | Fe      | 2b        | 0.000, 0.500, 0.833              | 0.04              |
|          |         |       |                           | Fe      | 2b        | 0.500, 0.000, 0.947              | 0.03 / 0.04       |
|          |         |       |                           | Fe      | 2b        | 0.500, 0.000, 0.729              | 0.18 / 0.19       |

**Fig. 1.** (color online) Calculated cold enthalpy ($U+pV$) of formation (0 K) of various Fe-Au compounds with respect to constituent elemental decomposition (a) at 140 GPa (b) at 200 GPa. Calculated enthalpies per atom for (c) Cmcn-AuFe$_4$ structure with respect to the mixture of elemental Fe and Au (d) Pmmn-AuFe$_3$ and I4/m-AuFe$_4$ structures with respect to the mixture of elemental Fe and Au.
The Au-Au bonds are 2.45 Å, and the Fe-Fe bond lengths range from 2.14-2.35 Å. While the Au-Au bond lengths are 2.35 Å and the Fe-Fe bond lengths are 2.29 Å, which is shorter than that observed in the other Fe-Au phases at 200 GPa, with each Au atom gaining 0.26e- and the Fe atoms at the edges of the Fe layers losing 0.19e-. The Fe atoms in the interior of the layers have greatly reduced partial charges of 0.03 and 0.04e-. A similar negative oxidation state in Au was reported for caesium auride (CsAu) (35, 36).

Conversely, for I4/m-AuFe4 at 200 GPa, each Au atom lies at the center of the unit cell and is coordinated to 12 Fe atoms, in a geometry similar to what is observed in the ionic lattices of some actinide complexes such as [Th(NO3)6]2- (37). Here, each Au atom is cationic, losing 0.40e-, while each Fe atom gains 0.10e-, making them anionic. Fe is known to become highly electronegative at such high pressures and a similar charge-transfer mechanism has been reported for Fe and Ni in the Xe-Fe/Ni system (23).

Finally, for Cmcm-AuFe4 at 140 GPa, the Au atoms each lose 0.34e-, again making them cationic. However, the two distinct Fe environments in the crystal have very different atomic charges, similar to what was reported in α-Mn (38). The Fe atoms at the first 8g sites directly bonded to the Au are also cationic and lose between 0.33e- and 0.37e-. Since they have comparable charges to the Au atoms, we will refer to these Fe atoms as pseudo-Au atoms. The Fe atoms at the second 8g sites (in the interior of the Fe layer) gain between 0.51e- and 0.53e- each to become anions. Therefore, the Cmcm-AuFe4 phase is stabilized through electron transfer from Au and pseudo-Au atoms to Fe atoms to give regions of alternating charge.

**Electronic structure of Fe-Au phases.** The calculated band structures (Fig. S5) show that all the three Fe-Au systems reported in this work are metallic. The electronic structures of states (DOS) projected to orbitals (Fig. 3) reveal that the states in the vicinity of the Fermi energy level are primarily Fe 3d states, with some contribution from Au 5d states. This implies that the Fe 3d and Au 5d states are responsible for the metallicity of the phases reported here.

The results of Bader charge analysis are shown in Tables 1 and S2, as well as Fig. S3. The observed atomic charges vary significantly between the three phases and, even within a given material, are highly dependent on the coordination environments. As expected from its greater electronegativity, Au acts as anion in the metastable Pmmn-AuFe3 phase at 200 GPa, with each Au atom gaining 0.26e- and the Fe atoms at the edges of the Fe layers losing 0.19e-. The Fe atoms in the interior of the layers have greatly reduced partial charges of 0.03 and 0.04e-. A similar negative oxidation state in Au was reported for caesium auride (CsAu) (35, 36).

**Dynamic, mechanical, and thermal properties of Fe-Au phases.** We established the dynamic stability of the various predicted phases of Fe-Au through the calculation of phonon dispersion relations (Fig. 4 a-c). All three show no imaginary frequencies throughout the BZ, indicating dynamic stability within the harmonic approximation. We further investigated the response of the three predicted phases to external strain...
which, in principle, is a measure of their elastic and mechanical stability (Table S1). The results indicate that all the predicted phases are elastically and mechanically stable and their Pugh’s ratio (42) also indicates that they are ductile.

At 200 GPa, two structures are predicted to be synthetically (Fig. 1b) with the I4/m-AuFe4 phase being the thermodynamic ground state and the Pmmn-AuFe3 phase being metastable. With an enthalpy difference of only \( \sim 40 \) meV/atom between I4/m-AuFe4 and the combination of the Pmmn-AuFe3 phase and hcp-Fe, differences in their vibrational free energies at high temperature could compensate for the enthalpy difference and reverse the stability ranking. Therefore, we calculated the Helmholtz free-energy evolution with temperature (\( T \)) at fixed volume (\( V \)) for both phases at 200 GPa within the harmonic approximation (Fig. 4d). The vibrational free-energy contribution is (43)

\[
F_{\text{vib}}(T) = \sum_{\omega} g(\omega)\hbar\omega - k_B T \sum_{\omega} g(\omega) \ln \left[ 1 - \exp \left( -\frac{\hbar\omega}{k_B T} \right) \right],
\]

where \( g(\omega) \) is the normalized density of states (phDOS) for the phonon branch \( \omega \) and \( k_B \) is Boltzmann’s constant.

The calculated temperature evolution of the relative free energies (Fig. 4d) reveals that I4/m-AuFe4 is preferred at ambient temperature up to \( \sim 1750 \) K. Between 1750 K and 2000 K, the two phases are effectively degenerate, while Pmmn-AuFe3 + hcp-Fe becomes preferable at high temperatures above 2000 K. This preference can be motivated by the presence of more low-frequency phonons (<4 THz) for Pmmn-AuFe3 (Fig. 4b) compared to I4/m-AuFe4 (Fig. 4c), which will have a greater contribution to the vibrational entropy. The latent heat absorbed in the I4/m-AuFe4 \( \rightarrow \) Pmmn-AuFe3 + hcp-Fe transition at 2000 K is estimated from the vibrational entropy to be \( 0.025 \) eV/atom (Fig. S9). The experimental implication of this observation is that the metastable Pmmn-AuFe3 phase could potentially be prepared by laser-heating a compressed mixture of Au and Fe (with a molar ratio consistent with the stoichiometry) above 2000 K.

### Thermal conductivity of Fe-Au

The thermal conductivity of solids is governed by the phonon vibrations, coupled with the scattering processes they encounter. During structural phase transitions driven by soft phonons, the phonon-assisted thermal conductivity is expected to be strongly modified, since the soft mode will experience a frequency and group velocity shift, which will in turn modify the allowed phonon scattering processes in the system. The modification of phonon modes also has significant implications for heat transport.

We computed the thermal conductivity of the three predicted Fe-Au intermetallic compounds by solving the Boltzmann transport equation (BTE) for a range of temperatures. The results are shown in Fig. 5a and highlight the significant effect of phase change on the thermal conductivity of these compounds. While the relaxation time approximation (RTA) usually underestimates the thermal conductivity (since it treats both Normal and Umklapp scattering as resistive processes (44)), we found that the RTA produces results within 0.5% of the iterative solution for all three phases at room temperature.

In the analysis of measured data, some (45) have concluded that the acoustic modes dominate thermal transport and that the optical modes contribute negligibly due to low group velocities. However, we have found that this assumption cannot explain the comparatively large thermal conductivity \( \left( k_{\text{ph}} \right) \) values for the Fe-Au systems studied in this work. From Fig. 4a-c, there is no gap between the acoustic and optical modes in the phonon dispersion in either Cmcm-AuFe4 or Pmmn-AuFe3 at 200 GPa, while a small gap exists for I4/m-AuFe4. Such gaps are often attributed to atomic mass differences and can suppress the interaction of acoustic phonons with optical phonons above the gap (46). To investigate further, we examined the contributions of each phonon mode from our BTE solution as shown in Fig. 5c and Fig. S4. At 300 K (Fig. S4), optical phonon modes contribute 51% of the total \( k_{\text{ph}} \) of Pmmn-AuFe3, while the contribution is 20% and 43% for Cmcm-AuFe4 and I4/m-AuFe4, respectively. At 2500 K (Fig. 5c), their contribution increases for all three phases, to 56%, 32%, and 54% for Pmmn-AuFe3, Cmcm-AuFe4, and I4/m-AuFe4, respectively. This observation is consistent with the trend predicted from the group velocity \( \left( v_g \right) \) for acoustic

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Fig. 3. (color online) Calculated electronic density of states projected to orbitals for (a) Cmcm-AuFe4 at 140 GPa, (b) Pmmn-AuFe3 at 200 GPa, and (c) I4/m-AuFe4 at 200 GPa. The black dashed line represents the Fermi energy level.

Fig. 4. (color online) Phonon dispersion relations for (a) Cmcm-AuFe4 at 140 GPa, (b) Pmmn-AuFe3 at 200 GPa, and (c) I4/m-AuFe4 at 200 GPa. Also shown is (d) the relative free energies of I4/m-AuFe4 and Pmmn-AuFe3 + hcp-Fe at 200 GPa as a function of temperature. The I4/m-AuFe4 structure at 0 K was used as the zero of energy.
Table 2. Calculated sound speed ($v_s$) and density at 200 GPa and 0 K for Pmmn-AuFe$_3$ and I4/m-AuFe$_4$ compared with simulation data (48) of inner Earth’s core model at 360 GPa and the PREM (15) data at 200 GPa.

| System            | Pmmn-AuFe$_3$ | I4/m-AuFe$_4$ | hcp-Fe | Fe$_{62}$C$_2$ | Fe$_{60}$C$_4$ | PREM  |
|-------------------|---------------|---------------|--------|---------------|---------------|-------|
| $v_s$ (km/s)      | 4.28          | 4.82          | 6.80   | 6.38          | 6.0           | 3.6   |
| Density (g/cm$^3$)| 17.72         | 16.88         | 14.25  | 14.10         | 13.82         | 13    |

Fig. 5. (color online) (a) Calculated lattice thermal conductivity ($k_{plh}$) of the three Au-Fe phases as a function of temperature, ranging from 300 to 3100 K. (b) Decomposition of the $k_{pl}$ of Au-Fe phases at 2500 K into contributions from the acoustic ($k_{aph}$) and optical ($k_{oph}$) modes. (c) Cumulative lattice thermal conductivity of Cmcm-AuFe$_3$ (140 GPa), Pmmn-AuFe$_3$ (200 GPa), and I4/m-AuFe$_4$ (200 GPa) as a function of the phonon mean-free-path at 2500 K.

To determine the length scales for thermal transport, the cumulative $k_{plh}$ with respect to the phonon mean free path is shown in Fig. 5b for the three phases of Au-Fe at 2500 K. This is informative for determining the length scales at which the phonons of each phase become relevant for heat conduction. Clearly, the I4/m-AuFe$_4$ phase is more sensitive to nano-structure compared to Pmmn-AuFe$_3$ and Cmcm-AuFe$_4$. This can be seen from the fact that the I4/m-AuFe$_4$ requires the least mean free path (< 100nm) to achieve its maximum, but the lowest lattice thermal conductivity and, as such, will transport heat more slowly.

**DISCUSSION**

Insight from elastic behavior of Fe-Au systems under pressure. The speed of elastic waves propagating through a material is a measurable property of condensed matter that is easily matched with seismic or experimental data when modeling the Earth’s interior. Using Navier’s relation (49, 50), we mapped the elastic properties space of the Fe-Au phases predicted in this study into longitudinal ($v_l$), transverse ($v_t$), and average ($v_m$) elastic wave speeds. These speeds are:

\[
v_l = \sqrt{\frac{G}{\rho}}, \quad [2]
\]

\[
v_t = \sqrt{\frac{3B + 4G}{3\rho}} \quad [3]
\]

and

\[
v_m = \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{\frac{1}{3}} \quad [4]
\]

where $B$ and $G$ are the bulk and shear modulus, respectively, and $\rho$ is the density of the material. The average wave speed is reported as the speed of sound ($v_s$) in Table 2. The $v_s$ therefore captures the elastic anisotropy and, by extension, sound wave anisotropy in the system, should it exist.

Compounds in the Earth’s interior each have different densities and sound speeds; thus, these values can be used in conjunction with seismic data to provide insight on its composition (15, 51–53). Seismological studies (18) suggest that the Earth’s core must include some light siderophile elements to explain its lower density than that of pure Fe (19–22). In addition to having a higher density, hcp-Fe has a much higher velocity of sound than predicted from models of the core, as shown in Table 2. While introducing light elements, as in Fe$_{62}$C$_2$ and Fe$_{60}$C$_4$ (48), improves agreement with the PREM density, it does so at the expense of worsening agreement in the sound speed.

The extracted density and sound speeds for the Pmmn-AuFe$_3$ and I4/m-AuFe$_4$ phases are also reported in Table 2. The Cmcm-AuFe$_3$ phase was not included because the pressure at which we are making this comparison is outside the stability range of this phase (Fig. 1c). Compared with hcp-Fe or other Fe-rich model structures (Fe$_{62}$C$_2$ or Fe$_{60}$C$_4$) (48), Pmmn-AuFe$_3$ and I4/m-AuFe$_4$ have average sound speeds that are very much closer to that from the PREM model (15). Particularly, the metastable Pmmn-AuFe$_3$ phase has $v_s$ that is closest to the PREM’s, further supporting the stabilization of the Pmmn-AuFe$_3$ over the I4/m-AuFe$_4$ at the Earth’s core’s (> 2000 K) temperature. However, the densities of Pmmn-AuFe$_3$ and I4/m-AuFe$_4$ are significantly higher than both hcp-Fe and the PREM model data. The results suggest that combining Fe and Au with Ni or other light elements to form ternary systems could yield calculated densities and sound speeds closer to the PREM data (54). Overall, the addition of Au to the base Fe leads to a decrease in seismic velocities towards the geophysical observations at the CMB and the outer core. We opine that, if Au is present, the Fe content that will be required to match precisely the Earth’s core profile would be less than what is required in the light-element-Fe alloys (48).
Implications for thermal conductivity at the CMB. The thermal conductivities of the Earth’s lower mantle and core greatly impact convection dynamics. They also determine the ease of heat transport from the core to the mantle, thereby maintaining the heat energy budget for the Earth’s geodynamo. As a result, there is a large body of work investigating thermal properties of iron and its alloys within a pressure-temperature regime relevant to the silicate mantle and core (55–57). Meanwhile, direct measurement of thermal conductivity under such extreme conditions still poses formidable challenges, so estimation of thermal conductivities from first-principles electronic structure calculations must suffice. Thus, identifying alloys and compounds of Fe with potentially high thermal conductivity is interesting as they could facilitate thermal convection at both the core-mantle boundary (CMB) and the inner-core boundary (ICB).

The coupling between mobile electrons and lattice vibrations dominates the heat transfer process of metals. The Wiedemann-Franz law (58) describes the relationship between electronic thermal conductivity and electrical resistivity as:

$$k = \frac{LT}{\varrho},$$

where \(L = 2.44 \times 10^{-8} W/\Omega K^2\) is the Lorentz number, \(T\) is the absolute temperature, and \(\varrho\) is the electrical resistivity. Thus, calculation of the electronic thermal conductivity of Fe-Au compounds is dependent on the knowledge of their electrical resistivity, which is scarce in the literature, especially for newly synthesized or predicted materials, and its determination falls beyond the scope of this paper. However, the Wiedemann-Franz law is a lower bound for the total thermal conductivity in a metal (56). While the addition of the electronic contribution would help to quantitatively estimate the total thermal conductivity of the Fe-Au systems, calculation of the total phonon thermal conductivity (including both acoustic and optical processes) gives a reasonable description of the heat transport mechanism (56).

The total phonon thermal conductivity \(k_{\text{ph}}\) in the predicted Fe-Au compounds could be as high as 68 W/mK in Pmnn-AuFe\(_4\) at 200 GPa and room temperature, and as low as 5.2 W/mK in I\(_4\)/m-AuFe\(_4\) at 200 GPa and 2500 K (Fig. 5a). Notably, the thermal conductivity of the CMB, corresponding to 136 GPa and 3750 K, is reported to be 90 W/mK (56). The pressure regime where Cmcm-AuFe\(_4\) is stable is therefore most representative of the CMB. Cmcm-AuFe\(_4\) has a \(k_{\text{ph}}\) of 6 W/mK at 140 GPa and 3100 K. The \(k_{\text{ph}}\) of the Cmcm-AuFe\(_4\) corresponds to 6.7% of the total thermal conductivity of the CMB. Given that the reported thermal conductivity in Ref. (56) already captured the electronic and vibrational contributions to the thermal conductivity (as well as those from any impurities), it then implies that the phonon process is significant in the Fe-Au compounds during heat transport at the CMB. Excess heat that is not transported by the mantle- or CMB-bound Fe-Au compounds is, instead, transported through compositional convection into the inner core (56). Unreacted Au, if available, may be transported through this process into the solid Earth’s inner core to form other stable Fe-Au compounds, such as Pmnn-AuFe\(_3\) and I\(_4\)/m-AuFe\(_4\).

In conclusion, we investigated the possible formation of stable Fe-Au compounds under pressure using density-functional methods. We found that, at high pressure, Au forms several stable compounds with Fe, which has strong implication for understanding the form that Au may take in the Earth’s mantle, CMB, and beyond. The Fe-Au intermetallic compounds are predicted to be stabilized by high pressure and electron transfer. Au exists as an anion in AuFe\(_3\) and as cation in two AuFe\(_4\) polymorphs, providing further evidence to support the striking chemistry of Au being able to adopt variable oxidation states at high pressure. At 140 GPa, Au attains a magnetic moment of 0.52\(\mu_B\) in Cmcm-AuFe\(_4\), making it ferromagnetic in nature. The speed of sound calculated for the various Fe-Au phases shows lower deviation from the PREM data compared to the other Fe-light element models compared. Furthermore, the computed thermal conductivity data for the various Fe-Au compounds shows that Fe-Au compounds have significant lattice thermal conductivity. This suggests that, beyond electronic phenomenon, the lattice vibrations also contribute to heat transport within the Earth’s core and at the CMB. The results from this study show that some part of the depleted Au could be mixed with Fe in the CMB and the outer region of the core. As such, our Fe-Au model could serve to explain the seismological structure of the upper part of the Earth’s interior, up to the core-mantle boundary, and some part of the outer core. Our work has strong implications for geoscience in the area of the Earth’s magnetic field and could be extended to study how Au is stored in the Earth’s solid, ferric inner core at pressures above 300 GPa.

MATERIALS AND METHODS

The crystal structure search was carried out using the particle swarm-intelligence optimization (PSO) algorithm using the Calypso program (59, 60). The structure search was performed for pressures of 0, 50, 100, 140, and 200 GPa, with simulation cells containing 1-4 formula units of Fe\(_x\)Au\(_{1-x}\). The stability of various phases with respect to decomposition was assessed by constructing their convex hull. Electronic structure calculations for structural optimization and property evaluations were performed with density-functional theory (DFT) and dynamic stability calculations with density-functional perturbation theory (DFPT) (61) as implemented in the Vienna Ab initio Simulation Package (VASP) (62) code. These calculations used the projector-augmented wave (PAW) (63) approach, in which the valence states of Au and Fe were treated as 5d\(^{10}\)6s\(^{1}\) and 3p\(^{6}\)3d\(^{7}\)4s\(^{1}\), respectively. The Perdew-Burke-Ernzerhof (PBE) (64) generalized gradient approximation (GGA) functional was selected and the planewave energy cut-off was set to 450 eV. The GGA+U framework was used to apply an on-site Coulomb interaction to improve treatment of the 3d electrons of Fe. The Hubbard U parameter was set to 8.6 eV (65, 66) and such treatment of Fe has previously shown good agreement with experimental results (67) over the pressure range of interest. To ensure that forces on all atoms were converged to within 1 meV/Å, the Monkhorst-Pack scheme was used to sample the Brillouin zone, with a \(k\) spacing of \(2\pi \times 0.02\) Å\(^{-1}\). Dynamical calculations for the thermal properties were carried out using the Quantum Espresso (QE) code (68), again with the PBE+U exchange-correlation functional. Well converged total energies were obtained using a planewave
kinetic-energy cut-off of 150 Ry and Monkhorst-Pack k-point meshes of $9 \times 9 \times 3$ and $8 \times 8 \times 8$ for AuFe$_3$ and AuFe$_4$, respectively.

To predict the thermal conductivity, the ShengBTE code (69) was used to iteratively solve the Boltzmann Transport Equation (BTE): 

$$F_{\lambda} = \tau_0^\lambda (\Omega + \Delta \Omega).$$

[6]

Here, $F_{\lambda}$ is the generalized mean free path, $\tau_0^\lambda$ is the relaxation time of mode $\lambda$ in the relaxation time approximation (RTA), and $\Delta \Omega$ gives the deviation of the solution from the RTA. The phonon assisted thermal conductivity ($k_{ph}$) tensor can then be obtained as

$$k_{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} n_0^0 (n_0^0 + 1) (\hbar \omega)^2 v_{\alpha\lambda} F_{\beta\lambda},$$

[7]

where $\alpha$ and $\beta$ are the three coordinate directions ($x, y,$ and $z$). $k_B$, $T$, $\Omega$, and $N$ are Boltzmann’s constant, the temperature, the unit-cell volume, and the number of $\mathbf{q}$-points in the integral over the BZ, respectively. The sum runs over all the phonon modes $\lambda$, $\hbar$ is the reduced Planck constant, and $\omega_\lambda$ is the phonon frequency. For the first iteration step, $\Delta \Omega$ is set to zero, which is equivalent to starting the iterative procedure from the RTA solution. The solution is converged when the relative phonon frequency. For the first iteration step, $\Delta \Omega$ is set to zero, which is equivalent to starting the iterative procedure from the RTA solution. The solution is converged when the relative phonon frequency is less than $10^{-5}$ W/mK. To solve the BTE, we used a $4 \times 4 \times 1$ supercell to calculate the third-order interatomic force constants (IFCs) for the Pmnm and Cmmm phases, and a $3 \times 3 \times 3$ supercell for the I4/m phase.

The force cut-off distance was set such that the interaction range includes the five nearest neighbors for AuFe$_3$ and the three nearest neighbors for AuFe$_4$. Meshes of $7 \times 7 \times 5$ and $5 \times 5 \times 5$ $\mathbf{q}$-points were used to calculate the second-order IFCs needed to compute the $k_{ph}$ of AuFe$_3$ and AuFe$_4$, respectively.

Data Availability. All study data are included in the article and/or SI Appendix.

Supporting Information Appendix (SI). The supporting information contains additional computational results, including plots of the zero-point energy (ZPE)-corrected convex hull, equation of states, 2D-projected crystal structures with Bader charge distributions, thermal conductivity at 300 K, electronic band structures, projected electronic density of states, vibrational entropies evolution with temperature, elastic modulus data and atomic charge distributions.

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References.

1. Bernard J Wood, Michael J Walter, and Jonathan Wade. Accretion of the earth and segregation of its core. Nature, 441(7095):825–833, 2006.

2. DJ Stevenson. Models of the earth’s core. Science, 241(4852):811–819, 1988.

3. Robert Sprague Jones. Gold in Meteorites and in the Earth’s Crust, volume 603. US Government Printing Office, 1968.

4. William F McDonald and S-S Sun. The composition of the earth. Chemical Geology, 120 (3-4):223–253, 1995.

5. Thomas J Ahrens. Global earth physics: a handbook of physical constants, volume 1. American Geophysical Union, 1995.

6. George R Helfrich and Bernard J Wood. The earth’s mantle. Nature, 412(6846):501–507, 2001.

7. Douglas R McKay and Daniel A Peters. The midas touch: Gold and its role in the global economy. Plastic Surgery, 25(1):61–63, 2017.
ations in various crystal systems. Physical Review B, 90(23):224104, 2014.
43. Pasquale Pacone, Stefano Baroni, and Stefano de Gironcoli. α ↔ β phase transition in In: A theoretical study based on density-functional perturbation theory. Physical Review B, 57 (17):10421, 1998.
44. John M Ziman. Electrons and phonons: the theory of transport phenomena in solids. Oxford university press, 2001.
45. Zhi Guo, Amit Verma, Xufei Wu, Fangyuan Sun, Austin Hickman, Takekazu Masui, Akito Kuramata, Masataka Higashikawa, Debdeep Jena, and Tengfei Luo. Anisotropic thermal conductivity in single crystal β-gallium oxide. Applied Physics Letters, 106(11):111908, 2015.
46. Ankit Jain and Alan JH MaGaughey. Thermal conductivity of compound semiconductors: Interplay of mass density and acoustic-optical phonon frequency gap. Journal of Applied Physics, 116(7):073503, 2014.
47. Ruqiang Guo, Xinxiang Wang, and Bading Huang. Thermal conductivity of skutterudite CoSb₂ from first principles: substitution and nanoeengineering effects. Scientific Reports, 5(1):1–9, 2015.
48. Yunguo Li, Lidunka Vočadlo, and John P Brodholt. The elastic properties of hcp-Fe alloys under the conditions of the earth's inner core. Earth and Planetary Science Letters, 493:118–127, 2018.
49. Orson L Anderson. A simplified method for calculating the debye temperature from elastic constants. Journal of Physics and Chemistry of Solids, 24(7):909–917, 1963.
50. Edward Schreiber, Orson L Anderson, Naohiro Soga, and James F Bell. Elastic constants and their measurement. 1975.
51. Lidunka Vočadlo. Ab initio calculations of the elasticity of iron and iron alloys at inner core conditions: Evidence for a partially molten inner core? Earth and Planetary Science Letters, 254(1-2):227–232, 2007.
52. Anastasia P Kantor, Innokenty Yu Kantor, Alexander V Kurnosov, Alexei Yu Kuznetsov, Natalia A Dubrovinskaia, Michael Krisch, Alexei A Bossak, Vladimir P Dmitriev, Vadim S Urusov, and Leonid S Dubrovinsky. Sound wave velocities of fcc Fe–Ni alloy at high pressure and temperature by mean of inelastic X-ray scattering. Physics of the Earth and Planetary Interiors, 164(1-2):83–89, 2007.
53. Jin Liu, Jung-Fu Lin, Ahmet Atatas, and Werri Bl. Sound velocities of bcc-Fe and Fe₀.₈₅Si₀.₁₅ alloy at high pressure and temperature. Physics of the Earth and Planetary Interiors, 233:24–32, 2014.
54. Yu He, Shichuan Sun, Duck Young Kim, Bo Gyu Jang, Heping Li, and Ho-kwang Mao. Superionic iron alloys and their seismic velocities in earth's inner core. Nature, 602(7898):258–262, 2022.
55. Wonjin Yong, Richard A Secco, Joshua AH Littleton, and Reynold E Sliper. The iron invariance: implications for thermal convection in earth's core. Geophysical Research Letters, 46 (20):11065–11070, 2019.
56. Hitoshi Gomi, Kanji Ono, Kai Hirose, Stéphane Labrosse, Razvan Caracas, Matthieu J Verstraete, and John W Hernlund. The high conductivity of iron and thermal evolution of the earth's core. Physics of the Earth and Planetary Interiors, 224:98–103, 2013.
57. Nico de Koker, Gerd Steinle-Neumann, and Wojtch Vitek. Electrical resistivity and thermal conductivity of liquid Fe alloys at high P and T, and heat flux in earth's core. Proceedings of the National Academy of Sciences, 109(11):4070–4073, 2012.
58. Orson L Anderson. The Grüneisen parameter for iron at outer core conditions and the resulting conductive heat and power in the core. Physics of the Earth and Planetary Interiors, 109 (3-4):179–197, 1999.
59. Yanchao Wang, Jian Lv, Li Zhu, and Yanming Ma. Crystal structure prediction via particle-swarm optimization. Physical Review B, 82(9):094116, 2010.
60. Yanchao Wang, Jian Lv, Li Zhu, and Yanming Ma. Claypsy: A method for crystal structure prediction. Computer Physics Communications, 183(9):2063–2070, 2012.
61. Stefano Baroni, Stefano De Gironcoli, Andrea Dal Corso, and Paolo Giannozzi. Phonons and related crystal properties from density-functional perturbation theory. Reviews of Modern Physics, 73(2):515, 2001.
62. Georg Kresse and Jürgen Hafner. Ab initio molecular dynamics for liquid metals. Physical Review B, 47(1):558, 1993.
63. Georg Kresse and Daniel Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. Physical Review B, 54(3):1758, 1996.
64. John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. Physical Review Letters, 77(18):3865, 1996.
65. Matteo Cococcioni and Stefano De Gironcoli. Linear response approach to the calculation of the effective interaction parameters in the LDA+U method. Physical Review B, 71(3):035105, 2005.
66. Arnab Majumdar, S Tse John, Min Wu, and Yansun Yao. Superconductivity in fep 5. Physical Review B, 96(20):201107, 2017.
67. HK Mao, Y Wu, LC Chen, JF Shu, and Andrew P Jephcoat. Static compression of iron to 300 GPa and Fe₁₋₀₃₉₆ alloy to 260 GPa: Implications for composition of the core. Journal of Geophysical Research: Solid Earth, 95(B13):21737–21742, 1990.
68. Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L Chiarotti, Matteo Cococcioni, Imsamia Dabo, et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter, 21(39):395502, 2009.
69. Wu Li, Jesús Carrete, Nebil A Katcho, and Natalio Mingo. Shengbte: A solver of the boltzmann transport equation for phonons. Computer Physics Communications, 185(6):1747–1758, 2014.