Spin crossover in ferropericlase from first-principles molecular dynamics

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Ferropericlase, (Mg,Fe)O, is the second-most abundant mineral of the Earth’s lower mantle. With increasing pressure, the Fe ions in the material begin to collapse from a magnetic to non-magnetic spin state. We present a finite-temperature first-principles phase diagram of this spin crossover, finding a broad pressure range with coexisting magnetic and non-magnetic ions due to favorable enthalpy of mixing of the two. Furthermore, we find the electrical conductivity of the mineral to reach semi-metallic values inside the Earth.

Ferropericlase, (Mg\(_{1-x}\)Fe\(_x\))O, is an Fe-bearing transition metal oxide that makes up some 20% of the total volume of the Earth’s lower mantle. Each Fe ion in this mineral assumes an octahedral coordination environment, which leads to crystal field splitting, i.e., separation of the Fe 3d shell of electrons into a higher-energy \(e_g\) and a lower-energy \(t_{2g}\) group. At low pressure, the ground-state electronic configuration of Fe\(^{2+}\) is a high-spin state with four unpaired electrons giving a total spin of \(S = 2\). On compression, three effects come into play which ultimately cause a spin transition or magnetic collapse to the low-spin state, \(S = 0\). Firstly, the crystal field splitting grows due to increased overlap of the Fe and O valence orbitals, while secondly, the electronic bands are broadened in energy due to increased confinement, making the high-spin state increasingly unfavorable. Thirdly, the low-spin state is favored by the smaller size of the low-spin Fe ion via the \(P\Delta V\) contribution to the free energy.

Ever since the discovery of the spin transition in Fe\(_{0.94}\)O beyond 60 GPa at room temperature and later in ferropericlase between pressures of 50 to 70 GPa, it has become apparent that the phenomenon affects mechanical, compositional, and electronic properties, and thus holds potentially significant implications for the physics and chemistry of the Earth. Interest in spin transitions is not, however, limited to geoscience, with applications in, e.g., nanoclusters and thin films showing great technological potential.

Experimental work utilizing x-ray emission spectroscopy (XES), optical spectroscopy, Mössbauer spectroscopy (MSB), and equation-of-state (EOS) data gathered from high-pressure x-ray diffraction experiments has, to date, probed the spin transition in ferropericlase up to pressures of \(P = 140\) GPa and temperatures of \(T = 2000\) K. On the theoretical side, approaches based on analytical mean-field theory and static first-principles calculations augmented by quasi-harmonic phonon computations have treated the spin transition as in fact a smooth spin crossover, an approach consistent with published experiments. This crossover proceeds, with increasing pressure, from all Fe ions assuming the high-spin state, through to a mixed-spin phase with coexisting high-spin and low-spin ions, to eventually all ions assuming the low-spin state.

Previous theoretical work has been based on static calculations and has assumed that the mixed-spin state is stabilized entropically, yielding a narrow crossover at low temperatures that disagrees with experiment. Moreover, experiment and theory have not explored geophysically important properties such as the band structure and electrical conductivity. In this Letter, we take a different approach that combines first-principles molecular dynamics with free-energy minimization to simulate the high-temperature properties of the spin crossover directly. Our results reveal a new physical picture of the crossover, where the mixed-spin phase is stabilized through enthalpy rather than entropy, giving a finite broadness for the crossover even at vanishing temperatures. Additionally, we predict the EOS up to the conditions at the base of Earth’s mantle (140 GPa, 4000 K), and find that the electrical conductivity of ferropericlase reaches semi-metallic values at the bottom of the lower mantle, with significant geophysical implications.

Our simulation setup is built on molecular dynamics (MD) simulations within density functional theory (DFT), as implemented in the VASP package. We consider a cubic simulation cell of 64 atoms with periodic boundary conditions, adopting an Fe concentration of \(x_{Fe} = 25\%\), with the Fe ions arranged in a regular superlattice with two nearest-neighbor distances between any two neighboring Fe ions. In order to obtain an efficient simulation setup with well-converged values for internal energy and pressure (within 5 meV/atom and 0.2 GPa), we sample the Brillouin zone at the Baldereschi point for a lattice of simple cubic symmetry and use a planewave cutoff energy of 500 eV. The projector-augmented wave method is used to avoid explicit calculation of the core electron orbitals. To decide on the best feasible approximation to the exchange and correlation part of the total energy functional, we compared the EOS from conjugate-gradient relaxed static calculations to experiment at 300 K, using the local-density approximation (LDA) and two different generalized-gradient approximations (GGA, PBE and PBEsol). Of these functionals, PBEsol proved clearly superior.

Unfortunately, the PBEsol functional fails to fully capture the strong correlation between the 3d electrons of the
Fe ions, which is manifested as a spin transition pressure of only 18 GPa for $x_{Fe} = 3.125\%$, whereas the experimental estimate is closer to 50 GPa [12]. As meta-GGA type functionals [24–27] that we tested brought no alleviation to this problem, and as hybrid functional calculations utilizing the exact Fock exchange of the DFT system of quasi-electrons are computationally too demanding for MD, we use the $+U$ method [28] to approximate the aforementioned correlation effects. Based on our calculations on the dependence of the spin transition pressure on $U$, an empirical estimate for $U$ from optical spectroscopy data [12], as well as our own hybrid functional [29] computations, we settled on $U - J = 2.5$ eV. We then performed our PBEsol+$U$ MD simulations in the NVT ensemble using the Nosé-Hoover thermostat. Each simulation was run with a timestep of 1.0 fs for a total of 10 ps to reach thermal equilibrium, followed by 10 ps over which all physical time averages were computed. A total of three isotherms, $T = 2000$, 3000, and 4000 K were simulated for compressions that result in pressures of approximately 0 to 200 GPa, to encompass existing experimental data and the conditions of the lower mantle of the Earth. These dynamic computations were complemented with a set of static calculations, where the crystal structure was relaxed using conjugate gradients.

In order to capture the continuous character of the spin crossover and to thus produce a first-principles phase diagram of the phenomenon, we minimize the Gibbs free energy $\Delta G(P, T, f) = G(P, T, f) - G(P, T, 0)$ at each $P$ and $T$ with respect to $f$, the fraction of Fe ions in the high-spin state. As we find a vanishingly small amount of intermediate spin ($S = 1$) Fe in our simulations, we define $f \equiv \langle \mu_{Fe} \rangle / \langle \mu_{HS} \rangle$, where $\mu_{Fe}$ and $\mu_{HS}$ denote the Fe magnetic moment and the same when all Fe ions are in the high-spin state, respectively, and $\langle \rangle$ denotes an average over Fe ions and time. To map $\Delta G(P, T, f) = \Delta H - T \Delta S$ as a function of $f$, we perform constrained-moment and free-moment calculations, the former producing a low-spin ($f = 0.0$) and high-spin ($f = 1.0$) phase and the latter producing two mixed-spin phases along each isotherm. The enthalpy $H$ of a given phase $f$ is obtained directly from the MD simulation, as is the electronic contribution to the entropy $S_{el}$ [30, 31] (we set the electronic temperature equal to the ionic temperature). The vibrational entropy $S_{vib}$ and entropy $S_{conf}$ due to site-switching of high spins and low spins we evaluate through the method of thermo-dynamic integration [32, 33]. The last contribution to the entropy, $S_{mag}$ due to the fully disordered paramagnetic state of the moments above the Néel temperature of $\sim500$ K [34], we compute from the expression $S_{mag} = k_B \sum_i \ln(\mu_i + 1)$, where $\mu_i$ is the total magnetic moment of Fe ion $i$, and $k_B$ is the Boltzmann constant. We thus obtain $\Delta G(P, T, f)$ at four values of $f$ for each $P$ and $T$, and to find the equilibrium $f$, we interpolate and minimize $\Delta G(P, T, f)$ with respect to $f$ using a free second-order polynomial [36].

The resulting phase diagram for the spin crossover is presented in Fig. [1]. Strikingly, we find a broad pressure interval of coexisting high-spin and low-spin ions at all temperatures, even at fully static conditions ($T = 0$ K in the phase diagram). Another interesting feature of the phase diagram is the weak temperature-dependence of the stability field of the mixed-spin phase up to $\sim3000$ K. The shape of our phase diagram is thus fundamentally different from previous theoretical work [10, 17, 18], where the mixed-spin phase was stabilized through an ideal mixing entropy, resulting in a completely sharp spin transition at $T = 0$ K. We predict $f \approx 0.5$ at the core-mantle boundary, also at odds with previous computations, which have found significantly smaller high-spin fractions. Comparison of our static results to existing experimental EOS, XES, and MSB data at 300 K shows overall good agreement (Fig. [2a,b]). Previous computations show a much narrower crossover than EOS, XES, and MSB data, and our present results. Our results for the EOS at all simulated temperatures are presented in Fig. [2], displaying good agreement with experimental high-temperature data.

The finite width of the spin crossover even at vanishing temperatures is due to favorable enthalpy of mixing $\Delta H_{mix}$ of the high-spin and low-spin ions (Fig. [3]). We trace the favorable $\Delta H_{mix}$ to packing considerations arising from the volumes of alternating high-spin and low-spin Fe-O octahedra. Due to occupation of $e_g$ orbitals, the high-spin octahedron is larger than the low-spin octahedron, and the Mg-O octahedron is intermediate in size. When high-spin and low-spin Fe in (Mg,Fe)O are brought close together, the system can exploit the willingness of high-spin Fe-O octahedra to expand and their neighboring low-spin octahedra to contract with respect to the MgO crystal (see inset of Fig. [3]), resulting in lower internal energy and forces and hence lower enthalpy than expected from ideal mixing of high-spin and low-spin Fe.

![FIG. 1. Our first-principles phase diagram of the spin crossover in ferropericlase. The black line is a geotherm from Ref. [37].](image)
These results are consistent with indications that Fe ions in (Mg,Fe)O tend to cluster at high pressure. Our finding is, however, in sharp contrast to previous computational work on the spin crossover, where the high-spin and low-spin ions have been assumed to form an ideal solid solution. The favorable $\Delta H_{\text{mix}}$ that stabilizes the mixed-spin phase in our static simulations persists in the dynamical simulations (Fig. 3).

Increasing temperature favors the high-spin state because of the favorable contribution to the free energy from the $S_{\text{mag}}$ term and to a lesser extent the $S_{\text{vib}}$ term. Over the range of temperatures that we have considered, the magnetic entropy dominates over the electronic entropy, which favors the low-spin state. The mixed-spin phase region becomes slightly broader with increasing temperature due to the increase in $S_{\text{conf}}$ with increasing temperature. $S_{\text{conf}}$ increases with temperature due to the increased occurrence of spontaneous interchanges of high-spin and low-spin moments among the Fe sites in the mixed-spin phase.

We find that the vibrational entropy is greater for high-spin ions than for low-spin ions. This we relate to the shape of the valence charge density of the Fe ion in the high-spin state which, considering a sole Fe ion in MgO at static conditions and zero pressure, results in a less symmetrical Fe-O octahedron (two axes expanding, one contracting) than for the low-spin state (all axes contracting uniformly). This underlying differential distortion, as quantified in our NVT simulations by the difference in octahedral quadratic elongation between the high-spin and low-spin phases, persists at finite temperature, leading to larger mean squared displacements of the high-spin Fe ions and hence larger $T S_{\text{vib}}$ in the

FIG. 2. a) The EOS of ferropericlase at static conditions compared to experimental data gathered at 300 K. We construct the total EOS by interpolating $V = V(P, f)$ linearly between the four spin phases $f$, where the EOS for each phase is a fit to the third order Birch-Murnaghan EOS. b) Our static result for $f$ compared to XES and MSB data as well as previous computational results at 300 K. c) Our thermal EOS for all simulated temperatures along with experiment at 2000 K.

FIG. 3. Enthalpy (solid lines) and internal energy (dashed lines) of mixing of high-spin and low-spin Fe at static conditions, along with enthalpy of mixing at 2000 K and 91 and 64 GPa (green octagons, left to right, respectively), 3000 K and 98 and 73 GPa (orange pentagons), and 4000 K and 106 and 81 GPa (red squares). Inset: Distribution of octahedral volumes at 2000 K and $f = 0.50$ for Fe-O octahedra of high-spin Fe (blue solid line) and low-spin Fe (red solid line). The corresponding static results are shown by the dashed vertical lines. The black dash-dotted line denotes octahedral volume for $f = 1.0$ and 0.0 for static and 2000 K results.
corresponding phase [36].

The partitioning of Fe between ferropericlase and the major lower mantle phase (Mg,Fe)SiO₃ perovskite has important implications for understanding the structure, dynamics, and geochemistry of the Earth’s lower mantle [5]. We assess the effect of the spin transition on the partitioning by computing the ratio ln(K_f/K_i,0), where K_f is the partition coefficient assuming the equilibrium f, and K_i,0 is the coefficient assuming f = 1.0. Assuming no subsequent spin transition in the perovskite, we find ln(K_f/K_i,0) to lie approximately in the range 0 to 1.5 along the geotherm [36], much less than the value of ~10 estimated by Badro et al. [7]. Our much more moderate result for the effect of the spin transition on the partitioning appears in better agreement with the relatively weak pressure-dependence of K_f found in experiment [1].

The electrical conductivity of the lower mantle is important for understanding anomalies in Earth’s rotation via electromagnetic coupling of mantle and the underlying core, and the relationship between observations of the geomagnetic field and its source through the filter of a potentially conductive mantle. However, no measurements or ab initio predictions of the conductivity of ferropericlase at conditions of the deep lower mantle are available. Using the Kubo-Greenwood method to compute the electronic component of σ as implemented in VASP [43, 44], we find σ = 4.0 ± 0.4 × 10⁴ S/m at conditions close to the bottom of the mantle (P = 136 GPa, T = 4000 K), approximately half the recently obtained value of 9 × 10⁴ S/m for FeO in similar conditions [47], consistent with the experimental result that σ increases with Fe concentration [48]. From the electronic density of states, it is evident that the metallization of the mineral from its initially insulating state is due to the 3d electrons of the Fe ions forming broad bands that lead to a significant density of states at the Fermi level, an effect due to both pressure and temperature. The spin crossover itself serves to increase σ, as an increase in the concentration of low-spin Fe implies increased density of states near the Fermi level of the crystal [49].

The predicted semi-metallic value of electrical conductivity of ferropericlase at the core-mantle boundary might be invoked to explain the highly conductive layer in this region inferred from observations of the planet’s nutations and anomalies therein [49, 50]. Assuming the pyrolitic volume fraction of 20% for ferropericlase in the lower mantle, the presently obtained electrical conductivity for the mineral, and taking the surrounding perovskite phase to be insulating, the Hashin-Shtrikman minimum-maximum bounds [51] for the conductivity of the mixture are zero and 5.7 × 10³ S/m, respectively. Adopting the maximum value and the half-way value, a simple calculation shows that respectively 18 or 35 km of lower-mantle material is enough to give the required minimum conductance of 10⁸ S to explain the nutation observations. A more highly conductive mantle than previously assumed may also require revision of the interpretation of surface measurements of the Earth’s magnetic field.

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SUPPLEMENTAL MATERIAL TO “SPIN CROSSOVER IN FERROPERICLASE FROM FIRST-PRINCIPLES MOLECULAR DYNAMICS”

Details of the free-energy computations

To compute the full Gibbs free energy for a given isotherm for the high-spin phase ($f = 1.0$), low-spin phase ($f = 0.0$), and for $f$ intermediate between 0.0 and 1.0, we start by constructing the pressure-volume equation of state (EOS) for each $f$. For $f = 1.0$ and 0.0, we perform the MD simulations in the canonical $NVT$ ensemble over a range of compressions in such a way that the total number of unpaired electrons in the supercell is constrained to correspond to either four or zero per Fe ion, respectively. We fit a third-order Birch-Murnaghan EOS \cite{1} to the resulting pressure-volume points.

In order to construct the EOS for $f$ intermediate between 0.0 and 1.0, we first perform a set of free-moment MD simulations, \textit{i.e.}, simulations where the number of unpaired electrons is not constrained, using various compressions. Each such run produces a certain average value for $f$. We choose two such pressure-volume points, each with a different $f$ intermediate between 0.0 and 1.0, to represent a point along the EOS of ferropericlase at each of these two $f$, respectively (see Fig. 1a). We compute the volume for each such intermediate $f$ at all other pressures via

$$V(P, f) = V(P, 0) + g(f) \Delta V(P),$$

where $\Delta V(P) = V(P, 1) - V(P, 0)$, and $g(f) = [V(P, f) - V(P, 0)]/\Delta V(P)$ is assumed to be constant and equal to the value computed directly from our free-moment simulation for each $f$. The inset of Fig. 1 illustrates that this is a good approximation and a sensible ansatz for computing the EOS of mixed-spin phases over the entire pressure range of our calculations. Examples of the magnetic structure for each $f$ are shown in Fig. 2.

From the EOS for each value of $f$, we compute the Helmholtz free energy $F = E - T(S_{el} + S_{vib} + S_{conf})$ by integrating the thermodynamic identity $P = -(\partial F/\partial V)_T$. At this stage, the free energy of each spin phase $f$ relative to the other phases is unknown. To resolve this, we employ adiabatic switching within the Kirkwood coupling scheme to compute the free energy of a given phase $f$ relative to $f = 0.0$. The joint potential energy function for switching from $f = 0.0$ to an arbitrary value of $f$ with the coupling parameter $\lambda$ going from
FIG. 1. The final result for the EOS at each value of $f$, this example being for $T = 3000$ K. The EOS for $f = 1.0$ and $f = 0.0$ are fitted to data points from simulations with constrained moments (marked by circles). The EOS for $f = 0.65$ and $f = 0.47$ are constructed starting from free-moment simulation points (marked by crosses). Inset: Explicit test of the method used to construct the EOS for $f$ intermediate between 0.0 and 1.0, at static conditions. The large symbols indicate points from which the EOS were constructed, small symbols indicate points calculated explicitly after the construction of the EOS.

The free energy difference between $f = 0.0$ and a given $f$ is computed as the integral

$$\Delta F = F_f - F_{f=0.0} = \int_0^1 d\lambda \langle E_f - E_{f=0.0} \rangle_\lambda,$$

which, from simple geometrical arguments, is equal to $-1/2 \times (d\langle E_{f=1.0} - E_{f=0.0} \rangle/d\lambda)_{\lambda=1}$, provided the perturbation term of Eq. 4 is small (we find 4 to 13 meV/atom throughout all calculations). We thus constrain the slope of the integrand at $\lambda = 1$, and using the three constraints, take a fully constrained second-order polynomial to model the integrand. For $f$
FIG. 2. Magnetic moment of each Fe ion in the 64-ion supercell as a function of time after the initial 10 ps equilibration, in units of the high-spin Fe moment. Data are shown for $f = 0.0$ (a), $f = 1.0$ (b), $f = 0.76$ (c), and $f = 0.49$ (d) at $T = 4000$ K. The inset in (d) is the corresponding data for $f = 0.39$ at $T = 2000$ K.

intermediate between 0.0 and 1.0, we use $\lambda = 1$ and the fluctuation term of Eq. 4 as in [2].

In Fig. 3 we present an example of the integrand and an assessment of the relative precision of the approximations detailed above, showing that overall the method looks sufficiently precise for the present purposes.

Finally, we add on the magnetic entropy $S_{mag}$ to the free energy of each spin phase $f$, and move on to analyze the results in the $NPT$ ensemble, i.e., in terms of Gibbs free energy. To find the equilibrium high-spin fraction at each pressure and temperature, we interpolate $\Delta G(P, T, f) = G(P, T, f) - G(P, T, 0)$ with a free second-order polynomial between the four values of $f$ and find the minimum of that polynomial in the interval $f \in [0, 1]$ (See Fig. 4 for an example). We consider this method of interpolation a more neutral choice than using a third-order polynomial or natural splines, both of which seemed to produce spurious and artificial features into the interpolation.
FIG. 3. a) The integrand of Eq. 3 at \( T = 3000 \) K at a lattice constant of 3.93 Å for \( f = 1.0 \), using the approximation of constraining the integrand only at \( \lambda = 0 \) and 1 (linear fit) and the approximation of constraining additionally the slope of the integrand at \( \lambda = 1 \) (quadratic fit). The values of the integrand at \( \lambda = 0 \) and 1 are shown for reference. b) The value of the integral of Eq. 3 for \( f = 1.0 \) for all isotherms and different levels of approximation. Using only \( \lambda = 0 \) or 1 results in overestimation or underestimation of \( \Delta F \), respectively. The linear and quadratic fit agree well with the approximation of using \( \lambda = 1 \) and the fluctuation term of Eq. 4 implying good precision for the chosen approximations.
FIG. 4. Finding the equilibrium value of \( f \) at \( T = 3000 \) K and \( P = 120 \) GPa through second-order polynomial interpolation and minimization.

Explaining the vibrational entropy results

Populating the spin-up and spin-down \( t_{2g} \) and \( e_g \) states of a single Fe ion within an MgO lattice unevenly to produce the high-spin configuration entails a valence electron density around the ion which results in a non-uniformly distorted Fe-O octahedron, contrary to the situation in the low-spin state. We quantify the distortion of the Fe-O octahedra in the dynamic simulations by using the mean octahedral quadratic elongation \( \langle \lambda_{\text{oct}} \rangle \), and find Fe-O octahedra at \( f = 1.0 \) to be generally more distorted than their counterparts at \( f = 0.0 \). In Fig. 5 we show that the difference in mean squared displacements of the Fe ions between \( f = 1.0 \) and \( 0.0 \) are correlated with the difference in \( \langle \lambda_{\text{oct}} \rangle \) between the two phases. This
FIG. 5. Explaining the results for the vibrational entropy difference between \( f = 1.0 \) and \( f = 0.0 \), this example being at \( T = 3000 \) K. The difference between the two phases in mean squared displacements \( \langle r(t)^2 \rangle \) of the Fe ions with respect to their mean positions is correlated with the difference in octahedral elongation, \( i.e. \), the degree of distortion of the Fe-O octahedra. The difference in vibrational entropy \( T S_{\text{vib}} \) between \( f = 1.0 \) and \( f = 0.0 \) is of the order of 15 meV/atom here. The mean octahedral volume is the same for both phases in these \( NVT \) simulations.

implies that the ionic network at \( f = 1.0 \), \( i.e. \), with all Fe ions in the high-spin state, is more distorted than at \( f = 0.0 \), with all Fe ions in the low-spin state, leading to larger nuclear excursions and hence the observed larger vibrational entropy.

Results on Fe partitioning

Results for the ratio of the two partition coefficients described in the main article are shown in Figs 6a and b.

Electronic density of states and metallization

In Fig. 7, we show the electronic density of states (DOS) of ferropericlase. Increasing temperature and pressure causes the DOS near the Fermi level to increase significantly, and
FIG. 6. a) Ratio of partition coefficient of Fe between ferropericlase and perovskite assuming the equilibrium high-spin fraction ($K_f$) and all Fe in the high-spin state ($K_{1.0}$). b) Bilinear interpolation of the results of a), along with a geotherm [5] (white solid line).

hence electrical conductivity to increase, eventually up to semi-metallic values. Collapsing the Fe moments to the low-spin state, as during the spin crossover, further increases the DOS near the Fermi level.
FIG. 7. Total and projected DOS of ferropericlase illustrating the effect of pressure and temperature as well as high-spin fraction on the DOS near the Fermi level. The plots are shifted so that the Fermi level is at 0 eV.

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