

Is low-spin Fe^{2+} present in Earth's mantle?

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Abstract

Recently, X-ray spectroscopy indicated that the low-spin (LS) electronic configuration of Fe^{2+} and Fe^{3+} ions substituting in silicate perovskite of various compositions, and also in magnesiowüstite is stable at room temperature above pressures of ~ 49 to 120 GPa [J. Badro, G. Fiquet, F. Guyot, J.-P. Rueff, V.V. Struzhkin, G. Vanko, G. Monaco, Iron partitioning in Earth's mantle: toward a deep lower mantle discontinuity, *Science* 300 (2003), 789–791.; J. Badro, J.-P. Rueff, G. Vanko, G. Monaco, G. Fiquet, F. Guyot, Electronic transition in perovskite: possible non-convecting layers in the lower mantle, *Science* 305 (2004) 383–386.; J. Li, V.V. Struzhkin, H.K. Mao, J. Shu, R.J. Hemley, Y. Fei, B. Mysen, P. Dera, V. Prakapenka, G. Shen, Electronic spin state of iron in lower mantle perovskite, *Proc. Natl. Acad. Sci.* 101 (2004) 14027–14030.; J.M. Jackson, W. Sturhahn, G. Shen, J. Zhao, M.Y. Hu, D. Errandonea, J.D. Bass, Y. Fei, A synchrotron Mössbauer study of $(\text{Mg,Fe})\text{SiO}_3$ perovskite up to 120 GPa, *Am. Mineral.* 90 (2005) 199–205.; J.F. Lin, V.V. Struzhkin, S.D. Jacobsen, M.Y. Hu, P. Chow, J. Kung, H. Liu, H.K. Mao, R.J. Hemley, Spin transition of iron in magnesiowüstite in the Earth's lower mantle, *Nature* 436 (2005) 377–380.]. Simple thermodynamic relationships combined with crystal field theory provide a minimum Clausius–Clapeyron slope of ~ 0.23 to 0.4 GPa/K for the high-spin (HS) to low-spin transition of Fe ions in perovskite, consistent with lower mantle temperatures stabilizing the disordered HS state. This computation of $\partial P/\partial T$ utilizes experimentally determined parameters only (P and T at the transition), and is supported by microstructural analysis of the change in volume and entropy considerations. Similarly, $(\partial P/\partial T)_{\text{min}} \sim 0.18$ to 0.31 GPa/K for magnesiowüstite. High spin Fe^{2+} should be stable in silicates throughout Earth's mantle for compositions of $\text{Fe}/(\text{Mg}+\text{Fe}) \sim 0.1$, consistent with disorder prevailing at high temperature, although partial conversion of octahedral Fe^{3+} to LS may occur. Similarly, partial conversion of octahedral Fe^{2+} in magnesiowüstite to the LS is possible for Fe-rich compositions, which transform at relatively low pressures.

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1. Introduction

Recent X-ray spectroscopic studies of volumetrically important phases in the lower mantle indicate that Fe ions transform from high-spin (HS) to low-spin (LS) electronic configurations at pressures of ~ 49 to 120 GPa and at room temperature [1–4]. Mössbauer data on

$\text{Mg}_{0.95}\text{Fe}_{0.05}\text{SiO}_3$ with the perovskite structure are consistent with transformation of Fe^{3+} ions to the low spin state at about 70 GPa, whereas Fe^{2+} ions remain in the high spin state to 120 GPa [5]. The spin state of Fe^{2+} influences the physical and chemical properties of its host mineral, and therefore has ramifications for mantle geophysics and geochemistry (e.g. [6–9]).

Because spin-pairing creates order, the entropy (S) decreases upon transition from the HS to the LS state. The volume (V) also decreases, because outlying

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electron orbitals are depopulated, resulting in a positive Clausius–Clapeyron slope:

$$\partial P/\partial T = \Delta S/\Delta V. \quad (1)$$

Spin-pairing can be a sharp or gradual transition. Whether LS Fe exists in Earth’s mantle depends crucially on the slope, because temperatures inside the Earth far exceed the ambient temperature conditions of the experiments, whereas pressures in the deepest mantle are comparable to run conditions. Badro et al. [2] predict a low Clapeyron slope of 0.0083 GPa/K, based on a very large value of $\Delta V=2.73 \text{ cm}^3/\text{mol}$ for (Mg,Fe) SiO_3 with the perovskite structure (henceforth termed perovskite). Clearly, their ΔV is overestimated, primarily due to their use [2] of ionic radii for 6-, not 8-coordinating anions. Compared to octahedral sites, spin-pairing on a cubic site should not produce as much contraction because some outlying orbitals remain populated (Fig. 1). Second, although the radius of HS iron is well-constrained, since this was inferred from crystallographic parameters of many oxides and fluorides using consistent anion radii, the radius of LS iron is uncertain, because this estimate involves pyrite (FeS_2) [10] which is not ionic, but covalent [11] and thus its size is underestimated. Third, such large ΔV is observed for reconstructive transformations involving coordination changes of Si, i.e., silicate spinel \rightarrow magnesiowüstite + silicate perovskite or pyroxene \rightarrow majoritic garnet (e.g. [12]). In contrast, no bonds are broken during spin-pairing, and the structural changes are minor. Specifically, much of the contraction is localized in that the spin transition involves only 1/20th of the cation sites in perovskite (based on $\text{Fe}/(\text{Fe}+\text{Mg}) \sim 0.1$ in these studies and that Fe^{3+} may substitute for Si whereas Fe^{2+} substitutes for Mg [13]). That the volume change for spin-pairing is significantly smaller than ΔV values known to accompany coordination changes involving the entire unit cell have been demonstrated for ferroperricite (magnesiowüstite) by Lin et al. [4].

Larger $\partial P/\partial T \sim 0.018 \text{ GPa/K}$ for perovskite was estimated by Li et al. [3] using Schläfer and Gliemann’s [14] relationship (the point-charge model):

$$\chi \sim R^{-5} \quad (2)$$

where χ is the splitting between energy levels (Fig. 1) and R is the cation–anion distance. As Li et al. [3] stated, the result is approximate. In particular, the bulk modulus of perovskite was used to ascertain the response of the transition to pressure and temperature whereas Eq. (2) concerns only the local environment of the Fe impurity ions.

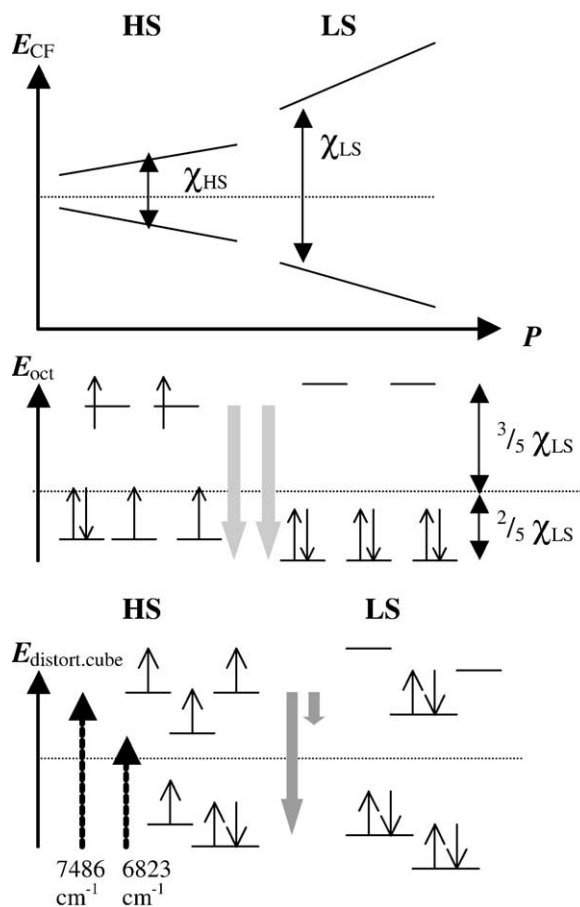


Fig. 1. Energy levels for d-electron orbitals in Fe^{2+} in a crystal field (after [6,19]). This diagram does not include pairing energy (see text). Left side = high spin state. Right side = low spin state. Top = schematic of the response of the levels to pressure. Middle = schematic of the placement of the d-electrons in the possible levels for ideal octahedral coordination as in (Mg,Fe)O. As pressure increases, separation (splitting = χ_{HS}) of the energy levels in the HS state increases. Upon transition to the LS state, electronic energy due to the crystal field decreases (light gray arrow). For the ideal octahedral site, one transition exists (middle). Although the splitting (χ_{LS}) differs upon transition, the levels will still straddle the value for the electronic energy of the unperturbed ion in a crystal field (dotted line), wherein all d-electron orbitals have the same electronic energy. The HS to LS transition occurs when the change in electronic energy (light gray arrow) at least equals the energy involved in forming 2 more pairs of electrons. Bottom = schematic of energy levels for a distorted cubic site such as in mantle perovskite. Visible absorption peaks (dotted arrows, labeled with frequencies) suggest that the two highest levels are degenerate [22]. Two spin-pairing transitions exist (dark gray arrows). As one of the upper levels remains populated in the LS state, the Fe^{2+} ion in cubic coordination does not contract as much as in octahedral coordination.

A similar relationship, $\chi \sim V^{-3/2} \sim R^{-9/2}$ attributed to Sherman [15] was used by Sturhahn et al. [16] to determine the P, T conditions for spin-pairing in

magnesiowüstite. A continuous cross-over is inferred with a partially paired (intermediate) spin state following $\partial P/\partial T \sim 0.015$ GPa/K (Fig. 3 in [16]). Sherman's [15] approach was also applied to magnesiowüstite by Lin et al. [4] resulting in $\partial P/\partial T = 0.018$ GPa/K. The Clapeyron slopes for (Mg,Fe)O [4,16] differ little from that for perovskite [3] because the point charge model is the basis of all calculations.

A Clapeyron slope of ~ 0.01 GPa/K for FeO was estimated by Ohnishi [17] also by using Eq. (2) and by assuming an ambient volume and an equation of state for the LS state, based on ionic radii from covalent pyrite. Ohnishi [17] considered his value to be rough.

The above estimates of the Clausius–Clapeyron slope are based on generalizations (ionic radii and/or a point charge model) because structural and spectroscopic measurements needed to compute ΔV and ΔS at appropriate conditions are unavailable for perovskite, and only partially available for magnesiowüstite [4]. It is difficult to evaluate the accuracy of calculations that are based on similar assumptions. Therefore, alternative approaches to calculate $\partial P/\partial T$ are needed to assess which spin state of Fe ions is stable at mantle conditions. The present report provides two additional estimates of $\partial P/\partial T$ for spin-pairing in perovskite and magnesiowüstite that are independent of each other and of the previous results. The predicted Clausius–Clapeyron slopes are sufficiently large to suggest that the transition from HS to LS Fe²⁺ in perovskite is unlikely at the high temperatures found in Earth's mantle, although partial conversion of octahedrally coordinated Fe³⁺ ions is not precluded.

2. Thermodynamics of the high-spin to low-spin transition

Most high-pressure phase transitions are precipitated by resistance of a given structure to contraction. Rearrangement of the atomic lattice to provide a denser phase is governed by the equation of state [$V(T,P)$] of each phase and by ΔV being negative. Spin-pairing differs significantly in that the driving factor is instead pressure-induced changes in electronic energy levels which in turn lead to a (secondary) volume change. To understand the process, thermophysical properties connected with the electrons are focused on.

Simple approaches are taken because so few of the relevant parameters are known. Section 2.1 evaluates the change in internal energy (E) based on microscopic behavior associated with electronic transitions. This information and a thermodynamic identity allow evalu-

ation of Eq. (1) (in Section 2.2) based solely on experimentally determined run conditions. Sections 2.3 to 2.5 follow a classical approach in which Eq. (1) is evaluated by estimating ΔS from the effect of disordering, and ΔV from micro-structural relationships for the relevant phases.

Sherman's [15] approach is not used to calculate ΔS and ΔV : (1) This is based on a point charge model, which is not warranted for realistically dilute compositions. (2) The total angular momentum (J) is used whereas the spin quantum number (s) better describes the behavior of transition metal elements [18]. (3) Visible spectra of the low spin state in silicates are unknown.

2.1. Internal energy from crystal field theory and spectroscopic measurements

Electronic energies of the 5 geometrically distinct d-orbitals of Fe²⁺ are split in an ideal octahedral field (Fig. 1) or ideal cubic field (not shown) due to interactions with coordinating oxygen atoms (e.g., [6,8,19]). In the low spin state, all electrons are paired, resulting in a lower crystal field stabilization energy (CFSE). Pairing electrons require additional energy to overcome their mutual Coulombic repulsion and to compensate for loss of exchange possibilities (e.g. [19]). The total pairing energy for creating one electron pair in a d-orbital around a free Fe²⁺ ion (E_{pair}) is calculated to be 229 kJ/mol Fe²⁺ [20,21]. For a complexed ion, these values would be reduced by 15–30% due to sharing with the coordinating ligands (the cloud effect; e.g. [19]). Electronic energy associated with orbital splittings is obtained from diagrams such as Fig. 1 and measured absorption spectra (e.g. [6,8]). The crystal field stabilization energy (CFSE) is $-0.4 \chi_{\text{HS}}$ for the HS state, and $-2.4 \chi_{\text{LS}}$ for the LS state in the ideal octahedral site, where χ is the splitting (Fig. 1). At ambient pressure, $\chi_0 \sim 7000 \text{ cm}^{-1} = 83 \text{ kJ/mol}$ from visible spectroscopy of Fe-bearing perovskite [22,23], as indicated in Fig. 1, which is typical of ferrous iron in silicate and oxide minerals [8,24]. If χ_{HS} and χ_{LS} are similar, as suggested by the small volume change in (Mg,Fe)O [4], then transition of one electron from the HS to LS state at $P \sim 1$ atm would reduce the internal energy due to the crystal field by the same splitting $\chi_0 \sim 83 \text{ kJ/(mol Fe}^{2+})$, which is considerably smaller than E_{pair} . For this reason, the HS state is stable at low pressure. The above arguments hold regardless of the specific geometry of the site and whether one or two electronic transitions occur (Fig. 1).

As pressure increases, frequencies of absorption bands connected with transition metals generally

increase, due to an increase in the splitting between the electronic levels (e.g. [24,25], discussed further below). Transition from the HS to LS state will occur when the electronic energy difference between the levels involved in the transition (Fig. 1) overcomes the energy associated with electron pairing [26–28]. For each electron,

$$\Delta E_{\text{ele}} = E_{\text{pair}} + \Delta \text{CFSE} \leq 0 \quad (3)$$

describes the conditions of the HS to LS transition. It is unnecessary to quantify the change in χ_{HS} with pressure, or to estimate χ_{LS} , or perform a structure-specific calculation of E_{pair} : the essential fact is that $\Delta E_{\text{ele}} \leq 0$ at the P and T conditions of the HS to LS transition. The electronic energy at the transition may be negative as χ_{LS} can be larger than χ_{HS} due to contraction of the metal–oxygen bond (Fig. 1), but it should not be positive.

The thermal electronic contribution to the internal energy (E_{th}) may be relevant at the high temperatures of the mantle. This contribution is rarely considered for insulators, e.g., [29] and has not been applied to Fe ions. As a very rough comparison, for Fe metal at mantle temperatures of ~ 2500 K, $E_{\text{th}} = 8$ kJ/mol which is only 10% of ΔCFSE and 3% of E_{pair} [30]. The difference ΔE_{th} between low and high-spin iron would be smaller. In the mean-field potential approach, ΔE_{th} is proportional to the difference between the electronic density of states of HS and LS Fe (Eq. (13) in [31]). The electronic density of states equals roughly the number of electrons in the various energy levels as a function of their energy. From Fig. 1, the HS state has electrons in higher energy levels and thus ΔE_{th} is negative. Results for metallic Fe suggest that thermal electronic effects should not alter Eq. (3).

Other additional contributions to the internal energy may exist. Any type of change which produces negative ΔE does not affect Eq. (3) or the results in Section 2.2. For example, the smaller size of LS state of Fe^{2+} compared to the HS state, should reduce lattice strain, providing an additional negative contribution to ΔE . Any additional positive *electronic* contributions to ΔE that oppose the transition simply cause the transition to occur at a higher pressure where such effects summed with E_{pair} equal the change in CFSE. For other, unknown changes to the internal energy to be important, their size must be large because the two terms governing this electronic transition (CFSE and E_{pair}) are large. The size of ΔE from effects other than electronic can be roughly estimated from ΔE of other phase transitions. At ambient pressure, $\Delta H = \Delta E + P\Delta V \cong \Delta E$, where H is enthalpy.

Minor structural rearrangements (such as α - to β -quartz and ortho- to clino-enstatite) have $|\Delta H| = |\Delta E| \sim 0$ to 1.6 kJ/mol-K [32], which is small compared to CFSE and E_{pair} . Also, ΔH correlates with ΔV (Tables 5 and 6 in [32]). Measured $|\Delta V| = 0.135$ cm³/mol for the spin transition in $\text{Mg}_{0.4}\text{Fe}_{0.6}\text{O}$ ([4], see Section 2.4), suggests values of $|\Delta H| = |\Delta E| \sim 1.7$ kJ/mol-K based on tabulated data in [32], which is much smaller than CFSE and E_{pair} .

Furthermore, negative values for ΔE are corroborated by measurements of ΔH for temperature induced spin transitions in XCoO_3 perovskites, where X is a lanthanide. For light rare earth cobaltites, ΔH is about -400 J/mol for HS \rightarrow LS transitions [see summary by 27], about $\sim 1/100$ th of either CFSE or E_{pair} . Heavy rare earth cobaltites have smaller negative values of ΔH and thus ΔE . This analysis and the above example supports the view that Eq. (3) is valid and that electronic terms dominate the internal energy of spin-pairing transitions.

Eq. (3) can also be tested by comparing calculated to measured transition pressures. From optical spectroscopy at ambient conditions, perovskite has two electronic transitions at 6823 and 7486 cm⁻¹ [22] which provides $\Delta \text{CFSE} \sim -7500$ and -700 cm⁻¹ = -85 and -8 kJ/mol. Using $E_{\text{pair}} = 190$ kJ/mol Fe accounts for the cloud effect. Bands shifts are roughly 100 cm⁻¹/GPa for many different types of Fe absorption [24,33,34], suggesting that the first transition occurs at ~ 90 GPa and that the second at ~ 160 GPa. For magnesiowüstite, absorption bands at 11,600 and 10,000 cm⁻¹ ([35], the site is slightly distorted) give $\Delta \text{CFSE} = -132$ and -114 kJ/mol, suggesting transitions at 50 and 105 GPa. Agreement is good with the X-ray spectroscopy and Mössbauer measurements which indicate transitions at ~ 50 GPa for high Mg magnesiowüstite [1,4] and at 70 to 132 GPa for perovskite [2,3,5], given the uncertainty in the pressure shift for the absorption bands of a factor of 2, that E_{pair} is estimated, and that ΔCFSE may be larger than that suggested by absorption spectroscopy at ambient conditions (Fig. 1). Agreement is worse for the second spin-pairing of Fe^{2+} , as expected, because the energy levels change after the first spin-pairing event. This exercise supports Eq. (3) representing the energetics of spin-pairing.

2.2. The minimum Clausius–Clapeyron slope

Phase transitions occurring at constant temperature and pressure are described by

$$\Delta G = \Delta E - T\Delta S + P\Delta V = 0, \quad (4)$$

where G is the Gibb's free energy, and thus the volume change is obtained from

$$\Delta V = (T\Delta S - \Delta E)/P, \quad (5)$$

where P and T are the conditions at the transition. Note that ΔE cannot be strongly negative or Eq. (5) would provide positive values of ΔV , inconsistent with contraction of the orbitals upon conversion of HS to LS state. Because ΔS is negative, and ΔE is negative or zero, the largest possible magnitude for ΔV is obtained from by setting $\Delta E=0$ in Eq. (5), giving $\Delta V_{\max}=T\Delta S/P$. Combining this result with Eq. (1) sets a lower limit on the Clapeyron slope:

$$(\partial P/\partial T)_{\min} = P/T. \quad (6)$$

If ΔE is slightly positive, as may be suggested by a thermal electronic term, then ΔV is smaller than ΔV_{\max} calculated here, and the lower limit set in Eq. (6) still holds (M. Bukowinski, pers. communication).

Interestingly, the minimum Clapeyron slope is determined solely by the conditions of the transition, which are known, although discrepancies exist between results from various research groups (discussed below). The transitions are expected to be gradual, as sharp transitions are generally associated with spin-pairing being accompanied by a structural phase transition [27]. For this reason, the average pressure of the room temperature experiments is used. Eq. (6) holds for any phase change which has negative signs for all of ΔE , ΔS , and ΔV .

For magnesiowüstite, the transition is gradual over ~49 to 58 GPa for $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$ [1], ~54 to 67 GPa for $\text{Mg}_{0.75}\text{Fe}_{0.25}\text{O}$, and ~84 to 102 GPa for $\text{Mg}_{0.40}\text{Fe}_{0.60}\text{O}$ [4]. The average transition pressure provides $(\partial P/\partial T)_{\min} \sim 0.18, 0.20,$ and 0.31 GPa/K for the above three compositions in order of increasing Fe content. The compositional dependence of the Clausius–Clapeyron slope is connected with ΔS being proportional to Fe content.

For perovskite, Badro et al. [2] inferred that the transition occurred in two steps, with one spin-pairing of Fe^{2+} occurring at 70 GPa, resulting in an intermediate state, and the final spin-pairing occurring at 120 GPa, consistent with the distorted cubic site (Fig. 1, see also [3]). Measurements on Al-free and Al-bearing perovskite to 145 GPa by Li et al. [3] instead indicate a gradual transition. Mössbauer data are consistent with a gradual transition of Fe^{3+} to the LS state around 70 GPa, whereas Fe^{2+} remains HS up to 120 GPa for $\text{Mg}_{0.95}\text{Fe}_{0.05}\text{SiO}_3$ [5]. This result differs from the X-ray spectroscopy studies of $\text{Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3$ which indicate that half of

the Fe^{2+} is transformed to the intermediate state at 100 GPa [3], and that transition is complete to the LS state at 120 GPa [2]. One explanation for the discrepancies is that the transition pressure depends on total Fe content or ferric/ferrous ratios. Second, non-hydrostatic stress could also be important as grinding is known to affect spin-pairing [e.g., 27]. Third, charge transfer existing between Fe^{3+} and Fe^{2+} in the HS state, as inferred from visible spectroscopy [22] indicates that some Fe^{3+} and Fe^{2+} occur in adjacent sites. Pairing could affect the transition pressure and would occur to varying degrees among the various samples since concentrations are dilute ($\text{Fe}^{3+}/\text{Fe}^{2+} \sim 0.1$ and $\text{Fe}_{\text{tot}}/\text{Mg} \sim 0.1$). Fourth, interpreting the changes in X-ray spectra as spin-pairing of Fe^{2+} may be incorrect.

Transformation of Fe^{3+} at ≥ 70 GPa [5] is expected to occur in all perovskite samples, as follows. All perovskite samples examined have ~10% of their iron as ferric [13], and that the smaller octahedral site where this probably resides should transform at lower pressures. Only one electron is involved so the spread in pressure should be narrower than that of Fe^{2+} . Also, models of the HS to LS transition in FeSiO_3 predict that ions in the octahedral site transform at lower pressure (<135 GPa) than in the distorted site (~1 TPa) [36]. For Fe^{3+} spin-pairing in perovskite, $(\partial P/\partial T)_{\min} \sim 0.23$ GPa/K.

If interpretations of X-ray emission studies are correct that Fe^{2+} in perovskite is entirely in the LS state by 120 to 145 GPa [2,3], then an average of 132 GPa is appropriate for the final pairing. Transition to the mixed state is equivocal but probably ~100 GPa. These pressures may be on the low side, given the Mössbauer results [5]. For Fe^{2+} in perovskite, $(\partial P/\partial T)_{\min} \sim 0.33$ GPa/K for the first pairing and ~0.43 GPa/K for complete pairing.

The post-perovskite phase, which is stable at conditions in the deepest mantle, has a site for Fe similar to that in perovskite: large, distorted, and with a high coordination number [e.g., 37,38,39]. The electronic nature of the HS to LS transition means that coordination of the Fe^{2+} ion is the overriding factor in determining the transition pressure. To first order, spin-pairing in the ppv phase will behave in the same manner as perovskite, and will have a high slope.

2.3. Magnetic and electronic contributions to the entropy

The magnetic contribution to the entropy is $S_{\text{mag}} = R \ln(2s+1)$ per iron atom in the formula unit where R is the gas constant and s is spin quantum

number [18]. Because $s=2$ for Fe^{2+} in the HS state, and $s=0$ in the LS state (Fig. 1), the change in magnetic entropy from HS to LS is $-1.34 \text{ J}/(\text{mol}\cdot\text{K})$, referenced to the formula unit of perovskite (or ppv) or $(\text{Mg},\text{Fe})\text{O}$, and given a composition near $0.1 = \text{Fe}/(\text{Fe} + \text{Mg})$. This quantity is independent of T and P .

Electronic entropy (S_{ele}) should be important for magnesiowüstite as its Fe site resembles the slightly distorted octahedral site in fayalite (e.g. [40]). From Wood [41], $S_{\text{ele}} = -R \sum p \ln p$ where p is the probability that the electron is located on a given energy level. For Fe^{2+} with three degenerate low-lying electronic levels (Fig. 1), $S_{\text{ele}} = 0.913 \text{ J}/(\text{mol}\cdot\text{K})$ referenced to the formula unit of $\text{Mg}_x\text{Fe}_{1-x}\text{O}$, with composition $\text{Fe}/(\text{Fe} + \text{Mg}) = 0.1$. For the low spin state of Fe^{2+} , S_{ele} is identically zero (e.g. [6]).

If the perovskite site is sufficiently distorted to lift the degeneracies of the electronic orbitals of Fe^{2+} , then the 6th electron resides in the lowest energy level, and electronic entropy for the HS state in a distorted site is negligible [42]. However, if the two lowest lying energy levels are degenerate, which is consistent with spectroscopic data [22], then $S_{\text{ele}} = 0.577 \text{ J}/(\text{mol}\cdot\text{K})$ referenced to the formula unit of perovskite, given a composition with $0.1 = \text{Fe}/(\text{Fe} + \text{Mg})$. Electronic entropy due to charge transfer is neglected due to low concentrations of Fe^{3+} .

At mantle conditions ΔS is underestimated because S_{ele} strongly increases with T [41,43]. Using fayalite as a proxy for the behavior of Fe^{2+} , suggests that $\partial S/\partial T = 0.0005$ [43] to $0.0025 \text{ J}/(\text{mol}\cdot\text{K}^2)$ [41]. At mantle temperatures ($\sim 2500 \text{ K}$), ΔS_{ele} should be 2.2 to $7.2 \text{ J}/\text{mol}\cdot\text{K}$ for magnesiowüstite and 1.8 to $6.8 \text{ J}/\text{mol}\cdot\text{K}$ for perovskite.

2.4. Independent estimates of ΔV from micro-structural relations

The perovskite structure consists of a sublattice of large oxygen anions, with voids sufficiently large to accommodate the cations (Fig. 2a). Because of this and that Fe^{2+} ions only occupy $\sim 10\%$ of one out of two cation sites in $(\text{Mg},\text{Fe})\text{SiO}_3$, the associated volume change should be small. For magnesiowüstite, a larger volume change is expected because a larger fraction of the cation sites is impacted, and for the specific arrangement of cations and anions in this structure (Fig. 2b), the cations have a greater effect on the volume.

The 8-coordinated cation site in perovskite is quite large with O–O bond lengths near 2.5 \AA [44]. Ideal coordination with the 8 O^{2-} anions touching (Fig. 2a) provides a void with radius of 0.94 \AA (Fig. 2ac). This

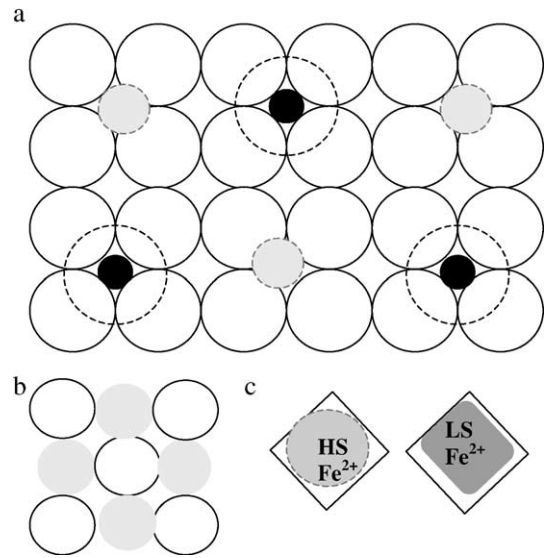


Fig. 2. Structure schematics. (a) Idealized 2-D projection of the cubic perovskite structure. The basal plane contains O^{2-} anions (open circles) and Si^{4+} cations (black circles). Adjacent layers contain O^{2-} anions (dotted rim open circles) and Mg^{2+} cations (grey circles). The next layer is a repeat of the basal plane of O and Si atoms. The small cations occupy interstitial voids within the oxygen sublattice. (b) Layer of the cubic magnesiowüstite structure. Here, the O and Mg ions together form a close packed array. (c) Schematic of the divalent cation site in perovskite and ppv. Square depicts size of the void ($r=0.988 \text{ \AA}$). HS Fe^{2+} (medium grey) should be larger (radii not provided by [10]). LS Fe^{2+} (dark grey) may or may not be smaller than HS, as mainly the shape changes: pairing moves electrons away from the anions and into the “corners” of the void. Also, the outer electron levels in perovskite remain populated in the LS state (Fig. 1).

size void is in excellent agreement with measured Mg–O (2.2 \AA) and O–O bond lengths in perovskite [44] and is consistent with ionic radii tabulations [10]. The octahedral site in MgSiO_3 can also be described in terms of touching O anions. Given this result, expansion of the unit cell of perovskite with substitution of a larger cation (Fe) for Mg [45,44] is interpreted as opening the voids and pushing the O anions apart.

Because the smallest attainable void size is limited by the size of the O anions, the smallest size that the unit cell can reach upon conversion to LS Fe^{2+} is that of MgSiO_3 . The O^{2-} radius inferred from bond lengths [44] and Fig. 2 is 1.26 \AA , which is smaller than 1.4 \AA from ionic radii compilations [10], suggesting that the oxygens and the 8-coordinated site are compact even at 1 atm. Therefore, if LS Fe^{2+} is smaller than Mg^{2+} it would not promote further contraction. However, the energy level diagram for a distorted cubic site (Fig. 1, bottom) suggests that LS Fe^{2+} is probably close to the size of HS Fe^{2+} as one of the spin pairs lies in an orbital that is strongly repulsed by the anions, and therefore

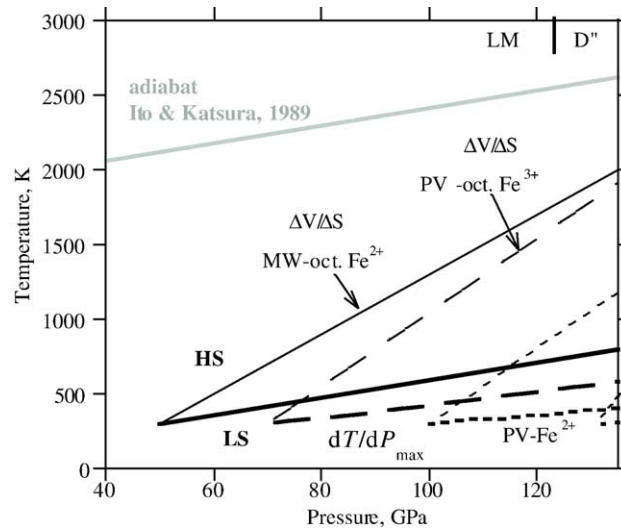


Fig. 3. Comparison of mantle temperatures to Clapeyron slopes. Grey line = adiabat of Ito and Katsura [48], which provides a lower limit to temperatures in D', since this may be a thermal boundary layer. Solid lines = magnesiowüstite. Dashed and dotted lines = transitions in perovskite seen at various pressures by different authors (see text). Heavy lines = Clapeyron slopes from Eq. 6. Light lines = Clapeyron slopes calculated from ΔS and ΔV , which overestimates of the stability of the LS state, since S depending on T results in flattening of the curves at high pressure.

significantly larger than Mg^{2+} . On this basis, ΔV due to spin-pairing in perovskite is overestimated by the difference in volume of MgSiO_3 and $(\text{Mg}_{0.88}\text{Fe}_{0.12})\text{SiO}_3$ perovskite compositions. Using structural data from Mao [45], $\Delta V = -0.045 \text{ cm}^3/\text{mol}$. The bulk moduli of these compositions are the same within experimental uncertainty [45], and so ΔV is unaffected by pressure.

High-pressure, room temperature X-ray diffractometry (XRD) showed that ΔV is insignificant for $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$ and ca. -1.6% for $\text{Mg}_{0.40}\text{Fe}_{0.60}\text{O}$ [4], which corresponds to $-0.135 \text{ cm}^3/\text{mol}$. Since this value was determined at the pressure of the transition, compressibility is not relevant. The volume change for magnesiowüstite is larger than ΔV of perovskite, as expected. For comparison, the volume change is also estimated from the 1 atm difference between MgO and $\text{Mg}_{0.40}\text{Fe}_{0.60}\text{O}$ (calculated from crystallographic data on end members [40]), giving $\Delta V = -0.49 \text{ cm}^3/\text{mol}$. Using a Birch–Murnaghan equation of state and accounting for the compositional dependence of the bulk moduli of magnesiowüstite [46] leads to $\Delta V \sim -0.19 \text{ cm}^3/\text{mol}$ near 60 GPa, which is reasonably close to the experimental values. The volume difference between MgO and $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$ similarly suggests $\Delta V = -0.139 \text{ cm}^3/\text{mol}$ at 1 atm, and $\Delta V \sim -0.056 \text{ cm}^3/\text{mol}$ near 60 GPa. The latter corresponds to $\Delta V = -0.65\%$ at ~ 65 GPa, which is similar to the experimental uncertainty in XRD data (see Fig. 2 in [4]), and thus consistent with no volume change being resolved by XRD [4]. This trend is dictated by the measurements and that

$\Delta V = 0$ for Fe-free MgO . The good agreement supports our estimates for ΔV of perovskite.

Small ΔV exists because the HS to LS transition mostly changes the shape of the Fe ion. Specifically, the LS cation better fits the void (Fig. 2c) because orbitals which point towards the 6 coordinating oxygens have been depopulated in favor of orbitals which point away.

2.5. Calculation of the Clausius–Clapeyron slope based on entropy and structure

From Eq. (1) and the information in Sections 2.3 and 2.4, $\Delta S/\Delta V \sim 0.03$ to 0.04 GPa/K for HS to LS transitions in perovskite. For $\text{Mg}_{0.83}\text{Fe}_{0.17}\text{O}$ and $\text{Mg}_{0.4}\text{Fe}_{0.6}\text{O}$, $\Delta S/\Delta V \sim 0.04$ to 0.06 GPa/K , respectively. Temperature should negligibly change ΔV , given that thermal expansivity varies little among isostructural compounds (e.g. [47]). Accounting for the estimated effect of temperature on S_{elec} increases the slope at mantle conditions to 0.05 to 0.15 GPa/K for perovskite and 0.08 to 0.2 GPa/K for magnesiowüstite. The slope presented in this section is more uncertain than that derived from energy considerations in Section 2.2, and thus less restrictive.

3. Discussion

Two independent estimates for the Clausius–Clapeyron slope of spin-pairing in perovskite are larger by a factors of ~ 2 to 40 than previous estimates. The

classical approach based on estimates of ΔS and ΔV suggests that values of $\partial P/\partial T$ for the HS to LS transition in deep mantle phases are fairly large, but this approach is an underestimate. The thermodynamic approach (Eq. (6)) provides $\partial P/\partial T_{\min}$ based on ΔE being negative for HS to LS transitions. As this approach only uses experimentally determined parameters, it should be robust and indicates that HS Fe is stable in the mantle, whereas the classical approach suggests that partial conversion of octahedrally coordinated Fe ions to the LS state is not precluded, evaluated through comparison to the mantle adiabat of Ito and Katsura [48] in Fig. 3.

Specifically, at lower mantle conditions of >2500 K, the LS state in perovskite and ppv should occur at $P > 900$ GPa, which is ~ 6 times larger than pressures of 135 GPa at the core–mantle boundary. It is not expected that low-spin Fe^{2+} exists in silicate perovskite or ppv within Earth's mantle, particularly if the lowest pressure transitions are connected with Fe^{3+} , as indicated by Mössbauer study [5]. Partial conversion LS Fe^{3+} could exist, if this transition initially at 70 GPa is spread out over pressure as temperature increases, similar to the calculations by Sturhahn et al. [16]. Similarly, complete stability of LS Fe^{2+} in magnesiowüstite in Earth's mantle is unlikely as pressures near 500 GPa are required near 2500 K. Partial conversion to LS Fe^{2+} in magnesiowüstite seems likely for the Fe-rich compositions, which transform at lower pressures, cf. [1] to [4]. That the various samples were heated between measurements is immaterial, as the spin state is not quenchable.

Fig. 3 indicates that the LS state in perovskite and magnesiowüstite is stable at temperatures far below the mantle adiabat. Even if this transition is spread over a substantial P, T range, the HS state is still expected at mantle conditions. The less restrictive analysis using ΔS and ΔV corroborates that the HS state is stable in perovskite (Fig. 3). For magnesiowüstite, partial transformation to the LS state might occur in D'' ; if the transition is spread out over a wide range of temperature and if LS Fe^{2+} is as small as Mg^{2+} . However, stability of LS Fe^{2+} in magnesiowüstite seems unlikely because (1) temperatures in D'' are probably above the adiabat, which increases the likelihood of stability of the HS state being stable in D'' , and (2) the strong temperature dependence of S_{ele} makes the curves in Fig. 3 become progressively less steep (by $\sim 1/3$) as P increases.

4. Conclusions

High temperatures promote disorder, thereby stabilizing the HS state. Other dense silicate and oxide miner-

als should behave similarly to the perovskite and magnesiowüstite phases discussed in this report. Due to the dominance of perovskite and ppv mineralogies, Fe^{2+} is expected to occur in high spin state inside the Earth, and strongly influences the physical properties of the mantle and its constituent phases.

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