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Citation: Shim, Sang-Heon et al. "Electronic and magnetic structures of the postperovskite-type Fe₂O₃ and implications for planetary magnetic records and deep interiors." Proceedings of the National Academy of Sciences 106.14 (2009): 5508-5512.

As Published: <http://dx.doi.org/10.1073/pnas.0808549106>

Publisher: National Academy of Sciences

Persistent URL: <http://hdl.handle.net/1721.1/50247>

Version: Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

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Electronic and magnetic structures of the postperovskite-type Fe_2O_3 and implications for planetary magnetic records and deep interiors

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Edited by Russell J. Hemley, Carnegie Institution of Washington, Washington, DC, and approved February 3, 2009 (received for review August 28, 2008)

Recent studies have shown that high pressure (P) induces the metallization of the Fe^{2+} -O bonding, the destruction of magnetic ordering in Fe, and the high-spin (HS) to low-spin (LS) transition of Fe in silicate and oxide phases at the deep planetary interiors. Hematite (Fe_2O_3) is an important magnetic carrier mineral for deciphering planetary magnetism and a proxy for Fe in the planetary interiors. Here, we present synchrotron Mössbauer spectroscopy and X-ray diffraction combined with ab initio calculations for Fe_2O_3 revealing the destruction of magnetic ordering at the hematite \rightarrow Rh_2O_3 -II type (RhII) transition at 70 GPa and 300 K, and then the revival of magnetic ordering at the RhII \rightarrow postperovskite (PPv) transition after laser heating at 73 GPa. At the latter transition, at least half of Fe^{3+} ions transform from LS to HS and Fe_2O_3 changes from a semiconductor to a metal. This result demonstrates that some magnetic carrier minerals may experience a complex sequence of magnetic ordering changes during impact rather than a monotonic demagnetization. Also local Fe enrichment at Earth's core-mantle boundary will lead to changes in the electronic structure and spin state of Fe in silicate PPv. If the ultra-low-velocity zones are composed of Fe-enriched silicate PPv and/or the basaltic materials are accumulated at the lowermost mantle, high electrical conductivity of these regions will play an important role for the electromagnetic coupling between the mantle and the core.

spin ordering | electrical conductivity | high pressure | phase transition

The origin of the magnetism in hematite (Fe_2O_3) has long drawn interest. It is a ubiquitous mineral on the oxidizing surfaces of the terrestrial planets, such as Earth and Mars, and is an important magnetic carrier mineral for deciphering the magnetic history of the planets. Furthermore, it serves as a proxy for the phases in the Earth's core and mantle, as oxygen may be an important alloying elements in the core and as Fe enters the dominant silicate and oxide phases in the mantle. Fe_2O_3 has a stability field for the postperovskite (PPv) - type crystal structure (1) to which the dominant lower mantle silicate transforms at the pressure (P)-temperature (T) conditions corresponding to the D'' region (bottom 200- to 400-km-depth region of the mantle) (2-4).

A previous study (5) showed a large increase in electrical conductivity in FeO at mantle related P , suggesting that the Fe^{2+} -O bonding character changes from covalent/ionic to metallic. An ab initio study (6) predicted a magnetic collapse of Fe in silicates and oxides at high P , perhaps within the deep mantle. A high-spin (HS) \rightarrow low-spin (LS) transition has been observed in silicates and oxides at mantle related P (7-9). These transitions can induce changes in important properties, such as elasticity, optical properties, electrical conductivity, and element partitioning (7, 10, 11). Recent ab initio studies suggested that structure and composition can have enormous influence on the spin transition, e.g., yielding large and opposite trends in transition pressure with composition for perovskite (Pv) and ferropericlasite (Fp) (12, 13). Therefore, it is

important to investigate how these electronic and magnetic transitions will be influenced by structural transitions and compositional variations existing in the deep Earth's interior.

Some iron oxides and sulfides carry important paleomagnetic records. However, impacts can disturb or even erase the records. For example, magnetic fields can be generated during a shock event, providing a possible explanation for high magnetic remanence found in young lunar glasses (14). In addition, a recent study suggested that randomization of paleomagnetic records by impact-generated fields may be responsible for the weak magnetic field intensity observed at the impact basins of Mars (15). As shown for pyrrhotite (16), impacts can demagnetize minerals, providing an alternative interpretation for the weak fields at the impact basins. Yet, high- P behaviors of most magnetic carrier minerals are not well studied.

Several intriguing changes have been observed in Fe_2O_3 at $40 \leq P \leq 60$ GPa: a large increase in density (14%) and a drastic drop in resistivity (17-19), a phase transition to a Rh_2O_3 -II (RhII) type structure (20), disappearance of magnetic hyperfine fields during the hematite \rightarrow RhII transition (19), and the HS \rightarrow LS transition of Fe (21).

Although Fe end member is stable in the MgO-FeO system that forms the second most abundant mantle phase, it is not stable and therefore not accessible experimentally for PPv in the MgSiO_3 - FeSiO_3 system that forms the most abundant phase in the D'' region. It has recently been found that the PPv phase is stable at 2,000 K and 60 GPa with an Fe_2O_3 stoichiometry (1). Furthermore, some studies suggested that a substantial amount of Fe in Mg-silicate Pv and PPv are Fe^{3+} ($\text{Fe}^{3+} / \sum \text{Fe} = 0.1 \sim 0.7$) at mantle P - T conditions due to crystal chemistry effects (22, 23). Therefore, Fe_2O_3 provides opportunities to understand the properties of Fe end-member PPv.

Here, we report the synchrotron Mössbauer spectroscopy (SMS) and X-ray diffraction (XRD) of Fe_2O_3 -PPv as well as the other Fe_2O_3 polymorphs at high P . We find that Fe in both the octahedral (hereafter B) and bipolar-prismatic (hereafter A) sites are magnetically ordered and, combined with our ab initio calculations, Fe in at least one of the two sites is in a HS state in PPv. Therefore, Fe_2O_3 undergoes a series of transitions: magnetic insulator with HS $\text{Fe}^{3+} \rightarrow$ nonmagnetic semiconductor with LS $\text{Fe}^{3+} \rightarrow$ magnetic metal with at least half of Fe^{3+} in HS, during

Author contributions: S.-H.S. designed research; S.-H.S., A.B., D.M., and K.C. performed research; W.S., J.Z., M.L., and V.P. contributed new reagents/analytic tools; S.-H.S., A.B., D.M., and W.S. analyzed data; and S.-H.S., A.B., and D.M. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/cgi/content/full/0808549106/DCSupplemental.

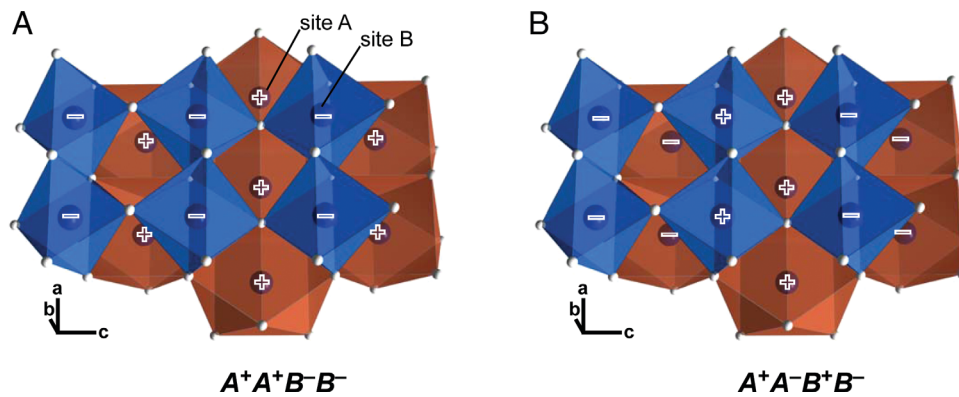


Fig. 3. The spin ordering in the PPv-type Fe_2O_3 . The red and blue spheres represent the bipolar-prismatically (site A) and octahedrally (site B) coordinated Fe^{3+} ions, respectively. The gray spheres represent oxygen atoms. The crystallographic orientations of the models are shown at A and B, Lower Left. We denote magnetic arrangements using + and – for up and down moments, respectively.

spin state in Fe_2O_3 -PPv, we have conducted ab initio calculations [GGA+U, see supporting information (SI) *Appendix* for calculation details]. We focus on three symmetry distinct collinear HS ferromagnetic (FM) and AFM arrangements in the Fe_2O_3 -PPv primitive unit cell, and three corresponding structures with LS on the B site, because we found the A site does not go LS (see below). An additional supercell magnetic arrangement was explored and is discussed in the *SI Appendix*.

First, we consider the two symmetrically distinct AFM arrangements and one FM arrangement in the primitive cell: $A^+A^+B^-B^-$, $A^+A^-B^+B^-$, and $A^+A^+B^+B^+$, where + and – are spin up and down, respectively, and A and B represent bipolar prismatic and octahedral sites, respectively (Fig. 3). In $A^+A^+B^-B^-$, all Fe atoms in the A site are + and all Fe atoms in the B site are – through AFM interaction along the [111] direction. All spin arrangements along the edge-sharing, [100], and corner-sharing, [001], directions are FM in $A^+A^+B^-B^-$. Arrangement $A^+A^-B^+B^-$ is AFM along [001] and [101] in the B and A sites, respectively, and FM along the edge-sharing direction, [100], in both the A and B sites. These arrangements are modeled with both HS and LS Fe^{3+} on the B site. Because we found no stable LS state on the A site up to 150 GPa, we only consider LS in the B site. Note that the $A_{HS}^+A_{HS}^+B_{LS}^+B_{LS}^+$ (FM) and $A_{HS}^+A_{HS}^+B_{LS}^-B_{LS}^-$ arrangements (the subscripts indicate the spin state of Fe) have a net magnetic moment per primitive cell $12\mu_B$ and $8\mu_B$, respectively. Therefore, the latter arrangement is ferrimagnetic. However, $A_{HS}^+A_{HS}^+B_{LS}^+B_{LS}^-$ has no net magnetic moment, i.e., AFM (see *SI Appendix* for details).

The calculated enthalpies of the different magnetic arrangements and spin states are shown in Fig. 4 for PPv. At low P , arrangements with HS Fe^{3+} are more stable than those with LS Fe^{3+} on the B site. Among the HS structures there is a significant gain in stability for AFM over FM arrangements by up to 100 meV per atom. There is no magnetic ordering transition at high P if Fe^{3+} remains HS. However, we find the $A^+A^-B^-B^-$, $A^+A^-B^+B^-$, and $A^+A^+B^+B^+$ (FM) arrangements all undergo a P -induced spin transition on the B site from HS to LS. For the most stable magnetic arrangement the spin transition occurs at a critical pressure, P_c , of 68 GPa. Below P_c , the most stable magnetic arrangement is $A_{HS}^+A_{HS}^+B_{HS}^-B_{HS}^-$. Above P_c , the most stable arrangement is $A_{HS}^+A_{HS}^-B_{LS}^+B_{LS}^-$. The P_c is very close to the values of 70 GPa where PPv has been measured in SMS work. Because the choice of the Coulomb interaction (U) is somewhat ambiguous and influences P_c ($U = 4$ eV lowers P_c to 50 GPa and $U = 7$ eV raises P_c to 110 GPa), we consider both $A_{HS}^+A_{HS}^+B_{HS}^-B_{HS}^-$ and $A_{HS}^+A_{HS}^-B_{LS}^+B_{LS}^-$ magnetic arrangements as candidates for the experimentally observed phase.

The pressure at which the B site Fe^{3+} undergoes a spin transition depends on the magnetic ordering: it occurs at 25 GPa for $A^+A^+B^+B^+$ (FM), at 55 GPa for $A^+A^-B^+B^-$, and at 75 GPa for

$A^+A^-B^-B^-$, demonstrating that the AFM arrangements stabilize HS Fe^{3+} on the B site to higher P . The spin transition to LS Fe^{3+} on the B site brings $A^+A^-B^-B^-$, $A^+A^-B^+B^-$, and $A^+A^+B^+B^+$ all within 25 meV of each other, suggesting that different magnetic orderings with LS B site are nearly degenerate in energy and all more stable than the same arrangements with HS Fe^{3+} at high pressures. The stable spin arrangements in our ab initio calculations can be also rationalized by considering the crystal structure of PPv combined with superexchange theory (28) (see *SI Appendix*).

In our SMS, the QS observed for both sites (-0.31 and 0.48 mm/s) in PPv are consistent with Fe^{3+} ions in the HS state (26). The QS of LS Fe^{3+} is expected to be higher than what we observed for PPv (29), as best shown in the high QS found in Fe_2O_3 -RhII (Table 1), which has all Fe^{3+} in LS according to X-ray emission spectroscopy (21). We obtain small differences in isomer shift, $\Delta IS = 0.30 \pm 0.02$ mm/s, between the two different Fe sites, indicating that the spin and oxidation states of the two Fe sites are likely to be the same (29). From these results and the ab initio calculation, we conclude that the magnetic ordering observed in SMS is likely to be $A_{HS}^+A_{HS}^+B_{HS}^-B_{HS}^-$.

The high B_{Hf} of site 1 is also consistent with HS Fe^{3+} (Table 1). However, the B_{Hf} of site 2 (19.2 T) is lower than expected

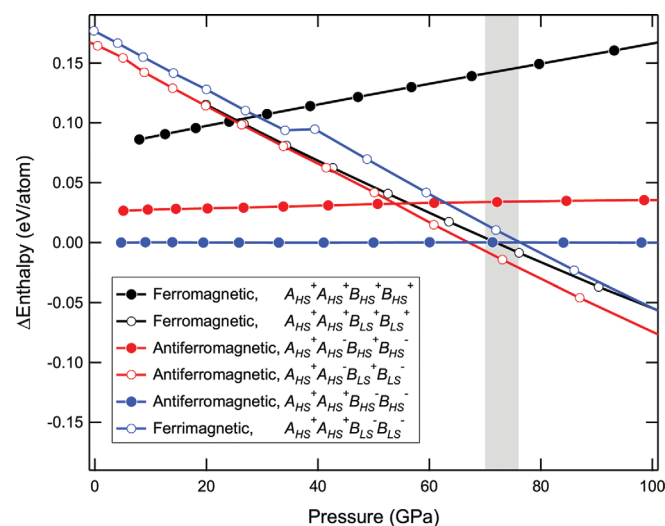


Fig. 4. Stability of different magnetic arrangements and spin states in Fe_2O_3 -PPv at high P . A reference state consisting of a polynomial fit to the enthalpy of $(A_{HS}^+A_{HS}^+B_{HS}^-B_{HS}^-)$, which is the stable state at ambient pressure, is subtracted off each curve. The gray area indicates the P where we measured the SMS of PPv. See the text for the notations.

ACKNOWLEDGMENTS. We thank B. Weiss and T. L. Grove for discussions that improved this article and the editor and two anonymous reviewers for helpful comments and suggestions. This work was supported by the National Science Foundation (NSF) Grants EAR0738655 (to S.H.S.) and EAR0738886 (to D.M.), respectively. K.C. is supported by a Department of Energy (DOE) National Nuclear Security Administration Stewardship Science Graduate

Fellowship. Measurements were performed at Sectors 3 and GeoSoilEnviro-Cars (GSECARS) at Advanced Photon Source. GSECARS is supported by the NSF and DOE. Use of Sector 3 was supported in part by the Consortium for Materials Properties Research in Earth Sciences under NSF Cooperative Agreement EAR 06-49658. Use of the APS was supported by the DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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