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Valence and spin states of iron in (Mg,Fe)SiO₃ perovskite and post-perovskite at pressures of the Earth's lower mantle

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Earth's lower mantle is believed to contain ~75 vol.% (Mg,Fe)SiO₃ perovskite, 20 vol.% (Mg,Fe)O ferropericlasite, 5 vol.% CaSiO₃ perovskite. In the lowermost ~200 km of the mantle, (Mg,Fe)SiO₃ adopts the post-perovskite structure [1,2]. While the properties and behaviour of pure MgSiO₃ phases are well understood (see e.g. ref. [2-5]), the effects of impurities - most importantly iron and aluminium, are poorly known and the existing experimental studies are contradictory. Here, we perform *ab initio* simulations that address the valence and spin states of iron impurities in MgSiO₃ polymorphs. In agreement with [6] we find a valence disproportionation reaction: $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^0_{\text{metal}}$. This highly exothermic (and somewhat counterintuitive) reaction results in the predominance of Fe³⁺ impurities in lower mantle silicates and produces free metallic iron. It occurs both in perovskite and post-perovskite, Al-free and Al-rich, at all lower mantle pressures. In presence of Al³⁺, iron forms Fe³⁺-Al³⁺ coupled substitutions in perovskite, but separate Fe³⁺-Fe³⁺ and Al³⁺-Al³⁺ substitutions in post-perovskite. Only the high-spin state is found for Fe²⁺ impurities at all mantle pressures, while Fe³⁺ impurities on the Si-site are low-spin at all pressures in both phases. Fe³⁺ impurities on the Mg-site are in the high-spin state in post-perovskite at all mantle pressures, but in perovskite we predict a high-spin - low-spin transition. The pressure at which this transition occurs strongly depends on the Al³⁺ content and according to our calculations increases from 76 GPa for Al-free to 134 GPa for Al-bearing perovskites. This explains previous experimental results [e.g., 7,8], which were thought to contradict each other. These findings have important geophysical implications [9].

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Investigation of Mn site configuration in wurtzite and rock-salt Zn_{1-x}Mn_xO by means of XAS experiments under pressure

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The diluted magnetic semiconductor (DMS) alloy Zn_{1-x}Mn_xO and other wide gap DMS are the object of increasing interest since Dietl et al. [1] predicted ferromagnetic behavior at room temperature in these materials.

Thin films of this material, deposited on sapphire have been reported to keep the wurtzite structure for Mn atomic proportions up to 30% [2] or 35% [3]. There have been a few reports on ferromagnetic behavior at low temperature (45 K) [4] and at room temperature [5, 6] but the subject remains controversial as some authors report spin-glass [7] or paramagnetic behavior [3].

Some authors attribute the ferromagnetic behavior to the presence of Mn nanoclusters while EXAFS measurements indicate that Mn atoms are in substitutional configuration on Zn sites [4, 8], but they do not report a full XANES analysis that would be far more sensitive to the site configuration

In this context, EXAFS and XANES experiments under pressure are relevant as they would give very valuable information about the site configuration of Mn atoms in Zn_{1-x}Mn_xO at different pressures and in different crystalline phases (wurtzite and rock-salt) which, combined with other techniques, can provide a deep insight on the origin of ferromagnetism in this DMS alloy.

The main results obtained in this study are:

- A phase transition to rocksalt occurs above 7 GPa for both compositions.
- The transition corresponds to a tetrahedral (octahedral configuration).
- A modification of the pre-edge feature and of the XANES is observed.
- The Mn-O distance is similar in the low pressure phase for both compositions but differs slightly in the high pressure phase. In any case they are larger than the Zn-O distances in pure ZnO.
- The second neighbor distance (Mn-Zn) for Zn_{0.95}Mn_{0.05}O is smaller than the equivalent distance Zn-Zn in pure ZnO, while the third one is identical.
- The local compressibilities for both compositions are the same than the compressibility for ZnO
- The transition is reversible for 5% Mn in ZnO, but irreversible for 25% Mn in ZnO

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