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Electronic spin transitions in iron-bearing $MgSiO_3$ perovskite

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Abstract

The electronic spin state of iron in perovskites with the chemical composition $Mg_{0.9375}Fe_{0.0625}SiO_3$, $Mg_{0.8750}Fe_{0.1250}SiO_3$ and $Mg_{0.9375}Fe_{0.0625}Si_{0.9375}Fe_{0.0625}O_3$, have been determined at 0 K and various pressures between 40–160 GPa, using *ab initio* methods. The results indicate that ferric iron exhibits a wide range of spin transition pressures between about 60–160 GPa, while ferrous iron has a much narrower span, between about 130–145 GPa. In general, the lowest spin transition pressures are associated with the most energetically favorable substitution configurations, where iron atoms are closest together. The effect of spin state on calculated elastic properties is found to be small.

Keywords: ab initio; iron; perovskite; spin transitions; elastic properties; lower mantle

1. Introduction

The lower mantle is believed to be predominantly composed of iron-bearing magnesium silicate perovskite, coexisting with small amounts of magnesiowüstite and calcium silicate perovskite [1], which transforms to post-perovskite in the lowermost few hundred kilometers [2]. In addition, 5–20 km thick ultra-low velocity regions [3], postulated to comprise an iron-rich phase [4–6], are observed, in places, at the core–mantle boundary. In order to interpret seismic data and construct geophysical models of the lower mantle it is essential to have a detailed knowledge of the physical and chemical properties of these iron-containing phases.

Previous theoretical studies have examined the effect of incorporating ferrous [7] and ferric [8] iron on the elastic and seismic properties of magnesium silicate perovskite, under lower mantle pressures. These report that the presence of ferrous or ferric iron, in the amounts expected in the lower mantle, causes a decrease in longitudinal and shear isotropic wave velocities of about 1 and 2%. In the case of ferric iron [8] the influence of the spin state of iron on the elastic properties was also investigated and found to be negligible. This is surprising in light of recent experimental work showing the spin state of iron in magnesiowüstite to have a sizeable effect on its bulk modulus [9]. It is possible that the effect may be more pronounced for ferrous iron than ferric, however, the degree to which the spin state of ferrous iron in perovskite affects its elastic and seismic properties remains unknown.

It has recently been shown that iron in perovskite undergoes a high to low-spin transition under pressures corresponding to those of the lower mantle [10,11]. If a

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large contrast exists in the physical properties of perovskite containing iron in a high and low-spin state, such a transition could, depending on its sharpness, result in a seismic velocity discontinuity at the related depth. Further geophysical implications of such a spin transition in the lower mantle also exist. In the first instance, because the spin state of iron influences its ionic radius, it could affect partitioning, leading to compositional layering [10,12]. It has also been postulated that the spin state of iron in lower mantle minerals influences thermal conductivity, and could, therefore, have a significant effect on mantle convection [10,13]. The exact mechanism of spin transitions of iron in perovskite is, however, still unclear, with some reporting a gradual decrease in spin [11,14], and others reporting that two distinct spin transitions are observed [10]. More detailed experimental investigations [15] and recent theoretical calculations [16] have connected the first of the two spin transitions to ferric iron, while the second has been postulated to be associated with ferrous iron [17]. Extrapolation of these results to lower mantle temperatures, by means of calculations based on simple thermodynamic relationships combined with crystal field theory [18], suggests that high to low-spin transitions may not occur in ferrous iron in perovskite until pressures that far exceed those of the lower mantle, although they could still occur in ferric iron.

Here we study spin transitions of iron in perovskite using *ab initio* calculations. In conjunction with results from our previous work [8,19] we establish a mechanism, related to substitution type, able to explain most experimental observations. In addition, we show that the elastic properties of perovskite incorporating ferrous iron in a high and low-spin state are very similar, particularly at the concentrations expected in the bulk of the lower mantle. These results, taken together, eliminate the possibility that a change in the spin state of ferrous iron in lower mantle perovskite could result in an observable seismic discontinuity.

2. Computational details

It is well-known that standard density functional methods can fail to predict the correct band structure of strongly correlated systems [20,21]. This has motivated the development of new methods, such as LDA+U [22], self-interaction correction [23] and the use of hybrid functionals [20]. Despite the availability of these techniques it is not possible to know *a priori* when standard density functional theory will fail, or which of these methods is the most suitable for a particular problem. For instance, standard density functional theory predicts iron oxide to be a metal [20,24] when it is known to be an insulator, and while using self-interaction correction methods [25,26], LDA+U [27,28] and hybrid functional methods [20] all correct for this, they do not give the same physical description of band gap formation. In addition, even though standard density functional theory calculations determine the wrong band structure, they do predict equation-of-state parameters well [24,29]. It is often assumed, therefore, as it is here, that standard density functional methods may be used to calculate other properties of transition metal oxides such as magnetic state, lattice parameters and elastic moduli [7,8,19,30].

Experimental investigations have shown that lower mantle perovskite is expected to have a ferrous iron to magnesium ratio of about 6% [1]. Though debate exists over the precise crystallographic location of iron in perovskite in the lower mantle, it is thought that both ferrous and ferric iron substitute into the pseudo-dodecahedral magnesium site, with ferric iron being charge-balanced by aluminum in the octahedral silicon site [31,32]. In earlier studies we investigated the spin state of ferric iron incorporated into magnesium silicate perovskite via charge coupled substitution with aluminum [19]. Here we broaden our investigation to include ferrous iron substituting for magnesium, and ferric iron incorporated via a double charge coupled substitution (*i.e.* with ferric iron substituting into a magnesium and silicon site.) For this, a similar eighty atom magnesium silicate perovskite model was fabricated, but with a single magnesium atom substituted by ferrous iron. In addition to this, eight models: five containing two ferrous iron substitutions and three containing two ferric iron substitutions were also fashioned. The specific details of these substitutions and the names to which the models will subsequently be referred are listed in Table 1.

Simulations were performed using the projector-augmented-wave implementation [33,34] of the density functional theory based VASP simulation code [35,36].

Table 1
Initial fractional coordinates and separation of iron substitutions in iron bearing $MgSiO_3$ perovskite models at 80 GPa

Model	Fe_{Mg} ($Mg^{2+}\rightarrow Fe^{2+}$)	$Fe_{Mg'}$ ($Mg^{2+}\rightarrow Fe^{2+}$)	$d(Fe_{Mg}–Fe_{Mg'})$/Å
SSM1	(0.49, 0.04, 0.25)	(0.26, 0.29, 0.25)	3.12
SSM2	(0.74, 0.21, 0.75)	(0.26, 0.29, 0.25)	5.42
SSM3	(0.26, 0.79, 0.25)	(0.26, 0.29, 0.25)	4.68
SSM4	(0.51, 0.46, 0.75)	(0.26, 0.29, 0.25)	4.27
SSM5	(0.24, 0.21, 0.75)	(0.26, 0.29, 0.25)	3.30

Model	Fe_{Mg} ($Mg^{2+}\rightarrow Fe^{3+}$)	Fe_{Si} ($Si^{4+}\rightarrow Fe^{3+}$)	$d(Fe_{Mg}–Fe_{Si})$/Å
CCM1	(0.51, 0.46, 0.75)	(0.50, 0.25, 0.50)	2.58
CCM3	(0.49, 0.54, 0.25)	(0.50, 0.25, 0.50)	3.12
CCM5	(0.01, 0.96, 0.75)	(0.50, 0.25, 0.50)	5.47