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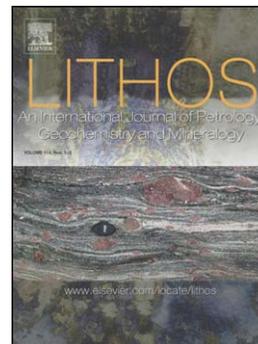
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Electronic spin state of Fe,Al-containing MgSiO₃ perovskite at lower mantle conditions

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Abstract

We have investigated silicate perovskite with composition Mg_{0.83}Fe_{0.21}Al_{0.06}Si_{0.91}O₃ relevant for the lower mantle at pressures up to 81 GPa and temperatures up to 2000 K using conventional Mössbauer spectroscopy and synchrotron Nuclear Forward Scattering (NFS) combined with double-sided laser heating in a diamond anvil cell. Room temperature Mössbauer and NFS spectra at low pressure are dominated by high-spin Fe²⁺, with minor amounts of Fe³⁺ and a component assigned to a metastable position of high-spin Fe²⁺ in the A-site predicted by computational studies. NFS data show a sharp transition (< 20 GPa) from high-spin Fe²⁺ to a new component with extremely high quadrupole splitting, similar to previous studies. Mössbauer data show the same transition, but over a broader pressure range likely due to the higher pressure gradient. The new Fe²⁺ component is assigned to intermediate-spin Fe²⁺, consistent with previous X-ray emission studies. NFS data at high temperatures and high pressures comparable to those in the lower mantle are consistent with the presence of Fe²⁺ only in the intermediate-spin state and Fe³⁺ only in the high-spin state. Our results are therefore consistent with the occurrence of spin crossover only in Fe²⁺ in Fe-, Al-containing perovskite within the lower mantle.

Keywords: silicate perovskite; Mössbauer spectroscopy; Nuclear Forward Scattering; lower mantle

1. Introduction

Magnesium silicate perovskite (Pv) is considered to be the most abundant constituent of the Earth's lower mantle with stability from a depth of 660 km to approximately 2700 km, which is several hundred kilometers above the core-mantle boundary (Liu, 1976). Pv incorporates notable amounts of iron and aluminum (5-10 mol%) into its structure (e.g., Lee et al., 2004). While the properties and behavior of pure MgSiO_3 Pv are mostly understood, the effects of these additional cations remain controversial.

The electronic spin state of iron in different valence states in Pv can strongly influence many properties of the Earth's interior such as thermal conductivity (Badro et al., 2004), electrical conductivity (Ohta et al., 2010; Potapkin et al., 2013), thermodynamic properties (Frost et al., 2004; McCammon, 1997). An accurate determination of the Fe spin state in Pv is complicated by the presence of two different crystallographic sites (a large distorted 8-12-coordinated site, hereafter referred to as A, and a smaller relatively undistorted octahedral site, hereafter referred to as B). Iron occurs both as ferrous (Fe^{2+}) and ferric (Fe^{3+}) in Fe-, Al-containing magnesium silicate perovskite (FeAlPv), with $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios up to at least 60% (Frost et al., 2004; McCammon, 1997), that strongly depend on the Al concentration (McCammon et al., 2004).

While it is well accepted that Fe^{2+} occupies exclusively the A-site, the site occupancy of Fe^{3+} is still under debate. Ferric iron has been observed to occupy either exclusively the A-site (McCammon et al., 2008; Potapkin et al., 2013) or both the A- and B-sites (Badro et al., 2004; Catalli et al., 2011, 2010; Hummer and Fei, 2012). Several studies have additionally predicted an exchange of Fe^{3+} from the A- to the B-site at high pressures (Catalli et al., 2011, 2010; Fujino et al., 2012); however the possibility of such exchange was disproved by recent single-crystal X-ray diffraction studies conducted at high pressure and high temperature (Glazyrin et al., 2013; Kuppenko et al., 2012).

The spin state of iron in iron-containing magnesium silicate perovskite (FePv) as well as in FeAlPv is also a matter of debate. Some studies conclude that Fe^{3+}_A undergoes high-spin (HS) to low-spin (LS) crossover (Jackson, 2005; Li et al., 2006), although the majority of studies do not observe spin

crossover in Fe^{3+}_A (Catalli et al., 2011, 2010; Fujino et al., 2012; Lin et al., 2012; McCammon et al., 2008; Potapkin et al., 2013). Meanwhile there is a general consensus that Fe^{3+}_B undergoes HS to LS crossover at mantle pressures in studies where Fe^{3+} is reported to occupy the B site (Catalli et al., 2011, 2010; Fujino et al., 2012; Lin et al., 2012). There is also general agreement that Fe^{2+} behavior undergoes a dramatic change at mantle pressures through the appearance of a new component with extremely high quadrupole splitting in Mössbauer spectra at high pressure (reviewed by McCammon et al., 2013), even though there are conflicting interpretations of this change: HS to intermediate-spin (IS) crossover (Lin et al., 2008; McCammon et al., 2010, 2008; Potapkin et al., 2013), HS to LS crossover (Badro et al., 2004) or a structural modification of the local environment (Lin et al., 2012).

Numerous theoretical studies have been made that examine the spin behavior of iron in different valence states and different crystallographic sites, but with often conflicting results (Bengtson et al., 2009, 2008; Caracas et al., 2010; Hsu et al., 2011, 2010; Li, 2005; Stackhouse et al., 2007; Umemoto et al., 2010; Zhang and Oganov, 2006). However one point on which all computational models agree in the instability of IS Fe^{2+} at all lower mantle pressures, which is in conflict with experimental results that show a decrease in the unpaired spin density of iron in FePv and FeAlPv (reviewed by McCammon et al., 2013).

Despite the many investigations, a systematic study of FeAlPv with mantle composition at mantle conditions is still lacking. Moreover all predictions of FeAlPv behavior at lower mantle conditions have been inferred by extrapolation of data measured at ambient temperatures or from *ab initio* calculations. Here we report the first *in situ* Nuclear Forward Scattering (NFS) study of FeAlPv with composition $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$ at pressure and temperature conditions of the lower mantle. The study is complemented by NFS and conventional Mössbauer spectroscopy measurements at high pressure and ambient temperature that provide high resolution data for the analysis of individual site and valence state contributions.

2. Experimental methods

The sample of FeAlPv was synthesized in the multianvil press from a mixture of MgO, SiO₂, Al₂O₃, ⁵⁷Fe₂O₃ (90% enriched) starting materials in a rhenium capsule at 26 GPa and 1800°C for 30 min. Before synthesis, the starting material was heated at 1273 K for 1 day in a CO-CO₂ gas-mixing furnace, in which oxygen fugacity was controlled at $\log f_{\text{O}_2} = -21$ to reduce Fe³⁺ to Fe²⁺. After the multianvil experiment, the recovered sample was characterized at ambient conditions using both the electron microprobe (JEOL, JXA-8200, under the operating conditions 15 kV and 15 nA) and Mössbauer spectroscopy. Results of electron microprobe analysis showed that the chemical composition of the sample is Mg_{0.828(18)}Fe_{0.208(13)}Al_{0.059(2)}Si_{0.911(23)}O₃ and Mössbauer spectroscopy showed the iron to be predominantly in the ferrous state ($\sim 20\%$ Fe³⁺/ΣFe).

Mössbauer spectra were recorded at room temperature in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 370 MBq ⁵⁷Co high specific activity source in a 12 μm thick Rh matrix with active dimensions of 500 μm x 500 μm. The velocity scale was calibrated relative to 25 μm thick α-Fe foil using the positions certified for (former) National Bureau of Standards standard reference material no. 1541; line widths of 0.36mm/s for the outer lines of α-Fe were obtained at room temperature. Spectra took 3-4 days each to collect. Centre shifts were calculated relative to α-Fe. Spectra were fitted using a full transmission integral with a normalized Lorentzian source lineshape using the MossA software package (Prescher et al., 2012). Mössbauer spectra of the FeAlPv sample were collected up to 72 GPa at room temperature (Fig. 1). The sample was annealed preceding data collection at all pressures above 30 GPa in order to relax stress.

Nuclear Forward Scattering (NFS) data were collected on the Nuclear Resonance (ID18) beamline (Rüffer and Chumakov, 1996) of the European Synchrotron Radiation Facility during operation in 4-bunch mode, with the beam focused to 6 μm vertical and 11 μm horizontal dimension using Kirkpatrick-Baez mirrors. All of the spectra were collected over 10-60 min each. NFS data were fit using the CONUSS package (Sturhahn, 2000). The centre shift was determined relative to a K₂Mg⁵⁷Fe(CN)₆ reference absorber. Room temperature NFS spectra were collected up to 81 GPa.

Additionally at 43, 63 and 81 GPa the sample was laser heated at 1200K-2000K and spectra were collected during laser heating.

High-pressure measurements were carried out using cylindrical-type diamond anvil cells (Kantor et al., 2012). Samples of FeAlPv were loaded together with a few ruby balls used as a pressure marker. The diamond anvils used had 250 μm culets. A 200 μm thick Re gasket was pre-indented to about 30 μm thickness and a 125 μm hole was drilled in the centre. Samples were loaded at room temperature and Ne was loaded as a pressure medium at a pressure of 1.2 kbar (Kurnosov et al., 2008).

For high temperature measurements a modified version of the portable double-sided laser heating system was used (Dubrovinsky et al., 2010, 2009; Kuppenko et al., 2012). The setup was installed at the ID18 beamline and consists of two SPI modulated fiber lasers (wavelength 1071 nm) with 100W maximum power and two laser heating heads. The system implements π -shapers (Prakapenka et al., 2008) that convert an initial Gaussian-shaped beam to one with a flat top distribution with ~ 50 μm FWHM in order to provide homogeneous heating. The measurement of temperature was performed with the standard spectroradiometry method (Shen et al., 2010) using an Ocean Optics QE650000 spectrometer.

3. Results

At low pressures the Mössbauer spectra were fitted to three doublets, one assigned to HS Fe³⁺ with ~ 1 mm/s quadrupole splitting (QS) and ~ 0.35 mm/s centre shift (CS) and two assigned to HS Fe²⁺ (QS ~ 1.6 mm/s and ~ 2.5 mm/s, both CS ~ 1 mm/s), based on their hyperfine parameters. Up to 37 GPa the spectra remain nearly unchanged with only moderate decrease of the CS and increase of the QS of all components (Fig. 2). At 37 GPa a new component begins to emerge, similar to all previous Mössbauer studies of Al-free FePv (Lin et al., 2008; McCammon et al., 2010, 2008; Narygina et al., 2010; McCammon et al., 2013), which is accompanied by an intensity reduction of the HS low QS

Fe^{2+} doublet. The new component has $QS > 3$ mm/s and $CS \sim 1$ mm/s. With further pressure increase the relative area ratio of the new component grows at the expense of the HS low QS doublet. The relative area ratios of the HS high QS Fe^{2+} ($\sim 10\%$) and Fe^{3+} ($\sim 20\%$) components remain essentially unchanged as a function of pressure. As discussed further below, we regard the two HS Fe^{2+} components to correspond to the two different configurations of Fe^{2+} in the A-site first introduced by Hsu et al. (2010). Based on arguments already presented in McCammon et al. (2008), Narygina et al. (2010) and McCammon et al. (2013), the new Fe^{2+} component is assigned to IS Fe^{2+} . The zero pressure NFS spectrum of FeAlPv is dominated by quantum beats arising from the HS Fe^{2+} component with $QS \sim 1.6$ mm/s and $CS \sim 1$ mm/s (Fig. 3). The deviation of the fit at 0 GPa can be due to additional components that are present only at low pressure, such as from a small degree of amorphization due to the metastability of FeAlPv at ambient conditions. These components are not normally resolvable in a conventional Mössbauer spectrum due to peak overlap. Good fits to the NFS spectra are obtained above 35 GPa after annealing at high temperatures, and hyperfine parameters and the relative abundance of components are in good agreement with our Mössbauer data. At 35 GPa high frequency beats begin to appear, arising from a new high QS component. The relative abundance of the dominant low pressure HS Fe^{2+} component starts to decrease from this pressure and reduces to zero at 58 GPa (Fig. 2, 3). The QS of the new component increases rapidly from 3.0 mm/s at 35 GPa to 4.2 mm/s at 57 GPa. Upon further compression no further changes of the spectra are observed.

High temperature NFS spectra of FeAlPv (Fig. 4) are more challenging to fit. The approach that is most consistent with all available information comprises two QS components, one with $QS \sim 0$ and $CS \sim -0.7$ mm/s, and one with $QS \sim 0.5-1.2$ mm/s and $CS \sim 0$ mm/s. The relative abundance of the near zero QS component is equal within uncertainty to the proportion of Fe^{3+} , while likewise the relative abundance of the second component is equal to the total Fe^{2+} proportion. After temperature quenching, the relative abundance and hyperfine parameters of all components return to their original values before heating.

The misfit seen in the fits in Fig. 4 can be attributed to several factors. The spectra are fit to two components with distinct hyperfine parameters; however both CS and QS will vary due to small deviations of temperature during data collection. The data therefore represent a superposition of multiple spectra arising from slightly different hyperfine parameters. However incorporating such an approach in the fitting process is not statistically meaningful due to the increased number of degrees of freedom, even though the conclusions would be unchanged. We emphasize the robustness of the fits shown in Fig. 4 despite their apparent flat appearance, and that the derived hyperfine parameters fulfill all of the required consistency checks (trends in CS, QS and relative abundance with pressure and temperature). Nevertheless we explored other possible fits of the high temperature NFS data and present one alternative in the supplementary material.

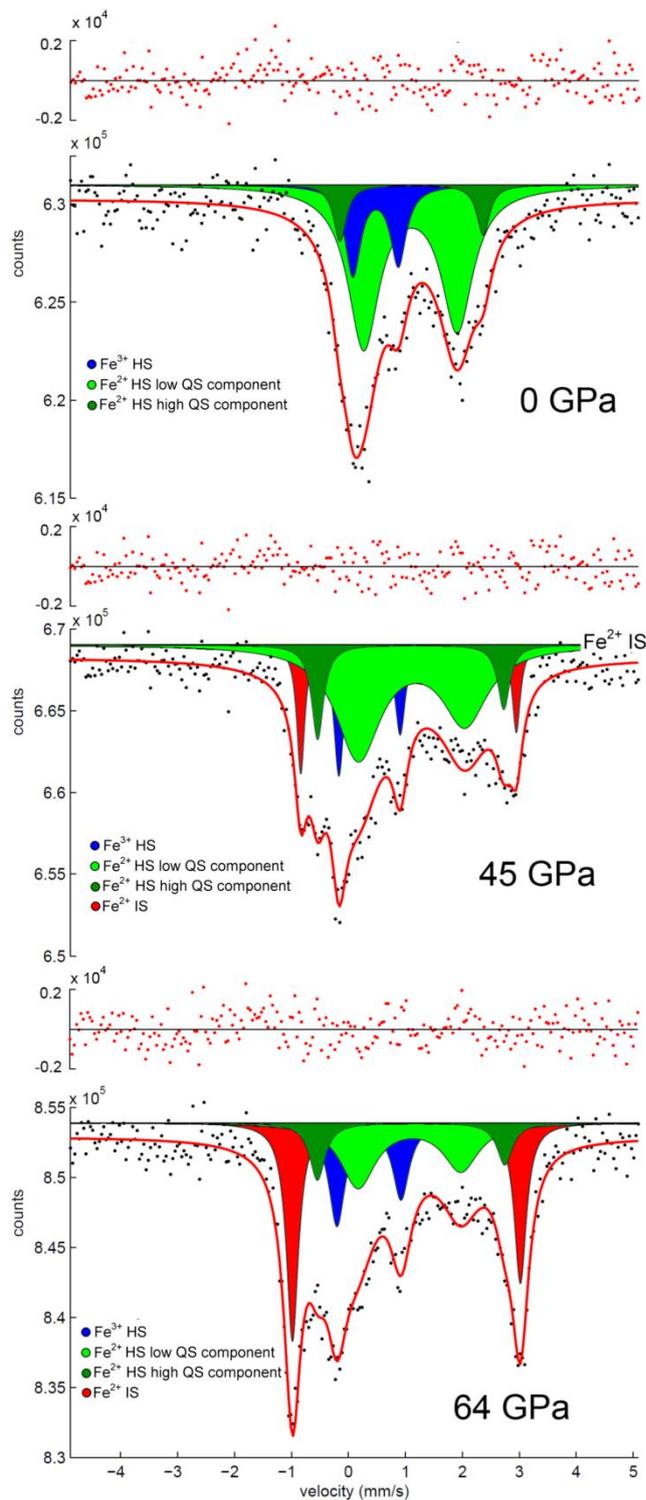
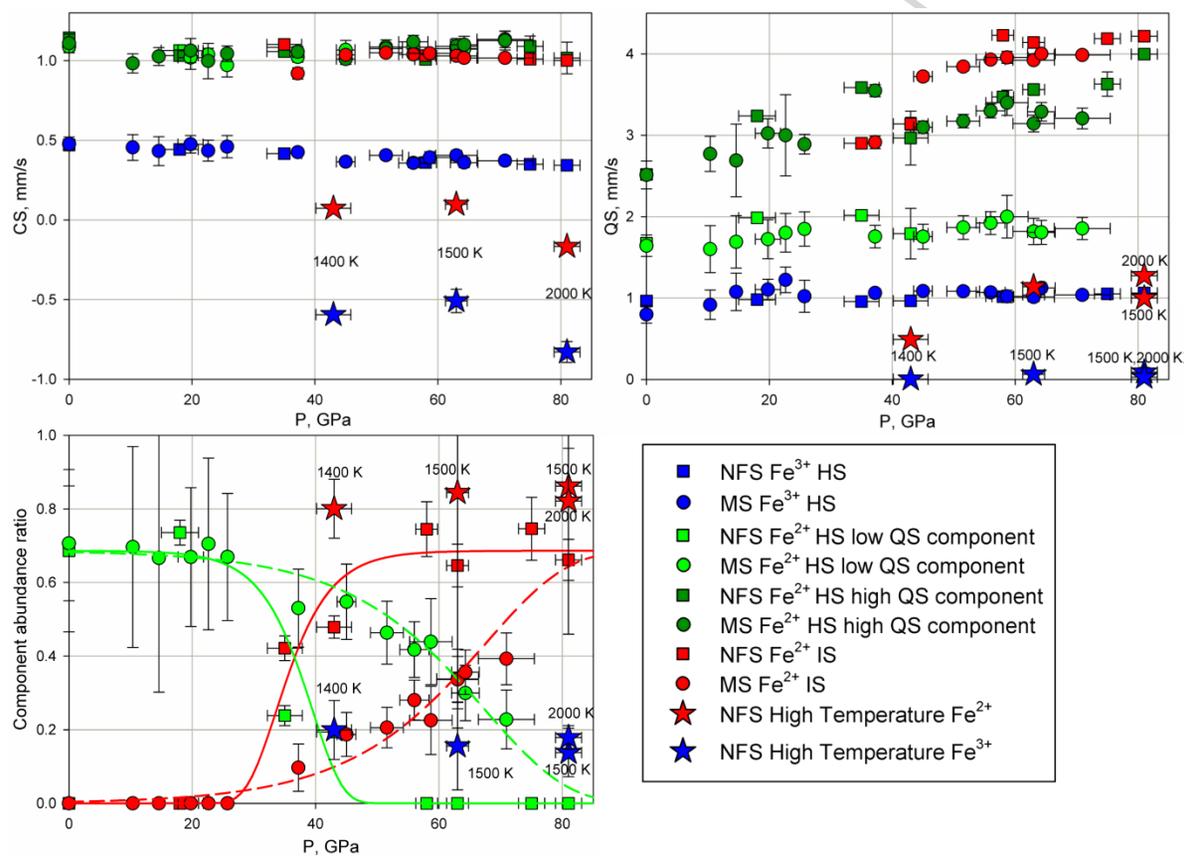


Fig. 1. Selected high-pressure conventional Mössbauer spectra of $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$ perovskite at room temperature. The solid lines show the theoretical fit and the residual is indicated above each spectrum.

Fig. 2. Effect of pressure on the hyperfine parameters of $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$ perovskite as measured by Mössbauer spectroscopy (MS) and nuclear forward scattering (NFS): (a) Centre shift (CS); (b) Quadrupole splitting (QS); (c) Relative abundance. Green and red curves indicate the trends of the relative abundance for the Fe^{2+} high-spin (HS) low QS and Fe^{2+} intermediate-spin (IS) components, respectively, while the dashed and solid curves indicate the trends for the MS and NFS data, respectively. For clarity the relative abundance of the Fe^{3+} and HS high QS Fe^{2+} components are not shown, which remain relatively constant at all pressures at values of 20% and 10%, respectively.



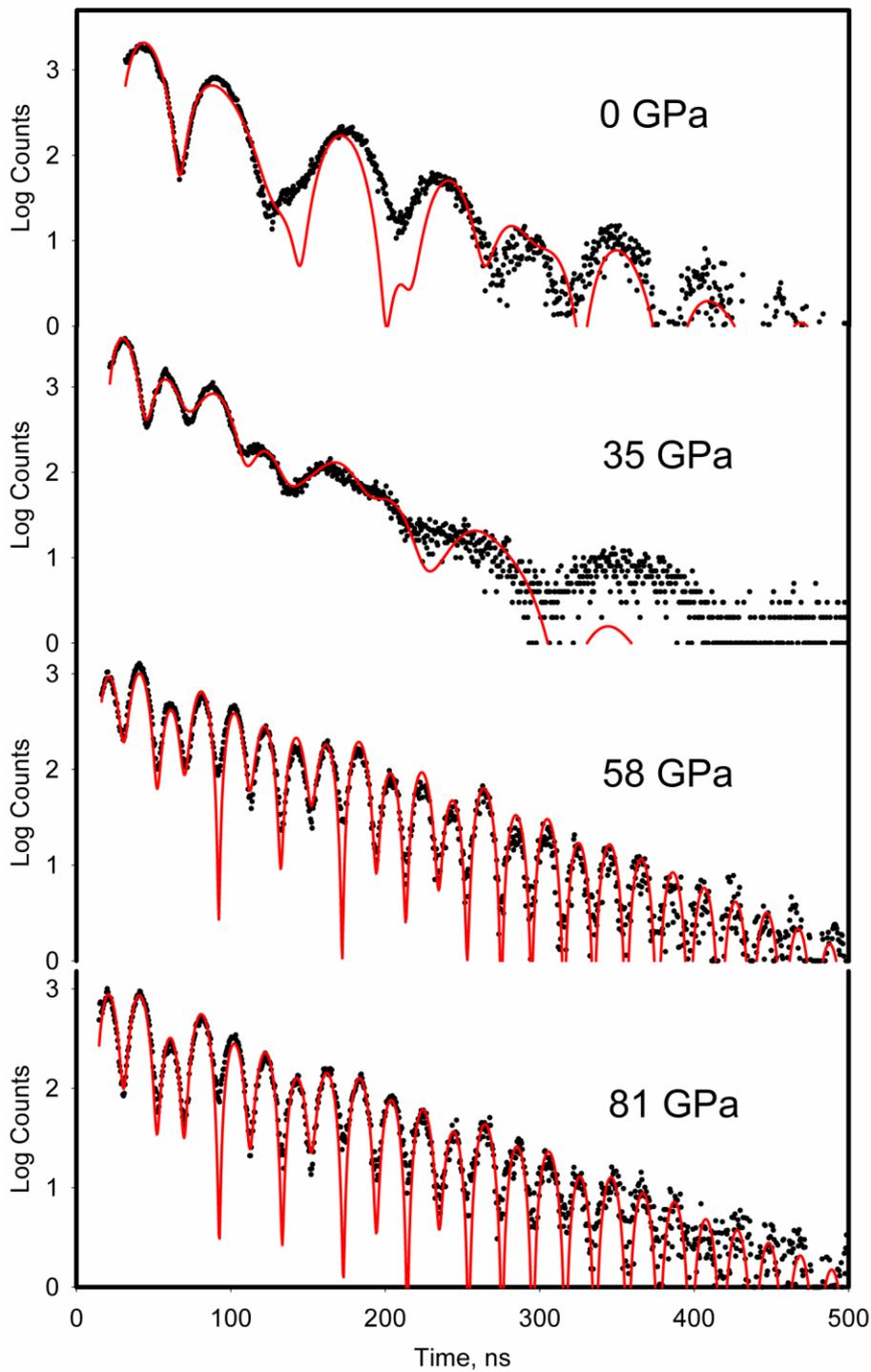


Fig. 3. Selected high-pressure NFS spectra of $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$ perovskite at room temperature. The solid lines show the theoretical fits.

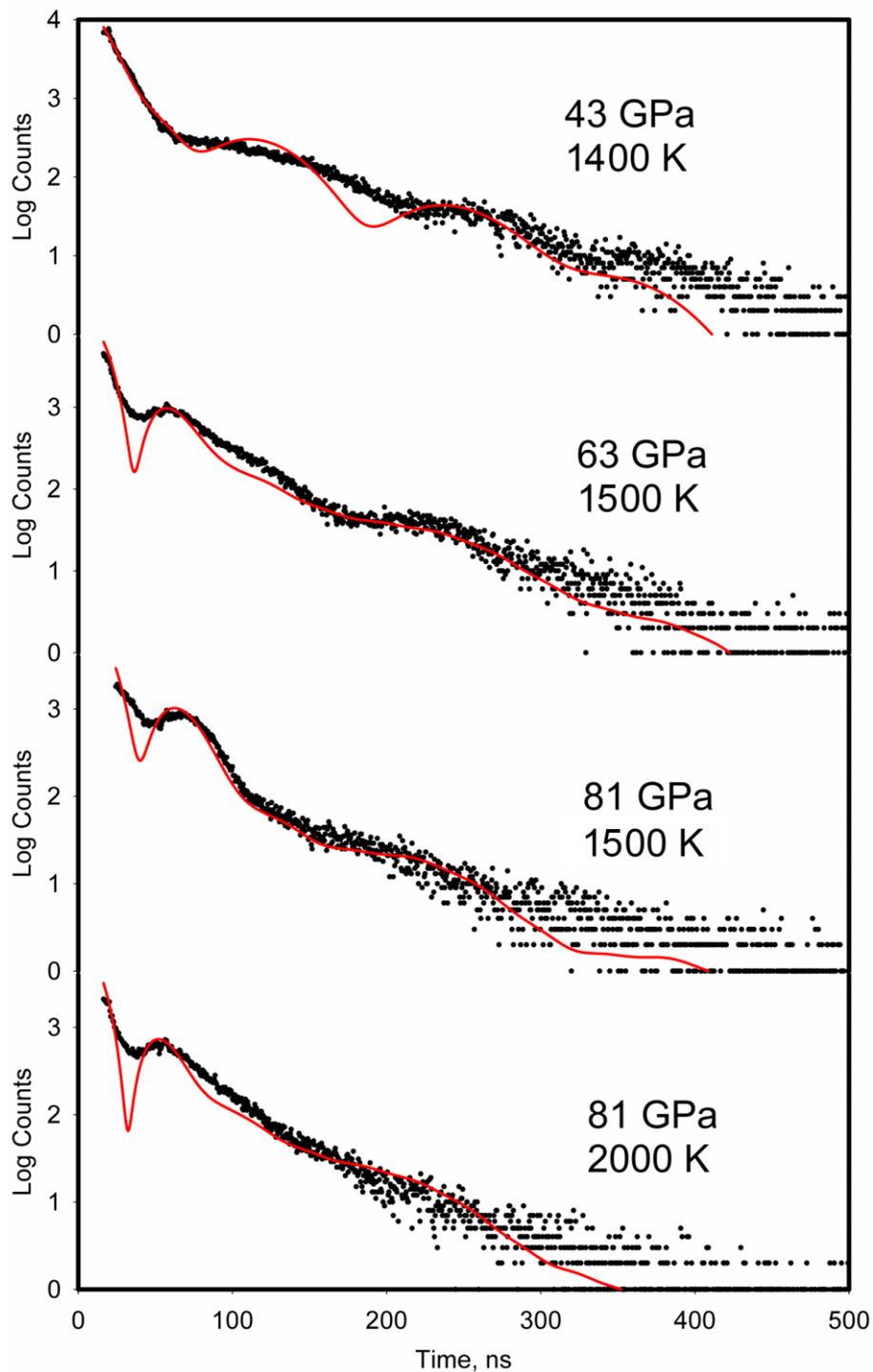


Fig. 4. High-pressure NFS spectra of $\text{Mg}_{0.83}\text{Fe}_{0.21}\text{Al}_{0.06}\text{Si}_{0.91}\text{O}_3$ perovskite at high temperature. The solid lines show the theoretical fits.

4. Discussion

There is an ongoing debate regarding the nature of Fe^{2+} in FePv and FeAlPv at high pressure. There is general agreement that a dramatic change occurs in Mössbauer and NFS spectra through the appearance of a new high QS component with increasing pressure, but the community is polarised as to whether this represents HS to IS crossover, or stable HS Fe^{2+} undergoing a change in the local environment of the A-site. The latter hypothesis is particularly favoured by computational studies that show the presence of multiple discrete atomic configurations of Fe^{2+} in the A-site that has been postulated to explain observations in Mössbauer and NFS data (Bengtson et al., 2009; Hsu et al., 2011, 2010; Umemoto et al., 2010). Our room temperature FeAlPv spectra, similar to those published in the literature for both FePv and FeAlPv with similar compositions (McCammon et al., 2010, 2008; Narygina et al., 2009; Potapkin et al., 2013) and derived hyperfine parameters that fall within ranges defined by previous data (reviewed by McCammon et al. 2013), provide an explanation for these results from computational studies.

Ab initio calculations have reported that Fe^{2+} may occupy metastable positions in addition to the dominant position of lowest energy within the large A-site cage in the perovskite structure, and thus Fe^{2+} may experience different electrical field gradients. It is therefore possible for iron to have the same spin state and crystallographic coordination, yet different QS (Bengtson et al., 2009; Hsu et al., 2011, 2010; Umemoto et al., 2010). We suggest that our Mössbauer spectra show evidence for two HS configurations, namely that the HS low QS component (light green in Figs. 1 and 2) corresponds to the stable position of Fe^{2+} within the A-site and that the HS high QS component (dark green in Figs. 1 and 2) corresponds to a metastable position of Fe^{2+} within the A-site. Thus at ambient conditions, ~10% of Fe^{2+} atoms occupy a metastable position.

We observe a dramatic difference in the behavior of HS high QS and low QS Fe^{2+} components with pressure (Fig. 2). The QS of the HS high QS Fe^{2+} component (dark green in Figs. 1 and 2) increases gradually with pressure over the entire pressure range and its abundance ratio (~ 10% of total Fe)

remains unchanged within experimental error at all examined pressures. In contrast the relative abundance of the HS low QS Fe^{2+} component (light green in Figs. 1 and 2) starts to decrease at 35 GPa at the expense of increasing relative abundance of a new Fe^{2+} component with high QS (red in Figs. 1 and 2). The transition to the new component is much sharper in the NFS data (35-55 GPa) compared to the Mössbauer data (35-85 GPa), which we attribute to the well focused nature of the synchrotron beam which significantly reduces pressure gradients in the radial direction, in contrast to conventional Mössbauer spectroscopy where absorption spectra are acquired from the entire pressure chamber due to the significantly larger beam size. X-ray diffraction studies show no significant increase of structural distortion in this pressure range (Boffa Ballaran et al., 2012; Catalli et al., 2011, 2010; Lundin et al., 2008); hence it is unlikely that the transition is caused by a change in the structure. The most plausible cause for the change in relative abundance of the Fe^{2+} components is spin crossover, and further arguments in favour of assignment of the new component to IS Fe^{2+} are discussed in the literature (reviewed by McCammon et al., 2013).

In the high temperature NFS spectra the component with almost zero QS is inferred to be due to Fe^{3+} , since it is well known that temperature causes a decrease in QS of HS Fe^{3+} (Kantor et al., 2009) and its relative abundance is equivalent to the value for Fe^{3+} in the room temperature spectra. The second component in the high temperature NFS spectra is therefore assigned to Fe^{2+} because of consistency with the total Fe^{2+} abundance. Previous studies have demonstrated that temperatures around 1000 K promote HS to IS crossover and stabilize the IS state relative to the HS state (Lin et al., 2008; McCammon et al., 2008), and our data are consistent with these observations.

The CS values provide a measure of the mean temperature of the sample. There are two main contributions to the CS – isomer shift and second order Doppler shift (SOD) (e.g., Greenwood and Gibb, 1971; Housley and Hess, 1966). The SOD varies approximately linearly with temperature for both Fe^{2+} and Fe^{3+} components in the high-temperature Debye limit, which can be estimated as $\Delta\nu = -7.3 \cdot 10^{-4}$ mm/s/K. Therefore the SOD provides a measure of the temperature of exactly those atoms

which are responsible for the spectral signal. We obtain temperatures based on the change in CS between spectra collected under hot and cold conditions (assuming that the isomer shift does not change with temperature) of 1690(13) K, 1530(50) K and 1900(3) K for the spectra at 43 GPa, 63 GPa and 81 GPa, respectively, which is in good agreement with spectroradiometry measurements (1400 K, 1500 K and 2000 K, respectively). Our previous experiments (Kupenko et al., 2012) showed that large discrepancies can occur between optically measured temperatures and temperatures deduced from the SOD in samples that are thick or where the laser and X-ray beams are not well aligned. The good agreement between the temperatures determined by the two different methods in this study therefore indicates that the internal temperature of the sample is close to that of the surface temperature, and hence that the double-sided laser heating setup provides homogeneous heating of the sample.

5. Conclusion

At ambient temperature and pressures above 35 GPa Fe^{2+} in FeAlPv occurs predominantly in a component assigned to the IS state with a minor proportion assigned to the HS state located in a metastable next nearest neighbor environment position within the A-site. The component assigned to IS Fe^{2+} is stable at pressures and temperatures corresponding to those in the lower mantle and we observe no evidence of spin crossover of Fe^{3+} up to 81 GPa and 2000 K. We therefore conclude that iron in FeAlPv in the lower mantle occurs almost entirely as Fe^{2+} in the IS state and Fe^{3+} in the HS state.

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Figure captions

Fig. 1. Selected high-pressure conventional Mössbauer spectra of Mg_{0.83}Fe_{0.21}Al_{0.06}Si_{0.91}O₃ perovskite at room temperature. The solid lines show the theoretical fit and the residual is indicated above each spectrum.

Fig. 2. Effect of pressure on the hyperfine parameters of Mg_{0.83}Fe_{0.21}Al_{0.06}Si_{0.91}O₃ perovskite as measured by Mössbauer spectroscopy (MS) and nuclear forward scattering (NFS): (a) Centre shift (CS); (b) Quadrupole splitting (QS); (c) Relative abundance. Green and red curves indicate the trends of the relative abundance for the Fe²⁺ high-spin (HS) low QS and Fe²⁺ intermediate-spin (IS) components, respectively, while the dashed and solid curves indicate the trends for the MS and NFS data, respectively. For clarity the relative abundance of the Fe³⁺ and HS high QS Fe²⁺ components are not shown, which remain relatively constant at all pressures at values of 20% and 10%, respectively.

Fig. 3. Selected high-pressure NFS spectra of Mg_{0.83}Fe_{0.21}Al_{0.06}Si_{0.91}O₃ perovskite at room temperature. The solid lines show the theoretical fits.

Fig 4. High-pressure NFS spectra of Mg_{0.83}Fe_{0.21}Al_{0.06}Si_{0.91}O₃ perovskite at high temperature. The solid lines show the theoretical fits.

HIGHLIGHTS

- We investigate (MgFe)(SiAl)O₃ perovskite at lower mantle pressures and temperatures
- At 300 K a transition from high- to intermediate-spin Fe²⁺ is observed at ~35 GPa
- The intermediate-spin Fe²⁺ is stable at lower mantle conditions
- We observe no evidence of spin crossover of Fe³⁺ up to 81 GPa and 2000 K