Spin crossover in (Mg,Fe)O: A Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy data

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A high-pressure Mössbauer spectroscopy study of a spin crossover in $(Mg_{0.8}Fe_{0.2})O$ ferropericlase is presented. A low-spin subspectral component appears at about 55 GPa, but there is a significant pressure region over which both high-spin and low-spin states are stable, before the high-spin component disappears completely above 100 GPa. These results are only partly consistent with recent x-ray emission spectroscopy (XES) results, and the discrepancy is likely due to assumptions used in analyzing the XES data that are not fully satisfied at high pressure. An alternative method of XES data analysis based on spectral decomposition is presented, which is fully consistent with the Mössbauer data and allows the extraction of additional information from the XES data.

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Ferropericlase $(Mg_{1-x}Fe_x)O$ with $x \sim 0.2$ is one of the main minerals constituting the Earth's lower mantle, and its high-pressure and high-temperature properties are of great importance for the Earth sciences. Spin-state changes of Fe^{2+} in ferropericlase will influence many of its properties, including bulk density, elasticity, and heat and electrical conductivity. For these reasons, a knowledge of the pressure dependence and characteristics of the spin crossover transition in ferropericlase is necessary for understanding the constitution and properties of the Earth's lower mantle. This study presents results from a high-pressure Mössbauer spectroscopy study of spin crossover in ferropericlase and proposes a revised analysis of recent x-ray emission measurements[1] of a similar material in view of the experimental data.

Until a few years ago, there were only two methods that could reliably detect changes in iron spin state at high pressures in samples within a diamond anvil cell (DAC): optical and near-infrared absorption spectroscopy and Mössbauer spectroscopy (MS). Recently, with the rapid development of synchrotron radiation facilities, the ability to measure high-resolution x-ray emission spectra of the Fe $K\beta$ line in the DAC appeared.[1–6] X-ray emission spectroscopy (XES) contains information of the electronic state of iron, and, in particular, of its spin state (presence or absence of $3d$-electron magnetic moments). The ability of XES to measure the spin crossover of iron at high pressures was demonstrated for metallic iron[2] and iron sulphide FeS (Ref. 3), and in both cases the transition pressures were in good agreement with those obtained using Mössbauer spectroscopy.

Recently, XES measurements of ferropericlase were reported[1] and showed a high-spin (HS) to low-spin (LS) transition in Fe^{2+} above 50 GPa; $Mg_{0.75}Fe_{0.25}O$ and $Mg_{0.6}Fe_{0.4}O$ were found to transform from 54 to 67 GPa and from 84 to 102 GPa, respectively. Motivated by the significant implications of the transition for the properties of the Earth's lower mantle, we undertook an independent study of ferropericlase using Mössbauer spectroscopy.

The methodology of Mössbauer spectroscopy measurements in the DAC at high pressures is given elsewhere.[7] Briefly, we used diamonds with 250 μm culet size and a Re

gasket that was preindented to $\sim$25 μm and then drilled with a 125-μm-diam hole. Several small ($\sim$1 μm diam) ruby chips were loaded together with the sample for pressure calibration and evaluation of the pressure gradient.[8] The sample was a synthetic powder $(Mg_{0.8}Fe_{0.2})O$ ferropericlase with $\sim$60% enrichment with ^{57}Fe. We recorded conventional transmission Mössbauer spectra as a function of pressure, which show a quadrupole-split doublet at low pressure in agreement with existing data. The center shift of the absorption is consistent with high-spin Fe^{2+}. Above $\sim$50 GPa a new spectral component appears, whose relative area increases with pressure (Fig. 1). The new component shows a significantly lower center shift compared to HS Fe^{2+} and negligible quadrupole splitting, consistent with a low-spin state of Fe^{2+}. The relative area of the LS component, which is related to its abundance, increases with increasing pressure until just over 100 GPa, where the LS component constitutes 100% of the spectrum (Fig. 1). To represent the change in spin state, the relative areas of the HS ($S=2$) and LS ($S=0$) components can be recalculated into an average spin number S (Fig. 2). Details of Mössbauer spectra processing and Fe^{2+} hyperfine parameters for the HS and LS states are given in the online supplementary materials.[9] The onset of the Fe^{2+} spin transition in ferropericlase is consistent between XES and Mössbauer data for samples with similar composition, but while the pressure interval over which the transition occurs is relatively narrow in the XES data ($<$15 GPa), it is relatively broad in the Mössbauer data (ca. 50 GPa), which show the HS state to persist up to significantly higher pressures (Fig. 2). The width of the pressure interval over which the spin transition occurs has significant implications for the properties of the lower mantle, the main and most important being that spin crossover in ferropericlase will not cause a sharp discontinuity in any physical property of the mantle. This motivates a closer look at both the Mössbauer and XES data.

Experimental artifacts such as pressure gradients and thickness effects can be ruled out as causing the wide pressure interval of the spin transition in the Mössbauer data. Pressure gradients were determined for each measurement
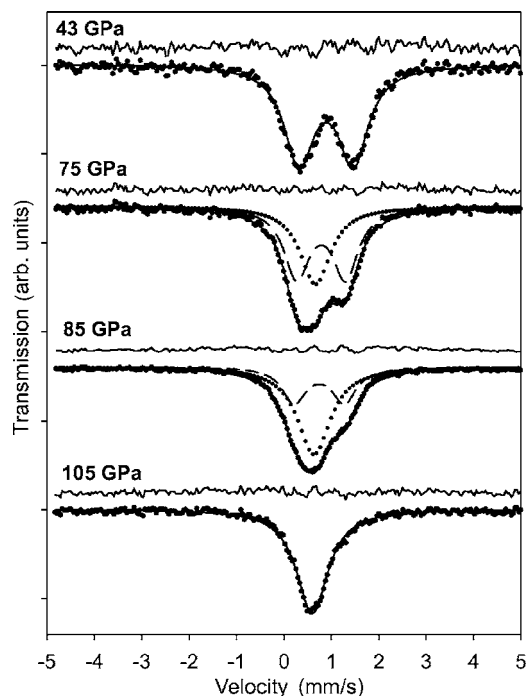
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FIG. 1. Room-temperature Mössbauer spectra of $(Mg_{0.80}Fe_{0.20})O$ ferropericlase at different pressures: (solid circles) experimental points; (solid lines) total fit; (dashed lines) high-spin Fe^{2+} absorption; (dotted lines) Fe^{2+} low spin absorption. The residual is shown above each spectrum, and the velocity scale is relative to α-Fe at ambient conditions.

FIG. 2. (Color online) Average spin number S of ferropericlase as a function of pressure. $(Mg_{0.80}Fe_{0.20})O$ was studied using Mössbauer spectroscopy (this study, solid circles); $(Mg_{0.75}Fe_{0.25})O$ was studied using XES (Ref. 1) [open diamonds—comparative analysis, red (dark gray) triangles—decompositional analysis in this study].

based on the fluorescence of ruby chips located in the center and at the edge of the sample chamber, and were not larger than 2–6 GPa. We accounted for thickness effects (the dimensionless effective Mössbauer thickness of the sample was estimated to be ~15 at pressures during the spin crossover) by using the full transmission integral when fitting the Mössbauer data,[9] which provides an accurate determination of low-spin abundance. We therefore consider the Mössbauer data to accurately represent the stability of the HS and LS states of Fe^{2+}. In fact, the characteristics of spin crossover in ferropericlase (broad transition region, smooth and continuous change of low-spin fraction, absence of hysteresis) are consistent with the most common type of spin transition in divalent iron compounds (the so-called type a);[10] in other words, the broad and smooth transition is not unusual for Fe^{2+}.

Mössbauer spectroscopy is a mature technique for spin transition measurements with a well-established theoretical basis.[10,11] It serves as a primary standard for the relatively young x-ray emission spectroscopy technique, where methods of data analysis are still evolving. Fe $K\beta$ XES data consist of a strong asymmetric $K\beta$ peak at ~7058 eV. At ~7044 eV a weak $K\beta'$ peak is observed, which appears due to the magnetic moments of Fe $3d$ electrons. Therefore, it should disappear for a LS state of Fe^{2+}. Traditionally, experimental XES data of a material that is believed to undergo a spin crossover at high pressures have been analyzed by subtraction of the highest pressure spectrum from all the rest, with further examination of the residual peaks.[1–6] This type
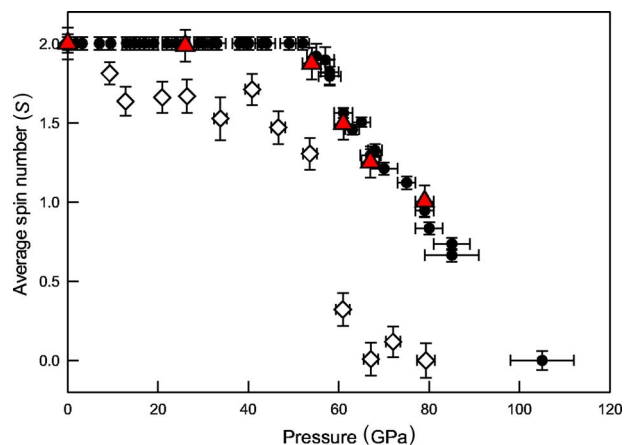
of analysis involves the following assumptions: (i) At ambient (initial) pressure the material is in a purely HS state; (ii) at highest (final) pressure the material is in a purely LS state; (iii) the energy separation between the $K\beta'$ and $K\beta$ peaks remains constant with pressure.

In the case of ferropericlase the energy difference ΔE between the $K\beta'$ and $K\beta$ peaks changes significantly with pressure, which leads to a misinterpretation of the XES data.[9]

We propose a more consistent method for XES data analysis. Currently one of the most frequently used methodologies for spectral data analysis is a least-squares decomposition of the spectrum into several peaks of a given shape. This type of analysis has been applied successfully to XES Mn-$K\beta$ emission edge data for various manganese com-
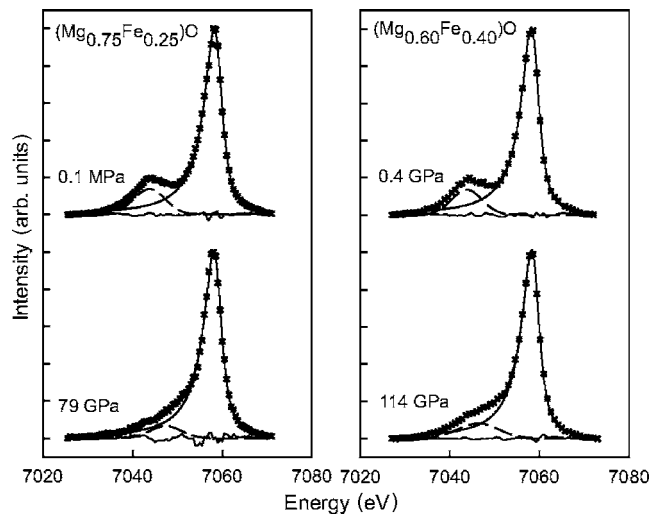

FIG. 3. Experimental XES data of $(Mg_{0.75}Fe_{0.25})O$ at 0.1 MPa and 79 GPa (left) and $(Mg_{0.60}Fe_{0.40})O$ at 0.4 and 114 GPa (right) fitted using the decompositional method (this study): (crosses) experimental absorption; (dashed line) Gaussian $K\beta'$ peak; (solid line) main Pearson IV $K\beta$ peak. Residuals are shown under each spectrum. Experimental data are from Ref. 1.

pounds.[12] In contrast to Mn, however, the main $K\beta$ peak in Fe XES data shows strong asymmetry, so a single Lorentzian peak profile is not appropriate. For the purpose of a spin crossover study, XES data should be deconvoluted into two peaks, corresponding to the $K\beta'$ and $K\beta$ peaks, where the value of peak intensities can be obtained from the least-squares fitting procedure.

The shape of the main asymmetric $K\beta$ peak is defined by a multiple finite state interaction between the $3p$ core and partially occupied $3d$ shell.[1–6] Although all of these interactions could not be accounted for separately, it is nevertheless possible to use a statistical distribution function to model the total effect. We found that the main $K\beta$ peak in ferropericlase XES data[1] could be described using a Pearson IV $I(E)$ function in the form

$$I = \frac{Ac\exp\left[c\tan^{-1}\left(\dfrac{E+\dfrac{Wc}{2}-m}{W}\right)\right]}{W\left[\exp\left(\dfrac{c\pi}{2}\right)-\exp\left(-\dfrac{c\pi}{2}\right)\right]\left[1+\dfrac{\left(E+\dfrac{Wc}{4}-m\right)^2}{W^2}\right]}, \quad (1)$$

where m is the peak position, A is the peak integrated area, W is the peak width, and c is the shape coefficient describing the peak asymmetry. The weak $K\beta'$ peak can be described sufficiently with a simple Gaussian function. Resulting fits of the XES data of $(Mg_{0.75}Fe_{0.25})O$ and $(Mg_{0.60}Fe_{0.40})O$ ferropericlase at the lowest and highest pressures are shown in Fig. 3. The shape of the main $K\beta$ peak (W and c coefficients) was refined only for the lowest pressure spectra, and was then fixed for the high-pressure spectra. Least-squares fitting was performed using PEAKFIT software.

The relative area (in % of total absorption) of the Gaussian $K\beta'$ peak as a function of pressure is shown in Fig. 4(a). At low pressures (i.e., where only HS Fe^{2+} is stable) the area of the $K\beta'$ peak remains constant ($\sim 13\%$) for both ferropericlase compositions. Above ~ 50 GPa in $(Mg_{0.75}Fe_{0.25})O$ the $K\beta'$ integrated intensity starts to decrease and reaches half of its value at 79 GPa. The average spin number S, calculated from the $K\beta'$ peak area, is in perfect agreement with Mössbauer data (Fig. 2). For $(Mg_{0.60}Fe_{0.40})O$ the $K\beta'$ integrated intensity starts to decrease only at the highest pressure (114 GPa). As an independent test of the method, we calculated the total area of each normalized XES spectrum [Fig. 4(a), inset]. The total area is independent of the fitting model, and should not be affected by the relative peak positions and line shapes. The total area should decrease at the point where spin crossover starts as the $K\beta'$ peak begins to lose intensity. As is seen clearly in Fig. 4(a) (inset), the total areas for both ferropericlase compositions decrease at exactly the pressures where spin crossover is determined to occur according to decompositional analysis [Fig. 4(a)].

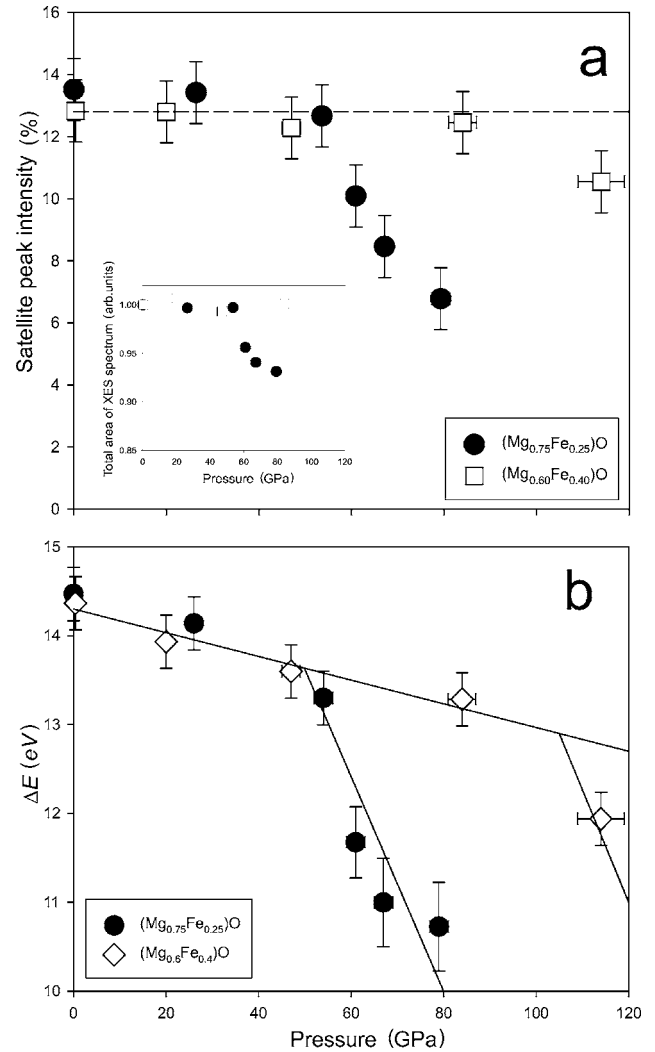Figure 4(b) shows the energy difference between the $K\beta'$

FIG. 4. (a) Area of the satellite $K\beta'$ peak (in % of total absorption) for $(Mg_{0.75}Fe_{0.25})O$ (solid circles) and $(Mg_{0.60}Fe_{0.40})O$ (open squares) ferropericlase. Inset: analytical total area of XES ferropericlase spectra. Note that the trend is identical to that in the main figure. (b) Energy difference between the $K\beta'$ and $K\beta$ peaks of ferropericlase as a function of pressure as determined from decompositional analysis. Experimental data are from Ref. 1.

and $K\beta$ peaks obtained by least-square fitting for the two ferropericlase compositions. ΔE decreases linearly with pressure in the high-spin region [up to 50 GPa for $(Mg_{0.75}Fe_{0.25})O$ and up to ~ 105 GPa for $(Mg_{0.60}Fe_{0.40})O$]. The slope of the line ($\sim -1.3 \times 10^{-2}$ eV/GPa) can, in principle, provide an estimate of the pressure dependence of the exchange integral J, $\delta J/\delta P$. The spin number S starts to decrease at the point of the spin transition, and the slope increases to about -1.2×10^{-1} eV/GPa. The width of the satellite $K\beta'$ peak increases with pressure (Fig. 3), reflecting the increased covalency of Fe-O chemical bonding upon compression due to the stronger overlap of electron wave functions.

Independent analysis of the Lin *et al.*[1] XES data by Rueff using an absolute integrated difference (AID) analysis[13] gives results that are in excellent agreement with results of the present study.[14] The main disadvantage of the AID analy-

sis is the requirement of a reference Fe^{2+} low-spin XES spectrum, in contrast to the decompositional analysis proposed here.

In this study we presented Mössbauer data of $(Mg_{0.8}Fe_{0.2})O$ ferropericlase that show a pressure-induced spin crossover that occurs over a wide pressure interval, in contrast to results of a recent XES study of a similar composition.[1] The width of the pressure interval has significant implications for the properties of the Earth's lower mantle, including bulk density, elasticity, and transport prop-erties. We propose a decompositional method of XES data interpretation that avoids erroneous assumptions inherent in the comparative analysis method, gives perfect agreement with results of our Mössbauer study, and potentially allows the extraction of additional information from the XES data.

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