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Synchrotron Mössbauer spectroscopic study of ferropericlase at high pressures and temperatures

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Abstract

The electronic spin state of Fe^{2+} in ferropericlase, $(Mg_{0.75}Fe_{0.25})O$, transitions from a high-spin (spin unpaired) to low-spin (spin paired) state within the Earth's mid-lower mantle region. To better understand the local electronic environment of high-spin Fe^{2+} ions in ferropericlase near the transition, we obtained synchrotron Mössbauer spectra (SMS) of $(Mg_{0.75},Fe_{0.25})O$ in externally heated and laser-heated diamond anvil cells at relevant high pressures and temperatures. Results show that the quadrupole splitting (QS) of the dominant high-spin Fe^{2+} site decreases with increasing temperature at static high pressure. The QS values at constant pressure are fitted to a temperature-dependent Boltzmann distribution model, which permits estimation of the crystal-field splitting energy (Δ_3) between the d_{xy} and d_{xz} or d_{zy} orbitals of the t_{2g} states in a distorted octahedral Fe^{2+} site. The derived Δ_3 increases from approximately 36 meV at 1 GPa to 95 meV at 40 GPa, revealing that both high pressure and high temperature have significant effects on the 3*d* electronic shells of Fe^{2+} in ferropericlase. The SMS spectra collected from the laser-heated diamond cells within the time window of 146 ns also indicate that QS significantly decreases at very high temperatures. A larger splitting of the energy levels at high temperatures and pressures should broaden the spin crossover in ferropericlase because the degeneracy of energy levels is partially lifted. Our results provide information on the hyperfine parameters and crystal-field splitting energy of high-spin Fe^{2+} in ferropericlase at high pressures and temperatures, relevant to the electronic structure of iron in oxides in the deep lower mantle.

Keywords: Ferropericlase, diamond-anvil cell, spin transition, Mössbauer spectroscopy, high pressures, high temperatures

Introduction

Electronic spin-pairing transitions of iron and associated effects on the physical properties of host mineral phases have been reported in lower-mantle minerals including ferropericlase, silicate perovskite, and possibly in post-perovskite at lower-mantle pressures (e.g., see Lin and Tsuchiya 2008 for a recent review). The spin transition of iron in ferropericlase with about 20 mol% iron begins at ~50 GPa and room temperature (Badro et al. 2003; Speziale et al. 2005; Lin et al. 2005a, 2006a, 2007a, 2007b; Gavriliuk et al. 2006; Kantor et al. 2006; Persson et al. 2006). At lower-mantle pressure-temperature conditions, a broad spin transition zone in ferropericlase occurs between ~1000 km in depth to 2200 km, i.e., spanning much of the lower mantle (Sturhahn et al. 2005; Tsuchiya et al. 2006; Lin et al. 2007c). The spin transition of iron is important to our understanding of the geophysics and geodynamics of the Earth's lower mantle (e.g., Lin et al. 2008) because it affects the density (Lin et al. 2005a; Speziale et al. 2005; Fei et al. 2007), incompressibility (Lin et al. 2005a; Tsuchiya et al. 2006; Speziale et al. 2007), and sound velocities (Lin et al. 2006b; Crowhurst et al. 2008) of the host minerals. The transition also reduces radiative thermal conductivity (Goncharov et al. 2006; Keppler et al. 2007) and electrical conductivity (Lin et al. 2007d) in the low-spin ferropericlase. Furthermore, elastic mode-softening within the transition was recently reported (Crowhurst et al. 2008).

Electronic transitions of Fe^{2+} in ferropericlase have been studied by Mössbauer spectroscopy at high pressures (Speziale et al. 2005; Garviliuk et al. 2006; Kantor et al. 2006; Lin et al. 2006b), absorption spectroscopy at high pressures (Goncharov et al. 2006; Keppler et al. 2007), and by X-ray emission spectroscopy at high pressures and/or temperatures (Badro et al. 2003; Lin et al. 2005a, 2007c). X-ray emission spectroscopy of the Fe*K*β peak is sensitive to the net spin moment of the 3*d* electrons and has been used to derive the fraction of the high-spin to low-spin states at high

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pressures and temperatures (Lin et al. 2007c). These recent results show that the local 3*d* electronic environment of the iron ions in ferropericlase is pressure and temperature dependent. However, hyperfine parameters including quadrupole splitting (QS) and isomer shift (IS), of Fe^{2+} in ferropericlase at simultaneous high pressure-temperature conditions have not been determined experimentally. In particular, the magnitude of the QS depends on the temperature, spin orbital coupling, crystal-field symmetry and splitting, and bond covalency (Bancroft 1973; Maddock 1997). Here we determine the QS of Fe^{2+} in ferropericlase as a function of pressure and temperature to evaluate the site distortion, crystal-field splitting energies, and bond covalency of the lattice. This information enables us to determine considerably more precise estimates of the crystal-field parameters and the crystal-field stabilization energies (Burns 1985, 1993). Although some of the crystal-field splittings have been determined from the infrared absorption spectra at high pressures (i.e., Mao and Bell 1972; Shankland et al. 1974; Shen et al. 1994; Goncharov et al. 2006; Keppler et al. 2007), the crystal-field splittings within the lower t_{2g} orbitals (Δ_3) in Fe^{2+} in lower-mantle ferropericlase remains illusive at high pressures and temperatures.

Here we determine the hyperfine parameters of the Fe^{2+} electronic structure in ferropericlase at high pressures and temperatures, employing externally heated diamond anvil cells (EHDAC) and laser-heated diamond anvil cells (LHDAC) to measure high-pressure and high-temperature synchrotron Mössbauer spectra at sectors 16 and 3 of the Advanced Photon Source, Argonne National Laboratory (APS, ANL). The derived QS values are used to evaluate the crystal-field splittings of high-spin Fe^{2+} in ferropericlase at pressures and temperatures relevant to the lower mantle.

Experimental methods

Polycrystalline $(Mg_{0.75},Fe_{0.25})O$ samples with 95% and 20% ^{57}Fe enrichment were synthesized by sintering stoichiometric mixtures of MgO and ^{57}Fe powder at 1378 to 1478 K for 8 h under a controlled CO_2-CO atmosphere near the iron-wüstite buffer (Lin et al. 2006a). Analyses of the traditional Mössbauer and synchrotron Mössbauer spectra (SMS) of the samples showed that the ferric iron (Fe^{3+}) content of the samples was below the detection limit of Mössbauer spectroscopy and magnetite (Fe_3O_4) was not detected in the X-ray diffraction pattern. The 95% ^{57}Fe-enriched ferropericlase had been used in previous studies (Lin et al. 2006a, 2006b, 2007d) and was used for the EHDAC experiments in this study, whereas the 20% ^{57}Fe-enriched ferropericlase was used in the LHDAC experiments because sample thickness was typically 10–15 μm in the LHDAC experiments.

SMS experiments in an EHDAC were carried out at the undulator beamline 16-IDD of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A monochromatic X-ray beam of ~14.4125 keV with 2 meV bandwidth was used to excite the nuclear resonance of the ^{57}Fe nuclei in the sample (Sturhahn 2004; Sturhahn and Jackson 2007). A cleanup aperture 20 μm in diameter was used to direct the X-ray beam onto the sample in an EHDAC. The polycrystalline ^{57}Fe-enriched $(Mg_{0.75},Fe_{0.25})O$ samples were compressed between two flat diamonds to ~1–3 μm in thickness prior to loading a pressure medium in the DAC, providing an effective thickness (a parameter to describe the total intensity and the influence of the sample thickness on the shape of the SMS spectra in this composition) between two and three (Gavriliuk et al. 2006; Lin et al. 2006a). A rhenium gasket was pre-indented to a thickness of 25 μm with an 80 μm diameter sample hole. A small flake of the sample with ~60 μm diameter was loaded into the sample chamber in the EHDAC with flat diamonds of a culet size of 200 μm in the EHDAC. Subsequently, NaCl was loaded into the sample chamber as the pressure medium and a few small Sm:YAG and ruby spheres were placed close to the sample for pressure measurements (Mao et al. 1978; Hess and Schiferl 1992). Temperatures of the sample chamber were measured using two K-type thermocouples attached to the diamond anvils, and controlled within ±10 K using a feedback controlled power supply (Bassett et al. 1993). Pressures at room temperature were measured using the Sm:YAG (Hess and Schiferl 1992) and ruby (Mao et al. 1978) luminescence peaks, while pressures at high temperatures were measured in situ using an online optical system and the temperature-corrected Sm:YAG luminescence peak (Hess and Schiferl 1992). Quasi-isobaric conditions were achieved by adjusting pressures during heating.

SMS experiments in the LHDAC were carried out at the undulator beamline 3-IDB of the APS, ANL. A monochromatic X-ray beam of approximately 14.4125 keV with 1 meV bandwidth and 7 μm in diameter was used for the experiments. The $(Mg_{0.75},Fe_{0.25})O$ samples with 20% enrichment measuring ~10–15 μm thick and 50 μm in diameter were loaded into symmetric DACs with Re gaskets. The ^{57}Fe enrichment with the sample thickness was comparable with the effective thickness between two to three (Gavriliuk et al. 2006; Lin et al. 2006a). Dried NaCl layers were sandwiched between the samples in the DACs and used as the thermal insulators and pressure medium. A few small ruby spheres were also placed close to the sample for pressure measurements. The samples in the DACs were first compressed to high pressures and then laser-heated by two infrared laser beams of ~30 μm in diameter at the sample position. Temperatures were determined from the thermal radiation spectra of the laser-heated samples fitted to the Planck radiation function. The laser-heating system has been described elsewhere (Lin et al. 2005b).

The SMS spectra were recorded by an avalanche photodiode detector in the forward direction (Toellner et al. 1994). After the SMS spectrum of the sample had been collected, thin stainless steel foil ($Fe_{55}Cr_{20}Ni_{25}$) of 0.5 μm in thickness was placed outside of the DAC serving as a reference for possible IS measurements; however, because of the strong temperature effect on the QS, derivation of a reliable IS at high pressure-temperature requires a much larger time window (see further discussions below). The collection time for each SMS spectrum was between one and four hours. The SMS spectra were evaluated with the MOTIF (Shvyd'ko 1999) and CONUSS (Sturhahn 2000) programs to derive the QS values at high pressures and temperatures.

Experimental results

SMS spectra of $(Mg_{0.75},Fe_{0.25})O$ were collected up to 65 GPa and 800 K in the EHDAC (Fig. 1) and 71 GPa and 2000 K in the LHDAC (Fig. 2). The quantum beats, generated from the QS of the high-spin state of Fe^{2+} in the sample, are consistent with previous studies at high pressures (Gavriliuk et al. 2006; Lin et al. 2006a). Traditional Mössbauer and SMS spectra of the start-

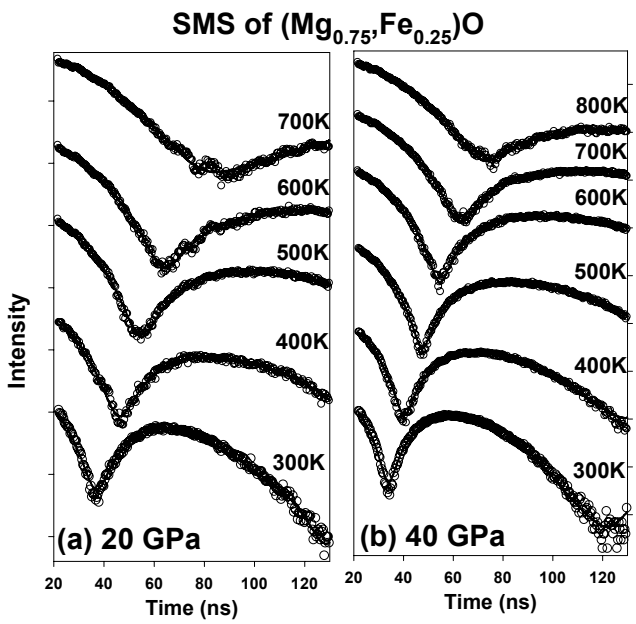

Figure 1. Representative SMS spectra of ferropericlase, $(Mg_{0.75},Fe_{0.25})O$, at (**a**) 20 GPa and (**b**) 40 GPa as a function of temperature, collected using the EHDAC at sector 16 of the APS. Open circles: experimental data; black lines: modeled spectra with two doublets. The sample thickness was ~1–3 μm.

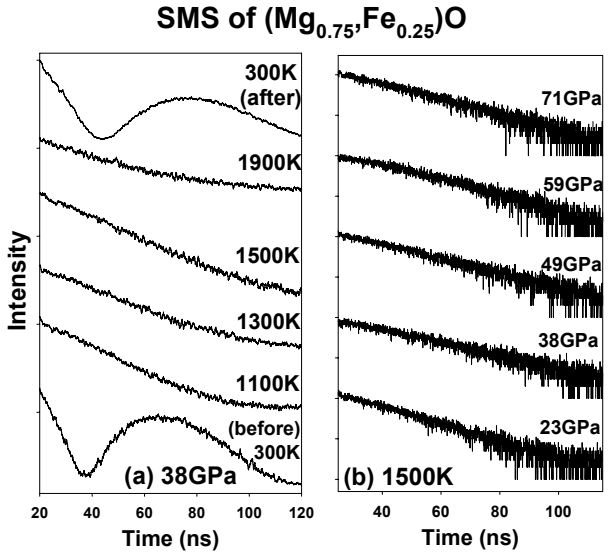

FIGURE 2. Representative SMS spectra of ferropericlase, $(Mg_{0.75}, Fe_{0.25})O$, at (**a**) 38 GPa and (**b**) 1500 K collected using a LHDAC at sector 3 of the APS. The enrichment of ^{57}Fe in the sample was ~20%, and the initial sample thickness was ~10–15 μm. The spectra in **a** were smoothed for clarity by averaging 10 data points. A very strong temperature effect on the QS shows the absence of quantum beats in the Mössbauer spectra at high temperatures.

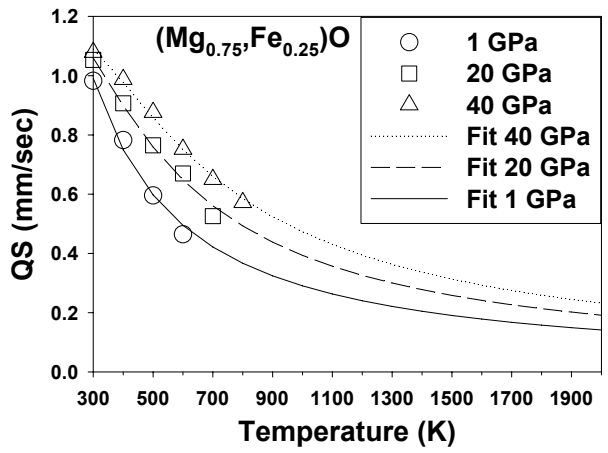

FIGURE 3. QS of ferropericlase, $(Mg_{0.75},Fe_{0.25})O$, at high pressures and temperatures. The QS of the dominant Fe^{2+} site slightly increases with increasing pressure at room temperature (Lin et al. 2006a) but decreases with increasing temperature. The QS values are used to derive the energy separation between the t_{2g} energy levels, assuming $\Delta_1 \approx \Delta_2 \approx \Delta_3$ (see Figs. 4 and 5 and Discussion for details). Lines are fits to the QS values at constant pressures using Equation 2 (Ingalls 1964; Bancroft 1973).

ing samples at ambient conditions can be satisfactorily fitted to two doublets modeled with a dominant high-spin Fe^{2+} site and a minor high-spin Fe^{2+} site, consistent with previous reports (Dobson et al. 1998; McCammon et al. 1998). SMS spectra of the sample at high pressures and temperatures are thus fitted to the two-doublets model; however, statistical distribution of reciprocal positions of the iron ions in the sample may result in further distribution of iron ions in the nearest neighbor positions and thus the hyperfine parameters, the QS and IS values.

Using the two-doublets model, the derived QS values of the dominant high-spin Fe^{2+} site under room temperature increase slightly with increasing pressure and are consistent with high-spin Fe^{2+} in octahedral coordination in ferropericlase (Lin et al. 2006a). At a constant pressure, the QS values of the dominant site drop significantly with increasing temperature, indicating a strong temperature effect on the QS (Fig. 3). The SMS spectra collected from the LHDAC experiments show no observable quantum beats within the time window of 146 ns, even when the pressure-temperature conditions were within the high-spin state (Fig. 2) (Lin et al. 2007c). These SMS spectra without quantum beats also manifest the very high-temperature effect on the QS of the high-spin Fe^{2+} in ferropericlase. Our evaluations also show that high pressure-temperature behavior of the minor doublet is similar to that of the main doublet. This behavior can be attributed to their similar local crystal environments and consequently to their crystal contributions to the QS, whereas the electronic structure significantly contributes to the change of the QS at high pressures and temperatures. We thus focus our discussion on further modeling of the behavior of the major doublet at high pressures and temperatures.

DISCUSSION

To understand the temperature effect on the high-pressure QS and to estimate the crystal-field splittings of high-spin Fe^{2+} in ferropericlase at high pressures, we have modeled the QS values of the dominant high-spin Fe^{2+} in the octahedral site in ferropericlase using Ingalls' model (Ingalls 1964). In Ingalls' model, the octahedral high-spin Fe^{2+} site is inherently subject to a Jahn-Teller distortion (Kambara 1979), which removes degeneracy of the t_{2g} and e_g orbitals and gives rise to a large crystal-field splitting energy (Δ_C) (Fig. 4) (Burns 1985, 1993). The QS of the octahedral Fe^{2+} depends on the covalency of the bonds (α^2), the spin-orbit coupling parameter (λ_0), temperature (T), and relative splittings of the lower 3*d* energy levels, Δ_1 and Δ_2 (Fig. 4c) (Ingalls 1964; Hazony and Axtmann 1971; Bancroft 1973). Following the discussion by Bancroft (1973), the roles of α^2 and λ_0 on the QS are neglected for simplicity, leading to a simplified parameterized equation for the Fe^{2+} in the distorted octahedral site:

$$QS = QS_0 F(\Delta_1, \Delta_2, T) \quad (1)$$

where QS_0 is the QS at absolute zero temperature for an ideal ionic Fe^{2+} site, and F is the reduction function relating the difference between the valence contribution (q_{val}) and lattice contribution (q_{lat}) to the QS. The lattice contribution is usually much smaller than the valence contribution and is generally of opposite sign to the valence contribution (Ingalls 1964). Neglecting the lattice contribution, and assuming that Δ_1 and Δ_2 values are similar in the octahedral site (i.e., $\Delta_1 \approx \Delta_2 \approx \Delta_3$) and remain constant over the temperature range, the QS of the Fe^{2+} can be related to the temperature using the Boltzmann distribution of the sixth 3*d* electron (which is of opposite sign to the other five) over the 3*d* levels. The most approximate expression for the

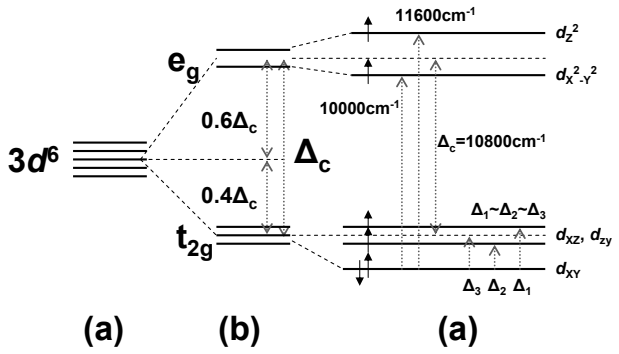

FIGURE 4. Energy level diagram of the high-spin Fe^{2+} in the octahedral site in ferropericlase based on the crystal field theory (Burns 1985, 1993). (**a**), free ion; (**b**), undistorted field; (**c**), distorted octahedral site. Δc = crystal-field splitting energy. Δ_1, Δ_2: energy separation between the lowest d_{xy} and upper d_{xz} and d_{zy} levels of the t_{2g} states in a distorted octahedral Fe^{2+} site, respectively. Δ_1 and Δ_2 are assumed to be same and are denoted as Δ_3 for simplicity. The energy separations in the diagram are not drawn to scale. Black arrows indicate electron spin, up or down. The sixth electron is shown to be in spin down and paired up with another electron in the lowest d_{xy} orbital. The diagram is revised from Burns (1985, 1993) and Bancroft (1973). The crystal-field energies between t_{2g} and e_g under ambient conditions are taken from Goto (1980) and Burns (1985), and have also been measured recently at high pressures (Goncharov et al. 2006; Keppler et al. 2007).

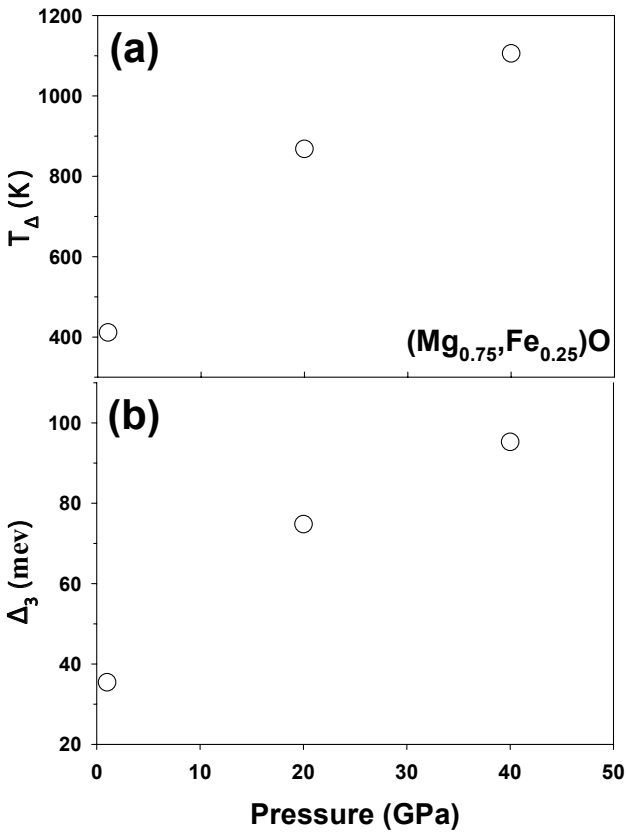

FIGURE 5. Derived T_Δ and Δ_3 of Fe^{2+} in the octahedral site in ferropericlase at high pressures. These parameters are derived from the QS values in Figure 3 at high pressures and temperatures using Equation 2 (Ingalls 1964; Bancroft 1973). The uncertainty in the derived Δ_3 is approximately ±10 meV.

QS of the high-spin Fe^{2+} in the octahedral site as a function of temperature and Δ_3 is:

$$QS(\Delta_3,T) = QS_0 \frac{1-\exp(-\Delta_3/kT)}{1+2\exp(-\Delta_3/kT)} = QS_0 \frac{1-\exp(-T_\Delta/T)}{1+2\exp(-T_\Delta/T)} \quad (2)$$

where k is Boltzmann constant and T_Δ is Δ_3/k in Kelvin (Figs. 3–5) (Ingalls 1964; Bancroft 1973). The T_Δ and Δ_3 can thus be estimated from fitting the experimentally derived QS values at high temperatures and constant pressures using Equation 2 (Fig. 5). The Δ_3 of ferropericlase is 36 meV at 1 GPa, 75 meV at 20 GPa, and 95 meV at 40 GPa. These results in general show that the Δ_3 increases with increasing pressure, indicating a higher degree of the energy separation between the d_{xy} and d_{xz} or d_{zy} orbitals of the t_{2g} states in a distorted octahedral Fe^{2+} site at higher pressures.

The above-mentioned model is sensitive to the temperature range of the experimental QS values. For example, the Δ_3 at 1 GPa is likely not as reliable as that at 20 and 40 GPa because of the limited temperature range used (Fig. 3). It is thus desirable to fit the equation to an extended temperature range of the QS values to derive more reliable values of Δ_3. However, paramagnetic high-spin ferropericlase transforms to the anti-ferromagnetic state at lower temperatures and high pressures (Speziale et al. 2005), whereas our laser-heated SMS data show no quantum beats, limiting the extension of the temperature range. If fits using Equation 2 deviate significantly from the experimental QS values over an extended temperature range, the α^2, λ_0, and q_{lat} to the QS should be taken into account (Ingalls 1964; Hazony and Axtmann 1971; Huggins 1975). The evaluation of the deviation in turn may permit further understanding of the effect of these parameters on the QS at high pressures and temperatures.

The temperature-dependent Boltzmann distribution model had also been used to estimate the energy separation of the two lowest e_g levels in Fe^{2+} in almandine end-member garnet, using high-temperature Mössbauer data (Huggins 1975). The derived Δ_1 for almandine under ambient pressure is ~138 meV (1100 cm^{-1}) (Huggins 1975), much larger than the values we derived for ferropericlase. We note that almandine exhibits the highest QS of 3.5–3.7 mm/s in nature, which indicates a very high degree of site distortion.

Our high pressure-temperature SMS results reveal that high temperatures significantly lower the QS value of the high-spin ferropericlase, which is similar to the behavior of the observed QS across the spin transition at high pressures and room temperature (Speziale et al. 2005; Lin et al. 2006a). If the broadening of the spin transition at high temperatures, namely the spin crossover, is a result of the thermal fluctuations between the HS and LS states (Sturhahn et al. 2005; Tsuchiya et al. 2006), the high-temperature contribution to the QS and the splitting of the energy levels observed in this study likely leads to a broader spin crossover region at high temperatures and pressures. That is, a larger splitting should broaden the spin crossover because the degeneracy of energy levels is partially lifted, providing further information on the extended width of the spin crossover in fer-

ropericlase in the lower mantle (Lin et al. 2007).

In this study, we have measured SMS spectra of ferropericlase up to 71 GPa and 2000 K. Our results show that quadrupole splitting (QS) of the dominant high-spin Fe^{2+} site decreases significantly with increasing temperature at a constant pressure. The QS values at a constant pressure are fitted to a temperature-dependent Boltzmann distribution model, which permits estimation of the separation of the crystal-field splittings between the d_{xy} and d_{xz} or d_{zy} orbitals of the t_{2g} states in a distorted octahedral Fe^{2+} site. The derived Δ_3 increases from approximately 36 meV at 1 GPa to 95 meV at 40 GPa, revealing that both high pressure and temperature have significant effects on the 3*d* electronic shells of Fe^{2+} in ferropericlase. The SMS spectra collected from the laser-heated diamond cells lack quantum beats within the time window of 146 ns, indicating that the QS significantly decreases at very high temperatures. The results provide new information on the hyperfine parameters and crystal-field splittings of the high-spin Fe^{2+} in ferropericlase at high pressures and temperatures and indicate that the local electronic structure of iron in the lower-mantle oxide, (Mg,Fe)O, is strongly pressure and temperature dependent.

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