American Mineralogist, Volume 94, pages 594–599, 2009

Synchrotron Mössbauer spectroscopic study of ferropericlase at high pressures and temperatures

Jung-Fu Lin,[1,*] Alexander G. Gavriliuk,[2,3] Wolfgang Sturhahn,[4,5] Steven D. Jacobsen,[6] Jiyong Zhao,[4] Michael Lerche,[7] and Michael Hu[8]

[1]Department of Geological Sciences, Jackson School of Geosciences, the University of Texas at Austin, Austin, Texas 78712, U.S.A.
[2]Institute for High Pressure Physics, Russian Academy of Sciences, 142190, Troitsk, Moscow region, Russia
[3]Institute of Crystallography, Russian Academy of Sciences, Leninsky pr. 59, Moscow 119333, Russia
[4]Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.
[5]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, U.S.A.
[6]Department of Earth and Planetary Sciences, Northwestern University, Evanston, Illinois 60208, U.S.A.
[7]HPSynC, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.
[8]HPCAT, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

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