

Effects of composition and pressure on electronic states of iron in bridgmanite

SUSANNAH M. DORFMAN^{1,2,*}, VASILY POTAPKIN³, MINGDA LV^{1,§}, ERAN GREENBERG^{4,†},
ILYA KUPENKO^{3,5}, ALEKSANDR I. CHUMAKOV⁵, WENLI BI^{6,7}, E. ERCAN ALP⁶, JIACHAO LIU¹,
ARNAUD MAGREZ⁸, SIÂN E. DUTTON^{9,‡}, ROBERT J. CAVA⁹, CATHERINE A. MCCAMMON^{10,||}, AND
PHILIPPE GILLET²

¹Department of Earth and Environmental Sciences, Michigan State University, East Lansing, Michigan 48824, U.S.A.

²Earth and Planetary Science Laboratory, Institute of Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

³Institute of Mineralogy, University of Münster, D-48149 Münster, Germany

⁴School of Physics & Astronomy, Tel-Aviv University, Tel-Aviv 6997801, Israel

⁵ESRF-The European Synchrotron, 71, Avenue des Martyrs, 38000 Grenoble, France

⁶Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

⁷Department of Geology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, U.S.A.;

Department of Physics, University of Alabama at Birmingham, Birmingham, Alabama 35294, U.S.A.

⁸Crystal Growth Facility, Institute of Physics, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

⁹Department of Chemistry, Princeton University, Princeton, New Jersey 08544, U.S.A.

¹⁰Bayrisches Geoinstitut, University of Bayreuth, 95447 Bayreuth, Germany

ABSTRACT

Electronic states of iron in the lower mantle's dominant mineral, (Mg,Fe,Al)(Fe,Al,Si)O₃ bridgmanite, control physical properties of the mantle including density, elasticity, and electrical and thermal conductivity. However, the determination of electronic states of iron has been controversial, in part due to different interpretations of Mössbauer spectroscopy results used to identify spin state, valence state, and site occupancy of iron. We applied energy-domain Mössbauer spectroscopy to a set of four bridgmanite samples spanning a wide range of compositions: 10–50% Fe/total cations, 0–25% Al/total cations, 12–100% Fe³⁺/total Fe. Measurements performed in the diamond-anvil cell at pressures up to 76 GPa below and above the high to low spin transition in Fe³⁺ provide a Mössbauer reference library for bridgmanite and demonstrate the effects of pressure and composition on electronic states of iron. Results indicate that although the spin transition in Fe³⁺ in the bridgmanite B-site occurs as predicted, it does not strongly affect the observed quadrupole splitting of 1.4 mm/s, and only decreases center shift for this site to 0 mm/s at ~70 GPa. Thus center shift can easily distinguish Fe³⁺ from Fe²⁺ at high pressure, which exhibits two distinct Mössbauer sites with center shift ~1 mm/s and quadrupole splitting 2.4–3.1 and 3.9 mm/s at ~70 GPa. Correct quantification of Fe³⁺/total Fe in bridgmanite is required to constrain the effects of composition and redox states in experimental measurements of seismic properties of bridgmanite. In Fe-rich, mixed-valence bridgmanite at deep-mantle-relevant pressures, up to ~20% of the Fe may be a Fe^{2.5+} charge transfer component, which should enhance electrical and thermal conductivity in Fe-rich heterogeneities at the base of Earth's mantle.

Keywords: Bridgmanite, Mössbauer spectroscopy, iron oxidation state, lower mantle