Raman spectroscopy on pressure-induced spin transitions in garnets

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The importance of garnets within the Earth's mantle, the high symmetry of the garnet structure (space group $Ia\bar{3}d$), and the manifold cation and anion substitution mechanisms make garnets an ideal model system to study pressure-induced spin-pairing transitions of 3*d*-transition-metal cations. Specifically, the spin-pairing behavior in andradite may serve as a benchmark for that of Fe^{3+} located on the octahedral B-site of iron-bearing magnesium silicate perovskite [1].

We have studied synthetic cubic andradite, $Ca_3Fe_2[SiO_4]_3$, and natural tetragonal henritermierite, $Ca_3Mn_2[SiO_4]_2[O_4H_4]$, at pressures up to 80 GPa using Raman spectroscopy, single-crystal synchrotron X-ray diffraction and quantum-mechanical calculations based on density functional theory. Isosymmetric phase transitions were observed in the pressure ranges 60-70 GPa and 55-70 GPa, which are associated with high spin-to-low spin electronic transitions in octahedrally coordinated Fe^{3+} and Mn^{3+}, respectively [2] [3]. Changes in the vibrational properties will be discussed with respect to the structural compression and results from theoretical calculations.

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[1] Lin *et al*. (2013) *Rev. Geophys* **51**, 244-275. [2] Friedrich *et al*. (2014) *Phys. Rev. B* **90**, 094105. [3] Friedrich *et al*. (2015) *Phys. Rev. B*, in revision.