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SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

An X-ray magnetic circular dichroism (XMCD) study of Fe ordering in a synthetic $MgAl_2O_4$-Fe_3O_4 (spinel-magnetite) solid-solution series: Implications for magnetic properties and cation site ordering

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Abstract

Fe $L_{2,3}$-edge XAS and XMCD studies have been used to unravel structural trends in the $MgAl_2O_4$–Fe_3O_4 solid solution where thermodynamic modeling has presented a challenge due to the complex ordering arrangements of the end-members. Partitioning of Fe^{3+} and Fe^{2+} between tetrahedral (Td) and octahedral (Oh) sites has been established. In the most Fe-rich samples, despite rapid quenching from a disordered state, Fe^{2+}_{Td} is not present, which matches the ordered, inverse spinel nature of end-member magnetite (Mgt) at room temperature. However, in intermediate compositions Al and Mg substantially replace Fe and small amounts of Fe^{2+}_{Td} are found, stabilized, or trapped by decreasing occurrence of the continuous nearest neighbor Fe–Fe interactions that facilitate charge redistribution by electron transfer. Furthermore, in the composition range ~$Mgt_{0.4–0.9}$, XAS and XMCD bonding and site occupancy data suggest that nanoscale, magnetite-like Fe clusters are present. By contrast, at the spinel-rich end of the series, $Mgt_{0.17}$ and $Mgt_{0.23}$ have a homogeneous long-range distribution of Fe, Mg, and Al. These relationships are consistent with the intermediate and Fe-rich samples falling within a wide solvus in this system such that the Fe-clusters occur as proto-nuclei for phases that would exsolve following development of long-range crystalline order during slow cooling.

Unit-cell edges calculated from the spectroscopy-derived site occupancies show excellent agreement with those measured by X-ray powder diffraction on the bulk samples. Calculated saturation magnetic moments (M_s) for the Fe-rich samples also show excellent agreement with measured values but for the most Mg-rich samples are displaced to slightly higher values; this displacement is due to the presence of abundant Mg and Al disrupting the anti-parallel alignment of electron spins for Fe atoms.

Keywords: $MgAl_2O_4$-Fe_3O_4 spinel solid solutions, Fe $L_{2,3}$ X-ray absorption spectroscopy, Fe $L_{2,3}$ X-ray magnetic circular dichroism, Mg and Fe *K*-edge extended X-ray absorption fine structure spectroscopy, octahedral and tetrahedral site occupancies, calculated unit-cell parameters, calculated magnetic moments, spinel-magnetite solvus, hypothetical high-temperature ordering model