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Microstructure and magnetism in the ilmenite-hematite solid solution: A Monte Carlo simulation study

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ABSTRACT

The energetics of magnetic and cation ordering have been modeled using an atomistic approach based on empirical exchange interaction parameters. The model has been applied to the study of magnetic and cation ordering in the ilmenite-hematite solid solution via Monte Carlo simulations, providing new insight into the effect of nanoscale microstructures on the magnetic properties of this system. The lowest energy state for intermediate compositions is an intergrowth of cation-disordered antiferromagnetic (AF) hematite and cation-ordered paramagnetic (PM) ilmenite, separated by mixed Fe^{2+}/Fe^{3+} "contact layers." The intergrowth carries a stable defect moment ("lamellar magnetism") due to the presence of uncompensated spins. The net magnetization is parallel to the spin alignment direction, i.e., perpendicular to the spin-canted magnetization of the AF hematite. Contact-layer spins are coordinated to fewer magnetic neighbors than bulk spins and thus disorder more rapidly on heating. This leads to a decrease of net moment with increasing temperature. A small net moment is present, however, up to the Néel temperature of the AF hematite phase. The maximum temperature for acquisition of a chemical remanent magnetization due to lamellar magnetism is 800 ± 25 K, corresponding to the temperature for the eutectoid reaction PM hematite → AF hematite + PM ilmenite. If only cation interactions are considered, Fe^{3+} and Fe^{2+} in the contact layers become ordered so that Fe^{3+} shares an octahedral face with Fe^{3+} in the neighboring hematite layer and Fe^{2+} shares an octahedral face with Ti^{4+} in the neighboring ilmenite layer. If both cation and magnetic interactions are considered, however, an alternative ordering scheme is stabilized, whereby Fe^{3+} shares an octahedral face with Ti^{4+} in the neighboring ilmenite layer and Fe^{2+} shares an octahedral face with Fe^{3+} in the neighboring hematite layer.

The model has been used to investigate the nature of exchange coupling between ordered/antiordered domains and disordered antiphase boundaries, with a view to elucidating the mechanism of self-reversed thermoremanent magnetization. Antiphase boundaries are enriched in Fe relative to the ordered/antiordered domains, with enhanced enrichment observed in simulations performed within the PM hematite + PM ilmenite miscibility gap. Monte Carlo simulations of magnetic ordering show no evidence of self-reversal in systems containing two equally well-ordered ferrimagnetic (FM) domains separated by Fe-enriched AF boundaries. Systems displaying partial long-range order, however, do display self-reversed magnetization. Partial long-range order is characterized by a mixture of highly ordered Ti-rich FM domains and poorly ordered Fe-rich domains with a weak FM moment. The magnetic ordering temperature of the poorly ordered Fe-rich domains is significantly higher than that of the highly ordered Ti-rich domains, and act as the "*x*-phase." Evidence in support of the proposed mechanism from neutron diffraction and transmission electron microscopy is presented.

Keywords: Magnetism, microstructure, ilmenite, hematite