Magnetic contributions to corundum-eskolaite and corundum-hematite phase equilibria: A DFT cluster expansion study

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ABSTRACT

Magnetic contributions have the potential to significantly influence predicted phase stability within alloy and mineral mixing phase diagrams, yet have been historically challenging to incorporate due to a significant increase to phase space sampling. In this work, we employ a computational protocol that includes spin orientation as an additional configurational component within multi-component cluster expansions between magnetic and non-magnetic metal oxide alloys [calculated using density functional theory (DFT) and the generalized gradient approximation]. This approach was used to determine the effect of magnetic contributions to corundum-eskolaite and corundum-hematite phase equilibria from first principles.

Two-component cluster expansions of the magnetic components of eskolaite and hematite were first performed showing the ability of this method to properly calculate their respective magnetic properties. Two-component cluster expansions were then performed for non-magnetic Al(III) and ferromagnetic Cr(III) and Fe(III), and phase diagrams were calculated for later comparison. Finally, a non-magnetic Al(III) and “up” and “down” magnetic configurations for anti-ferromagnetic Cr(III) and Fe(III) were performed. Magnetic contributions to the calculated phase diagram for the corundum-eskolaite system were shown to be inconsequential but are vital for accurate determination of the corundum-hematite solvus.

Keywords: Phase diagram, mineral mixing, magnetic states, corundum

INTRODUCTION

Corundum-eskolaite, α-(Al,Cr)₂O₃ and corundum-hematite, α-(Al,Fe)₂O₃ phase equilibria have been extensively researched in experimental studies (Jacob 1978; Sitte 1985; Chatterjee et al. 1982; Atlas and Sumida 1958; Turnock and Eugster 1962; Feenstra et al. 2005), but little work has been done to describe these 28 solid solutions from first-principle calculations (Pinney et al. 2009; Chatterjee et al. 2016; Eremin et al. 2008). This is perhaps due to additional complexity introduced by magnetic degrees of freedom present in both the Cr(III) and Fe(III) cations and the difficulty required to accurately calculate these contributions. More accurate modeling of these magnetic properties and their influence on phase equilibria would allow for better understanding of the underlying phenomena governing these systems and make predictive finite temperature structures more accessible for further study.

Corundum, hematite, and eskolaite are isostructural R3c space group minerals that are important compounds in the production of many industrial materials. Additionally, hematite and eskolaite both exhibit unique magnetic properties making them of high interest for a multitude of spintronics applications (Pattanayak et al. 2021; Khan et al. 2015; Borisov et al. 2005; He et al. 2010). Alloy composition is often a guiding factor in material design of these systems, and accurate simulations of alloy compositions are highly desirable.

Prior computational work for both systems has been confined to ab initio energy calculations of dilute limit substitutions (Chatterjee et al. 2016) and pair configurations (Pinney et al. 2009) within moderately sized supercells or from classical molecular dynamics free energy calculations yielding associated phase equilibria diagrams (Eremin et al. 2008). While the MD simulations provide complete solvus line calculations, they rely on interaction potentials using fitted parameters to better model thermodynamics. Presently, to the authors’ knowledge, there are currently no complete first-principle solvus line calculations for these systems.

Accurate determination of phase equilibria in AB alloys is typically performed through cluster expansion (CE) calculations (Sanchez et al. 1984), where ensemble average free energies can be determined rapidly and used to create phase diagrams. This method normally examines atomic configurations only, e.g., A B site configurations in binary alloys, but can be extended to capture magnetic effects as well. This is achieved through a multi-component cluster expansion (van de Walle 2009), where “up” and “down” magnetic moments at each spin polarized A/B cation site is included as an additional configurational component. This approach may be essential for the eskolaite and hematite systems since they are both anti-ferromagnetic at low temperatures and capturing these low energy states are essential for determining mixing energies.