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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