

Thermodynamics of the $R\bar{3}$ to $R\bar{3}c$ phase transition in the ilmenite-hematite solid solution

RICHARD J. HARRISON,^{1,*} UDO BECKER,¹ AND SIMON A.T. REDFERN²

¹Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster, Germany

²Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.

ABSTRACT

The thermodynamics of cation ordering in the ilmenite-hematite solid solution $(\text{FeTiO}_3)_x(\text{Fe}_2\text{O}_3)_{1-x}$ were re-examined in view of a recent in-situ neutron diffraction study of the $R\bar{3}$ to $R\bar{3}c$ phase transition. A macroscopic thermodynamic model is developed, in which the excess enthalpy of ordering is described by a fourth-order polynomial function of the long-range order parameter, Q , and the excess entropy is described by the configurational point entropy. The enthalpy coefficients are determined as a function of composition by fitting to the neutron diffraction data. The fourth-order energy coefficient increases smoothly with increasing Ti-content, indicating a change in the character of the transition from second-order ($x < 0.87$) to first-order ($x > 0.87$). Monte Carlo simulations confirm that the excess enthalpy is well described by a fourth-order polynomial, and demonstrate that the reduction in configurational entropy due to short-range ordering can be described by simply scaling the point entropy. This allows the enthalpy coefficients in the macroscopic model to be corrected for the effects of short-range ordering, yielding a revised estimate of $x = 0.92$ for the position of the tricritical point.

Monte Carlo simulations are used to study both ordering and exsolution in the solid solution, allowing the paramagnetic portion of the equilibrium phase diagram to be derived. The changing character of the phase transition is reproduced successfully by treating Fe^{2+} -Ti and Fe^{3+} -Ti interactions separately in the simulations. Intralayer Fe^{2+} -Ti interactions are negative (i.e., ordering of Fe^{2+} and Ti within the 001 layers is favored) whereas Fe^{3+} -Ti intralayer interactions are positive (i.e., separation of Fe^{3+} and Ti is favored). The λ -line for the $R\bar{3}$ to $R\bar{3}c$ phase transition intersects the low-temperature miscibility gap at a tricritical point near $x = 0.6$ and $T = 800$ °C, in reasonable agreement with previous thermodynamic models of the solid solution.