The influence of iron substitution on the magnetic properties of hausmannite, 
\[ \text{Mn}^{2+}(\text{FeMn})_{2}^{2+}\text{O}_{4} \]

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ABSTRACT

The occurrence of hausmannite with an apparent Curie temperature close to 750 K, instead of 41.8 K was recently described from hydrothermally altered manganese ore from the Kalahari manganese field, South Africa. The unusual magnetic properties were related to the substitution of \( \text{Fe}^{3+} \) for Mn in the hausmannite structure. Because of the large differences in the scattering lengths of Fe and Mn, \( b_{\text{Fe}} = 9.94 \) and \( b_{\text{Mn}} = -3.73 \) fm, respectively, we performed neutron powder diffraction experiments at 295 and 10 K on natural mineral separates and synthetic compounds to determine the influence of the Fe substitution on the crystal structure and the magnetic properties of the hausmannite. Rietveld refinements of synthetic Fe-rich hausmannite neutron powder diffraction patterns at 295, 60, and 10 K indicate some significant and interesting changes of magnetic properties and crystal structure of hausmannite, which are directly linked to an increasing amount of iron substituting for manganese. The unit-cell parameters of \( \text{Mn}_{3-x}\text{Fe}_{x}\text{O}_{4} \), in particular, illustrate decreasing Jahn-Teller distortion with increasing Fe content, whereas the Curie temperature was found to increase significantly with increasing Fe content. Nevertheless, this study indicates that the presence of Fe-rich hausmannite causes the unusual high-temperature ferrimagnetic behavior in the Kalahari manganese field.

INTRODUCTION

Hausmannite, ideally \( \text{Mn}_3\text{O}_4 \), is a magnetically hard material with a tetragonal distorted spinel structure. It commonly accompanies other Mn-oxide minerals in metamorphosed or hydrothermal manganese ores (Frenzel 1980). However, macroscopic, euhedral crystals of hausmannite, typically in the pseudo-octahedral habit of a tetragonal bipyramid, are scarce and have only been described from a few localities, including Ilmenau, Thuringia (Germany) and the giant Kalahari manganese field, Northern Cape Province (South Africa). Recently, fine-grained and massive hausmannite-rich manganese ores have been described from Kalahari, which display an unusual, strongly ferrimagnetic behavior at room temperature (Gutzmer et al. 1995). These unusual magnetic properties were attributed by Gutzmer et al. (1995) to the presence of Fe-rich hausmannite, which contains up to 11.3 wt% of \( \text{Fe}_2\text{O}_3 \). Mössbauer spectroscopy suggested that all iron in the magnetic hausmannite samples is trivalent (Gutzmer et al. 1995). Furthermore, the ferrimagnetic state of hausmannite is stabilized and enhanced by replacement of Mn\(^{3+}\) by Fe\(^{3+}\), an effect that is also observable in other spinels of the \( \text{Mn}_x\text{Fe}_{3-x}\text{O}_4 \) group, although on a different scale. Curie temperatures increase in these Néel ordered spinels with increasing Fe content, e.g., from 413 K in \( \text{Mn}_3\text{Fe}_2\text{O}_4 \) (synthetic ferrite) to 563 K in \( \text{MnFe}_2\text{O}_4 \) (jakobsite) and 858 K in \( \text{Fe}_3\text{O}_4 \) (magnetite). The purpose of this study is to test this tentative conclusion of Gutzmer et al. (1995).

PROPERTIES OF PURE HAUSMANNITE

Nuclear structure

The \( [\text{Mn}^{2+}\text{Mn}^{3+}\text{O}_4] \) is a “normal” spinel compound, with divalent Mn\(^{2+}\) ions in the tetragonal site (Goodenough and Loeb 1955; Sinha et al. 1957; Satomi 1961; Boucher et al. 1971; Jensen and Nielsen 1974; Chardon and Vigneron 1986). A cubic high temperature phase appears above 1473 K (Frenzel 1980). Below this temperature, the compound \( [\text{Mn}^{2+}\text{Mn}^{3+}\text{O}_4] \) has the tetragonal symmetry (space group no. 141, \( I4_{1}/amd \)) of a distorted spinel structure, with the O atom in position (16h), the Mn\(^{2+}\) (3d\(^0\)) ions in a (4a) tetrahedral site and the Mn\(^{3+}\) (3d\(^3\)) ions in a weakly distorted octahedral site (8d) (Satomi 1961). At room temperature, the lattice constants for the body-centered tetragonal unit cell are \( a = b = 5.7691(4) \) Å and \( c = 9.4605(7) \) Å (Satomi 1961). The oxygen position \( y_0 = 0.4723(3) \) and \( z_0 = 0.2592(2) \), is determined by the balance between the co-operative Jahn-Teller distortion around the Mn\(^{3+}\) site, stretching the spinel-lattice along \( [001] \), countered by the force of the tetrahedron preserving its regular form against the tetragonal deformation of the crystal (Satomi 1961; Sinha...