The atomic arrangement and electronic interactions in vonsenite at 295, 100, and 90 K

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ABSTRACT

Vonsenite, Fe2+Fe3+O2BO3, has been the subject of many studies in the materials science and condensed matter physics communities due to interest in the electronic and magnetic properties and ordering behavior of the phase. One such study, undertaken on synthetic material of end-member composition, reports X-ray diffraction structure refinements that indicate a phase transition from Pham to Pbnnm at or just below ~283 K, determined subsequently to arise from a Peierls-like instability. To compare the stability of the natural phase with that of synthetic material, we performed high-precision X-ray crystal-structure analyses at 295, 100, and 90 K (Rω = 0.0119, 0.0186, and 0.0183, respectively), Mössbauer spectroscopy at 295, 220, 150, 80, and 4.2 K, and wavelength-dispersive electron microprobe analysis on a vonsenite of near-end-member composition from Jayville, New York, U.S.A. The Pbnnm structure is observed at 100 and 90 K, suggesting similar phase stability for the natural and synthetic phases. Comparison of Mössbauer data and X-ray site occupancies between the natural and synthetic phases suggests a reinterpretation of Mössbauer site assignments. We conclude that the Peierls-like instability underlying the reported transition from Pham to Pbnnm in synthetic material also occurs in our specimen of natural near-end-member vonsenite at temperatures between 295 and 100 K.

Keywords: Vonsenite, phase transition, low-temperature structure refinements, Peierls-like instability

INTRODUCTION

Vonsenite, Fe2+Fe3+O2BO3, is the heterovalent-iron end-member of the ludwigite group of high-temperature contact-metamorphic oxyborates. Vonsenite forms a continuous isomorphic solid-solution series with ludwigite sensu stricto, Mg2Fe3+O2BO3 (Tschemark 1874). The ludwigite group minerals are common accessories in boron-rich magnesian and calcareous iron skarns after dolomites (Palache et al. 1951). Vonsenite is much less common than ludwigite.

Takéuchi et al. (1950) first determined the structure of a natural ludwigite, and Takéuchi (1956) refined the structure of a natural magnesian vonsenite (Fe1.625Mg0.375) using Weissenberg data. Mokeyeva (1968) refined the structure of two crystals of synthetic ludwigite, [(Mg1.18Fe1.55)(Al1.18)]BO3O2, and was first to report the distribution of Fe2+ and Fe3+ over the cation sites. Swinnea and Steinfink (1983) refined the structure of a crystal of synthetic end-member vonsenite, supporting many prior findings and surpassing earlier structure refinements by an order of magnitude in precision. Structure refinement was attained to R = 0.030 in space group Pham; the atom nomenclature of those authors is generally respected in later investigations, and we continue that practice in this work. Based on Mössbauer spectra, site distortions, and bond valence sums, the authors report that Fe2+ occupies Fe1 and Fe3. “Direct exchange” is reported between Fe2 and Fe4 [separated by 2.783 Å at 295 K (Table 1)], “direct exchange” is understood here to mean intervalence charge transfer, after the cited Burns (1981), though the authors do not express this claim categorically, resulting in an intermediate valence of Fe2.5+ on both sites. Significantly, Mössbauer spectra are reported to establish the presence of charge delocalization along [001] as a function of temperature.

The pivotal work of Swinnea and Steinfink (1983) set the stage for many studies of vonsenite structure, crystal chemistry, and electronic interactions by the materials science and condensed matter physics communities. These studies were undertaken to explore and understand the subtle, complex electronic and magnetic characteristics of the phase, its ordering behavior, and its manifestation of multiferroicity [see van den Brink and Khomskii (2008) for a technical introduction to multiferroicity; Maignan et al. (2017) assume familiarity with multiferroicity and discuss it specifically in vonsenite]. All such studies known to the present authors [cf. the exhaustive review of Sofronova and Nazarenko (2017)] were performed upon synthetic vonsenite powders and single crystals of ideal end-member composition,