Morin-type transition in 5C pyrrhotite

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ABSTRACT

We report the discovery of a low-temperature spin-flop transition in 5C pyrrhotite at \textasciitilde155 K that is similar to those seen in hematite at 260 K and FeS (troilite) at 440 K. The 5C crystal was produced by annealing a 4C pyrrhotite crystal at 875 K to produce a change in the vacancy-ordering scheme that developed during cooling. The 5C structure is confirmed by single-crystal X-ray diffraction and the stoichiometry and homogeneity by electron microprobe and SEM BSE mapping. Resonant ultrasound spectroscopy (RUS), heat capacity, and magnetization measurements from room temperature down to 2 K are reported. The transition is marked by a steep change in elastic properties at the transition temperature, a peak in the heat capacity, and weak anomalies in measurements of magnetization. Magnetic hysteresis loops and comparison with the magnetic properties of 4C pyrrhotite suggest that the transition involves a change in orientation of moments between two different antiferromagnetic structures, perpendicular to the crystallographic c-axis at high temperatures and parallel to the crystallographic c-axis at low temperatures. The proposed structures are consistent with a group theoretical treatment that also predicts a first-order transition between the magnetic structures.

Keywords: Pyrrhotite, palaeomagnetism, mineralogy, crystal structure

INTRODUCTION

The pyrrhotite system comprises several related structures having compositions Fe\textsubscript{1-x}S where 0 < x < 0.125. The best known of these structures are troilite (FeS) and 4C pyrrhotite (Fe\textsubscript{x}S\textsubscript{1-x}). 4C is so called because it is a superstructure with a 4 cell repeat along the c-axis with respect to the parent NiAs structure (Bertaut 1953; Powell et al. 2004). Other commensurate superstructures have been reported as 3C (Fleet 1971; Nakano et al. 1979), 5C (de Villiers et al. 2009; Elliot 2010; Liles and De Villiers 2012), and 6C (Koto et al. 1975; de Villiers and Liles 2010), while some are incommensurate (Nakazawa and Morimoto 1971; Morimoto et al. 1975; Yamamoto and Nakazawa 1982; Izaoa et al. 2007). Ferrimagnetic pyrrhotite (4C) is an important carrier of magnetic remanence on earth and possibly also on Mars (e.g., Rochette et al. 2005; Martin-Hernández et al. 2008), but 4C structures are not unique, and the other superstructure types have different structure/property relationships that are much less well known. The key issue in relation to the magnetic structures is how vacancies order on the cation sites as the stoichiometry changes and how the distribution of vacancies then controls the magnetic structures.

By adopting a group theoretical approach, Haines et al. (2019) have shown that the commensurate superstructures of pyrrhotite, which have different Fe/vacancy ordering schemes, are all likely to undergo a magnetically driven spin reorientation transition with accompanying small distortions of the crystal lattice at low temperatures. The prediction for the case of 5C pyrrhotite is for an abrupt spin-flop transition similar to the Morin transition in hematite. The present work focuses on the magnetic and elastic properties of a natural 4C crystal that transformed unexpectedly to 5C crystal after being heated above its concomitant vacancy ordering and Néel temperature of 595 K. We report a newly identified magnetic transition at \textasciitilde155 K in the 5C crystal and propose that it is a spin-flop transition between two antiferromagnetic structures, with an origin that is closely related to that of the magnetic transition already known in FeS at 440 K.

In general, 5C pyrrhotite is found to have a composition close to Fe\textsubscript{2}S\textsubscript{10}. However, Pósfai et al. (2000) reported a 5C polytype with composition Fe\textsubscript{5}S\textsubscript{8}. Konnyn et al. (2000) also presented some X-ray diffraction and magnetization measurements on multiphase samples, suggesting the possibility of pyrrhotite with a 5C structure having the stoichiometry close to the Fe\textsubscript{5}S\textsubscript{8} that is usually associated with the 4C structure. de Villiers et al. (2009) proposed space group \textit{Cmce} (no. 63, formerly \textit{Cmca}) as the correct crystallographic space group at room temperature. Elliot (2010) had claimed \textit{P2\textsubscript{1}c} for the room-temperature structure. Liles and De Villiers (2012) subsequently proposed \textit{P2\textsubscript{1}}, for the structure at both room temperature and 120 K. There do not appear to have been any studies of the magnetic structure.

In this work, we first establish the stoichiometry of the sample through electron microprobe analysis before going on to present a structural solution in the space group \textit{Cmce} based on single-crystal X-ray diffraction data collected on a single-crystal sample of 5C pyrrhotite at room temperature. We then present heat capacity, DC magnetization, and resonant ultrasound spectroscopy (RUS) measurements on a second single crystal over the range 2–300 K.