New metastable phases in an oxyborate compound obtained by an evolutionary algorithm and Density Functional Theory

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ABSTRACT

New metastable phases in the Fe homometallic ludwigite compound are obtained and studied using an evolutionary algorithm and Density Functional Theory. Our lowest energy monoclinic structure is identified as $P2_1/m$ with space group number of 11. This structure evolves towards the monoclinic structure as the result of the spin orbit coupling and a particular zigzag magnetic structure. A zigzag distortion in a class of three-leg ladders follows similar to the experimental one observed below the transition temperature of $T_c = 283$ K. In this distortion long and short bonds inside rungs alternating in a zigzag way along the ladder legs. Furthermore, a new type of zigzag structural ordering is observed in other two low-energy phases analyzed. In this case, the magnetic ordering behaves qualitatively similar to the experimental structure at 82 K, with antiferromagnetically coupled ferromagnetic rungs. Our calculations show that magnetic symmetry is not favorable for zigzag structural ordering. Finally, structural and magnetic properties will be discussed in comparison with the experimentally known phases.

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1. Introduction

Exciting properties like structural, transport and magnetic ones have been studied in a class of oxyborates known as warwickites [1–3] and ludwigites [4–10]. Interesting physical behavior like Wigner glass, the existence of a weak ferromagnetism or even charge ordering has been observed in ludwigite materials as consequence of strong correlations and low dimensional effects. Warwickites are characterized by one-dimensional structures called ribbons where the transition metals are randomly located [1,2]. Ludwigites in contrast, have a crystalline structure that consists of an assembling of subunits in the form of zigzag walls, with four nonequivalent octahedral sites occupied by divalent o trivalent metallic ions [5]. Warwickites (q = 1) and ludwigites (q = 2) present the following chemical formula $M_qO_qM'BO_3$ where M(M') are divalent (trivalent) 3d transition-metal ions.

Among the ludwigites, the semiconductor homometallic (M = M' = Fe) $Fe_3O_2BO_3$ is particularly interesting, not only because of its intrinsic properties but also because of the underlying physics of spin ladders. Its structure can be viewed as formed of two magnetic subsystems which can be considered as decoupled to a first approximation [5]. Each consists of three-leg spin ladders subunits

of Fe^{2+} and Fe^{3+} cations. The first type consists of triads (Fe4-Fe2-Fe4) of Fe^{3+} ions with one itinerant electron per rung, while the second one is formed by triads (Fe3-Fe1-Fe3) of Fe^{2+} ions. These three-leg ladders are present in our structures in Figs. 1 and 2 and clearly evidenced in Figs. 3 and 4 for the 1_O phase corresponding to Fig. 2. A perspective in the a-b (x-y) plane of the Fe4-Fe2-Fe4 triads can be observed in Fig. 3. In the same figure three near diagonal Fe (blue) atoms form the triads. In Fig. 3 can be observed that Fe4-Fe2-Fe4 triads share the same plane with the group $(BO_3)^{-3}$. Fe3-Fe1-Fe3 triads are shown in Fig. 4 as three near horizontal Fe atoms. Fe4-Fe2-Fe4 ladders exhibit charge ordering and structural phase transition at $T_c = 283$ K observed using specific-heat measurements [6] and X-ray diffraction [7]. This transition is accompanied by a change in the activation energy of the electrical resistivity [7]. Below T_c, each triad presents a short and long bond alternating along the ladder c-axis [7] giving a zigzag structural arrangement similar to the one presented in Fig. 5-a). The overall crystal structure is orthorhombic, space group Pbnm. In the high temperature phase all bonds become equal in the triads as can be observed in Fig. 5c) and the symmetry is orthorhombic, space group Pbam.

An antiferromagnetic transition at 112 K has been observed. This transition basically involves Fe^{3+} and Fe^{2+} within the first magnetic system [11,12]. The complementary Fe-ions are

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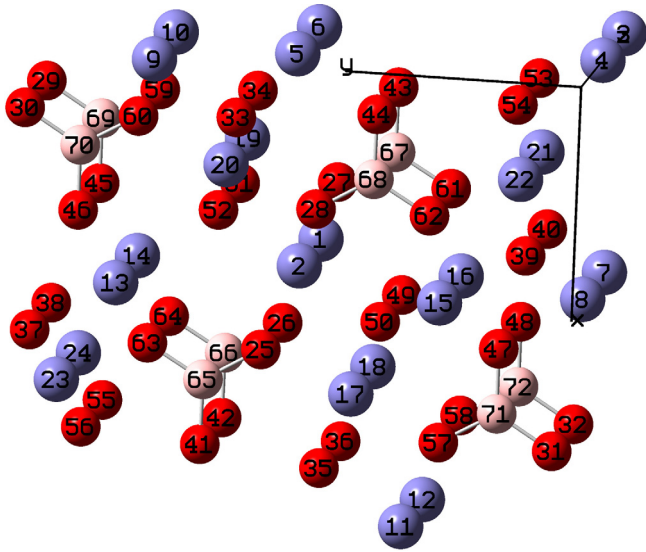 *E-mail address:* emapion2@gmail.com (E. Vallejo).

Fig. 1. Perspective of the 3D (three dimensional) unit cell of the 1_M_NC and 2_M structures. Blue, red and pink color corresponds to Fe, O and B atoms respectively. Numbering was included to identify atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
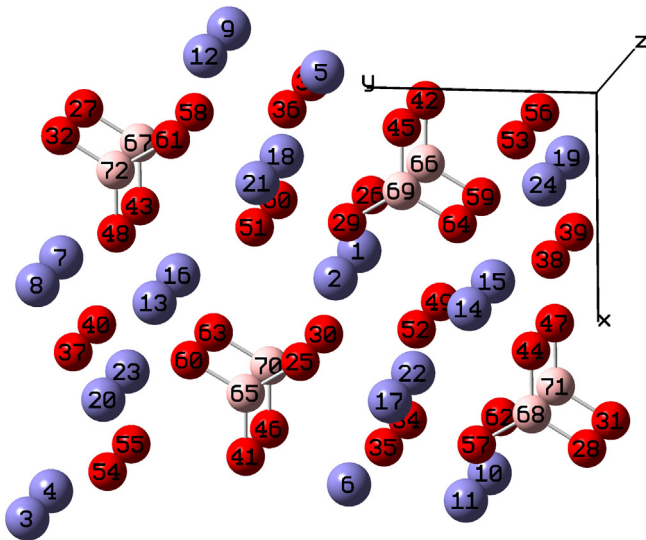

Fig. 2. Perspective of the 3D unit cell of the 1_O structure. Blue, red and pink color corresponds to Fe, O and B atoms respectively. Numbering was included to identify atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Perspective in the a-b (x-y) plane at z = c ∼ 1.5 Å of the Fe4-Fe2-Fe4 triads (three near diagonal Fe (blue) atoms) of the 1_O structure obtained from Fig. 2. Blue, red and pink color corresponds to Fe, O and B atoms respectively. Rectangle is a = 9.608 Å (red line) and b = 12.452 Å (green line) unit cell in accord to Table 1, and Fig. 2. Details in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Perspective in the a-b (x-y) plane at z = c ∼ 3.1 Å of the Fe3-Fe1-Fe3 triads (three near horizontal Fe (blue) atoms) of the 1_O structure obtained from Fig. 2. Blue and red colors correspond to Fe and O atoms respectively. Rectangle is a = 9.608 Å (red line) and b = 12.452 Å (green line) unit cell in accord to Table 1, and Fig. 2. Details in text. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

paramagnetic down to 74 K. Below 70 K all the sample becomes magnetically ordered. Mostly Fe^{3+} ions order in a weak ferromagnetism where canting of the magnetic hyperfine field for each Fe-ion is related to this order [5,6,12]. A total antiferromagnetic state is found below ∼ 40 K for this Fe-ludwigite. Below 40 K, two-dimensional antiferromagnetic magnons were proposed to explain the low-temperature T^2 behavior and disorder ($Fe^{3+} - Fe^{2+}$) was proposed to explain the large linear term of the specific heat in $Fe_3O_2BO_3$ [6] above 112 K. Transport measurements in Fe-Ludwigite show activated behavior with two characteristic energies above and below charge ordering at 220 K [5]. Theoretical investigation of spin exchange interactions and electronic structure were done using a spin dimer analysis [13] and the extended Hückel method [14] respectively. In contrast, an excitonic instability using a tight-binding model was studied in a three-leg ladder
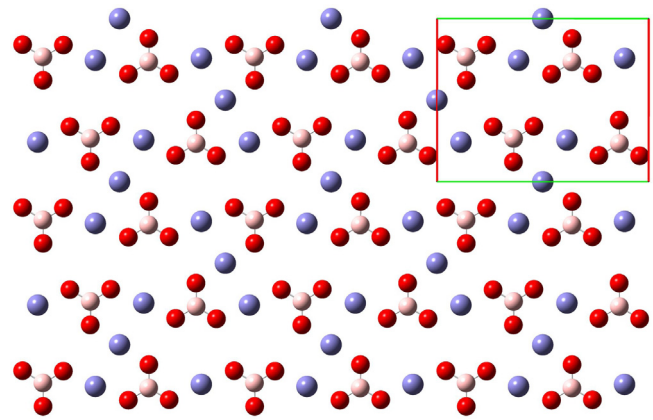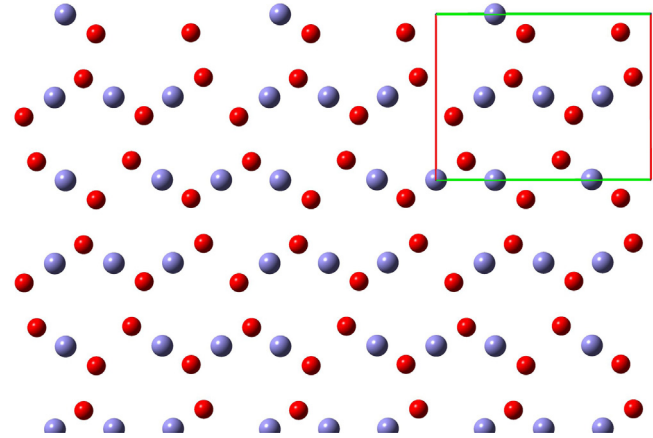
[15]. Nevertheless the important electronic, structural and magnetic correlation was taken into account by Vallejo and Avignon [16]. Spin and charge ordering was obtained resulting from the competition between double exchange and superexchange interactions. These interactions were proposed as a possible principal mechanism to study Ludwigites [16]. Double exchange interactions favor a ferromagnetic strong and short distance background of local spins. In contrast, superexchange interactions are responsible for antiferromagnetic ordering leading to interesting and unusual magnetic states [16]. Some of these magnetic phases obtained by Vallejo and Avignon are similar to these proposed to explain neutron powder diffraction experiments [11]. In the same way, similar magnetic behavior was found in a further theoretical work using density functional theory [17].

Contrastingly, the crystalline structure, space group and lattice parameters of the only other known homometallic oxyborate Co-based ludwigite $Co_3O_2BO_3$ are very similar to the previous Fe one at room temperature. These similarities suggest similar behaviors, nevertheless their physical properties are very distinct [18]. Structural distortion and two magnetic transitions (≃112 K and ≃70 K) are not found for the Co ludwigite [18]. Only one antiferromagnetic