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First principles calculation of magnetic order in a low-temperature phase of the iron ludwigite

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ABSTRACT

The magnetic order of a low-temperature dimerized phase of $Fe_3O_2BO_3$ is investigated through a density functional approach which considers full non-collinear spin–spin interactions, focusing on the 15 K crystalline structure. It is found that Fe spins in the $(Fe–Fe)^{5+}$ dimer, formed during the room temperature structural change of $Fe_3O_2BO_3$, are parallel and have little freedom to rotate under interaction with neighbor Fe atoms. While the Fe dimer behaves as a heavy single magnetic unit the spin magnetic moment of the third Fe^{3+} atom of the Fe *triad* has, on the contrary, much more freedom to rotate. This is responsible for a canted spin ordering, revealed by a rotation of $\sim 80^\circ$ of the trivalent Fe spin relative to the spin orientation of the dimer, due to spin–spin interaction with divalent Fe atoms outside the *triad*. Canting is thus seen to be responsible for the very low net magnetization, experimentally observed in this compound ($T < 40$ K).

1. Introduction

The renewed interest in the study of ludwigite compounds observed in the last decades was initially motivated by the low dimensionality of their crystal structure and its similarity with spinels [1–3]. After the discovery of a structural change in the Fe ludwigite [4,5], research has been mainly focused on understanding the mechanisms that cause the atomic instabilities. The structural change occurs at temperature $T_S = 283$ K and consists of an orthorhombic–orthorhombic transition that affects essentially a group of three Fe atoms. This iron *triad* stacks in one crystalline direction, forming a quasi-one-dimensional substructure that is responsible for the most interesting physical properties of this material [6–11].

Ludwigite is a metal oxo-borate of formula unit $M'_2MO_2BO_3$, where M′ and M are di- and trivalent metals. The crystalline structure consists of corrugated planes of oxygen octahedra filled with metals occupying 4 distinct crystal sites [6,12]. Trigonal BO_3 groups hold the planes together. Fig. 1 shows a polyhedral view of the $a \times b$ face of ludwigite, which has a flat orthorhombic unit cell ($a \sim 9$ Å, $b \sim 12$ Å and $c \sim 3$ Å), with 4 formula units. Considering the 4 different positions occupied by iron and 5 positions of oxygen atoms, the formula per unit cell of the mixed valence Fe ludwigite can be written as $(Fe4Fe2Fe4)_2(Fe3\ Fe1Fe3)_2(O2O4)_4(BO1O3O5)_4$. There are two Fe *triads*, 424 and 313, the former being associated with the complex behavior of this ludwigite, including the structural transition. In the high temperature phase the Fe2–Fe4 distance is 2.78 Å, the shortest observed in the Fe system of $Fe_3O_2BO_3$. Due to the structural transition, site 4 splits into 4a and 4b and inter-atomic distances change to 2.94 Å (Fe4b–Fe2) and 2.60 Å (Fe4a–Fe2). The transition could therefore be seen as a dimerization in the *triad*, with Fe4a-Fe2 forming the Fe dimer. Rietveld refinements show a doubling of the *c*-axis in the low temperature dimerized phase with alternation of the Fe2-Fe4a dimer along the *c*-axis [5]. Besides Fe ludwigite, $Co_3O_2BO_3$ is the only other homo-metallic ludwigite synthesized so far [13]. However, despite the strong similarity between the two mixed valence compounds, no structural transition was observed in the cobalt ludwigite [14,15].

Atomic instabilities were observed in other 2–3 mixed valence Fe oxides such as the spinel magnetite and the homo-metallic warwickite, Fe_2OBO_3, a different type of oxo-borate [1,16,18]. Both compounds undergo an orthorhombic–monoclinic transition driven by charge localization which forms a Wigner crystal phase [16–20]. Each of these materials exhibits one magnetic transition; Fe_3O_4 is ferromagnetic below $T_F = 858$ K and the warwickite becomes anti-ferromagnetic at $T_{AF} = 155$ K. No clear indication was found of interplay between charge localization and magnetism in these materials. Charge localization in magnetite occurs at 120 K (well below the magnetic transition) and in warwickite at

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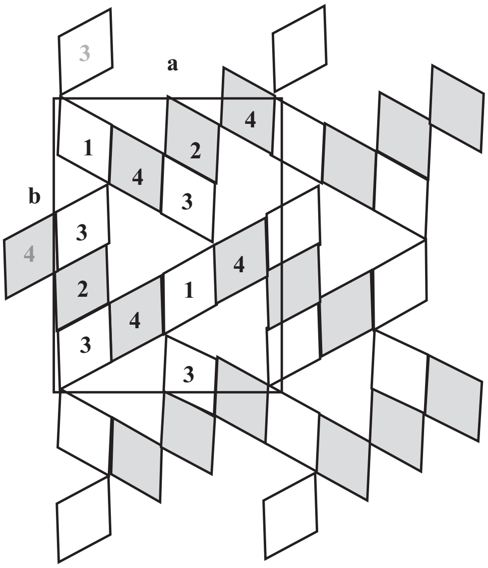

Fig. 1. Octahedral representation of $Fe_3O_2BO_3$, projected in the $a \times b$ plane, with unit cell indicated. Fe sites of the *triads* 424 and 313 are shown.

317 K (well above the magnetic transition) [16]. In $Fe_3O_2BO_3$, however, magnetism and charge ordering present more subtle behaviors that seem to be related, even though structural and magnetic transition temperatures differ. The first magnetic transition that occurs at 112 K, for instance, consists of an AF magnetic ordering which takes place mainly in the 424 *triad*, although Fe3 also begins to order magnetically in this temperature [3,8,9]. In the range 70–40 K, weak ferromagnetism was suggested with the inclusion of Fe1 in the magnetic order. Below 40 K the whole Fe spin system is ordered in a so-called 3D AF phase [3,9]. Thus, differently from magnetite and warwickite, in ludwigite there are three distinct magnetic phases, instead of one, all below the structural transition.

Formally, valences in the 424 group are (3+)(2+)(3+). However, like magnetism in the ludwigite, charge distribution presents different regimes, as seen from Mössbauer data obtained independently by Douvalis et al. [8] and Larrea et al. [9]. Results of both studies confirm the presence of divalent atoms attributed to Fe1 and Fe3 over a large temperature range (from 4 K to above 450 K). In the 424 group, good agreement is obtained within both studies for $T > 40$ K. Above 283 K there are two intermediate valences in the 424 *triad*, one close to 3^+ and the other close to 2+ associated to Fe4 and Fe2, respectively; at the structural transition (283 K) Fe4a reaches a valence close to that of Fe2 ($\sim +2.5$) while the charge of Fe4b approaches 3+, consistent with the dimerized structure. When magnetism sets in (112 K), the charge distribution continues to change although more smoothly. Between 112 K and 40 K there is an increasing tendency of uniformization of valences in the dimer, and that of Fe4b progressively approaching 3+.

Below 40 K results obtained by Douvalis et al. [8] and Larrea et al. [9] differ, both data confirming a tendency of the valences of the 424 *triad* to collapse into only two, pointing however to two possible arrangements $(Fe4b^{3+})(Fe2\text{–}Fe4a)^{5+}$ [8] and [9] $(Fe4b)^{2.5+}(Fe2)^{2+}(Fe4a)^{2.5+}$. More recently [11], from neutron diffraction data at 10 K, it was suggested that magnetic moments in the 424 *triad* are aligned ferromagnetically (F). AF alignment along *c* was assumed to satisfy the observed low magnetization of the sample. Earlier it had been suggested that, at very low temperatures, magnetic moments in the *triad* aligned antiferromagnetically [1,18]. Both studies find that magnetic moments in the group of Fe1 are opposite to those of Fe3, both perpendicular to the moments in the 424 *triad*. These results could be related to the interplay between magnetism and charge ordering in the 424 group since ferromagnetic alignment in a pair of Fe atoms favors electron hopping, leading to intermediate valence.

Theoretical research on $Fe_3O_2BO_3$ has been mainly based on one electron tight binding-based methodology. Realistic geometry-dependent electron–lattice interactions were studied by using the extended Hückel methodology with high spin band electronic configuration; local geometrical distortions of the oxygen octahedra were found to be related to the opening of a gap at the Fermi level of the minority spin band of the 424 *triad* [21]. The same methodology was used in an extensive study of spin exchange in both crystalline structures of $Fe_3O_2BO_3$ [22]. It was suggested that neighbor Fe spins are probably anti-parallel, independent of the pair. Tight binding models with infinite-U electron–electron repulsion on a three-leg ladder (3LL) system of Fe atoms have considered the possibility of Peierls instabilities being manifested in the structural transition [23]. More recently, Vallejo and Avignon [24]and Vallejo [25] included double and super-exchange terms in a tight binding hamiltonian to investigate the behavior of an itinerant electron in a trivalent, high-spin Fe triple describing the Fe4–Fe2–Fe4 rung. Phase diagrams relating spin exchange J and hopping parameters t provided general predictions of possible spin arrangements. They found that for reasonable parameters there is a tendency of ferromagnetic alignment in each rung, according to experimental predictions of Bordet and Suard [11]. These authors also suggest the presence of spin canting in the 424 *triad*.

In spite of considerable effort toward the understanding of the electronic and magnetic structure in the homo-metallic Fe ludwigite, a clear picture of the complex behavior of this material has not yet been given. A more detailed theoretical description of the system's magnetism could provide new insight into the behavior of this complex material. Thus we decided to do a first principles theoretical study of this compound by choosing the low-temperature dimerized phase of $Fe_3O_2BO_3$ for the following reasons: (i) neutron diffraction data and refined crystalline structure are available at $T = 10$ K and 15 K, respectively, (ii) in the range $\sim 5\text{–}\sim 40$ K, the magnetic arrangement and charge distribution are not expected to change considerably and (iii) it is a starting point to understand the more complex behavior around the structural transition. We use a first principles density functional theory taking into account, self-consistently, non-collinear spin–spin interactions. This is done by including in the exchange correlation functional the magnetization density, according to the methodology proposed by Hobbs et al. [26], available in the VASP computational code [27].

2. Computational details

The non-collinear spin-polarized electronic structure of Fe-ludwigite at 15 K has been obtained with periodic band-structure calculations using the first principles quantum-mechanical electronic structure density functional theory (DFT) program VASP [27]. The projector augmented wave potential and a plane wave basis set were employed using the Perdew–Burke–Emzerhof generalized gradient approximation (PAW-PBE) to describe the exchange and correlation. The Brillouin zone integration was performed using *K*-points grids of $2 \times 2 \times 3$ up to $4 \times 4 \times 5$ mesh within the Monkhorst–Pack scheme for electronic optimization and total energy calculations. Convergence is considered to be achieved when the total energy between two iterations is smaller than 1 meV. The electrons described as core in the PAW potentials are those composed of $[Ne]3s^2$ for Fe, leaving $3p^6 3d^7 4s^1$ valence electrons and [He] for both B and O leaving $2s^2 2p^1$ and $2s^2 2p^4$ valence electrons for B and O, respectively. Lattice parameters and