Journal of Magnetism and Magnetic Materials 401 (2016) 217–222

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

The superexchange interactions and magnetic ordering in low-dimentional ludwigite $Ni_5GeB_2O_{10}$

S.N. Sofronova [a,*], L.N. Bezmaternykh [a], E.V. Eremin [a,b], I.I. Nazarenko [b], N.V. Volkov [a,b], A.V. Kartashev [a], E.M. Moshkina [a,b]

[a] L.V. Kirensky Institute of Physics, Siberian Branch of Russian Academy of Science, 660036 Krasnoyarsk, Russia
[b] M.V. Reshetnev Siberian State Aerospace University, 660014 Krasnoyarsk, Russia

ARTICLE INFO

Article history:
Received 30 July 2015
Received in revised form
25 September 2015
Accepted 9 October 2015

Keywords:
Ludwigites
Magnetic order
Heat capacity
Exchange interactions
Ferrimagnetic

ABSTRACT

The ludwigite $Ni_5Ge(BO_5)_2$ belongs to a family of oxyborates which have low-dimensional subunits in the form of three-leg ladders unit structure. This material was studied by magnetic and thermodynamic measurements. $Ni_5Ge(BO_5)_2$ does not show full long-range magnetic order, but one goes into a partial ordering or spin-glass state at 87 K. The superexchange interactions were calculated in the framework of a simple indirect coupling model. Different models of magnetic structure of $Ni_5Ge(BO_5)_2$ and its unique magnetic behaviour was discussed.

1. Introduction

The ludwigites M_3BO_5 belong to the anhydrous oxyborates. In these materials, the metal ions form substructures such as ribbons, ladders and zigzag walls. The ludwigites are good examples of strongly correlated low dimensional systems with interesting physical properties. There are a charge-ordering phenomenon, the existence of two magnetic subsystems ordering independently at different temperatures in orthogonal directions, a spin-glass magnetic ordering, a reversal magnetization in these materials [1–5].

The specific-heat measurements show the long-range magnetic ordering in the whole system only in homometallic ludwigites (Fe_3BO_5 and Co_3BO_5) [6,7], the exception is $Co_5Sn(BO_5)_2$ [8]. In the heterometallic compounds with a magnetic metal ions there are no a true thermodynamic magnetic transitions. The magnetic ordering of the Fe^{3+} ions is observed in Co_2FeBO_5 and Ni_2FeBO_5, but the magnetic moments of diavalent subsystem (Co or Ni) freeze at low temperatures [7–9]. Nonmagnetic ions (Ti^{4+}, Mg^{2+}, Ga^{3+}) destroy long-range magnetic order and lead to spin-glass freezing in $Co_5Ti(BO_5)_2$ [10], $CoMgGaBO_5$ [11]. As cited above, despite being doped by nonmagnetic ions, $Co_5Sn(BO_5)_2$ has long range magnetic order below 82 K which is, surprisingly, the highest critical temperature found so far in the ludwigites [8]. This critical temperature can be explained by the absence of double-exchange interactions, which are usually present in the ludwigites and that give rise to a strong competition.

In order to extend our understanding of the interactions mechanism in the transition metal ludwigites, it is necessary to investigate materials of $Ni_{3-x}Me_xBO_5$ family (Me = Ge, Ti, Sn, Mn, Ga, Al, Cr, V). Many of these compounds were grown [12–17] before but there is no information about its physical properties.

This paper is the first step in studying of $Ni_{3-x}Me_xBO_5$ family. We present the study of the magnetic and thermodynamic properties of $Ni_5Ge(BO_5)_2$. We discuss the possible magnetic orderings in $Ni_5Ge(BO_5)_2$ and compare it with other investigated ludwigites.

2. Synthesis and structure

The single crystals of $Ni_5Ge(BO_5)_2$ with a ludwigite structure were synthesized by the spontaneous crystallization method. The flux was prepared in a platinum crucible with the volume $V = 100\ cm^3$ at the temperature $T = 1100\ °C$ by sequential melting of reactants taken in a molar ratio $Bi_2Mo_3O_{12}$:B_2O_3:Li_2CO_3:NiO:GeO_2 = 1:2.4:2:1.14:0.23. The total mass of reactants was 71 g. In the prepared flux, the phase crystallizing within a sufficiently wide (about 40 °C) high-temperature range was $Ni_5Ge(BO_5)_2$ with the ludwigite structure. The saturation temperature of the flux was $T_{sat} = 970\ °C$.

* Corresponding author.
E-mail address: ssn@iph.krasn.ru (S.N. Sofronova).

http://dx.doi.org/10.1016/j.jmmm.2015.10.024
0304-8853/

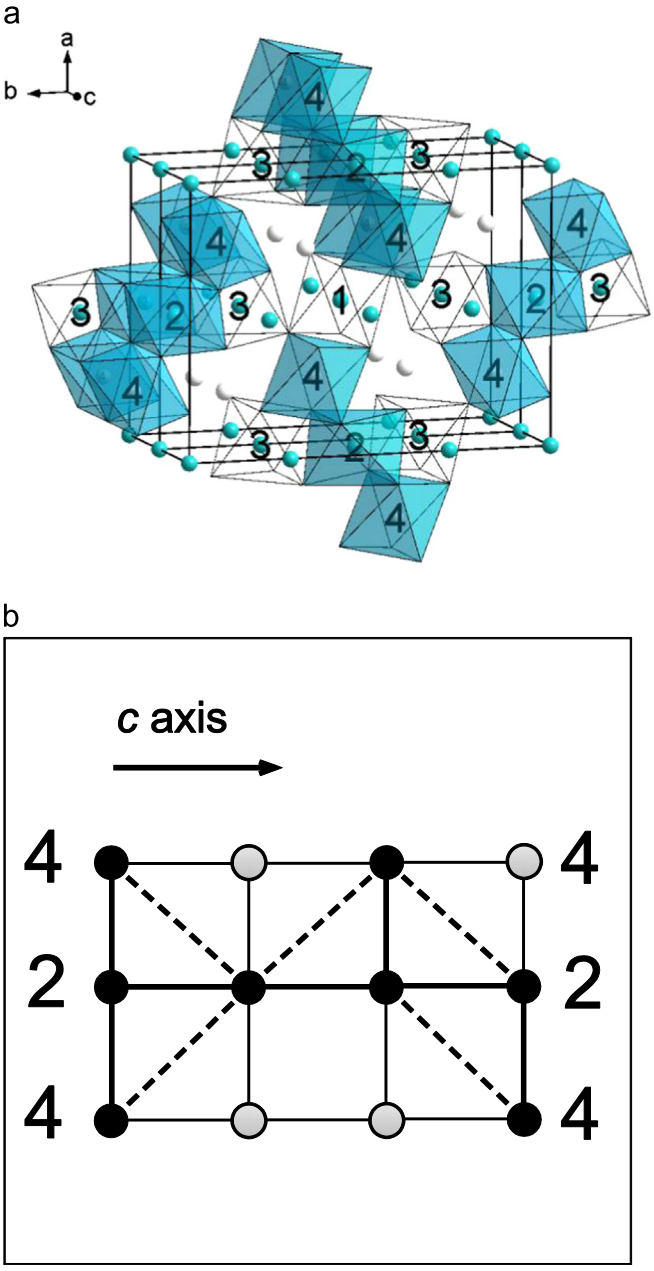

Fig. 1. (a) The structure of $Ni_5Ge(BO_5)_2$ crystal. (b) The subunit formed by the metal sites 4–2–4. The site 4 is occupied randomly by Ge and Ni ions in a proportion 0.5:0.5. Dark circles are Ni ions. The light circles are Ge ions. The 180° superexchanges are shown by the dashed lines. The 90° superexchanges are shown by the solid lines.

After homogenization of the flux at $T=1100$ °C for 3 h, the temperature was first rapidly reduced to $(T_{sat}-10)$ °C, and then slowly reduced with a rate of 4–12 °C/day. In 3 days, the growth was completed, the crucible was withdrawn from the furnace, and the flux was poured out. The grown single crystals in the form of black orthogonal prisms with a length up to 6 mm and a transverse size of about 0.3 mm were etched in a 20% water solution of nitric acid to remove the flux remainder.

A single-crystal x-ray diffraction of $Ni_5Ge(BO_5)_2$ showed that the structure of our single-crystals is the same as the structure was solved by Bluhm in the work [17]. We used the structural data from the Bluhm's paper [17]. The $Ni_5Ge(BO_5)_2$ crystal belongs to the $Pbam(D_{2h}^{16})$ space group with the lattice parameters $a=9.18$ Å, $b=12.14$ Å, and $c=2.98$ Å (Fig. 1). The unit cell involves two formula units. The sites 1(2b), 2(2c), 3(4h) are exclusively occupied by Ni. The site 4 (4g) is occupied randomly by Ge and Ni ions in a proportion 0.5:0.5 [17].

Table 1
The Ni–Ni bond lengths (Å) in $Ni_5Ge(BO_5)_2$.

Ni_i–Ni_j, i, j – crystallographic positions	R (Å)
Ni_4–Ni_4, Ni_1–Ni_1, Ni_2–Ni_2, Ni_3–Ni_3	2.98
Ni_4–Ni_3	3.084, 3.344
Ni_2–Ni_3	2.763
Ni_4–Ni_2	3.049
Ni_4–Ni_1	3.003
Ni_1–Ni_3	3.411

The ludwigite crystal structure consists of low-dimensional subunits: two three-leg ladders (3LLs) of different types. The ions in the 4–2–4 sites form so-called triads arranged as the rungs of the three-leg ladder of type I. Direct exchange is usually possible in the 4–2–4 ladders which have the smallest intermetallic distances (see Table 1). The Goodenough rule predicts that the 180° superexchange interaction Ni^{2+}–Ni^{2+} in triads of type I are strongly antiferromagnetic, as the 90° superexchange interaction Ni^{2+}–Ni^{2+} in triads of type I are ferromagnetic (Fig. 1(b)) [18]. The ions in the 3–1–3 sites form a three-leg ladder of type II. Triads of type II have the biggest intermetallic distances (see Table 1). The columns of edge-sharing octahedral form zigzag walls spreading along the crystallographic c axis.

3. Magnetic measurements

The magnetic measurements were performed using PPMS and MPMS facilities (Quantum Design) at the temperatures of 2–300 K in the magnetic fields up to 70 kOe. Figs. 2 and 3 present temperature dependences of magnetization and temperature dependences of inverse magnetic susceptibility of $Ni_5Ge(BO_5)_2$. Zero-field cooled (ZFC) and field cooled (FC) dc magnetization measurements were performed with applied fields of 1 kOe (Fig. 2) and 25 kOe (Fig. 3) oriented along the a, b, and c axes of single crystal. The magnetization curves have a sharp kink pointing out the occurrence of magnetic ordering near $T=87$ K. The temperature dependences of magnetization along the a and b axes show splitting of the curves corresponding to FC and ZFC regimes. The temperature dependence of the inverse dc magnetic susceptibility

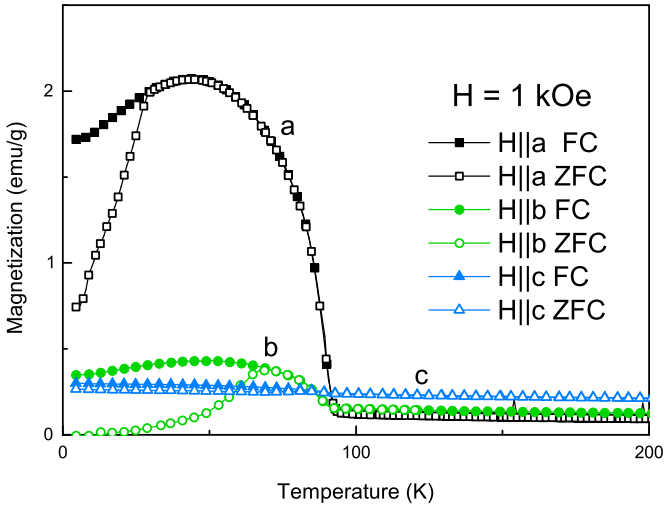

Fig. 2. The temperature dependences of magnetization in an applied field of 1 kOe oriented along the a, b, and c axes of single crystal in both regimes: zero-field cooled (ZFC) and field cooled (FC).