

Mossbauer magnetization and resistivity studies of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$

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Abstract

Single crystals of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ were prepared by spontaneous crystallization using a solution melt technology for the first time and its structure, electronic and magnetic properties were investigated by X-ray diffraction, Mossbauer spectroscopy, magnetization and electrical measurements. Room-temperature Mossbauer measurements indicate that “localized” (Fe^{2+} , Fe^{3+}) and “delocalized” ($\text{Fe}^{2.5+}$) states in ratio 0.31:0.345:0.345 distributed over two crystallographically non-equivalent positions exist. The results of magnetic measurements show that warwickite is a P-type ferrimagnet below $T = 130$ K. Resistivity measurements show a variable-range-hopping when electron–electron interactions cause a soft Coulomb gap in the density of states at the Fermi energy.

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1. Introduction

Transition metal oxi-borates $\text{M}^{2+}\text{M}'^{3+}\text{BO}_4$ adopt the orthorhombic warwickite structure which consist of low-dimensional units (ribbons). Intrinsic disorder due to the random occupation of the different octahedral sites by different transition metals (M and M') together with the

low-dimensionality gives rise to a variety of interesting effects (antiferromagnetic Heisenberg chains, charge ordering, structure phase transition etc.) [1]. Recent studies of mixed-valence iron oxide Fe_2BO_4 have shown the existence of a monoclinic–orthorhombic structural transition at 317 K, with concomitant charge delocalization above this temperature [2].

In the present work, we report the Mossbauer magnetization and resistivity measurements on vanadium-substituted single crystals of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$.

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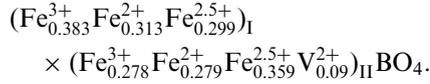
2. Experimental procedure

$\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ single crystals were prepared using a solution melt technology in $\text{Fe}_2\text{O}_3\text{--V}_2\text{O}_3\text{--B}_2\text{O}_3\text{--}(70\text{PbO}+30\text{PbF}_2 \text{ wt}\%)$. Single crystals of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ possess a regular shape and smooth surface with the needle form. A length of the needle is up to 1 cm and a thickness of 0.10–0.15 mm. Elemental composition of grown samples was determined by energy-dispersive X-ray spectroscopy (EDAX ZAF quantification procedure). X-ray diffraction was studied on a setup of the D8 ADVANCE type using CuK_α radiation ($\lambda = 1.506 \text{ \AA}$). Room-temperature scans of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ over $2\theta = 13.4^\circ\text{--}89.7^\circ$ showed an orthorhombic structure (P_{nam}) with lattice parameters $a = 3.1727$, $b = 9.3831$, $c = 9.2317 \text{ \AA}$, $\beta = 89.993$ [3]. The temperature magnetization were measured on a vibration-sample magnetometer with a superconducting coil in the temperature range 80–140 K. The Mossbauer spectra were obtained using $^{57}\text{Co}(\text{Cr})$ source on single-crystal powders with a linear density of 5–10 mg Fe/cm and a natural room-temperature iron content. The DC resistivity measurements were performed in the temperature range 100–400 K.

3. Results and discussion

The room-temperature Mossbauer spectrum of a $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ single crystal represents a superposition of several quadrupole doublets. The fitted parameters indicate localized (Fe^{2+} , Fe^{3+}) and delocalized ($\text{Fe}^{2.5+}$) states distributed on two non-equivalent (with respect to local environment) crystallographic positions, I and II. The area ratio of $\text{Fe}^{2+}:\text{Fe}^{2.5+}:\text{Fe}^{3+}$ is 0.31:0.345:0.345. All doublets can be assigned to high-spin, octahedrally oxygen-coordinated Fe states. The isomer shift values of $\text{Fe}^{2.5+}$ are characteristic of a mixed valence of Fe^{2+} and Fe^{3+} states, which appears as a result of the fast electron exchange between these ions. The quadrupole splitting values of I and II sites are slightly different and show that the coordination octahedron on position II is more distorted than that in position I. Taking into account the condition of electroneutrality, the

formal valence of vanadium is 2+. The cations distribution over crystallographic positions can be written as follows:



A comparison of the same distribution for the unsubstituted Fe_2BO_4 [4] suggests that vanadium replaces Fe^{2+} ions in position II and changes the ratio of localized:delocalized states in I and II positions.

Magnetization measurements have revealed a magnetic ordering transition at $T_C = 130 \text{ K}$ [3], whereas the long-range magnetic order in Fe_2BO_4 is established at 155 K. We have assumed that a broad maximum observed at $T = 60 \text{ K}$ can be attributed to the temperature of the maximum deference in magnetization of two sublattices (I and II). This conclusion is in agreement with the existence of P-type ferrimagnetism found in the unsubstituted Fe_2BO_4 using neutron scattering [5]. Fig. 1 shows the temperature dependence of magnetization in $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ at fields of $H = 100, 500$ and 1000 Oe and zero field. The external field is applied parallel to the a -axis of a needle crystal. All curves were measured in the heating regime from liquid nitrogen temperature to 140 K after the sample was cooled at zero field. There is a feature at about $T = 120 \text{ K}$. The peak bifurcation

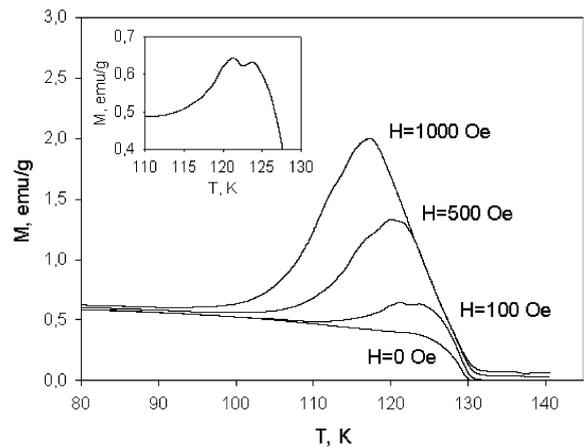


Fig. 1. Magnetization of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ as function of temperature at zero field, 100, 500 and 1000 Oe. The inset shows the features of the $M(T)$ curve at 100 Oe.

arises at $H = 100$ Oe (see inset of Fig. 1). The peak is increased while the “splitting” becomes lower manifested as field is increased. The saturation moment per formula in the warwickite $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ is $0.1\mu_B$ at 4.2 K, that is greater than that reported for Fe_2BO_4 ($0.06\mu_B$). This difference could correspond to the decreasing of average spin at substitution of the Fe ions by V ions.

The warwickites with $M = M'$ in general demonstrate a semiconducting behaviour and a charge ordering. This process is accompanied by a lattice distortion characteristic of the Jahn–Teller effect (Mn_2BO_4) and the formation of Wigner mini-crystals (Fe_2BO_4) [6]. The last system undergoes the charge ordering below 317 K with simultaneous origin of monoclinic distortions.

The temperature dependence of the electric resistance for $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ single crystals is typical of 3d metal borates such as VBO_3 and solid solutions $\text{Fe}_{1-x}\text{V}_x\text{BO}_3$ [7] and exhibit a sharp increase in the resistivity and tend to “dielectrization” at low temperature. As temperature is decreased from 400 K to 100 K the resistivity of $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ samples is increased by 10 orders of magnitude.

Investigation of the $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ single crystal revealed deviation from the linear temperature dependence, $\ln \rho(T) \sim T^{-1}$, characteristic for the activated conductivity of Fe_2BO_4 . Least-squares processing of the experimental data has shown different conductivity mechanisms being in different temperature intervals. The resistivity of the $\text{Fe}_{1.91}\text{V}_{0.09}\text{BO}_4$ samples exhibit activated-type conductivity as well as $\exp(T^*/T)^{1/2}$ behaviour in the

wide temperature range. We attribute the latter to Efros–Shklovskii variable-range hopping in the presence of a soft gap in the one-electron density of states at the Fermi level due to Coulomb interactions [8]. This leads to much lower conductivity at low temperatures.

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