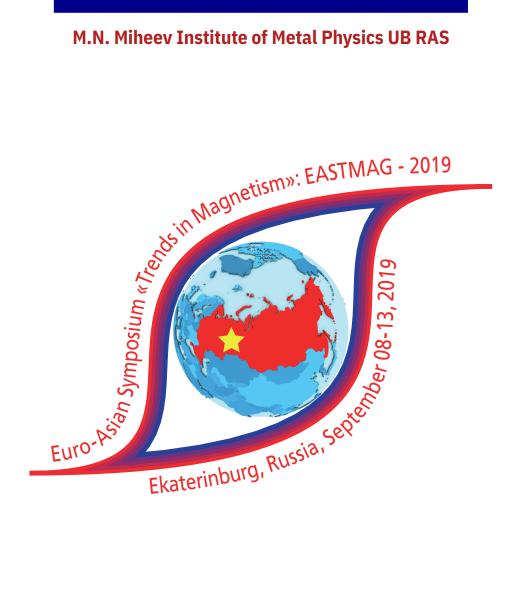
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## **BOOK OF ABSTRACTS. VOLUME I**



# HEAT CAPACITY, STRUCTURAL AND MAGNETIC PROPERTIES OF MIXED-VALENCE Pb<sub>3</sub>(Mn,Cu)<sub>7</sub>O<sub>15</sub>

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The family of crystals of Pb<sub>3</sub>(Mn,Me)<sub>7</sub>O<sub>15</sub> with different dopants Me is very attractive to study the low-dimensional magnetism phenomena due to the structural features of these crystals. In structure of Pb<sub>3</sub>(Mn,Me)<sub>7</sub>O<sub>15</sub> the magnetic ions form planes which connected through columns. The magnetic properties of parent compound which is Pb<sub>3</sub>Mn<sub>7</sub>O<sub>15</sub> are very complex. The paramagnetic behavior of Pb<sub>3</sub>Mn<sub>7</sub>O<sub>15</sub> is observed at temperatures down to  $\sim 250$  K. On further cooling, short-range correlations occur in the system and extensive antiferromagnetic clusters start forming at  $\sim 160$  K. At 70 K the long-range magnetic order is established, and low spontaneous magnetization is observed in all the ordered regions. At  $\sim 20$  K one more magnetic transition occurs in the crystals, which can be related to reorientation of a magnetic moment [1]. The different dopants (Li, Ga, Ge, Ru, Fe, Ni etc.) depending on concentration can change the magnetic properties as dramatically as slightly [2].

In this study, we systematically investigate the effect of substitution of cooper for manganese on the magnetic and structural properties of the  $Pb_3(Mn_{1-x}Cu_x)_7O_{15}$  single crystals. The choice of cooper as a substitute was imposed by the following circumstances. We assume that embedding of  $Cu^{2+}$  in our compound can firstly change the  $Mn^{3+}/Mn^{4+}$  ratio. Secondly, the octahedra occupied by the Jan-Teller  $Mn^{3+}$  ions will replace by Jan-Teller  $Cu^{2+}$ . Such replacement can significantly changes the exchange interactions between the planes that can dramatically changes the magnetic properties of  $Pb_3(Mn_{1-x}Cu_x)_7O_{15}$ .

The XRD investigations have shown that all the  $Pb_3(Mn_{1-x}Cu_x)_7O_{15}$  crystals belong to the hexagonal space group  $P6_3/mcm$ . Since the Mn2 (8h) sites in the structure are fully substituted by Cu all manganese ions have the valence 4+. The changes of the magnetic properties were not significantly what we were expecting. The broad peak at T=160 K moves to T=140 K and almost vanishes. The temperature of long-range magnetic order decreases to 60 K, but the temperature of reorientation of a magnetic moment increases to 30 K.

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#### **NEGATIVE MAGNETIZATION OF THE Ni<sub>5.33</sub>Ta<sub>0.67</sub>B<sub>2</sub>O<sub>10</sub> CRYSTALS**

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Oxyborates are interesting and wide group of compounds for studying the low-dimensional systems. Although oxyborates grow in different structures, almost all of these structures include low-dimensional elements such as walls [1], ladders [2], chains [3], and ribbons [4]. Ni<sub>5.33</sub>Ta<sub>0.67</sub>B<sub>2</sub>O<sub>10</sub> belong to wide group of compounds with the general chemical formula  $M_3$ BO<sub>5</sub> ( $M_6$ B<sub>2</sub>O<sub>10</sub>). The metallic ions in such compounds have different valence state due to the electroneutrality conditions. The mix of  $2^+ - 3^+$ ,  $2^+ - 4^+$  and  $2^+ - 5^+$  is possible. In Ni<sub>5.33</sub>Ta<sub>0.67</sub>B<sub>2</sub>O<sub>10</sub> divalent nickel and pentavalent tantalum is mixed. For the first time Ni<sub>5.33</sub>Ta<sub>0.67</sub>B<sub>2</sub>O<sub>10</sub> were grown in 1990-s, but only the structure were studied [5].

The small single crystal of  $Ni_{5.33}Ta_{0.67}B_2O_{10}$  were synthesised using the flux technique. The structure of these crystals is similar the structure obtained in [5]. Magnetic measurements of powder of  $Ni_{5.33}Ta_{0.67}B_2O_{10}$  were performed using PPMS-9. It was found that the magnetization curves show three features around 167, 43 and 25 K. In small field the magnetization in zero-field-cooling regime is negative. The compensation point occurs around 30 K (Fig. 1).

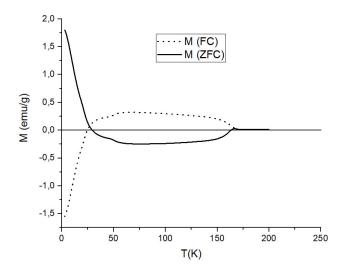


Figure 1. The temperature dependence of the magnetization in field-cooling (FC) and zero-field-cooling (ZFC) regimes in field 200 Oe

If the field more than 2 kOe the compensation point disappears (Fig. 2).

The magnetization behavior strongly depends on history the sample. The theoretical group analysis and an analysis of the possible magnetic structure using a simple indirect coupling model [6,7] based



# STRUCTURE AND MAGNETIC PROPERTIES OF THE $Mn_{3-x}Mg_xBO_5$ (x=1.6, 1.8) SINGLE CRYSTALS

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The single crystals of  $Mn_{1.4}Mg_{1.6}BO_5$  and  $Mn_{1.2}Mg_{1.8}BO_5$  have been grown by the flux method in the system  $Bi_2Mo_3O_{12}+B_2O_3+Na_2O+MgO+Mn_2O_3$ . The crystal structures were solved by means of single-crystal x-ray diffraction. The  $Mn_{1.4}Mg_{1.6}BO_5$  was found to crystallized in orthorhombic symmetry (Pbam(55)) with lattice parameters  $\alpha=18.3332(14)$  Å, b=12.5173(10) Å, c=3.0385(2) Å, V=697.28(9) ų. This material is isostructural to mineral "ortho-pinakiolite". The crystal structure contains seven crystallographically distinct metal atoms in octahedral coordination. The (Mg/Mn)O6 octahedra share edges to form a three-dimensional framework. The  $Mn_{1.2}Mg_{1.8}BO_5$  has a hulsite structure with monoclinic symmetry (Sp.gr. P2/m). The lattice parameters are  $\alpha=5.3266(4)$  Å, b=3.0180(2) Å, c=10.8743(7) Å,  $\beta=95.274(2)^\circ$ , V=174.07(2) ų. There are five symmetrically distinct sites. The  $Mg^{2+}$ ,  $Mn^{2+}$ , and  $Mn^{3+}$  ions have an octahedral coordination.

Magnetic properties highlighting the effect of crystal structure on the magnetic behavior have been studied. The analysis of magnetization and heat capacity data has shown that these compounds exhibit a spin-glass transition below  $T_{SG}=32$  for  $Mn_{1.4}Mg_{1.6}BO_5$  and 90 K for  $Mn_{1.2}Mg_{1.8}BO_5$ . The FC, ZFC and HC measurements have shown low-temperature anomalies at 6 and 8 K for x=1.4 and 1.8, respectively, which can indicate magnetic ordering. The spin-glass character is explained in terms of the substitutional disorder of Mg and Mn atoms. The results are discussed in compare with other Mg–Mn oxyborates such as the warwickites and ludwigites.

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