Charge-ordering and magnetism of Mn_2BO_4 oxyborate

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Oxyborates with general formula $M^{2+}M^{3+}BO_4$, which are isostructural to the mineral "warwickite", contain equal amounts of divalent and trivalent metal ions, and in a similar manner to magnetite Fe_3O_4 [1] it might undergo a charge ordering (CO). Three known mixed-valence warwickites Mn_2BO_4 [2], Fe_2BO_4 [3] and V_2BO_4 [4] demonstrate a temperature-induced CO transitions, which is accompanied by the orthorhombic → monoclinic symmetry lowering. The Fe_2BO_4 shows a rich electronic phase diagram with commensurately and incommensurately modulated charge ordered states at $T<T_{CO}$ = 340 K and the valence fluctuating state above T_{CO}. The CO in iron warwickite is supposed to be driven by electrostatic repulsion between the charges (Wigner crystallization), while the CO in manganese warwickite Mn_2BO_4 is associated with the orbital ordering in the presence of a x^2-y^2 hole localized at Mn^{3+}. The nature of CO in warwickites is the subject of hot discussions for two decades.

In this work we studied the long-range crystal structure, valence states and local structure around Mn atoms in Mn_2BO_4 through the temperature dependent X-ray powder diffraction (XRPD), Mn K-edge X-ray absorption (XAFS) spectroscopy, and heat capacity (HC) measurements. The XRPD, XAS and HC measurements were carried out in temperature ranges 298-973 K, 9-500 K, and 2-773 K, respectively.

The monoclinic symmetry (P21/n) was found to persist up to highest temperature measured. The *a*-lattice parameter shows negative thermal expansion in the T range 300-500 K. The BVS calculations were revealed large valence difference between two manganese sites that strongly supports the presence of CO up to high temperatures. The above estimations suggest that the Mn1 site is filled exclusively by Mn^{3+} ions, whereas the Mn2 site is occupied by Mn^{2+} ions. The pronounced temperature dependence of the Debye-Waller (DW) factor corresponding to the Mn-O coordination shell was found from the extended x-ray absorption fine structure (EXAFS) analysis and was associated with variations in the local distortions in MnO_6 octahedra and emergence of short-range magnetic correlations at low temperatures. Magnetization and heat capacity measurements establish the formation of an antiferromagnetic order at Neel temperature T_N=26 K. No any other anomalous were observed in the temperature dependence of HC, which could indicate structural phase transitions. In conclusion we discuss possible mechanisms of CO in Mn_2BO_4 and compare it with the CO observed in Fe_2BO_4.

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