Report on

Collaborative research on the ferroic properties of nickel iodine and nickel chlorine boracites

Four different ferroic properties that materials can have are ferroelasticity, ferroelectricity, ferromagnetism, and ferrotoroicity. Multiferroics possess more than one ferroic property and are important for potential applications. The objective of this research collaboration was to explore why certain compounds exhibit more than one ferroic property by studying two isostructural/isoelectronic multiferroics that show different ferroic properties.

Nickel iodine (Ni-I) boracite, $Ni_3B_7O_{13}I$, and nickel chlorine (Ni-Cl) boracite, $Ni_3B_7O_{13}Cl$, are isostructural are isostructural and isoelectronic, but their multiferroic properties are not identical. The structures of these boracites can be best described by analogy to the well-known peroskite oxides AMO_3, in which the MO_6 octahedra share their corners to form the three-dimensional framework and the element A occupies the center of each M_8 cube. From the viewpoint of perovskite, the formulas of the boracites can be rewritten as $(B_7O_{13})XNi_3$ (X = Cl, I). Namely, the B_7O_{13}, X and Ni play the role of A, M and O, respectively. In real structures, the –X–Ni–X–Ni– linkage along each of the three orthogonal directions undergoes a bond alternation ····X-Ni····X-Ni···· so as to form XNi_3 pyramids, as depicted in **Fig. 1a**, where the green and grey spheres represent the X and Ni atoms, respectively.

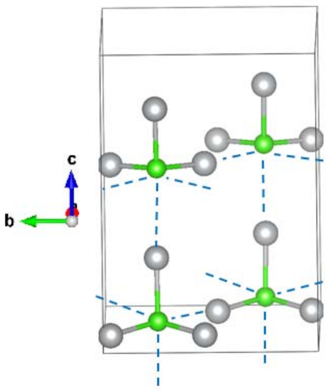

Fig. 1a

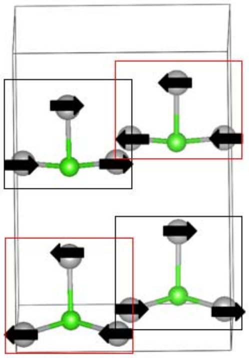

Fig. 1b

We determined the signs and magnitudes of 13 different spin exchange paths for Ni-I and Ni-Cl boracites by performing energy-mapping analysis based on DFT+U calculations. In addition, we carried out DFT+U+SOC calculations to determine the spin orientations. As summarized in **Fig. 1b**, the most important findings of our calculations are:

(a) that in each XNi_3 pyramid the three Ni^{2+} (S = 1) spins are ferromagnetically coupled, and these ferromagnetic exchanges are very strong,

(b) that these ferromagnetic XNi_3 pyramids are antiferromagnetically coupled along each of the three orthogonal directions.

The above two results are not in support of the magnetic structures of Ni-Cl and Ni-I boracites reported in the literature, which are presented in **Fig. 2a** and **2b**, respectively. Here the signs "+" and "-" indicate that the spins are pointed vertically out of the plane and vertically into the plane, respectively. In each XNi_3 pyramid of Ni-Cl (**Fig. 2a**) and Ni-I (**Fig. 2b**) boracites, two Ni^{2+} spins are antiferromagnetically coupled, and these two spins are orthogonal to the third Ni^{2+} spin. This cannot be correct by symmetry, because the three Ni^{2+} ions in each XNi_3 pyramid are practically equivalent. In the reported Ni-Cl magnetic structure (**Fig. 2a**), the two Ni^{2+} spins in each Ni-Cl····Ni linkage are antiferromagnetically coupled in all three directions, as found theoretically. In contrast, in the reported Ni-I magnetic structure (**Fig. 2b**), the two Ni^{2+} spins in each Ni-I···Ni linkage are antiferromagnetically coupled in only one direction but are ferromagnetically coupled in the remaining two directions. Given the isostructural nature between the Ni-Cl and Ni-I boracites, such a discrepancy as reported in the neutron diffraction studies is difficult to support. We are quite confident that our theoretical conclusions are correct.

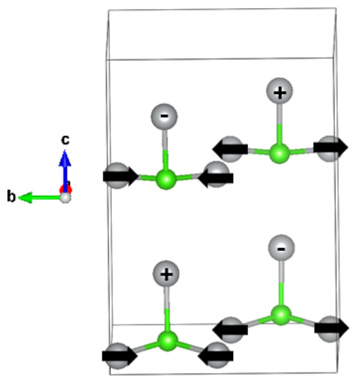

Fig. 2a: Ni-Cl

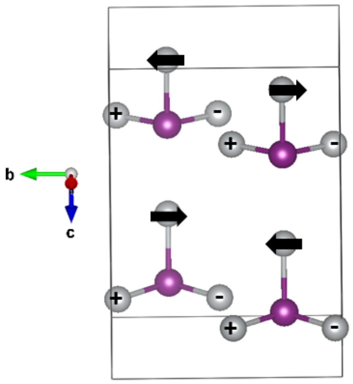

Fig. 2b: Ni-I

Planned calculations for the ferroelectric polarizations of the Ni-I and Ni-Cl boracites have not been completed yet. Whangbo's graduate student Elijah Gordon and Dr. Silvia Picozzi's group member, Dr. Aessandro Stroppa, will carry out these calculations in the coming months.

This report was prepared by M.-H. Whangbo on June 12th, 2015.

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