Experimental report

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Proposal: 5-31-2404 **Council:** 4/2015

Title: Non magnetic ions enhance magnetic order in the ludwigite Co5Sn(O2BO3)2

Research area: Physics

This proposal is a new proposal

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Samples: Co5Sn(O2BO3)2
Co3O2BO3

Instrument	Requested days	Allocated days	From	To
D1B	2	2	10/11/2015	12/11/2015

Abstract:

The ludwigites Co5Sn(O2BO3)2 and Co3O2BO3 belong to a family of oxyborates which presents low dimensional sub-units in the form of three leg ladders in its structure. The sub-units confer to these materials a strong anisotropy in their exchange interactions that provide to the ludwigites several interesting magnetic properties. The pure compound has a ferrimagnetic ordering near 43 K, while the Co5Sn(O2BO3)2 system has long range magnetic order below TN = 82 K. Surprisingly, the magnetic interactions are strengthened by the introduction of non-magnetic ions and the transition temperature of the whole system is the highest critical temperature found so far in the ludwigites. The determination of the magnetic structure in these systems will contribute to a complete understanding of the mechanism of the magnetic interactions in these materials, which in turn can help to understand many properties found in other ludwigites. For that reason we propose to carry out a temperature dependent neutron powder diffraction study on D1B in both compounds the pure one Co3O2BO3 and the doped one Co5Sn(O2BO3)2.

Report

Non magnetic ions enhance magnetic order in the ludwigite Co5Sn(O2BO3)2

A neutron powder diffraction (NPD) experiment was carried out in the D1B instrument of the Institut Laue-Langevin (ILL) in Grenoble. Two samples were measured: Co5Sn(O2BO3)2 and Co3O2BO3. 3 g of needle shaped black crystals well grinded were confined into a cylindrical vanadium can and put inside a cryostat. A wavelength of 1.28 °A was used, which corresponds, in D1B instrument, to the best compromise between flux, resolution and absorption of boron. The samples were cooled down to 2 K and diffraction patterns covering the angular range 0.8 to 128.8° were collected in 3h at 2, 30, 50 and 300K for Co3O2BO3 and at 2, 60, 100 and 300K for Co5Sn(O2BO3)2. The data were analyzed using the programs Fullprof Suite. The treatments included a full structural refinement of the crystal structure, with a single isotropic adp for each atom type. The neutron diffraction patterns show the occurrence of long-range magnetic order with the appearance of a set of magnetic peaks below T_N=82 K for Co5Sn(O2BO3)2 and T_N = 42 K for Co3O2BO3, accompanied by a small decrease of background intensity at low angles. See Fig. 1. The magnetic ordering temperature of both is consistent with previous magnetic measurements [1].The Co5Sn(O2BO3)2 presents also new peaks below 100 K at 2θ equal to 39, 43.6 and 63° suggesting a structural transition. Because of this unexpected structural transition we are programming to do single crystal x-ray diffraction to study this new structure before analyzing the magnetic structure below 80K. Therefore, in this report we focus on Co3O2BO3.

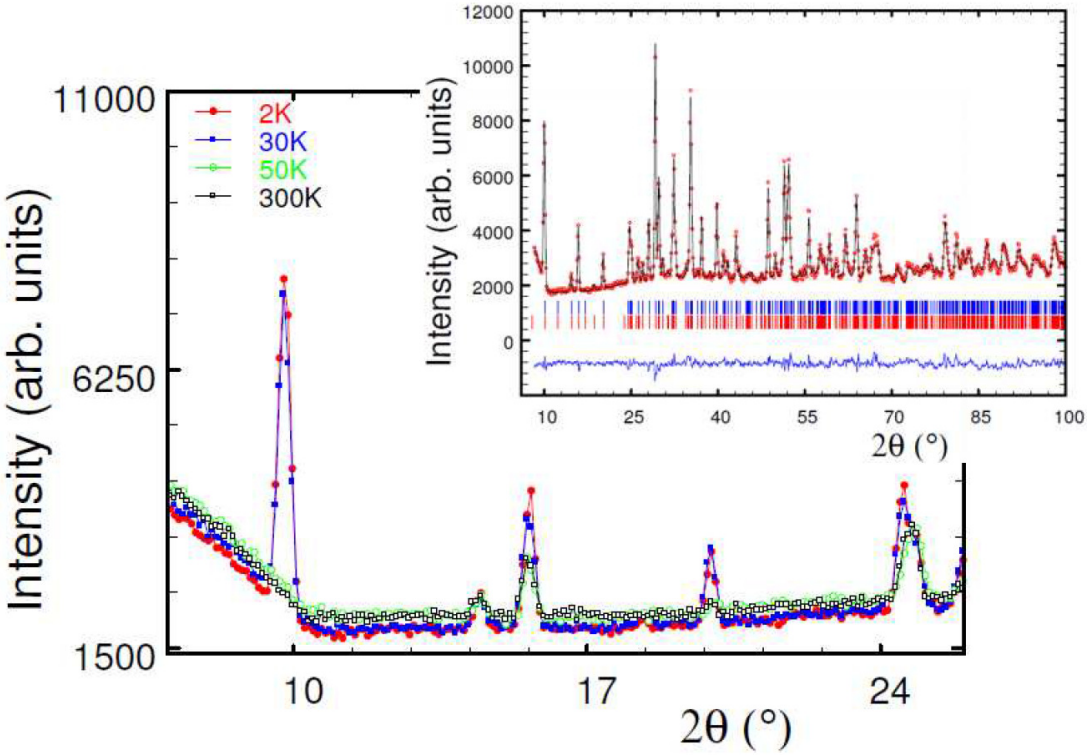
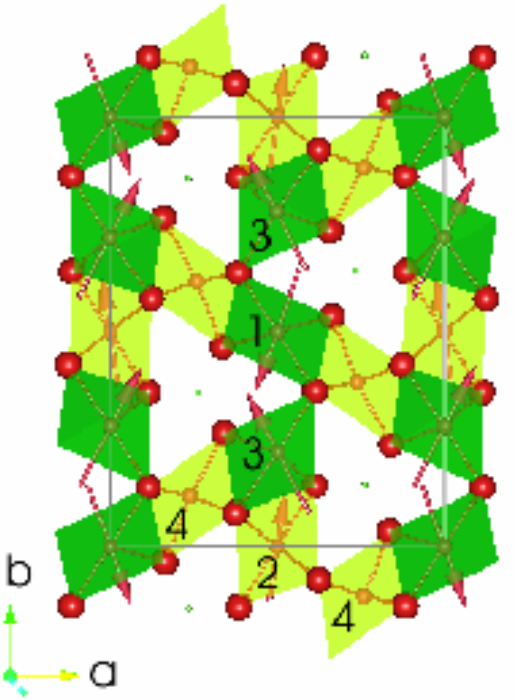


Figure1: Low angle part of the neutron diffractograms for Co3O2BO3 at 300, 50, 30 and 2 K. The set of magnetic peaks are clearly visible below 42 K, as well as magnetic diffuse scattering at the higher temperatures. Inset: Rietveld refinements (black line) of the NPD data (red dots) at 2 K. The difference between the experimental data and the Rietveld model is represented by the blue line. Blue (top) and red (bottom) tick marks correspond to the nuclear and magnetic reflection positions respectively.

We did not observe structural transitions in all range of measured temperatures with the changes of the magnetic structure between 2 and 30 K accounting for all variations in the spectra. The results

of the magnetic structure refinements at 2 K are given in Table I and the plot of the Rietveld refinement in Fig. 1. The NPD data at 2 K gives lattice parameters of *a*= 9.317(3) Å, *b* = 11.950(4) Å, *c*= 2.9646(7) Å. (R_{Bragg} = 8.0 %, R_F = 6.2 %). All magnetic contributions can be indexed with the nuclear unit cell, i.e., with a magnetic propagation vector **k**=0. The magnetic structure determination was done by symmetry analysis, following the representation analysis technique described by Bertaut using BasIreps software. For the Pbam space group, there were found eight real irreducible representations for the little group G_k associated to **k**=0, Γ_1 to Γ_8. Since a single magnetic ordering temperature is observed [1], it is expected that the magnetic structure is described within the same magnetic representation for all the magnetic sub-lattices. Only the odd irreducible representations (Γ_1, Γ_3, Γ_5, Γ_7) appear in the magnetic representation Γ_M for all the Wyckoff positions, being Γ 5 the one that best reproduces the experimental data (R_{mag} values: Γ_1=27.2 , Γ_3=25.9, Γ_5=8.6, Γ_7=13.4). The magnetic structure is shown in Fig. 2. The Co3O2BO3 system has a ferromagnetic spin configuration in the rungs of the 4–2–4 ladders with an effective moment of 8.2 μB per cell and a ferrimagnetic configuration in the rungs of the 3–1–3 ladders with about 8 μB per cell, which gives 1.4 μB per Co cation. All the moments are nearly parallel to the b-axis, making this the easy magnetization axis in accord with bulk magnetic anisotropy measurements [2]. Along the c-axis the moments in both ladders are ferromagnetically aligned. The magnetic moment in site 2 of the 4–2–4 ladder has a value consistent with a high spin state of the Co^{2+} ion, but the magnetic moment in site 4 is surprisingly small. This suggests that these sites are occupied by Co^{3+} ions in low spin states. The sites in the ladder 3–1–3 are all occupied by divalent Co^{2+} ions in high spin states. They are associated with the large magnetic moments shown in Table.



Atom (Wyckoff positions)	Mx	My	Mz	M
Co4 (4h)	-0.5(1)	-0.1(1)	0	0.5
Co3 (4g)	1.7(1)	3.38(8)	0	3.8
Co2 (2d)	0.4(2)	3.06(9)	0	3.1
Co1 (2a)	1.2(1)	-3.4(1)	0	3.6

Figure 1: Magnetic structure proposed for $Co_3O_2BO_3$ by NPD. The metal ions are situated within oxygen octahedra and the boron in trigonal coordination. The two sub-units in the form of 3LL are shown. The octahedra in the ladders 4-2-4 share edges and those in the ladders 3-1-3 share corners. The numbers indicate the crystallographic sites. Magnetic moments are ferromagnetically aligned along the c-axis. TABLE I: Magnetic moments of the ludwigite $Co_3O_2BO_3$ at 2 K for each direction in μB units. M represents the modulus of the magnetic moment vector.

The value of the magnetic moment expected for HS Co^{2+} is 3 μB and 1μB for the LS state, considering only the spin contribution as is usual for these systems. The values obtained in Table I indicate that there is a reasonable orbital contribution to the moments. Bulk 3d long range magnetic order in the system due to interaction between the 3LL is guaranteed by the presence of a magnetic Co ion on site 2 which is the one more strongly coupled to the 3–1–3 ladder [3]. We have submitted this study in Physical Review.

References

[1] D. C. Freitas, et al., *Phys. Rev. B* **77**, 184422 (2008). C. P. C. Medrano, D. C. Freitas, D. R. Sanchez, C. B. Pinheiro, G. G. Eslava, L. Ghivelder, and M. A. Continentino, *Phys. Rev. B* **91**, 054402 (2015).
[2] N. B. Ivanova et al., *Journal of Experimental and Theoretical Physics*, **113**, 1015 (2011); N.V. Kazak et al., *Solid State Phenomena* 152 & 153, 104 (2009).
[3] P. Bordet and E. Suard, *Phys. Rev. B* **79**, 144408 (2009).