Experimental report

14/05/2021

Proposal: 5-24-630 **Council:** 4/2019

Title: Investigation of a spin-state crossover in the ludwigite Co3O2BO3

Research area: Physics

This proposal is a continuation of 5-31-2404

Main proposer: Daniele Cristina SILVA DE FREITAS

Experimental team: Jose Alberto RODRIGUEZ VELAMAZAN

Local contacts: Jose Alberto RODRIGUEZ VELAMAZAN

Samples: Co3O2BO3

Instrument	Requested days	Allocated days	From	To
D20	2	1	22/01/2020	23/01/2020

Abstract:

There are two known homometallic ludwigite oxyborates, Fe3O2BO3 and Co3O2BO3. The structure of these materials has low dimensional units in the form of three legged ladders that confer to each of them unique magnetic and electronic properties. Fe3O2BO3 presents a staggered charge density wave (CDW) transition in the ladders near room temperature and two magnetic transitions, while Co3O2BO3 behaves quite conventionally, with a single magnetic transition and no CDW in spite of similar structural and electronic configurations. Neutron diffraction at low temperature in D1b instrument at ILL for first time in this system unraveled these differences. Far from a trivial explanation we uncovered a coexistence of low and high spin Co ions in well defined octahedral sites that seems to induce a subtle charge ordering phenomenon in the ladders. Two transitions were observed by several techniques at 450 K and 495 K. A gradual spin state crossover of Co3+ ions should occur near this region of temperature and this should induce a changes in the oxygen octahedra. In order to confirm this hypothesis, we propose to carry out temperature dependent NPD measurements on D20.

Report

Investigation of a spin-state crossover in the ludwigite $Co_3O_2BO_3$

A neutron powder diffraction (NPD) experiment was carried out in the D20 instrument of the Institut Laue-Langevin (ILL) in Grenoble. Black needle-shaped crystals of Co3O2BO3 were ground and placed inside a furnace. A wavelength of 1.36 Å was used, trying to have a best compromise between flux, resolution and absorption of boron. The sample was heated to 520 K and diffraction patterns covering the angular range 0.4 to 150.8° were collected in 1h in steps of 20 K. Close to the transitions temperatures (T1 = 450 K and T2 = 495 K), these steps were reduced to 5K. 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 did not show clearly structural transitions in all range of measured temperatures. We did not observe a clear structural transition in all range of measured temperatures. However, some changes were observed in the patterns approximately in the regions of temperature of the expected transitions (see fig1).

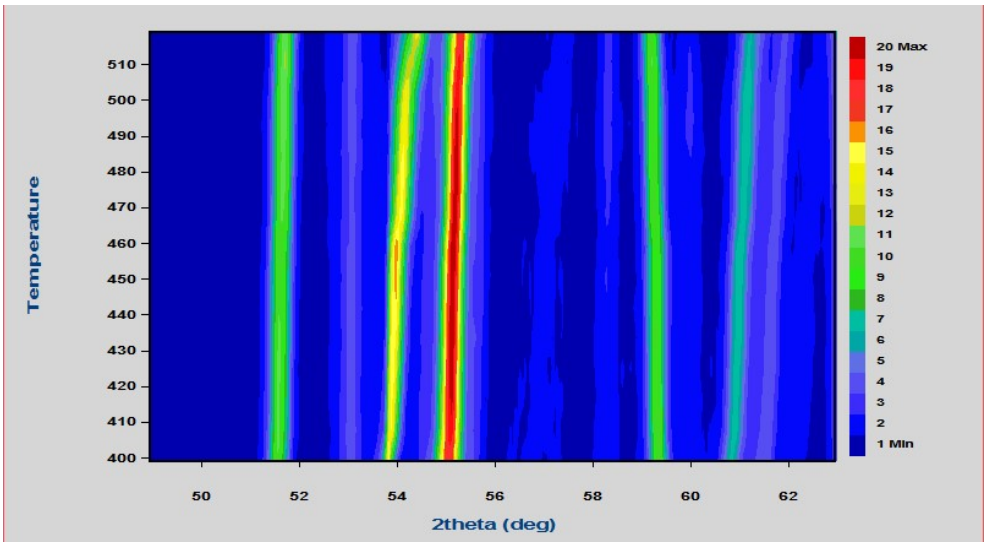

Figure1: Temperature dependence of the neutron diffractograms for Co3O2BO3.

The dependence of the lattice paramenter with temperature appears in Fig.2. The lattice parameters b, c and the cell volume increase with temperature but the lattice parameter a shows a negative temperature dependece. Il also has a clearly change of slope around T1 (see fig. 2). Trying to clarify the nature of these transitions, the average Co-O distances of the different octahedra were calculated using the Co-O distances obtained by the Rietveld refinement for all temperatures measured. As shown in Figure 3, these averages have different dependences with temperature. While for Co1 and Co3 the average distance remains nearly constant, for Co2 and Co 4 the evolution is negative and positive, respectively. For all the average Co-O distances a change of slope can be noticed around T1 (more clearly for Co2 and Co4). No clear change of tendency is observed around T2. Co1 and Co3 show average distances in the octahedra which are typical of a HS configuration.While Co2 presents an intermediate value, and Co4 a lower value, indicative of LS configuration.

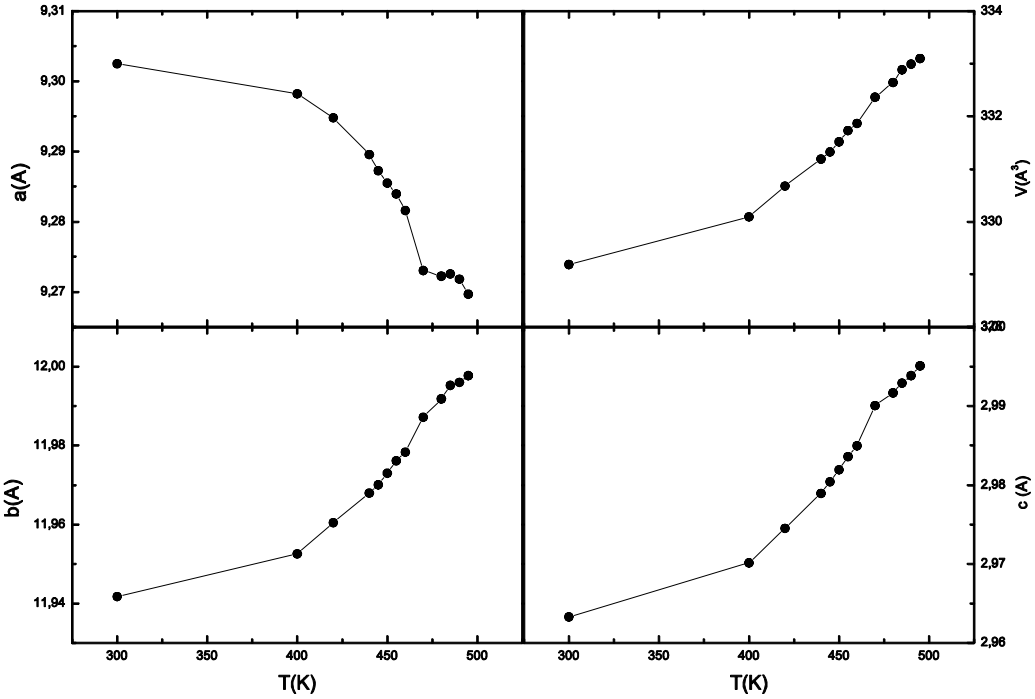

Figure2: Dependence with temperature of the lattice parameters of Co3O2BO3.

The magnetic structure has already been studied and an almost zero magnetic moment for CO4 was verified at 2 K, reinforcing the hypothesis of low spin at least at 2K [1]. Although the average Co4-O distance increases with temperature (showing, as stated before, a change in slope around T1), it does not reach the values of the other octahedra that are clearly in HS configuration. In this sense, it is not clear that a crossover from low spin to high spin occurs in this compound and other experiments must be taken. On the other hand, Co4-Co2-Co4 compose a three-legged ladder where a charge order was observed in the Fe3O2BO3 near 283 K[2]. Therefore, this is a strong indication that the Co3O2BO3 has also a charge order like that observed in Fe3O2BO3. Such possibility needs to be carefully investigated since no evidence of modification of the Pbam space group was noted in these neutron measurements.

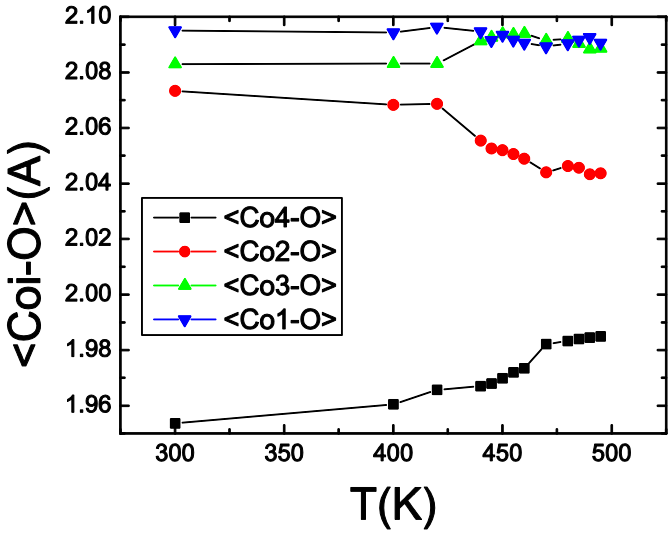

Figure3: Average Co-O distances of the different octahedra of Co3O2BO3 in function of temperature.

References

[1 D. C. Freitas, C. P. C. Medrano, D. R. Sanchez, M. Nuñez Regueiro, J. A. Rodríguez-Velamazán, and M. A. Continentino, Phys. Rev. B **94**, 174409 (2016).
[2] P. Bordet and E. Suard, *Phys. Rev. B* **79**, 144408 (2009).