Experimental Report

Proposal: **5-24-530** **Council:** 10/2012

Title: Structure and magnetism in the frustrated cobalt compound (Y,Ni)BaCo4O7+d

This proposal is resubmission of: 5-31-2248

Researh Area: Materials

Main proposer: **CUELLO Gabriel Julio**

Experimental Team: AURELIO Gabriela
CANTARGI Florencia

Local Contact: CUELLO Gabriel Julio

Samples: Y_1-x Ni_x Co_4 O_8
Y_1-x Ni_x Co_4 O_7

Instrument	Req. Days	All. Days	From	To
D2B	2	2	07/05/2013	09/05/2013

Abstract:

The objective of this project is to study the structural and magnetic diffraction of (Y,Ni)BaCo4O7+delta cobaltites and relate them to our on-going research of their magnetic and transport properties. In particular, we wish to study the crystallographic details of the structural transition reported to occur in Ni-doped samples at lower temperatures than in non-doped samples. By varying the oxygen content, we will also study the different oxygen arrangements. The development of long-range and short-range magnetic order is an issue of fundamental interest in the current literature. Given that Ni-doping introduces a disproportion of of the Co2+ / Co3+ ions and also does the oxygen content, we wish to correlate possible magnetic order with the Co2+ / Co3+ relation. We estimate that 2 days at the high-resolution D2B diffractometer and 2 days at D20 for following online the structural and magnetic phase transitions, are necessary to pursue our objectives.

Structure and magnetism in the frustrated cobalt compound $YBaCo_{4-x}Ni_xO_7$ and $Ca_{1-x}Sr_xBaCo_4O_7$
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D2B– May 2013

1. Samples and collected scans

We measured polycrystalline samples of $YBaCo_{4-x}Ni_xO_7$ and $Ca_{1-x}Sr_xBaCo_4O_7$ prepared by solid-state reaction, as summarized in Table 1. We also measured a NAC standard and a Si standard. We reproduced the instrumental resolution file provided by D2B's instrument scientists within experimental error using Fullprof.
Refined wavelength: 1.5943 ± 0.0001 Å

Sample	Composition	Temperature of scans
CBCo-2	$CaBaCo_4O_7$	300 K, 15 K
CSBCo-02	$Ca0.98\ Sr0.02\ BaCo_4O_7$	15 K, 70 K, 200 K, 300 K
CSBCo-05	$Ca0.95\ Sr0.05\ BaCo_4O_7$	300 K
LT-Co13	$YBaCo_4O_7$	300 K
CoNi-10-5	YBa Co3.90 Ni0.10 O7	300 K, 15 K, 80 K
CoNi-15-1	YBa Co3.85 Ni0.15 O7	300 K

2. Results

The present experiments belong to an ongoing research project on the effects of different cationic substitutions in the cobaltates $RBaCo_4O_7$. a highly frustrated system which offers a very peculiar scenario for the study of magnetism, electric transport, multiferroicity, absorption of gases, etc. The two selected systems were R=Y (substituted with Ni at the Co site) and R=Ca (substituted with Sr at the Ca site). They will be called hereafter Y-114 and Ca-114 in relation with their formula unit.

The objective of this particular study is to focus on the role of cationic disorder and size effects by performing partial substitutions at the Co site and at the Ca site to understand how this affects the structure and the magnetic and transport properties. The main objectives are:

- to detect magnetic transitions and correlate them to our macroscopic magnetization and transport measurements,
- to collect high-resolution data for a structural refinement in the substituted samples both at room temperature and temperatures below the observed features in the macroscopic physical measurements.
- to identify magnetic orderings and/or short range correlations

The experiments were successfully conducted, and very interesting and stimulating results were found. Some of the results were submitted for publication [Aurelio et al., submitted to Acta Materialia, 8 May 2015] and some are under preparation for submission. One of the studied systems will be a part of a PhD thesis which is about to be defended. In addition to the scans collected at D2B during the experiment, we could also collect two quick thermodiffractograms at the D20 instrument during a night shift which were extremely useful to interpret the data and to observe the magnetic transitions in two samples of the different systems.

For the system with R=Ca, the room temperature data were refined and combined with synchrotron XRD as well as X-ray absorption spectroscopy to analyse the substitution site of Sr. The results allowed to unequivocally conclude that the nominal substitution site is correct, despite other reports of Sr substituting at the Ba site. These results were recently submitted to publication in Acta Materialia.

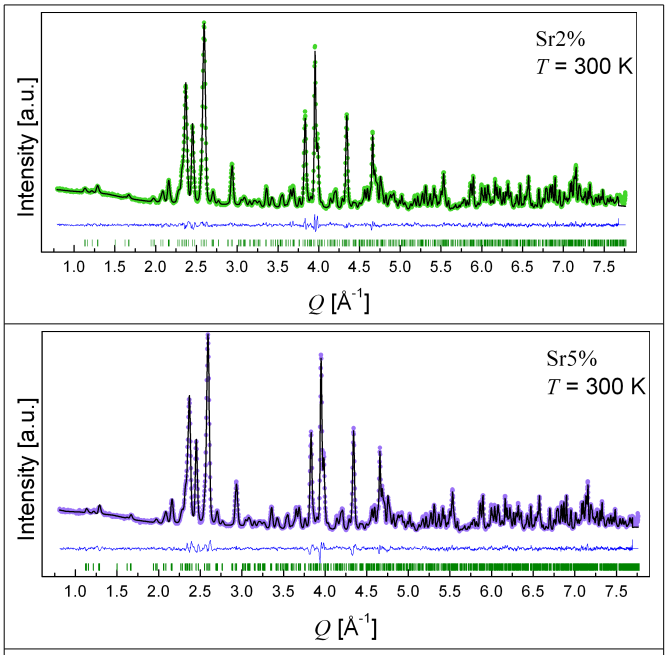

Fig.1 Rietveld refinement for samples Sr2% and Sr5% from NPD data collected at room temperature in the high–resolution diffractometer D2B at ILL. Vertical bars at the bottom indicate Bragg reflections from the orthorhombic P bn2 1 -phase. The line at the bottom corresponds to the difference between the experimental and calculated patterns.

Whereas the Sr-for-Ca substitution produces only a very small distortion in the lattice constants of the CaBaCo4O7 compound at room temperature, the effects on the magnetic behavior of the samples is very strong. Following the previous characterization of the macroscopic magnetization of the samples under different applied magnetic fields, frequency of AC-fields, temperature, etc. we performed the experiments at D2B at selected temperatures for samples Sr0%, Sr02% and Sr05% and in-situ neutron thermodiffraction at D20 for sample Sr02%. At the lowest temperature measured in D2B diffractometer, i.e. 15 K, almost no difference is observed between the parent compound and the Sr02% sample, as shown in Fig. 3 (nuclear and magnetic refinement). The magnetic phase was refined using a ferrimagnetic (FiM) model proposed by Caignaert et al. [1]. This result is also consistent with the macroscopic magnetization showing only a slight decrease between Sr0% and Sr02% at low temperature. All the magnetic reflections have a resolution–limited width, indicating that a full 3D, long–range order is achieved. No additional features are observed in the D2B data of the Sr02% sample.

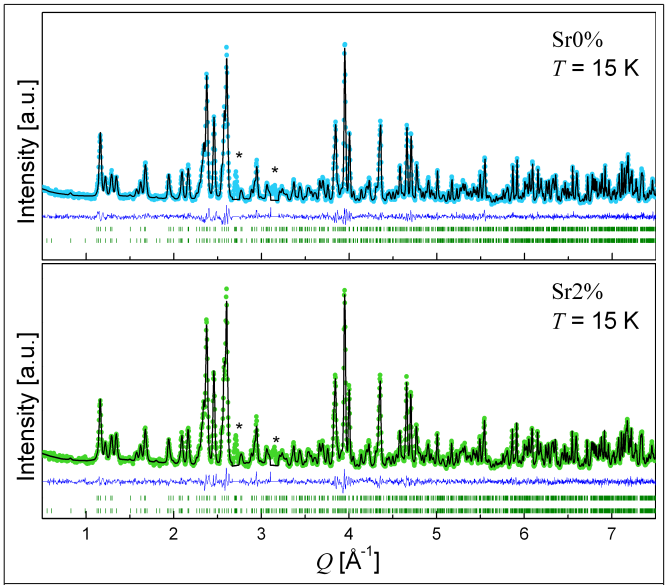

Fig.2 Rietveld refinement for samples Sr0% and Sr2% from NPD data collected at 15 K in the high–resolution diffractometer D2B. Vertical bars at the bottom indicate Bragg reflections from the orthorhombic Pbn2_1 phase and the magnetic phase proposed for the parent compound [1]. The line at the bottom corresponds to the difference between the experimental and calculated patterns. The asterisks indicate Bragg reflections coming from the cryostat.

For the parent compound, it is expected that the FiM phase disappears at 60 K and the sample becomes paramagnetic, only showing nuclear diffraction. However, a neutron thermodiffractogram for the Sr02% sample reveals more. We followed the evolution of the magnetic reflections with increasing temperature, between 20 K and 200 K at the D20 diffractometer using a wavelength λ = 1.3582 Å. The low-Q region, projected on the Q − T plane, is shown in Fig. 3. It is important to remark that the quality of these data only allow for a qualitative description, as the counting time is short (2 min) and the background is quite high, only the most intense magnetic peaks are well resolved. Nonetheless, we observe that the magnetic reflections corresponding to the FiM model discussed above vanish close to 60 K, in particular the (1 0 1) magnetic reflection at Q = 1.18 $Å^{-1}$. Moreover, between 50 K< T <80 K, a different kind of magnetic scenario is suggested by a diffuse magnetic scattering centered around Q ≈ 1.37 $Å^{-1}$, typical of short–range order (SRO). Above 80 K the SRO decreases and the only observed peaks are of nuclear nature, however there still remains an increased background around Q ≈ 1.37 $Å^{-1}$ indicating that magnetic correlations still persist up to 200 K.

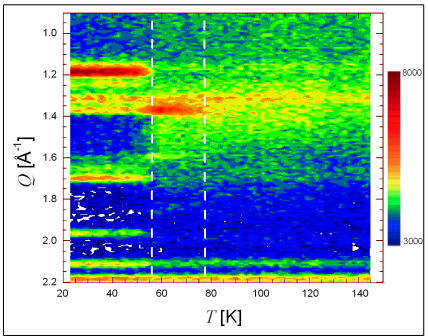

Fig.3 Projection on the Q−T plane of the thermodiffractograms for sample Sr02%. The dashed vertical lines are a guide to the eye, to help visualize the different regions.

Fig. 4 shows a more detailed picture of the features depicted in the thermodiffractogram using data from D2B at selected temperatures with 5 h of collection time. The long-ranged FiM phase with a flat background is sharp and clear only in the 15 K diffractogram. At 70 K the diffractogram is quite different, the FiM reflections have disappeared and the SRO with a main peak at Q ≈ 1.37 $Å^{-1}$ has appeared. Moreover, an important lattice distortion has occurred, as evidenced by the refined lattice parameters and atomic positions. Finally, the 200 K diffractogram in Fig. 4 shows that all reflections come only from the crystal lattice, but there persists a diffuse magnetic scattering.

The region of diffuse magnetic scattering characteristic of short–range correlations has been observed in many members of the $RBa(Co,X)_4O_7$ (X=Zn, Al, Fe) family and ascribed to an AFM kind of order. In this sample, a hint on the AFM nature of these correlations comes from our macroscopic magnetization measurements. On cooling, the onset of the SRO peak lies around 80 K and it persists until the development of the long–ranged FiM oder, which coincides perfectly with an observed plateau of the magnetization curves (both dc and ac), suggesting that some degree of AFM order is competing, decreasing the rate of magnetization growth expected for the PM phase and of course for the FiM phase when temperature is decreased.

These results have been combined with further measurements and a manuscript is now in preparation for submission.

Regarding the Y-114 system, data are still under processing an will be included in a PhD thesis on this subject which will be defended in the current year. We have confirmed that the lightly substituted Ni-per-Co samples still order antiferromagnetically below ~90 K, with the same AFM model proposed by Chapon *et al.* [2] and Khalyavin *et al.* [3] for the parent compound $YBaCo_4O_7$.

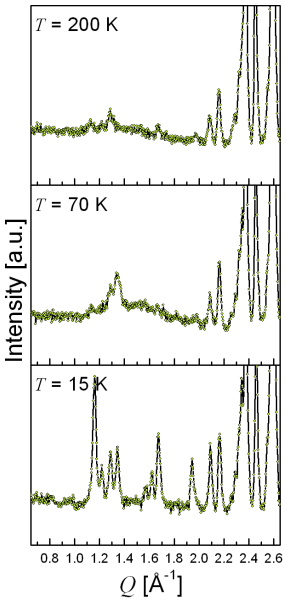

Fig.4 Low-Q data collected at D2B for sample Sr02% at 15 K, 70 K and 200 K, representative of the three different magnetic regions discussed in the text.

5. Summary

We have successfully performed the planned experiments in D2B and complemented with additional D20 data, which allowed us to scan the landscape of magnetic transformations occurring in the compounds $YBaCo_4O_7$ doped with Ni at Co site, and $CaBaCo_4O_7$ doped at the Ca site with Sr. The Sr-doping at the Ca site strongly affects the magnetic properties of the parent compound $CaBaCo_4O_7$, and we could correlate the features observed in the macroscopic magnetization with the evolution of magnetic peaks in the diffractograms. A temperature region with strong short range ordered magnetic correlations in observed. The nature of these correlations is now under further study as it is related to the always interesting topology of Kagomé and triangular frustrated lattices.

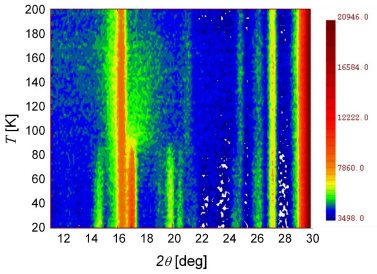

Fig.5 Projection on the 2θ−T plane of the thermodiffractogram for sample $YBaCo_{3.85}Ni_{0.15}O_7$.

The substitution of Ni at the Co site in the $YBaCo_4O_7$ system, on the other hand, has proven not to interrupt the development of long-ranged antiferromagnetism as in the parent compound, below 90K.

References

[1] V Caignaert, V Pralong, V Hardy, C Ritter, B Raveau, Physical Review B 81, 094417 (2010).
[2] L Chapon, P Radaelli, H Zheng, J Mitchell, Physical Review B 74, 172401 (2006).
[3] D D Khalyavin, P Manuel, B Ouladdiaf, A Huq, P W Stephens, H Zheng, J F Mitchell, L C Chapon, Physical Review B 83, 094412 (2011).