



	Experiment title: Electronic properties of the two-dimensional Mott system Ba(Co,Ni)S ₂ with a square lattice	Experiment number: HC-955
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Scientific background

BaCo_{1-x}Ni_xS₂ is a strongly correlated two-dimensional Mott system characterized by a competition between a paramagnetic (P) or antiferromagnetic (AF) insulating (I) ground state and a metallic (M) one controlled by temperature or electronic doping [1]. BaCoS₂ is an antiferromagnetic Mott insulator with a Néel temperature, $T_N \sim 305$ K. As shown by the phase diagram on **Figure 1** and [2], Ni-substitution for Co causes a decrease of T_N up to the critical value $x \sim 0.22$ for which the system becomes metallic.

The aim of the project is to unveil the electronic structure of both Co and Ni in the BaCo_{1-x}Ni_xS₂ system. The objectives are the determination of **(i-ii)** the spin state and the occupancy of the electronically active $3d z^2-r^2$ and x^2-y^2 orbitals but also to address the following open questions: **(iii)** the dependence of the above occupancy upon x , especially at the verge of the metal-insulator transition ($x_{cr} \sim 0.22$); **(iv)** the degree of hybridization of the above orbitals with the $3p(S)$ orbitals; **(v)** the orientation of the magnetic moments of the AF structure for $x = 0$.

Sample preparation and characterization

Four single crystals of size up to $0.5 \times 0.4 \times 0.1$ with $x = 0, 0.16, 0.22$ and 1 , corresponding to different electronic and magnetic states (see **Figure 1** and [2]), have been selected for the experiment. Samples were characterized by Energy Dispersive Spectroscopy for compositional measurements. X-ray diffraction studies and structural refinements enabled the determination of the nuclear structure with excellent reliability factors, $R_w \sim 1-2\%$. Magnetization curves (acquired with a VSM or VSM-SQUID) position the AFM to PM transition for $x = 0$ and $x = 0.16$ samples at $T \sim 295$ K and $T \sim 85$ K, respectively. Resistivity vs temperature measurements confirm the insulating state of the $x = 0$ and $x = 0.16$ samples and the metallic state of the $x = 0.22$ and $x = 1$ samples.

Experimental concerns

In the frame of this proposal, we performed X-ray Natural Linear Dichroism (XNLD) measurements at two temperatures, 315 K and 55 K. The samples were mounted in the cube equipped with a rotation stage with the c -axis oriented along z and the beam of a width $200 \times 50 \mu\text{m}^2$ parallel to the ab -plan. Thus the polarization was set vertically (along c -axis) or horizontally (in the ab -plan). The Co and Ni K-edge were recorded in the back-scattering mode with the 8 Si-diodes set-ups. Acquisitions of 2 to 4 hours for each spectrum were necessary to achieve reasonably high signal-to-noise-ratios. When Bragg diffraction peaks were present on a specific diode detector, the contribution of the latter was discarded before to make the difference between the c -axis and ab -plan polarized signals to obtain the XNLD characteristic.

Experimental results

Results are resumed on **Figure 2**. The dichroism *vs* energy, for both Co and Ni K-edge, show the presence of a clear anisotropy of all the samples. In the literature [3], edges of CoO and NiO structure are 7718.2 eV and 8344.2 eV respectively. Experimentally, we acquire 7718.1 eV for Co K-edge and 8341.2 eV for Ni K-edge. We can safely assume that Co and Ni ions are in divalent form as found by XES measurement before [4].

At 315 K, as Ni is substituted for Co, the dichroic signal at the Co K-edge is strongly modified, which suggests that Ni is likely to distort its site and induce a modification of the Co local environment. The Co 3d orbitals are also modified as a consequence of the electronic doping. On the other hand, the dichroic signal in the pre-edge region at the Ni K-edge is small and weakly dependent of the Ni content. That suggests the more isotropic structure of the Ni 3d orbitals as compared to Co ones. The latter description is not anymore valid at 55 K where a relation between dichroic signals and the long range magnetic order seems to exist. In the case of the Co K-edge, the metallic and PM $x = 0.22$ sample exhibits a XNLD signal different from the one of the insulating and AFM $x = 0$ and $x = 0.16$ samples. While in the case of the Ni K-edge, the metallic and PM $x = 0.22$ and $x = 1$ samples exhibit a XNLD signal different from the one of the insulating and AFM $x = 0.16$ sample. More data analyzes are in progress and will be compared to the theoretical calculations.

It will be interesting to acquire X-ray Magnetic Circular Dichroism (XMCD) spectra on these compounds in order to investigate both Co and Ni magnetic structures. The analysis of the XMCD in the pre-edge region will give a direct information on the valence and the spin-state of Co and Ni.

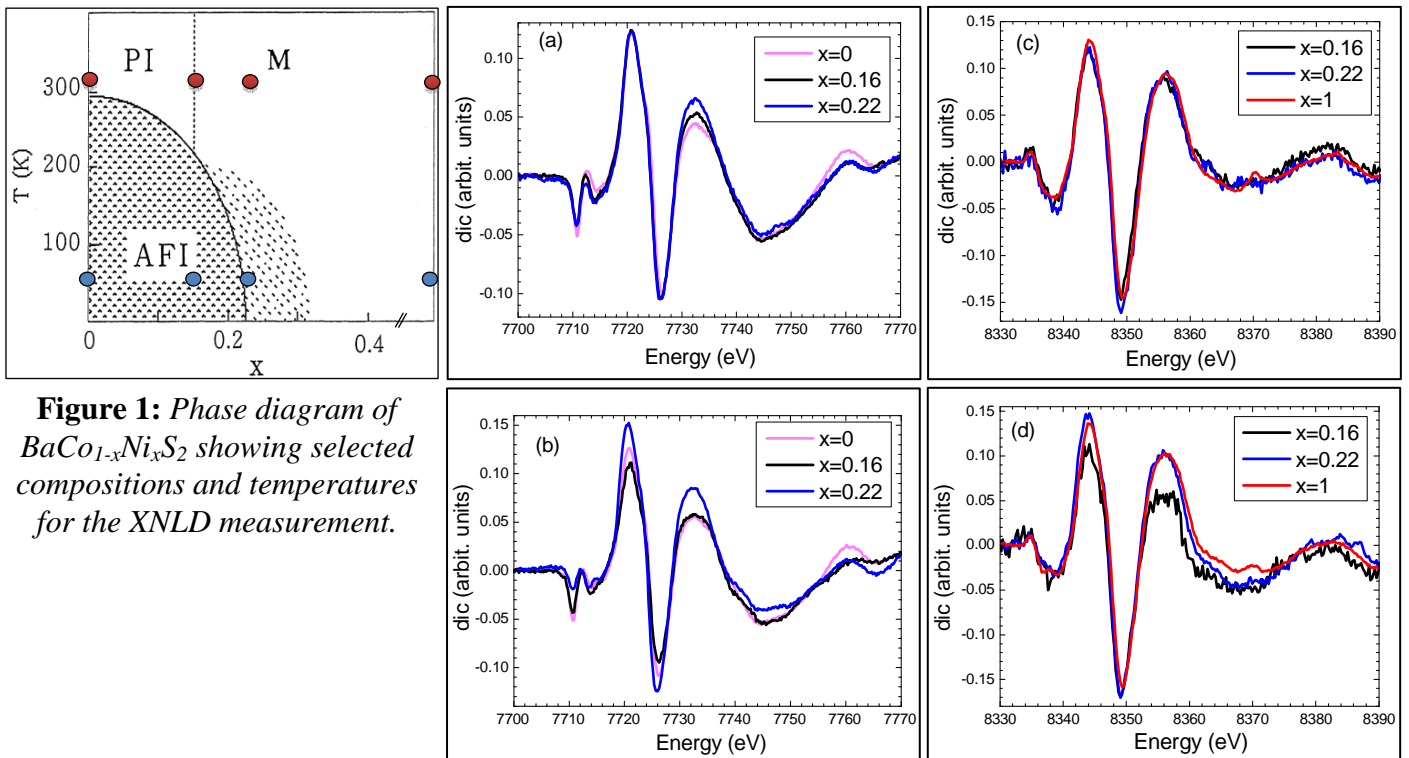


Figure 1: Phase diagram of $BaCo_{1-x}Ni_xS_2$ showing selected compositions and temperatures for the XNLD measurement.

Figure 2: Dichroism intensity versus photon energy of $BaCo_{1-x}Ni_xS_2$ for $x=0, 0.16, 0.22$ and 1 . (a) Co K-edge at 315K. (b) Co K-edge at 55K. (c) Ni K-edge at 315K. (d) Ni K-edge at 55K.

References:

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