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MS38 P07

Structural and magnetic study of cation substitution in layered cobaltites $Y(\text{Ba,Ca,Sr})\text{Co}_2\text{O}_{5.5}$ Gabriela Aurelio^a, Javier Curiale^a, Rodolfo D. Sánchez^a, Gabriel J. Cuello^b. ^a*Centro Atómico Bariloche, CNEA and CONICET, Argentina.* ^b*Institut Laue-Langevin, Grenoble, France.* E-mail: gaurelgio@cab.cnea.gov.ar

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In this work we present a study of the structural properties of $Y(\text{Ba, Sr,Ca})\text{Co}_2\text{O}_{5.5}$ layered cobaltites focussing on the role of cationic disorder and size effects by a partial substitution of Ba by the smaller cations Ca and Sr. We have synthesized the polycrystalline compounds $Y(\text{Ba}_{1-x}\text{Ca}_x)\text{Co}_2\text{O}_{5.5}$ with $x = 0, 0.05$ and 0.1 , and $Y(\text{Ba}_{1-y}\text{Sr}_y)\text{Co}_2\text{O}_{5.5}$ with $y = 0.05$ and 0.1 . We characterized the samples within the 5-570 K temperature range, using neutron diffraction, magnetic measurements and electrical resistivity experiments. Neutron powder diffraction (NPD) data were collected on the high-intensity two-axes diffractometer D20 and in the high-resolution powder diffractometer D2B. We have found that the alkaline earth doping strongly affects the magnetic properties of the parent compound $Y\text{BaCo}_2\text{O}_{5.5}$. With the partial substitution of Ba with smaller cations as Ca and Sr, we could highlight the competition between the AFM order observed in various $\text{R}\text{BaCo}_2\text{O}_{5.5}$ cobaltites (R is a rare earth), and the ferrimagnetic phase which is generally observed in a narrow temperature range. For the Ca series, the sample with $x = 0.05$ shows a small fraction of AFM phase which seems to coexist with a ferrimagnetic one below $T \approx 190$ K, whereas for $x = 0.1$ the AFM order is completely lost. A structural distortion is observed in our NPD data, associated to the metal-insulator transition. Recent studies in other members of the cobaltites family indicate that the distortion is due to a charge delocalization. For the Sr series a tetragonal structure is stabilized by the addition of Sr, and the ferrimagnetic order is replaced by an AFM phase for the sample with $y = 0.1$. The magnetic phases show even a more complex behaviour than in the Ca series. In addition, data collected at high temperature indicate that samples are irreversibly transformed at ≈ 550 K, where an orthorhombic to tetragonal transition is followed by a loss of oxygen in the structure. Until now, each of these phenomena had been analyzed separately in different rare-earth layered cobaltites, some showing orthorhombic symmetry, others tetragonal symmetry, some studied at low temperature, others at high temperature. It is for the first time that we can put all the ingredients together and show that not only the rare-earth is playing a role in the physics of the layered cobaltites, but also the disorder and size effects in the B-site, highlighting the delicate balance between highly competing structures, both crystallographically and magnetically.

MS38 P08

Crystal and Magnetic Structures of Co_2SiO_4 Olivine A. Sazonov^a, M. Meven^b, V. Hutanu^a, G. Heger^a, A. Gukasov^c, A. Goujon^c ^a*Institute of Crystallography,*

RWTH Aachen, D-52056 Aachen, Germany. ^b*ZWE FRM-II, TU Munich, D-85747 Garching, Germany.* ^c*Laboratory Leon Brillouin, 91191 CEA/Saclay, France.*

E-mail: andrew.sazonov@frm2.tum.de

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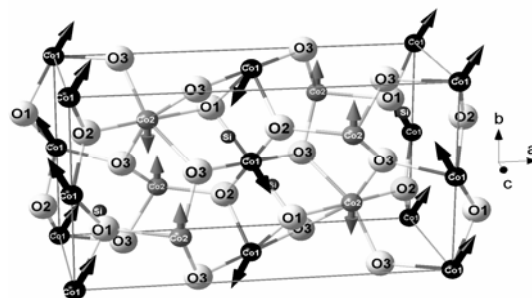
Olivine-type silicates, $M_2\text{SiO}_4$ ($M = \text{Mn, Fe, Ni, Mg, Ca}$), are a major and important component of the upper Earth's mantle. Therefore, the properties of these materials are of considerable interest in physics, geology and crystal chemistry. Olivine compounds are used as an important composition in some refractory materials, additives in cement concrete, acid-resistant containers, ceramic pigments, etc.

A remarkable feature of the orthorhombic olivine-type structure (space group Pnma, no. 62 [1]) consists in two crystallographically non-equivalent M positions: $M1(4a)$ and $M2(4c)$. Moreover, these systems are interesting due to the peculiarities of their magnetic structures. The magnetic properties of olivine compounds are quite complex and depend on type of M cation.

Synthetic Co_2SiO_4 also crystallizes in the olivine-type structure. The antiferromagnetic phase transition occurs in this compound at $T_N \approx 49$ K [2]. However, the magnetic properties of Co_2SiO_4 are not yet well understood. In order to understand the nature of magnetism in Co-olivines we have investigated crystal and magnetic structures of Co_2SiO_4 by means of both x-ray and neutron diffraction measurements.

A large Co_2SiO_4 single crystal (length = 1.5 cm, diameter = 0.5 cm) was grown by the zone melting method using a mirror furnace (Inst. of Cryst., RWTH Aachen). The phase purity and magnetostriction effect were checked using the high resolution x-ray powder diffraction (MILIDI, Inst. of Cryst., RWTH Aachen) in the temperature range from 19 to 300 K with Cu $K\alpha$ radiation. The unpolarized neutron diffraction measurements were done using the single crystal diffractometer HEiDi [3] at the hot source of the FRM-II (TU Munich, Germany). Data were collected at 2, 55 and 300 K with wavelength of 0.55 Å up to about $\sin\theta/\lambda \approx 1.1 \text{ \AA}^{-1}$. Polarized neutron flipping ratios were measured on the single crystal diffractometer 5C1 (LLB, France) using neutrons with $\lambda = 0.84 \text{ \AA}$. Data were collected in an external field of 7 T parallel to [010]. In order to get a saturated paramagnetic state the measurements were done above the magnetic ordering temperature ($T_N \approx 49$ K) at 70 and 150 K.

A schematic representation of both crystal and magnetic structures of Co_2SiO_4 are shown in the figure below.



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