maximal subgroups of index ≤4 of a representative group of each type of magnetic group in the superfamilies of these groups.

MS38 P05

Magnetic structure of the Kagomé mixed compound $(Co_{0.5}Ni_{0.5})_3V_2O_8$ N. Qureshi,[a,b] H. Fuess,[a] H. Ehrenberg[c] B. Ouladdiaf,[b] T. C. Hansen,[b] Th. Wolf,[d] C. Meingast,[d] Q. Zhang,[d] W. Knafo,[d,e] H. v. Löhneysen[d,e] [a]*Institute for Materials Science, University of Technology, Darmstadt, Germany.* [b]*Institut Max von Laue-Paul Langevin, Grenoble, France.* [c]*Leibniz Institute for Solid State and Materials Research, Dresden, Germany.* [d]*Research Center Karlsruhe, Institute of Solid State Physics, Karlsruhe, Germany.* [e]*Physics Institute, Karlsruhe University, Karlsruhe, Germany.*
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Keywords: magnetic structures, magnetic structure determination, neutron diffraction

$(Co_{0.5}Ni_{0.5})_3V_2O_8$ represents a mixed compound of the well investigated transition metal (M) orthooxovanadates $Ni_3V_2O_8$ (NVO) and $Co_3V_2O_8$ (CVO) labelled as Kagomé staircase structures, which are characterized by edge-sharing MO_6 octahedra isolated by nonmagnetic VO_4 tetrahedra. The crystallographic structure (orthorhombic space group Cmca) [1, 2] is interesting with respect to the magnetic properties as the magnetic ions form buckled planes of corner-sharing isosceles triangles representing an anisotropic variation of the ideal Kagomé net. Within these buckled planes, the Kagomé staircases, cross-tie ions on crystallographic (4a) sites link the linear chains of spine ions on (8e) sites. Due to the reduced symmetry of the Kagomé staircase geometry with respect to the ideal plane net the degree of frustration is lowered leading to interesting long range ordered magnetic structures. Magnetization and neutron diffraction experiments on a $(Co_{0.52}Ni_{0.48})_3V_2O_8$ powder sample [3] revealed only one magnetic phase transition into an antiferromagnetic ground state in contrast to the richness of magnetic phase transitions of its parent compounds [4, 5]. The magnetic structure is modulated by a composition dependent propagation vector $k=(\delta, 0, 0)$ with δ being 0.491(4) for $(Co_{0.52}Ni_{0.48})_3V_2O_8$ where a similarity to the NVO type magnetic structure was assumed [3]. Neutron single crystal diffraction experiments followed by group theory analysis produced a more detailed picture. The magnetic structure of $(Co_{0.5}Ni_{0.5})_3V_2O_8$ exhibits features, which differ from the predominantly collinear alignment of its parent compounds NVO and CVO, which exhibit a variety of magnetic structures with magnetic moments mainly oriented along the *a* axis [4-7]. The averaged magnetic moments of the statistically distributed Ni^{2+} and Co^{2+} ions are oriented in the *a-c* plane. They point either towards or away from the centers of the respective isosceles triangles of the Kagomé staircase structure if viewed as a projection along the *b* axis. The spin arrangement is close to a 120° configuration as expected for antiferromagnetically ordering systems on a Kagomé lattice. This result shows once again that the competition of the exchange interactions along various coupling pathways in this particular crystallographic system results in a variety of different interesting magnetic structures.

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MS38 P06

Magnetic structure of $Ba_7Co_6BrO_{17}$ Pascal Roussel, Matthieu Kauffmann, Olivier Mentré *UCCS CNRS UMR8181, Université de Lille, 59652 Villeneuve d'Ascq, France.* E-mail: pascal.roussel@ensc-lille.fr

Keywords: magnetic perovskite materials, neutron powder diffraction, new materials

At the basis of the search for original electronic and magnetic behaviour, a number of studies focus on the prospecting for new complex structural types within "hot" topics such as cobaltites (strong competition between magnetic ground states, attractive thermoelectricity, superconductivity …). In this context, we recently synthesized by solid state reaction the new $Ba_7Co_6BrO_{17}$ compound ($P6_3/mmc$: a=5.6611(1) Å and c=33.5672(8) Å) [1]. This cobaltite is built from a close-packing of $[BaO_3]$ and $[BaOBr]$ layers with a 14H stacking sequence (c'chhcc')$_2$, which creates Co_4O_{15} tetramers of face-sharing octahedra connected to their extremities to isolated tetrahedra by corner-sharing. This material is strongly related to the 12H-$BaCoO_{2.6}$ [2] and 6H-$Ba_6Co_6ClO_{16}$ [3] cobaltites, with the existence of common blocks. Measurement of the magnetic susceptibility χ against T has been performed under applied magnetic field of 1 T. The experiment reveals the existence of two transitions at 60 K and 30 K. The curve was fitted to the Curie-Weiss law in the paramagnetic domain (above 60 K), leading to the values $p_{eff}=3.12$ $\mu B/Co$ and $\theta=55K$ This paramagnetic effective moment can be explained by assuming Co^{3+} S=1 and Co^{4+} S=3/2 i.e. cobalt atoms at the intermediate spin-state (considering the spin-only approximation). The positive θ value indicates important ferromagnetic exchanges among the structures. In order to understand the magnetic properties of this cobaltite, we collected neutron powder diffraction data on the G41 diffractometer (LLB Saclay, France). The pattern below 60 K revealed the onset of new reflections, this fact being ascribed to the occurrence of long-range magnetic ordering and confirming the magnetic transition previously reported. All those magnetic reflections were indexed in a commensurate lattice related to the crystallographic one by a propagation vector k=[000]. Among all the possible magnetic models, only those for which the exchange interactions between two tetrahedral cobalt orders antiferromagnetically went to convergence with acceptable reliability factors. The magnetic structure can be described as the antiferromagnetic coupling of ferromagnetic blocks (Co_4O_{15} + 2 CoO_4 units). This kind of magnetic structure has been previously reported for 6H-$Ba_6Co_6ClO_{16}$ [4].

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MS38 P07

Structural and magnetic study of cation substitution in layered cobaltites Y(Ba,Ca,Sr)Co$_2$O$_{5.5}$ <u>Gabriela Aurelio</u>[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: <u>gaurelio@cab.cnea.gov.ar</u>

Keywords: cobalt compounds, transition metal-rare earth oxides and intermetallics, neutron powder diffraction

In this work we present a study of the structural properties of Y(Ba, Sr,Ca)Co$_2$O$_{5+\delta}$ 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(Ba$_{1-x}$Ca$_x$)Co$_2$O$_{5.5}$ with x = 0, 0.05 and 0.1, and Y(Ba$_{1-y}$Sr$_y$)Co$_2$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 YBaCo$_2$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 RBaCo$_2$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≈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 Ba-site, highlighting the delicate balance between highly competing structures, both crystallographically and magnetically.

MS38 P08

Crystal and Magnetic Structures of Co$_2$SiO$_4$ Olivine <u>A. Sazonov</u>[a], M. Meven[b], V. Hutanu[a], G. Heger[a], A. Gukasov[c], A. Goujon[c] [a]*Institute of Cristallography,* *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: <u>andrew.sazonov@frm2.tum.de</u>

**Keywords: antiferromagnetics, neutrons, x-rays**

Olivine-type silicates, M_2SiO$_4$ (M − 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$_2$SiO$_4$ 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$_2$SiO$_4$ 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$_2$SiO$_4$ by means of both x-ray and neutron diffraction measurements.

A large Co$_2$SiO$_4$ 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 Kα 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 sinθ/λ ≈ 1.1 Å^{-1}. Polarized neutron flipping ratios were measured on the single crystal diffractometer 5C1 (LLB, France) using neutrons with λ = 0.84 Å. 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$_2$SiO$_4$ are shown in the figure below.
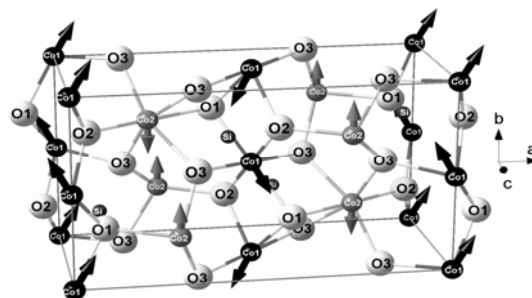
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