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High spin frustration in Co based *Swedenborgites*

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**Abstract.** The spin correlations in a series of cobaltate polycrystalline samples with *Swedenborgite* structure, $A$BaCo$_3$B$_4$O$_7$ ($A = Y, Ca,$ and $B = Co, Fe, Al, Zn)$, were studied by means of diffuse polarized neutron scattering. The alternate stacking of kagome and triangular Co layers forms a tetrahedral Co-network with geometrical frustration of antiferromagnetically (AF) coupled spins, which typically suppresses long-range order even at low temperatures (~1 K) despite Curie-Weiss temperatures in the order of 1000 K. The generic diffuse magnetic scattering as found in Y$_{0.5}$Ca$_{0.5}$BaCo$_4$O$_7$ reveals two dimensional (2D) spin correlations on the kagome sublattices towards the entropically favoured $\sqrt{3} \times \sqrt{3}$ structure and suggests a decoupling of layers by low spin states $S = 0$ on triangular sites. Co-substitution by Al and Zn yields similar diffuse magnetic scattering, however, spin dilution results in even more disordered spin liquid or spin glass states. With $B = Fe$ or Co, differences in the magnetic scattering evolve, indicating the onset of spin correlations perpendicular to the kagome layers and non-vanishing spin states on the triangular sites. Geometrical frustration prohibits any 3D long-range order when the characteristic 2D spin correlations with the $\sqrt{3} \times \sqrt{3}$ motif is present. We observe long-range order only in YBaCo$_4$O$_7$ and CaBaCo$_3$FeO$_7$ showing rather distinct ordering wave-vectors.

### 1. Introduction

Atomic networks of triangles can be found in many crystal structures, among which are the simple *fcc* lattice and several complex compounds, e.g. pyrochlores, spinels, garnets, jarosites, and magnetoplumbites. This structural feature has an important influence on magnetic properties. Particularly, triangular topologies impose a severe geometrical frustration on spins with antiferromagnetic coupling, lowering or fully suppressing Néel order and leading, in general, to complex spin structures. Some of these structures contain sublattices of a 2D prototype of geometric frustration formed by corner sharing triangles: the kagome lattice, which attracted significant interest because its ground states show an infinite manifold.

In the *Swedenborgite* type structure (SbNaBe$_4$O$_7$), the Be substructure can be described as kagome layers, constituting $\frac{3}{4}$ of all Be, and trigonal interlayer sites ($\frac{1}{4}$ of all Be) [1]. Full Co substitution was realized in the isostructural YBaCo$_4$O$_7$ [2] (figure 1), where intriguing magnetic properties were expected due to the strong AF coupling between the magnetic Co ions. A further intriguing fact about the *Swedenborgite* type structure, apart from the lack of inversion symmetry, is the unusual super-exchange situation: all Co-O-Co angles are close to the tetrahedral angle (109.5°) and, still, the spin to spin coupling is remarkable, implying the presence of covalence and hybridisation of oxygen.
Magnetic order was reported in the parent compound YBaCo$_4$O$_7$ by different groups \cite{3, 4}, however oxygen non-stoichiometry was suggested as reason for symmetry lowering and upheaval of magnetic degeneracy. In contrast, a spin-liquid like state was observed in the closely related Y$_{0.5}$Ca$_{0.5}$BaCo$_4$O$_7$ \cite{5}, where the relatively higher oxidation and low spin state of Co at interlayer sites have been proposed to explain the magnitude of the diffuse magnetic scattering and the apparent magnetic decoupling between the kagome layers \cite{6}. The diffuse magnetic neutron scattering intensity is consistent with the spin correlations approaching a predicted 2D spin structure of staggered chirality \cite{7}, namely the $\sqrt{3} \times \sqrt{3}$ structure. This recent close experimental approach to the ground state was in contrast to \cite{8} and in qualitative agreement with what has been seen for other kagome systems like the jarosites \cite{9,10}. A preference for staggered chirality has also been observed in magnetoplumbite compounds \cite{11}. The low temperature 2D spin correlations that evolve, undisturbed by any significant 3D coupling, indicate a ground state with algebraically decaying correlations \cite{7, 12 and Refs therein}, for which only octopolar ordering is predicted \cite{12}. Here, we present new stoichiometric variants with 2D spin correlations by non magnetic substitutions on the cobalt site by Al$^{3+}$ and Zn$^{2+}$ further using Y$^{3+}$ and Ca$^{2+}$ as charge compensation outside the magnetic substructure. Also, the tetrahedral Co-coordination of the parent compound provides an excellent example of high geometrical frustration for a 3D spin system with possibility of spin-liquid ground states. By replacing one Co by Fe$^{3+}$, with $S = 5/2$ or half-integer spin, it is plausible to avoid Co$^{3+}$ $S = 0$ low spin states on the triangular lattice sites inducing three dimensional spin coupling; partial Fe-substitution may still preserve the decoupled state, which is also discussed below for the charge compensated (Y$^{3+}$/Ca$^{2+}$) compounds. These new compositions of the Co based Swedenborgite have been reported among others \cite{13} and, in this paper, magnetic neutron diffuse scattering data, cleanly separated by polarization analysis, will be presented to investigate the effect of chemical substitution on the nature of present spin correlations.

2. Experiment

The preparation of the different polycrystalline samples is described together with atomic structure and basic physical properties elsewhere \cite{1, 5, 6, 13-15}. Specific heat measurements were done in a PPMS (Quantum Design) at zero field. A well-sintered part from each polycrystalline sample was selected to ensure good thermal conductivity within the sample. Powdered samples of typically 5 cm$^3$
have been prepared for neutron diffraction experiments. All diffraction data of polarized neutrons with a wavelength of 4.75 Å were performed at the DNS spectrometer in Jülich [16, 17]. An aluminium tube was used as sample holder and a steady flow of He was used as cooling agent. The separation of pure magnetic scattering from the coherent scattering of the atomic structure and spin-incoherent scattering, essentially from Co, has been achieved by measuring spin-flip and non-spin-flip cross-sections with neutron polarization along orthogonal directions \( x, y, \) and \( z \) (vertical) and longitudinal polarization analysis. Typically, the instrumental polarization was better than 90%, as determined by a \( \text{Ni}_{0.89}\text{Cr}_{0.11} \) reference with only non-spin-flip scattering, and taken into account for corrections to ideal polarization.

3. Results and Discussion
The investigated \textit{Swedenborgites} can be distinguished into two groups: those with magnetic short-range order (SRO, figure 2a) and those with magnetic long-range order (LRO, figure 2b). In all cases it is clear that the dominating spin-spin interaction is strongly anti-ferromagnetic, since the magnetic scattering factor approaches zero at infinite coherence \((Q = 0)\). Although the data is resolution limited, it is clear that the LRO in figure 2b is three dimensional as the Bragg intensities are symmetrical in shape. The spin-liquid like compounds depicted in figure 2a show qualitatively and quantitatively very similar and asymmetric patterns, indicating a common scenario as found in \( \text{Y}_{0.5}\text{Ca}_{0.5}\text{BaCo}_4\text{O}_7 \) [6] with \( S = 3/2 \) \( \text{Co}^{2+} \) ions and characteristic 2D spin-correlations of a \( \sqrt{3} \times \sqrt{3} \) ground state.

With Fe substitution, the \( \text{YBaCo}_3\text{FeO}_7 \) compound shows additional intensity particularly at the characteristic wave-vector of the \( \sqrt{3} \times \sqrt{3} \) structure, however, a second diffuse peak rising near 1.7 Å\(^{-1}\) might indicate a coupling between the kagome layers. A first observation from the LRO materials, in figure 2b, is that they have two different magnetic structures, as several of the observed magnetic ordering vectors are only present in one of the two diffraction patterns. Note that \( \text{YBaCo}_3\text{O}_7 \) still exhibits some diffuse scattering with a maximum near 3.93 Å \((Q \approx 1.6 \text{ Å}^{-1})\), meaning that a part of the spins remains disordered or slowly fluctuating. The observed \( k \)-vectors in \( \text{YBaCo}_3\text{O}_7 \) agree well with what has been seen for \( \text{YbBaCo}_4\text{O}_7 \) [18], where an orthorhombic magnetic super cell was suggested \((a_{\text{hex}} = a_{\text{orth}}, b_{\text{hex}} \times \sqrt{3} = b_{\text{orth}}, c_{\text{hex}} = c_{\text{orth}})\). However, it is also possible to index the same vectors with a hexagonal cell with doubled \( a \) axes. In fact, it is possible to index the magnetic intensities of \( \text{CaBaCo}_3\text{FeO}_7 \) with a similar unit cell as for \( \text{YBaCo}_3\text{O}_7 \). However, additional scattering contrasts arise from the larger Fe moment \((S = 5/2)\) in comparison to Co and the different extinction conditions reveal a different symmetry and magnetic structure. Further studies and analysis of this completely new magnetic structure of \( \text{CaBaCo}_3\text{FeO}_7 \) will be reported elsewhere.

Assuming an \( a \) axis in the hexagonal setting of 6.35 Å, it is easy to see that the (200)-reflection of the \( \sqrt{3} \times \sqrt{3} \) structure better suits the diffuse intensities of all SRO compounds (thin vertical line in figure 2a) than the (100)-reflection of the \( q_0 \)-structure (dashed vertical line in figure 2a), a degenerate competing structure with uniform chirality (see Ref.6). The data were divided by the square of the single-ion magnetic form-factor and normalized to the self-correlation term, which implies an approximation of the different moments by an average effective magnetic moment. This allows to perform a Fourier-analysis of the magnetic diffuse scattering in terms of spin correlations \(< S_i \cdot S_{i+n}>\), which we confine to the distances and coordinations within a single kagome layer (figure 3a). Spin correlations of all systems are essentially within the bounds of the frustrated antiferromagnetic structures [-0.5,1] providing physically meaningful results, which indicates the adequacy of this approach. A clear preference is observed for the \( \sqrt{3} \times \sqrt{3} \) structure, which for nearest neighbour exchange is entropically favoured with respect to the alternative \( q_0 \)-structure. This further clarifies the conclusions drawn from figure 2a, including the characteristic wave vector of the diffuse peak in \( S(Q) \).

One may also note the closeness of the nearest neighbour spin correlation to the lower bound of the ordered structure reflecting \( kT < < J \).
Figure 2. Magnetic neutron scattering of Co-Swedenborgites at low temperature, separated by polarisation analysis and calibrated by the spin-coherent scattering of Co. (a) Spin-liquid like diffuse scattering for the compounds exhibiting short-range magnetic order at $T = 1.2$ K. Two insets show the two possible variants of chiral spin order on a kagome layer. Green lines indicate the crystallographic unit cells and the red lines mark the magnetic unit cells. (b) Magnetic Bragg intensities for the two compounds with long-range magnetic order. Arrows indicate significant intensities and the asterisk marks a diffuse intensity still present in YBaCo$_4$O$_7$.

The valence distribution seems to be important for the spin correlations; for example, YBaCo$_3$ZnO$_7$ and CaBaCo$_3$AlO$_7$ contain both Co$^{7/3}$, the distribution of Zn or Al, respectively, on the Co sites is similar in both cases according to X-ray data [13] (Zn/Al occupies 50% of Co1 and 20% of Co2 sites), and the observed diffuse magnetic scattering from these two materials are almost identical. Changing the average Co valence from Co$^{7/3}$ in CaBaCo$_3$AlO$_7$ to Co$^{8/3}$ in CaBaCo$_3$ZnO$_7$ has a significant influence on the scattering. According to X-ray data, in CaBaCo$_3$ZnO$_7$ almost all Zn enters the kagome substructure but, still, the total scattering increases slightly and so does the spin correlation length; the FWHM is significantly narrower in CaBaCo$_3$ZnO$_7$ at the same temperature (1.2 K). This observation may be surprising in view of the higher spin-dilution in the kagome layer for the Zn-compound. On the other hand spin dilution in highly frustrated AF is less effective in reducing the spin correlations because locally frustration is diminished; the magnitudes of the magnetic scattering are, at least, inconsistent with expected Co-spin states for these two compounds. This unexpected behaviour may also result from possible mixed spin states or covalence effects. A structure determination by neutrons or anomalous x-ray diffraction could clarify the aspect of the Zn occupation.

Comparing YBaCo$_3$FeO$_7$ with CaBaCo$_3$FeO$_7$, the magnetic sublattice contains the same magnetic ions (“Co$_3$Fe”), but the obviously higher Co valence in the latter results in magnetic LRO, where only SRO is observed in the former. The same observation is made when comparing YBaCo$_3$ZnO$_7$ with CaBaCo$_3$ZnO$_7$; equal magnetic sublattice “Co$_3$Zn” but the average Co valence of $+7/3$ and $+8/3$, respectively, again causes the latter to exhibit a stronger ordering tendency. For comparison, data from Y$_{0.5}$Ca$_{0.5}$BaCo$_4$O$_7$ [5] has been added to figure 2a and it is obvious that the intensities of this data end up below those from CaBaCo$_3$ZnO$_7$ but above the intensities of CaBaCo$_3$AlO$_7$. Note that the data is normalized for one Co and can thus be directly compared. Accordingly, a possible connection appears when comparing the relative scattering intensities with the average Co valence: CaBaCo$_3$ZnO$_7$ (Co$^{2.667}$), Y$_{0.5}$Ca$_{0.5}$BaCo$_4$O$_7$ (Co$^{2.375}$), and CaBaCo$_3$AlO$_7$ (Co$^{2.333}$) showing that an increase in the average Co valence increases the ordering tendencies independent on where the chemical substitution is made.
The presence of Co$^{3+}$ might rule for more covalence and thus stronger orbital overlap due to hybridisation enhancing the exchange, which would be an understandable reason for changes in correlation lengths. However, YBaCo$_4$O$_7$, without any substitution, exhibits magnetic LRO although the mean valence of Co is mere $+2.25$, which does not follow this trend.

3D ordering in the *Swedenborgite* structure is, however, in view of the tetrahedral coordination, a highly nontrivial case: for antiferromagnetic (as well as ferromagnetic) nearest neighbour coupling via the trigonal interlayer sites, the expected $\sqrt{3} \times \sqrt{3}$ ordering on adjacent kagome layers will be completely frustrated. Therefore, comparably weak interactions between more distant spins may lift the infinite ground state degeneracies and determine a new 3D ordered structure as seen in CaBaCo$_3$FeO$_7$. Apparently, in YBaCo$_3$FeO$_7$ the spin correlations still reveal significant similarity to the $\sqrt{3} \times \sqrt{3}$ ordering motif, which traps the system in a spin-liquid like state and prohibits LRO.

To confirm the magnetic transition of the compounds with LRO, specific heat measurements were done. In both cases, when fitting the data below 10 K with a $T^3$ function, the Debye-temperature is close to 100 K. At high temperatures, heat capacities of both compounds almost reach the theoretical limit $3RN = 324.1 \text{J} \times \text{mol}^{-1} \times \text{K}^{-1}$ (dashed line in figure 3b), as expected. An anomaly at 143 K is clearly visible for CaBaCo$_3$FeO$_7$, but only a faint change of slope can be seen close to 100 K for YBaCo$_4$O$_7$. For CaBaCo$_3$FeO$_7$, no other specific heat measurement is known, but Soda *et al.* [4] also observed a small contribution at about 100 K for YBaCo$_4$O$_7$, which they called $Tc2$ and discussed it as a structural phase transition. A further transition was also reported to exist around 70 K, but our data do not show this.

4. Conclusions
There is a strong effect upon doping the Co based *Swedenborgite* system (YBaCo$_4$O$_7$), either on the Y site or on the Co site. Even though YBaCo$_4$O$_7$ exhibits at least partially magnetic LRO, not minding the remaining diffuse scattering below 100 K, almost all chemical substitutions, investigated here, result in a break-down of 3D order and exhibit only magnetic SRO, even at temperatures below $|T/TcW| \sim 10^3$. An exception to this was CaBaCo$_3$FeO$_7$, which evolved an even more pronounced LRO, *i.e.* no diffuse scattering remained, than the undoped material, but with a different spin structure.

Considering the doped materials with magnetic SRO, we observe a larger range of the spatial spin correlations for higher average Co-valence, which may indicate covalence of Co$^{3+}$ and enhanced exchange due to orbital overlap. Generally, the diffuse neutron scattering from the magnetic SRO compounds exhibits an asymmetric broad peak close to the expected q-vector for the $\sqrt{3} \times \sqrt{3}$ spin...
structure, suggesting a dominant 2D character of the spin correlations and clearly ruling out any preference for the \( q = 0 \) structure. This underlines the stability of the staggered \textit{versus} uniform chirality for the 2D kagome antiferromagnet with nearest neighbour exchange lattice, as expected by entropy consideration and expressed by Villain’s principle of \textit{order by disorder}.

The distinct 3D ordering of YBaCo\(_4\)O\(_7\) and CaBaCo\(_3\)FeO\(_7\) may appear to be more exceptional among the present selection of Co-substituted \textit{Swedenborgites}, however, it can be also rationalized by the unusual strong 3D frustration between the kagome layers that arises from the tetrahedral coordination. There are further aspects of charge ordering with ordered high and low spin states of Co\(^{2+}\) and Co\(^{3+}\) ions \([6,19]\) that may depend on temperature, magnetic field, oxygen stoichiometry, or unknown subtle effects and may create a huge diversity of interesting phenomena in this new class of materials.

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