

MAGNETIC STRUCTURES OF TRANSITION METAL (Mn, Co, Ni, Cu) HYDROXYSULFATES

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Recently, there has been widespread interest in hydrothermal synthesis particularly in creating porous compounds. In our case, hydrothermal synthesis has been used for the elaboration of 3d transition metal hydroxysulfates. Such compounds have been carefully studied by mineralogists [1], where the principal interests were the identification of the crystal phases and the mechanism of their formation with respect to their geographic location. However, the magnetic characterizations of the minerals are sparse and this stimulated the study of the relations between structure and magnetic properties.

With $M = \text{Cu}$, two compounds are obtained, $\text{Cu}_3(\text{OH})_4\text{SO}_4$ and $\text{Cu}_4(\text{OH})_6\text{SO}_4$ corresponding to the minerals antlerite and brochantite [2-3], respectively. The structure of the former contains triple chains of edge-sharing copper octahedra, running in the b -axis direction and connected to each other by sulfate groups. Neutron powder data collected on 94% deuterated sample on G4.1 diffractometer allow the determination of the magnetic structure and its thermal evolution, the D atomic positions and the H/D ratio being refined from 3T2 data. Below $T_N = 5 \text{ K}$, the magnetic structure can be viewed as a copper triple chain consisting of ferromagnetic outer chains, with magnetic moments in the c -axis direction ($0.88(5) \mu_B$), antiparallel to each other (Figure 1). As regards the central chain, the best fit gives a zero magnetic moment on metal ions, explained by some misorientation of the magnetic moments (idle spin behaviour). The triple chains are then AF coupled to each other [4].

For $\text{Cu}_4(\text{OH})_6\text{SO}_4$, double chains of edge-shared copper octahedra are corner-shared to give rise to corrugated planes. The magnetic structure (below $T_N = 7 \text{ K}$) consists of neighbouring ferromagnetic chains antiparallel to each other. The moments are quite weak, $0.16(5)$ and $0.45(4) \mu_B$, in agreement with the low signal magnitude. Moreover, at low θ values, the evolution with temperature of the diffraction signal has been related to the presence of ferromagnetic clusters [5].

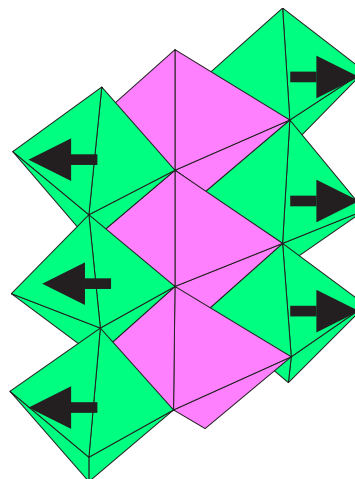


Figure 1. View of a triple chain in $\text{Cu}_3(\text{OD})_4\text{SO}_4$ with the magnetic moments as arrows pointing in the c -axis direction.

For $M = \text{Mn}$, Co and Ni , numerous new compounds have been obtained by hydrothermal synthesis and we will focus on the isostructural $\text{M}_3(\text{OD})_2(\text{SO}_4)_2(\text{D}_2\text{O})_2$ family. The structure contains zig-zag chains of edge-shared $\text{M}(1)$ octahedra running in the c -axis direction. $\text{M}(2)$ octahedra are corner-shared to the $\text{M}(1)$ chains building up corrugated planes. In the case of $M = \text{Ni}$ [6], all magnetic moments ($2.00(4)$ and $1.67(6) \mu_B$ for $\text{Ni}(1)$ and $\text{Ni}(2)$, respectively) are aligned along the b -axis direction and this magnetic structure is observed for any T below $T_N = 29 \text{ K}$. The magnetic model is slightly different in the case of $M = \text{Mn}$ and Co . For the former [7], the magnetic moments of $\text{Mn}(2)$ ions ($4.44(7) \mu_B$) are aligned along the c -axis direction, those of $\text{Mn}(1)$ ions ($4.34(7) \mu_B$) being located inside the bc -plane and making an angle around 20° with the c -axis direction. When the temperature raises up to $T_N = 26 \text{ K}$, the $\text{Mn}(1)$ moment moves towards a direction closer to the b -axis with a value of 74° with respect to the c -axis at 25 K . For $M = \text{Co}$, all moments are oriented along the c -axis direction with values of $2.99(6)$ and $3.31(7) \mu_B$ for $\text{Co}(1)$ and $\text{Co}(2)$, respectively. The magnetic structure is

observed up to $T_N = 42$ K. For $M = \text{Mn}$ and Co , another feature clearly appears on the neutron powder diffractograms. An increase in the background is evident and gives rise to a broad hump with a maximum around $2\theta = 30^\circ$ that is visually clearer for data recorded at T close to T_N , where its intensity reaches a maximum. Moreover, other less visible humps are also present. These broad humps are magnetic in origin and have been related to magnetic short-range ordering (SRO). Therefore, a second magnetic phase with the same structure and irreducible representation, but with a different coherence length, has been refined. Such an approach supposes that the volume distribution of both magnetic phases is homogeneous. Some differences appear between Mn and Co concerning the SRO phase. Whereas for Mn the broad hump is visible down to the lowest measurement temperature (1.4 K), it disappears below 34 K in the case of cobalt. For Co , the moments are oriented along the c -axis direction and are in the bc -plane for Mn , their direction turning towards the b -axis.

Other hydroxysulfates are under study to determine their magnetic structure. The substitution of the sulfate group by the seleniate one allows for

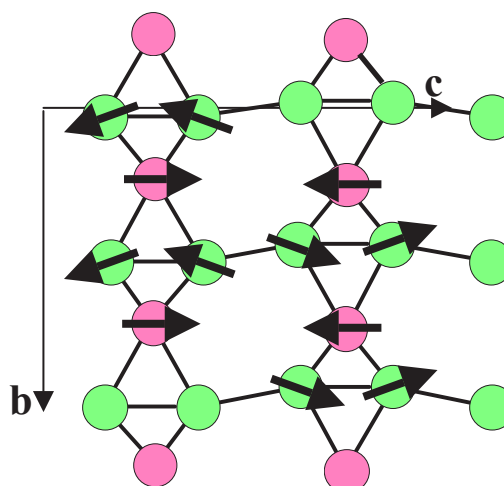


Figure 2. Projection on the bc -plane of the magnetic structure of $\text{Mn}_3(\text{OD})_2(\text{SO}_4)_2(\text{D}_2\text{O})_2$ with $\text{Mn}(1)$ in green and $\text{Mn}(2)$ in pink.

copper a structure similar to antlerite, $\text{Cu}_3(\text{OH})_4\text{SeO}_4$, to be obtained. Below $T_N = 8$ K, an incommensurate magnetic structure is evidenced.

References.

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