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A long sequence of studies of the olivine-type silicates, M_2SiO_4, provided abundant data, especially at/above room temperature and ambient pressure. However, there is still a lack of information on the magnetic properties for some olivines. One of the less investigated olivine-type silicates is a synthetic Co-olivine, Co_2SiO_4.

According to neutron diffraction measurements Co_2SiO_4 has an orthorhombic crystal structure with the space group *Pnma* (see, for example, [1,2]). There are two crystallographically inequivalent Co sites, namely Co1 (4a) site of inversion symmetry and Co2 (4c) site of mirror symmetry.

According to magnetization measurements, an antiferromagnetic phase transition occurs in this compound ($T_N \approx 50$ K) [3]. Neutron diffraction studies of Co_2SiO_4 single crystals have clearly shown that the magnetic cell coincides with crystallographic one ($\mathbf{k} = 0$) and that the magnetic structure corresponds to the Shubnikov magnetic space group *Pnma*. Cobalt magnetic moments on *M*2 are parallel to the *b*-axis whereas on *M*1 they are canted for the whole temperature range below T_N (Fig. 1). The magnetic moments on both sites are different and equal to about 3.9 and 3.3 μ_B/Co^{2+} ion for Co1 and Co2, respectively. These values well exceed the theoretical spin-only moment of 3 μ_B/Co^{2+} ion in high-spin state ($t_{2g}^5e_g^2$, $S = 3/2$). The large magnetic moment which strongly exceeds 3 μ_B/Co^{2+} was also found in another neutron diffraction experiment on single crystal [3]. Most probably the orbital contribution is very significant and different for two Co species [3].

On the other hand, in the recent theoretical work [4] the calculated orbital magnetic moment was found to be very small (less than 0.05 μ_B/Co). This is at least 10 times smaller than the values predicted from our and literature data [1,3] according to the neutron diffraction experiments. The difference between calculation and experiment might result from the fact that the simple collinear magnetic structure was considered for the calculation [4].

So, the question about the orbital contribution to magnetic moment in Co_2SiO_4 is still open. In that case, an additional independent method should be used for direct determination of the ground state magnetic properties of the Co ions and, in particular, of the spin and orbital contributions to their

magnetic moments. X-ray magnetic circular dichroism (XMCD) is the powerful method to study the effects of orbital magnetism.

Therefore, we have initially performed XMCD measurements of Co_2SiO_4 on the Co *K* edge using ID12 Beamline. The experiment was performed at different temperatures from 5 K to 150 K in an applied external magnetic field of 6 T. The direction of magnetic field was close to the crystallographic *b*-axis.

These measurements have shown very interesting temperature changes of the pre-edge peaks. The intensity variation of one of these peaks (Fig. 2) has a close correlation with the magnetization measurements. Here, one peak shows antiferromagnetic behavior and another one is ferromagnetic-like in the temperature range 20 K - 50 K. The ferromagnetic-like behavior of the second peak is unusual taking into account bulk antiferromagnetic properties of Co-olivine. Moreover, abrupt and strong changes were observed below about 20 K (see Fig. 2), that was not observed in any other study. These changes clearly show an orbital-type transition which takes place at about 20 K.

In general, the features of XMCD in the pre-edge region are related to the 1s to 3d transition. The pre-edge peak is prohibited by the selection rule within the approximation of the dipole transition. The quadrupole contribution in this system would be approximately 10^{-2} smaller than the dipole one. Therefore, the appearance of these pre-edge peaks suggests a possibility that there is a hybridization between the 3d states of neighboring Co ions via 2p state of O, i.e. by means of superexchange coupling.

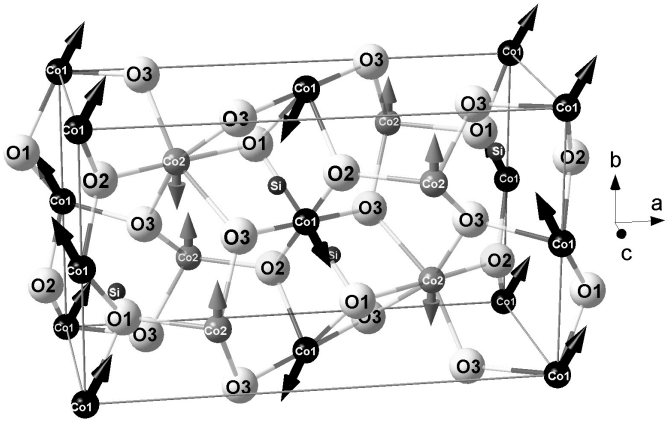

Fig. 1. Co_2SiO_4 magnetic structure.

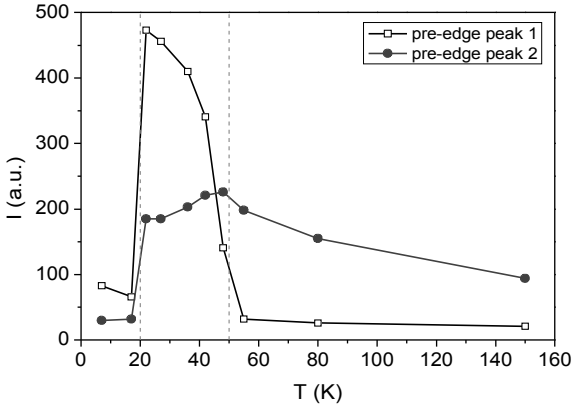

Fig. 2. Variation of pre-edge peak areas of the XMCD signals.

However, in order to understand the above mentioned unusual response of Co_2SiO_4 in XMCD spectra additional experiments on the both Co *K* and *L* edges in an applied magnetic field along different crystallographic directions are still necessary.

References

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