Neutron diffraction and X-ray magnetic circular dichroism studies of the Co_2SiO_4 magnetic properties

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Abstract. Synthetic Co_2SiO_4 crystallizes in the olivine structure (space group $Pnma$) with two crystallographically non-equivalent Co positions and shows antiferromagnetic ordering below $50\,K$. We have studied the magnetic properties of Co_2SiO_4 by means of both non-polarized and polarized neutron diffraction as well as X-ray magnetic circular dichroism. Measurements with non-polarized neutrons were made at $2.5\,K$ whereas polarized neutron diffraction experiments were done at $70\,K$ and $150\,K$ in an external magnetic field of $7\,T$ parallel to the b axis. Symmetry analysis of the Co_2SiO_4 magnetic structure proves that it corresponds to the magnetic (Shubnikov) group $Pnma$ which allows the antiferromagnetic configuration (G_x, C_y, A_z) for the $4a$ site with inversion symmetry $\bar{1}$ (Co1 position) and $(0, C_y, 0)$ for the $4c$ site with mirror symmetry m (Co2 position). The polarized neutron study of the magnetization induced by an applied field indicates a delocalization of the magnetic moment from Co towards neighbouring O due to the superexchange coupling. This is also in agreement with X-ray magnetic circular dichroism measurements performed at the Co K-edge in the temperature range $7\,K$–$150\,K$ in an external magnetic field of $6\,T$ applied close to the b axis of Co_2SiO_4. An important orbital contribution to the total magnetic moment of Co^{2+} in Co_2SiO_4 predicted by non-polarized neutron diffraction was independently proven by means of the X-ray magnetic circular dichroism and polarized neutron diffraction studies which indicate an orbital to spin magnetic moment ratio $\mu_L/\mu_S \approx 0.3$.

1. Introduction

The general chemical formula for olivine, which is a major phase of the earth's upper mantle, is M_2SiO_4 (M – divalent transition metal). The olivine-type silicates have an orthorhombic crystal structure with the space group $Pnma$ (No. 62 according to [1]), in which four formula units are contained in the unit cell ($Z = 4$).

In the crystal structure, the Si atoms are coordinated by four O atoms to form isolated SiO_4 tetrahedra connected via the cations M. These cations are surrounded by six O atoms and occupy two distinct octahedral sites; $M1$ is located on a centre of symmetry (Wyckoff position $4a$) and $M2$ on a mirror plane (Wyckoff position $4c$).

The magnetic properties of olivines have been studied a number of times over the past 40

years. The magnetic structure of olivines is found to be quite complex and strongly depends on the type of the cation M.

Below about $50\,\mathrm{K}$, the less studied Co-olivine was found to be magnetically ordered with the magnetic cell equal to the crystallographic cell. It was initially decided that the moments of Co^{2+} on both $M1$ an $M2$ sites are parallel to the b axis and antiferromagnetically coupled [2, 3]. Lottermoser *et al* [4] and Lottermoser and Fuess [5] found a slight deviation of the magnetic moment on $M1$ from the b axis for the whole antiferromagnetic region.

In the present paper the magnetic properties of Co_2SiO_4 were studied in more detail by means of both non-polarized and polarized neutron diffraction as well as X-ray magnetic circular dichroism (XMCD) measurements.

2. Experiment

Crystal growth was performed by the floating-zone method using a mirror furnace (see [6] for more detailed information). For the measurements, small Co_2SiO_4 single crystals were cut from the large as-grown crystal.

To obtain high accuracy in determination of both the nuclear and magnetic structure parameters, a Co_2SiO_4 single crystal was studied on the four-circle diffractometer HEiDi [7] at the hot neutron source of the FRM II reactor, TUM, Germany. Measurements using a short wavelength of $0.552(1)\,\text{Å}$ up to $\sin\theta/\lambda < 1.1\,\text{Å}^{-1}$ in the temperature range from $300\,\mathrm{K}$ down to $2.5\,\mathrm{K}$ were performed. Detailed experimental and refinement data can be found elsewhere [6].

The magnetization density distribution for Co_2SiO_4 was obtained from polarized neutron single-crystal diffraction. These measurements were performed at the ORPHÉE reactor, LLB, France. Polarized neutron flipping ratios were measured on the lifting-counter diffractometer 5C1 using neutrons with wavelength $\lambda = 0.845\,\text{Å}$. Data were collected in an external field of $7\,\mathrm{T}$ above the ordering temperature ($T_N \approx 50\,\mathrm{K}$) at $70\,\mathrm{K}$ and $150\,\mathrm{K}$. For both temperatures, one set of flipping ratios was measured with the field applied parallel to the crystallographic b axis of Co_2SiO_4.

The X-ray magnetic circular dichroism (XMCD) measurements were performed at beamline ID12 at the ESRF, France. Co K-edge absorption spectra were obtained from total fluorescence yield measurements using circularly polarized X-rays in the temperature range $7\,\mathrm{K}$–$150\,\mathrm{K}$. The XMCD signal was obtained from the difference in absorption for parallel and antiparallel alignments of the helicity of the X-ray beam with respect to an external magnetic field of $6\,\mathrm{T}$ applied in a direction close to the b axis of Co_2SiO_4. To avoid experimental artefacts, the external magnetic field direction and the circular polarization of X-rays were alternately flipped.

3. Results and Discussion

3.1. Non-polarized neutron diffraction

The neutron diffraction experiments on the single crystal were performed in order to verify the model of the Co_2SiO_4 magnetic structure suggested in Refs. [4, 5]. A total of 3226 Bragg reflection intensities were measured at $2.5\,\mathrm{K}$. After averaging 1424 independent reflections remained. After applying the criterion $I > 2\sigma(I)$, 1070 observed reflections were used for the nuclear and magnetic structure refinement. Structural parameters of Co_2SiO_4 were obtained from Rietveld refinements using the program FULLPROF [8]. The nuclear and magnetic structures were refined simultaneously.

All observed superstructure reflections were indexed with a magnetic propagation vector $\mathbf{k} = (0, 0, 0)$. The chemical space group of Co_2SiO_4 remains $Pnma$ down to $2.5\,\mathrm{K}$ according to our synchrotron and neutron diffraction data [6]. In the framework of the representation analysis, which was developed by Bertaut [9], it was shown that there are only eight possible one-dimensional irreducible representations for $Pnma$ associated with the propagation vector $\mathbf{k} = (0, 0, 0)$. The only irreducible representation consistent with the observed magnetic reflections of
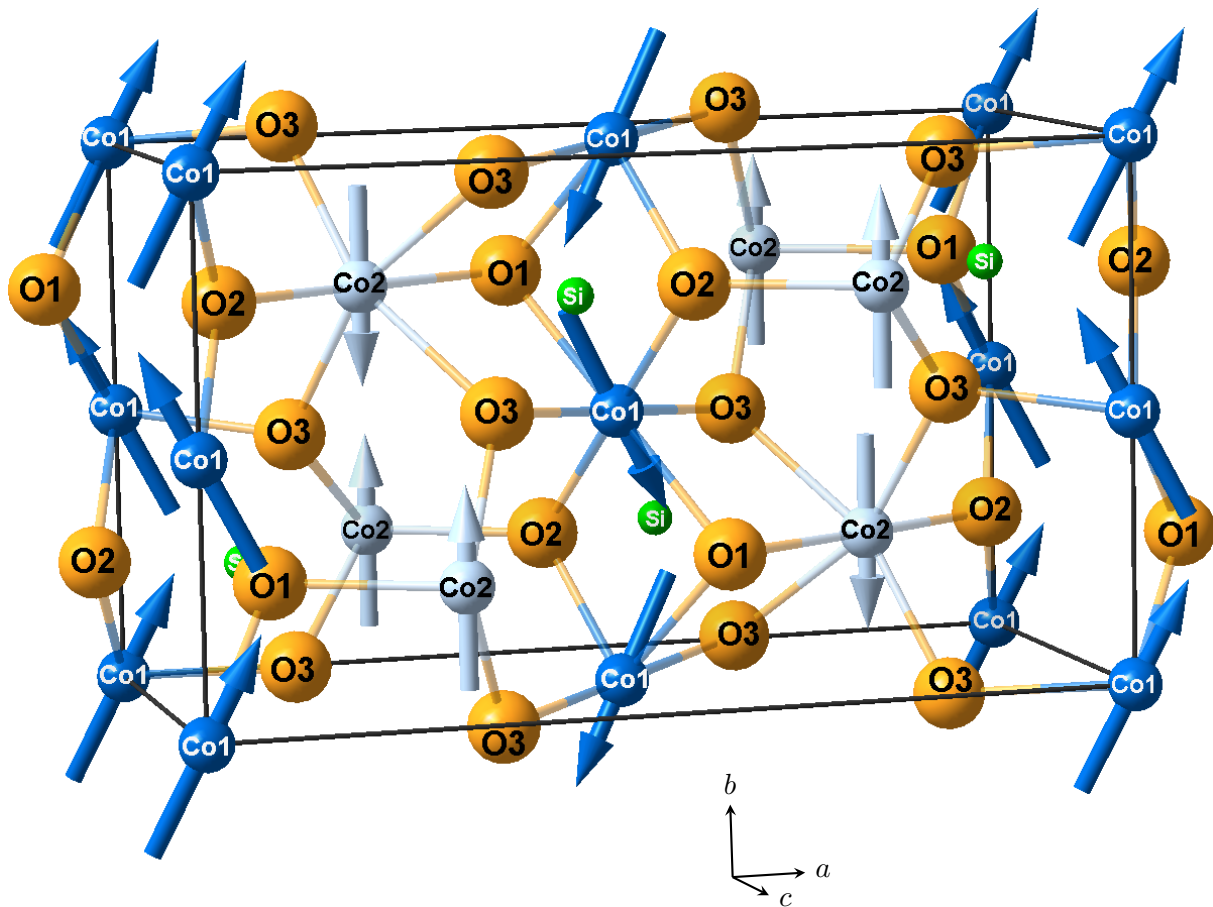
Figure 1. Graphical representation of the crystal and magnetic structures of Co_2SiO_4.

Co_2SiO_4 corresponds to the magnetic (Shubnikov) group $Pnma$. It allows the antiferromagnetic configuration C_y for both $4a$ and $4c$ sites as well as additional antiferromagnetic G_x and A_z components in the case of $4a$.

The magnetic moments of Co2 have a collinear arrangement along b, whereas the Co1 moments are canted with respect to all crystallographic axes (see figure 1). This confirms the magnetic model which was obtained by fitting the neutron diffraction data of Co_2SiO_4 collected at $4.2\,K$ [4, 5]. However, in those works the magnetic moments on both Co sites were found to be similar ($3.90 \pm 0.10\,\mu_B$ and $3.84 \pm 0.08\,\mu_B$ for Co1 and Co2, respectively) in contrast to our results ($3.87 \pm 0.03\,\mu_B$ and $3.35 \pm 0.02\,\mu_B$ for Co1 and Co2, respectively, with $R = 0.033$ and $wR = 0.044$). It is worth noting that the spin-only magnetic moment of Co^{2+} in the high-spin state ($t_{2g}^5 e_g^2$, $S = 3/2$) is $3\mu_B$.

3.2. Polarized neutron diffraction
In order to get further information on the magnetic interactions in Co_2SiO_4, experiments with polarized neutrons were carried out. The classical polarized neutron diffraction technique [10] is used to study the magnetization distribution around magnetic atoms in ferromagnetic and paramagnetic materials. It is much more difficult to make such measurements in antiferromagnetic systems [11]. One way to study the magnetization density distribution in antiferromagnetic compounds is to perform polarized neutron flipping ratio measurements in

Table 1. Induced ferromagnetic moments of Co_2SiO_4 from polarized neutron flipping ratio measurements at 70 K.

Atom		Magnetic moment (μ_B)
Co1:	μ_S	0.76 ± 0.02
	μ_L	0.24 ± 0.09
Co2:	μ_S	0.15 ± 0.02
	μ_L	0.04 ± 0.01
O1		0.09 ± 0.02
O2		0.01 ± 0.02
O3		0.04 ± 0.01

$R = 0.045$, $wR = 0.023$

special conditions, namely in the paramagnetic state (above T_N) and in an applied external magnetic field. This gives an information about the magnetization induced by the field. The flipping ratios R measured by polarized neutron diffraction are, for each Bragg reflection, the ratio between the intensity diffracted with spin up (I^+) and the intensity diffracted with spin down (I^-):

$$R = \frac{I^+}{I^-} = \frac{(F_N + \mathbf{F}_M^\perp)^2}{(F_N - \mathbf{F}_M^\perp)^2} \, ,$$

where F_N is the nuclear structure factor and $\mathbf{F}_M^\perp$ is the projection of the magnetic structure factor $\mathbf{F}_M$ into the scattering plane.

For the data collection at 70 K, a total of 207 Bragg reflection flipping ratios for Co_2SiO_4 were measured up to $\sin\theta/\lambda \approx 0.62$ Å^{-1} ($\lambda = 0.845$ Å). These yielded 113 independent reflections. A data collection at 150 K was also performed up to $\sin\theta/\lambda \approx 0.62$ Å^{-1} and a total of 218 Bragg reflection flipping ratios were measured yielding 114 independent reflections. Subsequently, we calculated the magnetic structure factor, assuming that the nuclear one is the structure factor known from our accurate non-polarized single-crystal neutron diffraction measurements [6]. The experimental flipping ratios were used directly in the refinement using the MAGLSQ program from CCSL [12]. The results of the refinement for the measurement at 70 K in a magnetic field of 7 T parallel to the b axis are summarized in table 1.

The Co^{2+} ions in the high-spin state have a relatively strong spin-orbit coupling that makes the orbital angular momentum contribute to the total magnetic moment. Therefore, we tried to refine the orbital part of the Co magnetic moment in addition to the spin one. Thus, the refined average ratio μ_L/μ_S is found to be about 0.3. This ratio can be used now to estimate the spin and orbital components of the Co magnetic moment using the non-polarized neutron diffraction data. The refinement also revealed a non-negligible amount of magnetic moment on the three different oxygen positions. We interpret this effect as a delocalization of magnetic moment from the cations towards neighbouring oxygen ions on superexchange pathways. Polarized neutron diffraction data also suggest that the exchange interactions between the Co1 ions via O are weaker compared to those between Co2. That is, the most important exchange interactions are antiferromagnetic and act through the paths Co2–O–Co2.

3.3. X-ray magnetic circular dichroism
In order to evidence the existence of the orbital contribution to the total magnetic moment of Co^{2+} in Co_2SiO_4, the XMCD experiments were performed at the Co K-edge. The experimental XMCD spectra are shown in figure 2 in comparison with isotropic X-ray absorption near edge
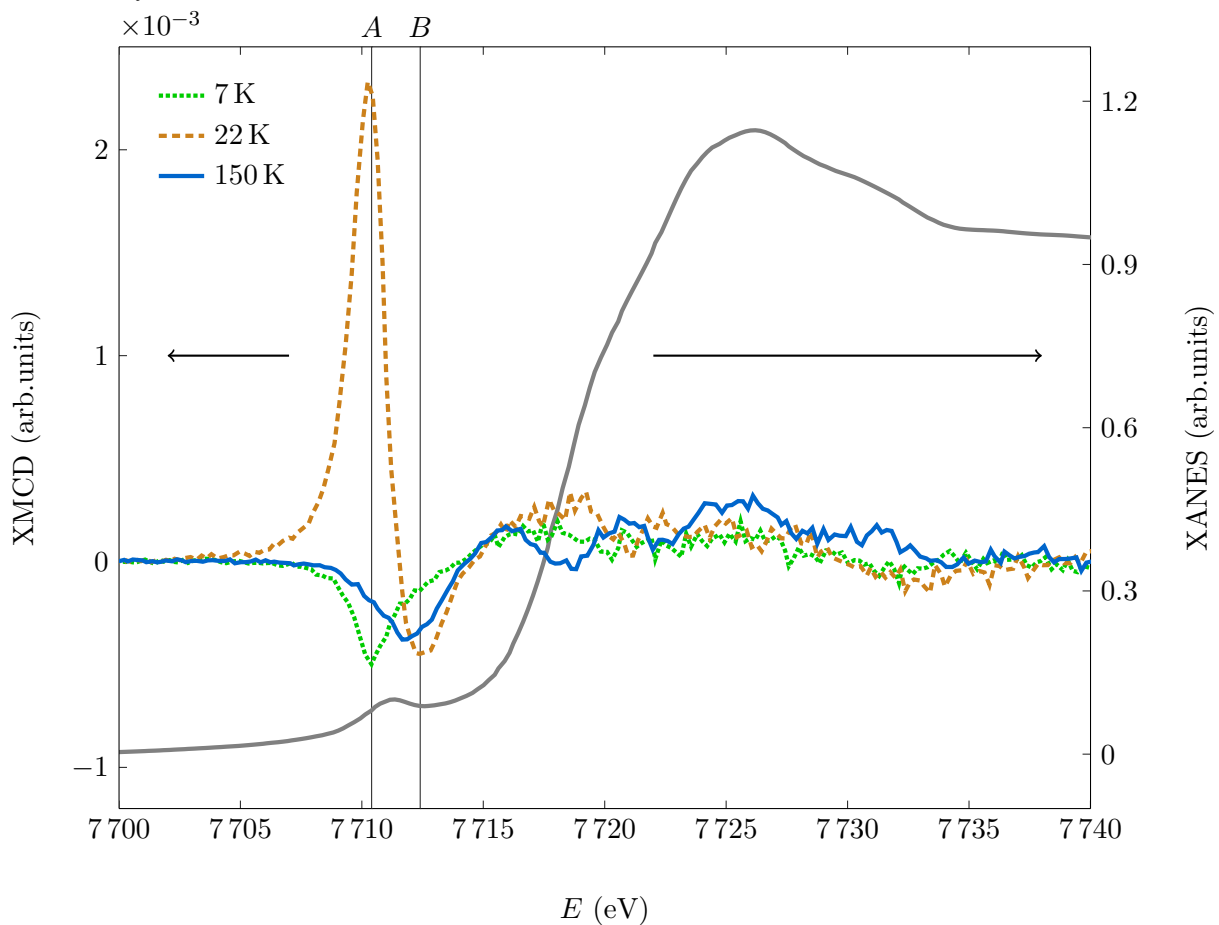
Figure 2. XMCD (left Y-scale) and XANES (right Y-scale) spectra of Co_2SiO_4 measured at the Co K-edge under a magnetic field of $\pm 6\,T$ along the beam (close to the b axis). Only three selected temperatures are shown for simplicity.

structure (XANES) spectra. The isotropic XANES spectra were obtained as an average of the X-ray absorption spectra recorded with left- and right-circular polarization. Characteristic XANES structures which were observed at all measured temperatures give rise to a rather weak pre-edge maximum at $7711\,eV$ and a shoulder at $7720\,eV$ whereas the main absorption edge peaks at $7726\,eV$.

The observed pre-edge structure is a typical feature of XANES K-edge spectra of $3d$ transition metals with rather localized $3d$-states, and are usually associated with admixtures of $1s \rightarrow 3d$ transitions. While being formally electric-quadrupole transitions which are usually very weak compared to the dipole transition $1s \rightarrow 4p$, a strong electric-dipole character can mix in due to indirect hybridization between $3d$ and $4p$ orbitals on adjacent sites through the ligand states. Appearance of the pre-edge peaks in Co_2SiO_4 can be explained by taking into account a hybridization between the $3d$ states of neighbouring Co ions via the $2p$ state of O. This is in agreement with our polarized neutron diffraction data.

We now consider the XMCD signals shown in figure 2. The prominent part of the Co XMCD consists of a double peak structure with a splitting of about $2\,eV$, centred around the pre-edge feature in the X-ray absorption spectrum. The pre-edge peaks at various temperatures have almost the same energies of about $7110\,eV$ (peak A) and $7112\,eV$ (peak B). On the other hand, a dramatic change in sign and intensity of these peaks is found with increase of temperature (see

figure 2). At the moment, there is no clear understanding of such strong change of the XMCD spectra and additional experiments are required to clarify this phenomenon.

The effective operators responsible for XMCD at the K-edge in both electric dipole and in electric quadrupole transitions have a pure orbital nature [13, 14]. Therefore, the rather intense XMCD signals ($\sim 0.2\%$ with respect to the edge jump) at the pre-edge indicate a strong orbital contribution to the total Co magnetic moment in Co_2SiO_4. However, its quantitative determination from the K-edge XMCD can only be obtained by a combination of experiment and theoretical calculations. As a matter of comparison, the ratio XMCD/XANES of about 0.2% was roughly estimated as the moment of the order of $1\,\mu_B$ per Co^{2+} in the Co-doped TiO_2 film from the Co K-edge measurements [15].

4. Conclusion

Non-polarized neutron diffraction measurements show that the ordered magnetic structure of orthorhombic Co_2SiO_4 corresponds to the magnetic (Shubnikov) group $Pnma$ which allows the antiferromagnetic configuration (G_x, C_y, A_z) for the $4a$ site with inversion symmetry $\bar{1}$ (Co1 position) and $(0, C_y, 0)$ for the $4c$ site with mirror symmetry m (Co2 position). The magnetic moments were found to be $3.87 \pm 0.03\,\mu_B$ and $3.35 \pm 0.02\,\mu_B$ for Co1 and Co2, respectively. Both Co1 and Co2 moments exceed the spin-only value of $3\mu_B$ for Co^{2+} in the high-spin state. Compared to literature data, an excellent agreement between the magnetic moments of Co1 is seen, whereas the values for Co2 are different [5].

An important orbital contribution to the total magnetic moment of Co^{2+} in Co_2SiO_4 was proven by the X-ray magnetic circular dichroism as well as polarized neutron diffraction studies, which indicate an orbital to spin magnetic moment ratio $\mu_L/\mu_S \approx 0.3$. According to this, the excess magnetic moment of Co^{2+} above the theoretical expectation of the spin-only value of $3\mu_B$ is caused by the orbital part. Both XMCD and polarized neutron flipping ratio measurements also suggest a hybridization between the $3d$ states of neighbouring Co ions via $2p$ state of O due to the superexchange interaction.

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