

“Peculiarities of Crystal and Magnetic Structures of Synthetic Co-Olivine, Co_2SiO_4 ”

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*Dedicated to
my wife Angelika Sazonova
for all her love and support*

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Kurzfassung

Verbindungen der chemischen Formel $M_2\text{SiO}_4$ mit Olivin-Struktur sind von grundsätzlicher Bedeutung für Geologen und Mineralogen aufgrund der großen Vorkommen von Olivinen im äußeren Erdmantel. Dabei ist M hauptsächlich Fe, Mg und Mn mit kleinen Anteilen an Ni, Ca, Co und Zn in Mischkristallen. Viele Studien haben Daten zu den Oxiden mit Olivinstruktur geliefert, insbesondere bei oder oberhalb von Raumtemperatur und bei hohen Drücken. Jedoch gibt es bei einigen Olivinen immer noch einen Mangel an Informationen zu den magnetischen Eigenschaften und dem Temperaturverhalten der Kristallstruktur unterhalb der Raumtemperatur. Eines der wenig untersuchten Silikate vom Olivintyp ist der synthetische Cobalt-Olivin, Co_2SiO_4 . Das Hauptziel der aktuellen Studie ist die genaue Bestimmung der Änderungen sowohl der Kristall- als auch der magnetischen Struktur von Co_2SiO_4 in einem breiten Temperaturbereich zwischen 2.5 K bis zu 500 K.

Synthetisches Co_2SiO_4 hat eine orthorhombische Kristallstruktur (Raumgruppe $Pnma$, Nr. 62) und zeigt unterhalb von rund 50 K eine magnetische Ordnung. Sowohl an Einkristallen (2.5 K–300 K) als auch an Pulvern (5 K–500 K) wurde Neutronendiffraktion für die genaue Bestimmung der Kristallstruktur angewendet. Die Gitterparameter wurden auch mittels Röntgen-Diffraktion zwischen 15 K und 300 K sowohl mit hochauflösenden Synchrotron- als auch Labor-Pulvermessungen bestimmt. Die orthorhombische Symmetrie mit der Raumgruppe $Pnma$ wurde für den gesamten Temperaturbereich zwischen 2.5 K und 500 K bestätigt.

Zur Parametrisierung der Zellkonstanten von Co_2SiO_4 wurde die molare spezifische Wärme gemessen und unter Berücksichtigung der Debye-Einstein-Gitterbeiträge, des magnetischen Anteils und des Schottky-Beitrags angepasst. Das Volumen der Einheitszelle wurde dann entsprechend der spezifischen Wärme berechnet. Es gibt einen klaren Hinweis auf eine anomale thermische Ausdehnung im Zusammenhang mit dem magnetischen Phasenübergang. Diese Anomalie in den Gitterkonstanten und des Volumens der Einheitszelle kann als Magnetostriktion aufgefasst werden.

Die genaue Symmetrieanalyse der magnetischen Struktur zeigt, daß diese mit der magnetischen (Shubnikov) Gruppe $Pnma$ übereinstimmt, welche die antiferromagnetische Konfiguration (G_x, C_y, A_z) für die $4a$ -Lagen mit

Inversionssymmetrie $\bar{1}$ (Co1 Position) und $(0,C_y,0)$ für die 4c-Lage mit Spiegelsymmetrie m (Co2 Position) zulässt. Die magnetische Anisotropie wurde mittels Anpassung der beobachteten $\chi(T)$ Kurven oberhalb von T_N an das Curie-Weiss-Gesetz untersucht und damit, die Curie-Weiss-Temperatur θ_{CW} und die effektiven magnetischen Momente μ_{eff} bestimmt.

Die magnetischen Momente aus den Neutronendiffraktionsmessungen ergaben $3.86 \pm 0.05 \mu_B$ und $3.37 \pm 0.04 \mu_B$ für Co1 bzw. Co2. Diese Werte sind viel größer als die reinen Spin-Werte für high-spin Co^{2+} ($3\mu_B$), was auf orbitale Beiträge hinweist. Dies stimmt auch mit Messungen sowohl der magnetischen Suszeptibilität als auch des magnetischen zirkularen Dichroismus von Röntgenstrahlung überein. Die sorgfältige Analyse der Neutronendiffraktionsmessungen als Funktion der Temperatur zeigt keine Änderung der Spinkonfiguration im gesamten Temperaturbereich des magnetisch geordneten Zustands.

Die magnetische Struktur von Co_2SiO_4 wurde auch mittels polarisierter Neutronenbeugung am Einkristall untersucht. Bei Temperaturen von 70 K und 150 K wurden Untersuchungen in einem äußeren Magnetfeld von 7 T parallel zur b -Achse durchgeführt. Diese Untersuchung der feldinduzierten Magnetisierung oberhalb von T_N zeigt eine Anisotropie, die bei hohen Temperaturen sehr gering ist, aber bei Annäherung an den magnetischen Phasenübergang stark ansteigt. Die Auswertung ergab außerdem einen nicht vernachlässigbaren Beitrag des magnetischen Moments auf den drei unterschiedlichen Sauerstoffpositionen. Dies wird als eine Delokalisierung des magnetischen Moments des Co^{2+} hin zu den benachbarten O aufgrund der Superaustauschwechselwirkung interpretiert.

Die Elektronendichteverteilung in Co_2SiO_4 wurde mittels Einkristall-Synchrotron-Diffraktion bei 12 K, 40 K und 300 K untersucht. Die Daten wurden sowohl mit Fourier- als auch Maximum-Entropie-Verfahren analysiert. Mit abnehmender Temperatur wurde eine Tendenz zur Ausdehnung der Valenzelektronendichte entlang der Richtung des magnetischen Moments durch eine Verlängerung des magnetischen Ellipsoids aus flipping-ratio Messungen mit polarisierten Neutronen gefunden. Die Annahme eines teilweise kovalenten Charakters der Co–O-Bindung wurde bestätigt.

Abstract

Compounds of the chemical formula $M_2\text{SiO}_4$ with olivine-type structure are of fundamental importance for geologists and mineralogists because of the presence of a huge amount of the olivines in the earth's upper mantle. Here, M is mainly Fe, Mg and Mn with small amounts of Ni, Ca, Co and Zn in mixed crystals. Many studies provided abundant data on the olivine-type oxides, especially at or above room temperature and at high pressure. However, there is still a lack of information on the magnetic properties and the thermal evolution of the crystal structure below room temperature for some olivines. One of the less studied olivine-type silicates is the synthetic cobalt olivine, Co_2SiO_4 . The main goal of the present study is to determine precisely the changes in both the crystal and magnetic structures of Co_2SiO_4 in a wide temperature range from 2.5 K up to 500 K.

Synthetic Co_2SiO_4 has an orthorhombic crystal structure (space group $Pnma$, No. 62) and shows magnetic ordering below ~ 50 K. Both single-crystal (2.5 K–300 K) and powder (5 K–500 K) neutron diffraction were applied to determine precise crystal structure parameters. Lattice parameters were also determined by means of both high-resolution synchrotron and laboratory X-ray powder diffraction measurements between 15 K and 300 K. The orthorhombic symmetry with space group $Pnma$ was found to be retained in the temperature range from 2.5 K up to 500 K.

In order to parameterize the cell parameters of Co_2SiO_4 the molar specific heat was measured and fitted taking into account the Debye–Einstein lattice contribution, the magnetic part and the Schottky contribution. The unit cell volume was then fitted based on the specific heat data. There is a clear evidence of an anomalous thermal expansion related to the magnetic phase transition. This anomaly in the lattice parameters and the unit cell volume can be attributed to magnetostriction.

Detailed symmetry analysis of the magnetic structure shows 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). Magnetic anisotropy was studied by fitting the observed $\chi(T)$

curves above T_N to the Curie-Weiss law, thus giving the Curie-Weiss temperatures θ_{CW} and effective magnetic moments μ_{eff} .

The magnetic moments from the neutron diffraction data were found to be $3.86 \pm 0.05 \mu_B$ and $3.37 \pm 0.04 \mu_B$ for Co1 and Co2, respectively. These values are much higher than the spin-only one for high-spin Co^{2+} ($3\mu_B$) indicating the orbital contribution. This is in agreement with both magnetic susceptibility and X-ray magnetic circular dichroism measurements. The accurate analysis of the neutron diffraction data as a function of temperature shows no change in the spin configuration in the whole temperature range of the magnetically ordered state.

The magnetic structure of Co_2SiO_4 has also been studied by means of polarized neutron diffraction on a single crystal. Measurements were made at temperatures of 70 K and 150 K in an external magnetic field of 7 T parallel to the b axis. This study of the magnetization induced by an applied field above T_N shows an anisotropy which is found to be rather small at high temperatures but becomes very strongly enhanced when approaching the ordering temperature. The refinement also revealed a non-negligible amount of magnetic moment on the three different oxygen positions which was interpreted as a delocalization of the magnetic moment from Co^{2+} towards the neighbouring O due to the superexchange coupling.

The electron-density distribution in Co_2SiO_4 was studied by means of single-crystal synchrotron X-ray diffraction measurements at 12 K, 40 K and 300 K. The data were analysed using both Fourier and maximum-entropy methods. A tendency to an elongation of the valence electron density along the direction of the magnetic moments with decrease of temperature was found in agreement with an elongation of the magnetic ellipsoids obtained from polarized neutron flipping-ratio measurements. The assumption of a partly covalent character of the Co–O bonding was confirmed.

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Chapter 1

Introduction

Orthosilicate olivine ($\text{Mg}_{1-x}\text{Fe}_x$) $_2\text{SiO}_4$ is a major phase in the solar system. It occurs in several types of meteorites and also on various planets and their moons. On Earth, the magnesium orthosilicate polymorphs are the dominant mineral phases of the top 660 km of the earth's mantle. It represents nearly 20% of the planet's volume. The composition of olivine in the upper mantle consists of $\sim 90\%$ forsterite, Mg_2SiO_4 , the magnesium-rich end member. Fayalite, Fe_2SiO_4 , is the iron-rich end member of the olivine-type silicate. Knowledge of its thermodynamic properties is crucial for undertaking many mineralogical, petrological and geophysical investigations. The T - x phase diagram at ambient pressure for the ($\text{Mg}_{1-x}\text{Fe}_x$) $_2\text{SiO}_4$ system was among the first of a transition metal bearing solid-solution mineral to be determined by experimental mineralogists [1]. Since that time, there have been a large number of experimental phase equilibrium and calorimetric studies undertaken in order to obtain a better description of the phase relations and thermodynamic properties of olivines.

The well-known discontinuity in seismic waves velocities at a depth of 410 km marks the transformation of Mg_2SiO_4 from the olivine structure (α phase) to the spinel structure (γ phase) with a narrow intermediate region

of stability for the β -spinel polymorph [2]. A second major discontinuity at a depth of 660 km is associated to the disproportionation of Mg_2SiO_4 into MgSiO_3 perovskite and MgO .

Natural ferromagnesian olivines contain minor amounts of additional divalent cations, including Ca, Mn, Ni and Co. Although concentrations of these elements in olivine are typically small ($\text{Ca} < 1.0\%$, $\text{Mn} < 1.0\%$, $\text{Ni} < 4000 \text{ ppm}$, $\text{Co} < 150 \text{ ppm}$ according to [3, 4]), their distribution relative to coexisting phases is important to understand the magmatic and planetary differentiation. Exchange of these elements between olivine and coexisting phases is also used in geothermometry. In the view of the many petrologic applications of equilibria involving minor components in olivine, it is necessary to develop a thermodynamic model for multicomponent olivine solutions. Once calibrated, such a model may be used to investigate mass transfer during igneous and planetary evolution and may be combined with thermodynamic treatments of coexisting phases to provide geothermometers and geobarometers.

Besides the fundamental importance for geologists and mineralogists, olivines display a surprising variety of chemical and physical properties. A large number of studies exist on olivine's structural and crystal-chemical properties, as well as lattice-dynamical behaviour (see, e.g., [5–9] and references therein). Because of the presence of $3d$ transition metal cations M (Fe^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+}), magnetic and electronic properties of the M_2SiO_4 olivines have also been studied rather intensively (see, e.g., [10–13] and references therein). In the following sections we briefly review some published results relevant to the present work.

1.1. Olivine structure

The crystal structure of Mg/Fe-olivine was determined long ago [14]. With the advent of the computer, using single-crystal diffractometers

and other different experimental techniques the structures of natural and synthetic olivines were redetermined and studied a number of times.

The general chemical formula for olivine is A_2BX_4 . The relatively large cations A^{2+} occupy the octahedral sites whereas relatively small cations B^{4+} are located in the tetrahedral sites. M_2SiO_4 (M – transition metal) compounds crystallizing with the olivine structure are characterized by a slightly distorted hexagonal close-packed array of oxygen anions in which one-eighth of the tetrahedral interstices are filled by silicon and one-half of the octahedral interstices are occupied by the divalent metal cation M . The olivine-type silicates have an orthorhombic crystal structure with the space group $Pnma$ (No. 62 according to [15]), in which four formula units are contained in the unit cell ($Z = 4$).

In the crystal, the Si ions are coordinated by four O ions to form isolated SiO_4 tetrahedra connected via divalent cations M . These cations are surrounded by six O ions and occupy two distinct octahedral sites: $M1$ is located on a centre of symmetry and $M2$ on a mirror plane. The polyhedral drawings of the corner- and edge-sharing MO_6 octahedra and isolated SiO_4 tetrahedra in the olivine structure are shown in figure 1.1.¹

With reference to figure 1.1 (see also figure 1 in [18]), one might expect the c cell dimension to be directly affected by variations in the radii, r_{M1} ² and r_{Si} , of the $M1$ and Si cations. The a dimension should be sensitive primarily to the mean effective radii, r_{M2} , of the cations occupying $M2$ octahedra, whereas the b dimension, which is parallel to the edge-sharing $-M1-M1-M1-$ spine of the octahedral chain presumably would be mostly affected by the mean radii of the cations occupying the $M1$ octahedra. Since there is an additional ‘chain’ of the corner-sharing $M2$ and Si polyhedra parallel to b , one must not underestimate the combined effects

¹This and the following molecular graphics were drawn with the programs DIAMOND [16] and VESTA [17].

²The parameters r_{M1} , r_{M2} and r_{Si} refer to the effective ionic radii (see [19]) of the atoms occupying the $M1$, $M2$ and Si sites, respectively.

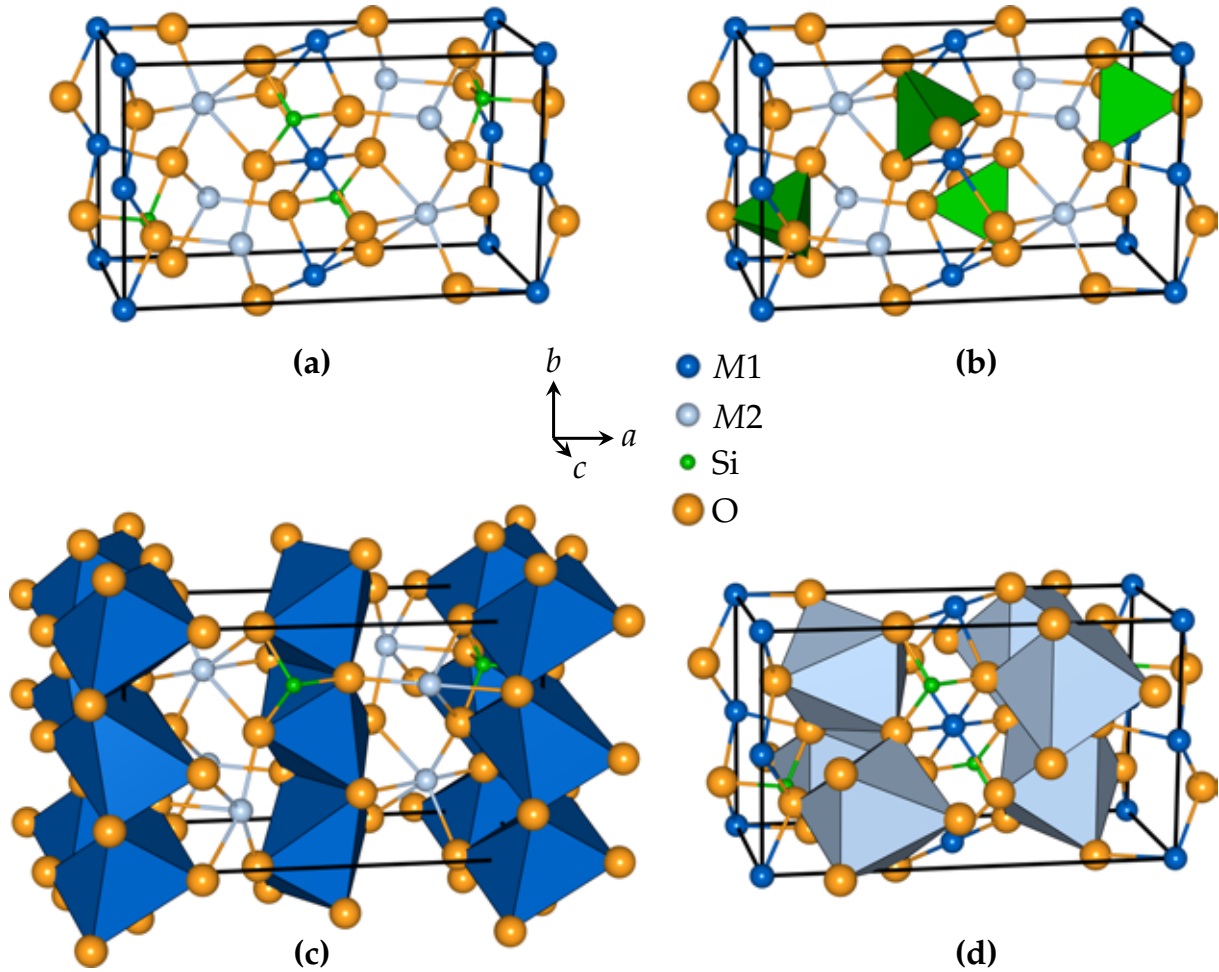


Figure 1.1. Polyhedral drawings of the M_2SiO_4 olivine structure. (a) The unit cell. (b) The framework of isolated SiO_4 tetrahedra. (c) The framework of edge-sharing M1 octahedra. (d) The framework of corner-sharing M2 octahedra.

of r_{M2} and r_{Si} on the b dimension. Thus, the unit cell volume will be a function of the mean effective radii of all constituent cations.

1.2. Magnetic properties of olivines

The magnetic properties of olivines received also much attention and were investigated a number of times over the past 40 years (see, e.g., [11, 20–27]). First, considering the case of Co-olivine, Nomura *et al.* [20] determined, using powder magnetic susceptibility measurements as well as neutron powder diffraction data, that a paramagnetic to

antiferromagnetic phase transition occurs in Co_2SiO_4 at ~ 49 K. Robie *et al.* [28] observed in heat capacity measurements of Co_2SiO_4 a sharp λ -peak at ~ 50 K corresponding to this transition.

Below T_N , the Co-olivine was found to be magnetically ordered with the magnetic cell equal to the crystallographic cell in space group $Pnma$. It was initially decided that the moments of Co^{2+} on both $M1$ and $M2$ sites are parallel to the b axis and antiferromagnetically coupled [20, 21]. Lottermoser *et al.* [22] and Lottermoser and Fuess [23] followed the neutron reflections of this composition over a range of temperatures below T_N , and found a slight deviation of the magnetic moment on $M1$ from the b axis for the whole antiferromagnetic region. The magnetic moments on both sites were found almost equal [$M1$: $3.9(1) \mu_B$ and $M2$: $3.84(8) \mu_B$ at 4 K] and exceed the spin-only value of $3 \mu_B$ [22].

The magnetization along the b axis in Co_2SiO_4 exhibits a metamagnetic double step transition at $H_j = 18$ T (figure 1.2), while those along the a and c axes show no anomaly up to 19 T [10, 29]. The b axis magnetization measured by pulsed fields of up to 41 T at 4.2 K are given in the inset to figure 1.2, which shows a slight hysteresis at H_j indicating a character of first-order transition. The magnetization at 41 T corresponds to the magnetic moment of $2.6 \mu_B$ per Co, which is substantially smaller than the observed moments of $M1$ or $M2$ sites at zero field by neutron experiments [22, 23]. At elevated temperatures, the transition becomes smeared, as shown in figure 1.2. At 15 K, the first-step curve still shows a discontinuous (first-order type) change while the second-step transition become already continuous. Above 30 K, the transitions are apparently of single step and second-order type.

Summarizing the various studies, it was proposed that olivines are magnetically ordered at low temperatures with the magnetic cell equal to the crystallographic cell. The magnetic structure is quite complex and the magnetic moments and their temperature dependences are different for the $M1$ and $M2$ sites. The magnetic moments of M at the $M2$ site are antiferromagnetically coupled and they are parallel to the one of the

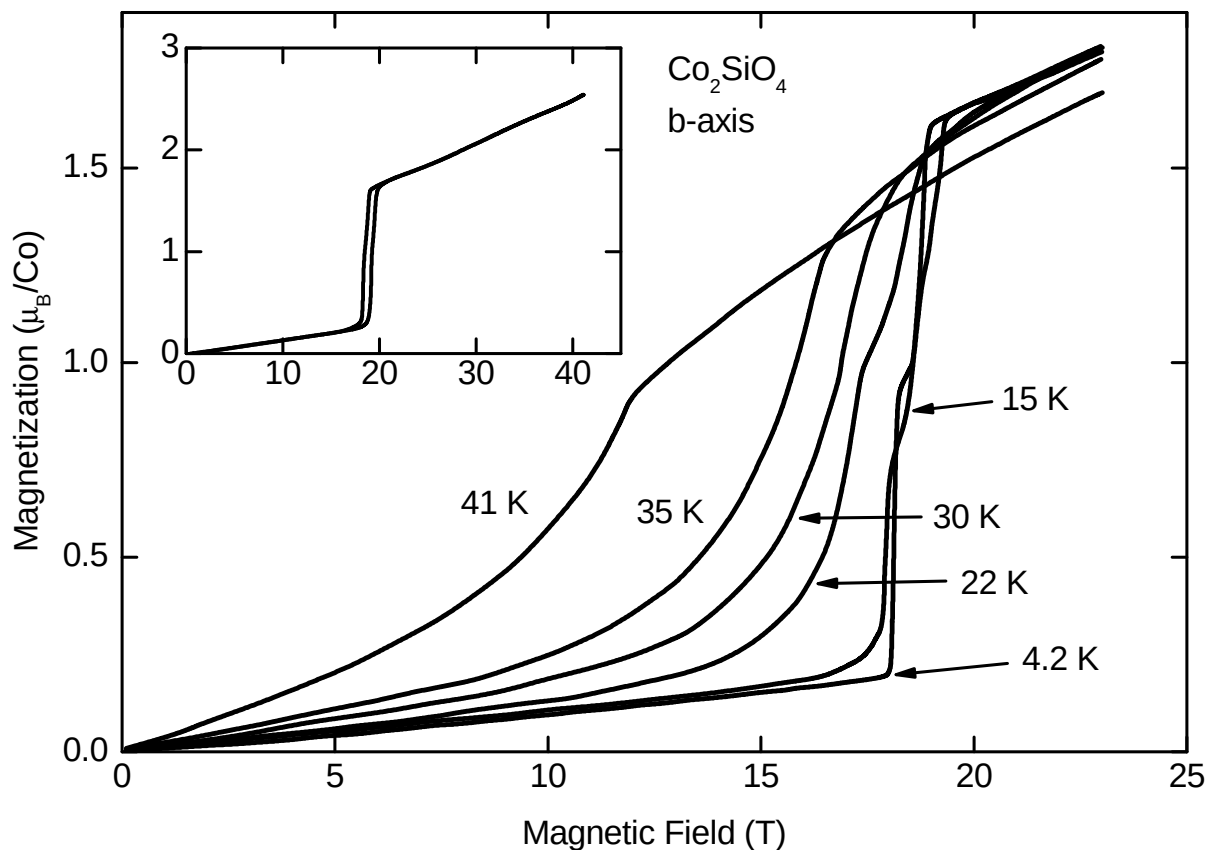


Figure 1.2. Magnetization curves of Co_2SiO_4 with fields along the b axis. The curves in the inset were obtained using pulsed magnetic fields of up to 41 T [10].

crystallographic axis; it is a for $M = \text{Mn}$ and b in the case of $M = \text{Fe}$ or Co . On the other hand, at the $M1$ site the moments of M are also coupled antiferromagnetically, but they are canted with respect to all three crystallographic axes at $T < T_N$. The thermal behaviour of the canting strongly depends on the type of the cation M . In Mn_2SiO_4 , the canting is very weak down to a temperature where it increases rapidly with decreasing temperature. In contrast, the canting in Fe_2SiO_4 increases monotonically with decreasing temperature.

A magnetic pre-ordering in Co_2SiO_4 above the Néel temperature (~ 49 K) was experimentally observed by means of the magnetic excitations measurements with neutron scattering [30]. Magnetization measurements also showed non-vanishing anisotropies above the transition temperature [30]. Short-range magnetic order above T_N was

also observed in Fe-olivine at least up to 80 K [31] or 130 K [27] and could potentially exist at temperatures up to 500 K based on Raman spectra recorded at different temperatures [32].

The electronic structure and magnetism in Co_2SiO_4 were studied by density functional theory within the generalized gradient approximation with the on-site Coulomb energy taken into account (GGA + U) [33]. It was found that the top of valence bands consists of the $\text{Co}(3d)\text{--O}(2p)$ hybridization. All calculated orbital magnetic moments were found to be very small and the calculated spin moments were found to be also smaller than the experimental values. The difference between calculated [33] and experimental [22, 23] data might result from the fact that a simplified collinear magnetic structure was considered.

1.3. Cation ordering

In olivines containing only one species and oxidation state of cation in both octahedral sites (e.g., Mg_2SiO_4), the $M1$ site is inherently 0.03–0.05 Å smaller than the $M2$ site, using an average $\langle M\text{--O} \rangle$ bond length as a measure of ‘size’. The $M1$ octahedron is also slightly more distorted than $M2$, even at high temperatures. The size and distortion differences arise from the fact that the $M1$ octahedron has twice as many shared edges as the $M2$ octahedron.

The cation distributions between the $M1$ and $M2$ sites of olivines were studied for many cation pairs (see, e.g., [6, 7, 9, 34–63] and references therein). In particular, Mg/Fe-olivines were studied most intensively because they are one of the most abundant minerals in the earth’s mantle. The cation distributions of Mg and other transition metals, such as Mg/Mn, Mg/Co and Mg/Ni, were also studied.

One important aspect of crystal-chemical studies was a determination of the nature of the long-range Mg/Fe distribution over the $M1$ and $M2$ octahedral sites. From the results obtained at ambient conditions, it can

be concluded that Fe^{2+} and Mg^{2+} are almost randomly distributed over the $M1$ and $M2$ sites. However, other divalent ions such as Ni and Co are strongly fractionated into the $M1$ site while Mn, Ca and Zn tend to prefer the $M2$ site in olivine.

Furthermore, ordering of some cations in the olivine structure is strongly dependent on the thermal history of the sample, and the potential for geothermometry has been postulated. For example, many Mg/Fe olivines are randomly disordered, but in a few cases Fe^{2+} prefers the $M2$ site [64] though most contain more Fe^{2+} in $M1$ than in $M2$ (up to 20% more in a lunar sample [65]). Contradictory data were obtained presumably due to $M1$ – $M2$ re-equilibration having occurred during quenching. Normal experimental quenching rates from high T are too slow to freeze-in the equilibrium cation ordering, and hence *in situ* experiments are required for studying ordering in such mineral systems in a systematic way. These *in situ* studies provided the first direct experimental confirmation of theoretical predictions [66] that Mg/Fe exchange reactions in olivine are effectively non-quenchable due to very rapid kinetics.

The non-convergent ordering of the (Ni,Mg)-olivines is controlled by the strong affinity of Ni for the $M1$ site, and only at $T > 800^\circ\text{C}$ the samples show a progressive, but slight, decrease in order. Co^{2+} shows a strong preference for the $M1$ site with an oscillatory behaviour; it decreases slightly at about 300°C , climbing up to nearly its original value at around 800°C and then decreases by about 30% at 1000°C . With increasing temperature, (Fe,Mg)-olivines show an initial tendency towards ordering with Fe^{2+} preferring the octahedral $M1$ site at lower temperatures, followed by a temperature region of disorder and finally, through a cross-over temperature of about 900°C , a switchover to anti-ordering with Fe^{2+} strongly preferring the octahedral $M2$ site between 900°C and 1300°C . In (Mn,Mg)- and (Mn,Fe)-olivines, Mn shows a preference for the $M2$ site at low T and becomes increasingly disordered

over the two sites at $T > 500^\circ\text{C}$. Both Co^{2+} and Ni^{2+} in the $(\text{Co,Ni})_2\text{SiO}_4$ solid solutions distribute randomly over the $M1$ and $M2$ sites.

Thus, the magnetic properties of olivines strongly depend on the M cation ordering and could, therefore, be controlled by a variation of the order parameter. For instance, a complete replacement of the paramagnetic ions by diamagnetic ones in the $M2$ position should result in a one-dimensional magnetic behaviour.

1.4. Goals of this study

Many studies provided abundant data on the olivine-type oxides, especially at or above room temperature and at high pressure. In spite of these numerous investigations, which shed much light on the structural, crystal-chemical, lattice dynamic, magnetic and thermodynamic properties of the olivine group of minerals, uncertainties and gaps in knowledge still persist. One of the less-studied olivine-type silicates is the synthetic cobalt olivine, Co_2SiO_4 . Synthetic samples of this composition are needed for measurements because Co_2SiO_4 does not occur in nature as a discrete mineral (natural materials have uncontrollable amounts of various other components).

The following areas need more investigation:

- The thermal evolution of the Co_2SiO_4 crystal structure below room temperature as well as the effect of magnetic ordering on the crystal structure needs further study. To our knowledge, the structural parameters of Co_2SiO_4 were published only from X-ray diffraction analyses at room temperature and above [67–70]. However, neutrons are the most appropriate probe for studies of both crystal and magnetic structures. Firstly, as the neutron interacts with nuclei, there is no fall-off in the scattering cross-section with increasing scattering angle. This enables us to determine the atomic distribution more precisely than in the case of X-rays.

Secondly, the fact that the neutron cross-sections do not depend on the atomic numbers means that light atoms (the O atoms in this case) can be localized as easily as heavy ones. Finally, the magnetic moment of neutrons allows the magnetic structures to be determined. Therefore, both single-crystal (section 3.2.1) and powder (section 3.1.3) neutron diffraction measurements (section 3.2.1) in a wide temperature range from 2.5 K up to 500 K were performed. The results were compared with those from laboratory (section 3.1.1) and synchrotron (section 3.1.2) X-ray powder diffraction studies as well as with previously reported room temperature literature data.

- The magnetic structure of Co_2SiO_4 and its thermal evolution require further analysis. The more recent works [22, 23] differ from those of earlier studies [20, 21] and the symmetry requirements were not discussed in detail in those papers. In order to examine the correctness of the derived models of the magnetic structure (section 6.3) as well as to follow its thermal evolution with high precision, the neutron diffraction experiments on both single-crystal (section 3.2.1) and powder (section 3.1.3) samples were performed. In addition, to parameterize with high accuracy the cell parameters of Co_2SiO_4 for subsequent thermal expansion calculations a model based on the specific heat capacity measurements (section 4.2.1) was applied.
- A third issue of interest concerns the effects of covalency, superexchange coupling and frustration in the magnetically ordered state of Co_2SiO_4 . Combined X-ray and neutron diffraction measurements is a powerful tool to investigate the electron-density distribution in crystals. On the other hand, the polarized neutron data give an important information about the magnetization density distribution. The high accuracy in the determination of the lattice parameters (sections 3.1.1, 3.1.2, 3.1.3), the atomic positions and

the atomic displacement parameters (section 3.2.1) is essential to interpret correctly the experimental electron and magnetization density maps obtained in our experiments with synchrotron radiation (section 5.1) and polarized neutrons (section 7.1) on single crystals.

- Finally, further measurements are necessary in order to clarify the influence of the orbital contribution to the total magnetic moment of Co^{2+} in Co_2SiO_4 . This is a poorly understood subject that has received little study in the past in spite of its importance. Moreover, the theoretical work [33] is in contrast to the experimental results [22, 23]. To clarify this, special techniques such as the polarized neutron flipping-ratio measurements (section 7.1) as well as the X-ray magnetic circular dichroism (section 8.1) studies of Co_2SiO_4 were performed. The results of the magnetic susceptibility measurements (section 6.2) were also considered.

Chapter 2

Sample preparation

2.1. Synthesis of powder sample

A five-gram sample of Co_2SiO_4 was prepared by conventional ceramic synthesis for the neutron powder diffraction measurements (see section 3.1.3). Stoichiometric amounts of the appropriate oxides CoO and SiO_2 were carefully ground in an agate mortar to a fine homogeneous black powder. Then, the mixture was pressed to a pellet and heated on air in an Al_2O_3 crucible to 1400 K at a rate of about 100 K per hour. After initial 48 hours at 1400 K, the sample was re-ground and the heating procedure was repeated. Finally, the sample was cooled in the furnace by switching off the power. Thus, a violet powder sample was obtained. The laboratory X-ray powder diffraction tests indicated a single phase product.

2.2. Single crystal growth

The same procedure (see section 2.1) was initially followed to obtain materials for the single-crystal growth. After the synthesis, the powder was re-ground and pressed hydrostatically under a pressure of about

55 MPa cm^{-2} in a plastic cylindrical balloon. Thus, a rod of $\sim 7 \text{ mm}$ in diameter and 80 mm in length was prepared and finally sintered at the same conditions as described above. The parts of this rod were then used as the feed and seed rods during the crystal growth procedure. Crystal growth was performed by the floating-zone method using a mirror furnace (Crystal System Inc., Model No. FZT-10000-H-II-VP). The furnace is equipped with four infra-red (IR) halogen lamps as the heat source of a maximum power of 1 kW each. Feed and seed rods were rotated in the furnace in opposite directions with a rotation speed of $\sim 30 \text{ r.p.m.}$ The growth rate was about 1.5 mm per hour . The length of the molten zone was $\sim 5 \text{ mm}$ and the power required to maintain this length value was $\sim 2 \text{ kW}$. Thus, a large dark violet single crystal with a dimension of about 7 mm in diameter and 15 mm in length was obtained after several cycles of the growth process. Figure 2.1 shows the grown Co_2SiO_4 single crystal.

To study structural parameters such as the atomic positions and atomic displacement parameters (ADPs) in detail, a small Co_2SiO_4 single crystal was cut from the large as-grown crystal and measured by single-crystal

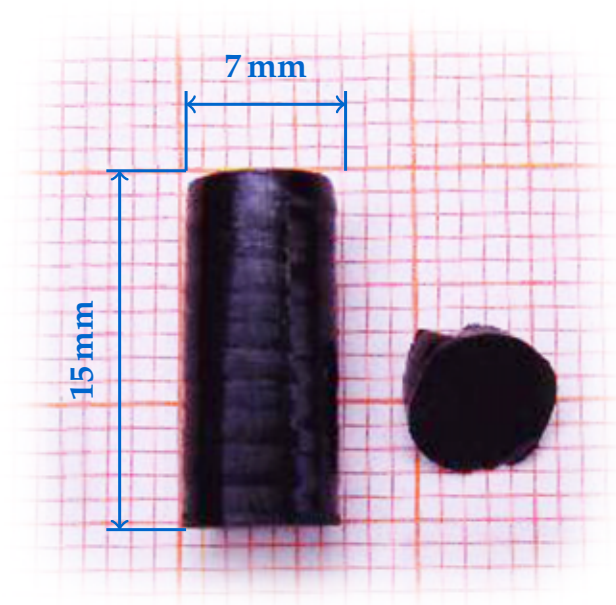


Figure 2.1. Co_2SiO_4 single crystal.

neutron diffraction (section 3.2.1). The parts of this crystal were also studied by means of specific heat (section 4.2.1) and dc magnetization (section 6.2) measurements as well as by polarized neutron diffraction (chapter 7) and X-ray magnetic circular dichroism (section 8.1). In order to determine the lattice parameters of Co_2SiO_4 , powder samples were finely ground from a part of the as-grown single crystal and studied by means of both conventional (laboratory) and synchrotron X-ray powder diffraction (see sections 3.1.1 and 3.1.2, respectively).

Chapter 3

Room temperature structure

As was already mentioned in the introduction, many studies provided abundant data on the olivine-type oxides, especially at or above room temperature and at high pressure. Some important aspects of the olivine structure (see, e.g., [71]) are summarized below.

Co_2SiO_4 crystallizes in the orthorhombic space group $Pnma$. There are two crystallographically non-equivalent Co^{2+} sites, namely Co1 (Wyckoff position $4a$) with inversion symmetry $\bar{1}$, and Co2 (Wyckoff position $4c$) with mirror symmetry m (see figures 3.1 and 3.2).

At room temperature the lattice constants are $a = 10.3005(1) \text{ \AA}$, $b = 6.0028(1) \text{ \AA}$ and $c = 4.7816(1) \text{ \AA}$.¹ The Co1 cation is coordinated by six O ions with Co–O distances ranging between $2.0929(2) \text{ \AA}$ and $2.1715(2) \text{ \AA}$ at room temperature and with an average $\langle \text{Co1–O} \rangle$ distance of $2.1200 \text{ \AA}$. The Co1O_6 octahedra are interconnected by common edges and form single chains along b (figure 3.2). The Co2 cations also form octahedra with Co–O distances within $2.0684(4) \text{ \AA}$ and $2.2250(6) \text{ \AA}$, and with an average $\langle \text{Co2–O} \rangle$ distance of $2.1402 \text{ \AA}$ at room temperature. The Co2O_6 octahedra are attached on alternate sides to the Co1O_6 chains in a way that the

¹Hereafter, standard deviations for the lattice constants as well as atomic distances and angles are shown in parenthesis.

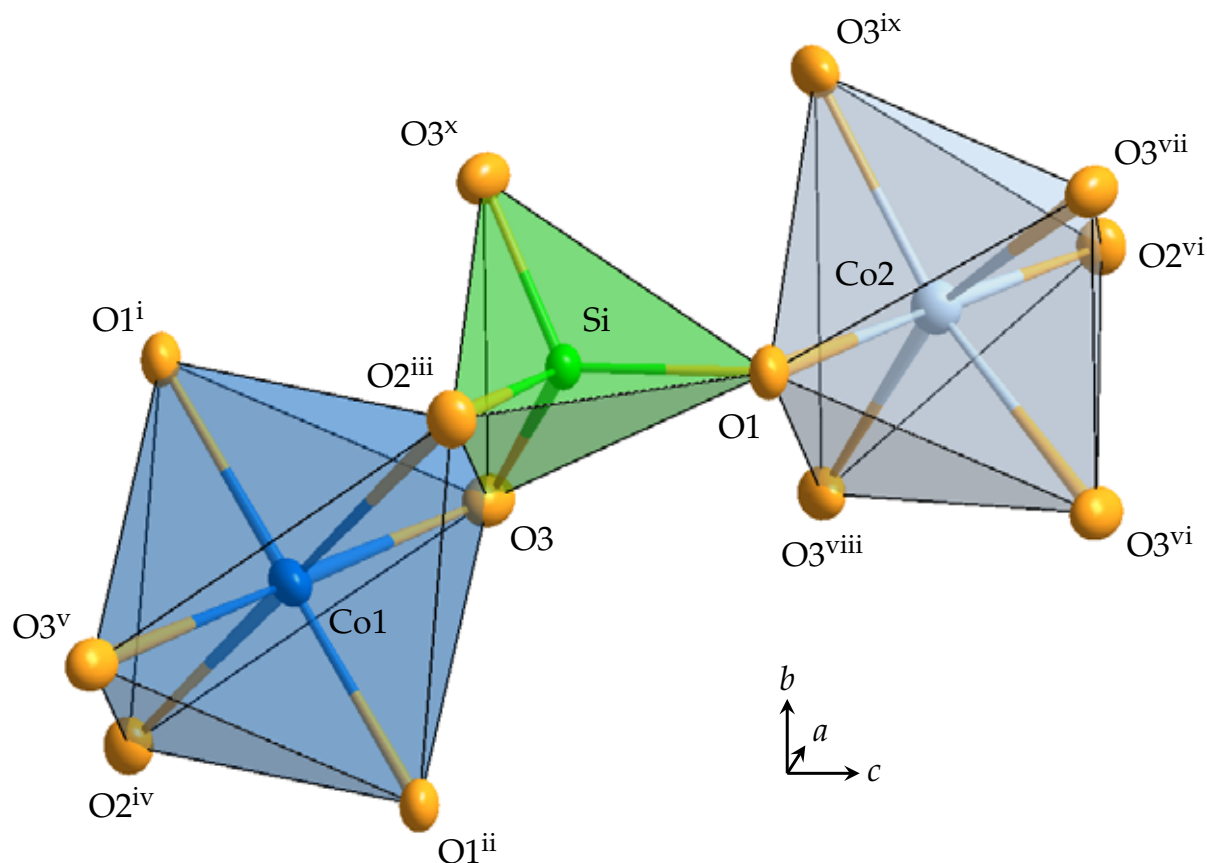


Figure 3.1. Clinographic view of the CoO_6 and SiO_4 polyhedra in Co_2SiO_4 at room temperature. Displacement ellipsoids are plotted at the 95% probability level. See table 3.5 for the symmetry codes.

whole arrangement of Co1O_6 and Co2O_6 octahedra forms zigzag chains along the b axis.

The Si cations are coordinated by four O ions forming the SiO_4 tetrahedra which are not linked (figures 3.1 and 3.2).

3.1. Lattice parameters

The lattice parameters at room temperature were initially obtained from both laboratory and synchrotron X-ray powder diffraction measurements [72].

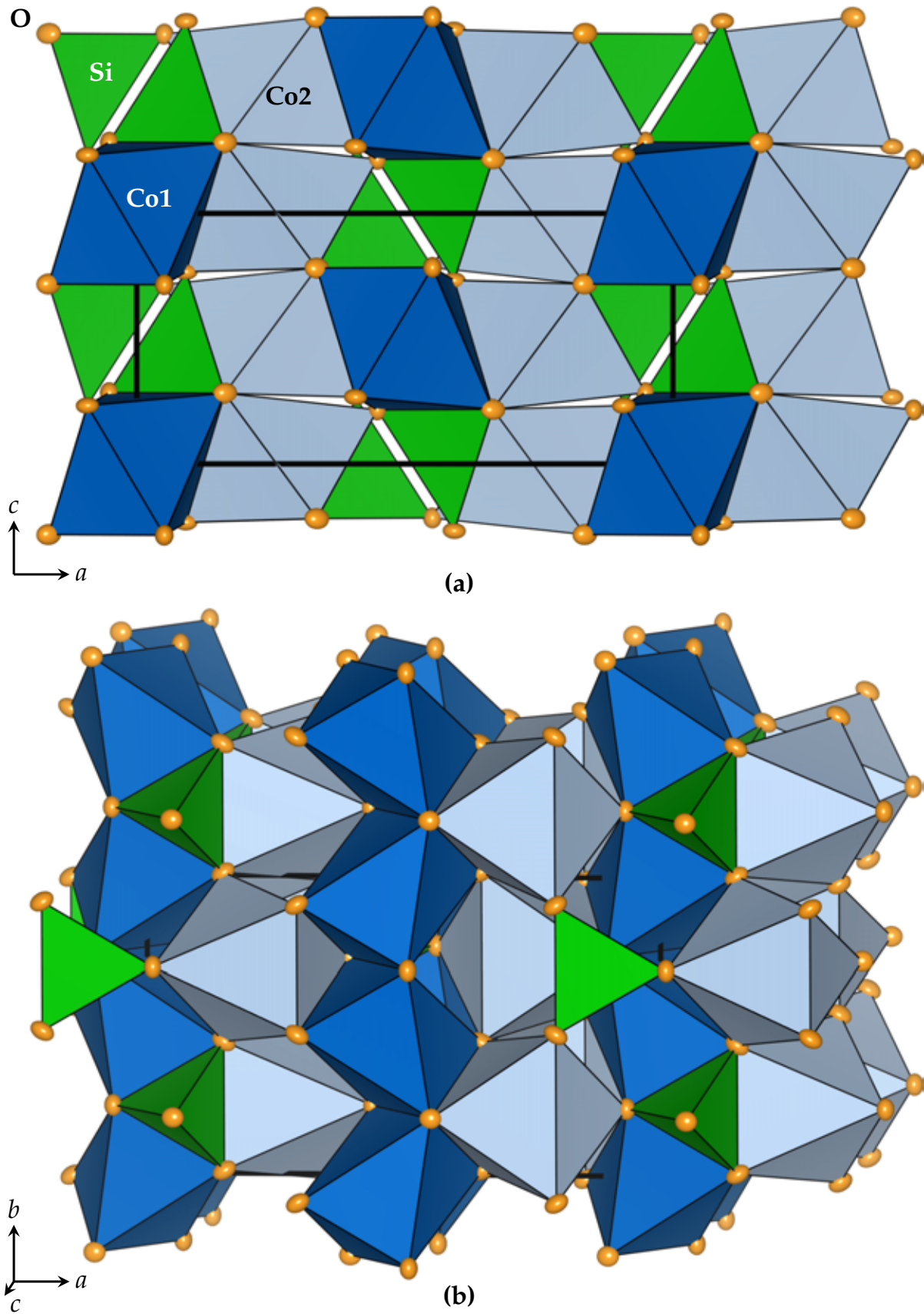


Figure 3.2. Structure of Co_2SiO_4 olivine at room temperature. (a) Projection onto the ac plane; (b) clinographic view. Displacement ellipsoids are plotted at the 95% probability level.

3.1.1. Laboratory X-ray powder diffraction

Powder sample of Co_2SiO_4 was finely ground from a part of the as-grown single crystal and studied by means of laboratory X-ray powder diffraction using the X'Pert PRO instrument (PANalytical) at the Institute of Crystallography, RWTH Aachen University, Germany. The data were collected in Bragg–Brentano geometry with $\text{Cu } K\alpha_{1,2}$ radiation. Owing to the θ – θ geometry of the diffractometer, the flat sample stayed fixed in the horizontal plane. The intensity was recorded by a position-sensitive detector (X'Celerator, PANalytical). The sample holder consisted of a copper plate mounted on top of a double-stage He closed-cycle refrigerator.

The temperature of the sample was controlled by two diode sensors and a stability of ± 0.1 K was achieved. One sensor was in direct contact with the sample holder, the other one was situated close to the heater at the cold-head itself.

Diffraction patterns were measured at various temperatures between 19 K and 300 K in the 2θ range from 10° to 120° . Silicon was used as an internal standard to ensure a high accuracy for the determination of the lattice parameters and to compensate for the temperature-dependent displacement errors. Lattice parameters of Co_2SiO_4 were obtained by whole pattern fitting using the LeBail method implemented in the program FULLPROF [73].

3.1.2. Synchrotron X-ray powder diffraction

In order to prove the results of our laboratory X-ray powder diffraction study, which revealed an unusual behaviour of the lattice parameters at low temperature, high-resolution experiments were carried out at the synchrotron facility HASYLAB/DESY (Hamburg, Germany) with the powder diffractometer at beamline B2 [74]. The powder sample consisted of a completely filled and sealed quartz capillary of 0.3×30 mm. It was mounted with a capillary spinner in Debye-Scherrer geometry inside a He

closed-cycle cryostat [75] equipped with a silicon diode as the temperature sensor. A wavelength of 0.50206(1) Å was selected from the direct white synchrotron beam using a Si(111) double flat-crystal monochromator and determined from eight reflection positions of a LaB₆ reference sample (NIST SRM 660a). The beam size of 0.4 × 3 mm at the sample position was cut by slits.

All diffraction patterns were collected using an on-site readable position-sensitive image-plate detector (2θ range 4°–55°) [76]. Several patterns were collected during the cooling process at a continuous temperature decrease down to 15 K with time intervals of approximately 10 min per pattern, whereas the data collection at fixed temperatures was applied during the heating from 15 K up to 300 K (on average approximately 30 min per pattern). Structure parameters of Co₂SiO₄ were obtained from the Rietveld refinements using the program FULLPROF [73]. Experimental and refinement details for synchrotron X-ray powder diffraction at selected temperatures are summarized in table 3.1.

Data obtained in both laboratory and synchrotron X-ray powder diffraction experiments correspond well to each other. They are also in close agreement with our additional neutron powder diffraction measurements (see section 4.1 for details) as well as with the literature data [20, 67–70].

3.1.3. Neutron powder diffraction

Accurate lattice parameters of Co₂SiO₄ were obtained from neutron powder diffraction [77]. These measurements were performed using the D20 diffractometer (Institut Laue-Langevin, Grenoble, France) in its high-resolution mode. The neutron wavelength was $\lambda = 1.87$ Å. Approximately two grams of Co₂SiO₄ were loaded into a standard ILL-type 7 mm Vanadium can.

Table 3.1. Experimental and refinement details of synchrotron powder diffraction on Co_2SiO_4 .

	180 K	100 K	15 K
<i>Crystal data</i>			
M_r	209.95	209.95	209.95
Cell setting, space group	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>
a, b, c (Å)	10.2928(1), 5.9927(1), 4.7795(1)	10.2891(1), 5.9899(1), 4.7785(1)	10.2876(1), 5.9877(1), 4.7789(1)
V (Å ³)	294.804(6)	294.499(6)	294.373(6)
Z	4	4	4
Radiation type	Synchrotron	Synchrotron	Synchrotron
Wavelength (Å)	0.50206	0.50206	0.50206
Specimen form, colour	Powder, violet	Powder, violet	Powder, violet
Specimen size (mm)	Capillary, 0.3×30	Capillary, 0.3×30	Capillary, 0.3×30
<i>Data collection</i>			
Data collection method	2θ scans	2θ scans	2θ scans
2θ range (°)	4–55	4–55	4–55
2θ step size (°)	0.004	0.004	0.004
<i>Refinement</i>			
Refinement method	Rietveld	Rietveld	Rietveld
R_p, R_{wp}	0.039, 0.050	0.041, 0.052	0.042, 0.054
R_{Bragg}, S	0.034, 3.21	0.037, 3.27	0.037, 3.22
Excluded region(s)	None	None	None
Profile function	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
No. of parameters	33	33	33
No. of data points	12751	12751	12751

Data were collected during every 6 min with a fixed ramp rate of 1 K for 6 min in the temperature range 5 K–100 K and 4 K for 6 min in the range 100 K–500 K. This procedure of fixed ramp rate and continuous data collection was applied to reduce the temperature gradient effects

across the sample. Each diffraction pattern was measured in the angle range of $10^\circ < 2\theta < 150^\circ$ with 2θ steps of 0.1° . Structural parameters of Co_2SiO_4 were obtained from the Rietveld refinements using the program FULLPROF [73].

3.2. Atomic positions and displacement parameters

3.2.1. Single-crystal neutron diffraction

To study structural parameters such as the atomic positions and atomic displacement parameters in more detail, especially those of the O atoms, as well as to obtain higher accuracy in determination of magnetic structure parameters, a small Co_2SiO_4 single crystal of $3 \times 2 \times 2$ mm was cut from the large as-grown crystal.

The sample was studied on the four-circle diffractometer HEiDi [78] at the hot neutron source of the FRM II reactor (Forschungsneutronenquelle Heinz Maier-Leibnitz), TU Munich, Garching, Germany. Using a Cu-(420) monochromator a short wavelength of $0.552(1) \text{ \AA}$ was obtained with a high flux density of $> 2 \times 10^6 \text{ neutrons s}^{-1} \text{ cm}^{-2}$. The large available q space ($\sin \theta / \lambda$ range) at this wavelength yields a large number of symmetrically non-equivalent measurable Bragg reflections. Thus, not only the positional parameters but also other parameters such as the ADPs can be refined with very small error bars $< 10^{-4}$. Additionally, typical sources of systematic errors such as the extinction effect are significantly dampened at this wavelength.

For low-temperature experiments a He closed-cycle cryostat was mounted in the Eulerian cradle of the diffractometer. The sample crystal was wrapped in Al foil in order to ensure homogeneity of the temperature. The temperature was measured and controlled by a diode sensor near the sample position and a stability of $\pm 0.1 \text{ K}$ was achieved. The absolute

temperatures of the measurements were obtained by using an additional temperature sensor at the sample position.

The corrected integrated intensities of the measured reflections were obtained using the program PRON2K.² Numerical absorption correction was performed with the program TBAR.³ The atomic positions and displacement parameters of Co_2SiO_4 were refined using the single-crystal option of the program FULLPROF [73]. Standard single-crystal refinement programs like SHELX or JANA2000 are not appropriate for the low-temperature data because of the additional magnetic contributions to the Bragg intensities below 50 K. On the other hand, JANA2006 [79] gave similar results as FULLPROF both for the crystal and magnetic structures parameters. Experimental and refinement details for single-crystal neutron diffraction at 2.5 K, 55 K and 300 K are summarized in table 3.2.

In order to prove the quality of our Co_2SiO_4 single crystal and to compare its structural parameters with those reported in the literature by Ghose & Wan [67], Miyake *et al.* [68], Morimoto *et al.* [69] and Tamada *et al.* [70], we performed a neutron diffraction study [72] at room temperature on the single-crystal diffractometer HEiDi at FRM II. The observed reflection profiles correspond to the instrumental resolution. This demonstrates the good quality of the crystal. Bragg reflection intensities were collected up to $\sin \theta / \lambda \approx 1.04 \text{ \AA}^{-1}$ [$\lambda = 0.552(1) \text{ \AA}$]. The stability of the experiment was controlled by the repeated measurement of standard reflections.

There were 2920 Bragg reflections measured and averaged over symmetry equivalents to yield a total of 1624 independent reflections with an internal R value of $R_{\text{int}} = 0.034$. Then, reflections with $I \leq 2\sigma(I)$ were deleted, and the remaining 1341 reflections were used for the

²Program for data reduction of DIF4. Version of the Institute of Crystallography, RWTH Aachen University.

³Program for calculating absorption, mean paths and extinction for single crystals (Paul Scherrer Institute, ETH Zurich).

Table 3.2. Experimental and refinement details of single-crystal neutron diffraction on Co_2SiO_4 .

	300 K	55 K	2.5 K
<i>Crystal data</i>			
M_r	209.95	209.95	209.95
Cell setting, space group	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>
a (Å), b (Å), c (Å), V (Å ³)	10.3005, 6.0028, 4.7816, 295.66	10.2869, 5.9889, 4.7781, 294.37	10.2864, 5.9872, 4.7785, 294.29
Z	4	4	4
Radiation type	Constant wave- length neutron diffraction	Constant wave- length neutron diffraction	Constant wave- length neutron diffraction
Wavelength (Å)	0.552(1)	0.552(1)	0.552(1)
μ (mm ⁻¹)	0.03	0.03	0.03
Crystal form, colour	Parallelepiped, dark violet	Parallelepiped, dark violet	Parallelepiped, dark violet
Crystal size (mm)	$3 \times 2 \times 2$	$3 \times 2 \times 2$	$3 \times 2 \times 2$
<i>Data collection</i>			
Diffractometer	Four-circle diffractometer	Four-circle diffractometer	Four-circle diffractometer
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Numerical	Numerical	Numerical
$T_{\min}$, $T_{\max}$	0.918, 0.946	0.915, 0.947	0.915, 0.947
No. of measured, independent [$I > 2\sigma(I)$] and observed reflections	2920, 1624, 1341	2118, 1465, 1098	3226, 1424, 1070
R_{int}	0.034	0.028	0.033
$\theta_{\max}$ (°)	37.4	37.9	37.9
<i>Refinement</i>			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.054, 1.28	0.029, 0.035, 1.10	0.033, 0.044, 1.49
No. of reflections	1341	1098	1070
No. of parameters	46	46	50
Weighting scheme	$w = 1/\sigma^2(F_o^2)$	$w = 1/\sigma^2(F_o^2)$	$w = 1/\sigma^2(F_o^2)$
Extinction method	Anisotropic	Anisotropic	Anisotropic
Extinction coefficients ($\times 10^{-3}$)	0.10(1), 0.28(1), 1.23(4), 0.04(1), -0.06(3), -0.04(6)	0.11(1), 0.07(4), 1.27(4), 0.18(3), 0.27(2), 0.03(4)	0.16(1), 0.35(4), 1.43(3), 0.00(3), 0.27(2), 0.22(4)

structure refinement. Lattice parameters were taken from the neutron powder diffraction data and fixed. Other starting parameters for the least squares refinements were obtained from Tamada *et al.* [70]. Positional parameters and anisotropic ADPs were refined in combination with an overall scale factor. Extinction effects were corrected according to an anisotropic model, as implemented in the program FULLPROF [73]. The results of the refinements are shown in figure 3.3 and table 3.2. The detailed structural parameters of Co_2SiO_4 at 300 K are presented in tables 3.3 and 3.4. Selected interatomic distances and angles in Co_2SiO_4 are summarized in table 3.5.

Our refined positional parameters at room temperature are in very good agreement [$< 2\sigma(I)$] with data from literature by Ghose & Wan [67], Miyake *et al.* [68], Morimoto *et al.* [69] and Tamada *et al.* [70]. For instance, a comparison of the Co–O distances at room temperature is shown in figure 3.4.

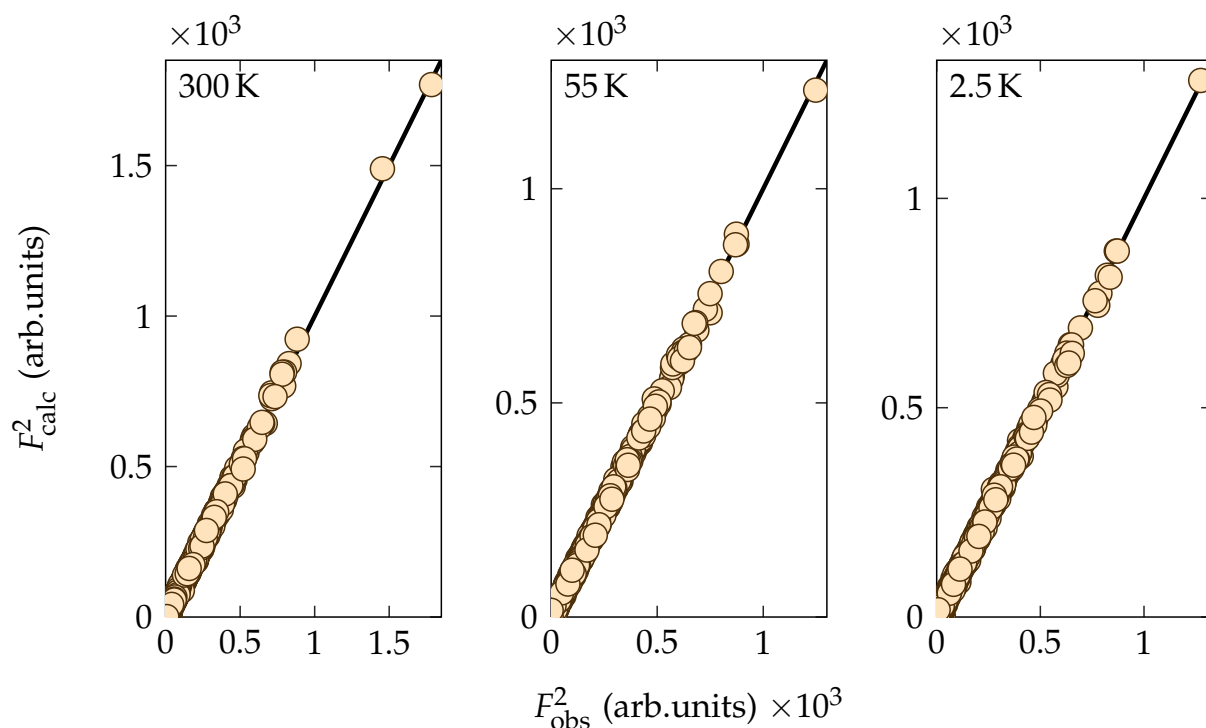


Figure 3.3. Results of the refinement for Co_2SiO_4 from our single-crystal neutron diffraction data at different temperatures. The experimental F^2 values (F^2_{obs}) are plotted against the calculated ones (F^2_{calc}).

Table 3.3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$) of Co_2SiO_4 from single-crystal neutron diffraction at different temperatures. Space group: $Pnma$. Atomic positions: Co1—4a(0, 0, 0); Co2—4c($x, \frac{1}{4}, z$); Si—4c($x, \frac{1}{4}, z$); O1—4c($x, \frac{1}{4}, z$); O2—4c($x, \frac{1}{4}, z$) and O3—8d(x, y, z).

	300 K	55 K	2.5 K
Co1			
x	0	0	0
y	0	0	0
z	0	0	0
$U_{\text{iso}}/U_{\text{eq}}$	0.00507(17)	0.00173(19)	0.00176(19)
Co2			
x	0.27645(7)	0.27603 (6)	0.27597(6)
y	0.25	0.25	0.25
z	0.99143(15)	0.99136(14)	0.99115(12)
$U_{\text{iso}}/U_{\text{eq}}$	0.00512(18)	0.00174(19)	0.00170(20)
Si			
x	0.09491(4)	0.09489(4)	0.09479(4)
y	0.25	0.25	0.25
z	0.42821(8)	0.42824(8)	0.42838(7)
$U_{\text{iso}}/U_{\text{eq}}$	0.00362(10)	0.00149(12)	0.00157(12)
O1			
x	0.09205(3)	0.09184(3)	0.09180(3)
y	0.25	0.25	0.25
z	0.76712(6)	0.76739(6)	0.76731(5)
$U_{\text{iso}}/U_{\text{eq}}$	0.00518(8)	0.00281(9)	0.00282(9)
O2			
x	0.44872(3)	0.44849(2)	0.44854(2)
y	0.25	0.25	0.25
z	0.21560(6)	0.21578(6)	0.21605(6)
$U_{\text{iso}}/U_{\text{eq}}$	0.00531(8)	0.00269(9)	0.00267(9)
O3			
x	0.16419(2)	0.16428(2)	0.16438(2)
y	0.03363(3)	0.03324(4)	0.03313(4)
z	0.28171(4)	0.28116(4)	0.28129(4)
$U_{\text{iso}}/U_{\text{eq}}$	0.00594(6)	0.00294(7)	0.00295(6)

$U_{\text{iso}}/U_{\text{eq}} = \frac{1}{3} (U^{11} + U^{22} + U^{33})$, where U^{ij} is an element of a mean-square displacement tensor (see table 3.4).

Table 3.4. Anisotropic atomic displacement parameters ($\text{\AA}^2$) of Co_2SiO_4 from single-crystal neutron diffraction at different temperatures.

		300 K	55 K	2.5 K
Co1	U^{11}	0.00657(18)	0.00245(16)	0.00235(14)
	U^{22}	0.00443(18)	0.00110(30)	0.00130(30)
	U^{33}	0.00420(17)	0.00165(15)	0.00161(13)
	U^{12}	−0.00098(16)	−0.00016(11)	−0.00022(14)
	U^{13}	−0.00018(15)	0.00004 (12)	0.00005(12)
	U^{23}	−0.00058(15)	−0.00010(14)	−0.00009(15)
Co2	U^{11}	0.00445(17)	0.00171(16)	0.00234(15)
	U^{22}	0.00567(18)	0.00160(20)	0.00080(30)
	U^{33}	0.00525(18)	0.00188(15)	0.00204(14)
	U^{12}	0	0	0
	U^{13}	0.00029(15)	−0.00018(12)	0.00004(13)
	U^{23}	0	0	0
Si	U^{11}	0.00404(11)	0.00182(10)	0.00199(9)
	U^{22}	0.00415(11)	0.00111(15)	0.00123(18)
	U^{33}	0.00265(10)	0.00153(10)	0.00149(9)
	U^{12}	0	0	0
	U^{13}	0.00006(9)	−0.00002(7)	0.00012(7)
	U^{23}	0	0	0
O1	U^{11}	0.00661(8)	0.00346(8)	0.00355(7)
	U^{22}	0.00588(8)	0.00295(13)	0.00291(15)
	U^{33}	0.00304(8)	0.00201(8)	0.00201(7)
	U^{12}	0	0	0
	U^{13}	0.00014(7)	0.00005(6)	0.00002(6)
	U^{23}	0	0	0
O2	U^{11}	0.00435(8)	0.00223(8)	0.00232(7)
	U^{22}	0.00661(8)	0.00289(12)	0.00278(15)
	U^{33}	0.00497(8)	0.00293(8)	0.00291(7)
	U^{12}	0	0	0
	U^{13}	−0.00005(7)	0.00006(6)	0.00003(6)
	U^{23}	0	0	0
O3	U^{11}	0.00727(6)	0.00352(6)	0.00363(5)
	U^{22}	0.00542(6)	0.00222(9)	0.00215(10)
	U^{33}	0.00515(6)	0.00308(5)	0.00306(4)
	U^{12}	0.00191(5)	0.00071(4)	0.00076(5)
	U^{13}	0.00033(5)	0.00017(5)	0.00006(5)
	U^{23}	−0.00027(5)	−0.00014(5)	−0.00019(5)

Table 3.5. Interatomic distances (Å) and angles (°) of Co₂SiO₄ from single-crystal neutron diffraction at different temperatures.

	300 K	55 K	2.5 K
<i>Co1 Octahedron</i>			
Co1–O1 ⁱ , Co1–O1 ⁱⁱ	2.0955(2)	2.0907(2)	2.0901(2)
Co1–O2 ⁱⁱⁱ , Co1–O2 ^{iv}	2.0929(2)	2.0896(2)	2.0885(2)
Co1–O3, Co1–O3 ^v	2.1715(2)	2.1678(1)	2.1691(2)
⟨Co1–O⟩	2.1200	2.1160	2.1159
O1 ⁱ –Co1–O1 ⁱⁱ	180.00	180.00	180.00
O1 ⁱ –Co1–O2 ⁱⁱⁱ , O1 ⁱⁱ –Co1–O2 ^{iv}	86.90(2)	86.96(2)	86.96(2)
O1 ⁱ –Co1–O2 ^{iv} , O1 ⁱⁱ –Co1–O2 ⁱⁱⁱ	93.10(1)	93.04(1)	93.05(1)
O1 ⁱ –Co1–O3, O1 ⁱⁱ –Co1–O3 ^v	84.87(1)	84.92(1)	84.95(1)
O1 ⁱ –Co1–O3 ^v , O1 ⁱⁱ –Co1–O3	95.13(2)	95.10(1)	95.05(2)
O2 ⁱⁱⁱ –Co1–O2 ^{iv}	180.00	180.00	180.00
O2 ⁱⁱⁱ –Co1–O3, O2 ^{iv} –Co1–O3 ^v	74.15(1)	74.29(1)	74.30(1)
O2 ⁱⁱⁱ –Co1–O3 ^v , O2 ^{iv} –Co1–O3	105.85(2)	105.72(1)	105.70(2)
O3–Co1–O3	180.00	180.00	180.00
<i>Co2 Octahedron</i>			
Co2–O1	2.1813(8)	2.1759(6)	2.1756(7)
Co2–O2 ^{vi}	2.0731(8)	2.0731(6)	2.0751(6)
Co2–O3 ^{vii} , Co2–O3 ^{vi}	2.2250(6)	2.2193(5)	2.2194(5)
Co2–O3 ^{viii} , Co2–O3 ^{ix}	2.0684(4)	2.0647(4)	2.0629(4)
⟨Co2–O⟩	2.1402	2.1361	2.1359
O1–Co2–O2 ^{vi}	178.32(4)	178.30(3)	178.26(3)
O1–Co2–O3 ^{vii} , O1–Co2–O3 ^{vi}	81.62(3)	81.71(2)	81.76(2)
O1–Co2–O3 ^{viii} , O1–Co2–O3 ^{ix}	91.09(3)	91.13(2)	91.15(2)
O2 ^{vi} –Co2–O3 ^{vii} , O2 ^{vi} –Co2–O3 ^{vi}	97.02(3)	96.92(2)	96.83(2)
O2 ^{vi} –Co2–O3 ^{viii} , O2 ^{vi} –Co2–O3 ^{ix}	89.87(3)	89.84(2)	89.85(2)
O3 ^{viii} –Co2–O3 ^{vi} , O3 ^{ix} –Co2–O3 ^{vii}	88.60(2)	88.69(2)	88.67(2)
O3 ^{viii} –Co2–O3 ^{vii} , O3 ^{ix} –Co2–O3 ^{vi}	159.48(2)	159.75(2)	159.76(2)
O3 ^{vii} –Co2–O3 ^{vi}	71.43(2)	71.60(2)	71.63(2)
O3 ^{viii} –Co2–O3 ^{ix}	110.80(2)	110.49(2)	110.52(2)
<i>Si Tetrahedron</i>			
Si–O1	1.6208(5)	1.6207(4)	1.6199(4)
Si–O2 ⁱⁱⁱ	1.6554(5)	1.6555(4)	1.6551(5)
Si–O3, Si–O3 ^x	1.6392(3)	1.6397(3)	1.6409(3)
⟨Si–O3⟩	1.6387	1.6389	1.6392
O1–Si–O2 ⁱⁱⁱ	113.50(3)	113.47(3)	113.56(3)
O1–Si–O3, O1–Si–O3 ^x	115.80(3)	115.90(2)	115.88(2)
O2 ⁱⁱⁱ –Si–O3, O2 ⁱⁱⁱ –Si–O3 ^x	102.62(3)	102.58(2)	102.59(2)
O3–Si–O3 ^x	104.81(2)	104.69(2)	104.62(2)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, y - \frac{1}{2}, -z + 1$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (v) $-x, -y, -z$; (vi) $x, y, z + 1$; (vii) $x, -y + \frac{1}{2}, z + 1$; (viii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (ix) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (x) $x, -y + \frac{1}{2}, z$.

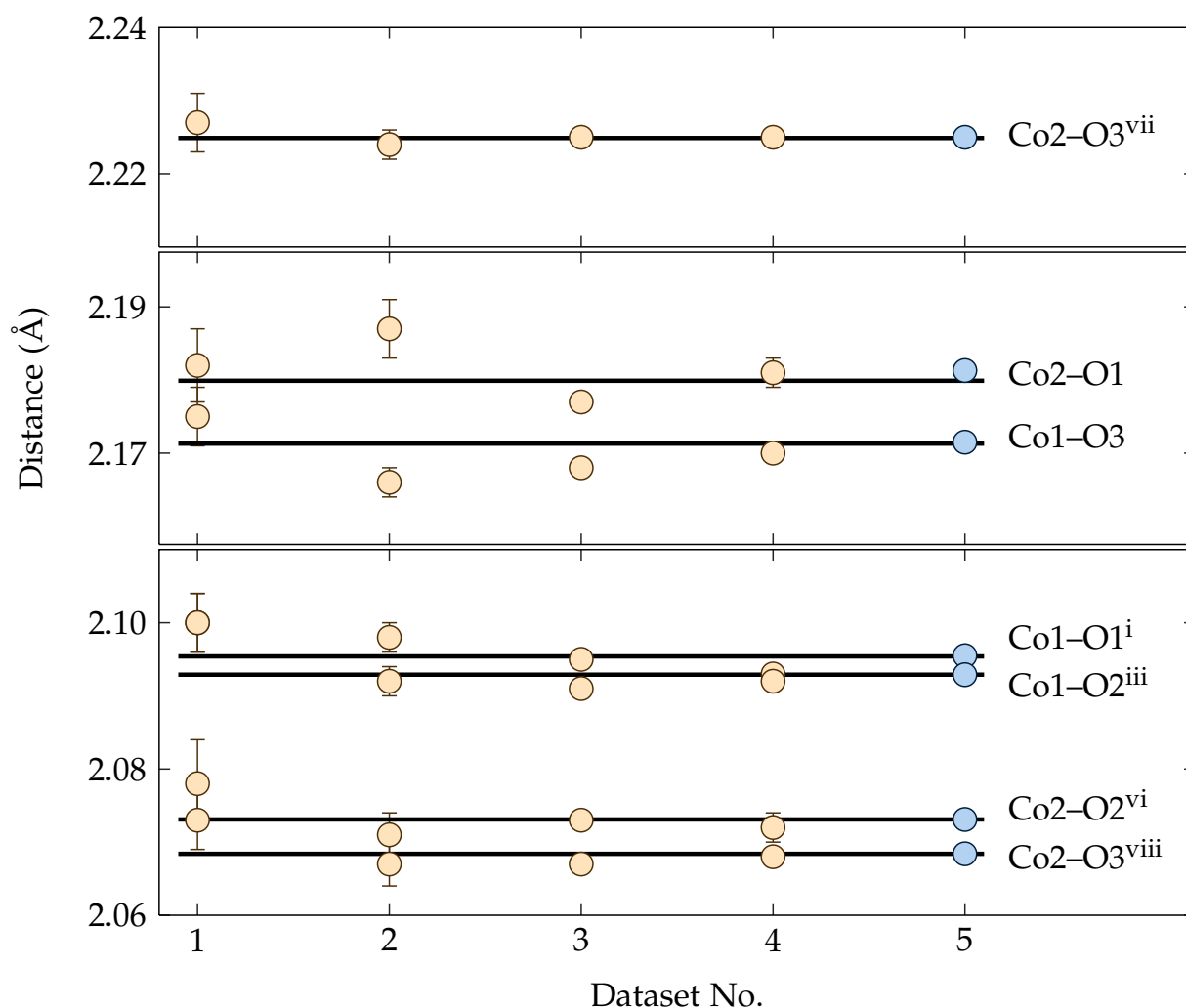


Figure 3.4. Comparison of the Co–O distances from different measurements at room temperature. Dataset No.: 1 corresponds to [69], 2 — [67], 3 — [70], 4 — [68], 5 — our single-crystal neutron diffraction data. Error bars are smaller than the symbols if not visible. Solid lines represent weighted averaged values calculated for all measurements. See table 3.5 for the symmetry codes.

It is worth noting that Bragg intensities contain information on the electron-density distribution (X-ray diffraction) or the nuclear densities (neutron diffraction) smeared by dynamic and static displacements. In many combined X-ray and neutron diffraction studies it has been shown that for non-H atoms satisfactory correspondence between the positional parameters determined by these two techniques can be achieved, see, for instance, our example in figure 3.4.

On the contrary, the agreement between the ADPs determined in parallel X-ray and neutron experiments is very often less satisfying because of numerous systematic errors. For precise work, even in the case of neutrons, measurement of many equivalent reflections with a crystal of good quality is necessary. See, for instance, the $\sin \theta / \lambda$ dependence of the displacement parameters in figure 3.5 determined from our single-crystal neutron diffraction measurements at room temperature.

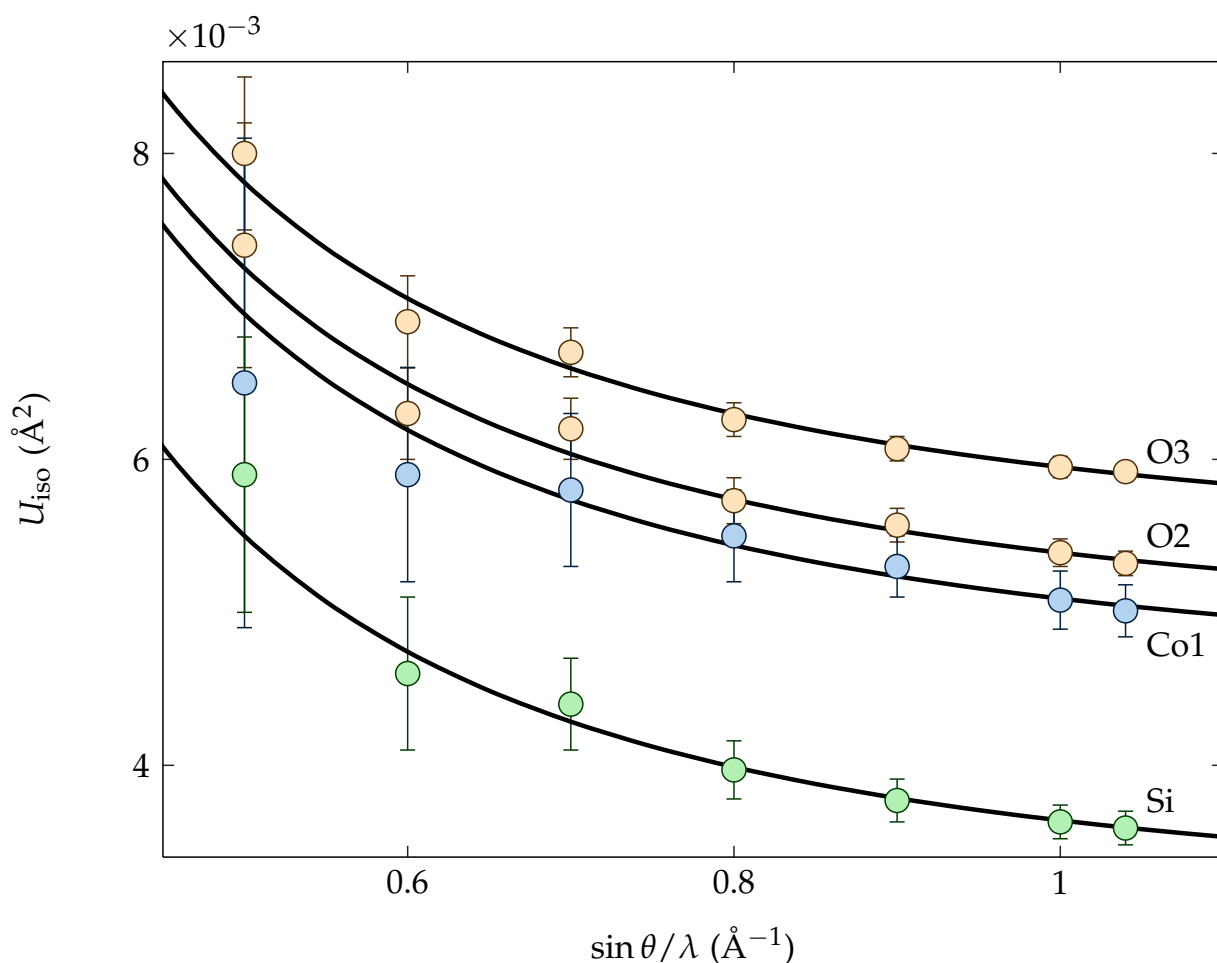


Figure 3.5. An example of accuracy of the refined isotropic ADPs for Co_2SiO_4 as a function of measured $\sin \Theta / \lambda$ range from our single-crystal neutron diffraction data at room temperature. The fits are used as guides to the eye.

Chapter 4

Structural variations with temperature

4.1. Lattice parameters

Figure 4.1 shows the variation of the lattice parameters and the unit-cell volume of Co_2SiO_4 with temperature over the complete temperature range covered in our X-ray powder diffraction experiments (15 K–300 K). The Rietveld fit of the synchrotron powder diffraction data at 35 K is shown in figure 4.2 as an illustration. Refinement results for selected temperatures are summarized in table 3.1. The lattice parameters of Co_2SiO_4 exhibit an anomaly at ~ 50 K (figure 4.1). Neither splitting of reflections due to symmetry changes nor broadening were observed in the powder diffraction patterns in the temperature range from 300 K down to 15 K; the patterns were successfully indexed according to the space group $Pnma$. Note that both the laboratory and synchrotron X-ray powder diffraction data are in perfect agreement, without any adjustment.

In order to parameterize with high accuracy the cell parameters of Co_2SiO_4 for subsequent thermal expansion calculations we performed the additional neutron powder diffraction measurements in the extended

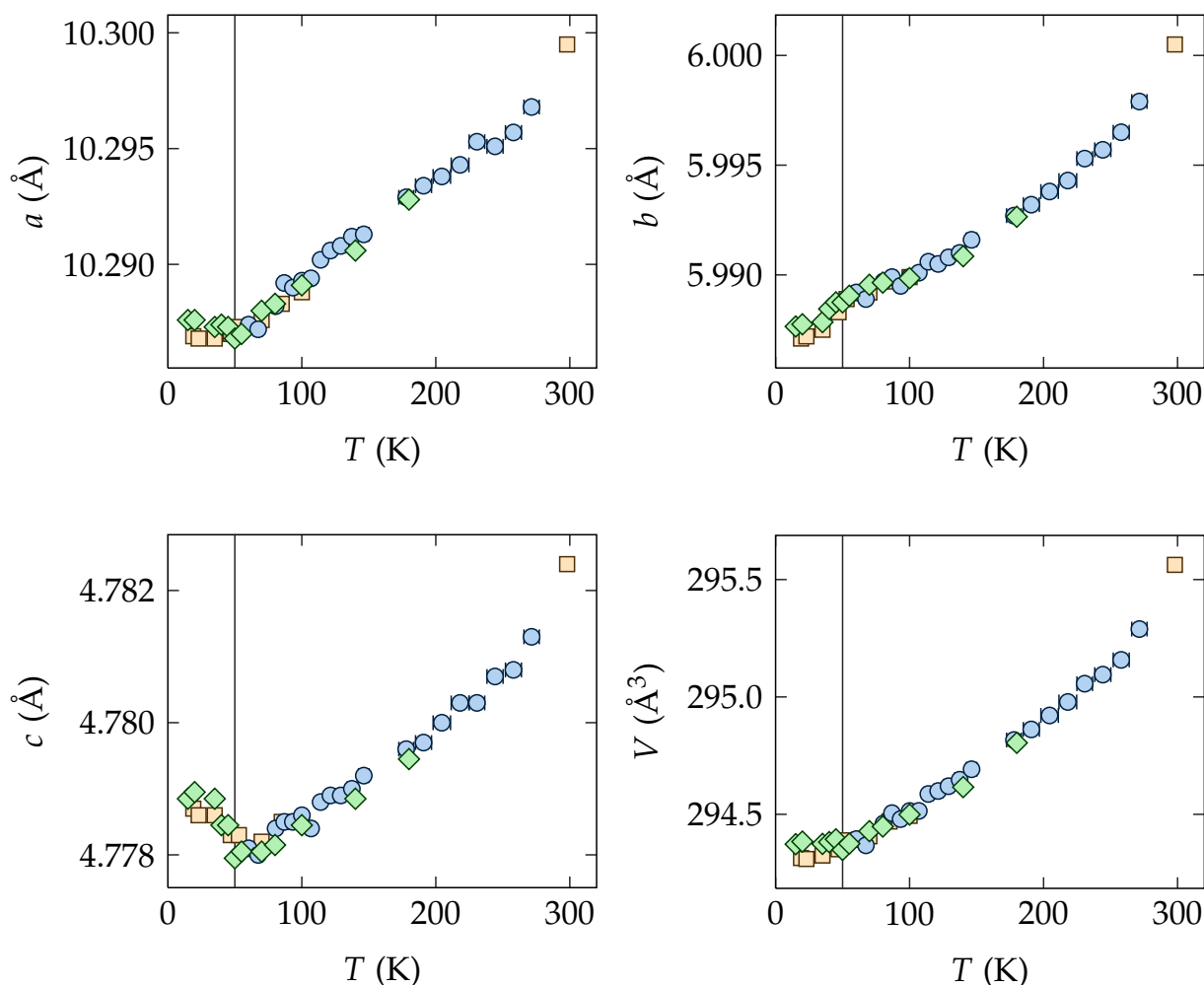


Figure 4.1. Temperature dependence of the lattice parameters and the cell volume of Co_2SiO_4 . Symbols represent the results of our laboratory ($\square$) as well as synchrotron X-ray diffraction measurements. In the last case, the results of measurements during the cooling ($\circ$) and heating ($\diamond$) procedures are shown. Error bars from the refinement are smaller than the symbols.

temperature range between 5 K and 500 K. The refined lattice parameters and the unit cell volume of Co_2SiO_4 as a function of temperature are shown in figure 4.3. These data are in perfect agreement with the results of both the laboratory and synchrotron X-ray powder diffraction measurements (see figure 4.1). Figure 4.4 shows a typical neutron powder diffraction pattern of Co_2SiO_4 measured at room temperature along with the results of the Rietveld refinement of the orthorhombic $Pnma$ crystal structure.

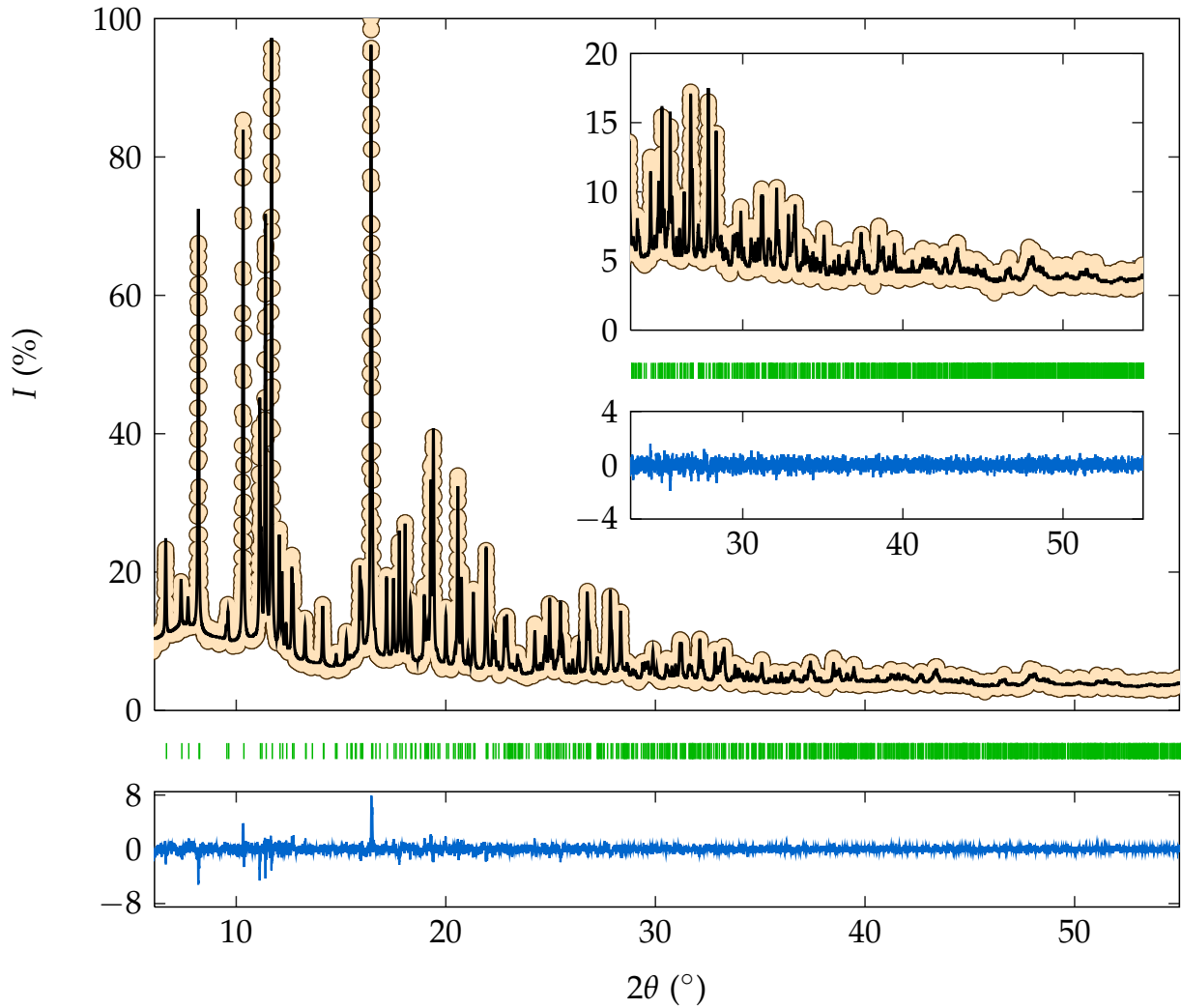


Figure 4.2. High-resolution synchrotron powder diffraction data (○), Rietveld fit (—) and allowed Bragg reflections (|) for Co_2SiO_4 at 35 K. The lower trace (—) is the difference, $I_{\text{obs}} - I_{\text{calc}}$, on the same scale. A magnified view in the 2θ range from 23° to 55° is inserted.

As was already found in our X-ray powder diffraction experiments (figure 4.1), the lattice parameters of Co_2SiO_4 exhibit an anomaly at about 50 K (figure 4.3). The neutron patterns at all temperatures were successfully indexed according to the space group $Pnma$ in agreement with former X-ray diffraction data. Furthermore, our single-crystal neutron data did not show any reflections violating the $Pnma$ symmetry. Thus, we conclude that the $Pnma$ symmetry is retained in the temperature range from 5 K up to 500 K. The anomaly in the anisotropic thermal expansion can therefore be associated with the magnetic phase transition

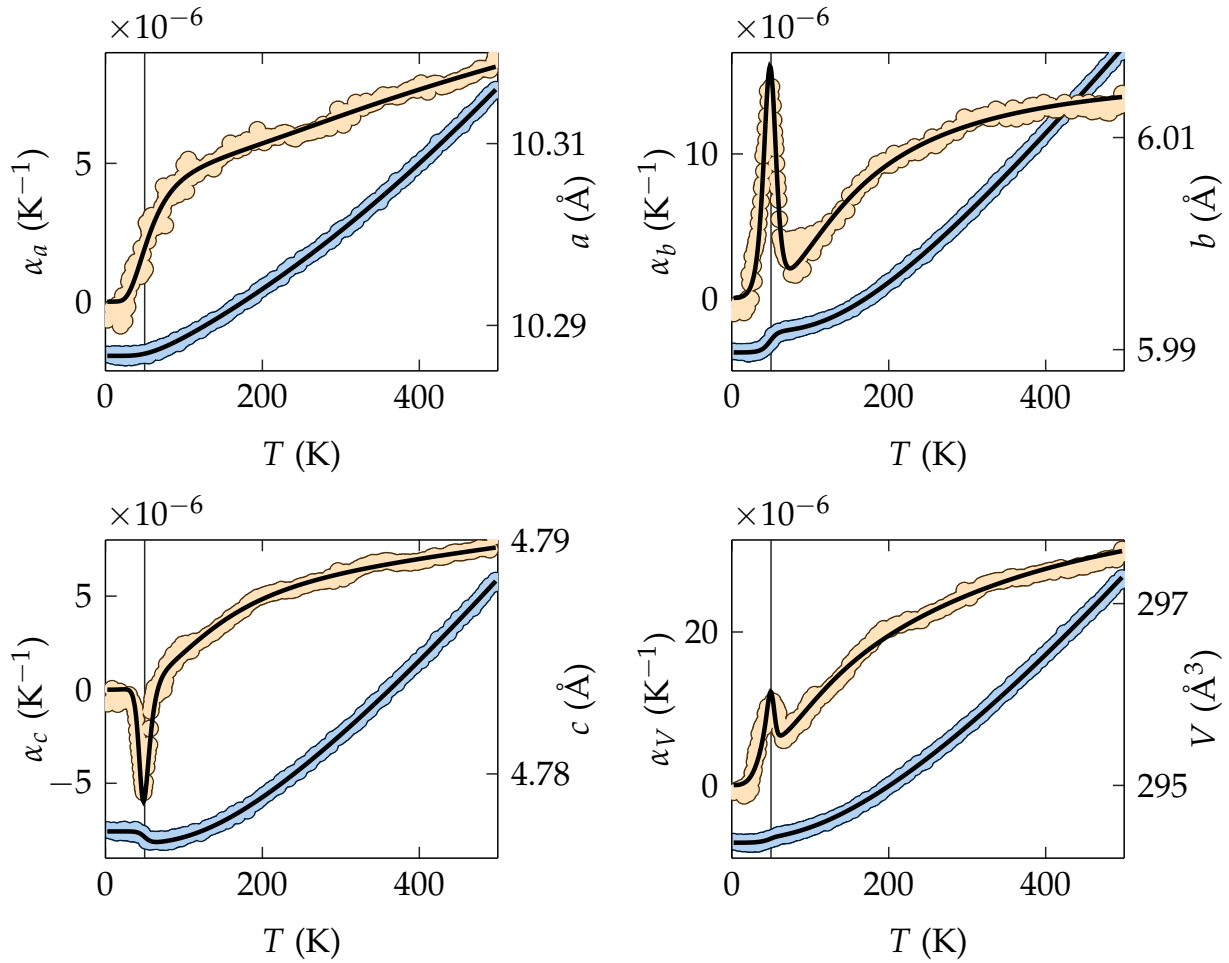


Figure 4.3. Temperature dependencies of the lattice parameters and the cell volume of Co_2SiO_4 (●; right Y-scales) as well as the thermal expansion coefficients (○; left Y-scales) according to the powder neutron diffraction measurements. The points for the expansion were obtained by numerical differentiation of the unit-cell parameters (equation 4.1). Error bars for the lattice parameters and the cell volume are smaller than the symbols. The solid curves (—) represent a fit (see details in the text).

taking place at 50 K [23, 24]. The lattice parameters as well as the unit cell volume show variations at this temperature which can be related to magnetostriction effects. An abrupt elongation and contraction below approximately 50 K were observed along the c and b axes, respectively, whereas the lattice parameter a remains constant in the range between 5 K and 50 K (see figure 4.3). Anomalous contraction of the cell volume observed below 50 K (see figure 4.3) indicates the domination of the b axis in anomalous thermal expansion of Co_2SiO_4 at low temperature.

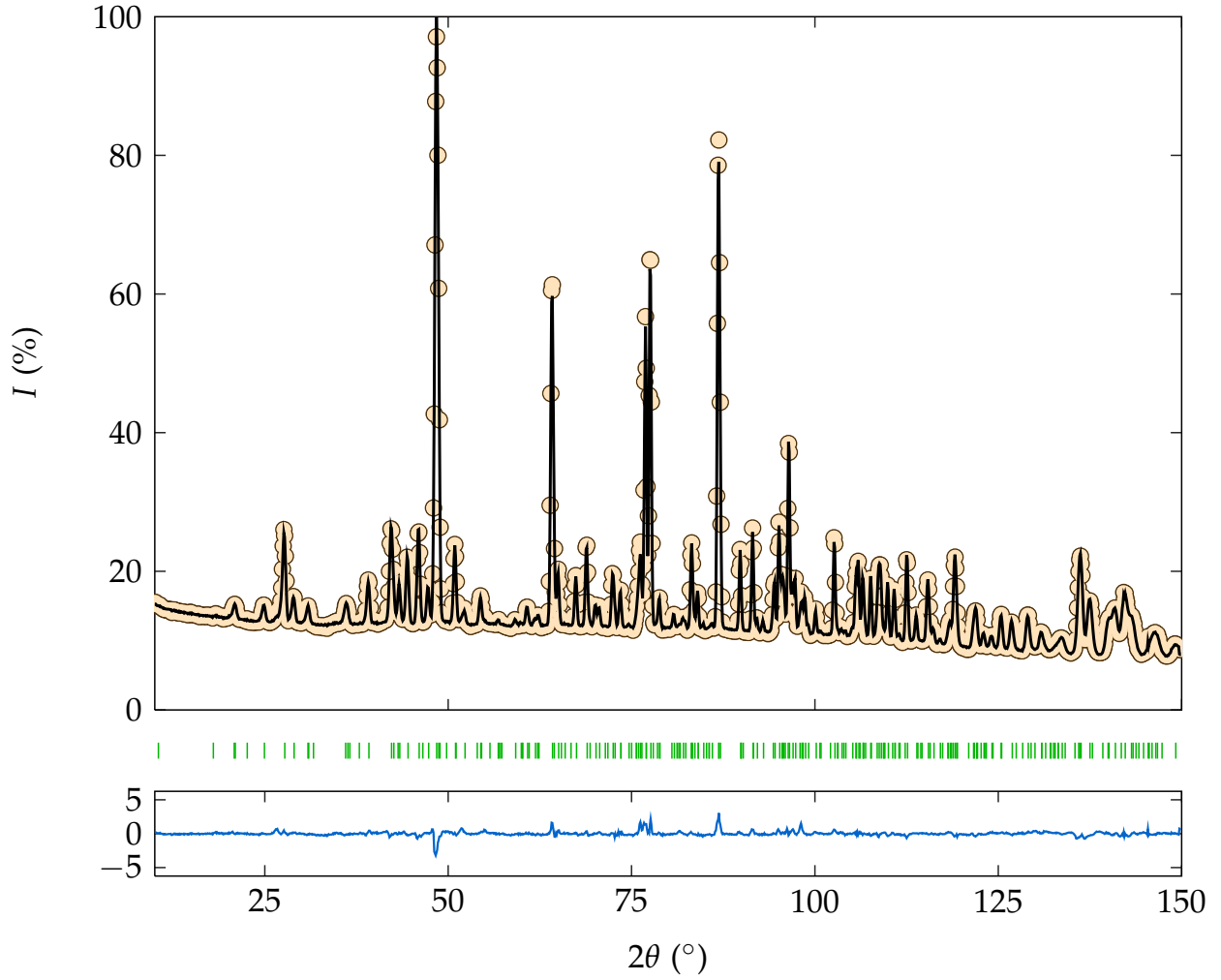


Figure 4.4. Neutron powder diffraction pattern (○), Rietveld fit (—) and allowed Bragg reflections (|) for Co_2SiO_4 at room temperature. The lower trace (—) is the difference, $I_{\text{obs}} - I_{\text{calc}}$, on the same scale.

Thermal expansion curves (presented in figure 4.3) were calculated by numerical derivation

$$\alpha_l(T) = \frac{1}{l} \frac{\partial l}{\partial T}, \quad (4.1)$$

where l denotes the lattice parameters (a , b , c) and the unit cell volume (V), T is the temperature, and $\alpha_l(T)$ are the linear thermal expansion coefficients (TEC) in the a , b and c directions for $l = a$, b and c , or volumetric thermal expansion coefficient for $l = V$, respectively.

As a consequence of equation 4.1, $l(T)$ is related to TEC $\alpha_l(T)$ as

$$l(T) = l(T_0) \exp \left[\int_{T_0}^T \alpha_l(x) dx \right], \quad (4.2)$$

where $l(T)$ denotes the lattice parameters and the unit cell volume at a chosen temperature T and T_0 is the lowest reached temperature.

4.2. From thermal expansion to specific heat

In the case of the volumetric thermal expansion, a physically meaningful interpretation of the expansion curve and, therefore, of the unit cell volume can be obtained in quasiharmonic approximation via the Grüneisen relation

$$\alpha_V = \frac{\gamma}{B_S V} C_P, \quad (4.3)$$

where γ is the Grüneisen parameter, B_S is the adiabatic bulk modulus and C_P is the specific heat at constant pressure.

Usually γ , B_S and V display modest changes with temperature and the volumetric thermal expansion coefficient α_V varies with temperature similar to the specific heat. Assuming the parameter $\frac{\gamma}{B_S V}$ to be independent of temperature, the α_V may be calculated using the fitted C_P . A direct calculation of $\frac{\gamma}{B_S V}$ through the experimentally obtained C_P and numerically differentiated TEC α_V (via equation 4.1) shows the ratio $\frac{C_P}{\alpha_V} = \frac{\gamma}{B_S V}$ to be almost constant. The maximal temperature deviation of $\frac{\gamma}{B_S V}$ from the mean value does not exceed 5% in the temperature range from 50 K up to 500 K. The abrupt change of both α_V and C_P near the magnetic phase transition at 50 K as well as the small absolute values of these parameters at low temperatures lead to an increase of the oscillation and uncertainty of $\frac{\gamma}{B_S V}$ with respect to its mean value. The solid curves in figure 4.3 represent the best fit of both the experimental lattice parameters and the thermal expansion to the model described below in detail.

4.2.1. Specific heat model

The specific heat of Co_2SiO_4 was measured at the Physics Department (E21, Technical University of Munich, Garching, Germany) using the

heat capacity option of a Physical Property Measurement System (PPMS, Quantum Design, USA) based on a relaxation technique. Data were taken in zero magnetic field and in the temperature range from 5 K to 300 K. For these measurements the sample was a plate of 0.3 mm thickness and a 11.5 mg weight obtained from the as-grown single crystal. The absolute accuracy of the data was better than 1% over the entire temperature range.

Thus obtained specific heat C_P of Co-olivine is plotted versus temperature in figure 4.5. The C_P of Co_2SiO_4 is characterized by the classical picture of the lambda transition around T_N : with increasing temperature the specific heat rises gradually on the low-temperature

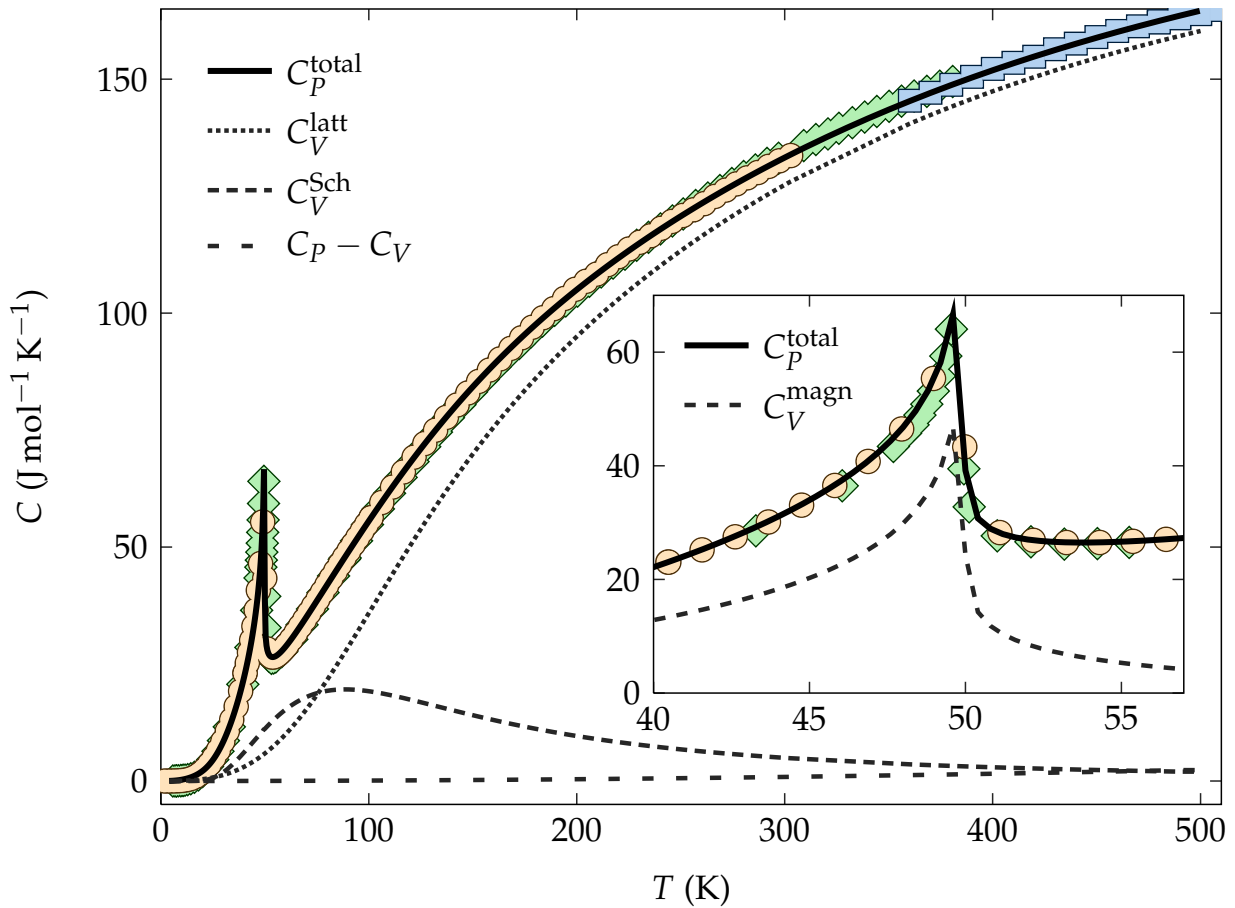


Figure 4.5. The experimental specific heat of Co_2SiO_4 as a function of temperature according to our (○) and literature data (◇ — [28], □ — [80]). The lines are specific heat calculated from numerical fits as described in the text. The inset shows an expanded view of the paramagnetic-antiferromagnetic transition region.

side of the transition and falls sharply on the high-temperature side. In figure 4.5 our measured specific heat [77] is shown together with literature data. It is noteworthy that the Co-olivine specific heat reported by Robie *et al.* [28] for the temperatures from 5 K to 380 K is in very good agreement with our measurements [77] over the common temperature range. We have also combined our specific heat results for the range from 5 K to 300 K with the data from [80] between 360 K and 500 K to complete the specific heat for higher temperatures.

The specific heat of a crystalline substance consists of a number of contributions (see, e.g., [81]). In the case of Co_2SiO_4 , the measured overall specific heat was fitted as the superposition of

$$C_P = C_P^{\text{latt}} + C_P^{\text{Sch}} + C_P^{\text{magn}}, \quad (4.4)$$

where C_P^{latt} is a lattice vibrational contribution, C_P^{Sch} is a Schottky contribution, and C_P^{magn} is a magnetic contribution.

One may extend equation 4.4 to include more components, such as contributions from the free electrons, anharmonic effects, crystal defects, etc. However, these contributions are small in this particular case and will not be taken into account. For example, the contribution from the free electrons is negligible because the Co-olivine is an insulator [82]. The anharmonic effects may play a role only at temperatures higher than those covered in the experiment. The defect contribution is not taken into account due to the high quality of the single crystals used in the measurements.

Determination of C_V^{latt}

The lattice contribution to the specific heat was determined using a sum of Debye (D) and Einstein (E) functions with the respective coefficients k_D and k_E :

$$\frac{C_V^{\text{latt}}}{R} = k_D D\left(\frac{\Theta_D}{T}\right) + k_E E\left(\frac{\Theta_E}{T}\right), \quad (4.5)$$

where R is the universal gas constant, Θ_D and Θ_E are Debye and Einstein temperatures, respectively.

D and E are described via following equations:

$$D\left(\frac{\Theta_D}{T}\right) = 9 \frac{1}{(\Theta_D/T)^3} \int_0^{\Theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx,$$

$$E\left(\frac{\Theta_E}{T}\right) = 3 (\Theta_E/T)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}.$$

The characteristic temperatures Θ_D , Θ_E and coefficients k_D , k_E were determined by fitting the model to the experimental data. Table 4.1 summarizes the fitted parameters for equation 4.4. Hereafter, for a rough estimate of how well the model fits the data we use the value R according to equation:

$$R = 1 - \frac{\sum(I_{\text{fit}} - I_{\text{obs}})^2}{\sum(I_{\text{obs}} - \langle I_{\text{obs}} \rangle)^2}, \quad (4.6)$$

where I_{obs} are the measured values and I_{fit} are the calculated values from the fit.

Table 4.1. Coefficients from the fit of the experimental specific heat of Co_2SiO_4 to equation 4.4.

Parameter	Coefficient
k_D	0.776 ± 0.014
Θ_D (K)	570 ± 17
k_E	0.311 ± 0.009
Θ_E (K)	1250 ± 28
k_S	0.615 ± 0.058
Θ_S (K)	84 ± 2
K^-	1.337 ± 0.019
m	2.958 ± 0.093
K^+	0.370 ± 0.023
n	3.263 ± 0.947
A_1 ($\text{J mol}^{-1} \text{K}^{-2}$) $\times 10^{-6}$	-10.0 ± 0.2
A_2 ($\text{J mol}^{-1} \text{K}^{-3}$) $\times 10^{-6}$	7.7 ± 0.2
R^*	0.999987

* according to equation 4.6.

For the Debye temperature we obtained from our specific heat fit [77] a value of $\Theta_D = 570 \pm 17$ K, which is rather close to 551 K calculated from the room temperature elastic constants by Sumino [83].

Determination of C_V^{Sch}

For materials containing cobalt ions, e.g., GeCo_2O_4 , an additional contribution to the specific heat was observed near 100 K [84]. This phenomenon has been attributed to a Schottky anomaly arising from the thermal population of the Co lowest lying excited states due to the spin-orbit coupling.

To interpret our data, we consider a scheme that has been used to understand the properties of fayalite, Fe_2SiO_4 [85]. In octahedral coordination with a crystal field of cubic symmetry the $3d$ -orbitals of a transition metal (Co in our case) split into a low lying t_{2g} triplet and a higher lying e_g doublet. The magnitude of the splitting in olivines is rather large ($\sim 9000 \text{ cm}^{-1}$). Both e_g and t_{2g} level further split due to the low symmetry of the $M1$ and $M2$ sites. At the end, spin-orbit coupling may further split the ground state. As it was assumed in [85] the details of the ground-state splitting within this spin-orbit sub-manifold are different for the $M1$ and $M2$ sites, not only because the relative strength and symmetry of the axial fields are different, but also because the exchange splitting depends on the details of the moment coupling and geometry.

In the case of fayalite and tephroite (Mn_2SiO_4) a shoulder in the specific heat was observed below the Néel temperature. It was suggested that the origin of this shoulder is a thermal population of the spin-orbit manifold on the $M1$ site [85]. The shoulder in tephroite occurs at a slightly lower temperature than that in fayalite (20 K). This was explained in terms of a narrower spin-orbit manifold in Mn_2SiO_4 caused by the smaller spin-orbit coupling parameter of the Mn^{2+} ion ($\lambda \sim 60 \text{ cm}^{-1}$) as compared with that of Fe^{2+} ($\lambda \sim 100 \text{ cm}^{-1}$) [86]. The Co^{2+} and Ni^{2+} ions have much larger spin-orbit coupling parameters ($\lambda \sim 170$ and 630 cm^{-1} ,

respectively) [86]. These values are sufficiently large that essentially no thermal excitation within the spin-orbit manifold occurs in cobalt olivine up to the Néel temperature. So the temperature of the Schottky anomaly is expected to be above 50 K for Co-olivine and much higher in the case of Ni-olivine.

Dachs *et al.* [87] demonstrated that the Schottky contribution C_V^{Sch} to the specific heat of fayalite can be determined by the expression

$$\frac{C_V^{\text{Sch}}}{R} = (2.4 \Theta_S / T)^2 \frac{e^{-2.4 \Theta_S / T}}{(1 + e^{-2.4 \Theta_S / T})^2}, \quad (4.7)$$

where Θ_S is the temperature maximum of the Schottky anomaly. Thus we applied equation 4.7 for the case of Co-olivine. Table 4.1 summarizes the fitted parameters.

Determination of C_V^{magn}

The contribution to the specific heat due to the thermal anomaly at the magnetic transition temperature can now be deconvoluted by subtracting of the calculated non-magnetic contribution from the measured specific heat. On the other hand, Inden [88] noted that the magnetic transition in ferromagnetic metals followed a nearly universal behaviour when modelled by

$$\frac{C_V^{\text{magn}}}{R} = \begin{cases} K^- \ln \frac{1 + (T/T_C)^m}{1 - (T/T_C)^m}, & \text{for } T < T_C; \\ K^+ \ln \frac{(T/T_C)^n + 1}{(T/T_C)^n - 1}, & \text{for } T > T_C, \end{cases} \quad (4.8)$$

with parameters K^- , K^+ , m and n . It should be noted that Inden suggested $m = 3$ and $n = 5$. Different values for the exponent are required for the long- (low temperature) and short-range (high temperature) types of order.

The Inden model is being widely applied for thermodynamic calculations involving not only metal alloys, but also (anti)ferromagnetic oxides by fitting of m and n parameters in addition to K^- and K^+ .

Therefore, we used equation 4.8 to describe the λ -peak in the specific heat related to the paramagnetic-antiferromagnetic transition of Co_2SiO_4 . A summary of the fitted parameters is given in table 4.1.

Conversion between C_V and C_P

The above mentioned theoretical analyses are given for C_V instead of measured C_P . The small difference between C_V and C_P can be evaluated according to a thermodynamic relationship

$$C_P - C_V = \frac{T \alpha^2 V}{\kappa},$$

which require information on the coefficient of thermal expansion (α), the volume of the material (V) and the isothermal compressibility (κ). On the other hand, it was shown (see, e.g., [87, 89]) that the difference between C_P and C_V becomes important at elevated temperatures and its approximately quadratic behaviour can be modelled as

$$C_P - C_V = A_1 T + A_2 T^2, \quad (4.9)$$

where A_1 and A_2 are fit parameters.

The values obtained for A_1 and A_2 (see table 4.1) are close to those calculated for forsterite and fayalite [87].

4.2.2. Magnetic contribution to specific heat

Once the expression for C_P and the set of fitted parameters was identified, the global fitting was applied whereby all the terms appearing in equation 4.4 are treated together. Results of the cobalt olivine specific heat regression analysis, based on the data from [80] at temperatures above 360 K and our measurements below 300 K [77], are shown in figure 4.5. An inset to figure 4.5 illustrates in more detail the temperature region containing the paramagnetic-antiferromagnetic transition. The black solid line in figure 4.5 is the best fit of the complete function to the

experimental results. Excellent agreement is demonstrated over the entire temperature range from 5 K to 500 K.

Figure 4.6 plots the magnetic contribution to the specific heat C_p^{magn} together with its fitted curve as a function of temperature. The excess entropy that occurs upon passing from the magnetically ordered state to the paramagnetic state may be determined from equation:

$$\Delta S^{\text{magn}} = \int_0^\infty \frac{C_p^{\text{magn}}}{T} dT. \quad (4.10)$$

The magnetic entropy as a function of temperature is shown in the inset to figure 4.6. The entropy change associated with the magnetic

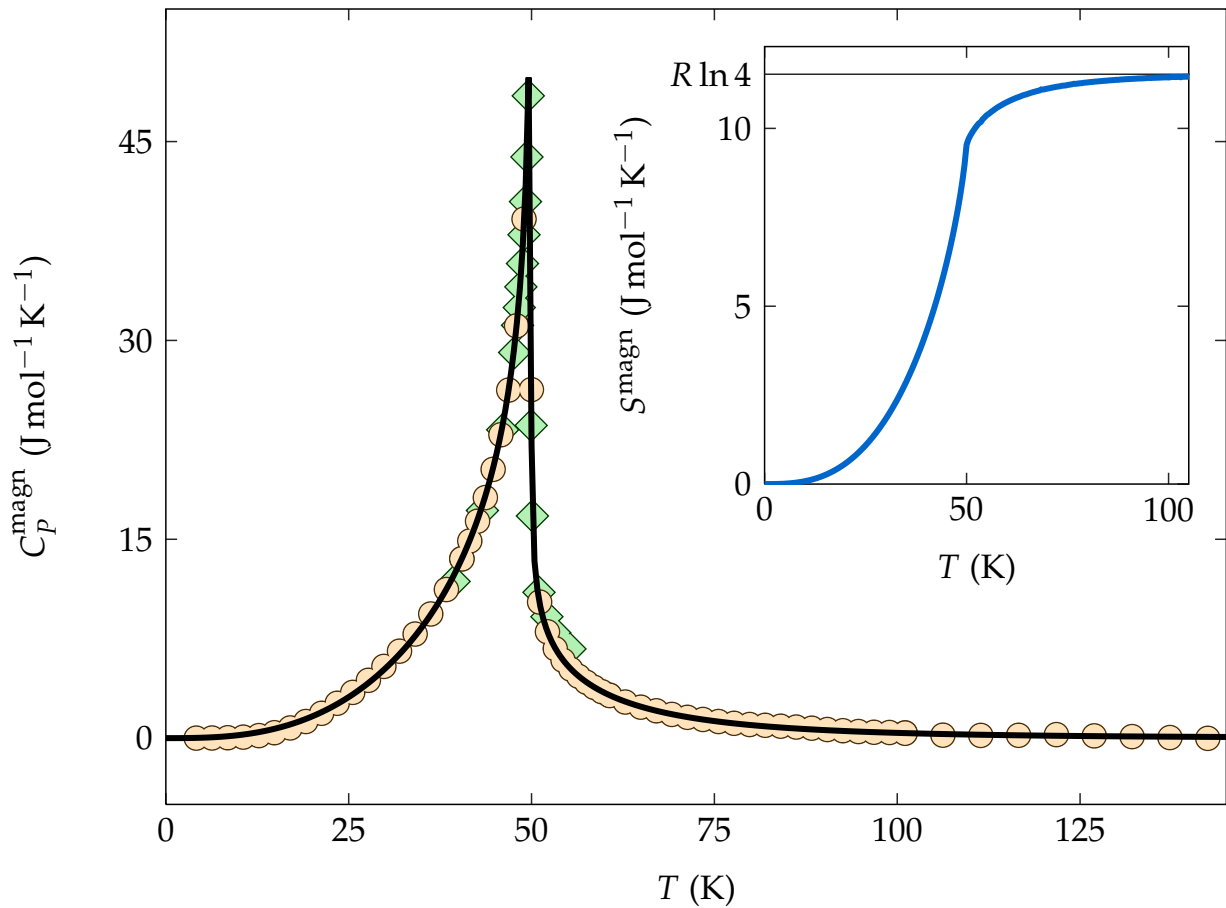


Figure 4.6. Magnetic contribution to the specific heat of Co_2SiO_4 as a function of temperature according to our (○) and literature data (◇ — [28]). The solid curve is the specific heat calculated from a fit as described in the text. The magnetic contribution to the entropy is shown in the inset.

transition, determined from the fitted Inden model (equation 4.8) parameters is equal to $\Delta S^{\text{magn}} = 11.64 \pm 0.09 \approx R \ln 4$ in our case. Another approach was used by Robie *et al.* [28] in order to separate the magnetic contribution of the specific heat from the total measured one. In that paper the authors used both C_P data for Mg_2SiO_4 and $\gamma\text{-Ca}_2\text{SiO}_4$ with the corresponding states model to estimate the lattice entropies of Co_2SiO_4 . That is, Mg_2SiO_4 and $\gamma\text{-Ca}_2\text{SiO}_4$ were used as the references, because they have no magnetic contribution. Using that approach [28], the magnetic entropy of Co_2SiO_4 was found to saturate at $2R \ln 2 = R \ln 4$ for $T \gg T_N$ as well.

Since the magnetic entropy may be defined in terms of the mean atomic moment β (in Bohr magnetons) as

$$\Delta S^{\text{magn}} = R \ln (\beta + 1),$$

we have calculated from our measurements that $\beta \approx 3.1 \mu_B$. This value corresponds to the high-spin state of Co^{2+} (HS, $t_{2g}^5 e_g^2$, $S = 3/2$) and is in agreement with neutron diffraction (section 6.3) and magnetic susceptibility (section 6.2) measurements.

4.3. Back to thermal expansion and unit cell volume

The line (A) in figure 4.7 shows the result obtained from the fitting of equation 4.2 to the unit cell volume data in the temperature region close to the paramagnetic-antiferromagnetic transition. The α_V is defined via the equation 4.3, where the coefficient $\frac{\gamma}{B_S V}$ was treated as a fit parameter, and C_P was obtained from the fitting of equation 4.4 to the specific heat data with only the exception of the magnetic contribution C_p^{magn} . This means that the magnetic contribution C_p^{magn} was considered as zero in the first approximation. The fit to the data is excellent over the temperature range above 50 K.

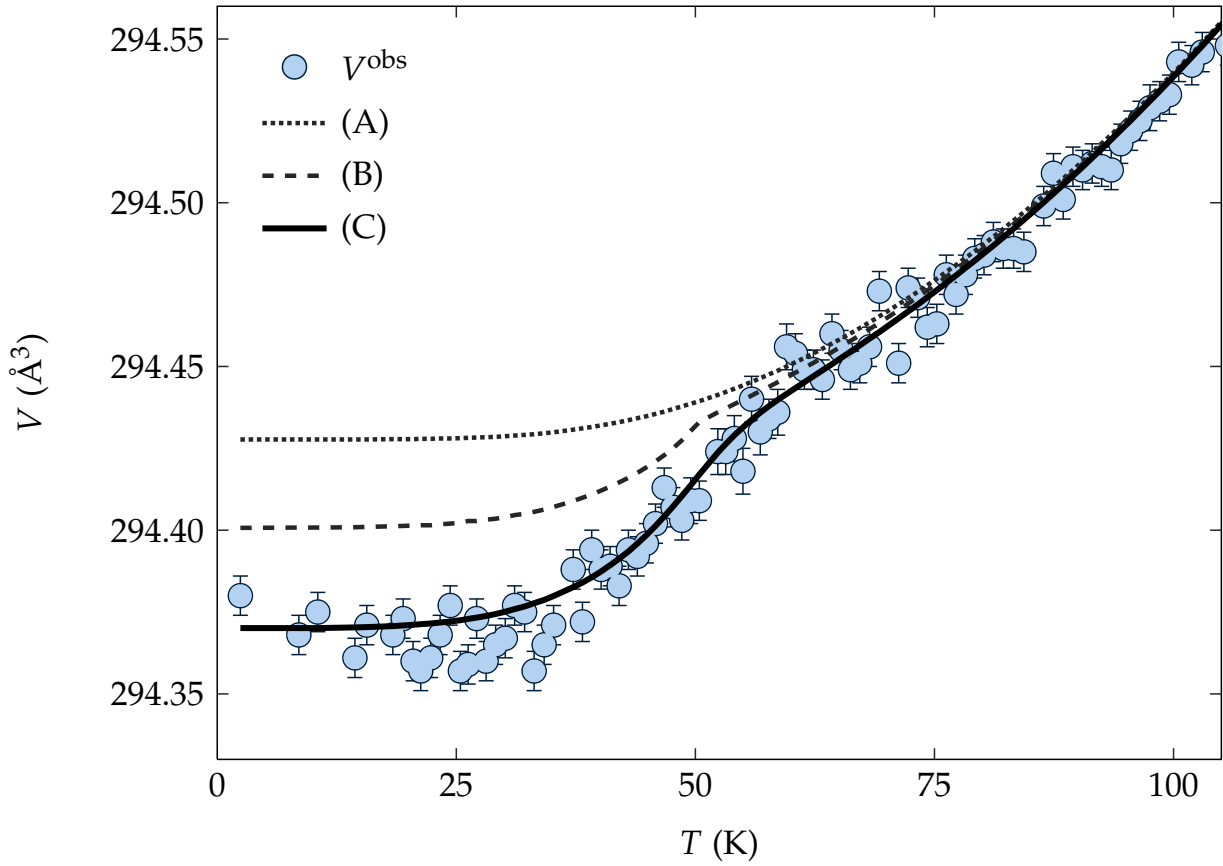


Figure 4.7. Temperature dependence of the unit cell volume of Co_2SiO_4 . The curves represent different fits (see details in the text): the line (A) indicates no magnetic contribution, (B) corresponds to the magnetic contribution from equation 4.8, and (C) shows the magnetic contribution from equation 4.11

Taking into account the magnetic contribution from the fit of C_V^{magn} (equation 4.8) leads to an improvement of the unit cell volume description denoted as line (B) in figure 4.7. The anomalous contraction of V below approximately 50 K is therefore associated with the magnetic phase transition at this temperature. However, the fit below 50 K is still not perfect. For TEC α_V , one does not observe a sharp λ -peak as in the specific heat C_p , but instead a broad asymmetric peak. To fully describe α_V by means of equation 4.3 we used the function

$$C_V^{\text{magn}*} = k_m^* \frac{1}{1 + \exp\left(-\frac{T-T_N}{w_1^*}\right)} \left[1 - \frac{1}{1 + \exp\left(-\frac{T-T_N}{w_2^*}\right)} \right], \quad (4.11)$$

as an empirical modified description of the magnetic contribution. In this equation, k_m^* is a scaling factor, w_1^* and w_2^* describe the peak width centered around T_N on the low-temperature side of the transition and on the high-temperature side, respectively. The corresponding fit parameters are given in table 4.2.

The lines in figure 4.3 show the result obtained from the fitting of equation 4.2 using the modified magnetic contribution $C_V^{\text{magn}*}$ which is described by equation 4.11. Excellent agreement is demonstrated now also for the temperature range from 5 K to 50 K [see line (C) in figure 4.7].

The same model was applied to fit the lattice parameters as in the case of the unit cell volume with the exception that no physically meaningful interpretation of the fit parameters is considered. Note that whereas the unit cell volume V as well as the lattice parameters b and c are affected by the magnetic phase transition at about 50 K, the lattice parameter a displays no significant effect (figure 4.3). This point is better illustrated in figure 4.8, which shows the comparison between the measured and fitted data in the region of the antiferromagnetic phase transition for Co_2SiO_4 on an expanded temperature scale. Table 4.2 summarizes the fitted parameters associated with the calculation of the unit cell volume of Co_2SiO_4 to equation 4.2 with the modified magnetic contribution $C_V^{\text{magn}*}$ (equation 4.11) instead of C_V^{magn} (equation 4.8) in equation 4.4.

Table 4.2. Coefficients from the fit of the experimental unit cell volume of Co_2SiO_4 to equation 4.2 with modified $C_V^{\text{magn}*}$ according to equation 4.11.

Parameter	Coefficient
k_m^*	1.76 ± 0.46
w_1^* (K)	7.21 ± 2.58
w_2^* (K)	6.01 ± 1.78
k_V	0.1857 ± 0.0006
V_0 ($\text{\AA}^3$)	294.365 ± 0.004
R^*	0.99998

* according to equation 4.6.

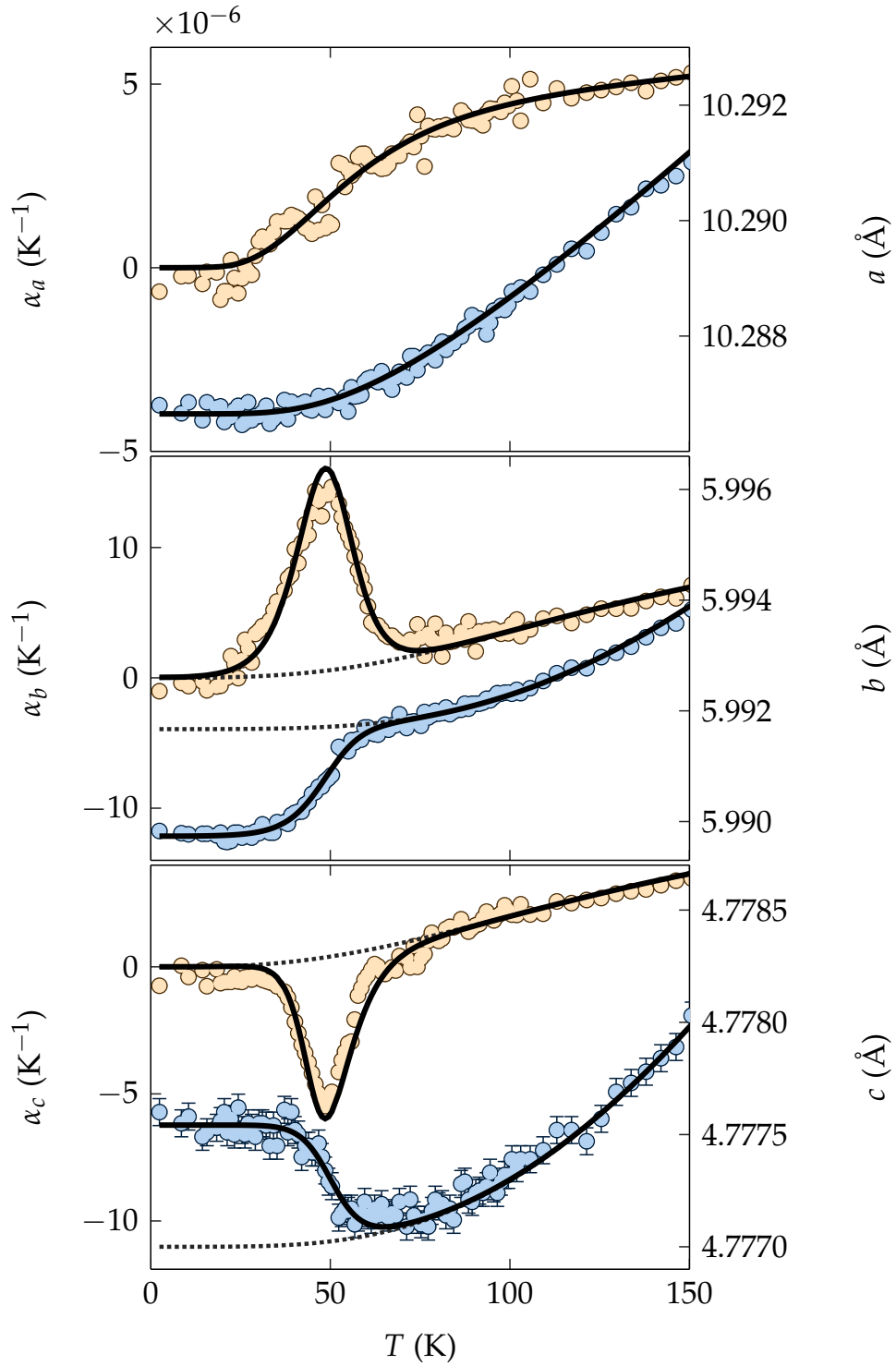


Figure 4.8. Temperature dependencies of the lattice parameters of Co_2SiO_4 (●; right Y-scales) as well as the thermal expansion coefficients (●; left Y-scales) in the temperature region close to the magnetic phase transition. Error bars for the lattice parameters are smaller than the symbols if not visible. The dashed (·····) and solid (—) curves represent a fit without and with the magnetic contribution, respectively (see details in the text).

In general, variations of the lattice parameters of Co_2SiO_4 with temperature are smaller than 0.5% (figure 4.9) over the complete temperature range covered in our powder neutron diffraction experiments (5 K—500 K). The maximal change in the lattice parameters due to the magnetic phase transition at least ten times smaller, but still observable with accurate measurements.

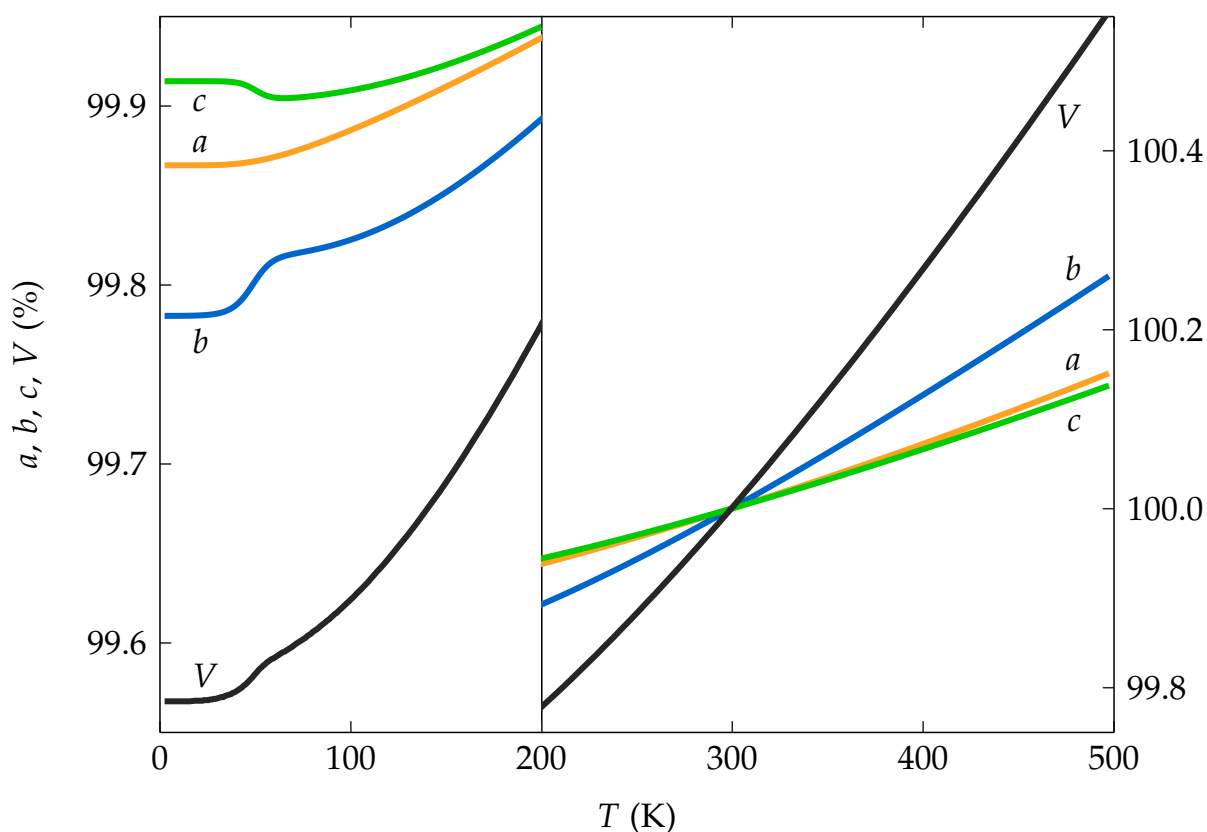


Figure 4.9. Variation of the lattice parameters and the cell volume of Co_2SiO_4 with temperature (in percents). The room temperature was chosen as 100%.

4.4. Atomic positions, interatomic distances and angles, ADPs

The influence of temperature on the atomic positions is also expected to be weak. This can be studied by means of interatomic distances and angles. It

is important to consider this point because the superexchange interactions strongly depend on the values of distances and angles between magnetic cations and non-magnetic anions [90–93].

For the data collection at 55 K, a total of 2118 Bragg reflection intensities up to $\sin \theta / \lambda \approx 1.1 \text{ \AA}^{-1}$ [$\lambda = 0.552(1) \text{ \AA}$] were measured with the single-crystal neutron diffractometer HEiDi. After averaging over all symmetry equivalents, 1465 independent reflections remained ($R_{\text{int}} = 0.028$). A total of 1098 reflections satisfied the criterion $I > 2\sigma(I)$ and were used for the structure refinement. A data collection at 2.5 K was also performed up to $\sin \theta / \lambda \approx 1.1 \text{ \AA}^{-1}$ [$\lambda = 0.552(1) \text{ \AA}$] and a total of 3226 Bragg reflection intensities was measured. After averaging 1424 independent reflections remained ($R_{\text{int}} = 0.033$). After applying the criterion $I > 2\sigma(I)$, 1070 observed reflections were used for the structure refinement. Result of the refinements at 55 K and 2.5 K are shown in figure 3.3. The structural parameters of Co_2SiO_4 at 55 K and 2.5 K are presented in tables 3.3 and 3.4. The data for the selected interatomic distances and angles in Co_2SiO_4 are summarized in table 3.5.

Increasing temperature causes a smooth, almost linear expansion of the average $\langle \text{Co-O} \rangle$ distance, which is shown in figure 4.10 together with the individual interatomic distances Co–O and the volumes of CoO_6 octahedra. The slope coefficients for the individual interatomic distances slightly differ from each other as well as from the average distance but the difference is not significant taking into account the experimental uncertainty. In general, variations of the Co–O interatomic distances with temperature are smaller than 0.8%. The same is true for the O–Co–O angles (figure 4.11): most of them remain constant within the experimental error. The powder neutron diffraction data correspond to the single-crystal measurement. There might be a small indication of the magnetic phase transition near 50 K in the Co–O distances (figure 4.10). However, the precision of atomic coordinates and hence interatomic distances is principally reduced with respect to the determination of lattice parameters.

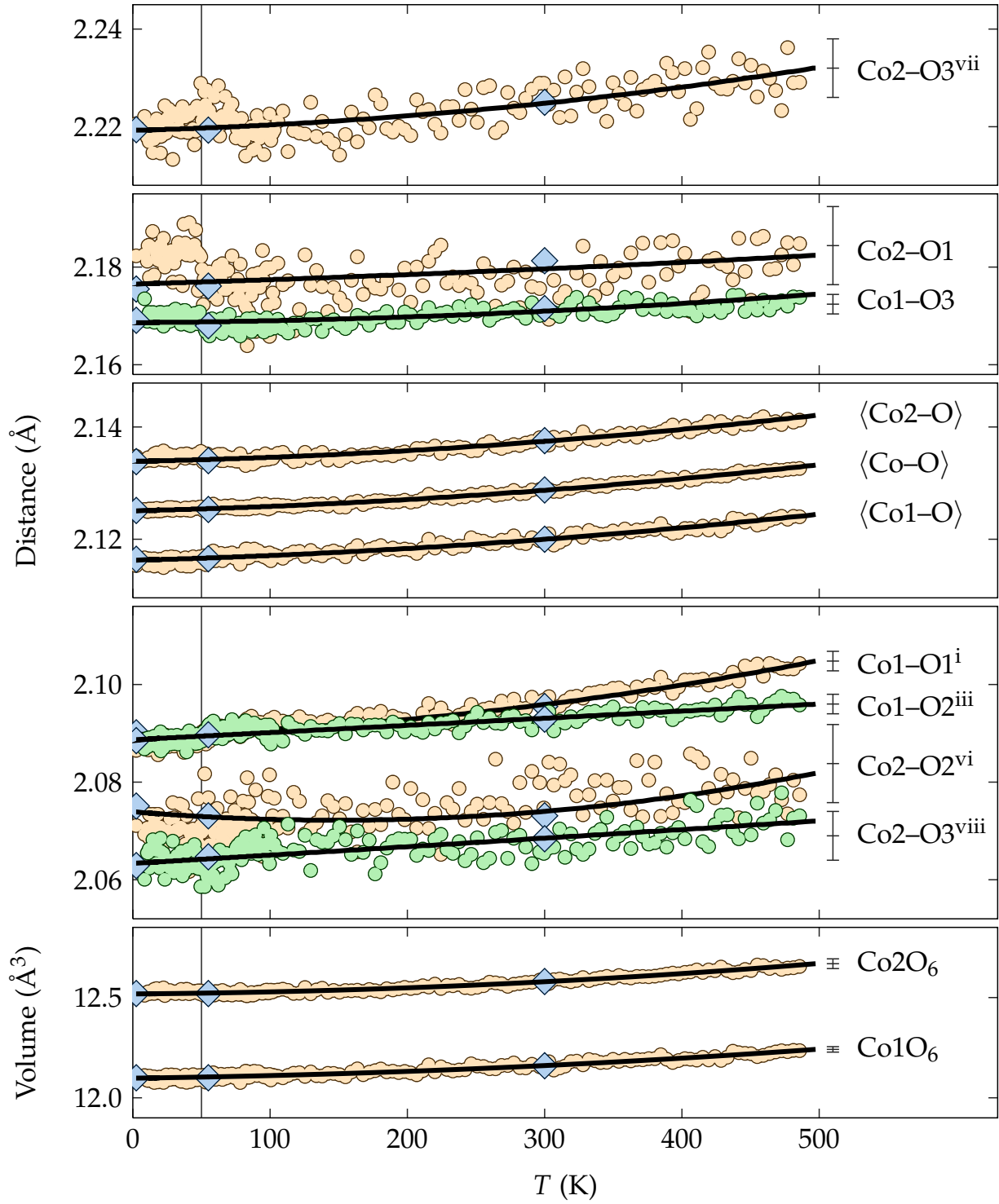


Figure 4.10. Temperature dependence of the Co–O distances and CoO_6 octahedra volumes for Co_2SiO_4 . Circles ($\circ$ and $\bullet$) mark the results of the powder neutron diffraction measurements (error bars shown at the right) whereas rhombs ($\diamond$) mark the results of the single-crystal neutron diffraction measurements (error bars from the refinement are smaller than the symbols). The fits (—) are used as guides to the eye (second order polynomial fit). See figure 3.1 and table 3.5 for the symmetry codes.

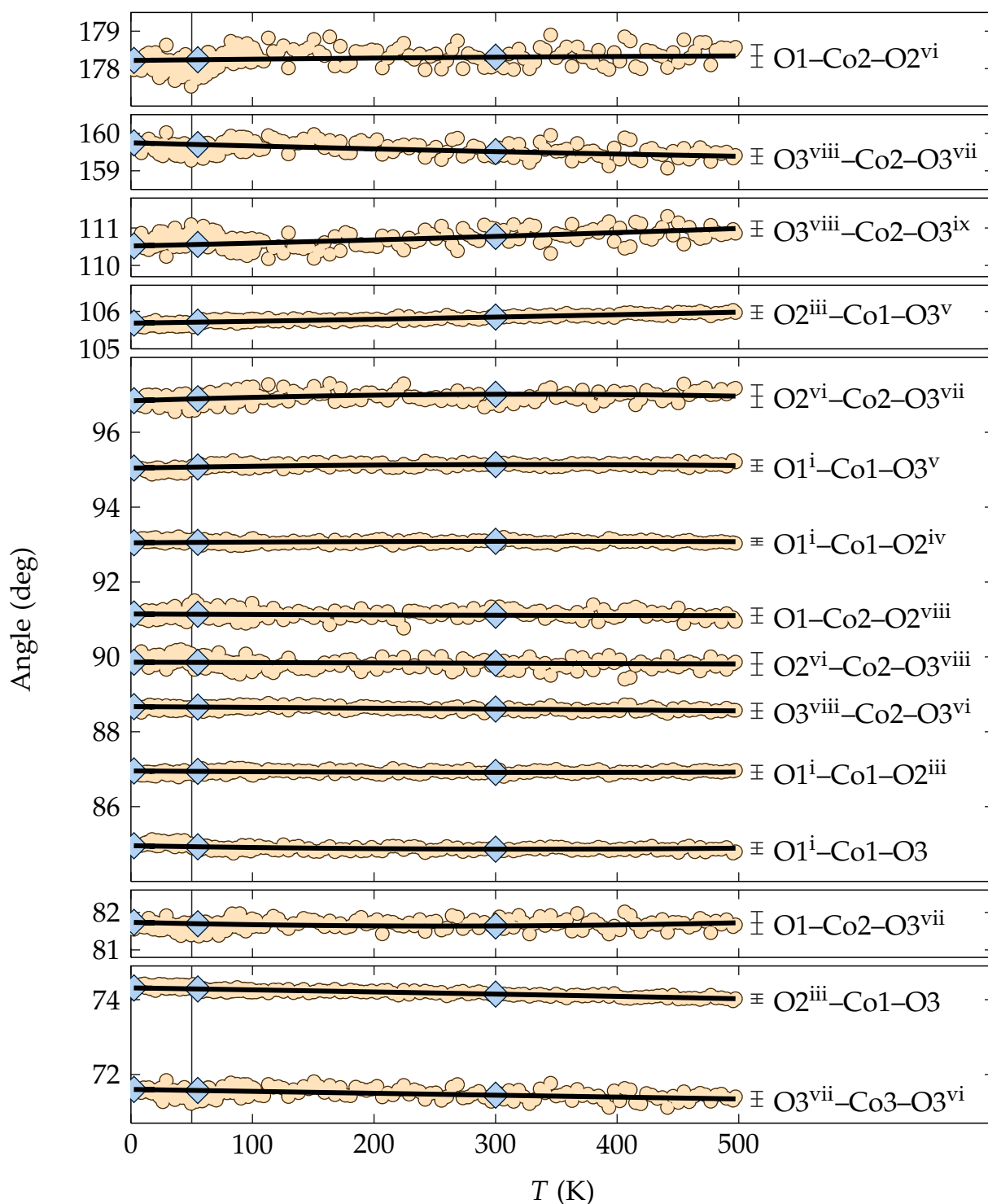


Figure 4.11. Temperature dependence of the O–Co–O angles for Co_2SiO_4 . Circles (○) mark the results of the powder neutron diffraction measurements (error bars shown at the right) whereas rhombs (◈) mark the results of the single-crystal neutron diffraction measurements (error bars from the refinement are smaller than the symbols). The fits (—) are used as guides to the eye (second order polynomial fit). See figure 3.1 and table 3.5 for the symmetry codes.

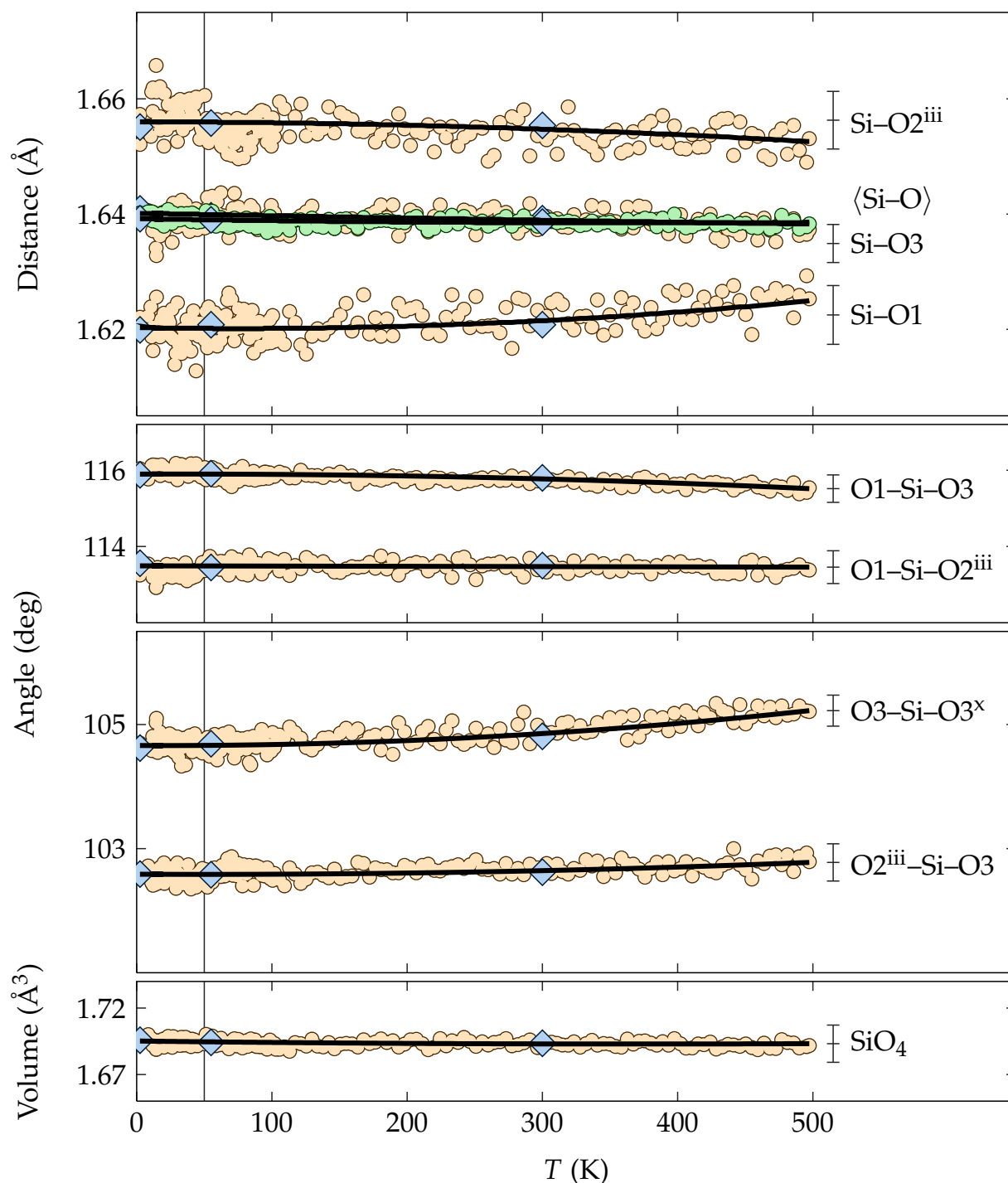


Figure 4.12. Temperature dependence of the Si–O distances, O–Si–O angles and SiO_4 tetrahedra volumes for Co_2SiO_4 . Circles (○ and ●) mark the results of the powder neutron diffraction measurements (error bars shown at the right) whereas rhombs (◊) mark the results of the single-crystal neutron diffraction measurements (error bars from the refinement are smaller than the symbols). The fits (—) are used as guides to the eye (second order polynomial fit). See figure 3.1 and table 3.5 for the symmetry codes.

In silicate compounds isolated SiO_4 tetrahedra generally behave as rigid units if a parameter of state like the temperature is changed. This also holds true for Co_2SiO_4 . Only minor changes in the SiO_4 geometry are observed (figure 4.12). Most of the Si–O distances, O–Si–O angles and SiO_4 tetrahedra volumes remain constant within experimental error for the temperature range from 5 K up to 500 K.

The temperature dependencies of the atomic displacement parameters of Co_2SiO_4 are shown in figure 4.13. At very low temperatures, the thermal motion is close to constant at the zero-point motion. The equivalent ADPs of Co1 and Co2 as well as of O1 and O2 are very similar and much larger than that of Si at room temperature. At low

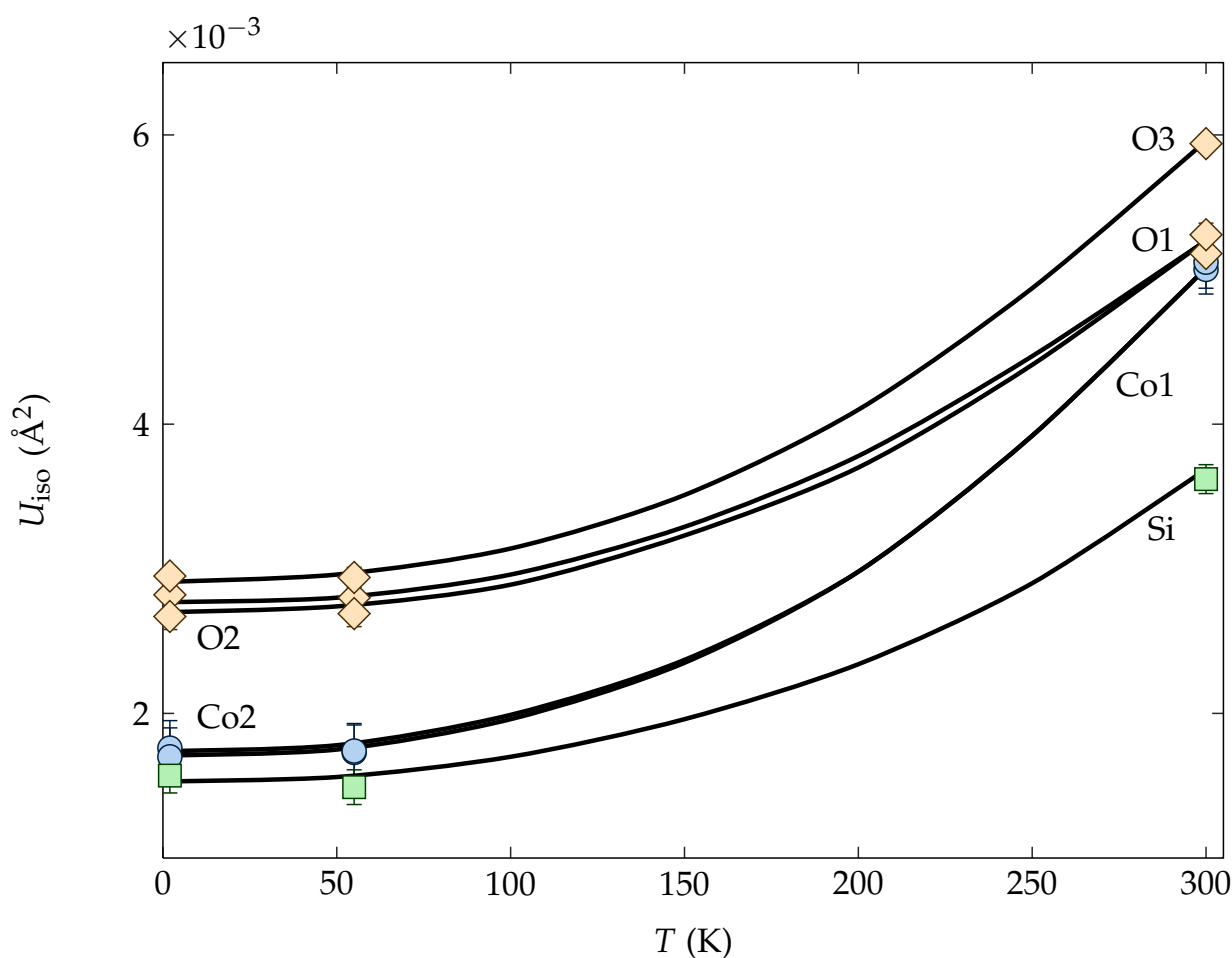


Figure 4.13. Temperature dependence of the isotropic ADPs for Co_2SiO_4 according to the results of our single-crystal neutron diffraction measurements. The fits are used as guides to the eye.

temperatures all ADPs remain constant, at least between 55 K and 2.5 K. The values for Co1, Co2 and Si are now very similar and almost two times smaller than those of the O atoms.

Chapter 5

Electron densities

5.1. Single-crystal synchrotron X-ray diffraction

In order to study the electron-density distribution of the Co-olivine, single-crystal synchrotron diffraction measurements were performed. Several fragments of a crushed part of the Co_2SiO_4 single crystal (see section 2.2) were mechanically ground and polished to the shape of spheres with diameters between $150\text{ }\mu\text{m}$ and $200\text{ }\mu\text{m}$. Then, sulfuric acid was used to clean the surfaces of the samples. The quality of the crystals was initially tested on a laboratory X-ray Laue diffractometer. Thus, two crystals were selected for the data collection. The single-crystal diffraction data were collected on a Huber four-circle diffractometer in fixed vertical diffraction geometry at beamline D3 at the synchrotron facility HASYLAB/DESY (Hamburg, Germany). The beam was monochromated by a Si(111) double-crystal monochromator. In order to follow the evolution of the electron density with temperature the measurements were performed above and below the magnetic phase transition ($T_N \approx 50\text{ K}$). The data were collected at 12 K and 40 K using a point detector (NaI scintillation counter) and at 300 K with a two-dimensional detector (*Marresearch GmbH* CCD165 system). A double-stage He closed-cycle cryostat was used to cool the

sample. The energy of the synchrotron radiation was selected according to wavelengths of 0.5000 Å and 0.4770 Å for low temperature and room temperature measurements, respectively. Three standard reflections were measured every two hours as a check of the stability of the experimental setup. Experimental details are given in table 5.1.

5.2. Fourier transform

Since the $3d$ shell is the outermost shell and known to be responsible for the magnetic properties for the iron group ions, the distributions of $3d$ electrons at the Co1 and Co2 sites are of particular interest. The aspherical electron-density distributions around the cobalt ions were initially studied by means of inverse Fourier transform (Fourier syntheses).

The electron distribution in a crystal may be obtained from the measured X-ray amplitudes and calculated values of their phases. The amplitude of the elastic scattering of the contents of the unit cell or structure factor F is given by

$$F(\mathbf{H}) = \int_{\text{unit cell}} \rho(\mathbf{r}) e^{2\pi i \mathbf{H} \cdot \mathbf{r}} d\tau, \quad (5.1)$$

where ρ is the time-averaged electron density at the point described by the vector $\mathbf{r}$. $\mathbf{H}$ is a reciprocal lattice vector

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \quad (5.2)$$

where h, k and l are the Miller indices and $\mathbf{a}^*, \mathbf{b}^*$ and $\mathbf{c}^*$ the reciprocal space basis vectors.

As described by equation 5.1, the structure factors are the Fourier transform (Fourier analysis) of the electron density ρ . According to the Fourier transform theorem, ρ is, therefore, the inverse Fourier transform of the structure factors

$$\rho(\mathbf{r}) = \int F(\mathbf{H}) e^{-2\pi i \mathbf{H} \cdot \mathbf{r}} d\mathbf{H}, \quad (5.3)$$

Table 5.1. Experimental and refinement details of synchrotron single-crystal diffraction on Co_2SiO_4 .

	300 K	40 K	12 K
<i>Crystal data</i>			
M_r	209.95	209.95	209.95
Cell setting, space group	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>	Orthorhombic, <i>Pnma</i>
a ,	10.3005,	10.2864,	10.2864,
b ,	6.0028,	5.9872,	5.9872,
c (Å)	4.7816	4.7785	4.7785
V (Å ³)	295.66	294.29	294.29
Z	4	4	4
D_x (Mg m ⁻³)	4.715	4.737	4.737
Radiation type	Synchrotron	Synchrotron	Synchrotron
Wavelength (Å)	0.4770	0.5000	0.5000
μ (mm ⁻¹)	3.688	4.237	4.237
Crystal form, colour	Sphere, violet	Sphere, violet	Sphere, violet
Crystal size (mm)	0.160	0.160	0.160
<i>Data collection</i>			
Diffractometer	Huber four- circle diff- ractometer	Huber four- circle diff- ractometer	Huber four- circle diff- ractometer
Detector	CCD area detector	NaI scintillation counter	NaI scintillation counter
Data collection method	ω scans	ω scans	ω scans
No. of measured, independent and observed reflections	5967, 2786, 2128	1820, 757, 712	2231, 935, 908
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.063	0.046	0.048
θ_{max} (°)	39.7	28.5	37.9
<i>Refinement</i>			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$,	0.046, 0.047,	0.020, 0.028,	0.019, 0.029,
S	1.38	1.64	1.70
No. of reflections	2128	712	908
Extinction method	Isotropic type I, Gaussian	Isotropic type I, Gaussian	Isotropic type I, Gaussian
Extinction coefficient	0.17(3)	0.11(2)	0.10(2)

As $F(\mathbf{H})$ are only different from zero at discrete points in reciprocal space, the integral may be replaced by a summation

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} F(\mathbf{H}) e^{-2\pi i \mathbf{H} \cdot \mathbf{r}}, \quad (5.4)$$

where V is the volume of the unit cell.

In general, the structure factor F in equation 5.4 is a complex quantity which may be described by both its magnitude $|F|$ and its phase ϕ . It is well known that the phases $\phi(\mathbf{H})$ cannot be measured directly. To evaluate $\rho(\mathbf{r})$, they must be calculated according to 5.1 for which at least an approximate estimation of $\rho(\mathbf{r})$ is required. A significant simplification occurs when the structure contains a crystallographic centre of symmetry [$\rho(\mathbf{r}) = \rho(-\mathbf{r})$] and, therefore,

$$\phi(\mathbf{H}) = 0^\circ \text{ or } 180^\circ.$$

A superposition of spherical atoms centered at the nuclear position is a sufficiently close approximation to the density in a crystal to give a reliable prediction of the sign of the structure factors for all but a few of the very weak reflections.

Single-crystal X-ray diffraction data were used for the reconstruction of the electron density in the unit cell. As a first step, we performed a refinement of the independent spherical atom model against all data. Some details of the refinement as well as the reliability factors of the fit are summarized in table 5.1. An isotropic extinction type I correction with Gaussian mosaic distribution was applied during the refinement, based on the approximation that the crystal is a sphere with radius 0.160 mm. All refinements and Fourier maps calculations were performed with the program JANA2006 [79]. The spherical atom model refinement was used to obtain scaled and phased observed structure factors. A Fourier map in the plane of the chemical bonds is shown in figure 5.1. No electron density in the bonds is evident due to the series termination effects. There are even positive walls and negative ditches between the atoms, where the density of the bonding should be visible.

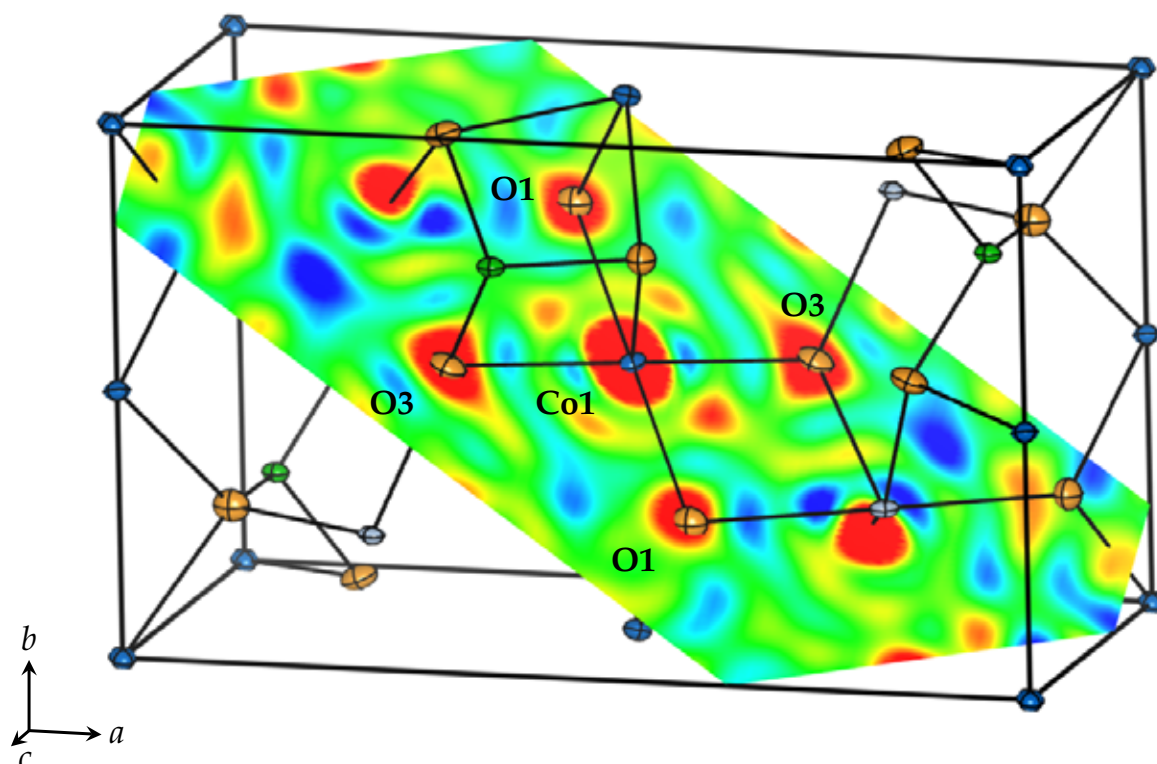


Figure 5.1. Electron-density distribution of Co_2SiO_4 at 12 K from the Fourier synthesis with contour range from $-8 \text{ e}/\text{\AA}^3$ (blue) to $10 \text{ e}/\text{\AA}^3$ (red). A section which intersects the Co1O_6 octahedron and contains the Co1, O1 and O3 atoms is shown together with the schematic representation of the crystal structure.

5.3. Maximum-entropy method

The maximum-entropy method (MEM) is another tool to study the electron-density distribution. When compared with the conventional Fourier synthesis the MEM is more informative. As shown in figure 5.1, in Fourier synthesis the electron densities will be biased due to the series termination error and negative electron density that prevents clear understanding of bonding between the atoms. MEM analysis usually overcomes these problems.

The exact electron-density distribution would be obtained if all the structure factors were known without any ambiguities. It is however, impossible to collect exact values of all the structure factors by X-ray

diffraction methods. The number of observed structure factors by the experiment is limited and they have some errors. From the viewpoint of the information theory, it is not appropriate to use an inverse Fourier transform to reconstruct density distribution by using a limited number of observed structure factors.

A valuable feature of the MEM is that all types of information gained from a diffraction experiment can be used in a maximum-entropy calculation of the electron-density distribution: phased reflections, unphased reflections, intensities of groups of overlapping reflections, and even reflections with a remaining ambiguity in the phase [94].

The maximum-entropy method is based on the Bayesian statistical theory. The entropy S is defined as

$$S = - \sum_{j=1}^N \rho_j \log \left(\frac{\rho_j}{r_j} \right), \quad (5.5)$$

where ρ_j is the electron density at position j within the unit cell ($j = 1 \dots N$) and r_j is the reference density.

The maximum of S will give the most probable electron density of the crystal. The reference density r_j can incorporate any pre-knowledge about the problem. If there is no further information available, it is chosen flat which means the density values of all voxels are the same. The experimental data are introduced in so-called constraints C . It should be noted that MEM is model free at this point, but there are several models incorporated with the constraints.

Reflections with known magnitude and phase are combined in the F -constraints:

$$C_F = \frac{1}{N_F} \sum_{j=1}^{N_F} \frac{|F_j^{\text{calc}} - F_j^{\text{obs}}|^2}{\sigma_j^2}, \quad (5.6)$$

where F_j^{calc} and F_j^{obs} are the calculated and observed structure factors, respectively, N_F is the number of reflections contributing to the sum, and $\sigma = \sigma(|F|)$ is the estimated error.

Reflections with the phases not known, or groups of overlapping reflections are collected into the G -constraints:

$$C_G = \frac{1}{N_G} \sum_{j=1}^{N_G} \frac{(G_j^{\text{calc}} - G_j^{\text{obs}})^2}{\sigma_j^2}, \quad (5.7)$$

with the ‘mean structure-factor modulus’

$$G^j = \sqrt{\frac{\sum_i m_i |F_i|^2}{\sum_i m_i}},$$

where m_i denotes the multiplicity of a reflection.

In powder diffraction both types of constraints are needed. There is almost no chance to get a good result without using the F -constraints, since phase information is needed to pin the electron density to atoms. However, it is advisable to use all available information, not only the F -constraints.

The measurement information is introduced through a constraint function C with the ‘pseudo-Lagrange parameter’ λ . The basic equation is

$$\rho_j = r_j \exp \left(-\frac{\lambda \delta C}{\delta \rho_j} \right), \quad (5.8)$$

used iteratively [95–97]. The different constraint functions C are summed up and then used in equation 5.8.

The MEM expects the given F_{obs} . Obviously the raw data (integrated intensities) have to be corrected and normalized to match that condition. In order to determine the phases of the structure factors an approximate model is used. The obtained F_{calc} of the best model are used to apply all corrections in a single step:

$$F_{\text{obs}}^{\text{electron}}(\mathbf{H}) = \frac{F_{\text{calc}}^{\text{electron}}(\mathbf{H})}{|F_{\text{calc}}(\mathbf{H})|} |F_{\text{obs}}(\mathbf{H})|, \quad (5.9)$$

where the superscript ‘electron’ denotes values equal to the Fourier transform of the corresponding electron density.

The deviations between the calculated F_{calc} and the real/observed F_{obs} structure factors are contained in their magnitude, since the phases determine the positions of the atoms in the unit cell mainly. A good fitting model should give the proper phases, even if it does not cover all properties of the structure. Therefore, MEM can be used to determine structural features beyond that of a reasonable fitting model.

As was already mentioned, the spherical atom model refinement was used to obtain scaled and phased observed structure factors from the single-crystal X-ray diffraction measurements (see table 5.1). These data were used in the F -constraint of the MEM. Calculations according to the MEM were performed with the program PRIMA [98] from the computer software package VENUS [99]. PRIMA is a MEM analysis program to calculate electron densities from X-ray diffraction data and nuclear densities from neutron diffraction data.

In the present analysis, the total number of electrons in the unit cell was fixed to be $F(000) = 400\text{e}$. The electron density was defined on a grid of $204 \times 120 \times 96$ pixels over the unit cell to ensure good spatial resolution, which corresponds to a pixel size of $0.05 \times 0.05 \times 0.05 \text{ \AA}^3$. The number of independent reflections used was 2128, 712 and 908 for 300 K, 40 K and 12 K, respectively. The reliability factor of MEM, R_F was 0.042 for 300 K, 0.022 for 40 K and 0.023 in the case of 12 K. They were calculated according to

$$R_F = \sqrt{\frac{\sum |F_{\text{obs}} - F_{\text{calc}}|}{\sum |F_{\text{obs}}|}}. \quad (5.10)$$

The MEM electron density at 12 K in the section which intersects the Co1O_6 octahedron is shown in figure 5.2. In comparison to the Fourier map (figure 5.1), the MEM map is smooth and more detailed. It shows no unrealistic negative density, which is the characteristic of the MEM procedure. Artefacts are not critical to the interpretation of the bonding, even though they are still present. The MEM is therefore more suited to determine the electron density in the bonds and other fine structure of the electron density than the Fourier synthesis.

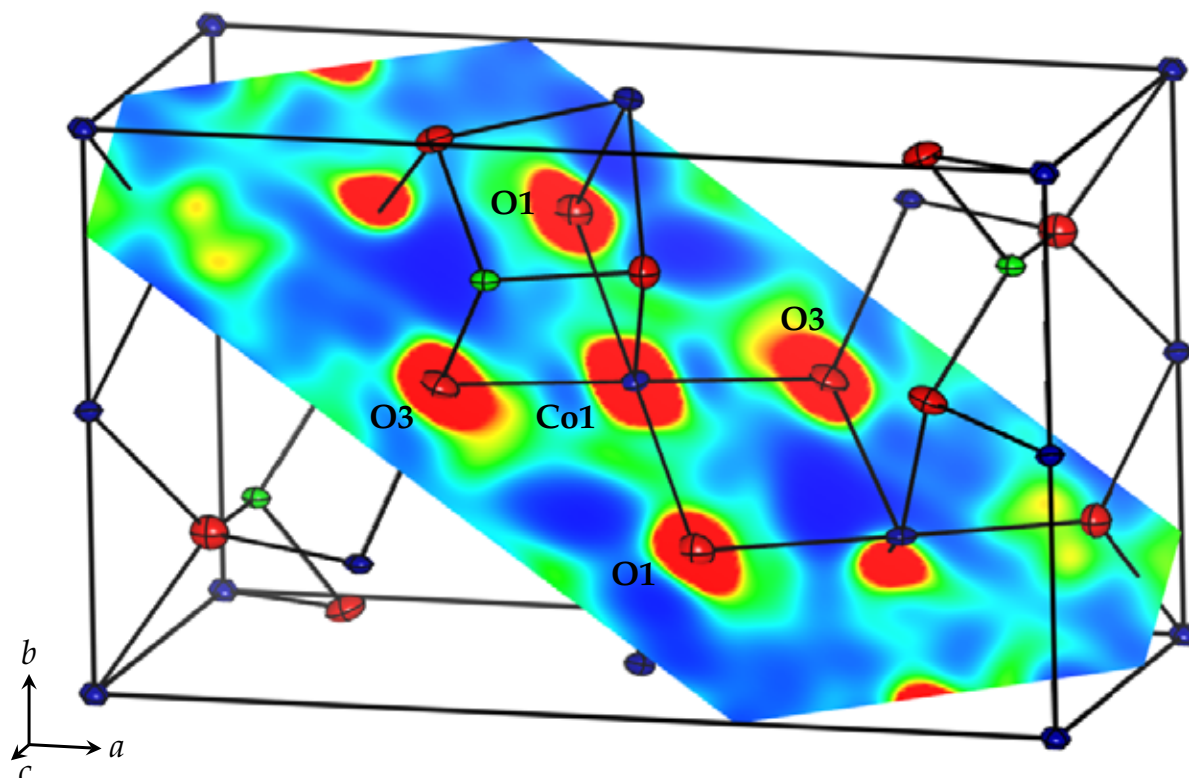


Figure 5.2. MEM electron-density distribution in Co_2SiO_4 at 12 K with contour range from $0.0 \text{ e}/\text{\AA}^3$ (blue) to $0.4 \text{ e}/\text{\AA}^3$ (red). A section which intersects the Co1O_6 octahedron and contains the Co1, O1 and O3 atoms is shown together with the schematic representation of the crystal structure.

From the MEM analysis, a covalent bonding feature is found between Co and O ions (see figure 5.2). It is considered that this covalent bonding of Co–O is attributed to the overlapping of electron densities due to the Co-3*d* and O-2*p* orbital hybridization.

Figure 5.3 shows isosurfaces of electron densities determined from the single-crystal synchrotron diffraction data of Co_2SiO_4 at 300 K, 40 K and 12 K by MEM. The isosurface level was set to $2.4 \text{ e}/\text{\AA}^3$. It is worth noting that the local maxima of the electron densities are identified with the atomic positions and no residual charges are seen at any other regions.

It is also found from the MEM analysis that owing to the more uniform distribution of the surfaces at 300 K, they are distinguished from those at 40 K and, especially, at 12 K (figure 5.3). There is a tendency to elongation

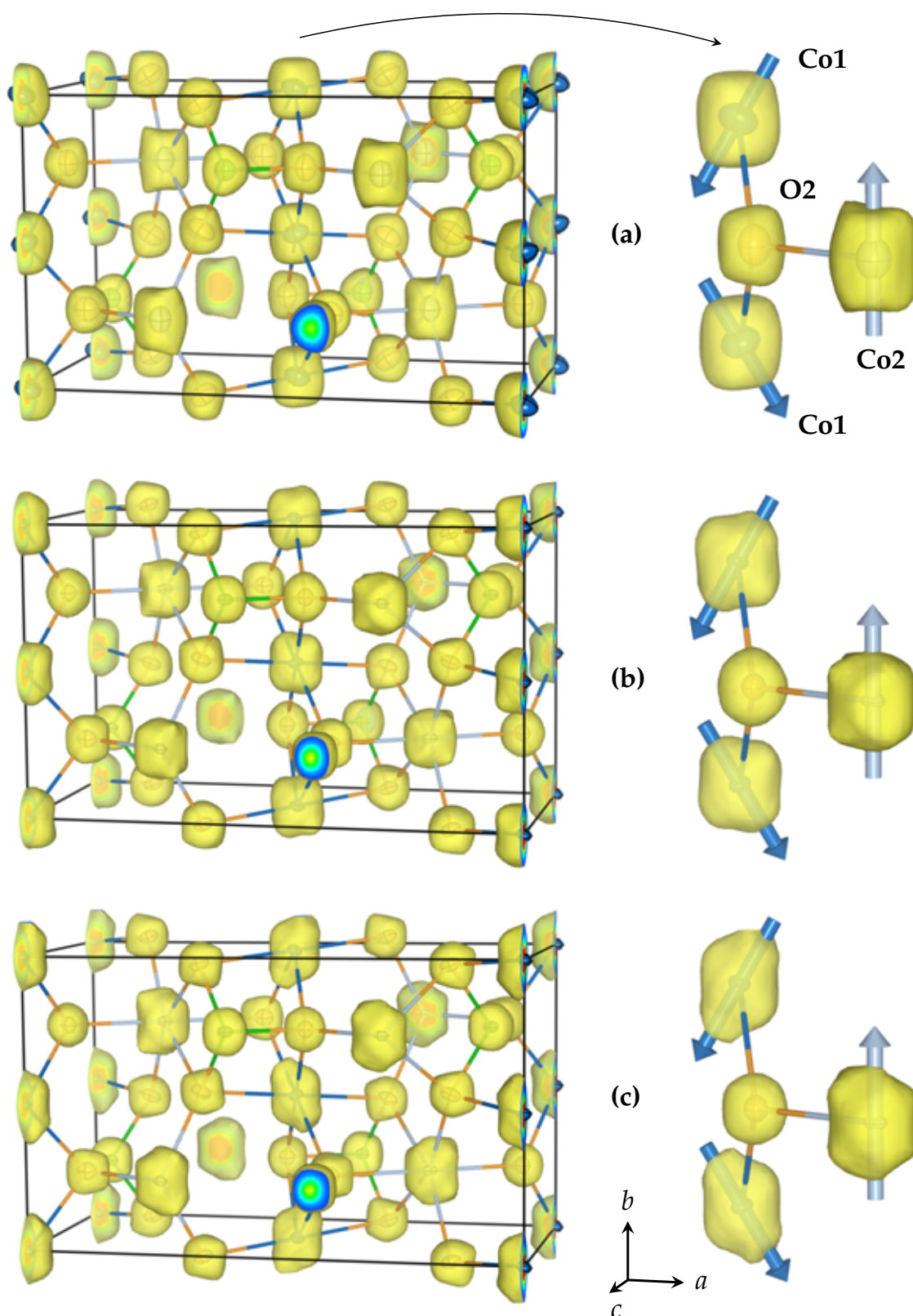


Figure 5.3. Three-dimensional MEM electron-density distribution in the unit cell of Co_2SiO_4 at (a) 300 K, (b) 40 K and (c) 12 K are shown with an isosurface level of $2.4 \text{ e}/\text{\AA}^3$. A magnified view of the central part for every temperature is also shown. The magnetic moments as determined at 2.5 K are plotted for illustration (see text for details).

of the electron density along the direction of the magnetic moments with decrease of temperature. The values and the directions of the Co magnetic moments were obtained from the single-crystal neutron diffraction measurements at 2.5 K (see section 6.3); they are plotted in the same way at temperatures below and above the magnetic phase transition temperature ($T_N \approx 50$ K) only for illustration.

5.4. Deformation densities

Another possible way to overcome the problem of the Fourier transform of F_{obs} (figure 5.1) is to calculate a difference Fourier map. That means it is desirable to subtract from the total electron density the density corresponding to a superposition of spherical atoms at the nuclear positions. This superposition represents the distribution prior to the process of chemical bonding. The difference function

$$\rho_{\text{deform}}(\mathbf{r}) = \rho(\mathbf{r}) - \sum_{\text{atoms}} \rho_{i,\text{spherical atom}}(\mathbf{r}), \quad (5.11)$$

therefore, represents the deformation of the charge distribution on chemical bond formation and is described as the deformation density.

Equation 5.11 requires knowledge of the positional parameters of the nuclei at which the spherical density functions are centered and of the thermal vibrational parameters of the nuclei. The combined use of X-ray and neutron diffraction provides a method which is independent of a priori assumptions on the nature of the electron-density deformations. If the atomic positional parameters and the thermal smearing factors are obtained by neutron diffraction, one can then calculate the X-rays scattering of the density in the crystal by using tabulated spherical atom X-ray scattering factors

$$F_{\text{calc,N}} = \sum_{\text{atoms}} f_i e^{2\pi i \mathbf{H} \mathbf{r}_i} T_i, \quad (5.12)$$

where the symbol 'N' indicates that neutron atomic parameters were used in the calculation of the X-ray scattering. The deformation density is then

given by an expression similar to 5.4

$$\rho_{\text{deform}}^{\text{X-N}}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} (F_{\text{obs,X}} - F_{\text{calc,N}}) e^{-2\pi i \mathbf{H} \mathbf{r}}. \quad (5.13)$$

In centrosymmetric crystals with very few exceptions $\phi_{\text{X}}(\mathbf{H}) = \phi_{\text{N}}(\mathbf{H})$ ($= 0$ or π) so that equation 5.13 reduces to

$$\rho_{\text{deform}}^{\text{X-N}}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} (|F_{\text{obs,X}}| \frac{|F_{\text{calc,N}}|}{F_{\text{calc,N}}} - F_{\text{calc,N}}) \cos 2\pi \mathbf{H} \mathbf{r}. \quad (5.14)$$

The difference Fourier maps $\rho_{\text{deform}}^{\text{X-N}}$ were compared with the difference MEM maps $\rho_{\text{diff}}^{\text{MEM}}$ obtained as

$$\rho_{\text{diff}}^{\text{MEM}} = \rho^{\text{MEM,X}} - \rho^{\text{MEM,N}}.$$

They are shown in figure 5.4 for 300 K as an illustration. Both Fourier synthesis and MEM give comparable results at three measured temperatures (300 K, 40 K and 12 K). However, the MEM maps are again smoother and seem to be more reliable. Therefore, we used the MEM reconstruction to plot the three-dimensional electron deformation density in the Co_2SiO_4 unit cell. Figure 5.5 shows isosurfaces of electron densities determined from the single-crystal synchrotron diffraction data of Co_2SiO_4 at 300 K, 40 K and 12 K by MEM.

The room temperature picture coincides with the hypothesis that the Co e_g -electrons occupy both the $d_{x^2-y^2}$ and d_{z^2} orbitals at 300 K and give rise to three-dimensional hybridization with six ligand oxygens. The dramatic change of the deformation density features was found by Fourier synthesis and MEM with temperature decrease (see figure 5.5). It is evident that the two positive lobes become negative at 40 K and 12 K while the four other lobes remained positive.

The negative density on the deformation maps may indicate the vacancy of the d_{z^2} orbital and, therefore, a change of the spin state of Co^{2+} from HS ($t_{2g}^5 e_g^2$, $S = 3/2$) to LS ($t_{2g}^6 e_g^1$, $S = 1/2$) with decrease of temperature. However, this is in contradiction with the high value of the Co magnetic moment found from the neutron diffraction measurements

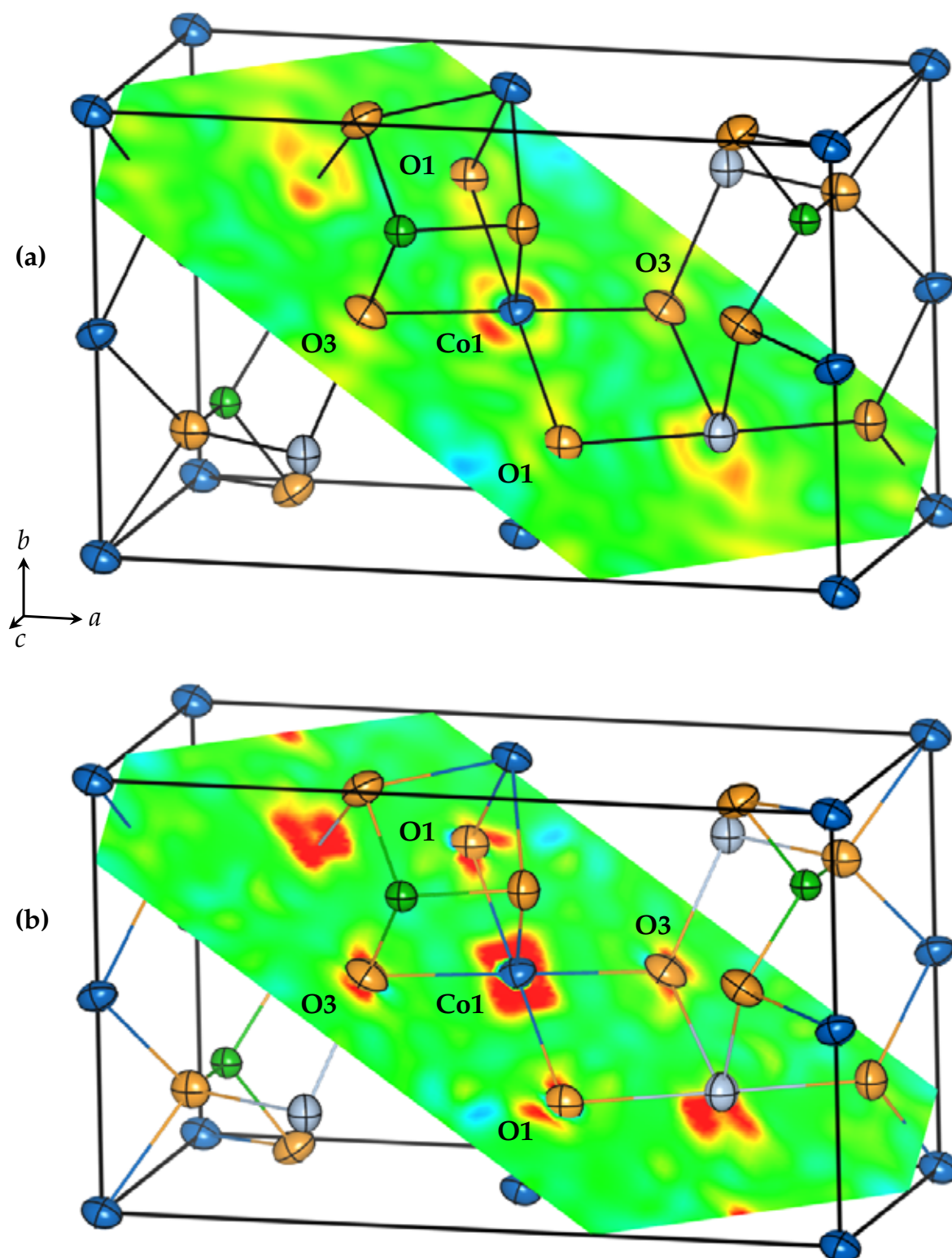


Figure 5.4. Sections through the O1–Co1–O3 plane of difference Fourier and MEM maps at 300 K. (a) Difference Fourier map with ρ from $-1.25 \text{ e}/\text{\AA}^3$ (blue) to $1.15 \text{ e}/\text{\AA}^3$ (red). (b) Difference MEM map with ρ from $-1.00 \text{ e}/\text{\AA}^3$ (blue) to $1.00 \text{ e}/\text{\AA}^3$ (red).

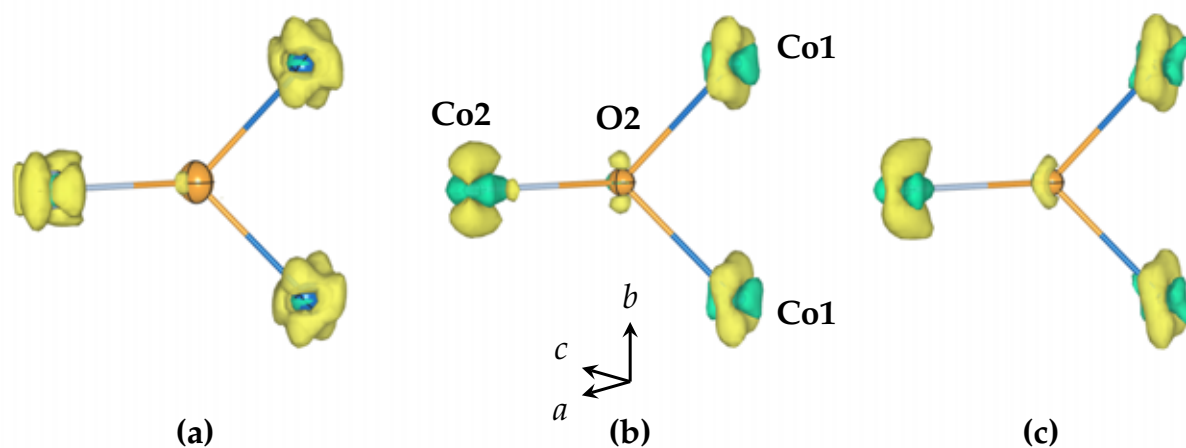


Figure 5.5. Three-dimensional MEM electron deformation densities around the Co1, O2 and Co2 atoms in Co_2SiO_4 at (a) 300 K, (b) 40 K and (c) 12 K. The isosurface levels were set at $1 \text{ e}/\text{\AA}^3$ (yellow) and $-1 \text{ e}/\text{\AA}^3$ (blue).

(see section 6.3). So, there is no clear understanding of this change of the deformation density with temperature. Additional experiments are further required to clarify this phenomenon.

Chapter 6

Magnetic structure

6.1. Crystal structure aspects

Some important aspects of the olivine structure (see section 3 for details) with respect to an understanding of the magnetic structure of Co_2SiO_4 are summarized below. The Co_2SiO_4 crystal structure can be considered as an arrangement of the CoO_6 octahedra in layers perpendicular to the c axis at $z = 0$ and $z = 0.5$ (see figure 6.1). The Co1 ions are located exactly in these layers whereas the Co2 ions are slightly shifted along the c axis.

The Co1O_6 octahedra are interconnected by common edges and form single chains along the b axis (figures 6.1 and 6.2). The Co2O_6 octahedra are attached on alternative sides to the Co1O_6 chains in a way that the whole arrangement of Co1O_6 and Co2O_6 octahedra forms zigzag chains along the b axis (figure 6.1). A section of the resulting three dimensional arrangement of the Co^{2+} ions forming zigzag chains in layers perpendicular to the c axis is shown in figure 6.1. These chains are separated by SiO_4 tetrahedra (not shown for simplicity). Besides the two Co1O_6 neighbour octahedra (figure 6.2a) there are four corner-shared Co2O_6 octahedra and two common-edge Co2O_6 octahedra (figure 6.2b) for every Co1O_6 . On the other hand, each Co2O_6 octahedron has four

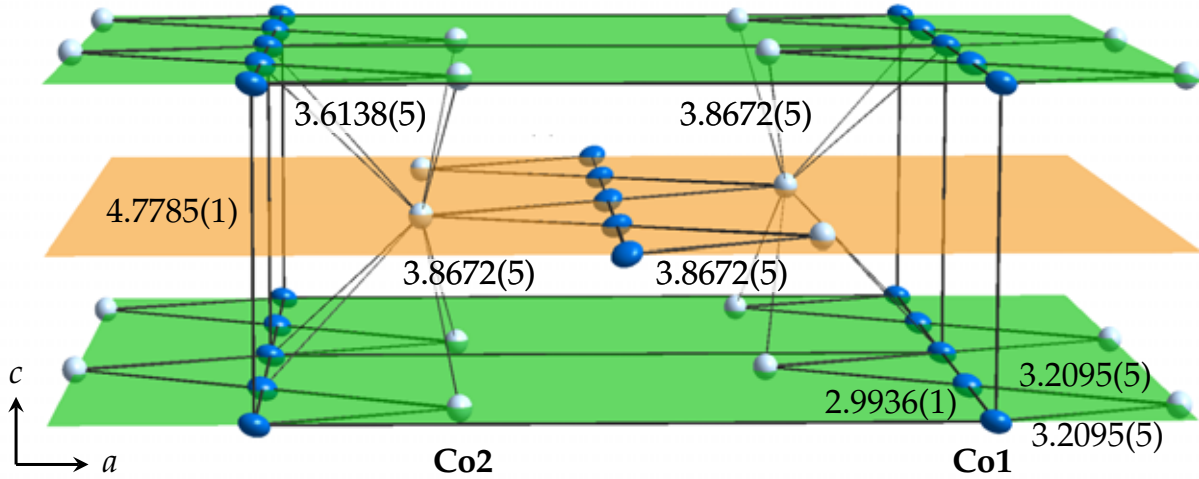


Figure 6.1. Perspective drawing of the arrangement of Co^{2+} ions along the b axis in Co_2SiO_4 . Some distances are marked for clarity.

Co_2O_6 neighbours with common corners (figure 6.2c). Moreover, there are four Co_1O_6 neighbour octahedra connected to Co_2O_6 by common corners and two by common edges (figure 6.2d).

According to our single-crystal neutron diffraction measurements [72, 100], the interatomic distances between the Co^{2+} ions within the zigzag chain lie in the range from 2.9936(1) Å to 3.2095(5) Å at room temperature. The Co–Co distances between the near-neighbour chains are in the range from 3.6138(5) Å to 3.8672(5) Å. All other distances between the Co ions are larger than the double spacing between the layers [4.7785(1) Å]. In general, the variation of the above mentioned interatomic distances with temperature is smaller than half a percent in the range from 300 K down to 2.5 K.

6.2. Magnetic susceptibility studies

The dc magnetization measurements were performed using a MPMS-5 SQUID magnetometer (Quantum Design, USA) at the Berlin Neutron Scattering Center (BENSCH), Hahn Meitner Institute (HMI), Berlin, Germany. For these measurements, a single-crystal sample with

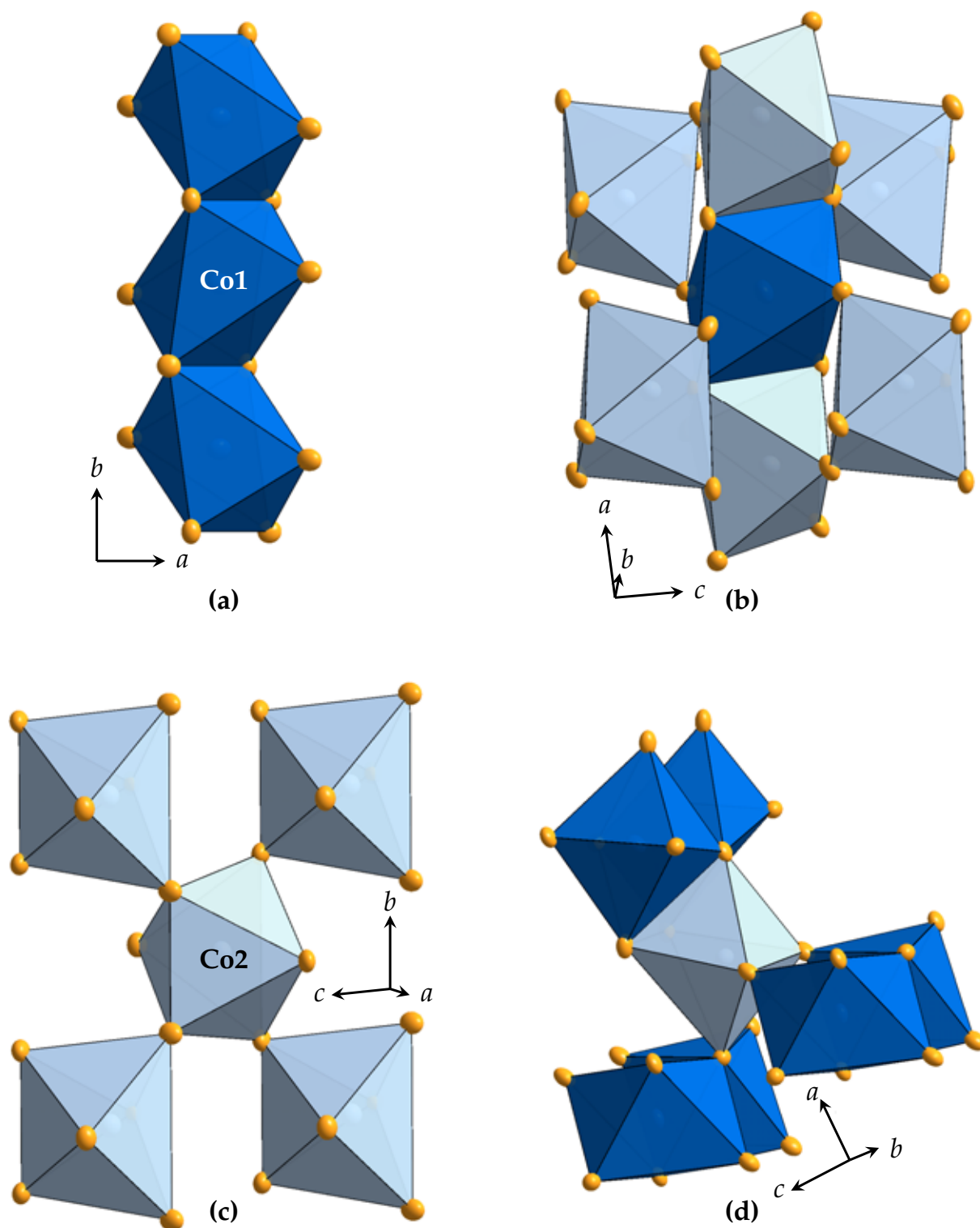


Figure 6.2. All possible arrangements of the CoO_6 octahedra in Co_2SiO_4 (see text for details). (a) Co1O_6 neighbours of Co1O_6 , (b) Co2O_6 neighbours of Co1O_6 , (c) Co2O_6 neighbours of Co2O_6 and (d) Co1O_6 neighbours of Co2O_6

dimensions of $2 \times 2 \times 2 \text{ mm}^3$ and a mass of 37.1 mg was cut from the as-grown Co_2SiO_4 crystal, with the three axes of the unit cell along the edges of the cube. The sample was placed in a plastic container and brought into a measuring position using a straw. The temperature dependences of the magnetization $M(T)$ were measured on warming from 5 K to 330 K in a field of 5 T after a field cooling (FC) or zero field cooling (ZFC) procedure. The difference between the FC and ZFC measurements was found to be negligible.

6.2.1. Paramagnetic region

The dc magnetic susceptibility χ of a Co-olivine single crystal is plotted as a function of temperature in figure 6.3. Hereafter, we denote $\chi(T)$ with an applied field along the a , b and c crystallographic axes by χ_a , χ_b and χ_c , respectively. The average magnetic susceptibility χ_{av} , defined as $\chi_{\text{av}} = (\chi_a + \chi_b + \chi_c)/3$, is shown in the inset to figure 6.3.

As seen in figure 6.4, the inverse magnetic susceptibilities $\chi_\alpha^{-1}(T)$ ($\alpha = a, b, c$) are linear in the temperature range from about 80 K up to 330 K indicating a paramagnetic behaviour. The extrapolations of the linear portion of $\chi_\alpha^{-1}(T)$ intersect the negative temperature axis implying that the dominant magnetic interactions are antiferromagnetic by nature. The susceptibility strongly depends on the direction of the applied external magnetic field. That is, the three $\chi_\alpha(T)$ curves do not coincide at least up to 330 K. This indicates a strong magnetic anisotropy in the paramagnetic phase, which can be studied by fitting the observed $\chi(T)$ curves from 80 K to 330 K to the Curie-Weiss law

$$\chi = \frac{C}{T - \theta_{\text{CW}}}, \quad (6.1)$$

where C is the Curie constant and θ_{CW} is the Curie-Weiss temperature.

Any constant, temperature-independent susceptibility terms, such as diamagnetic, Pauli paramagnetic, or instrumental background effects,

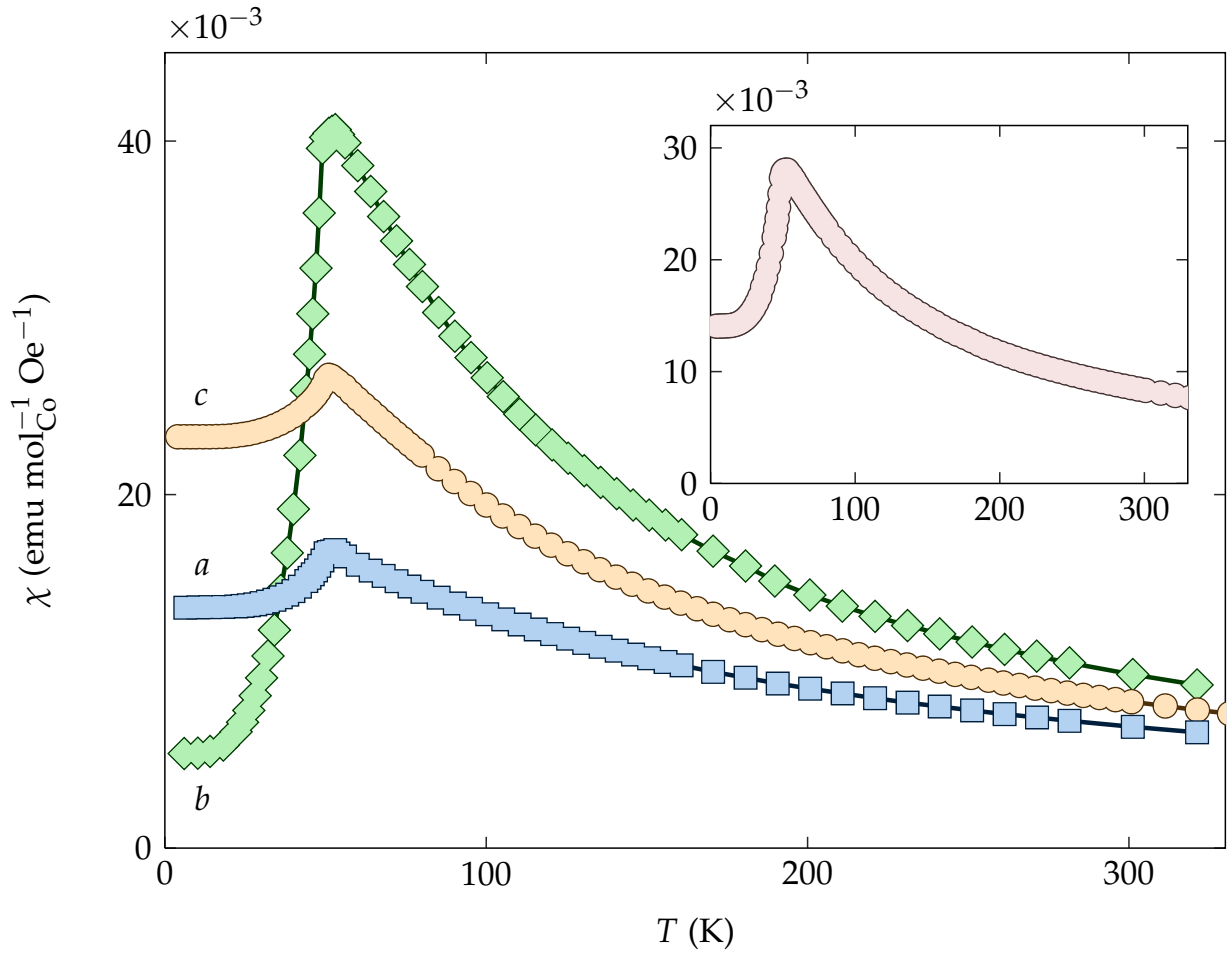


Figure 6.3. Temperature dependencies of the dc magnetic susceptibilities $\chi_\alpha(T)$ ($\alpha = a, b, c$) of Co_2SiO_4 in an applied field of 5 T along the crystallographic axes a, b and c . The inset shows the average magnetic susceptibility χ_{av} , defined as $\chi_{\text{av}} = (\chi_a + \chi_b + \chi_c)/3$.

were taken to be negligible. The best fits were obtained with parameters listed in table 6.1, and results of fits are shown in figure 6.4.

We would like to compare the $\chi(T)$ data reported by Hagemann *et al.* [11] for their polycrystalline Co_2SiO_4 sample with our single-crystal data [100]. For this purpose, we fitted the $\chi_{\text{av}}(T)$ curve (see inset to figure 6.3) to the Curie-Weiss law (equation 6.1). The fitted value of $\theta_{\text{CW}} = -45.7 \pm 0.5 \text{ K}$ is very close to that of -45.5 K reported in [11]. The fitted individual $\theta_{\text{CW}}^\alpha(T)$ ($\alpha = a, b, c$) are also in good agreement with those found in the literature; they are within a 7% deviation from the values determined previously in [24].

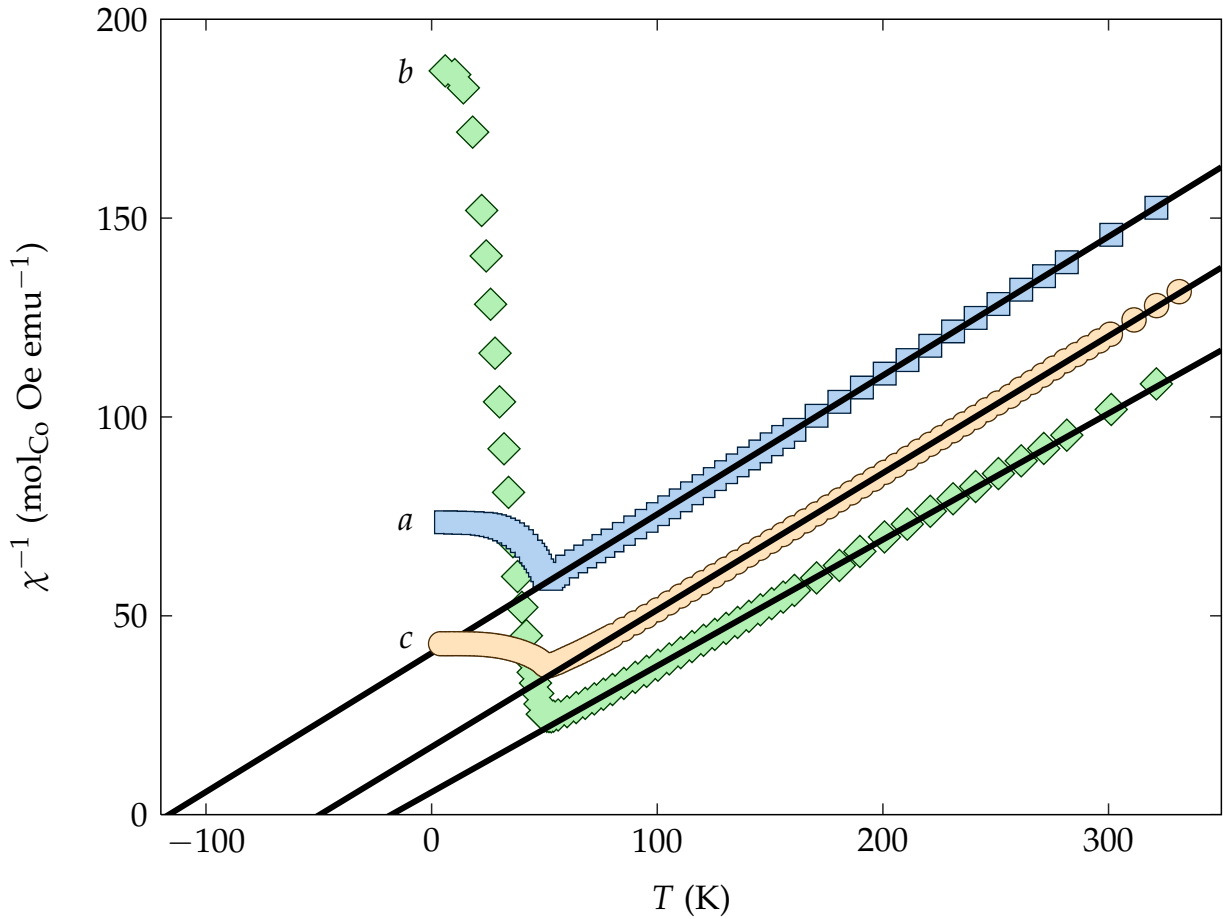


Figure 6.4. Temperature dependencies of the inverse dc magnetic susceptibilities $\chi_{\alpha}^{-1}(T)$ ($\alpha = a, b, c$) of Co_2SiO_4 as measured in an applied field of 5 T along the crystallographic axes a , b and c . The solid lines show a linear fit of the data in the temperature range from 80 K to 330 K to the Curie-Weiss law (see text).

The second and more important quantity which can be determined from the high-temperature data (paramagnetic phase) is the ionic effective magnetic moment. This quantity is calculated from the slope of the linear portion of the experimental $\chi^{-1}(T)$ curve. Namely, in the temperature range where the Curie-Weiss law is obeyed, the effective magnetic moment of an atom/ion can be calculated from the Curie constant C as

$$\mu_{\text{eff}} = \sqrt{\frac{3k_{\text{B}}C}{N_{\text{A}}}} \approx 2.827\sqrt{C}, \quad (6.2)$$

where k_{B} is the Boltzmann constant and N_{A} is Avogadro's number.

Table 6.1. The Curie-Weiss temperatures θ_{CW} , Curie constants C and effective magnetic moments μ_{eff} determined from the Curie-Weiss fits of high-temperature portions of the magnetic susceptibilities $\chi_{\alpha}(T)$ ($\alpha = a, b, c$) for Co_2SiO_4 .

α	θ_{CW} (K)	C (emu K mol ⁻¹)	μ_{eff} (μ_B)
a	-116.4 ± 0.9	2.87 ± 0.01	4.79 ± 0.01
b	-17.9 ± 1.5	3.15 ± 0.03	5.02 ± 0.03
c	-49.5 ± 0.6	2.91 ± 0.01	4.82 ± 0.01
av*	-45.7 ± 0.5	2.88 ± 0.01	4.80 ± 0.01

* From the fit of the average magnetic susceptibility χ_{av} (see text).

When only the spin moment is active for the Co^{2+} ion of the electron configuration $3d^7$ in the high-spin state ($S = 3/2$), we obtain $\mu_{\text{eff}} = g_S \sqrt{S(S+1)} \approx 3.87 \mu_B$, with $g_S = 2$. When the full orbital contribution ($L = 3$) is considered, $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} \approx 6.63 \mu_B$, with $g_J \approx 1.33$ for the total angular momentum $J = S + L$. The experimental $\mu_{\text{eff}}^{\alpha}$ ($\alpha = a, b, c$) values for the Co^{2+} ions in our Co_2SiO_4 lie between these limits (see table 6.1).

The average moment $\mu_{\text{eff}}^{\text{av}}$ of $4.80 \pm 0.01 \mu_B$ is obtained from the fitting of the average magnetic susceptibility χ_{av} . The value of $\mu_{\text{eff}}^{\text{av}}$ found here is close to those of $4.77 \mu_B$ and $4.87 \pm 0.10 \mu_B$ reported in [11] and [101], respectively. Therefore, the high value of the obtained effective moment in Co_2SiO_4 can be explained by a comparatively large component of the orbital angular momentum. This is in agreement with the observation that the orbital moment is not necessarily quenched in compounds with the 2/3 filled t_{2g} manifold.

It is also important to compare the properties of the cobalt olivine, Co_2SiO_4 , and more widely studied cobalt oxide, CoO . The local environment of the Co^{2+} ions in the Co-olivine is similar to that found in CoO . As far as the magnitude of the magnetic moment is determined primarily by the bonding symmetry of the Co^{2+} ions the magnetic moment of Co_2SiO_4 should be comparable to the moment found in the

cobalt oxide. The measured values for the effective magnetic moment of Co^{2+} in CoO are about $5 \mu_{\text{B}}$ [102–104]. This value is close to that of $4.80 \pm 0.01 \mu_{\text{B}}$ obtained for the average effective moment of Co_2SiO_4 . The literature values for the polycrystalline Co-olivines scatter in the range from $4.60 \mu_{\text{B}}$ to $5.09 \mu_{\text{B}}$ [11, 20, 101, 105, 106].

6.2.2. Magnetically ordered state

Around 50 K an anomaly in $\chi(T)$ is observed and below this temperature pronounced deviations from linearity in the $\chi^{-1}(T)$ plots occur (figures 6.3 and 6.4). The appearance of a relatively sharp peak in the susceptibility indicates the onset of a long-range antiferromagnetic order and correlates well with the negative sign of the obtained Curie-Weiss temperatures θ_{CW} (table 6.1).

The ordering temperature or Néel temperature T_{N} , determined by the temperature at the maximum of the $\chi(T)$ curves [107], is about 51 K. It should be noted that χ_b starts to drop rapidly at a slightly lower temperature of 49 K compared to that of 50 K for both χ_a and χ_c . The small difference of T_{N} for the three directions is consistent with the observation that the peak positions (which is another way to define T_{N}) in the curves of the derivative of the susceptibility, $d\chi/dT$, are located at 47 K for χ_b and 48 K in the case of χ_a and χ_c . In the specific heat measurements carried out on Co_2SiO_4 [28], a sharp anomaly was observed also at about 50 K, which confirms the appearance of magnetic ordering.

The $\chi(T)$ curves in figure 6.3 show strong magnetic anisotropy not only above T_{N} (paramagnetic phase) but also below T_{N} (antiferromagnetically ordered phase). Below the transition temperature, χ_b decreases rapidly with decreasing temperature, but it does not approach zero. This behaviour is in contrast to the χ_a and χ_c curves which decrease only slightly when passing T_{N} and stay almost constant below 30 K. This result indicates that the easy axis for the antiferromagnetic ordering in Co_2SiO_4 is the b axis. This is in agreement with the results of [10],

where it was shown that the magnetization along the b axis exhibits a metamagnetic-like double step transition at $H = 18$ T, while those of the a and c axes show no anomaly up to 19 T. Note that the predominant antiferromagnetic coupling of Co_2SiO_4 is so strong that the magnetization along the b axis does not saturate at 4.2 K even with an external field of 41 T [10].

The distinct difference in the temperature dependencies between the magnetic susceptibilities measured below T_N along different crystallographic directions is typical for antiferromagnetic single crystals. If an anisotropy precludes a rotation of the magnetic moments, a field applied along them gives rise to a susceptibility decreasing to zero when temperature decreases from T_N to 0 K ($\chi_{\parallel}$). When the field is perpendicular to the moments, the susceptibility remains nearly constant ($\chi_{\perp}$).

In Co_2SiO_4 , the following general trend of $\chi(T)$ is observed. The susceptibility χ_b has a strong $\chi_{\parallel}$ character, whereas χ_a and χ_c are dominated by $\chi_{\perp}$. This indicates that the main direction of the moments is along the b axis. The non-zero value of χ_b at zero temperature is most probably caused by the canting of the magnetic moments. That is, the magnetic structure is expected to be non-collinear and the canting is responsible for a certain amount of $\chi_{\perp}$ in χ_b . Moreover, the slight decrease of both χ_a and χ_c below T_N is due to the presence of some $\chi_{\parallel}$ contribution in the susceptibilities along the a and c axes. The susceptibility $\chi_a(T)$ is lower than $\chi_c(T)$ indicating the smaller component of the total magnetic moment to be along the a axis.

6.3. Symmetry analysis of the magnetic structure

The thermal evolution of the experimental neutron powder diffraction patterns collected below 100 K with small temperature increments of 1 K is presented in figure 6.5. The neutron patterns show the appearance of new

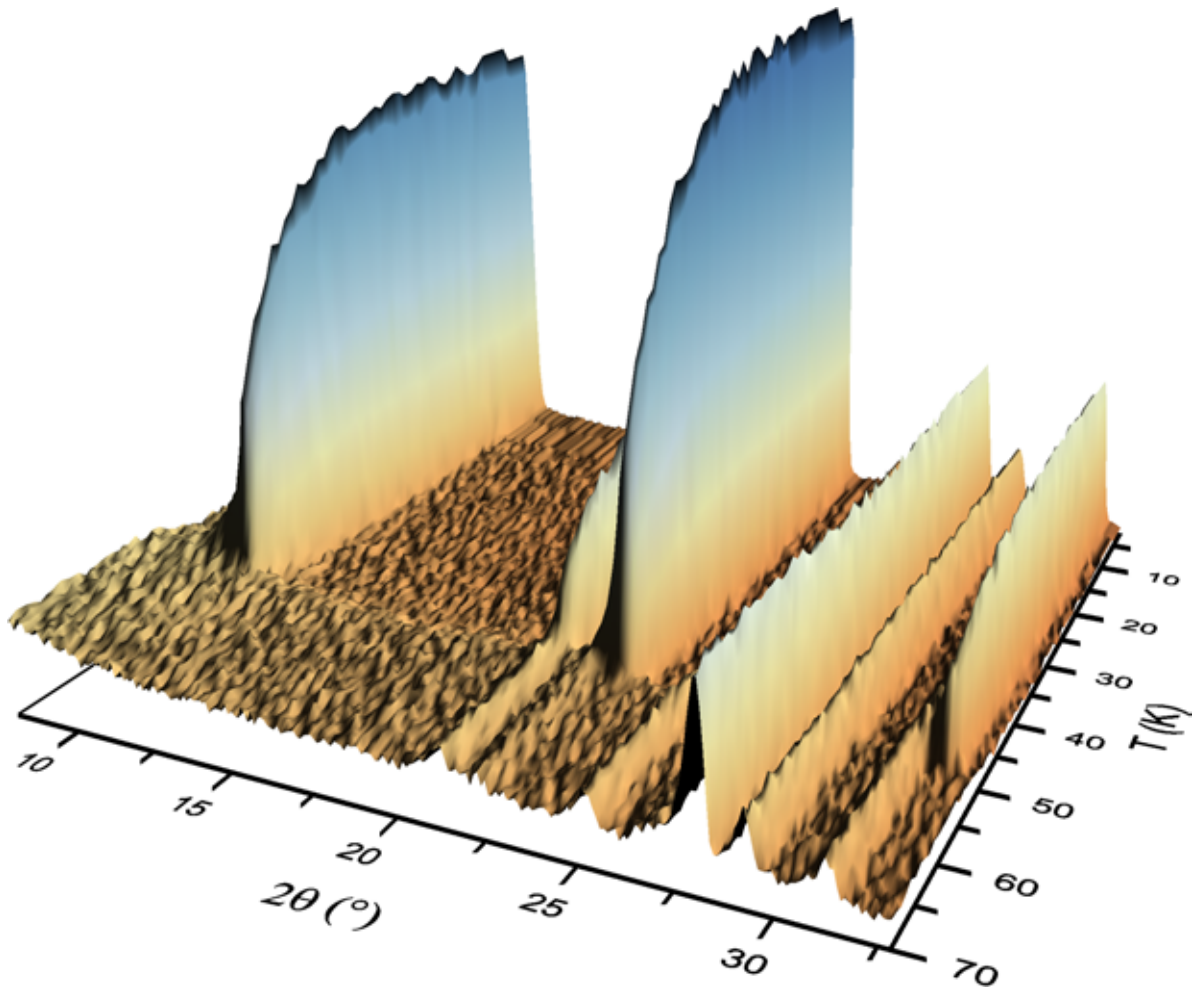


Figure 6.5. Thermal evolution of the neutron powder diffraction patterns of Co_2SiO_4 collected in the temperature range from 5 K to 100 K with temperature increment of 1 K.

Bragg peaks at about 50 K which are forbidden in the crystallographic space group $Pnma$. Allowed reflections are $(h00)$ where $h = 2n$; $(0k0)$: $k = 2n$; $(00l)$: $l = 2n$; $(hk0)$: $h = 2n$ and $(0kl)$: $k + l = 2n$ [15].

Figure 6.6 shows a typical neutron powder diffraction pattern of Co_2SiO_4 measured at 5 K as well as the results of the Rietveld refinement. The nuclear and magnetic structures were refined simultaneously in the antiferromagnetic region.

Along with anomalies observed in the specific heat (figure 4.5) and dc susceptibility measurements (figure 6.3), the presence of the new reflections can be attributed to the long-range magnetic ordering. The

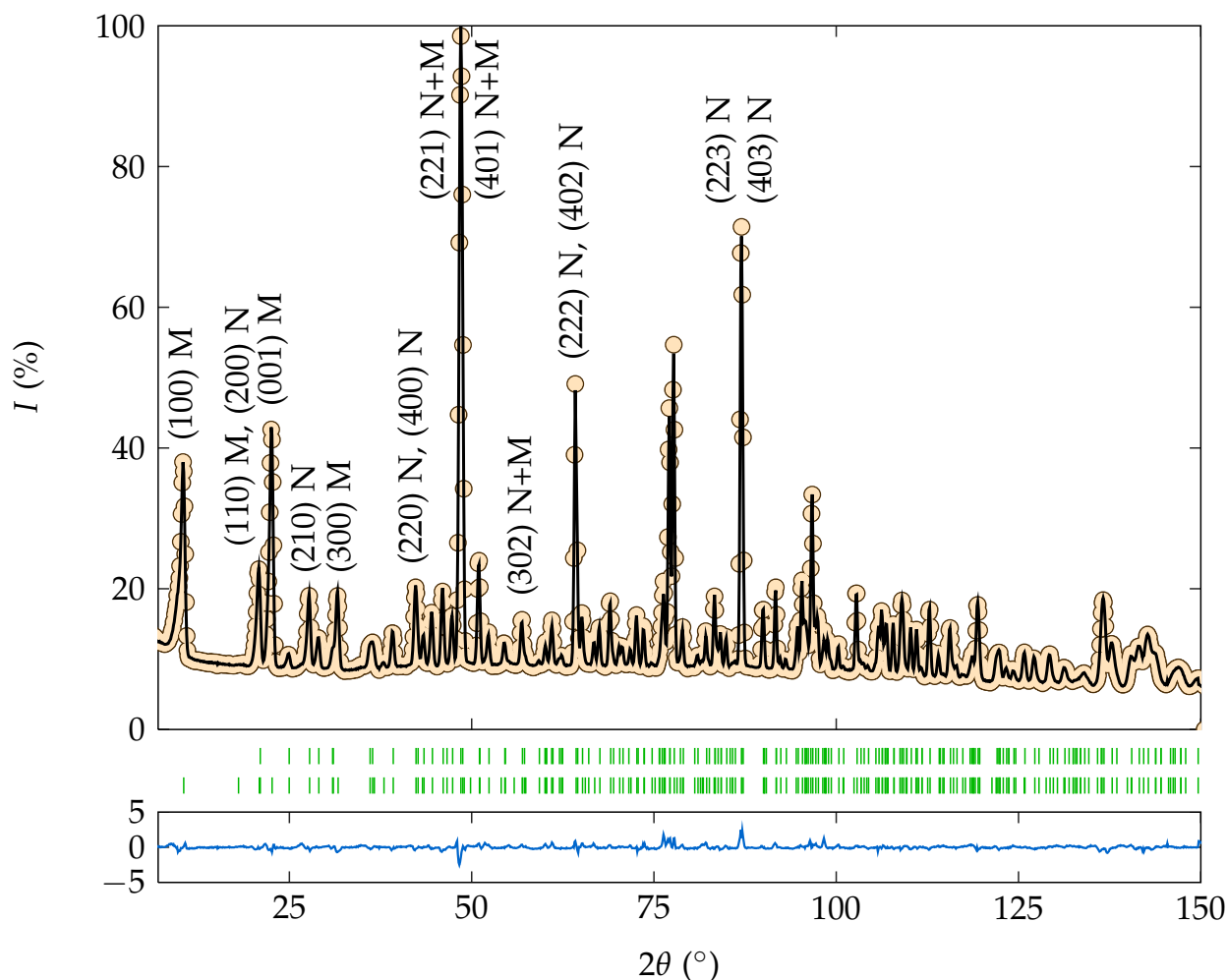


Figure 6.6. Neutron powder diffraction pattern (○), Rietveld fit (—) and allowed Bragg reflections (|) for Co_2SiO_4 at 5 K. The lower trace is the difference, $I_{\text{obs}} - I_{\text{calc}}$, on the same scale. The upper row of the Bragg reflections shows the nuclear phase and the lower row represents the magnetic peaks. Some of the Bragg peaks are indexed. ‘N’ and ‘M’ denote the nuclear and magnetic contributions, respectively.

strongest pure magnetic reflections are (001), (100), (110) and (300); they are labelled by ‘M’ in figure 6.6. Also there is an additional contribution to the intensity of the nuclear reflections, as can be seen, for instance, in the contribution to Bragg peaks at $2\theta \approx 48.5^\circ$ corresponding to (221) and (401). For the reflection (302) at $2\theta \approx 57^\circ$ about a half of the intensity at 5 K is due to magnetic scattering.

All observed superstructure reflections can be indexed with a magnetic propagation vector $\mathbf{k} = (0,0,0)$. This means no loss in translational

symmetry coming from the spin arrangement and identity of the magnetic and chemical cells. The chemical space group of Co_2SiO_4 remains $Pnma$ down to 2.5 K according to our synchrotron (section 3.1.2) and present neutron diffraction data. In this case, the propagation vector group G_k has the whole symmetry of the point group mmm (D_{2h}), which contains the rotational parts of the crystallographic space group $Pnma$ (D_{2h}^{16}).

The eight magnetic Co ions per unit cell in Co_2SiO_4 , which are distributed on two special $4a$ and $4c$ sites of the space group $Pnma$, produce two magnetic sublattices associated with these sites. In order to generate all possible magnetic structures that are compatible with the crystal structure, we have used the program for calculating irreducible representations BASIREPS from the FULLPROF suite [73]. In the framework of the representation analysis, which has been developed by Bertaut [108], it was shown that there are only eight possible one-dimensional irreducible representations Γ_i ($i = 1, 2, \dots, 8$) of mmm associated with the propagation vector $\mathbf{k} = (0, 0, 0)$. They are summarized in table 6.2 for the case of the crystallographic space group $Pnma$. The magnetic (Shubnikov) groups are also given together with the corresponding magnetic configurations for the $4a$ and $4c$ sites of $Pnma$ (table 6.2).

The fourfold positions ($4a$ and $4c$ in our case) allow one ferromagnetic and three antiferromagnetic configurations or modes:

$$\begin{aligned} F &= S_1 + S_2 + S_3 + S_4, \\ G &= S_1 - S_2 + S_3 - S_4, \\ A &= S_1 - S_2 - S_3 + S_4, \\ C &= S_1 + S_2 - S_3 - S_4, \end{aligned} \tag{6.3}$$

where S_n indicates the spin for the n -fold positions.

This means that a vector F_x , for instance, has a maximum value when all the moments are aligned ferromagnetically and is zero for any antiferromagnetic combination. It characterizes a ferromagnetic $F(++++)$ configuration. In a similar manner, the G_x , A_x and C_x

Table 6.2. The irreducible representations Γ_i and magnetic (Shubnikov) groups of $Pnma$ associated with $\mathbf{k} = (0,0,0)$ as well as the corresponding magnetic modes along x, y, z for the $4c$ and $4a$ positions.

Representation	4a			4c			Magnetic group
	x	y	z	x	y	z	
Γ_1	G	C	A	.	C	.	$Pnma$
Γ_2	C	G	F	C	.	F	$Pn'm'a$
Γ_3	F	A	C	F	.	C	$Pnm'a'$
Γ_4	A	F	G	.	F	.	$Pn'ma'$
Γ_5	.	.	.	A	.	G	$Pn'm'a'$
Γ_6	.	.	.	.	A	.	$Pnma'$
Γ_7	.	.	.	.	G	.	$Pn'ma$
Γ_8	.	.	.	G	.	A	$Pnm'a$

basis vectors as well as their y and z components can be obtained from equation 6.3. Finally, the sign change of the three magnetic moment projections μ_x, μ_y, μ_z for the sites $4a$ and $4c$ under those eight representations are listed in table 6.3 [109]. The symbols $F(++++)$, $G(+--+)$, $A(+--+)$, $C(++--)$ correspond to Bertaut's notations [108].

Although there are no general extinction rules, the very strong intensities of the magnetic reflections (100) and (001) allow a preliminary statement to be made concerning the magnetic structure. First, we consider that both the Co1 and Co2 ions contribute to magnetism in Co_2SiO_4 and that the basis functions for $4a$ and $4c$ belong to the same irreducible representation (this is usually the case). That is, we restrict the search to the magnetic structures having the highest possible symmetry.

The representations from Γ_5 to Γ_8 exclude any magnetic moment on Co1 (table 6.2) and cannot take part in the solution. The presence of the strong magnetic reflections (100) and (001) indicates that the primary component of the total magnetic moment is perpendicular to both the a and c axes at the same time. This is consistent with the b axis being

Table 6.3. The magnetic modes of the non-equivalent positions $4a$ and $4c$ for the eight possible magnetic space groups of $Pnma$ associated with $\mathbf{k} = (0,0,0)$.

	Position	$Pnma$				$Pn'm'a$				$Pnm'a'$				$Pn'ma'$			
i	$4a$	G	C	A	C	G	F	F	A	C	A	F	G				
1	$0, 0, 0$	+	+	+	+	+	+	+	+	+	+	+	+				
2	$0,1/2,0$	−	+	−	+	−	+	+	−	+	−	+	−				
3	$1/2,1/2,1/2$	+	−	−	−	+	+	+	−	−	−	+	+				
4	$1/2, 0, 1/2$	−	−	+	−	−	+	+	+	−	+	+	−				
	$4c$	.	C	.	C	.	F	F	.	C	.	F	.				
1	$x,1/4,z$	.	+	.	+	.	+	+	.	+	.	+	.				
2	$-x,3/4,-z$	.	+	.	+	.	+	+	.	+	.	+	.				
3	$1/2 + x,1/4,1/2 - z$	.	−	.	−	.	+	+	.	−	.	+	.				
4	$1/2 - x,3/4,1/2 + z$	.	−	.	−	.	+	+	.	−	.	+	.				

	Position	$Pn'm'a'$				$Pnma'$				$Pn'ma$				$Pnm'a$			
i	$4a$	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
1	$0, 0, 0$	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
2	$0,1/2,0$	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
3	$1/2,1/2,1/2$	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
4	$1/2, 0, 1/2$	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
	$4c$	A	.	G	.	A	.	.	G	.	G	.	A				
1	$x,1/4,z$	+	.	+	.	+	.	.	+	.	+	.	+				
2	$-x,3/4,-z$	−	.	−	.	−	.	.	−	.	−	.	−				
3	$1/2 + x,1/4,1/2 - z$	−	.	+	.	−	.	.	+	.	+	.	−				
4	$1/2 - x,3/4,1/2 + z$	+	.	−	.	+	.	.	−	.	−	.	+				

the easy axis according to magnetic susceptibility measurements (see section 6.2.2). Therefore, the contribution of Co^{2+} to (100) and (001) can only appear due to the mode C_y taking into account the extinction rules for the $4c$ site [110–112]. The same conclusion can be drawn also for the $4a$ site according to the limiting conditions from [113]. Hence the only irreducible representation consistent with these considerations is Γ_1 . This corresponds to the magnetic (Shubnikov) group $Pnma$ which 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 $4a$. This is also in agreement with the susceptibility measurements, which suggest the canted antiferromagnetic structure (section 6.2).

Good agreement between the observed and calculated intensities of the Co_2SiO_4 neutron diffraction patterns (see figure 6.6 as an illustration) indicates the correctness of the model used. Note that the single-crystal investigations make it possible to obtain higher accuracy in determination of both the nuclear and magnetic structure parameters. Therefore, the neutron diffraction experiments on a single crystal were performed in order to verify the model of the Co_2SiO_4 magnetic structure at low temperature (see section 4.4). Our single-crystal neutron diffraction results are found to be in perfect agreement with the powder data.

If the spin components of the two different ions belong to various one-dimensional irreducible representations, different magnetic groups would be involved and the ‘global magnetic symmetry’ would be the intersection of these two magnetic groups. In that case a ‘global Shubnikov group’ is of lower symmetry than the Shubnikov groups associated with the representations of the individual ions. From the point of view of representation theory there is no conceptual difficulty in admitting that in the same crystallographic space group there might be spin components belonging to different representations.

An example is TbFeO_3 [114], where it was found at 1.5 K that the Fe spins are in the G_x mode belonging to Γ_4 or $Pb'n'm$ and the Tb spins are in a non-collinear A_xG_y arrangement belonging to Γ_8 or $Pbnm'$. These two magnetic groups have the intersection $P2'_12'_12_1$. Moreover, there are also examples where the interactions between ions of the same nature sited in non-equivalent crystallographic positions lead to a lower symmetry than that associated with their individual representations. For instance, in $\text{Tb}_5\text{Si}_{2.2}\text{Ge}_{1.8}$ the Tb atoms are distributed among two $8d$ and one $4c$ sites of the space group $Pnma$. Below 75 K the magnetic structure of this

compound can only be described using the basis vectors of two different irreducible representations Γ_3 and Γ_7 [115].

Therefore, one can consider all the possible 32 intersections of 4 irreducible representations for the 4a site and those 8 representations for the 4c site. We have tested these variations and have found only a good agreement between fit and data for the intersections $G_x C_y A_z$ for Co1 as well as C_y for Co2. This again corresponds to Γ_1 or $Pnma$ for both Co1 and Co2 and is in agreement with the single Néel temperature observed for Co_2SiO_4 in different experiments. The reliability factors for this solution are at least ten times smaller than those for other configurations.

The Cartesian (μ_x , μ_y and μ_z) and spherical (μ , ϕ and θ) components of both the Co1 and Co2 magnetic moments are given in table 6.4. The magnetic structure of Co_2SiO_4 corresponding to the magnetic (Shubnikov) group $Pnma$ is shown in figure 6.7. The magnetic moments of Co2 have a collinear arrangement along b , whereas the Co1 moments are canted with respect to all crystallographic axes.

The canting angles for Co1 calculated from the refined magnetic moment values at 2.5 K are about 72° , 21° and 80° with respect to the a ,

Table 6.4. The Cartesian (μ_x , μ_y and μ_z) and spherical (μ , ϕ and θ) components of the Co1 and Co2 magnetic moments according to the single-crystal neutron diffraction data at 2.5 K. The directions of the magnetic moments for other cobalt ions in the unit cell could easily be obtained using the magnetic modes for the Schubnikov group $Pnma$ (see table 6.3)

	Co1 (0,0,0)	Co2 (x,1/4,z)
μ_x (μ_B)	1.18 ± 0.05	—
μ_y (μ_B)	3.61 ± 0.04	3.37 ± 0.04
μ_z (μ_B)	0.66 ± 0.18	—
μ (μ_B)	3.86 ± 0.05	3.37 ± 0.04
ϕ ($^\circ$)	71.9 ± 0.7	90
θ ($^\circ$)	80.2 ± 2.7	90

$$\chi^2 = 2.23, R[F^2 > 2\sigma(F^2)] = 0.033, wR(F^2) = 0.044.$$

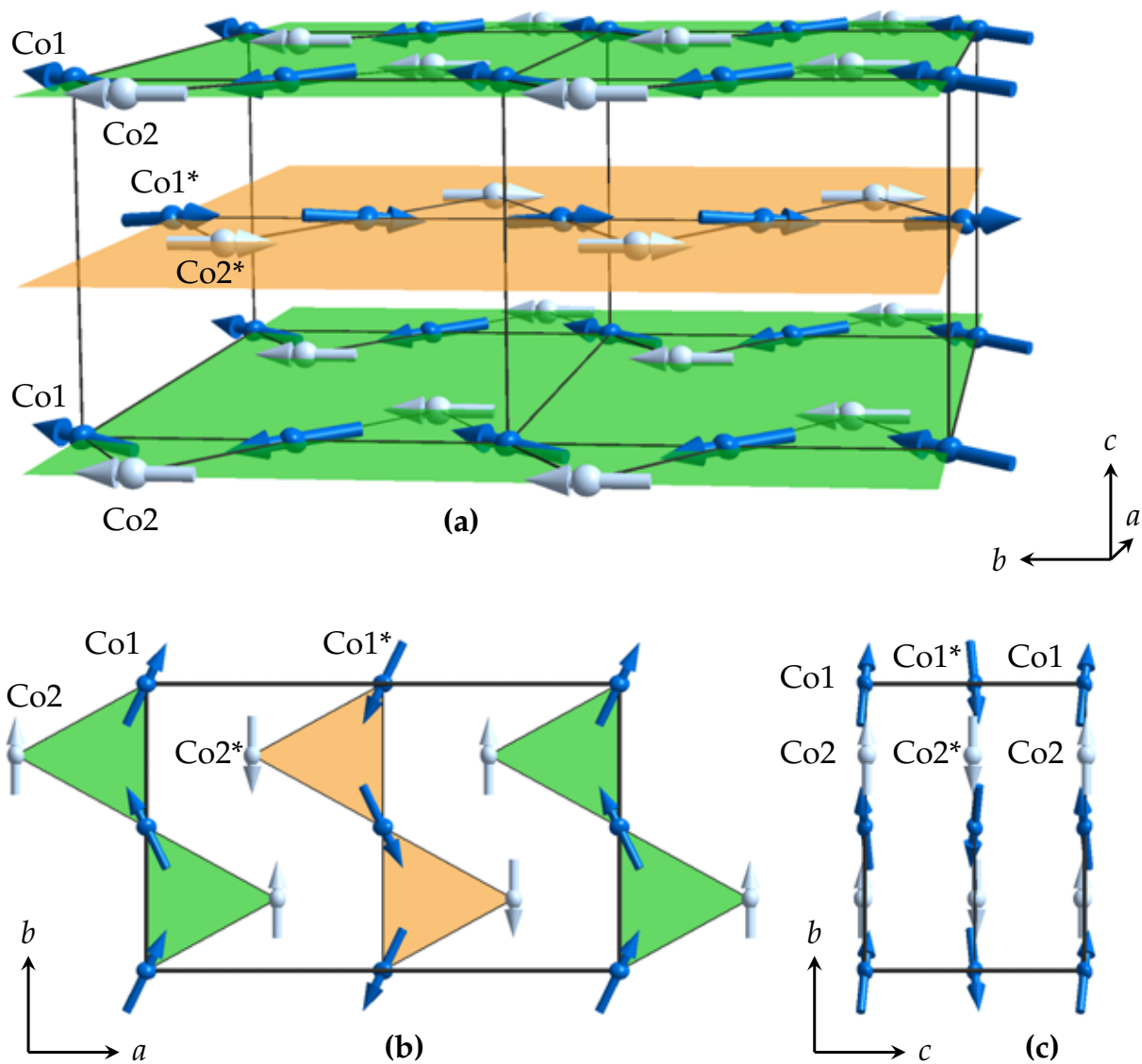


Figure 6.7. (a) Graphical representation of the magnetic structure of Co_2SiO_4 below 50 K. The non-magnetic atoms (Si and O) were excluded for simplicity. The figure shows the zigzag chains of Co in the layers perpendicular to c axis. (b) Projection of the magnetic structure on the ab plane. (c) Projection of the magnetic structure on the bc plane.

b , and c axes. This qualitatively confirms the magnetic model which was obtained by fitting the neutron diffraction data of Co_2SiO_4 collected at 4.2 K [22, 23]. 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; see table 6.4).

6.4. Thermal evolution of the magnetic structure

First we consider the thermal evolution of the crystal structure of Co_2SiO_4 in terms of the Co–O interatomic distances and Co–O–Co angles which are involved in the superexchange magnetic interactions.

Increasing temperature causes a smooth, almost linear expansion of the average Co–O distance. The slope coefficients for the individual interatomic distances slightly differ from each other as well as from the average distance, but the difference is not significant taking into account the experimental uncertainty. In general, variations of the Co–O interatomic distances with temperature are smaller than 1%. The same is true for the O–Co–O angles (figure 6.8): most of them remain constant within the experimental error. The powder neutron diffraction data correspond to the single-crystal measurement. There might be a small indication of the magnetic phase transition near 50 K in the Co–O distances. However, the precision of atomic coordinates and hence interatomic distances is principally reduced with respect to the determination of lattice parameters.

Now, we would like to consider the magnetic moments per Co^{2+} ion for the two cobalt sublattices, obtained from the neutron diffraction data. The temperature dependence of the magnetic moments per Co1 and Co2 ions is presented in figure 6.9. Besides the above mentioned powder and single-crystal (S1) measurements, additional single-crystal neutron diffraction experiments (S2) at several temperatures between 2 K and 45 K were carried out. Here, only a limited number of Bragg reflections with magnetic contribution was measured (from 23 to 95 reflections).

For a simple antiferromagnetic structure, the temperature dependence of the magnetic moment μ in the conventional molecular-field model can be expressed as

$$\frac{\mu}{\mu_0} = B_S \left(\frac{3S}{S+1} \frac{T_N}{T} \frac{\mu}{\mu_0} \right), \quad (6.4)$$

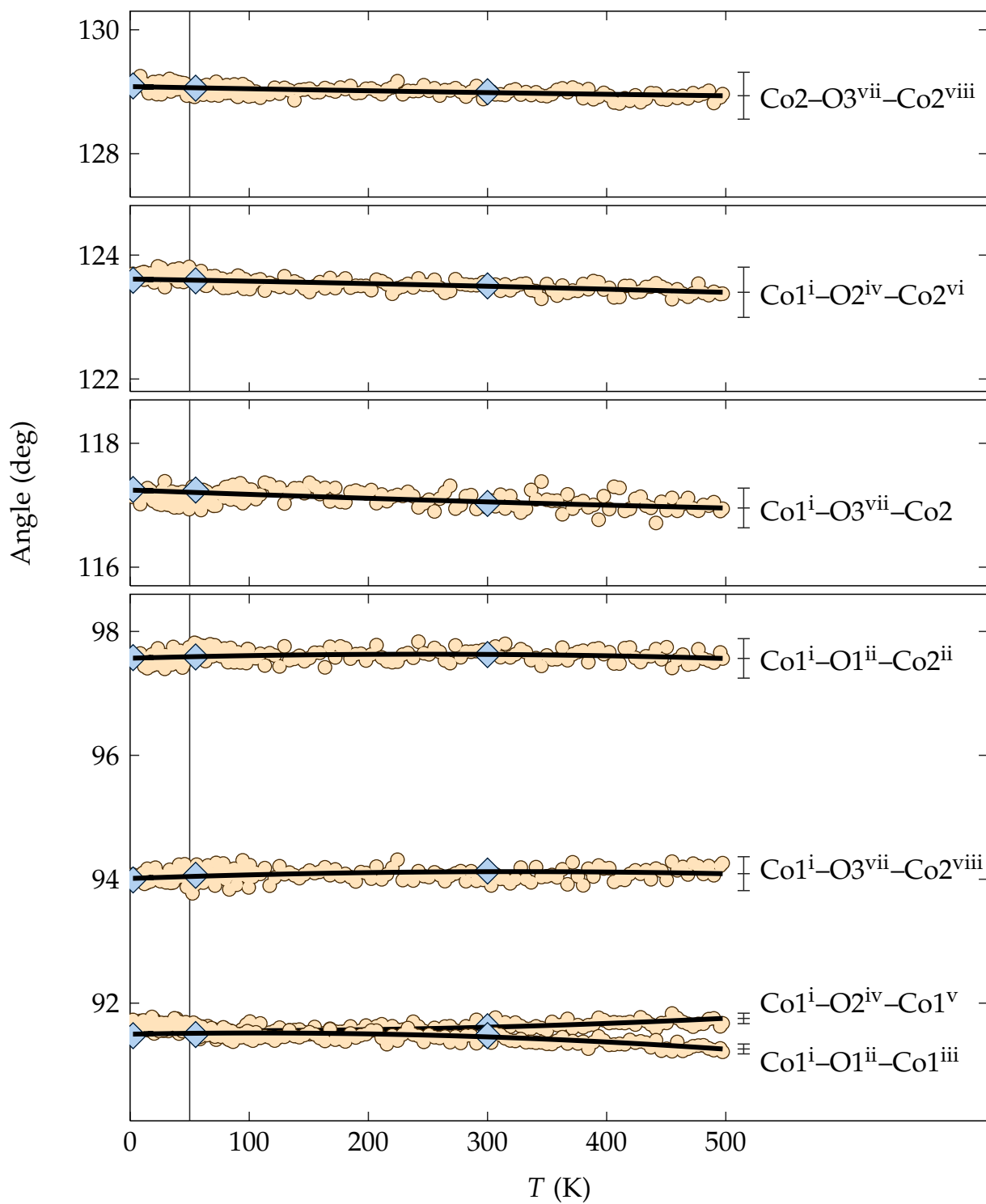


Figure 6.8. Temperature dependence of the Co–O–Co angles for Co_2SiO_4 . Circles (○) mark the results of the powder neutron diffraction measurements (error bars shown at the right) whereas rhombs (◊) mark the results of the single-crystal neutron diffraction measurements (error bars from the refinement are smaller than the symbols). The fits (—) are used as guides to the eye (second order polynomial fit). See table 7.3 for the symmetry codes.

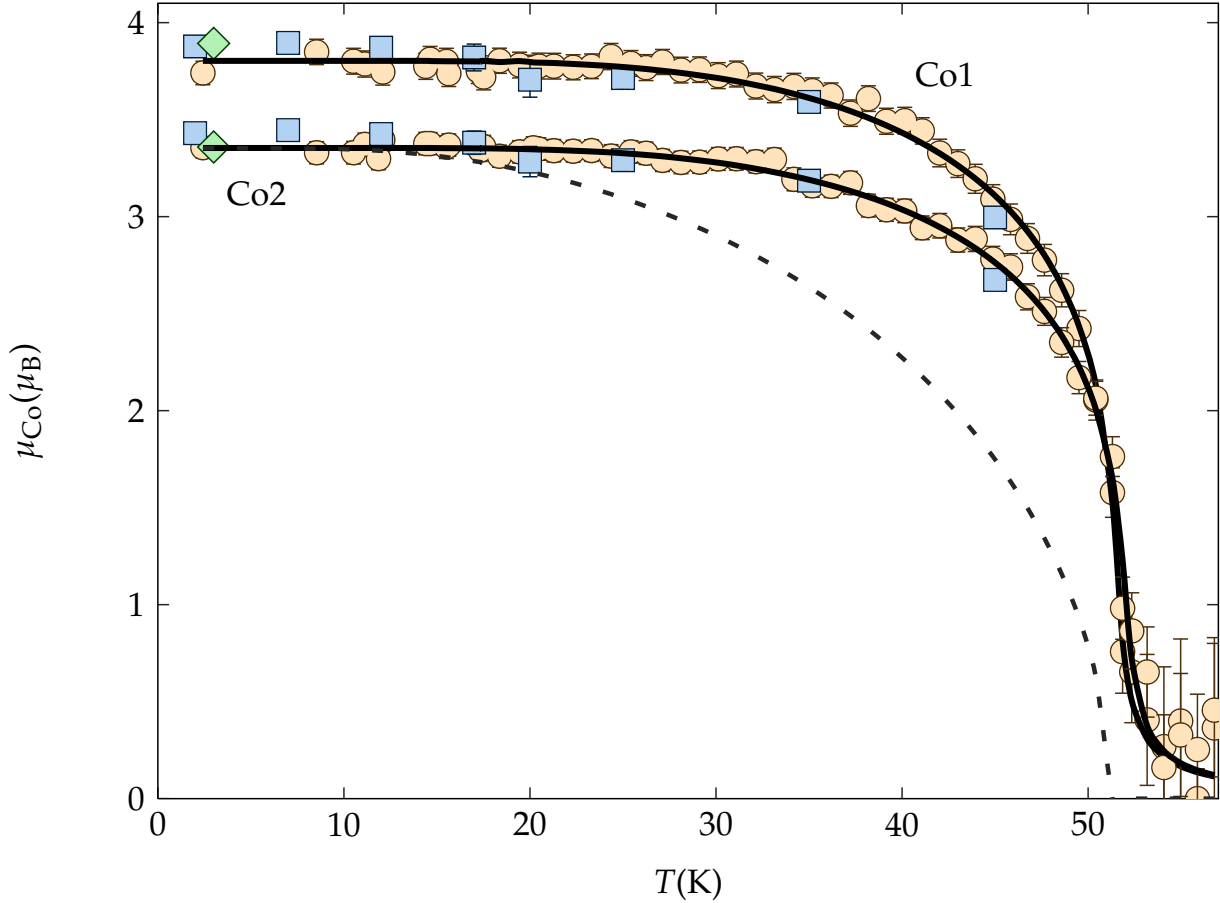


Figure 6.9. Temperature dependence of the Co magnetic moment for Co_2SiO_4 . The experimental data from single-crystal ($\diamond$ — S1 and $\square$ — S2) neutron diffraction experiments and powder ($\circ$) neutron diffraction measurements are shown together with fitting curves in the strongly modified molecular field model ($h \approx 0.62$, $a \approx 0.54$) for $S = 3/2$. The dashed line is an example of the deviation of $\mu_{\text{Co2}}(T)$ from the conventional molecular field model ($h = 0$, $a = 0$) for the spin $S = 3/2$.

where S is the spin of the system, μ_0 is the magnetic moment at $T = 0$ K, and B_S is the Brillouin function

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right).$$

In a first approach, we have attempted to fit the experimental data using the conventional molecular field model with $S = 3/2$ (high-spin state of Co^{2+}). An important feature of the dependencies in figure 6.9 is a very sharp increase of μ just below the Néel temperature. The

experimental magnetic moment values go much higher than the curve described by equation 6.4.

To compensate for this discrepancy, a modified molecular field model [116] was applied, which differs from the conventional form by the additional fitting parameters h and a ,

$$\frac{\mu}{\mu_0} = B_S \left(\frac{h}{T} + \frac{3S}{S+1} \frac{T_N[1 + a(\mu/\mu_0)]}{T} \frac{\mu}{\mu_0} \right), \quad (6.5)$$

where h is a fictive magnetic field modeling the effect of short-range magnetic order above T_N and a is a magnetoelastic parameter describing the magnetostrictive shift of T_N [116, 117]. Thus, we fitted the magnetic moment $\mu(T)$ curves (figure 6.9) to the modified molecular field model (equation 6.5) for HS Co^{2+} . Table 6.5 summarizes the fitted parameters.

Note that the magnetic anisotropy found in Co_2SiO_4 according to the magnetic susceptibility measurements (section 6.2) in the paramagnetic phase also cannot be explained by the conventional molecular field theory of antiferromagnetism, because such theory would predict that $\chi_\alpha(T)$ ($\alpha = a, b, c$) curves coincide above T_N [107].

The fitted values of the parameters h and a for the Co1 curve are close to those for Co2. Therefore, the ordering with decreasing temperature evolves with almost the same velocity for the two magnetic sublattices, although both end up with different resultant magnetic moments per ion. The non-zero values of the parameter h are in agreement with

Table 6.5. Coefficients from the fit of the experimental Co magnetic moment of Co_2SiO_4 in the modified molecular field model (equation 6.5) with $S = 3/2$.

	Co1 (0,0,0)	Co2 (x,1/4,z)
h	0.61 ± 0.18	0.63 ± 0.20
a	0.54 ± 0.04	0.54 ± 0.04
T_N (K)	49.9 ± 0.5	50.3 ± 0.6
μ (μ_B)	3.84 ± 0.03	3.39 ± 0.03
R^*	0.996	0.993

* according to equation 4.6.

the magnetic pre-ordering in Co_2SiO_4 above the Néel temperature, observed by means of the magnetic excitations measurements with neutron scattering [30].

The analysis of the neutron diffraction data as a function of temperature also shows that there is no change in the magnetic moment directions in the whole temperature range of the magnetically ordered state. As seen from figure 6.10, the Co1 canting angles in spherical representation (ϕ and θ) are independent of temperature within the experimental error. This is in agreement with the strong magnetic

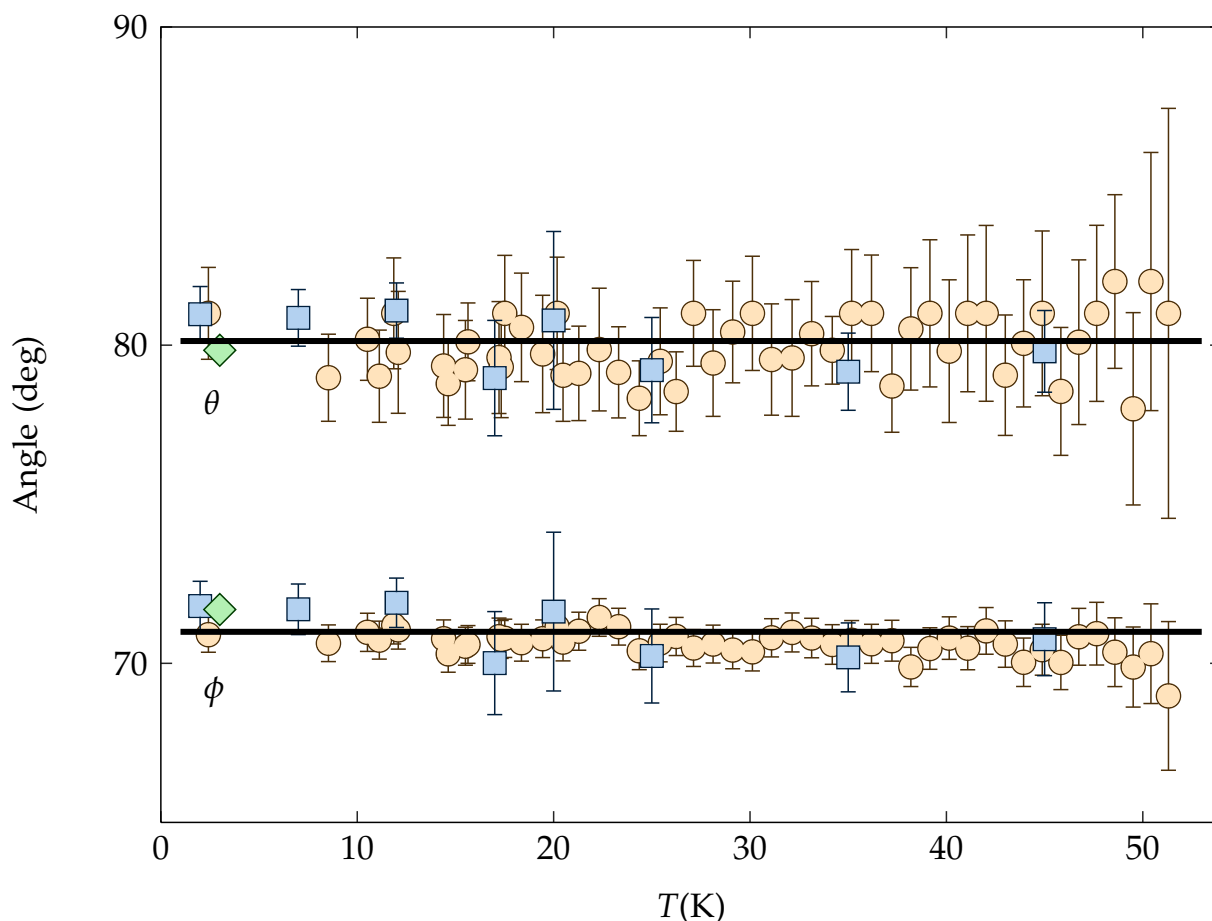


Figure 6.10. Temperature dependencies of the angles (see table 6.4) which describe the direction of the Co1 magnetic moment for Co_2SiO_4 . The experimental data from single-crystal ($\blacklozenge$ — S1 and $\blacksquare$ — S2) neutron diffraction experiments and powder ($\bullet$) neutron diffraction measurements are shown together with fitting curves (linear fit).

anisotropy found in Co_2SiO_4 at least for the temperature range from 5 K up to 330 K (see section [6.2](#)).

Chapter 7

Magnetization densities

In order to get further information on the relative strength of the exchange interactions in Co_2SiO_4 as well as for a graphic representation of the magnetic properties in the unit cell, experiments with polarized neutrons were carried out [100, 118]. The classical polarized neutron diffraction technique [119] 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 where the cross-section is not often polarization dependent and, therefore, the classical method is not applicable.

Up to now very few precise measurements have been made in antiferromagnetic structures with zero propagation vector ($k = 0$) [120]. One type of structures with $k = 0$ is that in which magnetic atoms of opposite spin are related by a centre of symmetry. In such structures the magnetic and nuclear scattering are superimposed, making separation of the nuclear and magnetic parts rather difficult. However, the newly developed technique of spherical neutron polarimetry (SNP) [121] allows a precise measurement of the magnetic scattering in such structures, and this can be applied to determine the antiferromagnetic magnetization distribution. For example, Cr_2O_3 belongs to the class of antiferromagnets

introduced above whose magnetic structure factors were successfully measured using SNP [120].

Another type of antiferromagnetic structures with $k = 0$ is considered if magnetic atoms, which are related by a centre of symmetry, have the same direction of spins. This is the case for Co_2SiO_4 (see section 6.3 for details). In such structures the SNP technique is expected to give the same results as the non-polarized neutron diffraction measurements. Therefore, the only way to study the magnetization density distribution in Co_2SiO_4 is to perform the polarized neutron the flipping-ratio measurements in special conditions, namely in paramagnetic state (above T_N) and in an applied external magnetic field. This gives information about the magnetization induced by the field and can help to understand the dominant magnetic interaction paths.

7.1. Polarized neutron diffraction

The magnetization density distribution for Co_2SiO_4 was obtained from polarized neutron single-crystal diffraction by using the flipping-ratio method. These measurements were performed at the ORPHÉE reactor (Laboratory Léon Brillouin, CEA Saclay, France). Polarized neutron flipping ratios were measured on the lifting-counter diffractometer 5C1 using neutrons with wavelength $\lambda = 0.845 \text{ \AA}$ obtained with a Heusler-alloy monochromator. Data were collected in an external field of 7 T above the ordering temperature ($T_N \approx 50 \text{ K}$) at 70 K and 150 K. For both temperatures, one set of flipping ratios was measured with the field applied parallel to the crystallographic b axis. The higher-order contamination was suppressed by means of an erbium filter to a level of less than 0.01%. The programs MAGLSQ and CHILSQ of the Cambridge Crystallography Subroutine Library [122] were used for least-squares refinements on the measured flipping ratios. The program for Fourier map calculations FOURIER from the FULLPROF suite [73] as well as

an enhanced version [94] of the maximum-entropy method program MEND [123] were used to calculate magnetization densities from the flipping-ratio data.

During the diffraction experiment neutrons with spin parallel (I^+) and antiparallel (I^-) to the axis of preferred magnetization are used. Their intensities may be described according to

$$I^\pm \sim (F_N \pm F_M^\perp)^2, \quad (7.1)$$

where F_N is the nuclear structure factor and $F_M^\perp$ is the projection of the magnetic structure factor F_M into the scattering plane:

$$F_M^\perp = \mathbf{e}_k \times (\mathbf{F}_M \times \mathbf{e}_k), \quad \text{with } \mathbf{e}_k = \mathbf{k}/|\mathbf{k}|, \quad (7.2)$$

where $\mathbf{e}_k$ is the unit vector in the direction of the scattering vector $\mathbf{k}$.

From equation 7.1 it is evident that for a reflection with both structure factors equal, one component of the intensity disappears whereas the other one is linearly polarized.

The polarized and monochromatized neutron beam traverses the cryoflipper where the precession frequency of the neutron spins is induced. By this device, it is possible to ‘flip’ the neutron spins antiparallel or parallel to an applied magnetic field with definite amounts of neutrons (n^+) and (n^-) with intensities I^+ and I^- , respectively.

The single crystalline sample alters the distribution of I^+ and I^- in a characteristic manner (depending on its spin structure), which is detected by a counter. 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^-):

$$R = \frac{I^+}{I^-} = \frac{(F_N + F_M^\perp)^2}{(F_N - F_M^\perp)^2}. \quad (7.3)$$

Taking into account the degree of polarization of the neutrons $p = (n^+ - n^-)/(n^+ + n^-)$, the efficiency e of the flipping as well as the angle

α between F_M and the scattering vector we get:

$$R = \frac{F_N^2 + 2p \sin^2 \alpha F_N F_M + F_M^2}{F_N^2 - 2pe \sin^2 \alpha F_N F_M + F_M^2} = \frac{1 + 2pq^2 \gamma + q^2 \gamma^2}{1 - 2peq^2 \gamma + q^2 \gamma^2}, \quad (7.4)$$

with $\gamma = F_M/F_N$ and $q^2 = \sin^2 \alpha$.

Thus, with measured R and F_N the magnetic structure factors can be derived.

7.2. Magnetization in the paramagnetic region

For the data collection at 70 K, a total of 207 Bragg reflection flipping ratios for Co_2SiO_4 were measured up to $\sin \theta / \lambda \approx 0.62 \text{ \AA}^{-1}$ [$\lambda = 0.845 \text{ \AA}$]. This yielded 113 independent reflections. A data collection at 150 K was also performed up to $\sin \theta / \lambda \approx 0.62 \text{ \AA}^{-1}$ and a total of 218 Bragg reflection flipping ratios were measured yielding 114 independent reflections. The average intensity of each set of equivalent reflections was calculated for up and down polarizations. 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 (see chapters 3 and 4). The measured values were used directly in the refinement using initially the MAGLSQ program. This program works from a very general expression for the flipping ratio in terms of the magnetic and nuclear structure factors. It adjusts the parameters of the magnetic model to obtain a least-squares fit to the observations [124].

The results of the refinement for flipping ratios measured at 70 K in a magnetic field of 7 T parallel to the b axis are summarized in table 7.1. As can be seen from the table, the model which account only the spin components (Model I, table 7.1) of the Co magnetic moment along the b axis does not fit well for the measured flipping ratios ($\chi^2 = 21.1$). Much better agreement ($\chi^2 = 4.6$) is obtained when the data were treated in

terms of the model which assigns a site susceptibility tensor χ (Model II, table 7.1) to each crystallographically independent site [124].

In the work of Gukasov and Brown [124], a new method of modelling the magnetic response of a crystal to an external magnetic field was put forward based on the concept of site susceptibility tensors χ . This formalism can properly and easily describe the local anisotropy in crystals containing several magnetic atoms in the unit cell. The site susceptibility is a second order tensor and hence its symmetry properties are very similar to those of the tensor U^{ij} describing the thermal motion of atoms. By analogy with the atomic displacement parameters, atomic susceptibility parameters (ASPs) were introduced. These ASPs can be visualized as magnetic ellipsoids whose diameters in any given direction are proportional to the magnetization which can be induced in that direction by a field (see [124] for more detail). If the local anisotropy is small, the magnetic ellipsoids approximate to spheres with diameters proportional to the induced magnetization. In other cases, anomalous elongation or flattening of ellipsoids will occur. It was suggested that

Table 7.1. Refinement of different models of the magnetic structure of Co_2SiO_4 from polarized neutron flipping-ratio measurements at 70 K.

Atom	Magnetic moment (μ_B)			
	Model I*	Model II**	Model III**	Model IV**
Co1: μ_S	0.77 ± 0.01	0.78 ± 0.01	0.75 ± 0.01	0.76 ± 0.01
μ_L	—	—	0.22 ± 0.06	0.18 ± 0.05
Co2: μ_S	0.15 ± 0.01	0.16 ± 0.01	0.14 ± 0.01	0.17 ± 0.01
μ_L	—	—	0.04 ± 0.02	0.04 ± 0.02
O1	—	—	—	0.05 ± 0.01
O2	—	—	—	0.03 ± 0.01
O3	—	—	—	0.03 ± 0.01
χ^2 (%)	23.1	5.1	4.3	2.8

* Refinement using the MAGLSQ program (see text).

** Refinement of the components of the Co1 site susceptibility tensor with the CHILSQ program.

anomalous ASPs may mediate a magnetic phase transition [124] in the same way as anomalous ADPs mediate structural transitions.

In the local susceptibility approach [124], the atomic site susceptibility tensor accounts for the linear paramagnetic response of the moments to an applied field of arbitrary direction. The magnetic moments are in general not parallel to the field, and the magnetic structure is not necessarily collinear, as reflected by the non-diagonal terms in the susceptibility tensor.

In Co_2SiO_4 the Co2 ion occupies a site with mirror symmetry m , which leads to the constraints $\chi_{23} = \chi_{12} = 0$ for the susceptibility tensor. On the other hand, the Co1 ion occupies a site with inversion symmetry $\bar{1}$ and, therefore, it is subject to no symmetry constraints. However, the χ_{11} , χ_{33} and χ_{13} susceptibility components could not be obtained from the refinement due to the limited measurements; a field was applied only along one direction (b axis) and, therefore, data are only available for reflections with $k = 0, \pm 1, \pm 2$. Thus, three independent components of χ need to be determined individually for Co1 and only one component for Co2. At both experimental temperatures (70 K and 150 K), the measured flipping ratios were now used to refine the components of the site susceptibility tensors with the CHILSQ program. This program takes into account the orientation of the field for flipping ratio and imposes the necessary symmetry constraints [124].

As it was already mentioned, the Co^{2+} ions in the high-spin state ($S = 3/2$) have a relatively strong spin-orbit coupling that makes the orbital angular momentum contributing to the total magnetic moment. Therefore, we tried to refine the orbital part in addition to the spin one. An improvement of the fit ($\chi^2 = 3.9$) was obtained by the refinement of the orbital component to the total magnetic moment of the Co ions (Model III, table 7.1).

Finally, superexchange and covalency effects were considered by attributing magnetic moments to the O ions. When the magnetic moments on oxygen were allowed to vary (Model IV, table 7.1), a refinement gave a

slightly better fit ($\chi^2 = 2.4$). The detailed results of this refinement are summarized in table 7.2.

The ferromagnetic components induced by external field are found to be comparably small and different for the two cation sites Co1 and Co2. This shows that there is a strong local anisotropy field which prevents full ferromagnetic alignment of the Co moments in a magnetic field up to 7 T. This is in agreement with the bulk magnetization measurements which also indicate large anisotropy (see figure 1.2). It can be seen that the susceptibility tensor component of Co2 remains smaller than that of Co1 at both measured temperatures. At 70 K the anisotropy of Co2 is so strong that a magnetic field of 7 T applied parallel to the b axis induces much smaller moment compared to Co1.

At 70 K one of the non-diagonal elements for Co1, χ_{12} , becomes rather large, showing that the principal axes of the representative ellipsoid do

Table 7.2. Site susceptibilities in Co_2SiO_4 obtained from the refinement on polarized neutron flipping ratios.

T (K)	χ^2 (%)	Atom	Site susceptibilities (μ_B)		
			χ_{22}^*	χ_{23}^*	χ_{12}^*
70	2.8	Co1: μ_S	0.76 ± 0.01	0.09 ± 0.02	0.23 ± 0.02
		μ_L	0.18 ± 0.05	—	—
		Co2: μ_S	0.17 ± 0.01	0**	0**
		μ_L	0.04 ± 0.02	0**	0**
		O1	0.05 ± 0.01	—	—
		O2	0.03 ± 0.01	—	—
		O3	0.03 ± 0.01	—	—
150	1.6	Co1: μ_S	0.30 ± 0.01	0.00 ± 0.01	0.09 ± 0.01
		μ_L	0.08 ± 0.03	—	—
		Co2: μ_S	0.20 ± 0.01	0**	0**
		μ_L	0.05 ± 0.01	0**	0**
		O1	0.02 ± 0.01	—	—
		O2	0.03 ± 0.01	—	—
		O3	0.02 ± 0.01	—	—

* χ_{11} , χ_{33} and χ_{13} susceptibility components could not be obtained from the refinement.

** Symmetry constraints $\chi_{23} = \chi_{12} = 0$ on susceptibility tensor for Co2.

not coincide with the crystal axes (see table 7.2). The orientation of the ellipsoids along the principal axes is very temperature dependent. Within the constraints the principal axes of the ellipsoids at 70 K are found to be oriented parallel to the directions of the magnetic moments in the magnetically ordered state (below 50 K). It should be noted that this orientation is not a consequence of any symmetry imposed on the susceptibilities, but is given naturally by the refinement. On the other hand, well above the magnetic phase transition at 150 K the non-diagonal elements of the susceptibility ellipsoids are close to zero. This shows that whilst the local anisotropy is rather small at high temperatures, it is very strongly enhanced when approaching the ordering temperature. The non-collinear magnetic structure can be seen to be the direct consequence of this high anisotropy; the molecular field leading to magnetic order can only orient the moments along the elongated axes of the ellipsoids, so it is along these directions that the moments finally order. The long axes of the ellipsoids are the easy axes of magnetization of the individual atoms and they do not coincide with the easy magnetization axis of the crystal as a whole.

The refinement also revealed a non-negligible amount of magnetic moments on the three different oxygen positions. We interpret this effect as a delocalization of magnetic moments from the cations towards neighbouring oxygen atoms on superexchange pathways.

7.3. Maximum-entropy reconstruction

In order to verify the correctness of the calculated magnetic moment values induced by a magnetic field and for a graphic representation of the magnetic properties in the unit cell, a Fourier inversion was initially applied to the experimental magnetic structure factors F_M^{obs} .

The results of the Fourier inversion were compared with a maximum-entropy reconstruction, which is another tool to study the density

distribution (see section 5.3 for details). Both techniques gave similar results. However, in comparison to the Fourier map, the MEM map is smoother, without any negative range and seem to be more reliable.

Figure 7.1 shows a superposition of sections of the magnetization density map parallel to the *ac* plane in the Co_2SiO_4 unit cell according to MEM. The most prominent features of the map are regions of positive density close to the Co positions. Due to a large preponderance of the cobalt magnetic moments, small details are not clearly visible on the conventional maps. However, by choosing appropriate scale we were able to observe small but distinct peaks around the oxygen positions (see figure 7.2).

The refinement also clearly shows the evidence for the magnetic moments near the positions of the O atoms (table 7.2). Moreover, the difference X-N Fourier and MEM maps (figure 5.4), which represent *d*-electron densities, show small, but distinct peaks around the oxygen positions. So there is an agreement between the electron and magnetization density distribution maps. This supports the assumption of a partly covalent character of the Co–O bonding and confirms that the superexchange interactions play a major role in the magnetic properties of Co_2SiO_4 . Similar behaviour was already reported by Lottermoser and Fuess [125] in the case of another olivine, Mn_2SiO_4 , where the occurrence of a magnetic moment of the oxygen atoms was shown.

7.4. Magnetic interactions

In order to find a relationship between the magnetic properties and the crystal structure of Co_2SiO_4 as well as to explain the negative signs of the Curie-Weiss temperatures, it is necessary to take into account the relative orientation of the magnetic moments on neighbouring magnetic sites (see figure 7.3).

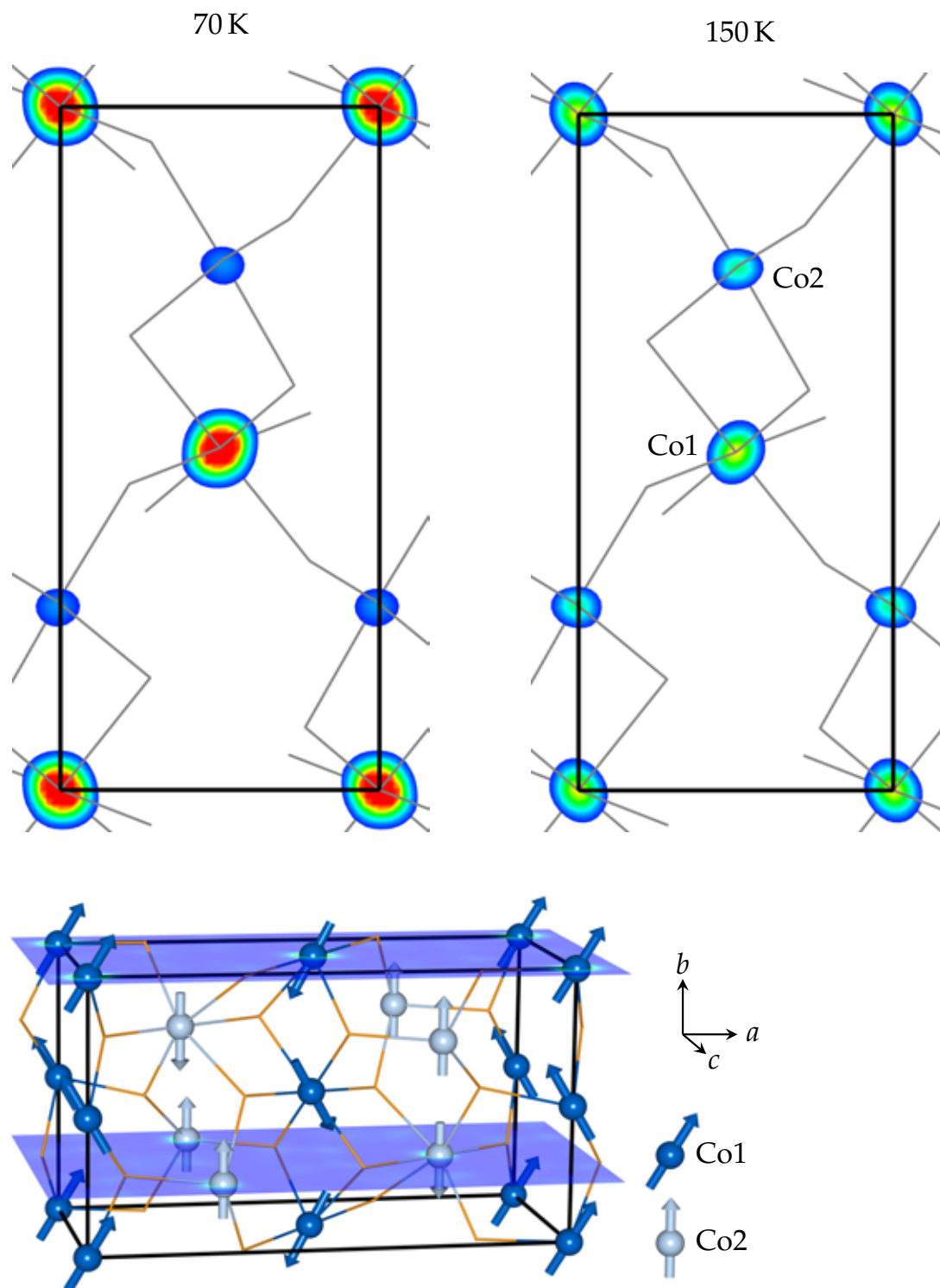


Figure 7.1. Maximum-entropy reconstruction of the density corresponding to the observed magnetization distribution of Co_2SiO_4 at 70 K and 150 K. Superposition of two sections of the magnetization density map perpendicular to the b axis is given for each temperature. These sections are shown in the bottom of figure together with the schematic representation of the magnetic structure. The magnetic moments as determined at 2.5 K are plotted for illustration.

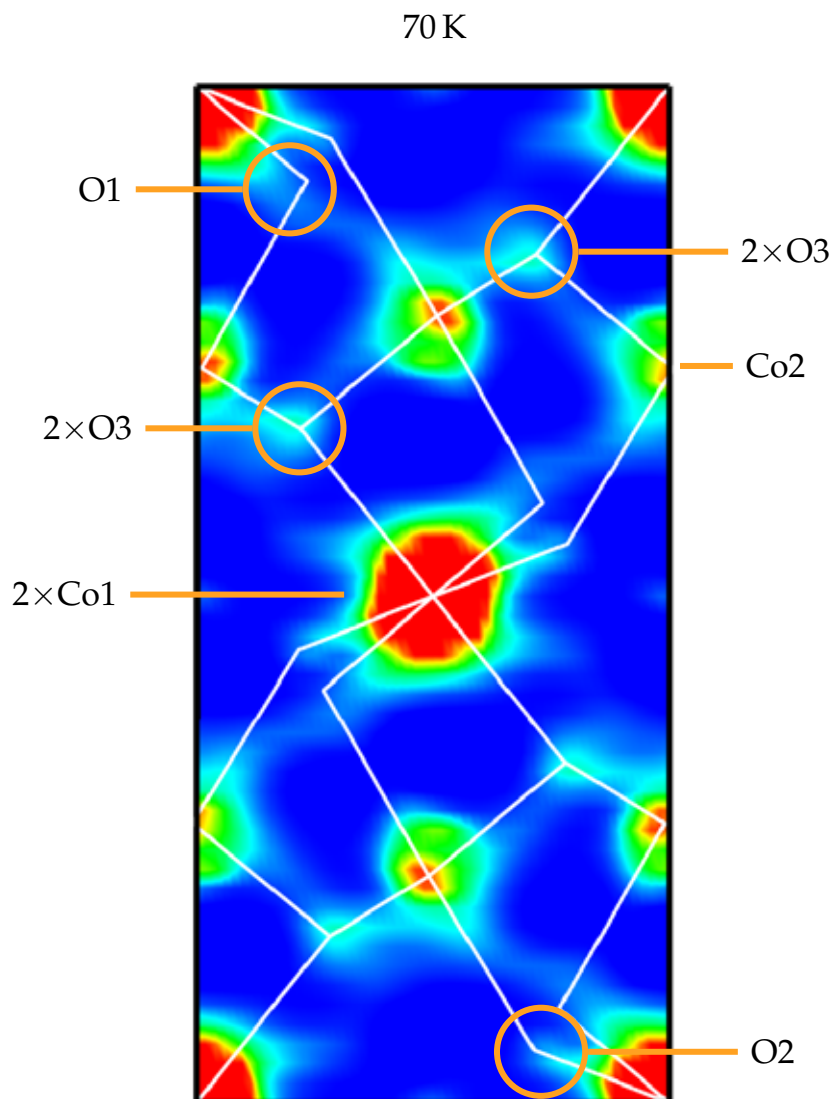


Figure 7.2. Maximum-entropy reconstruction of the density corresponding to the observed magnetization distribution of Co_2SiO_4 at 70 K with contour range from $0 \mu_{\text{B}}/\text{\AA}^3$ (blue) to $2 \mu_{\text{B}}/\text{\AA}^3$ (red). The projection of the full unit cell along the b axis is shown.

Because in Co_2SiO_4 , all cobalt–cobalt distances ($\geq 3 \text{\AA}$) are much larger than those between cobalt and oxygen ($2.09\text{--}2.22 \text{\AA}$), the direct exchange interactions (Co–Co) play a minor role.

In indirect magnetic interactions between two cations via one bridge oxygen ion, the origin of the interaction lies in the existence of excited states of the cation–anion–cation configuration. In the excited configurations, one or both of the electrons in a $2p$ oxygen orbital are excited into the empty, or partially filled, cation orbitals. The

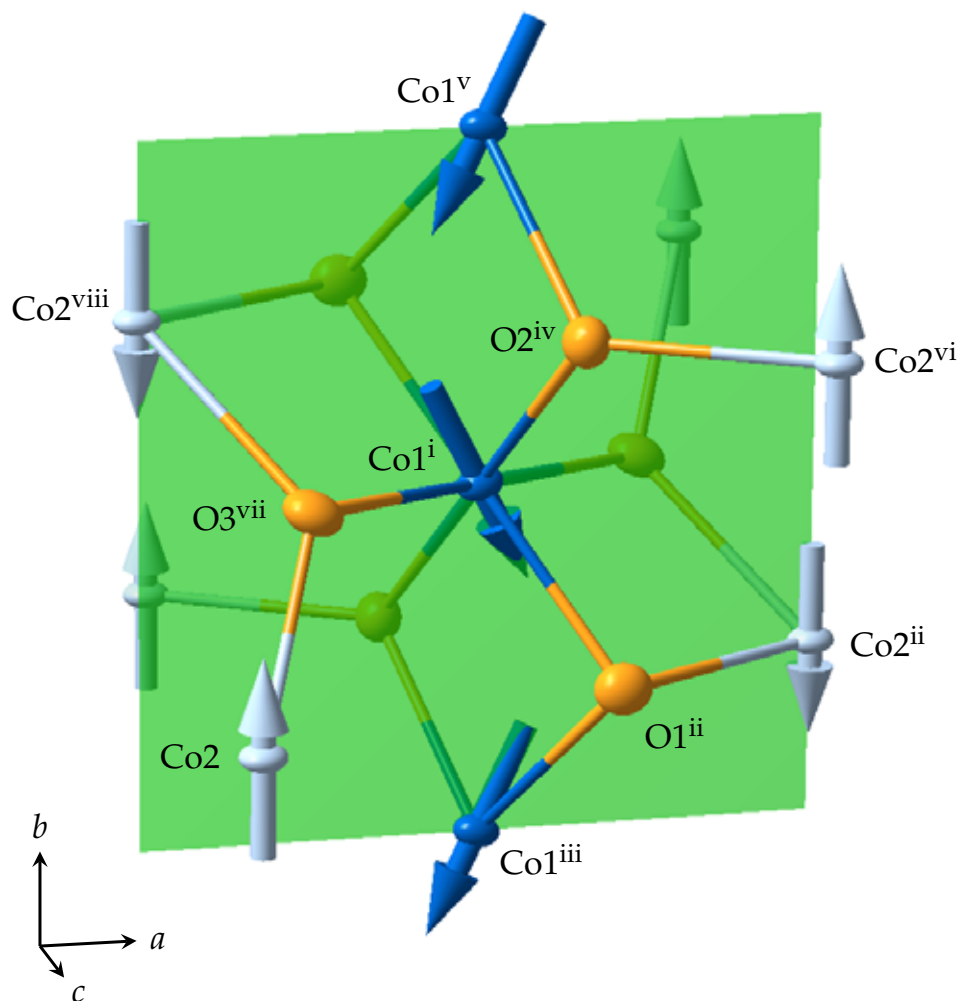


Figure 7.3. Graphical representation of the part of Co_2SiO_4 magnetic structure showing the different exchange paths between the Co ions via O. See table 7.3 for the symmetry codes.

magnetic coupling between neighbouring Co^{2+} moments in Co_2SiO_4 can be understood by invoking the indirect superexchange model of Kramers [90] and Anderson [91] taking also into account the Goodenough-Kanamori rules [92, 93]. It was shown that whenever octahedral-site cations are located on opposite sites of a common anion and the lines connecting the interacting cations to the intervening anion make an angle of 180° , cations interact antiferromagnetically if they have a half filled e_g orbital. Note that Co^{2+} in the HS state ($t_{2g}^5 e_g^2$) has two half filled e_g orbitals, namely $d_{x^2-y^2}$ and d_{z^2} . However, the case in which each cation is again surrounded octahedrally by anions, but the lines

connecting the interacting cations to the intervening anion make an angle of 90° , often leads to a weak ferromagnetic coupling. That is, the superexchange becomes stronger with more open angles and shorter bond lengths, favoring the overlap between oxygen and metal orbitals and, thus, enhancing the magnetic interactions.

In Co_2SiO_4 each Co1 ion is surrounded by eight near-neighbour cobalt ions ($2 \times \text{Co1}$ and $6 \times \text{Co2}$), whereas there are ten near-neighbour cobalt ions ($6 \times \text{Co1}$ and $4 \times \text{Co2}$) for every Co2 (see figure 6.2). The total number of the Co–O–Co paths is equal to twelve for both the Co1 and Co2 cations. All these exchange paths are described by seven indirect magnetic interactions via oxygen anions giving rise to antiferromagnetic or ferromagnetic coupling (table 7.3).

As can be seen from table 7.3 the signs of exchange interactions Co–O–Co are in good agreement with the prediction of the Goodenough-Kanamori rules [92, 93]. Two types of indirect predominantly ferromagnetic couplings occur between the Co1 cations via O1 and O2. According to the single-crystal neutron diffraction measurements at 2.5 K, the Co1–Co1 distance is $2.9936(1)\text{\AA}$. The Co1–O1–Co1 and Co1–O2–Co1 angles have values of $91.47(1)^\circ$ and $91.57(1)^\circ$, respectively. Two types of interactions between Co1 and Co2 via O1 and O3 are also predominantly ferromagnetic. The Co1–Co1 distance is $3.2103(6)\text{\AA}$. The Co1–O1–Co2 and Co1–O3–Co2 angles are $97.58(3)^\circ$ and $93.99(3)^\circ$, respectively. In addition, there are two types of predominantly antiferromagnetic coupling between Co1 and Co2 via O2 and O3. The Co1–Co2 distances are $3.6679(7)\text{\AA}$ and $3.6139(7)\text{\AA}$, whereas Co1–O2–Co2 and Co1–O3–Co2 are $123.59(3)^\circ$ and $117.25(3)^\circ$, respectively. Finally, only one type of superexchange interaction is considered between the Co2 ions via O3, giving rise to a strong antiferromagnetic coupling. In this case, the Co2–Co2 distance is $3.8675(7)\text{\AA}$ and the Co2–O3–Co2 angle is $129.09(3)^\circ$.

Thus, beside of the four negative and four weak positive superexchange interactions between the Co1 and Co2 ions, there are four predominantly ferromagnetic Co1–O–Co1 paths weakening the overall antiferromagnetic

Table 7.3. Interatomic distances (Å) and angles (°) in Co₂SiO₄ corresponding to the indirect magnetic interactions (from single-crystal neutron diffraction measurements—section 3.2.1). ‘F’ denotes the ferromagnetic (positive) type of exchange interactions, whereas ‘AF’ means antiferromagnetic (negative) coupling.

	Type	Co1*	Co2*	300 K	55 K	2.5 K
<i>between Co1 and Co1</i>						
Co1 ⁱ –O1 ⁱⁱ , Co1 ⁱⁱⁱ –O1 ⁱⁱ	F	2		2.0955(2)	2.0907(2)	2.0901(2)
Co1 ⁱ –O1 ⁱⁱ –Co1 ⁱⁱⁱ				91.48(1)	91.48(1)	91.47(1)
Co1 ⁱ –O2 ^{iv} , Co1 ^v –O2 ^{iv}	F	2		2.0929(2)	2.0896(2)	2.0885(2)
Co1 ⁱ –O2 ^{iv} –Co1 ^v				91.62(1)	91.54(1)	91.57(1)
<i>between Co1 and Co2</i>						
Co1 ⁱ –O1 ⁱⁱ	F	2	2	2.0955(2)	2.0907(2)	2.0901(2)
Co2 ⁱⁱ –O1 ⁱⁱ				2.1813(8)	2.1759(6)	2.1756(7)
Co1 ⁱ –O1 ⁱⁱ –Co2 ⁱⁱ				97.63(3)	97.59(2)	97.58(3)
Co1 ⁱ –O3 ^{vii}	F	2	2	2.1715(2)	2.1678(1)	2.1691(2)
Co2 ^{viii} –O3 ^{vii}				2.2250(6)	2.2193(5)	2.2194(5)
Co1 ⁱ –O3 ^{vii} –Co2 ^{viii}				94.13(1)	94.07(2)	93.99(3)
Co1 ⁱ –O2 ^{iv}	AF	2	2	2.0929(2)	2.0896(2)	2.0885(2)
Co2 ^{vi} –O2 ^{iv}				2.0731(8)	2.0731(6)	2.0751(6)
Co1 ⁱ –O2 ^{iv} –Co2 ^{vi}				123.50(4)	123.59(3)	123.59(3)
Co1 ⁱ –O3 ^{vii}	AF	2	2	2.1715(2)	2.1678(1)	2.1691(2)
Co2–O3 ^{vii}				2.0684(4)	2.0647(4)	2.0629(4)
Co1 ⁱ –O3 ^{vii} –Co2				117.03(3)	117.24(2)	117.25(3)
<i>between Co2 and Co2</i>						
Co2–O3 ^{vii}	AF		4	2.0684(4)	2.0647(4)	2.0629(4)
Co2 ^{viii} –O3 ^{vii}				2.2250(6)	2.2193(5)	2.2194(5)
Co2–O3 ^{vii} –Co2 ^{viii}				129.00(4)	129.05(3)	129.09(3)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + 1$; (v) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (vi) $-x + 1, y + \frac{1}{2}, -z + 2$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$.

* Number of the near-neighbour exchange paths for Co1 or Co2.

behaviour. In contrast to Co1, the Co2 ions have four additional strong antiferromagnetic interactions. Therefore, the geometrical arrangement and the competition between the ferromagnetic and antiferromagnetic

interactions seem to be responsible for the canted magnetic structure of the Co1 sublattice in contrast to the collinear structure for Co2.

Now we discuss the relative strength of the exchange interactions using the polarized neutron diffraction data. Above the antiferromagnetic phase transition ($T_N \approx 50$ K), the influence of temperature destroys the long-range magnetic order. By applying an external magnetic field we introduce an additional term to the competition between the exchange interactions and temperature. As seen from figure 7.3 and table 7.3 the influence of the external magnetic field differs for Co1 and Co2. It seems to be much easier to induce a ferromagnetic component for Co1 in contrast to Co2. Thus, at 150 K in a magnetic field of 7 T applied parallel to the b axis the induced magnetic moment on Co2 is smaller than that of Co1. This is even more prominent at 70 K (closer to T_N). Therefore, we 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. This is in agreement with the Goodenough-Kanamori rules [92, 93] considering the values of the Co2–O3–Co2 angle (table 7.3). This exchange is the strongest in absolute value and probably responsible for the overall antiferromagnetic behaviour of Co₂SiO₄.

These results can help us to describe a metamagnetic-like double step transition at $H \approx 18$ T (figure 1.2), which was observed from the $M(H)$ magnetization measurements of Co₂SiO₄ along the primary direction of the total magnetic moment (axis b). Most probably, with increasing field the spin-flop of the Co1 magnetic moments as more flexible component compared to the Co2 moments is visible as the first step in the $M(H)$ curves. Then, both increasing of magnetic field and influence of exchange interactions between Co1 and Co2 lead to a spin-flop of the Co2 moments and the second step on the $M(H)$ curves appear.

Chapter 8

Orbital contribution to magnetic moment

It is often considered that itinerant magnetism originates mainly from the spin contribution (μ_S) and that the spin-orbit-coupling is a weak perturbation. However, the orbital moment (μ_L) can be larger than 10% of the total magnetic moment (as in the case of 5d and 5f elements). In some cases, the orbital moment of the 3d transition metals is also non-negligible. From a certain point of view the orbital magnetism may be even more important: a finite orbital momentum L is an indication of a non-spherical charge distribution in solids. Such a non-spherical charge distribution is the primary source for the magnetic anisotropy energy and therefore determines the easy axis magnetisation direction. As it was already mentioned, the Co^{2+} ions in the high-spin state ($S = 3/2$) have a relatively strong spin-orbit coupling that makes the orbital angular momentum contributing to the total magnetic moment. X-ray magnetic circular dichroism (XMCD) is one of very few experimental techniques that allow us to separate the spin and orbital contributions to the total magnetic moment carried by an absorbing atom. Thus, 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 [118].

8.1. X-ray magnetic circular dichroism

Magnetic dichroism describes the phenomenon that the absorption of electromagnetic radiation by magnetized matter depends on the polarization of the radiation with respect to the direction of the magnetization. Describing magnetic dichroism, one has to distinguish between circular and linear forms of magnetic dichroism. Magnetic circular dichroism describes the different behaviour of left- and right-circularly polarized waves in a magnetic material.

X-ray magnetic dichroism appears in magnetic solids due to X-ray photoabsorption. In the X-ray regime photoabsorption results from electric multipole transitions which is the main interaction channel between electromagnetic radiation and solids. The absorption of radiation is influenced by an interplay of the polarization of the radiation and the magnetization M of the matter. This process can be described by an absorption coefficient $\mu^{(q)}(\omega)$ which denotes the absorption as a function of the photon energy $\hbar\omega$ for a given polarization q .

The physical origin of XMCD can be explained most easily with the so-called two-step model. The first step describes the excitation of a core electron by a circularly-polarized X-ray photon that carries an angular momentum ($+\hbar$ for a right-handed photon and $-\hbar$ for a left-handed photon), the corresponding helicity vector being parallel (right) or antiparallel (left) to the propagation direction. As a consequence of the conservation of angular momentum in the absorption process, the photon's angular momentum is entirely transferred to the photoelectron. Let us consider the photoelectron being excited from a spin-orbit-split core level (e.g., $L_{2,3}$ absorption edges): then the part of the angular momentum carried by the photon will be converted into spin via spin-

orbit coupling. The acquired spin moment is always parallel to the photon propagation direction but its sign depends on the helicity of the incident X-ray photon and on the spin-orbit coupling ($l + s$ at the L_3 and $l - s$ at the L_2). The magnetic properties of the sample are driving the second step. A polarized photoelectron occupies the states above the Fermi level and, if there is any imbalance in either spin or orbital momentum in the final states, the XMCD spectrum reflects the difference in the density of states with different spin or orbital moments. The sum of the XMCD spectra recorded at the L_2 and L_3 edges reflects only a difference in the orbital moments of the final states, while the difference is proportional to a spin polarization of the valence states. This is precisely the content of the magneto-optical sum rules. It is worth mentioning that the summation over two spin-orbit split edges is equivalent to what can be measured for a core level with no spin-orbit interaction. This implies that a dichroic effect at the K -edge is only due to the orbital moments in the valence shell.

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 K–150 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 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. Measurements, taken over several hours, were averaged in order to improve the signal-to-noise ratio.

A spin-dependent part of fluorescence intensity can be simply given as

$$\Delta q_f = \frac{I_0^+}{I_f^+} - \frac{I_0^-}{I_f^-}. \quad (8.1)$$

The XMCD at the N–S arrangement of the magnet parallel to X-ray beams is given as

$$\Delta q_f^+ = \frac{I_0^{-+}}{I_f^{-+}} - \frac{I_0^{++}}{I_f^{++}}. \quad (8.2)$$

On the other hand, the XMCD at the antiparallel S–N arrangement is given as

$$\Delta q_f^- = \frac{I_0^{--}}{I_f^{--}} - \frac{I_0^{+-}}{I_f^{+-}}. \quad (8.3)$$

In the first term of the superscript, + and – represent the right- and left-polarized X-rays, respectively; in the second term of the superscript, + and – denote the N–S and S–N arrangements, respectively. Then, the final XMCD is given as

$$\Delta q_f = \frac{\Delta q_f^- - \Delta q_f^+}{2}. \quad (8.4)$$

The experimental XMCD spectra at the Co *K*-edge of Co₂SiO₄ are shown in figure 8.1 in comparison with isotropic X-ray absorption near edge 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 main feature at the Co *K*-edge is an absorption step associated with the onset of core-level (1s) to the continuum transition. This feature, however, consists of a number of overlapping spectral peaks and will not be discussed here. Atomic-like transitions from the 1s core to empty 4p states also produce multiple peaks in the near-edge region. The multiplicity of these features is governed by the solid-state splitting of the 4p levels and by replication of 4p features associated with different 3d configurations. Finally, 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 → 3d transitions.

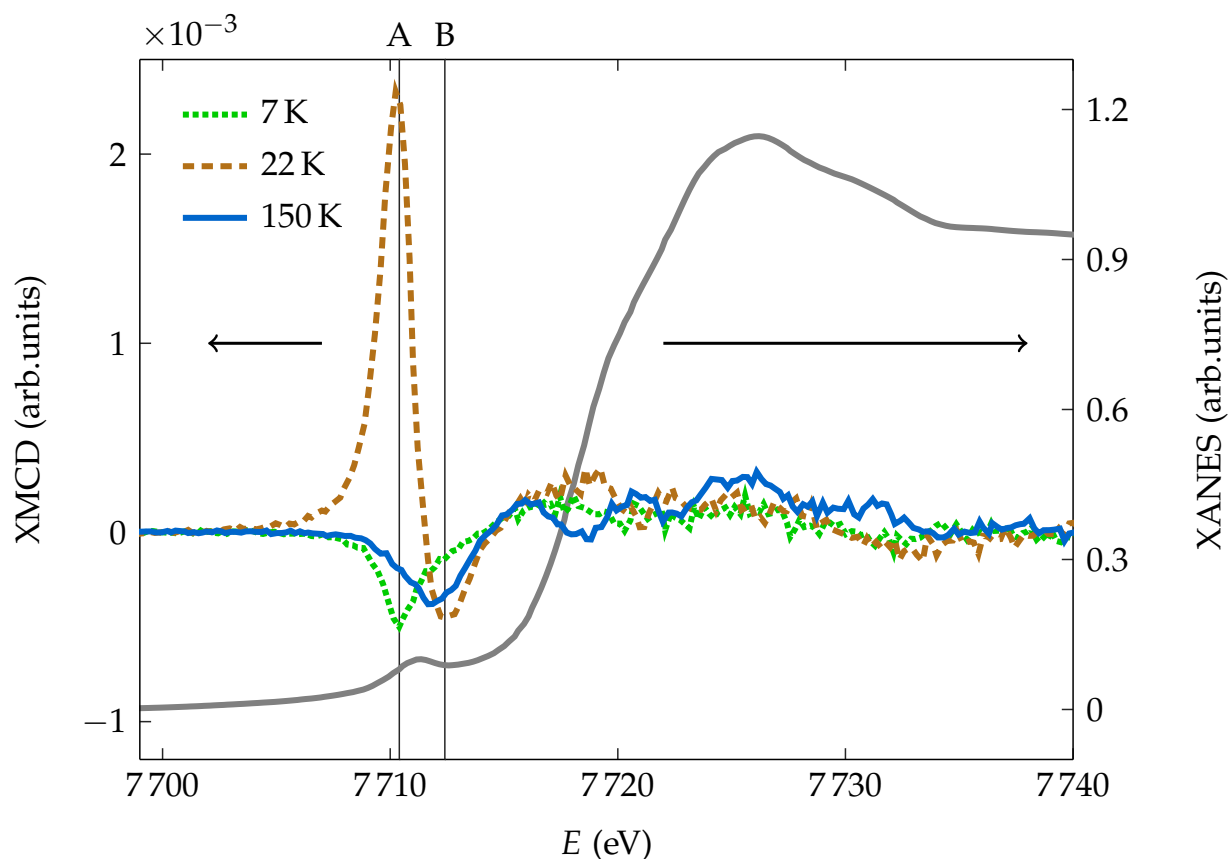


Figure 8.1. XMCD (left Y-scale) and XANES (right Y-scale) spectra of Co_2SiO_4 measured at the Co K -edge under a magnetic field of ± 6 T along the beam (close to the b axis). Only three selected temperatures are shown for simplicity.

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 the synchrotron X-ray diffraction (section 5.1) and polarized neutron diffraction (section 7.1) measurements on single crystals.

Increasing spectral weight of this pre-edge feature (within a given symmetry environment) is typically associated with an increasing d -hole count in $3d$ transition-metal compounds. In our case, the height of the

pre-edge peak is independent of temperature (see figure 8.1). Moreover, the pre-edge peak is always observed at the same energy of about 7711 eV.

We now consider the XMCD signals shown in figure 8.1. As seen in the figure, rather small positive peaks appear at the main edge. The prominent part of the Co XMCD consists of a double peak structure with a splitting of about 2 eV, centered 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 figures 8.1 and 8.2).

This dramatic change of the XMCD pre-edge peaks can be divided by three temperature regions. (a) Below ~ 20 K, the XMCD pre-edge features consist of two negative peaks. The intensity of peak *A* is higher than that of peak *B*, which is rather weak. (b) With temperature increase above ~ 20 K the peak *A* becomes abruptly positive and strong, whereas peak *B* remains negative and is now clearly visible. That is, in the temperature range ~ 20 – 50 K the strong positive-to-negative dispersion-type XMCD signal is observed in the vicinity of the XANES pre-edge. (c) Above ~ 50 K, both XMCD peaks are again negative, but peak *A* is much weaker now than peak *B* in contrast to the case (a).

Figure 8.3 shows the temperature dependence of these XMCD pre-edge peaks. Negative values denote the negative intensities of XMCD peaks. The pre-edge XMCD feature was fitted by two Gauss peaks as shown for three selected temperatures in the inset to figure 8.3. The peak positions were confirmed to be almost independent from temperature. The full width at half maximum (FWHM) of the peaks also do not significantly change with temperature. As seen from the figure, the integrated intensities of both *A* and *B* XMCD peaks exhibit two anomalies at ~ 20 K and ~ 50 K (figure 8.3). The later can be associated with the magnetic phase transition taking place at 50 K. On the other hand, the anomaly at 20 K is unexpected because there was no indication in the magnetic susceptibility data at the same experimental conditions.

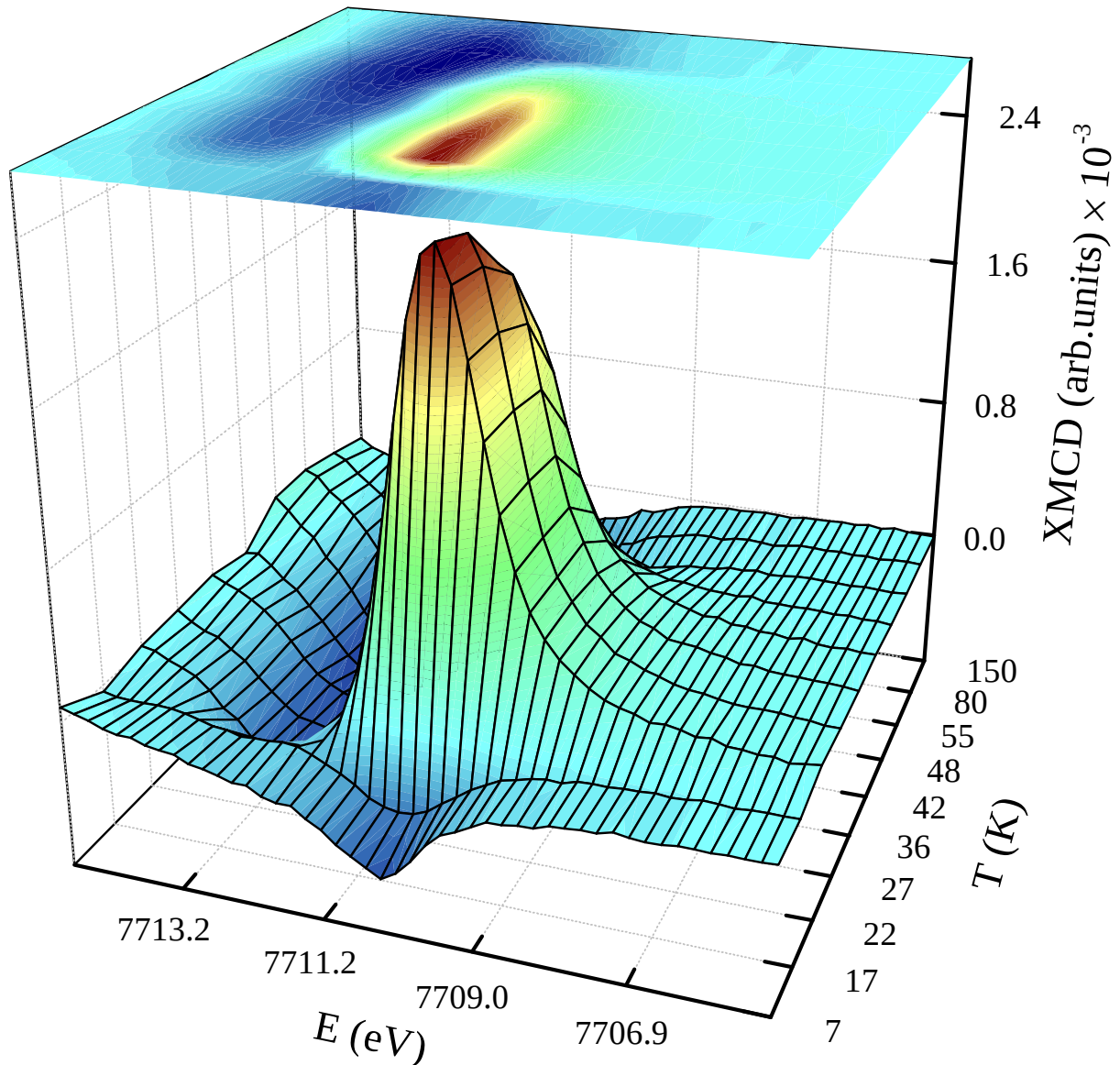


Figure 8.2. Thermal evolution of two XMCD pre-edge peaks of Co_2SiO_4 .

Additional measurements were performed at two temperatures 10 K and 30 K under the same magnetic field of $\pm 6 \text{ T}$ but with the beam perpendicular to the direction used in the first experiment (b axis), i.e. the beam now is in the ac plane. These measurements show the similar change in intensities of the pre-edge peaks with temperature. Therefore, the pre-edge structures seem to be qualitatively independent of the crystallographic direction. At the moment, there is no clear understanding of such strong change of the XMCD spectra with temperature in Co_2SiO_4 and additional experiments are required to clarify this phenomenon.

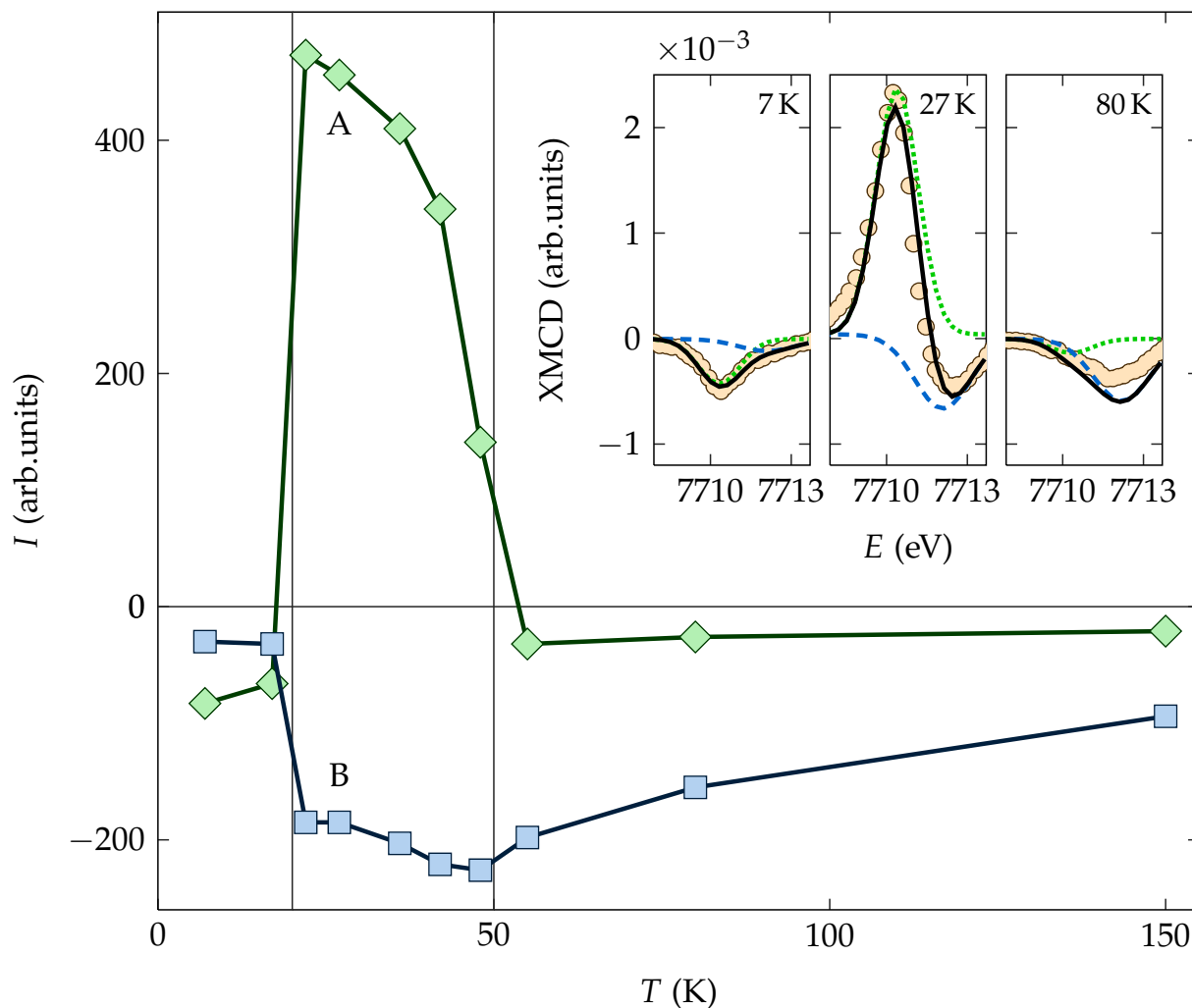


Figure 8.3. Thermal evolution of the integrated intensities for two XMCD pre-edge peaks of Co_2SiO_4 . The Gauss fits for three selected temperatures are shown in the inset.

The origin of pre-edge signals was already discussed above and assigned to Co^{2+} as XMCD at the Co K absorption edge is sensitive only to the magnetic states of the cobalt ions. In the case of the $L_{2,3}$ -edges, the XMCD sum rules are quite simple expressions (in contrast to the K -edge) to connect the XMCD spectrum of an absorbing atom in a solid to its spin and orbital magnetic moments. On the other hand, the effective operators responsible for XMCD at the K -edge in both electric dipole and in electric quadrupole transitions have a pure orbital nature [126, 127]. 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 [128]. That result was compared and is consistent with the results of other magnetic materials having comparable ratios of XMCD/XANES. We would like also to compare our data and the XMCD data at the Co K -edge for CoFe_2O_4 and FeCo_2O_4 with the spinel structure [129]. It was found, that in the vicinity of the pre-edge the concave patterns in CoFe_2O_4 change to a dispersion-type signal in FeCo_2O_4 . This was explained by the different spin state of Co^{2+} ions in the end-members of $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ferrite [129].

8.2. Neutron diffraction and magnetic susceptibility

As it was already mentioned, a strong spin-orbit coupling is probably the reason why the observed magnetic moments (neutron diffraction; chapter 6) in Co_2SiO_4 ($3.86 \pm 0.05 \mu_B$ and $3.37 \pm 0.04 \mu_B$ for Co1 and Co2, respectively) are higher than those expected on the basis of the spin-only contribution ($3\mu_B$). Moreover (see section 6.2.1), the effective magnetic moments along the three principal crystallographic axes determined from the susceptibility measurements of the single crystal Co_2SiO_4 are also much higher than the spin-only values. Thus, both techniques suggest some orbital contribution to the total magnetic moment. An unquenching of the orbital moment in Co^{2+} due to the strong spin-orbit coupling was also reported for other compounds containing cobalt ions. For example, it was shown in [130] that in CoFePO_5 the Co^{2+} magnetic moment of $3.45 \pm 0.05 \mu_B$ is greater than the spin-only value due to a non-negligible orbital contribution.

It is also important to compare again the properties of Co_2SiO_4 with those of CoO . It was shown that the calculated value of the Co total magnetic moment at 0 K amounts to $4.01 \mu_B$ in CoO [131]. Such theoretical outcome is in agreement with the experimental results of $3.80\text{--}3.98 \mu_B$ from the neutron diffraction measurements [132–134]. According to [131], the total magnetic moment of Co in CoO is built up from the spin moment of $2.62 \mu_B$ and the orbital moment of $1.39 \mu_B$. This leads to the $\langle L_z/S_z \rangle$ ratio of about 1.06 through the equation $\langle L_z/S_z \rangle = 2\mu_L/\mu_S$. So, the orbital moment in CoO is quite substantial being more than 1/3 of the total moment. This is in good agreement with the theoretical values of $\langle L_z/S_z \rangle = 0.92$ [135] and $\mu_L \approx 1 \mu_B$ [107, 136] as well as the experimental $\langle L_z/S_z \rangle$ values of 1.08 and 0.95 obtained from the XMCD [135] and non-resonant X-ray magnetic scattering (NRXMS) [137] measurements, respectively.

Thus, beside the coinciding values of the Co^{2+} effective moments in the paramagnetic phase, found for CoO and Co_2SiO_4 in the susceptibility measurements, the obtained magnetic moments from the neutron diffraction experiments in the magnetically ordered state are also similar. Therefore, the orbital magnetic moment in Co_2SiO_4 is roughly estimated to be of the order of $1 \mu_B$ per Co^{2+} as in CoO . This estimation is in agreement with that based on the XMCD to XANES ratio (section 8.1).

Our assumption also agrees with the polarized neutron diffraction measurements (section 7.1) according to which the orbital magnetic moment induced by the field was found for Co1 in Co_2SiO_4 at 70 K and 150 K. The obtained ratios μ_L/μ_S are similar for both temperatures; they are 0.22 ± 0.06 and 0.27 ± 0.07 at 70 K and 150 K, respectively. Assuming the μ_L/μ_S to be independent of temperature and magnetic field one could apply the averaged value of ~ 0.25 to estimate the spin and orbital components to the total magnetic moment obtained from non-polarized neutron diffraction measurements. This estimation is shown in figure 8.4, where the spin (μ_S) and orbital (μ_L) contribution were calculated from the total magnetic moment for Co1 measured by means of the neutron

powder diffraction measurements (see chapter 6 for details). As seen from the figure, μ_S is saturated at a value close to the spin-only moment of $3 \mu_B$ for Co^{2+} in the high-spin state ($S = 3/2$).

Therefore, we expect that the excess magnetic moment of $\sim 0.86 \mu_B$ (Co1) and $\sim 0.37 \mu_B$ (Co2) in Co_2SiO_4 is caused by the orbital contribution to the total magnetic moment. Spin-orbit coupling with this partially unquenched orbital moment is mainly responsible for the magnetocrystalline anisotropy in the cobalt olivine.

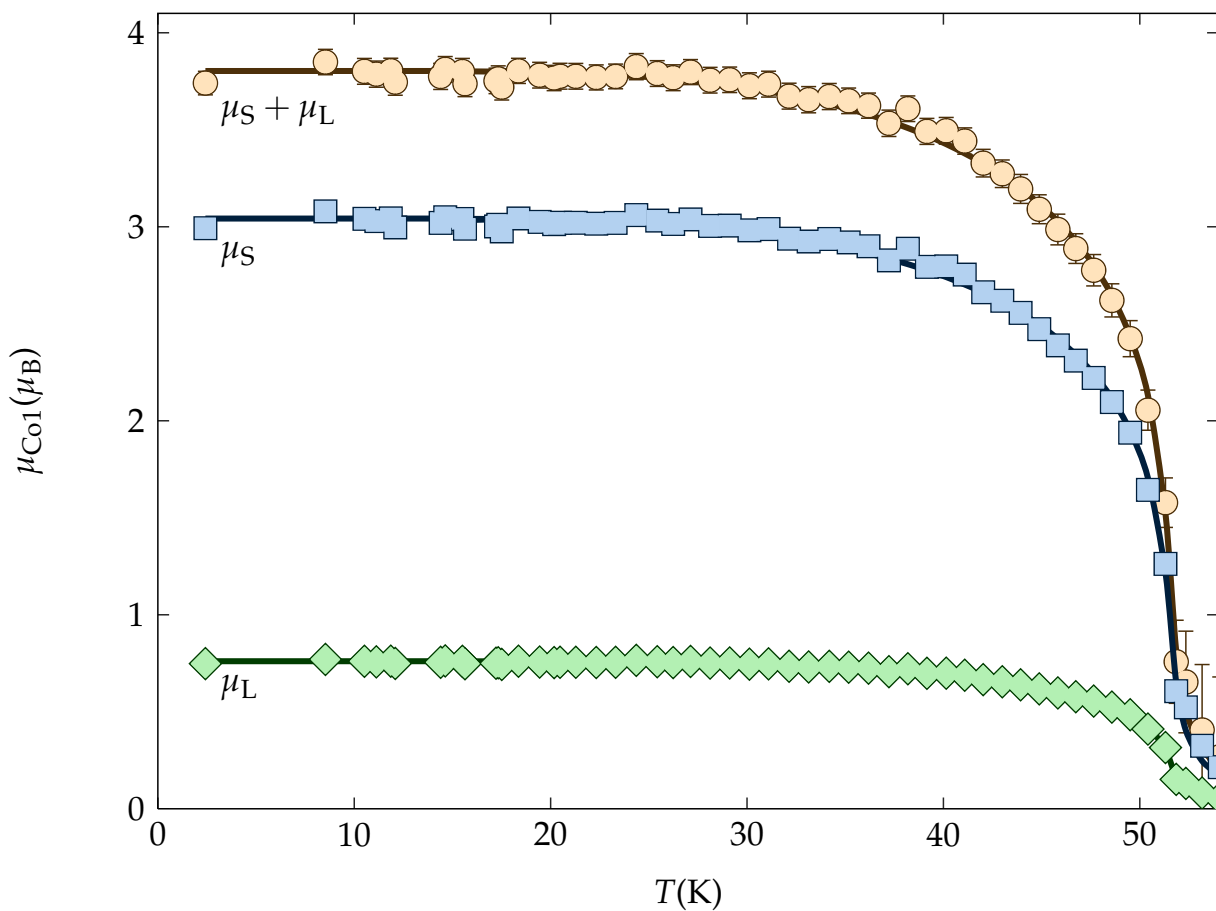


Figure 8.4. Temperature dependence of the Co1 spin (μ_S), orbital (μ_L) and total ($\mu_S + \mu_L$) magnetic moment for Co_2SiO_4 according to the neutron diffraction measurements by applying the ratio $\mu_L/\mu_S \approx 0.25$.

Chapter 9

Conclusions

Detailed structure analyses on Co_2SiO_4 were performed by single-crystal neutron diffraction using a short wavelength of $0.552(1) \text{ \AA}$ in the temperature range from 300 K down to 2.5 K. Measurements up to $\sin \theta / \lambda < 1.1 \text{ \AA}^{-1}$ yielded precise structure parameters for all atoms including O atoms. The data at room temperature are in good agreement with former X-ray results [20, 67–70].

The lattice parameters of Co_2SiO_4 were determined by both laboratory and synchrotron X-ray powder diffraction studies in the temperature range from 15 K to 300 K as well as by neutron powder diffraction measurements in the extended range between 5 K and 500 K with small temperature increments of 1 K to 4 K. These data are in perfect agreement and indicate a small but significant anomaly in the anisotropic lattice expansion close to the magnetic phase transition at 50 K. Below this temperature the lattice parameter b is shortened abruptly whereas c increases and a remains constant. The resulting volume of the unit cell thus shows anomalous contraction below 50 K. The interatomic distances and angles of Co_2SiO_4 do not show significant effects at the magnetic phase transition temperature. Moreover, there is no indication of any

structural phase transition. The orthorhombic symmetry with space group $Pnma$ is retained in the temperature range from 2.5 K up to 500 K.

In order to parameterize the cell parameters of Co_2SiO_4 with high accuracy the measured molar specific heat data in the temperature range from 5 K to 300 K were combined with previously available results [28, 80]. They were fitted considering the Debye-Einstein lattice contribution, the magnetic part reflecting the antiferromagnetic phase transition and the Schottky contribution due to the spin-orbit splitting of the Co^{2+} ground state. The Debye temperature calculated from the lattice specific heat was found to be in good agreement with the values calculated from the room temperature elastic constants [83]. In this way, the specific heat data on Co_2SiO_4 enabled a physically meaningful interpretation of the volumetric thermal expansion and, therefore, of the thermal evolution of the unit cell volume. The results show that the anomaly in the lattice parameters and the unit cell volume is caused by magnetostriction often occurring in magnetic compounds.

Non-polarized neutron diffraction measurements on both single-crystal and powder samples show that the ordered magnetic structure of orthorhombic Co_2SiO_4 is described as an antiferromagnetic arrangement of the Co^{2+} magnetic moments below $T_N \approx 50$ K with a magnetic propagation vector $\mathbf{k} = (0,0,0)$ in agreement with [22, 23]. Detailed symmetry analysis of the magnetic structure shows 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). This is in agreement with the magnetic susceptibility measurement $\chi(T)$, which also suggests a canted antiferromagnetic structure. The magnetic anisotropy was studied by fitting the observed $\chi(T)$ curves above T_N to the Curie-Weiss law. Thus the Curie-Weiss temperatures θ_{CW} and effective magnetic moments μ_{eff} were obtained.

The magnetic moments from the neutron diffraction data were found to be $3.87 \pm 0.03 \mu_B$ and $3.35 \pm 0.02 \mu_B$ for Co1 and Co2, respectively. Compared to literature data, an excellent agreement between the magnetic moments of Co1 is seen, whereas the values for Co2 are different [23]. Note that the results of our measurements on samples prepared by different methods (powder and single crystal) and by using different instruments (neutron powder and single-crystal diffractometers) are in good mutual agreement indicating that the moments on Co1 and Co2 are rather different than similar.

In order to follow the thermal evolution of the Co_2SiO_4 magnetic structure, the temperature dependence of the Co1 and Co2 magnetic moments obtained from neutron diffraction measurements was fitted in a modified molecular field model. The results indicate the importance of introducing a magnetoelastic parameter describing the magnetostrictive shift of T_N as well as show the magnetic pre-ordering above T_N . The precise analysis of the neutron diffraction data also shows that canting angles of the Co_2SiO_4 magnetic structure are independent of temperature, which is in agreement with the strong magnetic anisotropy found in Co-olivine.

Polarized neutron flipping-ratio measurements made at temperatures above T_N and with an external field of 7 T along the b axis were used to represent the magnetization density in the unit cell. These data were interpreted using the local susceptibility approach [124]. The site susceptibility tensors were determined and used to construct the magnetic ellipsoids within the experimental constraints. The local anisotropy is found to be rather small at high temperatures but becomes very strongly enhanced when approaching the ordering temperature. This anisotropy prevents full ferromagnetic alignment of the Co moments in magnetic fields up to 7 T, which is in agreement with the bulk magnetization measurements [10]. The longest axis of the magnetic ellipsoids may be considered as a local easy axis of magnetization. Both refinement and density maps revealed a non-negligible amount of magnetic moment on

the oxygen positions indicating a delocalization of magnetic moment from Co towards neighbouring O due to the superexchange coupling.

The relative strength of the exchange interactions was discussed based on the the non-polarized and polarized neutron data. The superexchange interactions Co2–O–Co2 are found to be much stronger than those between the Co1 ions and to be probably responsible for the overall antiferromagnetic behaviour of Co₂SiO₄.

Electron-density distribution in Co₂SiO₄ was studied by means of single-crystal synchrotron X-ray diffraction measurements. The data were analysed using both Fourier transform and maximum-entropy method. A tendency to elongation of the valence electron density along the direction of the magnetic moments with decrease of temperature is found in agreement with elongation of magnetic ellipsoids from polarized neutron flipping-ratio measurements. There is also an agreement between the electron and magnetization density maps which supports the assumption of a partly covalent character of the Co–O bonding. An appearance of the pre-edge peaks at the Co *K*-edge X-ray absorption near edge structure spectra in Co₂SiO₄ also suggests a hybridization between the 3*d* states of neighbouring Co ions via the 2*p* state of O. The X-ray magnetic circular dichroism measurements were 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 Co₂SiO₄.

An important orbital contribution to the total magnetic moment of Co²⁺ in Co₂SiO₄ was predicted by means of magnetic susceptibility and non-polarized neutron diffraction measurements. This prediction 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 $\mu_L/\mu_S \approx 0.25$. According to this, the excess magnetic moment of HS Co²⁺ ($S = 3/2$) above the theoretical expectation of the spin-only value of $3\mu_B$ is caused by the orbital part. Spin-orbit coupling with this partially unquenched orbital moment in Co²⁺ is mainly responsible for the magnetocrystalline anisotropy in the cobalt olivine.

Below ~ 20 K an unusual behaviour of XMCD signals was observed in the vicinity of the pre-edge peak of XANES, but no anomalies were found in the magnetic susceptibility data at the same experimental conditions. Therefore additional experiments are further required to clarify this phenomenon.

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