phys. stat. sol. (a) **109**, 589 (1988)

Subject classification: 75.25; S11.1

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Magnetic Structure of the Orthosilicates Mn_2SiO_4 and Co_2SiO_4

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The antiferromagnetic structure of the orthosilicates Mn_2SiO_4 (tephroite) and Co_2SiO_4 is determined on synthetic single crystals by neutron diffraction. In Mn_2SiO_4 the magnetic moments on the crystallographic M2-site are aligned almost parallel to the a-axis (space group Pnma). On the M1-site the spin arrangement is collinear and nearly parallel to a below $T_N = 47.1(1)$ K but pronounced canting away from the crystallographic axes is confirmed below about 20 K. The magnetic moments in the two crystallographic sites are significantly different at all temperatures below T_N with smaller moments on M1, and at 2 K both moments are smaller than the spin-only value of $5\mu_B$. In Co_2SiO_4 the moments on M2 are parallel to the b-axis whereas on M1 they are canted for the whole temperature range below the transition temperature ($T_N = 49.5(1)$ K) in contrast to results from earlier neutron powder diffraction measurements. The magnetic moments on both sites are only slightly different and exceed the spin-only value as a result of orbital contribution.

Die antiferromagnetische Struktur der Orthosilikate Mn_2SiO_4 (Tephroit) und Co_2SiO_4 wird durch Neutronenbeugung an synthetischen Einkristallen bestimmt. In Mn_2SiO_4 sind die magnetischen Momente der kristallographischen M2-Position nahezu parallel zur a-Achse ausgerichtet (Raumgruppe Pnma). Auf der M1-Position ist die Spinstruktur kollinear und annähernd parallel zu a unterhalb von $T_N = 47{,}1(1)$ K, aber eine ausgeprägte Spinkantung weg von den kristallographischen Achsen wird für Temperaturen unterhalb von 20 K bestätigt. Die magnetischen Momente der beiden kristallographischen Lagen sind deutlich verschieden für alle Temperaturen unterhalb von T_N, wobei M1 das wesentlich kleinere Moment aufweist. Bei 2 K sind beide Momente gegenüber dem Wert des reinen Spinmagnetismus reduziert. In Co_2SiO_4 sind die Momente der M2-Position parallel zu b, während für M1 im gesamten Temperaturbereich unterhalb der Ordnungstemperatur ($T_N = 49{,}5(1)$ K) ein Kantungswinkel mit den kristallographischen Achsen beobachtet wird. Dieses Ergebnis steht im Gegensatz zu früheren Beobachtungen an Neutronenpulverdaten. Die magnetischen Momente beider Lagen unterscheiden sich nur wenig und sind größer als die Werte des Spinmagnetismus, was auf einen Bahnanteil hindeutet.

1. Introduction

The orthorhombic olivine structure (space group Pnma) has two different octahedral sites, one (M1 or 4a) with local symmetry $\bar{1}$, the other (M2 or 4c) with site symmetry m. Previous neutron diffraction studies on powders of the olivine compounds of the 3d elements Mn and Co at 4.2 K [1 to 3] show that they order antiferromagnetically at low temperatures. For Mn_2SiO_4, a canted spin array was found, which was matched ambiguously by two different models [2, 3]. Both groups of authors agree on a collinear ordering of the magnetic moments on M2 parallel to the $\boldsymbol{a}$-axis and on a moment arrangement in a crystallographic plane of the moments on M1. But Cox et al. [2] propose the $\boldsymbol{a}$–$\boldsymbol{b}$ plane and Santoro et al. [3] the $\boldsymbol{a}$–$\boldsymbol{c}$-plane. Whereas the proposal of Cox et al.

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is consistent with the crystallographic symmetry, the other of Santoro et al. is not. These latter authors interpret an inflexion in the susceptibility curve in tephroite as a transition between a collinear and a canted antiferromagnetic structure. Cobalt-orthosilicate was considered as purely collinear antiferromagnetic in the low temperature region with moments aligned parallel to the ***b***-axis.

In order to determine more precisely the magnetic structures and to follow their thermal evolution, we reinvestigated the group of silicates of 3d elements with the olivine structure by magnetization measurements [4] and neutron diffraction on single crystals. The magnetic structure and the magnetization of Fe_2SiO_4 were published previously [5]. A preliminary account of a detailed Mössbauer study on Fe_2SiO_4 has been reported [6] and a summary of experimental results (magnetization, neutron diffraction, Mössbauer) is given in a review article [7].

2. Experimental

Single crystals of Mn_2SiO_4 and Co_2SiO_4 have been grown by Takei and coworkers [8, 9] by the floating-zone method under controlled atmosphere using focussed radiation heating.

Crystallographically oriented plates with 0.5 mm thickness and 5 mm diameter were cut from the middle of these crystals. The crystals were mounted inside a helium-gas-flow cryostat with one axis upside and the incident beam rectangular to the plane of the crystal for data collection with unpolarized neutrons on the D15 device of the ILL, Grenoble. An ω–2θ-scan technique was used and the neutron wavelength was $\lambda = 0.1175$ nm.

Two kinds of experiments were carried out in the antiferromagnetic region:

1. Some reflections which were characteristic of the spin canting were measured as a function of temperature.

2. Data sets of about 100 to 200 independent magnetic reflections were collected at temperatures corresponding to the canted or collinear antiferromagnetic regions.

The intensities of individual reflections were integrated. Structure factors were derived after background and Lorentz corrections.

3. Refinement

The total intensity of a Bragg reflection in a neutron diffraction experiment with unpolarized neutrons is proportional to the square of the nuclear structure factor (F_N) and the square of the projection of the magnetic structure factor on the scattering plane ($\boldsymbol{F}_M^{\perp}$):

$$I \sim F_N^2 + \boldsymbol{F}_M^{\perp 2} ,$$

where $\boldsymbol{F}_M^{\perp}$ is given by

$$\boldsymbol{F}_M^{\perp} = \boldsymbol{e}_k \times (\boldsymbol{F}_M \times \boldsymbol{e}_k)$$

with

$$\boldsymbol{e}_k = \boldsymbol{k}/|\boldsymbol{k}| ,$$

$\boldsymbol{k}$ is the scattering vector of the incident neutrons.

The conclusion of our previous study on Fe_2SiO_4 [5] was that the neutron data were better explained by a structure which follows the symmetry requirements of the olivine structure [2] than by the type of model proposed by Santoro et al. [3]. The inter-

pretation of the experimental results from the Mn_2SiO_4 and Co_2SiO_4 data was attempted with both models but again lead us to the same conclusion.

When symmetry requirements are followed the magnetic structure factor of the corresponding magnetic structure in Mn_2SiO_4 is for the M1-site

$$\boldsymbol{F}_M(M1) = \begin{pmatrix}\mu_a\\ \mu_b\\ \mu_c\end{pmatrix} f_{Mn}\left\{\begin{pmatrix}1\\1\\1\end{pmatrix} + \begin{pmatrix}1\\-1\\1\end{pmatrix}\cos \pi k + \right.$$

$$\left. + \begin{pmatrix}-1\\-1\\1\end{pmatrix}\cos \pi(k+l) + \begin{pmatrix}-1\\1\\1\end{pmatrix}\cos \pi(h+k+l)\right\} e^{-W}.$$

μ_a, μ_b, μ_c are the components of the magnetic moment along the crystallographic axes, f_{Mn} is the magnetic form factor from Watson and Freeman [10], and e^{-W} is the Debye-Waller factor. For the M2 site the magnetic structure factor $\boldsymbol{F}_M(M2)$ has a more complicated expression. However, the structure vectors are the same, and $\mu_b = 0$.

In the case of magnetic structure of Co_2SiO_4, the structure factors are obviously the same, except the form factor f_{Co} and the structure vectors. These are here the same as those for Fe_2SiO_4

$$\begin{pmatrix}1\\1\\1\end{pmatrix}, \begin{pmatrix}-1\\1\\-1\end{pmatrix}, \begin{pmatrix}-1\\-1\\1\end{pmatrix} \text{ and } \begin{pmatrix}1\\-1\\-1\end{pmatrix}.$$

On the M2-site, $\mu_a = 0$ and $\mu_c = 0$. The symmetry requirements are discussed in a subsequent paper by Ballet and Fuess [11].

Such magnetic structure factors lead to relations between the components of the moments and the reflections to which they contribute. These relations are reported in Table 1.

The refinement of the crystallographic and magnetic structures was carried out by a least-squares procedure using the Cambridge Crystallographic Subroutine Library. The crystal structure refinement in the paramagnetic region was based on the atomic parameters of previous X-ray measurements as starting values [1, 2]. The data were corrected for extinction (Mn_2SiO_4) and absorption and extinction (Co_2SiO_4). Nuclear and magnetic structure factors were refined simultaneously in the antiferromagnetic region.

Table 1

Extinction rules for the magnetic structure factors which are described in the text

k	$h + l$	Mn_2SiO_4	Co_2SiO_4
even	even	μ_c	
even	odd	μ_a	μ_b
odd	even		μ_c
odd	odd	μ_b	μ_a

Table 2

Magnetic moments (in μ_B), directions of the components of moments, agreement factors, and number of magnetic reflections for three temperatures in Mn_2SiO_4 and Co_2SiO_4

Mn_2SiO_4	2 K	4 K	20 K
moments of M1 (μ_B)	3.85(11)	3.86(11)	2.66(7)
cos (μ, a)	0.74(3)	0.74(2)	0.99(3)
cos (μ, b)	0.65(4)	0.66(4)	0.10(4)
cos (μ, c)	0.17(10)	0.15(13)	0.14(15)
moments of M2 (μ_B)	4.68(9)	4.55(7)	4.32(7)
cos (μ, a)	0.97(2)	0.99(2)	0.98(2)
cos (μ, b)	0	0	0
cos (μ, c)	0.24(6)	0.16(7)	0.19(7)
$R(F_M)$	0.049	0.042	0.039
$R_w(F_M)$	0.027	0.024	0.021
No. of reflections	96	97	96
Co_2SiO_4	2 K	20 K	40 K
moments of M1 (μ_B)	3.90(10)	3.89(7)	3.37(6)
cos (μ, a)	0.24(2)	0.21(1)	0.25(1)
cos (μ, b)	0.96(2)	0.97(1)	0.96(1)
cos (μ, c)	0.12(2)	0.12(1)	0.12(1)
moments of M2 (μ_B)	3.64(8)	3.71(5)	2.99(5)
cos (μ, b)	1	1	1
$R(F_M)$	0.041	0.048	0.041
$R_w(F_M)$	0.027	0.029	0.024
No. of reflections	76	166	102

As parameters we used the components of the magnetic moments indicated by the formulas mentioned above. The absolute magnetic moments could easily be derived from these components (Table 2). As a test for the goodness of the refinement we took the correspondence factor R which is defined as

$$R(F_M) = \sum_i |I_i^{obs} - I_i^{cal}| / \sum_i |I_i^{obs}|$$

and its weighted value

$$R_w(F_M) = \sum_i |w_i(I_i^{obs} - I_i^{cal})| / \sum_i |w_i I_i^{obs}|$$

with

$$w_i = 1/\sigma_i(I^{obs}) .$$

Both are also displayed in Table 2.

4. Results

4.1 Mn_2SiO_4

The intensities of the magnetic reflections (001) and (011) were measured as a function of temperature for tephroite (Fig. 1). The first one (001) is due to the component of the magnetic moment parallel to the a-axis and vanishes at $T_N = 47.1(1)$ K. The second one is due to a moment on M1 which is perpendicular to the a-axis. It decreases rapidly. Extrapolation of the pronounced decrease at low temperature yields a transition tem-

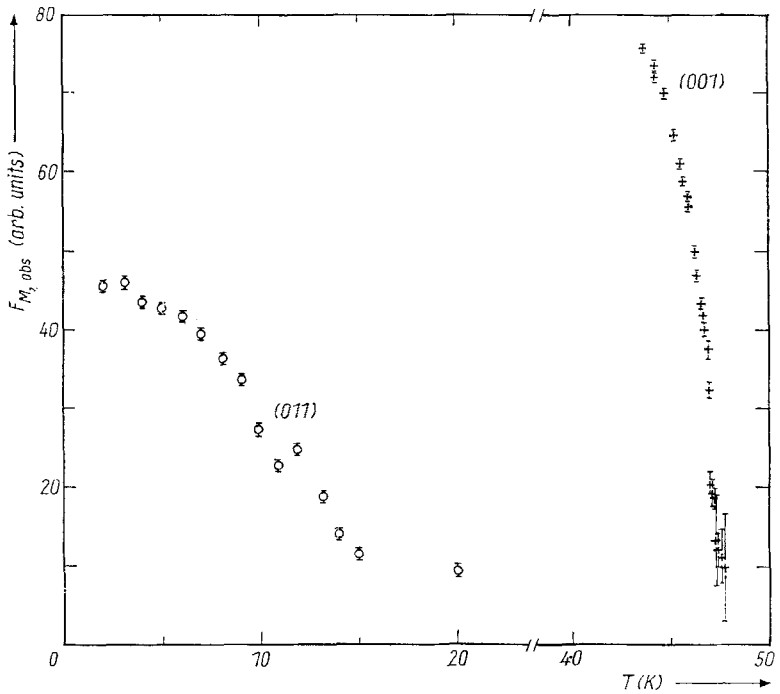

Fig. 1. Decrease of the magnetic amplitude in Mn_2SiO_4 for (001) which is due to the collinear spin arrangement and for the (011) reflections which is due to canting

perature of about 15 K, but a small canting still remains at 20 K. This observation confirms to some extent the assumption of a canted/collinear transition in the magnetic structure near 13 K proposed by Santoro et al. [3] based on their susceptibility measurements.

Data sets which contain reflections of the various groups stated above, were recorded at $T = 2$, 4.2, and 20 K. The refined parameters agree with the qualitative features of the temperature dependent experiments. The magnetic moments on both sites are lower than the spin-only value of $5\mu_B/Mn^{2+}$-ion especially on the M1 sites. Furthermore when temperature increases the moment on M1 decreases faster than the moment on M2 as already observed in Fe_2SiO_4 [5]. The spin directions for both sites are shown in Fig. 3.

Magnetization measurements [4] on Mn_2SiO_4 gave evidence for a weak ferromagnetism. However, this component would be too weak to be detected by neutron diffraction directly. A refinement of the neutron data including a ferromagnetic component on M2 did not alter the agreement between observed and calculated structure factors. The group theoretical analysis [11] does, however, reveal that such a ferromagnetic component is in agreement with the symmetry requirements. This component is therefore included in Table 2.

4.2 Co_2SiO_4

The neutron diffraction experiments on Co_2SiO_4 in the temperature range 4.2 K $<$ $< T < T_N = 49.5(1)$ K revealed magnetic intensities for reflections which could only occur if canting is present (Fig. 2). This is in contrast with results of previous neutron powder measurements [1]. The reflections given in Fig. 2 are connected with

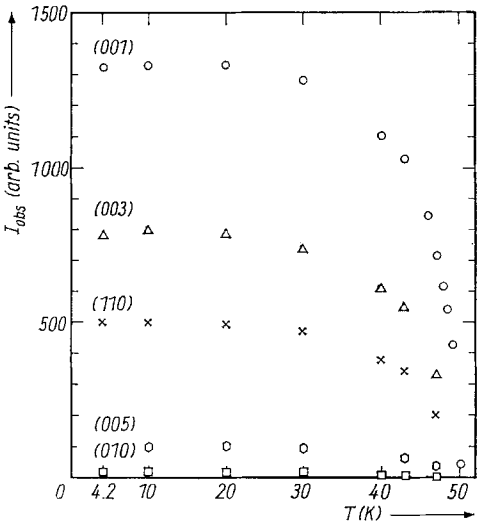

Fig. 2

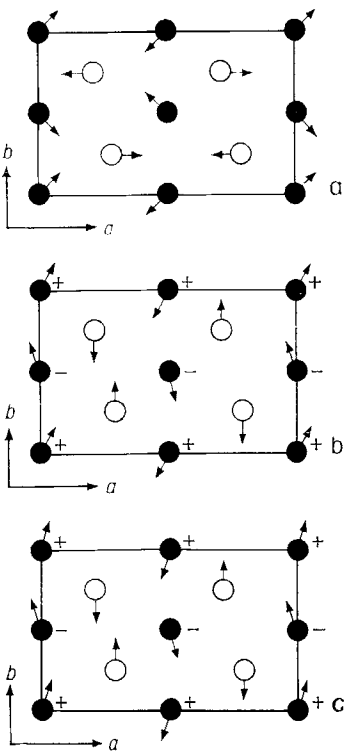

Fig. 3

Fig. 2. Intensity of five magnetic reflections in Co_2SiO_4 as a function of temperature below T_N
Fig. 3. The antiferromagnetic spin structure at 4.2 K projected on the ***a*–*b*** plane, ● moments on M1, ± indicates component in ***c***-direction, ○ moments on M2. a) Mn_2SiO_4, b) Fe_2SiO_4, c) Co_2SiO_4

the three components of the magnetic moment. The reflection (110) is representative for μ_a (001) (003), and (005) for μ_b and (010) for μ_c. Precise values of the canting angles were refined from data sets at $T = 4.2$, 20, and 40 K. The refined moments based on the structure factors described above are listed in Table 2. The canted magnetic moment on M1 has its main component parallel to the ***b***-axis but components along the ***a***- and ***c***-directions are detected. The canting angles are almost independent of temperature. The configuration is displayed in Fig. 3. The magnetic moments at 4.2 K are considerably higher than the spin-only value for both sites. This is attributed to a spin–orbit coupling for the Co^{2+}-ion. They decrease according to a Brillouin function with increasing temperatures below T_N.

5. Discussion

The three olivine structures Mn_2SiO_4, Fe_2SiO_4, and Co_2SiO_4 are crystallographically isomorphous but they differ in their antiferromagnetic properties. In the case of Mn_2SiO_4 the spin direction is essentially parallel to ***a*** with canting on the M1 position at 4.2 K. This canting disappears well below the Néel point ($T_N = 47.1$ K) at about 20 K. The magnetic moments on M2 are bigger than on M1. At 4 K a moment of $4.55\mu_B$ was found on M2 but only $3.86\mu_B$ on M1. At 20 K the moment on M2 is $4.32\mu_B$ whereas only $2.66\mu_B$ were observed for M1. The magnetic moments are, however, considerably lower than the spin-only value of $5\mu_B$. This has been attributed to covalency

which was shown in the electron density study of Fujino et al. [12] and in the preliminary results of our polarized neutron study on Mn_2SiO_4.

The magnetic structures of Fe_2SiO_4 [5] and Co_2SiO_4 are essentially similar (Fig. 3). In both cases the spins on M2 are parallel to the b-axis. The moments on M1 deviate from that direction and they have components along the three crystallographic axes. This canting is observed in the whole temperature range below T_N. The magnetic moments are higher in Fe_2SiO_4 and Co_2SiO_4 than the spin-only value indicating an orbital contribution to the magnetic moment. The moment on M2 (4.40(10) μ_B at $T = 23$ K) is considerably higher in Fe_2SiO_4 than on M1 (3.40(20) μ_B at 23 K) whereas the moments on both sites are similar in Co_2SiO_4 with a slightly higher value for M1. The canting angles decrease continuously in Fe_2SiO_4 below T_N but they remain almost constant in Co_2SiO_4 below T_N.

In all three olivines the moment on M2 decreases in a manner similar to the Brillouin function. But while in Co_2SiO_4 the decrease of the moment of M1 is similar, it falls off very quickly in Mn_2SiO_4 and Fe_2SiO_4 when the temperature increases above 0 K.

A mean-field analysis has provided a good understanding of the experimental details. Whereas the canting in Mn_2SiO_4 may be explained by a negative value of the M1–O–M1 exchange integral in agreement with the theoretical model by Santoro et al. [3], the canting in Fe_2SiO_4 and Co_2SiO_4 is due in this analysis to single-ion anisotropy [11].

Acknowledgements

The single crystals have kindly been given to us by Dr. Takei, Sendai, Japan. Helpful discussions with Dr. G. Amthauer, Dr. R. Müller, and Dr. W. Treutmann are gratefully acknowledged. Thanks are due to Dr. O. Ballet for critical reading of the manuscript. We are grateful to Dr. Jane Brown, Institut Laue-Langevin, Grenoble, for support during the experiments. This work has been funded by the German Federal Minister for Research and Technology (BMFT) under the contract 03 FU1 FRA-0.

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(Received December 10, 1987; in revised form July 19, 1988)