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ANTIFERROMAGNETISM IN SYNTHETIC OLIVINES

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Neutron diffraction measurements on single crystals of synthetic α-Fe_2SiO_4, α-Co_2SiO_4 and α-Mn_2SiO_4 in the antiferromagnetic state revealed different magnetic moments on the two crystallographic sites and determined the precise canting angles on the M1-position. The results for Fe_2SiO_4 were confirmed by Mössbauer-spectroscopy to a greàt extent.

1. Introduction

The metal cations in the silicates Fe_2SiO_4, Co_2SiO_4 and Mn_2SiO_4 (orthorhombic, space group: Pnma, four molecules per unit cell) occupy two crystallographic sites in the olivine structure: M1 (4a) with site symmetry $\bar{1}$ and M2 (4c) with m.

Susceptibility measurements on powders [1,2] revealed antiferromagnetic order at low temperatures. A transition from a collinear to a canted AF-structure was postulated for Fe_2SiO_4 and Mn_2SiO_4 whereas Co_2SiO_4 was found to be collinear antiferromagnetic without canting along the *b*-axis.

Powder neutron diffraction [1,2] at 4 K confirmed the spin canting for the crystallographic site M1 in Fe_2SiO_4 and Mn_2SiO_4. The spins on the M2 site are parallel to the *b*-axis for Fe_2SiO_4 and to the *a*-axis for Mn_2SiO_4. Santoro et el. [1] describe the canting in the *a–c* plane whereas Cox et al. [3] derive the *a–b* plane for Mn_2SiO_4. The two models [1,3] give different angles of the spins with the crystallographic axes for Fe_2SiO_4 (fig. 2).

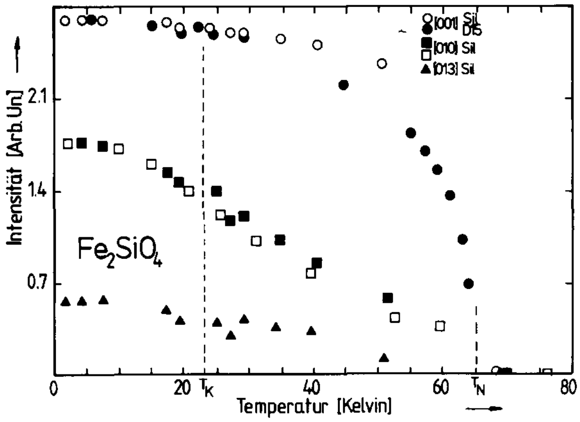

Fig. 1. Some magnetic reflections characteristic for canting in Fe_2SiO_4 as function of the temperature (Sil = measured at Siloe - reactor, Grenoble; D15 = measured at D15, ILL, Grenoble).

In this paper we report neutron diffraction studies on single crystals. A full account of our results on Fe_2SiO_4 is given, those on Mn_2SiO_4 and Co_2SiO_4 are briefly mentioned.

2. Experimental

Neutron diffraction was performed on plates of 5 mm diameter and 0.5 mm thickness (cut from crystals kindly provided by Dr. Takei, Sendai, Japan) on neutron facilities at the ILL and CENG, Grenoble and at Saclay, France.

Data sets of 100–200 reflections were collected at several temperatures. In addition, four to six reflections sensitive to the canting angles were followed as a function of temperature.

Further details are given in table 1 for Fe_2SiO_4. Nuclear and magnetic structure factors were refined simultaneously by least squares techniques. The parameters varied for the magnetic structure were: The moment on M2 and the components of the magnetic moment with the crystallographic axes on M1. The basic features of the resulting structures are in good agreement with the model [3], the agreement is less satisfactory with model [1]. Table 2 shows some calculated and observed structure factors at two temperatures in the antiferromagnetic state.

Table 1
Magnetic moments on M1 and M2 and angle cosines on M1 in synthetic Fe_2SiO_4 in the antiferromagnetic state

Site	10 K	23 K	35 K	50 K
M2 μ/μ_B	4.41(5)	4.4(1)	4.10(4)	3.74(7)
M1 μ/μ_B	4.4 (1)	3.4 (2)	2.8 (2)	2.1 (2)
$\cos(\boldsymbol{\mu},\boldsymbol{a})$	0.31(2)	0.21(3)	0.25(8)	0.08(5)
$\cos(\boldsymbol{\mu},\boldsymbol{b})$	0.77(1)	0.88(2)	0.89(1)	0.96(4)
$\cos(\boldsymbol{\mu},\boldsymbol{c})$	0.57(2)	0.43(2)	0.38(7)	0.27(3)
number of reflections	269	120	227	87

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Table 2
Some calculated and observed structure-factors (F_{calc} and F_{obs}) for Fe_2SiO_4 at two temperatures in the antiferromagnetic state

hkl	10 K		35 K	
	F_{calc}	F_{obs}	F_{calc}	F_{obs}
300	26.73	26.92	24.97	24.37
001	31.17	30.80	30.12	29.15
101	8.19	8.37	8.20	8.45
301	34.41	35.24	34.41	35.41
103	31.94	31.77	31.92	31.58
003	24.04	24.36	21.21	21.91
212	17.53	17.14	16.63	16.19
302	22.72	23.63	20.12	20.88
012	1.00	2.51	1.44	3.27
510	12.40	12.95	11.74	11.49

3. Results

3.2. *The magnetic properties of Fe_2SiO_4*

The intensities of several magnetic reflections are presented in fig. 1 as a function of temperature. The intensities of all reflections decrease steadily but with different slope. No anomalous behaviour is detected at $T = 23$ K. We therefore exclude a definite transition from a canted to a collinear structure. The continuous decrease of the magnetic intensities up to $T_N = 65.3$ K is interpreted as a gradual change of the canting angle and a decrease of the magnetic moments on both sites. The refinement of the parameters of the magnetic structure at 10, 23, 35 and 50 K confirms this conclusion. The magnetic moments of the two crystallographic sites are equal at 10 K but their temperature dependence produces a pronounced difference between 10 K to T_N. This difference is understood by the superexchange pathways of the two sites.

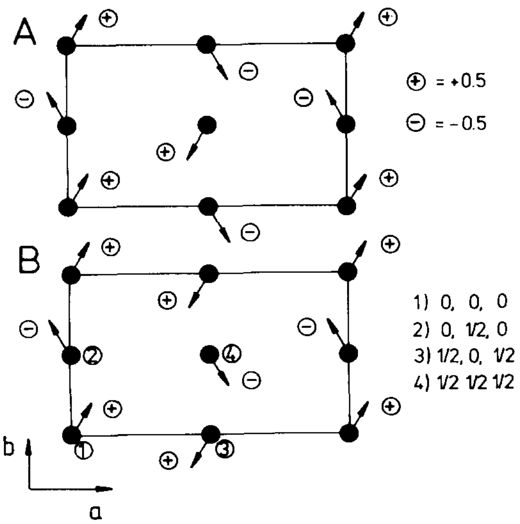

Fig. 2. Spin-canting in Fe_2SiO_4 according to the model of Cox et al. [3] (below) and Santoro et al. [1] (upper).

The magnetic moments on M2 are parallel to the *b*-axis below T_N whereas the canting persists on M1 up to the Néel temperature.

Additional Mössbauer measurements on a powder sample reveal a pronounced difference of the local magnetic fields between the two sites in agreement with a previous study [4]. The temperature dependence of the local magnetic fields does not show any anomaly between 4 and 40 K and confirms the conclusion from the neutron diffraction results. A full account of this work will be given elsewhere.

3.2. *The magnetic properties of Co_2SiO_4 and Mn_2SiO_4*

Our neutron diffraction results on Co_2SiO_4 reveal a slight deviation of the magnetic moment on M1 from the *b*-axis for the whole antiferromagnetic region. The previous powder study [2] described the magnetic structure as collinear. The magnetic moments on both sites are almost equal (M1: 3.9(1) and M2: 3.84(8) at 4 K) and exceed the spin-only value of $3\mu_B$ considerably.

The interpretation of the neutron data for Mn_2SiO_4 confirmed the canted structure on M1 and the collinear alignment on M2 for the temperature range from 4 to 20 K. From 20 K to $T_N = 47.1$ K the magnetic moments are (nearly) collinear.

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