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The Magnetic Structure of Mn_2GeSe_4

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The magnetic structure of the olivine type Mn_2GeSe_4 is investigated by powder neutron diffraction between 2 K and ambient temperature. Based on a number of "magnetic reflections" occurring below $T_c = 66$ K a model for the magnetic structure of the Mn^{2+} ions (d^5) is derived by structure refinements based on the FULLPROF program system. Most important result is an antiferromagnetic arrangement of the Mn^{2+} moments in successive layers along [001] ("easy direction"). This ordering evolves gradually with decreasing temperature as can be seen from the temperature dependence of the resultant magnetization of the two magnetic sublattices. The magnetization direction of one of the magnetic sublattices shows a weak tendency at low temperatures to deviate from the easy direction [001] towards [100]. The magnetic structure proposed for the title compound is comparable with the ones found for other magnetic thio- and seleno-olivines although a comprehensive picture for the magnetic properties of this group of solids is still lacking. The explanation for the "weak ferromagnetism" below $T_c = 66$ K with a saturation magnetization of about 0.5 μ_B per Mn^{2+} ion in a field of 7 T (2 K) as derived from earlier susceptibility measurements remains still speculative. It may result from local non-zero components that do not show up in the overall magnetic structure.

Introduction

Mn_2GeSe_4 is one of the rare ternary selenides that crystallizes in the olivine structure type with Se atoms forming a hexagonal close packing. The Mn^{2+} ions ($3d^5$) occupy half of the octahedral and the Ge^{4+} one eighth of the tetrahedral holes. Crystal structure and temperature dependence of the magnetic susceptibility for Mn_2GeSe_4 were recently determined[1]. Above 150 K the susceptibility shows a clear paramagnetic field independent Curie–Weiss behaviour with an extrapolated Curie temperature $\Theta = -240(5)$ K indicating predominant antiferromagnetic exchange interactions between the Mn^{2+} ions. Below 150 down to 66 K significant deviations from an ideal Curie–Weiss behaviour are observed until below $T_c = 66$ K the susceptibility increases and becomes clearly field dependent. Consequently $1/\chi$ drops sharply for the low field data which we ascribe to a weak ferromagnetic component that is saturated in the high field measurement.

In this paper we present the results of elastic neutron scattering measurements on powder samples obtained at the ILL Grenoble using the instruments D2B and D20. The model for the magnetic structure of Mn_2GeSe_4 at different temperatures is based on Rietveld refinements and discussed on the background of earlier susceptibility and magnetisation measurements. A particular problem of a detailed comparison between the susceptibility measurement and the magnetic structure as obtained by neutron diffraction is that the latter one is measured under *zero* field conditions whereas the magnetization measurements require a *non-zero* field. So a *weak* magnetization detected by a susceptibility measurement may not necessarily be reflected by the magnetic structure.

Results and Discussion

General

A few investigations concerning magnetic properties (susceptibility, magnetic structure) of sulfur and selenium containing olivines which are closely related to the title compound, have been carried out in the past. They were initiated by the surprising observation of a *sharp* local $1/\chi$ minimum between 83 and 85 K for Mn_2SiS_4[2,3,4] accompanied by the occurrence of "weak ferromagnetism". This effect might be related to "metamagnetism" occurring in certain antiferromagnetic compounds under special conditions as a function of an external field (see, for example, ref.[5]). Indeed below 85 K Mn_2SiS_4 is antiferromagnetic with a change of the easy direction from [010] to [100] between 83 and 85 K. Above 85 K the compound is paramag-

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netic. In particular the *sharp* local $1/\chi$ minimum is unique among the chalcogen containing olivines investigated so far. A further example is Mn_2SiSe_4 which is comparable to Mn_2SiS_4 in its *general* susceptibility behaviour, but is characterized by a *broad* local $1/\chi$ minimum between 66 and 30 K[6,7]. The Mn^{2+} ions in Mn_2SiSe_4 show an antiferromagnetic ordering (easy direction: [001]). A complex behaviour with respect to the temperature dependence of susceptibility and magnetization was discussed on the basis of several measurements in two independent publications for the olivine type Fe_2GeS_4 (T_N = 144 K)[3,8]. This compound shows an antiferromagnetic ordering below 144 K (easy direction [010]) followed by a change of the easy direction to [001] at lower temperatures. The susceptibility behaviour of Mn_2GeS_4 is unknown but its antiferromagnetic structure was determined at 4.2 K[9] (easy direction [010]).

The Olivine Structure

Some important aspects of the well known olivine structure[10] with respect to an understanding of the magnetic structure of Mn_2GeSe_4 are summarized subsequently. Olivine and spinel are frequent competitors for solids with the general chemical composition A_2BX_4. The olivine structure is preferred if relatively large cations (A = Mn^{2+}) occupy the octahedral and relatively small cations (B = Ge^{4+}) the tetrahedral holes. The opposite is true for spinel (further details see, for example, ref.[11,12]).

Concerning the magnetic structure it is important to mention that the $MnSe_6$ octahedra are arranged in layers perpendicular to [001] at $z \approx 0$ and $z \approx 0.5$. *Inside* the layers the octahedra share *common edges* and form zig-zag chains which are separated by $GeSe_4$ tetrahedra. Between successive layers along [001] the AX_6 octahedra share *corners* only (Figure 1). A section of the resulting three dimensional arrangement of the Mn^{2+} ions in layers perpendicular to [001] referring to the just mentioned zig-zag arrangement of $MnSe_6$ octahedra is shown in Figure 2. It can be seen that the Mn^{2+} ions form isolated triangular strands along [010]. In the (110) plane the strands are separated by $GeSe_4$ tetrahedra (not shown in Figures 1 and 2). Interatomic distances between Mn^{2+} ions inside the strands are around 400 pm between adjacent strands they are greater than 479 pm in all directions.

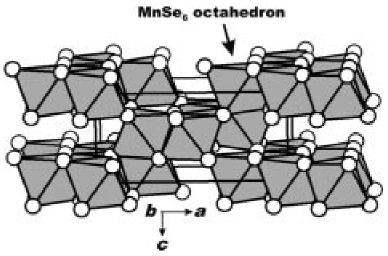

Figure 1. Section of the Mn_2GeSe_4 structure emphasizing the arrangement of the $MnSe_6$ octahedra. The $GeSe_4$ tetrahedra are omitted for clarity.

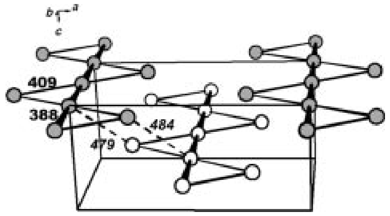

Figure 2. Perspective drawing of the arrangement of Mn^{2+} ions (approximately along [010]) in Mn_2GeSe_4 with shortest interatomic distances d(Mn–Mn) inside and between the strands.

Magnetic Structure and Magnetization

Figure 3 shows a Rietveld plot (3 K) and Figure 4 neutron scattering diagrams (D2B, low 2Theta section) for three different temperatures (3, 63 and 196 K). Upon cooling below 66 K five significant magnetic reflections with increasing intensity can be indexed as 100, 110, 300, 310 and 120. The Miller indices of these magnetic reflections can be assigned on the basis of the chemical unit cell, but apparently violate the a-glide plane in *Pnma*. They are similar to those ones found in the 1.4 K measurement for Mn_2SiSe_4[6,7] but are different from the ones found for Fe_2GeS_4[8] at 85 and 4.2 K.

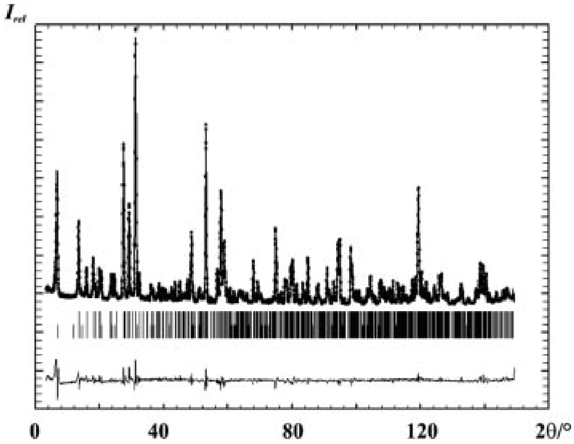

Figure 3. A Rietveld plot of a neutron scattering measurement of Mn_2GeSe_4 at 3 K.

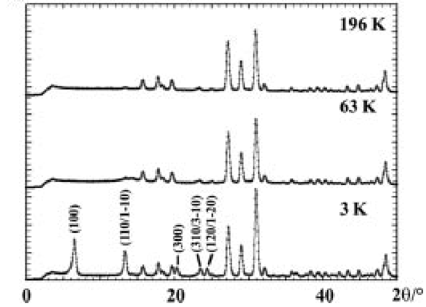

Figure 4. Neutron scattering diagrams for Mn_2GeSe_4 at 196, 63 and 3 K. The magnetic reflections are marked by their Miller indices.

As in the case of Mn_2SiSe_4, [001] reflections are basically absent (see however discussion below). This indicates an antiferromagnetic arrangement of Mn^{2+} ions in the layers at $z \approx 0$ and $z \approx 0.5$ with the magnetic vector aligned along [001] ("easy direction") similar to the magnetic structure of Mn_2SiSe_4 (see above). In accordance with Mn_2SiSe_4 we assumed for our initial Rietveld refinements (3 K data obtained with the D2B instrument) a model based on an ordered magnetic phase characterized by a $C_z(4a) - C_z(4b)$ coupling. 4a and 4b are the Wyckoff positions for the two crystallographically different Mn^{2+} ions and C_z refers to Bertauts notation[13] for this type of coupling in space group *Pnma*. Relevant refinement data for different temperatures based on the magnetic reflections are given in Table 1. Further details are discussed in ref.[14]

Table 1. Reliability factors for the chemical (R_B) and the magnetic structure (magnetic R) of Mn_2GeSe_4 between 10 and 65 K as obtained by Rietveld refinements with neutron powder data at different temperatures.

T/K	M_{4a}/μ_B	M_{4c}/μ_B	R_B/%[a]	Magnetic *R*/%[b]
10	4.11(4)	4.26(5)	2.76	9.99
12	4.05(4)	4.23(5)	3.36	10.1
15	3.97(4)	4.22(5)	2.87	10.7
17	3.90(4)	4.20(5)	2.80	11.0
20	3.84(4)	4.17(5)	2.77	11.3
24	3.74(4)	4.14(5)	3.09	12.0
28	3.61(4)	4.13(5)	3.08	12.7
32	3.48(4)	4.05(5)	3.30	13.8
36	3.30(4)	3.99(5)	3.34	15.2
43	3.06(4)	3.84(5)	3.64	17.4
46	2.82(4)	3.70(5)	3.92	19.6
49	2.64(4)	3.53(6)	4.21	21.9
52	2.46(4)	3.39(6)	4.38	24.9
55	2.29(5)	3.21(6)	4.26	28.3
57	2.04(5)	2.97(7)	4.95	33.2
59	1.94(5)	2.85(7)	4.96	34.7
61	1.72(6)	2.61(7)	5.17	40.9

[a] $R_B = [\sum_h |I_{obs,h} - I_{calc,h}|]/[\sum_h |I_{obs,h}|]$. [b] The magnetic R is defined as R_B but it is applied to magnetic intensities.

As a result of these initial calculations it can be stated that the magnetic structures of Mn_2SiSe_4 and the title compound (Figure 5, a) are similar, except a possible transverse component of one of the magnetic sublattices (see below). In most of the other chalcogeno-olivines investigated up to now such a transverse component of at least one magnetic sublattice is superimposed to the general antiferromagnetic order. Such transverse components evolve either continuously with decreasing temperature or they occur in an intermediate temperature range. A good example is the just mentioned Mn_2SiSe_4 where a transverse component was discussed but could not be verified significantly by the magnetic structure.[6,7] Indeed a closer inspection of details of the magnetic scattering diagrams of the title compound in combination with Rietveld refinements based on the D2B data showed a weak indication for a transverse component of *one* of the two magnetic sublattices (Figure 5, b). In particular the very weak and somewhat diffuse scattering intensity at the 2Theta position where the magnetic 001 reflection occurs (marked by an arrow in Figure 4) is a (weak) indicator for a possible deviation from the [001] direction. There is low significance but an apparent tendency from our refinement calculations that this deviation is associated to those Mn^{2+} ions which belong to the Wyckoff position 4(a). A final proof based on the existing data is, however, not possible presently.

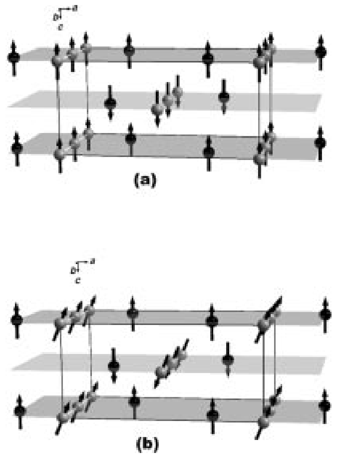

Figure 5. (a) The magnetic structure of Mn_2GeSe_4 as obtained by *initial* Rietveld refinements based on 3 K neutron scattering data. Mn atoms belonging to Wyckoff position 4(a): light gray balls, Wyckoff position 4(b): black balls. (b) Possible magnetic structure below 66 K including a deviation of the Mn^{2+} in Wyckoff position 4(a) from the easy direction [001] towards [100] (qualitative representation of the unknown inclination angle).

It is further interesting to look at the magnetization per Mn^{2+} ion for the two magnetic sublattices (Figure 6), derived from the evaluation of the D20 neutron data. One can see clearly that the successive ordering with decreasing temperature evolves with different velocities for the two sublattices, although both end up with a resultant magnetization per Mn^{2+} ion of 4.25 μ_B. This value corresponds to the one found for Mn_2SiSe_4 (4.5 μ_B see ref.[6,7]) and is in good agreement with the assumed d^5 configuration for Mn^{2+}.

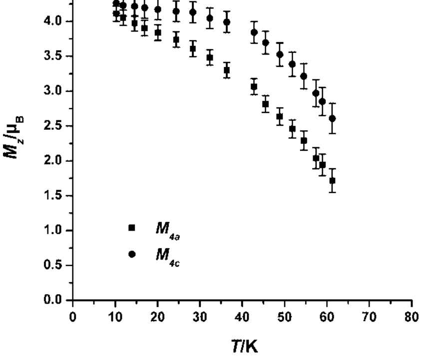

Figure 6. The resultant magnetization for the two magnetic sublattices as derived from the refinements of powder neutron diffraction diagrams between 10 and 60 K.

Neither the deviation alone nor the antiferromagnetic basis structure, however, account for the very weak resultant ferromagnetic magnetization ($< 0.05\ \mu_B$ per Mn^{2+} ion) of the title compound even in low fields at low temperatures. As Figure 7 shows this weak magnetization, which may result from non-compensating local components in the overall antiferromagnetic sample, saturates even in an external field of 7 T to about $0.5\ \mu_B$ per Mn^{2+} ion only.

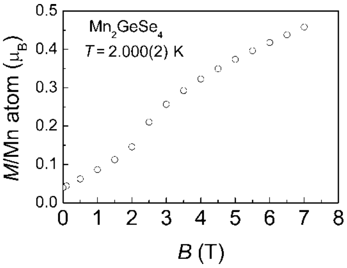

Figure 7. The resultant overall magnetization per Mn^{2+} at 2 K in an external field between 0 and 7 T.

One cannot expect from neutron powder diffraction data to reflect the origin of such a weak resultant magnetization in the magnetic structure. Speculations about magnetically non compensated grain boundaries and domain size effects as possible origins can be found in the literature (e.g., ref.[6,7]). Moreover we note the slight anomaly in the M vs. B curve (Figure 7) between 2 and 4 T which is not discussed in this paper but seems to be an indication for more subtle magnetic properties of the title compound.

Experimental Section

Powder samples of Mn_2GeSe_4 were obtained by the experimental procedure described in ref.[1] The neutron diffraction measurements were carried out with the D2B and D20 powder diffractometer at the ILL in Grenoble with samples contained in cylindrical vanadium containers and loaded into a standard helium flow cryostat. Data were collected at the temperatures 3 K, 63 K, 196 K (D2B) and with the instrument D20 in the temperature range $10\ K < T < 75\ K$ using different ΔT steps. The wavelength was 1.594 Å. Data sets cover a range in 2Θ up to 160° and have an angular resolution of 0.05°. The Rietveld method (Fullprof package[15,16]) was used to refine at first the chemical structure at room temperature. In subsequent refinement cycles based on low temperature data various refinement strategies were used. In these calculations the magnetic moment vectors of all eight Mn^{2+} ions in the Wyckoff positions 4(a) and 4(c) were refined either independently or partly fixed by constraints. The room-temperature data served as basis for the positional parameters of the chemical structure. In addition to the magnetic moment vectors only thermal parameters and lattice constants were refined with low-temperature data.

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