Magnetic structure of $MnS_2$: single-k or multiple-k, collinear or helical spin density wave?



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# Magnetic structure of $MnS_2$: single-$k$ or multiple-$k$, collinear or helical spin density wave?

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**Abstract.** The magnetic structure of the cubic type-III antiferromagnet $MnS_2$ has been investigated by unpolarized and polarized single-crystal neutron diffraction measurements. By applying a magnetic field up to 8 T parallel to [0, 0, 1] and [1, −1, 0] we have established that the magnetic structure of $MnS_2$ is actually of the single-$k$ type. Polarized neutron diffraction investigations using zero-field neutron polarimeter (CRYOPAD) have further established that the magnetic structure of $MnS_2$ is collinear and is not of the helical spin density wave (HSDW) type.

## 1. Introduction

The magnetic semiconductor $MnS_2$ orders with the type-III antiferromagnetic structure [1] which involves doubling of the unit cell along a cubic edge direction along which the spins are oriented. The antiferromagnetic phase transition at $T_N = 48$ K is found to be of first order [2–4]. The $Mn^{2+}$ ions in $MnS_2$ form a face centred cubic (FCC) lattice. The FCC lattice is inherently frustrated with regard to antiferromagnetic ordering and, therefore, exhibits many different types of antiferromagnetic ordering. Nearest-neighbour Ising antiferromagnets on the FCC lattice have zero-temperature ground states with large degeneracies which are not just due to symmetry [5, 6]. At any non-zero temperature, fluctuations break the degeneracies: entropy favours the ground state(s) about which the density of low-energy excitations is greatest, producing a well-defined long-range order. Villain *et al* [5] called this phenomenon 'ordering due to disorder' and noted that both thermal and quenched disorders could induce long-range order. This idea has been extended to the Heisenberg FCC antiferromagnets with only isotropic exchange coupling, which also have ground states with continuous degeneracies [7]. Again thermal fluctuations select special ground states, typically the collinear ones. $MnS_2$ is a typical example of such a Heisenberg antiferromagnet on a FCC lattice and therefore has been the subject of our systematic investigations. ,

The spatial configuration of the magnetic moments of the type-III magnetic structure based on a FCC lattice is specified by the wave vectors $k_1 = (2\pi/a)(\frac{1}{2}, 1, 0)$ and $-k_1$, $k_2 = (2\pi/a)(0, \frac{1}{2}, 1)$ and $-k_2$, $k_3 = (2\pi/a)(1, 0, \frac{1}{2})$ and $-k_3$ where $a$ is the lattice constant. The type-III antiferromagnet is associated with magnetic Bragg reflections at positions $G \pm k_i$ where $G$ is a reciprocal lattice vector and $i = 1, 2, 3$. Diffraction experiments cannot distinguish between a single-$k$ multidomain structure and multiple-$k$ structure in a cubic system without the application of magnetic field or uniaxial stress [8, 9]. Again there are two possible single-$k$ type-III antiferromagnetic structures. The first is collinear and corresponds to a single-spin density wave (SSDW) and the second variety is called the helical spin density wave (HSDW). The type-III HSDW structure has the additional property that magnetic Bragg reflections have a polarization-dependent cross-section [10] and the HSDW can therefore be distinguished from the SSDW by polarization analysis.

To understand the microscopic origin of the first-order phase transition in $MnS_2$ we have investigated the diffuse magnetic scattering above $T_N$ and magnetic excitations below $T_N$ [11]. The magnetic excitation spectra of $MnS_2$ are difficult to interpret unless the magnetic structure of $MnS_2$ is known with certainty. To distinguish between the different possibilities we have performed unpolarized neutron diffraction investigations on $MnS_2$ under a magnetic field of up to 8 T and have also performed polarized neutron investigations with zero-field neutron polarimetry. The results of these investigations will be described and discussed in the present paper. We have established that the magnetic structure of $MnS_2$ is in fact a collinear single-$k$ type.

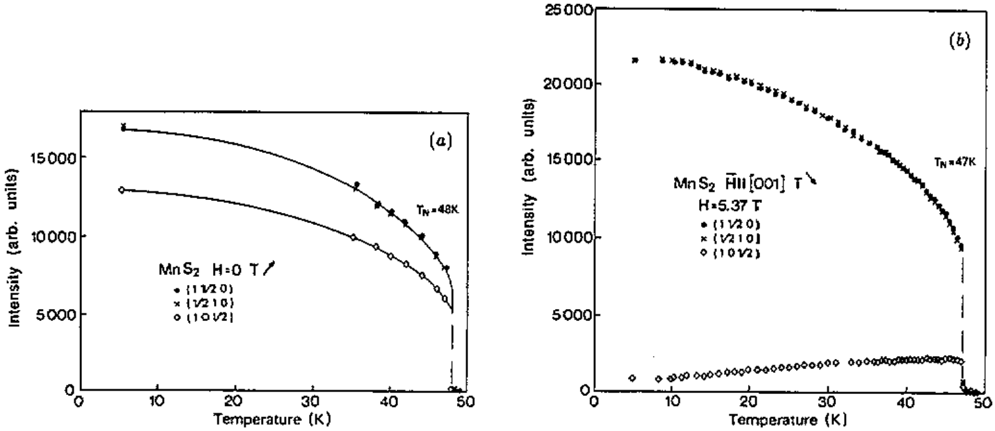
## 2. Experiment

### 2.1. Unpolarized neutron diffraction investigations in an applied magnetic field

We have used a natural single crystal (hauerite) of high purity for the present investigation. Two small pieces of about 4 mm in linear dimension were cut out of the original large single crystal (octahedron with linear dimensions of about 1 cm). The first crystal (crystal I) had the form of a semi octahedron with the sides of its basal square parallel to $\langle 1\,1\,0 \rangle$ and the perpendicular to the basal square parallel to [0 0 1]. The second crystal (crystal II) had an irregular form but was approximately a rectangular paralleopiped of size of about $2 \times 2 \times 4\ mm^3$. Unpolarized neutron diffraction measurements were performed with the D15 diffractometer of the Institut Laue–Langevin in Grenoble. The diffractometer was used in normal beam geometry at a neutron wavelength $\lambda = 1.174$ Å. The crystal was fixed on the sample stick of a helium cryostat with a superconducting magnet capable of generating vertical magnetic fields up to 10 T. We have investigated the temperature dependence of $\frac{1}{2}1 0$, $1\frac{1}{2}0$ and $1 0 \frac{1}{2}$ magnetic reflections of $MnS_2$ crystal I with magnetic fields applied parallel to [0 0 1] and [1, −1, 0]. We have also investigated the field dependence of the magnetic reflections with the magnetic field parallel to [1, −1, 0] on the $MnS_2$ crystal II.

### 2.2. Polarized neutron diffraction with the zero-field polarimeter

Crystal II was carefully aligned and mounted with its [0 0 1] axis vertical in the zero-field polarimeter CRYOPAD on the IN20 polarized beam triple-axis spectrometer at the Institut Laue–Langevin, Grenoble. The principle and operation of the CRYOPAD have been fully described elsewhere [12, 13]. In short, it allows both the input neutron beam polarization to be set to any desired angle and the magnitude and direction of the polarization in a diffracted beam to be found under the control of a PDP11/73 computer. The diffracting sample is kept in a field-free region and its temperature can be maintained in the range 1.5–315 K. The Heusler alloy monochromator and analyser crystal of IN20 were set to a wavelength of 1.532 Å. Although the CRYOPAD makes it possible to set the input polarization $\boldsymbol{P}$ to any desired angle, it is convenient from the point of view subsequent analysis to make scans in which $\boldsymbol{P}$ is varied in the three principal planes defined by the $x$-axis parallel to the scattering vector $\boldsymbol{\kappa}$, the $z$-axis vertical and the $y$-axis making the right-handed set.



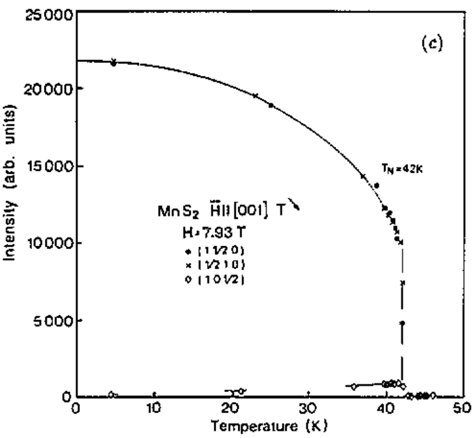




**Figure 1.** Temperature variation of the intensities of $\frac{1}{2}10$, $1\frac{1}{2}0$ and $10\frac{1}{2}$ magnetic reflection at (*a*) $H = 0$, (*b*) $H = 5.37$, (*c*) $H = 7.93$ T with magnetic applied parallel to [001].

## 3. Results of unpolarized neutron diffraction in magnetic fields

Figure 1(*a*) shows the temperature variation of the intensities of the $\frac{1}{2}10$, $1\frac{1}{2}0$ and $10\frac{1}{2}$ magnetic reflections at $H = 0$. Assuming a single-***k*** magnetic structure of $MnS_2$, these reflections correspond to the contributions of the same magnetic reflections from the $K_x$, $K_y$ and $K_z$ domains. The intensities from $K_x$ and $K_y$ domains are equal within the experimental accuracy whereas that of the $K_z$ domain is significantly smaller at all temperatures below $T_N$. Figures 1(*b*) and 1(*c*) show the temperature variations of the same reflections for magnetic fields $H = 5.37$ and 7.93 T applied parallel to [001]. The magnetic field was applied at 4 K. Next, the temperature was increased to a temperature above $T_N$ and the temperature variation of the intensities of the above-mentioned reflections was measured, while the temperature was decreased in steps. As expected for a multidomain single-***k*** structure the magnetic field applied parallel to [001] suppresses the intensity from the $K_z$ domain whereas that from the $K_x$ and $K_y$ domains increase in intensity. The sum of the intensities from the three domains remains, however, unchanged at all temperatures below $T_N$. On the other hand, the temperature dependence of the intensity from the $K_z$ domain is different from what one expects: this intensity decreases linearly with decreasing temperature. This is very unusual behaviour and is difficult to understand. Another unusual feature is that although the magnetic field was not exactly parallel to [001] but was tilted with respect to it by about a degree,

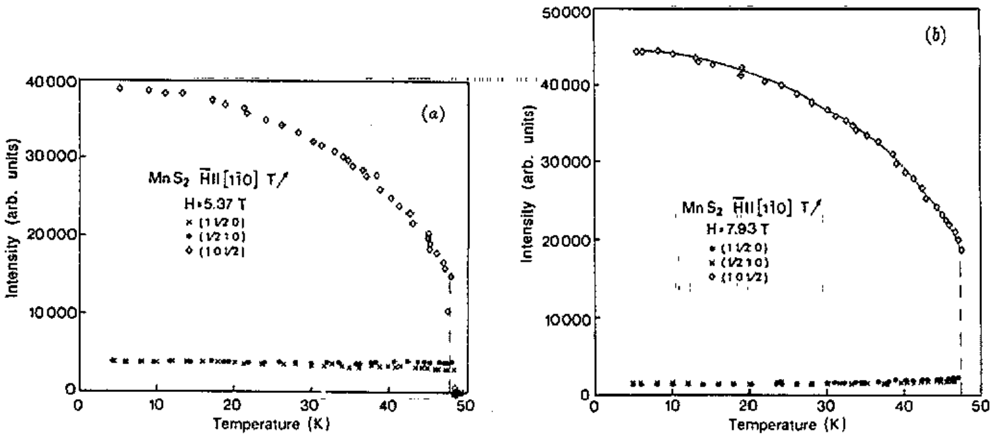



**Figure 2.** Temperature variation of the intensities of ½10, 1½0 and 10½ magnetic reflection at (*a*) $H = 5.37$ and (*b*) $H = 7.93$ T with magnetic field applied parallel to $[1-10]$.

the intensities from the $K_x$ and $K_y$ domains remain equal within experimental accuracy. At $H = 7.93$ T and $T = 4.2$ K the $K_z$ domain is practically depopulated. The magnetic phase transition at $T_N$ retains its first-order character up to $H = 7.93$ T. The Neél temperature decreases from $T_N = 48$ K at $H = 0$ to $T_N = 42$ K at $H = 7.93$ T. It seems likely that this decrease of $T_N$ at higher fields is not real but is caused by problems with the thermometry that we had during this measurement. This is also supported by the fact that in the subsequent measurements performed after removing the thermometric problems with magnetic field parallel to $[1, -1, 0]$ (see next paragraph) no such field variation of $T_N$ could be detected.

We have performed similar investigations with magnetic fields applied parallel to $[1, -1, 0]$. The results obtained are very similar. Figures 2(*a*) and 2(*b*) show the temperature dependence of ½10, 1½0 and 10½ magnetic reflections with $H = 5.36$ and 7.93 T applied approximately parallel to $[1, -1, 0]$. The magnetic fields were applied at 4 K and the measurements of the temperature variation of the intensities were performed as the temperature was increased by steps. For $H = 5.36$ T we have also measured the temperature variation of the intensities while the temperature was decreased. Some hystereses was observed. Just below $T_N$, the intensity of the 10½ reflection measured on cooling was less than that found on heating by a factor of about 1.2 whereas for ½10 and 1½0 the intensities were greater than those found on cooling by factors of 1.4 and 1.3, respectively. These differences disappeared at about 4 K. As expected, the applied magnetic field parallel to $[1, -1, 0]$ suppresses the intensities from the $K_x$ and $K_y$ domains and increases the intensity from the $K_z$ domain, the total intensity from the three domains remaining constant. At $H = 7.93$ T and $T = 4.2$ K the crystal is essentially a monodomain. Again the intensities of the depopulated $K_x$ and $K_y$ domains remain equal within experimental accuracy although the magnetic field was not exactly parallel to $[1, -1, 0]$ but was misoriented by about three degrees. The temperature dependence of these depopulated domains is also unusual: the intensities decrease with decreasing temperature.

So far we have discussed the results by assuming that the magnetic structure of $MnS_2$ is a multidomain single-$\boldsymbol{k}$ structure and have pointed out the unusual features of the experimental results obtained. However, the experimental results shown above do not prove conclusively that the magnetic structure of $MnS_2$ is of the single-$\boldsymbol{k}$ type. Instead

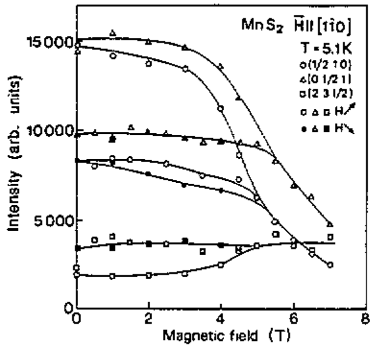



**Figure 3.** Magnetic field dependence of the intensities of $\frac{1}{2}10$, $0\frac{1}{2}1$ and $23\frac{1}{2}$ magnetic reflections at $T = 5.1$ K with magnetic applied parallel to [1 −1 0].

of saying 'the intensities from $K_x$, $K_y$ or $K_z$ domains' we could equally well refer to 'intensity contributions from the $K_x$-, $K_y$- or $K_z$-component of the modulation'. Moreover, the equality of the intensities from the $\frac{1}{2}10$ and $1\frac{1}{2}0$ reflections for $H = 0, 5.37$ and 7.93 T parallel to both [001] and [1, −1, 0] is suggestive of a double-**k** type of magnetic structure.

To distinguish between single-**k** and multiple-**k** of magnetic structures we have further investigated the magnetic field dependence of the $\frac{1}{2}10$, $0\frac{1}{2}1$ and $23\frac{1}{2}$ magnetic reflections at $T = 5.1$ K with the magnetic field applied parallel to the crystallographic [1, −1, 0] direction on a different single crystal (crystal II). The results are shown in figure 3. The reason for using a different crystal was to check whether the equal populations of the $K_x$ and $K_y$ domains of crystal I at $H = 0$ was just accidental. For this crystal the magnetic intensities from the $K_x$ and $K_y$ domains are practically equal at $H = 0$ but they differ in intensity more and more as the field is increased. The intensities of these reflections decrease with increasing magnetic field as expected for magnetic field applied parallel to [1, −1, 0], whereas the intensity of the $23\frac{1}{2}$ reflection increases (also as expected) with the magnetic field. One should note that we could not measure the intensity of the $10\frac{1}{2}$ reflection due to the geometrical restrictions and have measured the $23\frac{1}{2}$ reflection instead. The intensity of the $23\frac{1}{2}$ reflection, which is weaker by a factor of 1.7 than the $10\frac{1}{2}$ reflection, cannot be directly compared with the other two reflections. When the magnetic field was decreased from 7 T to lower values, the intensities of the $\frac{1}{2}10$ and $0\frac{1}{2}1$ reflections increase and follow the same curve only down to about 5 T. When the magnetic field is further decreased, the intensities do not regain their original values at $H = 0$ but show strong hysteresis. Similarly the intensity of the $23\frac{1}{2}$ reflection also shows hysteresis. If the sample is heated above the Néel temperature after the magnetic field is reduced to zero and then cooled to $T = 5.1$ K, the original intensities are regained. The behaviour proves conclusively that the magnetic structure of $MnS_2$ is actually of single-**k** type. For a multiple-**k** magnetic structure such hysteresis is not expected.

## 4. Results of zero-field neutron polarimetry

The polarization of a neutron beam scattered elastically by a pure magnetic reflection can be expressed in terms of the magnetic interaction vector $\boldsymbol{Q}$ as:

$$\boldsymbol{P}_s\, \partial\sigma/\partial\omega = -\boldsymbol{P}_i \boldsymbol{Q}\cdot\boldsymbol{Q}^* + \boldsymbol{Q}(\boldsymbol{P}_i\cdot\boldsymbol{Q}^*) + \boldsymbol{Q}^*(\boldsymbol{P}_i\cdot\boldsymbol{Q}) + i(\boldsymbol{Q}\times\boldsymbol{Q}^*). \qquad (1)$$

Figure 4 shows, in stereographic projection, the directions of the polarization of the

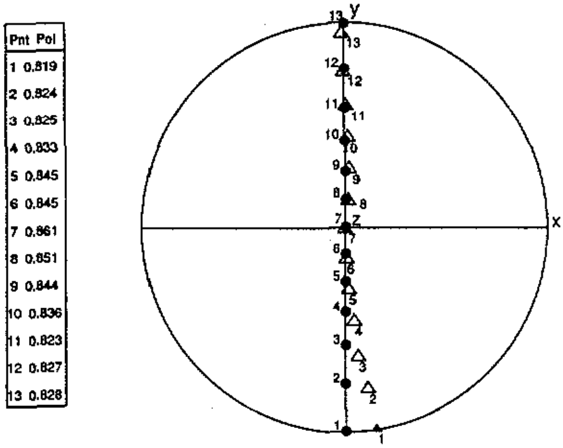



**Figure 4.** Stereographic projection showing the directions of polarization of the beam scattered by the $1\frac{1}{2}0$ reflection of $MnS_2$ for different directions of the incident polarization. Solid circles mark the directions of incident polarization in the upper hemisphere and open triangles the direction of the scattered polarization, the labelling numbers identify corresponding points. The magnitude of the scattered polarization for each direction is given in the table. Axes have been chosen with $x$ parallel to the $1\frac{1}{2}0$ scattering vector, $z$ parallel to [001] and $y$ completing the right-handed orthogonal set.

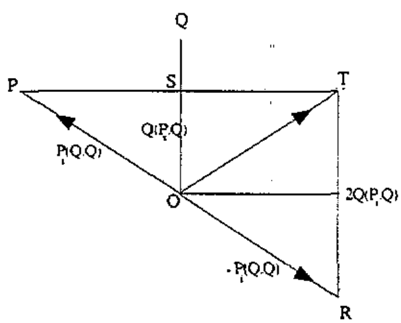



**Figure 5.** Vector diagram illustrating the rotation of the polarization.

beam scattered by the $(1\frac{1}{2}0)$ reflection of $MnS_2$ for different directions of incident polarization in the plane perpendicular to the scattering vector. The significant features of the results are that the vertical ($z$) component of polarization is inverted by the scattering process, but that the magnitude of the polarization is unchanged. This is the behaviour to be expected from a pure magnetic reflection whose magnetic interaction vector is horizontal. This result is therefore consistent with the SSDW model with spin direction parallel to $y$. For this model, $\boldsymbol{Q}$ is real and the rotation of the polarization can be understood with reference to figure 5. $OQ$ is parallel to $\boldsymbol{Q}$ and $OP$ parallel to the incident polarization and of length $\boldsymbol{Q} \cdot \boldsymbol{Q}$, the vector $OR$ then represents the first term in equation (1) and $OS$ the second. The third term is equal to the second and their sum can be represented by $RT$ so that the resultant scattered polarization direction is given by $OT$. The polarization thus precesses about $\boldsymbol{Q}$ by an angle of 180° and our results show that $\boldsymbol{Q}$ is horizontal. The HSDW model could give this behaviour only if the axis of the helix for the domain with propagation vector $(1\frac{1}{2}0)$ were [001]. For any other orientation $\boldsymbol{Q}$ would not be parallel to $\boldsymbol{Q}^*$ and the $\boldsymbol{Q} \times \boldsymbol{Q}^*$ term in equation (1) would lead either to a component of scattered polarization along the scattering vector, or to a degree of depolarization of the scattered beam if the two different chiralities of HSDW were present in equal proportions. This latter hypothesis can be ruled out by remembering that the $1\frac{1}{2}0$ reflection can equally well be considered as being generated from the 1 1 1 reflection by the propagation vector $0\frac{1}{2}1$ and the only spin direction perpendicular to [0 0 1] which has a consistent relationship to these two vectors is [0 1 0].

## 5. Summary and conclusions

We have investigated the magnetic structure of $MnS_2$ by unpolarized neutron diffraction in a magnetic field and also by polarized neutron diffraction with zero-field neutron polarometry. Our investigations have established that the magnetic structure of $MnS_2$ is collinear and single-$k$.

## Acknowledgments

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