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MAGNETIC ORDERING IN $MnSe_2$

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Neutron diffraction experiments on polycrystalline samples of $MnSe_2$ performed in the temperature range 1.8 to 54 K show a first-order magnetic phase transition at T_N = 49 K. The existence of the third-order harmonics below T_N shows the magnetic structure of $MnSe_2$ to be of commensurate square-wave type given by the wave vectors $\mathbf{k}$ = [1/3 0 1] and $3\mathbf{k}$ = [0 1 0].

AMONG THE HOMOLOGOUS SERIES of the pyrite-structure compounds MnX_2 (X = S, Se, Te), MnS_2 and $MnTe_2$ order with the well-known type III and type I antiferromagnetic structures, respectively [1]. The third compound $MnSe_2$ orders with a different magnetic structure and has been described (Fig. 1a) by the stacking of A- and B-type antiferromagnetic layers with the sequence A B $\bar{A}$ $\bar{B}$ $\bar{A}$ B which yields a magnetic unit cell (3a, a, a) three times larger than the chemical cell (a = 6.417 Å) [1]. However, a careful examination of the magnetic structure reveals that the proposed sequence is not the correct one because this would give rise to additional magnetic reflections, viz. [2/3 0 2].

$MnSe_2$ crystallizes with the pyrite-type structure with the primitive cubic space group $Pa\bar{3}$. The unit cell contains four sublattices denoted by 1, 2, 3, 4. The magnetic coupling between these sublattices is antiferromagnetic: $\mathbf{m}_1 = \mathbf{m}_2 = -\mathbf{m}_3 = -\mathbf{m}_4$. The sign of the magnetic moments (+ or −) in the other two crystallographic unit cells forming the magnetic unit cell is completely given by the knowledge of the wave vectors which in the present case are $\mathbf{k}$ = ⟨1/3 0 0⟩ and the third-order harmonic $3\mathbf{k}$ = 0. Thus the magnetic ordering correspond to a commensurate structure with a (+ − −) sequence, or (A B, $\bar{A}$ $\bar{B}$, $\bar{A}$ $\bar{B}$) (Fig. 1b).

However, considering only the magnetic atoms, Mn atoms are located in a face-centered-cubic Bravais lattice. Using this f.c.c. lattice the magnetic ordering is fully determined by the knowledge of the wave vectors which can be written as $\mathbf{k}$ = ⟨1/3 0 1⟩ and $3\mathbf{k}$ = ⟨0 1 0⟩ and the moment direction of the Mn atom 1. The moment direction has been found to be parallel to the commensurate component, i.e., ⟨1 0 0⟩.

The intensity of a magnetic superlattice peak at

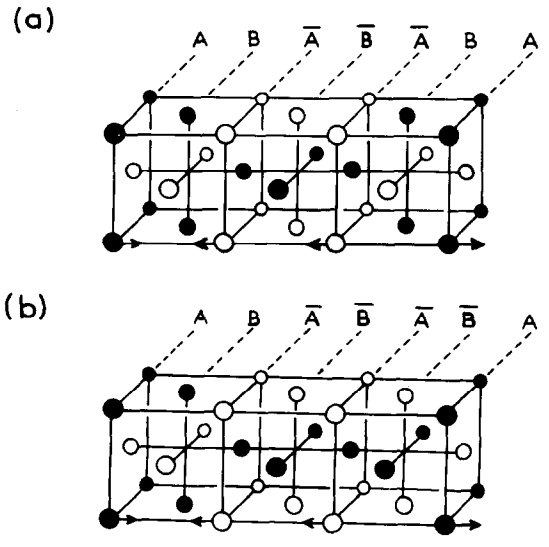

Fig. 1. (a) The magnetic structure of $MnSe_2$ proposed by Hastings *et al.* [1] at 4.2 K. The structure consists of layers (A B, $\bar{A}$ $\bar{B}$, $\bar{A}$ B) where $\bar{A}$ and $\bar{B}$ can be obtained from A and B by reversing the spin directions. The black and white circles represent the magnetic atoms having their magnetic moments oppositely directed, parallel to the magnetic axis indicated by the arrows. The Se atoms are not shown. b) The corrected magnetic structures of $MnSe_2$ compatible with the observed wave vector (AB, $\bar{A}$ $\bar{B}$, $\bar{A}$ $\bar{B}$).

the reciprocal point $\mathbf{h} = \mathbf{H} + \mathbf{k}$ within each Brillouin zone associated with the wave vector $\mathbf{k}$ is given by

$$I(\mathbf{h} = \mathbf{H} + \mathbf{k}) = (0.27)^2 f^2(\mathbf{h}) |\mathbf{m}_k|^2 \sin^2 \alpha, \quad (1)$$

where $\mathbf{H}$ is a reciprocal lattice vector, $\mathbf{m}_k$ is the Fourier component associated with the wave vector $\mathbf{k}$ and α is the angle between the moment direction and the scattering vector $\mathbf{h}$. For a powder sample the multiplicity of the reflection has to be taken into account.

The observed wave vectors $\mathbf{k}$ and $3\mathbf{k}$ define two sets of intensities. Each of these two sets allows us to determine the moment direction which has been found to be parallel to the commensurate component of the wave vector, i.e. [1 0 0] and the modulii of the two Fourier components $|\mathbf{m}_k|$ and $|\mathbf{m}_{3k}|$. The magnetic ordering is given by the sum of these two Fourier components by the equation

$$\mathbf{m}(\mathbf{R}_l) = \sum_{\mathbf{k}} \mathbf{m}_k e^{i\mathbf{k}\cdot\mathbf{R}_l},$$

with

$$\mathbf{m}_k = \frac{A_k}{2} e^{i\varphi_k} \hat{u}_k \quad \text{and} \quad \mathbf{m}_{3\mathbf{k}} = \frac{A_k}{4} e^{i\varphi_{3k}} \hat{u}.$$

We have then

$$\mathbf{m}(\mathbf{R}_l) = \left[\frac{A_k}{4} e^{i\varphi_{3k}} \cos 3\mathbf{k}\cdot\mathbf{R}_l + \frac{A_k}{2} e^{i\varphi_k} \cos \mathbf{k}\cdot\mathbf{R}_l\right] \hat{u}_k, \quad (2)$$

where $\hat{u}_k$ is the unit vector and φ_k and φ_{3k} are the phases corresponding to $\mathbf{k}$ and $3\mathbf{k}$, respectively.

It should be noted that a neutron diffraction experiment cannot determine the value of the phase φ_k and therefore the true magnetic structure remains undetermined. However, it is reasonable to assume that each Mn atom carries the same value of moment m_0 at low temperature. The reported magnetic structure with the corrected sequence (Fig. 1b) satisfies this condition and corresponds to a commensurate square-wave structure for which the ratio between the two Fourier components is well-defined by

$$|\mathbf{m}_k| = \frac{A_k}{2} = \frac{2}{3} m_0 \quad \text{and} \quad |\mathbf{m}_{3k}| = \frac{A_k}{4} = \frac{m_0}{3} \quad \text{with} \quad \varphi_k = 0, \quad \varphi_{3k} = \pi, \quad (3)$$

leading to

$$\mathbf{m}(\mathbf{R}_l) = m_0[-\tfrac{1}{3} \cos 3\mathbf{k}\cdot\mathbf{R}_l + \tfrac{4}{3} \cos \mathbf{k}\cdot\mathbf{R}_l]\hat{u}_k. \quad (4)$$

Now the important question to be answered is whether the structure remains complete square-wave-type or not up to T_N. Actually a first-order transition at T_N was first observed by Corliss and Hastings [2] suggesting the square-wave structure persists up to T_N, whereas Plumier and Sougi [3] have recently reported two successive transitions: a first order transition at $T^* = 48.5$ K from the square-wave structure to a sine-wave structure and the transition to the paramagnetic state at $T_N = 53$ K. However, these latter conclusions of Plumier and Sougi [3] are not convincing because in their spectrum at $T = 50.5$ K the third order harmonic (0 1 0) was still observed.

In order to clarify the magnetic ordering especially at higher temperatures close to T_N we have undertaken neutron diffraction on $MnSe_2$ and after the experiment was completed we came to know the recent work of Plumier and Sougi [3].

Powder samples of $MnSe_2$ were synthesized from the elements (Mn, crushed flakes, 99.99%, Johnson, Matthey & Co.; Se, powder, 99.99%, Koch Light Laboratories) using the sealed silica capsule technique. The X-ray Guinier photographs from the sample showed well-crystallized pyrite phase of $MnSe_2$ along with small amounts of unreacted Se. Neutron diffraction experiments were performed with the powder diffractometer equipped with a position sensitive detector located at the Siloe reactor of the Centre d'Etudes Nucléaires de Grenoble in the temperature range 1.8–54 K using a neutron wavelength of 2.50 Å.

The neutron diffraction pattern at $T = 1.8$ K is quite similar with that of [1]. The magnetic reflections can be readily indexed with the wave vectors $\mathbf{k} = [1/3\ 0\ 1]$ and $3\mathbf{k} = [0\ 1\ 0]$. The magnetic moment $m_0 = \frac{3}{2}|\mathbf{m}_k|$ is found to be 2.8 μ_B at 1.8 K. A part of the neutron diffraction pattern given in Fig. 2 shows the magnetic reflections $\langle 2/3\ 1\ 0\rangle$ associated with the wave vector $\mathbf{k} = [1/3\ 0\ 1]$ and the third order harmonic $\langle 1\ 0\ 1\rangle$ associated with the wave vector $3\mathbf{k} = [0\ 1\ 0]$ as a function of temperature in a heating cycle. At $T = 1.8$ K both reflections are well developed. Intensities of these reflections decrease continuously with temperature up to about 40 K following a Brillouin-type function but with an ordering temperature $T_N \simeq 65$ K (Fig. 3). At 40 K the sublattice magnetization corresponds to about 80% of the saturation value. At 47.7 K the magnetic reflection $\langle 2/3\ 1\ 0\rangle$ and the third-order harmonic 101 are still well defined but at 48.7 K the intensity of the $\langle 2/3\ 1\ 0\rangle$ reflection drops abruptly and the third-order $\langle 1\ 0\ 1\rangle$ reflection can no longer be observed with the present counting statistics. At 49.6 K none of the magnetic reflections are seen indicating that the first-order transition to the paramagnetic state occurs at $T_N = 49$ K. However, a broad critical scattering has been observed at the Bragg angle corresponding to the reflection $\langle 1/3\ 0\ 1\rangle$.

The above results show that the magnetic structure of $MnSe_2$ is of commensurate square-wave type at

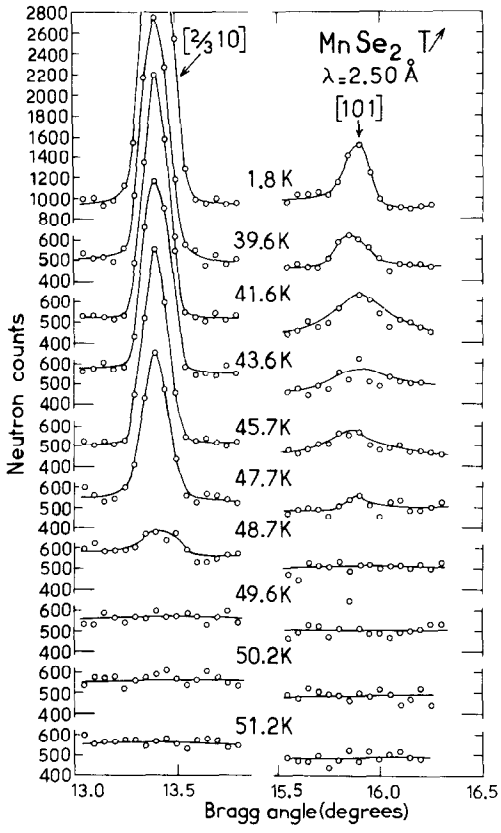

Fig. 2. Part of the neutron diffraction diagram of polycrystalline $MnSe_2$ obtained with the wavelength $\lambda = 2.50$ Å showing the temperature dependence of magnetic peak $\langle 2/3\ 1\ 0\rangle$ and the third-order harmonic $\langle 1\ 0\ 1\rangle$.

least in the temperature range 1.8–48 K in which the third order harmonic is clearly seen. At 48.7 K the third-order harmonic is not seen and therefore the modulation can theoretically be pure sine-wave type as was conjectured before [3, 4]. At 48.7 K the intensity of the $\langle 2/3\ 1\ 0\rangle$ reflection itself is very small, therefore the third-order harmonic which has an intensity less than the principal by a factor 4, is expected to be very feeble in intensity and can not be seen with the present counting statistics. We have calculated the ratio $|\mathbf{m}_k|/|\mathbf{m}_{3k}|$ of the Fourier components corresponding to the principal and the third-order harmonic. This ratio is found to be about 1/2 as expected and constant within the experimental accuracy in the whole temperature range except for temperatures

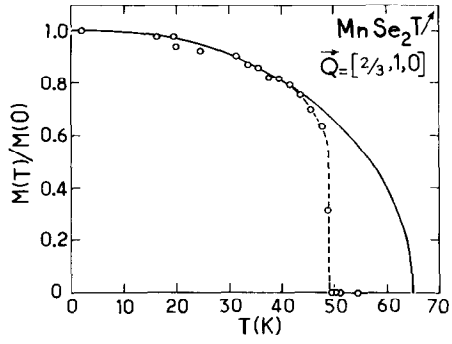

Fig. 3. Sublattice magnetization of $MnSe_2$ as a function of temperature calculated from the intensity of the $\langle 2/3\ 1\ 0\rangle$ reflection. Brillouin function $B_{5/2}$ has been fitted to the low-temperature data points. The dashed curve joins the data points.

very close to T_N where $|\mathbf{m}_{3k}|$ can not be determined with any reasonable accuracy. We therefore conclude that the magnetic ordering in $MnSe_2$ corresponds to a perfect square-wave in almost the entire temperature range below T_N. Dimmock's proposal [4] for the sine-wave modulation at T_N was based on the assumption of a second-order phase transition at T_N. Since the phase transition at T_N is of the first order the magnetic structure proposed by Hastings *et al.* [1] with the corrected sequence given in Fig. 1(b) is allowed up to T_N and the Landau–Lifshitz symmetry argument is no longer valid. We intend to perform experiments on single crystal of $MnSe_2$ in near future to investigate more carefully the magnetic structure very close to T_N and magnetic correlations above T_N.

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