Polarization dependence of magnetic Bragg scattering in YMn$_2$O$_5$

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Abstract

The polarization dependence of the intensity of elastic magnetic scattering from YMn$_2$O$_5$ single crystals has been measured at 25 K in magnetic fields between 1 and 9 T. A significant polarization dependence was observed in the intensities of magnetic satellite reflections, propagation vector $\tau = \frac{1}{2}, 0, \frac{1}{4}$, measured with both the [100] and [010] axes parallel to the common polarization and applied field direction. The intensity asymmetries $A$ observed in sets of orthorhombic equivalent reflections show systematic relationships which allow the phase relationship between different components of their magnetic interaction vectors to be determined. They fix the orientation relationships between the small $y$ and $z$ moments on the Mn$^{4+}$ and Mn$^{3+}$ sub-lattices and have allowed a further refinement of the magnetic structure, which determines the phases of the vector Fourier components with much higher precision. Systematic differences found between values of $A(hkl)$ and $A(\bar{h}\bar{k}\bar{l})$ suggest that there is a small modulation of the nuclear structure which has the same wavevector as the magnetic modulation and gives rise to a small nuclear structure factor for the satellite reflections. The magnitudes of the differences suggest shifts in the atomic positions of the order of 0.05 Å.

1. Introduction

YMn$_2$O$_5$ together with other members of the series of isostructural rare earth compounds (RMn$_2$O$_5$), exhibits multiferroic properties [1–3] of a type unique amongst known multiferroics. Whereas the magnetic structures giving rise to ferroelectricity in other materials are some form of spiral (cycloidal, conical etc) the magnetic order in the ferroelectric phases of RMn$_2$O$_5$ compounds has been shown to be only very weakly cycloidal, with the major components of the moments arranged nearly co-linearly in the $x$–$y$ plane and modulated as a spin density wave. The electric polarization and several other observations made on these phases can be explained within the framework of a simple, symmetric exchange model, in which polarization is generated by superexchange striction, effective even when the spins are perfectly collinear [4–6]. This is in sharp contrast to the mechanism proposed for the RMnO$_3$ series and other multiferroics, in which non-collinear spins are needed not only to break inversion symmetry, but also to generate atomic displacements, through the inverse Dzyaloshinsky–Moriya (IDM) effect [7, 8].

One of the difficulties encountered in studying the connection between magnetic structure and dielectric properties in these manganates is that, whether the ferroelectric polarization arises from exchange striction, or from cycloidal modulation of the magnetic structure, neither phenomenon contributes very much to the elastic scattering of either x-rays or neutrons. The relationship between the magnetic structure and the ferroelectric polarization can be demonstrated using neutron polarimetry [9] and resonant soft x-ray scattering [10]; atomic displacements induced by applied magnetic fields have been inferred from experiments with polarized synchrotron radiation [11], however none of these techniques can readily be applied to study in detail how these important features of the magnetic and nuclear structure respond to applied fields. In the present paper we demonstrate how such details can be studied using the well developed polarized neutron diffraction (PND) technique [12].

The intensity of elastic scattering $I^P$ of a neutron beam with polarization $P$ from a Bragg reflection of a magnetic crystal is given by

$$I^P \propto N^r + M_{\perp} \cdot M_{\perp}^* + 2\text{Re}(NP \cdot M_{\perp}^*) + P \cdot i(M_{\perp} \times M_{\perp}^*).$$  (1)
In this equation \( N \) is the nuclear structure factor for the reflection and \( \mathbf{M}_I \), the magnetic interaction vector, which is the projection on the plane perpendicular to the scattering vector of its magnetic structure factor. In most PND experiments, measurements are made of the polarization dependence of the intensities of the fundamental structural reflections in which most of the intensity usually comes from nuclear scattering (\( NN^* \gg \mathbf{M}_I \cdot \mathbf{M}_I^* \)). By contrast, the intensities of magnetic reflections from a simple antiferromagnet have no nuclear contribution and are independent of the direction of neutron polarization. The purely magnetic intensity scattered by the magnetic reflections can however be polarization dependent if the antiferromagnetic structure is such that the final term in equation (1) is non-zero. This will only occur if the magnetic structure is acentric and the moments are non-collinear (\( \mathbf{M}_I \not\parallel \mathbf{M}_I^* \)); the populations of centro-symmetrically related domains must be unequal and the scattering vector must not be perpendicular to the polarization direction. It is important because, unlike the total diffracted intensity, it is sensitive to just those details of the magnetic structure which give rise to its ferroelectric properties. The third term in equation (1) can contribute to the polarization dependence of antiferromagnetic reflections only if the nuclear structure is modulated with the same wavevector as the magnetic structure so that there is a finite nuclear contribution \( N \) to the structure factor. Any such nuclear scattering would give information about atomic displacements due to magnetic ordering.

The present experiment was undertaken to study whether PND can be used to study the origin of multiferroicity in a magnetic structure and to determine whether the field axis. This allowed access to reflections of 5 T and the ratios \( R \) of 1.5. The crystal was cooled to 25 K (\( T_N = 45 \) K) in a field of 5 T and the ratios \( R \) (flipping ratios) between the peak intensities diffracted with incident neutrons polarized parallel and anti-parallel to the field direction were measured for 160 magnetic satellite reflections \( hkl \) with \( h = \pm 0.5 \). Where possible all 8 orthorhombic equivalent \( hkl \) were included. The intensities of almost all the reflections measured were found to have a small but significant polarization dependence. To check whether this dependence arose solely because the crystal had been cooled through the Néel transition in a magnetic field, the field was reduced to zero, the crystal warmed to 45 K and cooled again to 25 K. A sub-set of reflections was remeasured first with 1 T and then with 3 T applied. Very little change in the flipping ratios was found. To be sure that the crystal had indeed passed the Néel transition in zero field, it was warmed to 75 K and again cooled to 25 K, all the time in zero field. Measurement of the same set of reflections in 1 T again gave nearly unchanged results. The crystal was remounted with a [010] axis parallel to the field direction and again cooled to 25 K in zero field. The flipping ratios of a group of 42 magnetic reflections \( hkl \) \( k = 0, -1, -2 \) were measured with 1, 3 and 9 T applied. Again, significant polarization dependence was found in the intensities of almost all the reflections with \( k \neq 0 \), but no significant effect due to increasing the field was observed.

### 3. Results

The polarized neutron intensity asymmetry \( A \) is defined as \( A = (I^+ - I^-)/(I^+ + I^-) \) where \( I^+ \) and \( I^- \) are the intensities scattered with neutrons polarized respectively parallel and anti-parallel to the polarization direction \( \mathbf{P} \). It can be calculated directly from the flipping ratios \( A = (R - 1)/(R + 1) \). The intensity asymmetries due to purely magnetic scattering (fourth term in equation (1)) have different symmetry properties from those due to nuclear magnetic interference (third term in equation (1)). Both \( \mathbf{M}_I(k) \) and \( N(k) \) obey Friedel’s law so

\[
\mathbf{M}_I(k) = \mathbf{M}_I(\bar{k})^* \quad \text{and} \quad N(k) = N(\bar{k})^* \\
\]

so that on reversal of the scattering vector \( \mathbf{M}_I(k) \times \mathbf{M}_I^*(k) \) changes sign whilst \( \text{Re}[N(k)\mathbf{M}_I^*(k)] \) does not. If \( A(k) \) and \( A(\bar{k}) \) are measured in normal beam geometry with the rotation axis parallel to the polarization direction then, setting \( |N|^2 + |\mathbf{M}_I|^2 = I \)

\[
A_M(k) = (\mathbf{M}_I(k) \times \mathbf{M}_I^*(k) \cdot \mathbf{P})/I \\
A_N(k) = 2\text{Re}(N(k)\mathbf{M}_I^*(k) \cdot \mathbf{P})/I \\
A_M(\bar{k}) = (\mathbf{M}_I^*(k) \times \mathbf{M}_I(k) \cdot \mathbf{P})/I \\
A_N(\bar{k}) = 2\text{Re}(N(k)\mathbf{M}_I(k) \cdot \mathbf{P})/I \\
\]

so

\[
A_M(k) = -A_M(\bar{k}) \quad \text{and} \quad A_N(k) = A_N(\bar{k}). \\
\]

Table 1 shows the intensity asymmetry \( A \) measured with each applied field for two reflections in each of the two crystal orientations, it can be noticed that the signs of \( A \) for reflections \( hkl \) and \( \bar{h}k\bar{l} \) are always different. In table 2 the asymmetries \( A \) of groups of orthorhombic equivalent reflections measured with both crystal orientations are listed. Within each group it can be seen that

- for the [100] orientation \( A(hkl) \approx -A(\bar{h}k\bar{l}) \approx A(\bar{h}k\bar{l}) \approx A(hkl) \)
- for the [010] orientation \( A(hkl) \approx A(\bar{h}k\bar{l}) \approx -A(hkl) \approx -A(\bar{h}k\bar{l}) \)

but that for the [100] orientation, where the geometry allowed measurement with \( h = \pm 0.5 \), \( A(hkl) \neq A(\bar{h}k\bar{l}) \). These
and axes parallel to the polarization direction.

Table 2. Polarized neutron intensity asymmetries $A$ measured at 25 K in different fields $H$ after cooling in 5 T and in zero field.

| $h$ | $k$ | $l$ | Field $||[100]$ |
|-----|-----|-----|----------------|
|     |     |     | $H = 5$ T$^a$ | $H = 1$ T$^b$ | $H = 3$ T$^b$ | $H = 1$ T$^c$ |
| 0.5 | 1.0 | 0.25 | $-0.033(2)$ | $-0.025(6)$ | $-0.041(2)$ | $-0.038(2)$ |
| 0.5 | 1.0 | $-0.25$ | $0.041(2)$ | $0.031(6)$ | $0.045(2)$ | $0.043(2)$ |
| 0.5 | 2.0 | 0.75 | $-0.015(4)$ | $-0.016(4)$ | $-0.031(7)$ | $-0.019(4)$ |
| 0.5 | 2.0 | $-0.75$ | $0.014(4)$ | $0.018(4)$ | $0.034(7)$ | $0.020(4)$ |

| $h$ | $k$ | $l$ | Field $||[010]$ zero field cooled |
|-----|-----|-----|----------------------------------|
|     |     |     | $H = 1$ T | $H = 3$ T | $H = 9$ T |
| 1.5 | 1.0 | 0.25 | $0.013(2)$ | $0.011(2)$ | $0.010(2)$ |
| 1.5 | 1.0 | $-0.25$ | $-0.010(3)$ | $-0.015(2)$ | $-0.011(2)$ |
| 0.5 | 1.0 | 1.25 | $0.019(5)$ | $0.029(5)$ | $0.032(7)$ |
| 0.5 | 1.0 | $-1.25$ | $0.054(10)$ | $-0.050(12)$ | $-0.0345(13)$ |

$^a$ Field cooled from 300 K in 5 T.
$^b$ Zero field cooled from 45 K.
$^c$ Zero field cooled from 75 K.

Table 2. Intensity asymmetries $A$ measured for groups of orthorhombic equivalent satellite reflections from YMn$_2$O$_5$ at 25 K with [100] and [010] axes parallel to the polarization direction.

| Polarization $||[100]$ | Polarization $||[010]$ |
|-------------------|-------------------|
| $h$ | $k$ | $l$ | $A(hkl)$ | $h$ | $k$ | $l$ | $A(hkl)$ |
| 0.50 | 1.00 | 0.25 | $-0.034(2)$ | 1.50 | 1.00 | 0.25 | $0.019(4)$ |
| 0.50 | 1.00 | $-0.25$ | $0.041(2)$ | 1.50 | 1.00 | $-0.25$ | $-0.021(4)$ |
| $-0.50$ | 1.00 | 0.25 | $-0.029(2)$ | $-1.50$ | 1.00 | 0.25 | $-0.016(3)$ |
| $-0.50$ | 1.00 | $-0.25$ | $0.032(2)$ | $-1.50$ | 1.00 | $-0.25$ | $0.015(6)$ |
| $-0.50$ | $-1.00$ | 0.25 | $-0.056(2)$ | | | | |
| $-0.50$ | $-1.00$ | $-0.25$ | $0.054(2)$ | | | | |
| $-0.50$ | $-1.00$ | 0.25 | $-0.079(2)$ | | | | |
| $-0.50$ | $-1.00$ | $-0.25$ | $0.076(2)$ | | | | |
| 0.50 | 2.00 | 0.25 | $-0.033(2)$ | | | | |
| 0.50 | 2.00 | $-0.25$ | $0.033(2)$ | | | | |
| $-0.50$ | 2.00 | 0.25 | $-0.022(2)$ | | | | |
| $-0.50$ | 2.00 | $-0.25$ | $0.019(2)$ | | | | |
| $-0.50$ | $-2.00$ | 0.25 | $-0.038(2)$ | | | | |
| $-0.50$ | $-2.00$ | $-0.25$ | $0.033(2)$ | | | | |
| $-0.50$ | $-2.00$ | 0.25 | $-0.064(2)$ | | | | |
| $-0.50$ | $-2.00$ | $-0.25$ | $0.062(2)$ | | | | |

symmetry relationships were found to apply to all the groups of equivalent reflections measured.

For the data presented in table 2, not only the signs, but also the magnitudes of $A(hkl)$ and $A(h\bar{k}\bar{l})$ differ. This suggests that $A$ contains contributions from both $A_M$ and $A_N$, but that the major contribution is from $A_M$, which dictates the sign; the difference in magnitude is then due to a smaller contribution from $A_N$. These observations show that the two centro-symmetrically related domains are unequally populated, and that this inequality was essentially unchanged by the different field cooling cycles. This suggests that the stability ofacentric domains in this crystal may be more strongly coupled to crystal imperfections than to magnetic fields of less than 10 T.

4. Magnetic scattering from YMn$_2$O$_5$

The manganese moments in YMn$_2$O$_5$ order at $\approx 45$ K to an antiferromagnetic structure with propagation vector $\mathbf{\tau} = \frac{1}{2} + \delta_x, 0, \frac{1}{2}$; below 40 K this incommensurate (HT-ICM) phase locks in to the commensurate CM phase with $\mathbf{\tau} = \frac{1}{2} + \delta_x, 0, \frac{1}{2}$; with further cooling below 23 K the structure again becomes incommensurate with $\mathbf{\tau} = \frac{1}{2} + \delta_y, 0, \frac{1}{2} + \delta_z$. The magnetic structure of the CM phase has been described in terms of zigzag antiferromagnetic chains of Mn moments lying in the $ab$ plane with weak $c$ components modulated in phase quadrature, giving the structure a cycloidal character [5, 13]. In these structure refinements the components of moment on all the Mn sub-lattices were allowed to vary independently, making the symmetry of the structural motif triclinic. A very similar structure, which conserves orthorhombic symmetry, has also been reported [14]. This latter structure is defined using a formalism based on the results of symmetry analysis [15, 16], which requires that the parameters describing order in the structure should transform according to one of the irreducible representations of its space group, specifically that one which minimises the free energy. For YMn$_2$O$_5$ with space group...
Table 3. Symmetry operators for space group \textit{Pbam} and the associated operations \(\hat{O}_j\) for \(\bm{\tau} = \frac{1}{2}, 0, \frac{1}{2}\) acting on the complex Fourier components. Each \(12 \times 12\) matrix operator \(\hat{O}\) is the outer product of a diagonal \(3 \times 3\) rotation matrix represented by the greek letters \(\epsilon, \rho, \tau\) or \(\xi\) and the \(2 \times 2\) matrices \(Q\) which give the characters of the elements.

| Operator \([\hat{R}_j, \hat{A}_j]\) | Operator \(\hat{O}_j\)\(^a\) |
|----------------------------------|----------------------------------|
| \(j\)                           | \(\hat{Q}_{11}\) | \(\hat{Q}_{12}\) | \(\hat{Q}_{21}\) | \(\hat{Q}_{22}\) | \(\phi_j\) |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|--------------|
| 1 \(E\)                         | \(\epsilon\)    | 0               | 0               | \(\epsilon\)    | 0             |
| 2 \(2\)                         | \(\tau\)        | 0               | \(\rho\)        | 0               | \(\rho\)      |
| 3 \(a_y\)                       | \(\frac{1}{2} + x, \frac{1}{2} - y, z\) | 0               | \(\xi\)         | 0               | \(\xi\)       |
| 4 \(b_x\)                       | \(\frac{1}{2} - x, \frac{1}{2} + y, z\) | 0               | \(\bar{\xi}\)   | 0               | \(\bar{\xi}\)  |
| 5 \(\bar{l}\)                   | \(\bar{x}, \bar{y}, \bar{z}\) | 0               | \(\epsilon^b\)  | \(\bar{\epsilon}^b\)| 0 | \(\bar{\epsilon}^b\) |
| 6 \(m_z\)                       | \(\frac{1}{2} - x, \frac{1}{2} + y, z\) | \(\rho^b\)      | 0               | \(\rho^b\)      | 0             |
| 7 \(2\) \(1\)                  | \(\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}\) | \(\bar{\epsilon}^b\) | 0               | \(\bar{\epsilon}^b\) | 0 |
| 8 \(2\) \(1\)                  | \(\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}\) | \(\epsilon^b\)  | 0               | \(\epsilon^b\)  | 0             |

\(a\) \(\epsilon, \rho, \tau\) and \(\xi\) represent diagonal rotation matrices with diagonal elements \(\epsilon = 1, 1, 1; \rho = -1, -1, 1; \tau = 1, -1, -1; \xi = -1, 1, -1\).

\(b\) Indicates that the operator \(Q\) is combined with conjugation.

Table 4. Phase differences between components of the magnetic interaction vectors \(\bm{M}_\perp\) for equivalent orthorhombic magnetic reflections in a structure with the symmetry of table 3. (Note: the relative signs of \(\phi_{3j}\) observed with the \([100]\) \((S_{yz})\) and \([010]\) \((S_{zx})\) orientations.)

| Indices | \(\phi_j\) | \(\phi_y\) | \(\phi_z\) | \(\phi_y - \phi_z\) | \(S_{12}\) | \(\phi_y - \phi_z\) | \(S_{zx}\) |
|---------|-------------|-------------|-------------|---------------------|-----------|---------------------|-----------|
| \(h k l\) | \(\phi_j\) | \(\phi_y\) | \(\phi_z\) | \(\phi_y - \phi_z\) | \(\phi_y - \phi_z\) | \(\phi_y - \phi_z\) | \(\phi_y - \phi_z\) |
| \(\bar{h} \bar{k} \bar{l}\) | \(\phi_j - \frac{\pi}{2}\) | \(\phi_y - \frac{\pi}{2}\) | \(\phi_z - \frac{\pi}{2}\) | \(\phi_y - \phi_z + \pi\) | \(\phi_y - \phi_z - \pi\) | \(\phi_y - \phi_z + \pi\) | \(\phi_y - \phi_z - \pi\) |
| \(h k l\) | \(-\phi_j\) | \(-\phi_y\) | \(-\phi_z\) | \(-\phi_y - \phi_z\) | \(-\phi_y - \phi_z + \pi\) | \(-\phi_y + \phi_z + \pi\) | \(-\phi_y - \phi_z + \pi\) |
| \(\bar{h} \bar{k} \bar{l}\) | \(-\phi_j + \pi\) | \(-\phi_y + \pi\) | \(-\phi_z + \pi\) | \(-\phi_y + \phi_z - \pi\) | \(-\phi_y + \phi_z - \pi\) | \(-\phi_y - \phi_z + \pi\) | \(-\phi_y - \phi_z - \pi\) |

\(\phi_{3j}\) are chosen to be \(\phi_{3j}^M\) for the Mn\(^{3+}\) ions.

To see the symmetry relationships between related orthorhombic magnetic interaction vectors it is convenient to write

\[
\bm{M}_\perp = \sum_{u=x,y,z} M_u \exp(i\phi_u) \quad \text{then} \quad (3)
\]

\(A_M = M_x M_z \sin(\phi_y - \phi_z)/|\bm{M}_\perp|^2 = A_M S_{yz}\)

\(A_M = M_x M_z \sin(\phi_y - \phi_z)/|\bm{M}_\perp|^2 = A_M S_{zx}\)

\(\text{for} \ P \parallel [010].\)

The symmetry relationships between the phases \(\phi_{3j}\) for a structure with the symmetry of table 3 are shown in table 4. \(S_{yz}\) and \(S_{zx}\) give the relative signs of the asymmetries observed in symmetrically related reflections measured with the \([100]\) and \([010]\) orientations. It confirms that this symmetry predicts the correct relationships.

5. Analysis of the data

The phase relationships imposed by the symmetry operators in real space (relating different domains) are the same as those imposed by the equivalent reciprocal space operators (relating equivalent reflections from the same domain), except that the real space operators also act on the polarization direction, whilst the reciprocal space ones do not.

For the symmetry used here the only domains which can occur are those having opposite propagation vectors \(\bm{\tau}\) and \(-\bm{\tau}\).
Each measurement of $A$ can contain contributions from both domains. If $L$ is integer, reflections $h, k, L + \frac{1}{2}$ have $k = g + \mathbf{r}$ for $\mathbf{r} = \frac{1}{2}, 0, 0$ and $k = g - \mathbf{r}$ for $\mathbf{r} = -\frac{1}{2}, 0, 0$. If the populations of these two domains are $p^+$ and $p^-$, with $\eta = (p^+ - p^-)/(p^+ + p^-)$, then for set of orthorhombic equivalent reflections measured with the [100] orientation:

$$A(hkl) = \eta M_x + A_{Nz} S_{Nz}(hkl)$$
$$A(h\bar{k}l) = -\eta M_x + A_{Nz} S_{Nz}(h\bar{k}l)$$
$$A(h\bar{k}\bar{l}) = \eta M_x - A_{Nz} S_{Nz}(h\bar{k}\bar{l})$$
$$A(h\bar{l}k) = -\eta M_x - A_{Nz} S_{Nz}(h\bar{l}k)$$

where the $S_{Nz}$ give the sign relationships between the $A_{Nz}$ for equivalent reflections since

$$A(hkl) = -A(h\bar{k}\bar{l}) \quad \text{and} \quad A(h\bar{k}l) = -A(h\bar{l}k)$$
$$S_{Nz}(h\bar{k}\bar{l}) = -S_{Nz}(h\bar{l}k) = 1$$

but

$$A(h\bar{l}k) \neq A(hkl) \text{ so } S_{Nz}(h\bar{k}l) = -S_{Nz}(h\bar{l}k) = -1.$$  

With these relationships the asymmetries measured with the [100] axis orientation can be used to obtain values for the quantities $\eta A_{Mz}$ and $A_{Nz}$ for each set of reflections measured. If

$$\langle A(hkl) \rangle = A(hkl) + A(\bar{h}\bar{k}\bar{l}) - A(h\bar{k}\bar{l}) - A(h\bar{k}l)$$
$$\langle A(h\bar{k}l) \rangle = A(h\bar{k}l) + A(h\bar{l}k) - A(h\bar{l}k) - A(h\bar{l}k)$$

then

$$\eta A_{Mz} = \frac{1}{4} \langle (A(hkl) - A(h\bar{k}l)) \rangle \quad \text{and} \quad A_{Nz} = \frac{1}{4} \langle (A(hkl) + A(h\bar{k}l)) \rangle.$$ 

The values obtained from the data measured at 25 K in 5 T are given in table 5. $A_{Nz}$ and $A_{Mz}$ cannot be extracted separately from the [010] axis data since only reflections $hkl$ with positive $k$ could be measured.

An initial estimate of $\eta = 0.55(4)$ was obtained by scaling the values of $M_x$ calculated using the structure [14] to the observations. The large standard deviation in $\eta$ shows that the fit with the calculations is not very good and for several reflections even the relative signs are inconsistent. The poor fit is not altogether surprising as the diffraction intensities and the polarization analysis results for $h0l$ reflections are largely dependent on the dominant $x$ component of the magnetic moments, whereas $A_{Mz}$ depends heavily on the $y$ and $z$ components of the interaction vectors and on the phase difference between them, to which the unpolarized neutron intensity and even the polarization analysis of $h0l$ reflections are insensitive. In order to test this possibility modifications were made to the CCSL programs [17] which calculate magnetic structure factors to use the formulation of equation (2). This then allowed a magnetic structure refinement to be carried out in which both the intensity data [13] and the $A_{Mz}$ data of table 5 were included. The asymmetries calculated from the structure factors include the neutron polarization. The degree of extinction was estimated from measurements of the intensities of nuclear reflections, its effect on the calculated values of both the asymmetries and magnetic intensities was small. The refinement led a structure which gave an equally good (or better) fit with the intensity data as well as fitting the $A_{Mz}$ data. The parameters of the structure of [14] and that obtained from the present refinement are compared in table 6.

It should be noted that the amplitude and phase of the order parameter cannot be determined independently of the magnetic moment vectors using diffraction data, and that both partners give the same diffracted intensity; the parameter values of table 6 have been calculated for a single partner (2 [14]) with $\sigma_2 = 1$.

### Table 5

| $h$ $k$ $l$ | $\langle A(hkl) \rangle$ | $\langle A(h\bar{k}l) \rangle$ | $\eta A_{Mz}$ | $\sigma^2 A_{Mz}$ |
|-------------|---------------------------|---------------------------|---------------|-----------------|
| 0.5 1 0.25  | -0.034(2)                 | -0.065(7)                 | -0.050(4)     | 0.0038          |
| 0.5 2 0.25  | -0.026(4)                 | -0.047(8)                 | -0.037(4)     | 0.0088          |
| 0.5 3 0.25  | -0.0111(14)               | -0.020(5)                 | -0.015(2)     | 0.0126          |
| 0.5 1 0.75  | 0.0152(12)                | 0.022(2)                  | 0.0187(14)    | 0.0513          |
| 0.5 1 1.25  | 0.0208(12)                | 0.028(4)                  | 0.024(2)      | 0.0268          |
| 0.5 2 0.75  | -0.0074(10)               | -0.011(2)                 | -0.0090(13)   | -0.0019         |
| 0.5 2 1.25  | -0.0128(13)               | -0.023(5)                 | -0.018(2)     | -0.0046         |
| 0.5 3 0.75  | 0.010(4)                  | 0.009(4)                  | 0.009(3)      | 0.0074          |
| 0.5 1 1.75  | -0.0107(11)               | -0.015(2)                 | -0.0127(11)   | -0.0061         |
| 0.5 1 2.25  | 0.005(2)                  | 0.004(2)                  | 0.0044(11)    | 0.0021          |
| 0.5 2 1.75  | -0.014(2)                 | -0.018(4)                 | -0.016(2)     | -0.0167         |
| 0.5 3 1.75  | -0.016(10)                | -0.027(10)                | -0.022(7)     | -0.0029         |

Observations: 0.55(4) 0.419(11) 917 55
6. Nuclear contribution to magnetic reflections in a modulated magnetic structure

The appearance of ferroelectricity coincident with a magnetic ordering transition is strongly indicative of small atomic displacements leading to electrical polarization linked to the magnetic order parameters. Whether these displacements are driven by IDM interactions [7, 8], superexchange striction [4–6], or by some other mechanism, they will necessarily give rise to additional nuclear scattering. It must, however, be emphasized that electrical polarization is a bulk property and therefore a necessity give rise to additional nuclear scattering. It is due solely to the displacements of the Mn ions, was fitted by least squares to the displace model in which

\[ r_{\ell \delta} + \delta_{\ell \delta} \]

where \( \delta_{\ell \delta} \) is a tensor representing the interaction giving rise to the displacements. If the displacements are small, so that \( \mathbf{k} \cdot \delta \ll 1 \), then the nuclear structure factor can be written:

\[ N + N_0 \approx \sum \exp i \mathbf{k} \cdot (\mathbf{\ell} + \mathbf{r}_i)(1 + i\mathbf{b}_i \mathbf{k} \cdot \delta_i). \]  

(5)

\( N \) is the nuclear structure factor for the unmodified structure and \( N_0 \) the additional scattering due to the displacements.

\[ N_0 = \sum_i b_i \exp i \mathbf{k} \cdot \mathbf{r}_i \sum_{\ell} \exp i \mathbf{k} \cdot \mathbf{\ell} \times \sum_m k_i \lambda_{im} (\sigma_r S_{r\ell m} e^{i\mathbf{\ell} \cdot \mathbf{r}_i} + \sigma_r^* S_{r\ell m}^* e^{-i\mathbf{\ell} \cdot \mathbf{r}_i}) = \sum_i b_i \exp i \mathbf{k} \cdot \mathbf{r}_i \sum_{\ell} k_i \lambda_{im} \times \sum_{\ell} \exp i \mathbf{\ell} \cdot (\mathbf{k} + \mathbf{\tau}) \sigma_r S_{r\ell m}^* + \exp i \mathbf{\ell} \cdot (\mathbf{k} - \mathbf{\tau}) \sigma_r S_{r\ell m}. \]  

(6)

The lattice sum of equation (6) is non-zero for the wavevectors \( \mathbf{k} = \mathbf{g} \pm \mathbf{\tau} \) characterizing the antiferromagnetic modulation and so can give rise to a polarization dependent cross-section for the antiferromagnetic reflections. Including the magnetic symmetry from equation (2)

\[ N_{3\delta} = \sum \exp i \mathbf{k} \cdot (\mathbf{R} + \mathbf{r}_i) \delta \]  

(7)

\(|\mathbf{M}_\parallel|^2 \gg |N_0|^2\) so that the nuclear contribution to the asymmetry is

\[ A_N \approx \sum R(\mathbf{N}_0 \mathbf{S} \cdot \mathbf{M}_\parallel)/|\mathbf{M}_\parallel|^2. \]  

(8)

An interaction between the magnetic polarity of the spin on an atom and the electric polarity of its nuclear environment, such as that represented by the tensor \( \lambda \), is the fundamental requirement for a magneto-electric effect and will be strongly linked to multiferroic behaviour. The polarization dependence of the intensities of the magnetic satellite reflections provides a means to study this effect.

If \( N_0 \) is expressed as \(|N_0| \exp i\phi_N\) then, for the [100] orientation

\[ A_N \approx 2 |N_0| |\mathbf{M}_\parallel \cos (\phi_N - \phi_a)|/|\mathbf{M}_\parallel|^2. \]  

(9)

In a model in which \( A_{N_0} \) is due solely to the displacements of magnetic atoms the symmetry operations on these vector displacements determine the relative signs of \( A_N \) for the orthorhombic equivalent reflections. The relationships between the \( \phi_a \) taken from table 4 and the \( \phi_{N_0} \) for displacements parallel to \( x, y \) and \( z \) are given in table 7. To obtain the observed relationship \( A_{N_0}(hkl) = -A_{N_0}(hk\ell) = -A_{N_0}(hk\ell) = A_{N_0}(hkk) \) with this model the signs associated with operators 1–4 must be \( |+ + + | + + + - - - + + - + + + - - - - \) and for displacements parallel to \( x, y \) and \( z \) respectively.

This model, in which the nuclear scattering is due just to the displacements of the Mn ions, was fitted by least squares to the values of \( A_{N_0} \) in table 8. In the result only the \( x \) displacement of Mn\(^{3+}\) had a non-zero value \( \delta(x) = 0.006(11) \). The values of \( A_{N_0} \) calculated with this displacement are also listed in

**Table 6. Parameters obtained from the magnetic structure refinement.**

| Ion | \( p \) | \( S\) (\( \mu_B \)) | \( \phi\) (deg) | \( S\) (\( \mu_B \)) | \( \phi\) (deg) |
|-----|-----|---------------|--------|---------------|--------|
| A\(^{b}\) Mn\(^{3+}\) | 1 | 3.62(4) | 45.0 | 0.44(7) | 45.0 |
| | 2 | 3.90(5) | 45.0 | 0.89(5) | 45.0 |
| Mn\(^{4+}\) | 1 | 2.50(4) | -124.3(9) | 0.78(4) | -123(5) |
| | 2 | 2.50(4) | -124.3(9) | 0.78(4) | -123(5) |
| B\(^{b}\) Mn\(^{3+}\) | 1 | 3.32(9) | 56.6(6) | 0.92(9) | 56.6(6) |
| | 2 | 3.78(9) | 56.6(6) | 0.92(9) | 56.6(6) |
| Mn\(^{4+}\) | 1 | 2.60(9) | -130(20) | 0.76(9) | -140(30) |
| | 2 | 2.60(9) | -130(20) | 0.76(9) | -140(30) |

\( a \) The \( S_p(r, \tau) \) refer to positions \( r = (0.0881, 0.8508, 0.5) \) for Mn\(^{3+}\) and \( r = (0.5, 0.2550) \) for Mn\(^{4+}\).

\( b \) The present refinement with \( S = \sum S_i \exp(i\phi_i), \sigma_1 = 0 \) and \( \sigma_2 = 1.0 \).

\( c \) The results of Kim et al [14] normalized to \( \sigma_1 = 0, \sigma_2 = 1.0 \) for comparison with A.
The exploratory experiment reported here was carried out using magnetic fields only, but the PND technique can be used with electric and magnetic fields applied simultaneously. Further experiments of this kind, made using both electric

### Table 7. Phase relationships between the nuclear contribution to the structure factors of orthorhombic equivalent magnetic reflections for displacement of magnetic ions in the x, y, and z directions.

| Operator number | 1 2 3 4 | 1 2 3 4 | 1 2 3 4 | 1 2 3 4 |
|-----------------|--------|--------|--------|--------|
| Displacement    | + + + + | + + + + | + + + + | + + + + |
| Sign of A_N    | + + + + | + + + + | + + + + | + + + + |
| Displacement    | x y z  | x y z  | x y z  | x y z  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_M     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_N     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_M     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_N     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_M     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_N     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_M     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_N     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_M     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_N     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_M     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |
| Relative        | h k l  | h k l  | h k l  | h k l  |
| Signs of A_N     | + + + + | + + + + | + + + + | + + + + |
| Displacements   | h k l  | h k l  | h k l  | h k l  |

### Table 8. Observed and calculated values of A_N using the least squares result \( \delta(x) = 0.006 \) for Mn\(^{3+}\) with all other displacements zero.

| \( h \) | \( k \) | \( k \) | \( A_N \) (obs) | \( A_N \) (calc) |
|--------|--------|--------|---------------|---------------|
| 0.50   | 1.00   | 0.25   | 0.015(3)      | 0.0005        |
| 0.50   | 2.00   | 0.75   | 0.010(4)      | 0.0001        |
| 0.50   | 3.00   | 0.25   | 0.004(2)      | 0.0015        |
| 0.50   | 1.00   | 0.75   | −0.004(1)     | −0.0010       |
| 0.50   | 2.00   | 1.25   | −0.004(2)     | 0.0010        |
| 0.50   | 3.00   | 0.75   | 0.002(1)      | −0.0002       |
| 0.50   | 2.00   | 1.25   | 0.005(2)      | 0.0002        |
| 0.50   | 3.00   | 0.75   | 0.001(3)      | −0.0019       |
| 0.50   | 1.00   | 1.75   | 0.0020(10)    | −0.0007       |
| 0.50   | 1.00   | 2.25   | 0.0000(10)    | 0.0010        |
| 0.50   | 2.00   | 1.75   | 0.002(2)      | −0.0001       |
| 0.50   | 3.00   | 1.75   | 0.006(7)      | 0.0051        |

It can be seen that the fit is not good which suggests that the displacements may not be confined the magnetic ions. The small number of data available preclude a more extensive analysis, however the results do show that displacements of the order of 0.05 Å (\( a\delta(x) \)) are required to account for the observations.

### 7. Conclusions

The results of the present experiments show that useful information about the magnetic structure can be obtained from measurements of the polarization dependence of the intensities of magnetic satellite reflections of antiferromagnetic multiferroic crystals. Analysis of the relationships between groups of reflections related by the symmetry operations of the paramagnetic space group yield unique information about the phase relationships between different components of the magnetic interaction vectors and hence the symmetry of the magnetic structure. This gives access to details of the magnetic structure to which unpolarized neutron intensity measurements are insensitive.

In the present experiment polarized neutron intensity asymmetry was found in the magnetic satellite reflections of YMn\(_2\)O\(_5\) at 25 K (\( \tau = \frac{1}{2}, 0, \frac{1}{2} \)) indicating an unequal population of centro-symmetrically related domains. The insensitivity of these intensity asymmetries to both field cooling and magnetic fields of up to 9 T suggests that the stability of such domains in this crystal is more strongly coupled to the crystal microstructure than to magnetic fields of less than 10 T. A small inequivalence between the asymmetries of Friedel pairs of reflections indicates the presence of two distinct contributions to A, one of which, \( A_M \), changes sign with reversal of the scattering vector and a second, \( A_N \), which does not. \( A_M \) is of purely magnetic origin whereas \( A_N \) could be due to a small nuclear scattering contribution to the otherwise purely magnetic reflections given by small atomic displacements modulated with the same wavevector as the magnetic moments.

The sign relationships between the \( A_M \) of equivalent reflections are in accordance with the proposed structure [14]. On the other hand their actual magnitudes agree rather poorly with those calculated from the parameters of the model. Including the \( A_M \) jointly with intensity data in a least squares refinement allows a good fit with both to be obtained. There is a big improvement in the precision with which the phases of the complex vector components are determined, however the only really significant difference between the two models is in the relative magnitudes of the \( y \) and \( z \) components of the Mn\(^{3+}\) ions. In the model of [14], the \( y \) and \( z \) components of the two vectors contributing to the Mn\(^{3+}\) moment are nearly equal, with \( y \approx 2z \), whereas in our model they differ, with \( y \approx 2z \) for one and \( z \approx 2y \) for the other.

A different set of rules govern the relationships between the signs of the \( A_N \) of equivalent reflections, and these allow the symmetry operations on the displacement vectors to be determined. Although the magnitudes of \( A_N \) suggest that displacements of order 0.05 Å occur, it was not possible the fit their values satisfactorily with a model in which only the magnetic ions are displaced. Much smaller ionic displacements (0.0005 Å T\(^{-1}\)) induced by an applied magnetic field have been observed in measurements of TbMn\(_3\)O\(_7\) using polarized synchrotron radiation [11], a difference much greater than needed to account for the difference in their electrical polarization ((P \( \text{Y Mn}_2\text{O}_5\)),/P \( \text{Tb Mn}_3\text{O}_7\) ≈ 5). The displacements observed in TbMn\(_3\)O\(_7\) were dominantly of oxygen, so it is possible that in YMn\(_2\)O\(_5\) also the atomic shifts driven by the staggered field may be predominantly of oxygen. More extensive data would be needed to enable such shifts to be quantified.

The exploratory experiment reported here was carried out using magnetic fields only, but the PND technique can be used with electric and magnetic fields applied simultaneously. Further experiments of this kind, made using both electric
and magnetic fields as parameters, would allow the magnetic structural origin of multiferroic behaviour to be studied in fine detail.

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