Noncentrosymmetric commensurate magnetic ordering of multiferroic ErMn$_2$O$_5$

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Abstract

The noncentrosymmetric magnetic structure of ErMn$_2$O$_5$ has been shown to be very similar to that of HoMn$_2$O$_5$ (Vecchini et al 2008 Phys. Rev. B 77 134434). The magnetic modulation at 25 K has propagation vector $\vec{k} = (1/2, 0, 1/4)$ and the symmetry imposes very few constraints on the magnetic configurations allowed. Only by combining the results of bulk magnetization measurements, powder and single crystal neutron diffraction and spherical neutron polarization analysis was it possible to distinguish clearly between different models. The susceptibility measurements show that the erbium magnetic moments are aligned parallel to the $c$-axis indicating strong single ion anisotropy. Spherical neutron polarimetry demonstrates the presence of two unequally populated chirality domains in ErMn$_2$O$_5$ single crystals. X-ray diffraction measurements on an ErMn$_2$O$_5$ powder using synchrotron radiation show that the buckling angles of the Mn–O–Mn bond change below the transition to the ferroelectric phase.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

At the present time there is considerable interest in the often complex physics of multiferroic materials such as RMn$_2$O$_5$ oxides (R = rare earths, Y, or Bi), see for instance [1–3], and the papers cited therein. A systematic powder neutron diffraction study of RMn$_2$O$_5$ compounds at room temperature [4] confirmed the centrosymmetric space group $Pbam$ (No. 55) for these compounds. The Mn-ions occupy one set (Mn1) of 4f $(0, 1/2, z)$ and one set (Mn2) 4h $(x, y, 1/2)$ sites whilst the R atoms occupy 4g $(x, y, 0)$ positions. It was concluded from bond valence considerations and bulk magnetic measurements that the 4f sites contain Mn$^{4+}$ ions and the 4h sites Mn$^{3+}$ ions. For multiferroic ErMn$_2$O$_5$ soft x-ray magnetic diffraction under an applied electric field confirms strong coupling between the ferroelectric and antiferromagnetic order parameters [5].

Studies of magnetic ordering in ErMn$_2$O$_5$ date from 1973, when magnetic neutron diffraction peaks were observed at 20 K in a powder neutron diffraction investigation [6] and indexed with $\vec{k} = (1/2, 0, 0.242(5))$. Helical magnetic ordering of the Mn moments and sinusoidal modulation of the Er moments was proposed. An early single crystal neutron diffraction study of ErMn$_2$O$_5$ [7] concluded that the magnetic ordering of both Mn and Er was sinusoidal at 1.5 and 25 K with $\vec{k} = (1/2, 0, 0.275(5))$ and $T_N = 44$ K.

The complex phase diagram of ErMn$_2$O$_5$ is described in [8]. At all temperatures below the Néel temperature ($T_N$ = 44 K) the magnetic structure is modulated with propagation vector $k$ close to $k_x = 1/2, k_y = 0, k_z = 1/4$. Just below $T_N$ both $k_x$ and $k_z$ are incommensurate: the 2D-ICM phase. On cooling below approximately 40 K $k_z$ locks to 1/4 giving the 1D-ICM phase and finally at 37.7 K $k_z$ locks in at 1/2 and this commensurate (CM) phase is stable down to low temperature.
Below about 10 K, the CM phase coexists with a further 1D-ICM phase with \( k_c = 0.271 \) at 2 K. Third order magnetic satellite peaks were observed in this phase indicating some squaring up of the sinusoidal modulation [9]. Below \( T \sim 35 \) K the compound is ferroelectric [10]. Further details of the phase diagram of ErMn2O5 have been elucidated by Fukunaga et al [9] who made simultaneous measurements of magnetic neutron diffraction, electrical polarization and dielectric permittivity \( \epsilon \). Weak ferroelectricity first appears in the 1D-ICM phase, but the peak of the permittivity occurs at the 1D-ICM to CM phase transition. Strangely the (1D-ICM) phase stable below 10 K is only weakly ferroelectric. This incommensurate low-temperature phase may be stabilized with respect to the commensurate phase by the application of external magnetic fields [10]. Hydrostatic pressure on the other hand has been shown to stabilize the commensurate ferroelectric phases of RMn2O5 (R = Tb, Dy, Y, Ho, Er) [11].

The commensurate antiferromagnetic (CM) structures of RMn2O5 (R = Tb, Dy, Ho; \( k = (1/2, 0, 1/4) \)) have been determined by Blake et al [12] from time-of-flight powder neutron diffraction data using group-theory symmetry arguments (concerning the latter see also [2]). Unfortunately for this structure the crystal symmetry imposes rather few constraints on the variables to be determined. Nevertheless all the magnetic moments were found to lie in the (001) plane. An alternative structure for the commensurate phases of RMn2O5 (R = Y, Ho, Er) has been proposed by Kimura et al [13] based on single crystal neutron diffraction measurements. It is a rather complicated spiral chain model, described in terms of a \( 2\alpha \times b \times 4\gamma \) magnetic super-cell, in which the magnetic moments have components along all three crystallographic axes. For ErMn2O5 the major components of the Er magnetic moments were along the \( c \)-axis at 20 K.

In the present paper we report measurements of the magnetic susceptibility of ErMn2O5 single crystals as well as a combined unpolarized and polarized neutron scattering study of the magnetic structure of this compound at \( T = 25 \) K. We show that the magnetic ordering of Mn in ferroelectric ErMn2O5 is similar to that found in the Ho compound [14]. Moreover we demonstrate that for a structure containing several magnetic sublattices and few symmetry constraints, it is only by combining precise single crystal neutron diffraction intensity measurements with quantitative spherical neutron polarimetry [15] on the same specimens that different possible magnetic configurations may be clearly distinguished.

2. Experimental techniques

The single crystals of ErMn2O5 were grown by the flux method as described in [16]. Their magnetic response was studied by measuring both dynamic and static susceptibilities. The dynamic magnetic susceptibility in zero static magnetic field was measured by the induction method at a frequency of 10 kHz in the temperature range 5–150 K. The static magnetic susceptibility was obtained using a vibrating sample magnetometer in magnetic fields up to 30 kOe.

The neutron diffraction work was carried out partly at the Swiss spallation neutron source SINQ [17], Paul Scherrer Institut, Villigen, Switzerland (PSI) and partly at the high-flux reactor of the Institut Laue Langevin, Grenoble, France (ILL). Powder neutron diffraction measurements were made using the DMC diffractometer at PSI [18, 19] and wavelength \( \lambda = 2.448 \) Å. The ErMn2O5 powder was contained in a cylindrical vanadium can (6.5 mm diameter 50 mm high) under an atmosphere of He gas. The sample was maintained at stable temperatures down to 1.5 K in an ILL type \(^3\)He cryostat. Single crystal diffraction measurements were made both at PSI and at ILL on two differently oriented samples of volume ∼50 mm³. The integrated intensities of reflections from the first crystal were measured on the four-circle single crystal neutron diffractometer TricS at PSI [20] using a wavelength \( \lambda = 1.18 \) Å. For the second, the measurements were made with the four-circle diffractometer D10 at ILL using a wavelength \( \lambda = 1.526 \) Å. The neutron diffraction data were evaluated by means of a current version of the FullProf program package [21]. For the single crystal data neutron absorption was neglected, but an anisotropic extinction correction involving 6 parameters was made.

Because of the complexity of the magnetic structure of ErMn2O5, we have also made neutron polarimetric measurements on both crystals. For these measurements the polarimeter Cryopad 2 [15] was installed on the D3 diffractometer at ILL. An incident polarized beam wavelength \( \lambda = 0.82 \) Å was obtained from a magnetized Heusler alloy monochromator and the polarization of the scattered beam analyzed using a spin polarized \(^3\)He filter. The first specimen was oriented with an [010] axis vertical which gave access to reflections of type \( h, 0, l \). With this orientation, neutron polarimetry measurements do not distinguish sensitively between the \( a \) and the \( c \)-axis components of moment. We therefore made additional measurements on a second crystal oriented with a \([1, 0, 2]\) axis vertical so that magnetic Bragg peaks with indices \( h/2, k, h/4 \) could be measured in the scattering plane.

3. Bulk magnetic measurements

The temperature dependence of the dynamic and static magnetic susceptibilities of ErMn2O5 along the three principal axes are shown in figures 1 and 2. The susceptibility measured along the \( c \)-axis is considerably higher than that in the two other axial directions. The susceptibilities along the \( a \)-and \( b \)-axes show diffusive maxima at temperatures above \( T_N \) and below \( T \sim 120 \) K. Such behavior is characteristic of short-range magnetic correlations above \( T_N \) that mask the anomaly in \( \chi_{a,b} \). The susceptibility along the \( c \)-axis can be described by a Curie-Weiss law \( \chi = C/(T - \theta_p) \) at all measured temperatures, although the slope of \( \chi^{-1}(T) \) changes slightly near \( T = 25 \) K. No anomaly is observed around \( T_N \), suggesting that the \( c \)-axis susceptibility is dominated by the magnetic response of Er. Fitting the susceptibility data to the Curie-Weiss law in the temperatures range 10–25 K gives \( \theta_p = -5.6 \) K and an effective magnetic moment \( \mu \sim 7 \mu_B \). This is rather less than the \( \sim 9 \mu_B \) expected for Er\(^{3+}\) (\(^{4I_{15/2}}\)) with strong spin–orbit coupling.
The unit cell of ErMn$_2$O$_5$ contains three different magnetic species Er$^{3+}$, Mn$^{3+}$, and Mn$^{4+}$. Since all crystals of the RMn$_2$O$_5$ family, including those with nonmagnetic R-ions (Y and Bi), have Néel temperatures $T_N$ near to 40 K, it can be concluded that it is the manganese ions which order magnetically at $T_N$. Spontaneous antiferromagnetic ordering of Er occurs below $|\theta_P| \sim 6$ K and at higher temperatures the Er-spins are polarized by the internal magnetic field arising from the Mn–Er exchange interaction. The susceptibility along the $c$-axis is paramagnetic at all temperatures up to the Néel temperature and is much higher than along the $a$- and $b$-directions, showing that the $c$-axis is the easy direction of magnetization for the Er$^{3+}$ moments. It is determined by the crystalline-electric-field anisotropy. On the other hand, the arrangement of the Er magnetic moments depends on the symmetry of the effective internal field which will be sensitive to spin reorientations in the Mn-sublattice. This is probably at the origin of the anomaly observed near 25 K.

4. Magnetic structure of ErMn$_2$O$_5$ in the commensurate phase

4.1. Single crystal neutron diffraction

In order to determine the magnetic structure of ErMn$_2$O$_5$ in the commensurate CM phase with propagation vector $\vec{k} = (1/2, 0, 1/4)$ two sets of integrated reflection intensities were collected on TriCS at SINQ from the first single crystal: 77 nuclear reflections were measured at 50 K in the paramagnetic state and 227 magnetic reflections at 30 K. Subsequently 227 nuclear and 186 magnetic reflections were measured at 25 K from the second crystal on D10 at ILL. The nuclear intensities were used mainly to obtain the scale factor for the magnetic intensities. Using isotropic temperature factors conventional nuclear $R_F$-factors of 8.8% and 8.4% were obtained for the two sets. Within limits of error the refined structural parameters agree with the presumably more precise 20 K nuclear parameters of ErMn$_2$O$_5$ published in [13]. The positional parameters were then fixed to the latter values and an overall temperature factor $B = 0$ was used in the magnetic refinements.

The best fit of the magnetic reflections to a model in which the magnitudes of the Mn moments were kept constant was obtained with a magnetic Mn configuration similar to that found in HoMn$_2$O$_5$ [14]. This same configuration was also obtained using the simulated annealing procedure [21]. To conform to the easy [001] direction determined from the susceptibility measurements, the modulated magnetic Er moments were assumed to be oriented parallel to [001], in agreement with Gardner et al [7]. This model gave magnetic $R_F$ factors of 12.1% ($R_F = 8.1\%$) and 15.6% ($R_F = 10.4\%$) for the 30 K and 25 K data sets, respectively (see figure 3). Using the helical configuration proposed in [13] gave significantly worse magnetic fits: $R_F$ factors of 17.6% and 19.4% for 30 K and 25 K, respectively.

A sketch of the noncentrosymmetric commensurate magnetic structure proposed for ErMn$_2$O$_5$ at 30 K is shown in figure 4. The refined values of the magnetic parameters are summarized for 25 and 30 K in table 1. Finally it is reassuring that the parameters of table 1 yield, without further refinement, an excellent fit to the profile intensities measured at $T = 30$ K on DMC, with nuclear and magnetic $R_{Bragg}$ factors of 1.9 and 10.5%, respectively.

4.2. Polarimetry

The relationship between the incident and scattered polarizations $\vec{P}$ and $\vec{P}'$ when a neutron beam is scattered by a magnetic system is given by the Blume–Maleev equations [22]. For magnetic Bragg scattering by an acentric antiferromagnetic structure with finite propagation vector $\vec{k}$, such as the model proposed for ErMn$_2$O$_5$ in section 4.1, these equations may be simplified to

$$\vec{P}' = \vec{P}(-|\vec{M}_\perp|^2) + 2\Re[\vec{M}_\perp(\vec{P} \cdot \vec{M}_\parallel)] - \Im(\vec{M}_\perp \times \vec{M}_\parallel)$$ (1)
Figure 3. Calculated magnetic neutron intensities ($F^2$) versus observed values for ErMn$_2$O$_5$ at (a) 30 K and (b) 25 K, respectively.

Table 1. Magnetic parameters of ErMn$_2$O$_5$. $M$ and $I$ are the real and imaginary magnetic Fourier components and magnitudes in units of $\mu_B$ and phase in units of $2\pi$, refined from single crystal neutron intensities at 30 and 25 K (upper and lower values, respectively). The third row is the result of the calculations of the magnetic Fourier components from the polarimetry data taken at $T = 25$ K. Estimated standard deviations of the parameters are given within brackets and refer to the last relevant digit.

| Ion   | $x$    | $y$    | $z$    | $M_x$ | $M_y$ | $M_z$ | $I_x$ | $I_y$ | $I_z$ | $I$   | Phase |
|-------|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|-------|
| Er1   | 0.137  | 0.171  | 0      | 0     | 0     | 0.3(1)| 0     | 0     | 0     | 0     | 0.250 |
| Er2   | 0.863  | 0.829  | 0      | 0     | 0     | 1.6(1)| 1.6(1)| 0     | 0     | 0     | 0.250 |
| Er3   | 0.637  | 0.329  | 0      | 0     | 0     | 1.80(5)| 1.80(5)| 0     | 0     | 0     | 0.250 |
| Er4   | 0.363  | 0.671  | 0      | 0     | 0     | 0.3(1)| 0     | 0.1(1)| 0     | 0     | 0.250 |
| Mn$^{3+}$1 | 0.412 | 0.350 | 0.5 | 3.28(5) | 0.82(9) | 0.3(1) | 0.3(1) | 0 | 0 | 0.82(6) | 0.82(6) | 0.125 |
| Mn$^{3+}$2 | 0.588 | 0.650 | 0.5 | -3.28(5) | 0.82(9) | 0.3(1) | 0.3(1) | 0 | 0 | -0.82(6) | 0.82(6) | 0.125 |
| Mn$^{3+}$3 | 0.912 | 0.150 | 0.5 | -3.28(5) | 0.82(9) | 0.3(1) | 0.3(1) | 0 | 0 | -0.82(6) | 0.82(6) | 0.125 |
| Mn$^{3+}$4 | 0.088 | 0.850 | 0.5 | -3.28(5) | 0.82(9) | 0.3(1) | 0.3(1) | 0 | 0 | -0.82(6) | 0.82(6) | 0.125 |
| Mn$^{4+}$a1 | 0  | 0.5 | 0.254 | -2.09(5) | 0.71(9) | 2.0(5) | 0 | 0 | -0.92(5) | 0.92(5) | 0.083(3) |
| Mn$^{4+}$a2 | 0.5 | 0 | 0.254 | 2.09(5) | 0.71(9) | 2.0(5) | 0 | 0 | -0.92(5) | 0.92(5) | 0.083(3) |
| Mn$^{4+}$b1 | 0.5 | 0 | 0.746 | 2.09(5) | 0.71(9) | 2.0(5) | 0 | 0 | -0.92(5) | 0.92(5) | 0.167(3) |
| Mn$^{4+}$b2 | 0 | 0.5 | 0.746 | -2.09(5) | 0.71(9) | 2.0(5) | 0 | 0 | -0.92(5) | 0.92(5) | 0.167(3) |
positive and negative incident polarizations. The scattered polarizations were corrected for the analyzer efficiency which was determined by measuring the polarization scattered by a nuclear reflection at intervals throughout the experiment. The independent elements of the polarization matrix which can be measured for this type of magnetic structure are:

\[ P_{yx} = -2\eta_c \Re(\langle M_{\perp y}M_{\perp z}^*\rangle)/|\vec{M}_\perp|^2 \]

where \( P_{yx} \) is the population of the two chirality domains.

Table 2 shows the independent elements of the polarization matrices obtained in the CM phase at 25 K, for the first and second crystal orientations, respectively. They have been averaged using the relationships between the elements of the polarization matrices:

\[ P_{xx} = -P_{-xx} = -1 \]

\[ P_{xy} = P_{xz} = P_{-xy} = P_{-xz} = 0 \]

\[ P_{yx} = P_{zx} = P_{-yx} = P_{-zx} \]

\[ P_{yy} = -P_{yz} = -P_{-yy} = P_{-yz} \]

\[ P_{yz} = P_{zy} = -P_{-yz} = -P_{zy} \]

The standard deviations, given in parentheses, have been estimated from the deviations of individual measurements from the means.

Neither of the two magnetic structures which had previously been proposed for ErMn₂O₅ are compatible with the polarimetric measurements. In the structure suggested by Buisson [6] the Mn moments on each sublattice rotate in the \( a-b \) plane with a helical modulation propagating in the \( c \) direction, the phase relationships between the different Mn sublattices lead to a canted arrangement of moments in the Mn planes at \( z = 0, \frac{1}{2} z \approx \pm \frac{1}{2} \frac{\pi}{4} \) and \( z = \frac{1}{2} \). Although the chiral character of this structure can account for the finite values observed for \( P_{yx} \), the \( P_{xy} \) elements calculated for the \( \frac{1}{2} \) \( 0 \ \frac{1}{2} \) and \( \frac{1}{2} \ 0 \ \frac{1}{2} \) reflections are very small: 0.055 and -0.020 respectively whereas the observed values: 0.90(2) and 0.57(5) are much larger. On the other hand in the magnetic structure proposed for ErMn₂O₅ by Gardner et al [7] the Er-and Mn-spins are confined to the \( a-c \) plane and hence the magnetic interaction vectors can have no component parallel to the
**Table 2.** Observed and calculated values of independent elements of the polarization matrices for ErMn$_2$O$_5$ at $T = 25$ K obtained with Cryopad on D3.

| $h$ | $k$ | $l$ | P$_{yy}$ Obs | P$_{yy}$ Calc | P$_{yx}$ Obs | P$_{yx}$ Calc | P$_{zz}$ Obs | P$_{zz}$ Calc |
|-----|-----|-----|-------------|--------------|-------------|--------------|-------------|--------------|
| 0.50 | 0.00 | 0.25 | 0.54(3)     | 0.53         | -0.71(3)    | -0.69        | -0.06(3)    | 0.01         |
| 1.50 | 0.00 | 0.75 | 0.35(2)     | 0.33         | 0.90(2)     | 0.90         | 0.06(2)     | 0.00         |
| 0.50 | 0.00 | 1.75 | -0.40(4)    | -0.35        | 0.85(2)     | 0.88         | 0.09(3)     | 0.00         |
| 2.50 | 0.00 | 1.75 | -0.62(4)    | -0.54        | 0.57(5)     | 0.69         | 0.11(4)     | 0.00         |
| 0.50 | 0.00 | 2.25 | -0.32(2)    | -0.29        | 0.89(1)     | 0.92         | 0.07(2)     | 0.00         |
| 0.50 | 0.00 | 0.25 | 0.49(5)     | 0.12         | -0.68(9)    | -0.99        | 0.04(6)     | 0.00         |
| 2.50 | 0.00 | 1.25 | 0.23(4)     | 0.31         | -0.95(2)    | -0.88        | 0.04(3)     | 0.00         |
| 0.50 | 1.00 | 0.25 | -0.50(2)    | -0.48        | -0.62(1)    | -0.63        | -0.31(1)    | -0.30        |
| 0.50 | 2.00 | 0.25 | -0.61(2)    | -0.62        | 0.33(1)     | 0.33         | -0.35(1)    | -0.34        |
| 1.50 | 2.00 | 0.75 | 0.62(2)     | 0.63         | -0.32(1)    | -0.25        | -0.29(1)    | -0.36        |
| 0.50 | 3.00 | 0.25 | -0.16(1)    | -0.14        | 0.39(1)     | 0.37         | -0.89(1)    | -0.91        |
| 1.50 | 3.00 | 0.75 | 0.26(2)     | 0.36         | 0.61(2)     | 0.70         | 0.69(3)     | 0.50         |

$b^*\text{-axis.}$ In this case the chiral part of the neutron cross-section ($M_\perp \times M_\perp^*$) vanishes for the $h0l$ reflections so that this model cannot account for the finite $P_{yx}$ observed. It can be concluded that the magnetic structure of ErMn$_2$O$_5$ must contain spin components along the $b$-axis. The helical model of the magnetic structure of ErMn$_2$O$_5$ recently proposed by Kimura [13] fulfills this criterion: the Mn-spins have a spiral modulation with components in both the $(a, c)$ and $(b, c)$-planes and the Er moments are parallel to the $c$-axis and have a sine-wave modulation. The elements of the polarization matrix calculated with this model yield much better agreement with the observations than either of the two structures discussed previously. For the $\frac{1}{2} 0 \frac{1}{2}$ Bragg reflection:

\[ P_{yx} = -0.40 \quad P_{yy} = 0.72 \quad P_{yz} = P_{yx} = 0 \]

calculated [13]

\[ P_{yx} = -0.32 \quad P_{yy} = 0.87 \quad P_{yz} = 0.06 \]

observed.

This model of the magnetic structure of ErMn$_2$O$_5$ at $T = 25$ K gives qualitative agreement with the polarization data. However, a least-square fit to the complete set of polarimetric data taking into account the two unequally populated chirality domains yielded, at best, $\chi^2 = 68$. This suggests, in agreement with the single crystal diffraction data, that Kimura’s model is not adequate.

The magnetic model which gave the best fit to the integrated intensity data is that shown in table 1 which is similar to the magnetic structure of HoMn$_2$O$_5$ [14] in the commensurate phase. The results obtained by fitting this model to the polarimetric data, is shown in table 1. The starting parameters were those obtained from the single crystal integrated intensity measurements and because the absolute size of the magnetic moments cannot be determined from neutron polarimetry when the propagation vector is non-zero, the $x$-component of the magnetic moment of Mn$^{3+}$ was fixed. The fit obtained, indicated by $\chi^2 = 8$, is very much better than that obtained for any of the other structures tried. For this model, the only orientation domains are those related by the inversion symmetry. These two domains have spin structures with opposite chiralities. The polarimetric measurements allow the chiral domain fraction $\eta_c$ to be determined. The inequality in population of the chiral domains in the two crystals studied were found to be very similar: the values determined were $\eta_c = 0.74(2)$ and 0.70(2) for the [010] and [102] crystals respectively.

5. X-ray diffraction with synchrotron radiation

A synchrotron x-ray diffraction measurement on a powder sample of ErMn$_2$O$_5$ was made to search for any lattice distortion which may occur on passing into the ferroelectric phase. The powder sample was contained in a glass capillary with a diameter of 0.3 mm. Diffraction patterns were collected at the high resolution powder diffraction station of the Materials Sciences beam-line at the Swiss Light Source (SLS). The wavelength was $\lambda = 0.618$ Å. All the data were taken whilst heating between 5 and 71 K in steps of 2 K. The diffraction lines observed as well as those found since the additional reflections allowed by $Pb21m$ (h0l with h odd) have zero intensity within the accuracy of the measurements. In addition no evidence for superlattice reflections corresponding to a lattice distortion of twice the magnetic propagation vector could be observed in our measurements on contrary to recent single crystal synchrotron investigations in HoMn$_2$O$_5$ [23]. The data therefore cannot confirm whether the true space group of the low-temperature crystal structure is lower than $Pbam$. The quality of the refinements was practically identical using any of the three space groups. The agreement factors are slightly better for $Pb21m$, perhaps due to the higher number of parameters refined. We have therefore chosen to discuss the results obtained for the refinement of the data in space group $Pbam$ in which there are the fewest parameters to be refined. This yielded excellent fits at all temperatures with space group $Pbam$ and isotropic temperature factors, e.g. at 25 K the agreement values: $R_{Bragg} = 4.4\%$, $R_{wp} = 11.2\%$ and goodness of fit $\chi^2 = 3.1$. Figure 5 shows that there are clear changes in the crystal structure, as reflected by changes in the unit cell parameters, below the temperature of the ferroelectric
transition. A study of the evolution of the structural parameters through the ferroelectric phase transition shows that it is the square pyramids of oxygen coordinating the Mn$^{3+}$ ions that are most affected, see figure 6. The oxygen atoms located in the base plane of the pyramids move along the $c$-axis at $T \sim T_C$ so that the Mn$^{4+}$–O–Mn$^{3+}$ and Mn$^{3+}$–O–Mn$^{3+}$ bond angles decrease on cooling. A sketch of the buckling distortion is shown in figure 7. The Mn$^{3+}$–Mn$^{3+}$ and Mn$^{3+}$–Mn$^{4+}$ distances however remain constant.

6. Discussion

As pointed out in the introduction the zero-field magnetic phase diagram of ErMn$_2$O$_5$ is complex and the crystal undergoes a series of magnetic phase transitions 2D-CM1 ⇒ 1D-ICM ⇒ CM ⇒ 1D-ICM on cooling below $T_N$. The exchange interactions in RMn$_2$O$_5$ (R = Rare-earth, Bi) have not yet been determined with precision but this series of ICM–CM–ICM transitions is characteristic of frustrated and competing exchange interactions [25]. In addition, centro-symmetry is lost in all the ordered magnetic phases allowing ferroelectricity and leading to a Dzyaloshinskii–Moriya interaction. Combination of these two effects is probably the cause of both the non-collinearity and the small cycloidal component in the magnetic structure of the commensurate phase.

The magnetic structure of ErMn$_2$O$_5$ in the commensurate phase is very similar to the one found for the commensurate
phase of HoMn$_2$O$_5$ [14] although in the Er compound the stronger single ion anisotropy forces the Er-spins to be aligned along the c-axis. Due to the Er–Mn exchange field, the Mn magnetic moments also have a larger c-component than found in the Ho compound.

Ferroelectric polarization with $\vec{k} = 0$, aligned along the b-axis, coexisting with magnetic ordering with non-zero $\vec{k}$, is allowed by the symmetry of $Pbam$ on all the Mn and Er sublattices for the irreproducible representation $\Gamma_4$. Similar symmetry analyses have been made in [24] and [3] for RMn$_2$O$_5$ crystals. Actually the point group symmetry of the magnetic structure determined here is monoclinic, retaining only the mirror plane perpendicular to $\vec{a}$. Already the fact that the mirror plane perpendicular to the c-axis is missing in the group $G_\mathbb{E}$ of the propagation vector (mm2) implies that the magnetic structure is noncentrosymmetric, and the Mn$^{4+}$ ions can split into two orbits. In addition the 2-fold rotation around the c-axis does not leave the magnetic configuration invariant. The symmetry of the magnetic structure is therefore only $Pb'$.  

7. Conclusion

In conclusion, we have determined the magnetic structure of ErMn$_2$O$_5$ in the commensurate phase. The arrangement of the Mn moments is very similar to that determined for HoMn$_2$O$_5$ [14]. This structure is in good agreement with powder, single crystal diffraction and neutron polarimetry measurements. It may be noted that the alternative structure proposed for ErMn$_2$O$_5$ [13] gives only slightly worse agreement with the integrated intensity data but can clearly be rejected using the polarimetric results. Because of the strong crystal field anisotropy the magnetic moments of Er are aligned along the c-axis and induce a larger c-component of the Mn-spins than that found in HoMn$_2$O$_5$. Neutron polarimetry reveals that the ferroelectric phase is characterized by unequal population of the two chirality domains. The x-ray diffraction measurements show that the average crystallographic structure distorts in the ferroelectric phase transition. The principal effect of the distortion is to change the buckling angles of the Mn–O–Mn bonds leaving the distances between Mn-ions unchanged.

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