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2010 J. Phys.: Condens. Matter 22 226002

(http://iopscience.iop.org/0953-8984/22/22/226002)

J. Phys.: Condens. Matter **22** (2010) 226002 (7pp) doi:10.1088/0953-8984/22/22/226002

Phenomenological theory of phase transitions in multiferroic $MnWO_4$: magnetoelectricity and modulated magnetic order

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Received 14 January 2010, in final form 11 April 2010
Published 12 May 2010
Online at stacks.iop.org/JPhysCM/22/226002

Abstract

The phenomenological theory of phase transitions in multiferroic $MnWO_4$ is suggested. The theoretical model uses the assumption that the magnetic order is driven by the instability in the (1/4; 1/2; 1/2) point of the Brillouin zone, which is justified by the symmetry of the low-temperature magnetic phase. It is shown that the experimentally observed incommensurate magnetic order is due to the Lifshitz invariants allowed for the corresponding order parameters. Invariants responsible for the magnetoelectric interaction are found and a schematic phase diagram is calculated. The influence of the magnetic field on the phase transition sequence is also analyzed. It is suggested that the description of the phase transitions in $MnWO_4$ starting from the orthorhombic praphase significantly simplifies the approach and allows us to draw important conclusions.

1. Introduction

Magnetoelectrics are materials in which magnetic and ferroelectric orders occur simultaneously. The revival of interest in these materials is due to the discovery of the giant magnetoelectric effect (see, for example, a recent review [1]). Strong coupling between the magnetic and ferroelectric subsystems [2] allows for interesting applications [1, 3] such as, for example, high precision magnetic field measuring devices and a new generation of data storage devices [4, 5]. The objects attracting the strongest interest of researchers include, for example, $BiFeO_3$ and the two huge classes $RMnO_3$ and RMn_2O_5 (where R is a rare-earth element).

The common feature of magnetoelectric materials is the existence of incommensurate magnetic ordering [6, 7]. Many multiferroics show complex phase diagrams with a variety of different incommensurately ordered phases [8]. Some of these incommensurate phases experience a ferroelectric order as well and in some multiferroics (such as, for example, RMn_2O_5) ferroelectricity exists in the commensurately ordered state [9].

Wolframite $MnWO_4$ is one of the Mn-containing multiferroics. It contains only one magnetic ion type, Mn^{2+}, which possibly simplifies its experimental as well as theoretical study. $MnWO_4$ experiences two different incommensurately ordered structures and a low-temperature commensurately ordered magnetic phase [10]. The ferroelectricity in it has been found in one of the incommensurate phases [11, 12], although there are indications that polarization also exists in the low-temperature commensurate phase [13].

$MnWO_4$ possesses a monoclinic structure at room temperature described by the space group $P2/c$ (C^4_{2h}) with $\beta \sim 91°$ and contains two Mn^{2+} ions in the unit cell. On lowering the temperature $MnWO_4$ undergoes a sequence of magnetic phase transitions at 13.5 K (T_N), 12.7 K (T_2) and 7.6 K (T_1), leading to the appearance of magnetically ordered states **AF3**, **AF2** and **AF1** [11], respectively. According to the neutron diffraction experiments [10, 14] the structure of the low-temperature commensurate magnetic phase **AF1** is described by the wavevector (±1/4; 1/2; 1/2), whereas the incommensurate phases **AF2** and **AF3** are characterized by the wavevector (−0.214; 1/2; 0.457). In the phases **AF1** and **AF3** the collinearly aligned magnetic moments are confined to the ac plane forming an angle of about 35° with the a axis (this direction is hereafter referred to as the easy axis), whereas in

the **AF2** phase there appears an additional component along the b axis.

The ferroelectric order along the b axis in $MnWO_4$ appears at the second phase transition at T_2 from the paraelectric **AF3** phase to the ferroelectric **AF2** one [11, 12]. The polarization P_b continuously changes through T_2, whereas it drops abruptly to zero at T_1. The dielectric constant ϵ_b shows a sharp peak at T_2 and a steplike change of about 0.08% at T_1 when the ferroelectric order disappears [11, 12].

Heyer *et al* [13] reported that the polarization along the a axis appears at either T_N or T_2 (they were unable to resolve between these two phase transitions). According to their data P_a persists in the commensurate **AF1** phase in contrast to P_b. The largest measured values of P_a are about six times smaller than those of P_b.

An applied external magnetic field influences the stability ranges of the magnetically ordered phases in $MnWO_4$. Magnetic fields applied along the a or c axes stabilize the **AF2** phase, reducing T_1 to the lowest measured temperatures for fields above 2–4 T [12, 15]. Influence on T_2 and T_N for these field directions is minor except that T_N reduces to T_2 for fields above 8 T (i.e. the **AF3** phase disappears) for magnetic fields along a. The magnetic field along the b axis stabilizes the **AF1** and **AF3** phases leading to the collapse of T_1 and T_2 at about 10 T [11, 12] while stronger fields induce a magnetically ordered phase with polarization along the a axis [11].

Different behavior is observed when the magnetic field is applied along the easy axis. For field strengths between about 2 and 12 T the **AF2** phase is stable up to the lowest measured temperatures. For fields above 12 T another low-temperature magnetically ordered phase **HF** appears [15, 16]. Neutron diffraction measurements [17] revealed that this high field phase **HF** has the same relative spin arrangement as **AF1**, except that the magnetic moments are switched perpendicular to the applied field within the ac plane.

In this work we consider the phase transitions in $MnWO_4$ using the phenomenological theory of phase transitions. The thermodynamic potential is constructed in terms of the relevant magnetic and ferroelectric order parameters. In our model we consider magnetic ordering with the commensurate wavevector $\vec{k} = (1/4; 1/2; 1/2)$. The appearance of incommensurate magnetic structures as well as magnetoelectricity is accounted for by taking into consideration Lifshitz invariants and magnetoelectric interactions allowed by the symmetry of the nonmagnetic phase. A schematic phase diagram is found.

2. Magnetic ordering and symmetry

There are attempts in the literature to theoretically describe the magnetoelectric behavior observed in experiments. Usually these models proceed from the assumption that the ferroelectricity is induced by incommensurate magnetic order. Whereas ferroelectric order is often observed in incommensurately ordered phases there are magnetoelectrics showing polarization in commensurate magnetic structures. The examples are $TbMn_2O_5$ [9, 18], $TbMnO_3$ under an applied magnetic field [19, 20] and possibly $MnWO_4$ [13].

Table 1. Irreducible representations of the C_{2h}^4 space group in the $(1/4; 1/2; 1/2)$ point of the Brillouin zone.

IR	C_2	I	σ_h	a_1	a_2, a_3
G_1	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
G_2	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$

The theoretical models accounting for magnetoelectricity include a continuous formulation and representation analysis (see, for example, [7, 21]). In the model of Mostovoy [7] an inhomogeneous magnetization **M**, which is assumed to appear at a Lifshitz point, induces polarization **P** via coupling of the form $\mathbf{P}(\mathbf{M}(\nabla \cdot \mathbf{M}) - (\mathbf{M} \cdot \nabla)\mathbf{M})$. This model, which has been employed to describe the magnetoelectricity in $TbMnO_3$ [7], is not sensitive to details of the crystal structure. Moreover, the magnetic order parameters essentially belong to the center of the Brillouin zone $\vec{k} = 0$, whereas the magnetic order is modulated with $\vec{k} \approx (0; 0.28; 0)$. From our point of view such a rapid spatial change of the order parameter renders the approximation invalid.

Harris [21] has applied representation analysis to the description of magnetoelectricity in $MnWO_4$. The model takes into account magnetic ordering with the wavevector $\vec{q}$ of the incommensurate phase. The magnetoelectric interaction is found to be due to the coupling of the form $\sigma_1(\vec{q})\sigma_2^*(\vec{q})P_b$, where the order parameters $\sigma_1(\vec{q})$ and $\sigma_2(\vec{q})$ transform according to two different irreducible representations (IR). Therefore, simultaneous condensation of these two IRs gives rise to polarization along the b axis P_b.

In contrast to Harris [21] and Mostovoy [7] we assume that the magnetic order is driven by the instability in the $(1/4; 1/2; 1/2)$ point of the Brillouin zone. This is justified by the fact that (i) the low-temperature commensurate magnetically ordered phase is described by this wavevector and (ii) the incommensurately ordered phases **AF2** and **AF3** possess the wavevector close to $\vec{k} = (1/4; 1/2; 1/2)$. We give symmetrical arguments both for the appearance and direction of the long-wavelength modulation and induced polarization. Thus, as will be shown below, the phases **AF2** and **AF3**, which possess the wavevector $(-0.214; 1/2; 0.457)$, are long-wavelength modulations of a magnetic structure with $\vec{k} = (1/4; 1/2; 1/2)$ appearing at distances of several tens of unit cells. In contrast to Harris [21] our approach does not require the introduction of the temperature dependence of the modulation vector or additional order parameters belonging to $\vec{k} = (1/4; 1/2; 1/2)$ in order to describe the phase transition to the low-temperature commensurate phase. Moreover, by introducing the orthorhombic praphase as shown in section 4 the whole sequence of phase transitions in $MnWO_4$ can be described using only a single magnetic order parameter.

Therefore we proceed with finding the magnetic representation for the Mn^{2+} ions connected to the star of the vector $\vec{k}$, which is composed of two arms $\vec{k}_1 = \vec{k}$ and $\vec{k}_2 = -\vec{k}$. In this point of the Brillouin zone the space group C_{2h}^4 possesses two irreducible representations which are given in table 1.

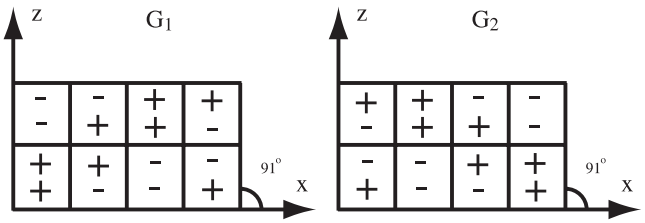

Figure 1. Schematic representation of the spin structure for the x and z components induced by the IRs G_1 and G_2. Each box corresponds to one unit cell of the lattice. For the y components of the spins the IRs should be interchanged.

The magnetic moments of the two Mn^{2+} ions in $MnWO_4$ can be expressed in the form

$$\vec{M}_1 = \begin{pmatrix} M_{1x}^{\vec{k}_1} \\ M_{1y}^{\vec{k}_1} \\ M_{1z}^{\vec{k}_1} \end{pmatrix} e^{i\vec{k}_1\vec{t}} + \begin{pmatrix} M_{1x}^{\vec{k}_2} \\ M_{1y}^{\vec{k}_2} \\ M_{1z}^{\vec{k}_2} \end{pmatrix} e^{i\vec{k}_2\vec{t}},$$

$$\vec{M}_2 = \begin{pmatrix} M_{2x}^{\vec{k}_1} \\ M_{2y}^{\vec{k}_1} \\ M_{2z}^{\vec{k}_1} \end{pmatrix} e^{i\vec{k}_1\vec{t}} + \begin{pmatrix} M_{2x}^{\vec{k}_2} \\ M_{2y}^{\vec{k}_2} \\ M_{2z}^{\vec{k}_2} \end{pmatrix} e^{i\vec{k}_2\vec{t}}.$$

The four quantities $M_{i\alpha}^{\vec{k}_j}$ for every direction α form a four-dimensional reducible representation, which can be decomposed into $G_1 + G_2$. The spin structures for the x and z components induced by the IRs G_1 and G_2 are schematically shown in figure 1 [10]. For the y components of the spins the IRs should be interchanged. In the following we define the orthogonal x, y and z axes parallel to the a axis, parallel to the b axis and perpendicular to both the a and b axes of the monoclinic cell, respectively.

The first phase transition at T_N from the paramagnetic phase to **AF3** is of second order and is connected with the condensation of IR G_1 as follows from neutron diffraction experiments [10]. It leads to the appearance of the ordered x and z components of the spins. The subsequent phase transition at T_2 to **AF2** is a second-order phase transition as well. It is connected with the instability with respect to the IR G_2 and consists in the ordering of the y component of the spins with the same pattern as for the x and z components [10].

In the low-temperature commensurate phase **AF1** only the x and z components of the spins are ordered, which is described by the single IR G_1.

In order to describe the phase transition sequence we construct the thermodynamic potential in terms of the invariants of the space group C_{2h}^4. Let us denote the x and z components of the order parameters as (η_x, ξ_x) and (η_z, ξ_z), respectively, which transform according to the IR G_1. The y components of the order parameter (η_y, ξ_y) transform according to the IR G_2. It should be noted that the order parameters $(\eta_\alpha, \xi_\alpha)$ $(\alpha = x, y, z)$ are odd under time reversal since they describe magnetic order.

The symmetry allows Lifshitz invariants:

$$\eta_\alpha \frac{\partial \xi_\alpha}{\partial x} - \xi_\alpha \frac{\partial \eta_\alpha}{\partial x}, \qquad \eta_\alpha \frac{\partial \xi_\alpha}{\partial z} - \xi_\alpha \frac{\partial \eta_\alpha}{\partial z}, \tag{1}$$

where $\alpha = x, y, z$. These invariants are responsible for the long-wavelength modulation of the phases **AF3** and **AF2** in the (x, z) plane as found in experiments.

The magnetoelectric interaction is expressed in the existence of the invariants

$$(\eta_x\eta_y + \xi_x\xi_y)P_y, \qquad (\eta_z\eta_y + \xi_z\xi_y)P_y, \tag{2a}$$

$$(\eta_x\xi_y - \xi_x\eta_y)P_xP_y, \qquad (\eta_z\xi_y - \xi_z\eta_y)P_xP_y, \tag{2b}$$

$$(\eta_x\xi_y - \xi_x\eta_y)P_zP_y, \qquad (\eta_z\xi_y - \xi_z\eta_y)P_zP_y, \tag{2c}$$

$$\eta_\alpha\xi_\alpha(\eta_\alpha^2 - \xi_\alpha^2)P_x, \qquad \eta_\alpha\xi_\alpha(\eta_\alpha^2 - \xi_\alpha^2)P_z, \tag{2d}$$

where $\alpha = x, y, z$ and P_x, P_y and P_z are the respective components of polarization. It should be noted that the existence of long-wavelength modulation of the magnetic order is not necessarily for the appearance of ferroelectric order.

The existence of Lifshitz invariants unambiguously shows that the corresponding order parameter induces improper ferroelectric phase states. Indeed, those symmetry operations, which correspond to the homomorphism kernel of the irreducible representation, i.e. the operations possessing unit matrices of the IR, do not change the components of the order parameter. Owing to the existence of the Lifshitz invariant they also should not change the polarization vector component lying along the modulation direction determined by the Lifshitz instability. Therefore, the lowest symmetry phase induced by the order parameter, which allows Lifshitz invariants, should be polar. Hence, in the general case, some of the higher symmetry phases induced by this order parameter are improper ferroelectric as well.

In the case of $MnWO_4$ the Lifshitz invariants (1) imply the existence of the invariants (2*d*). The point group symmetries of the low symmetry phases induced by both of the IRs G_1 and G_2 are C_s for the phase state (a, b) and C_{2h} for the phase states (a, a) and $(a, 0)$. Thus, the phase state (a, b) for both G_1 and G_2 is polar with the polarization lying in the xz plane.

The existence of invariants (2*a*) is possible due to the fact that the expressions $\eta_x\eta_y + \xi_x\xi_y$ and $\eta_z\eta_y + \xi_z\xi_y$ possess the same transformational properties (including translational invariance since their total wavevector $\vec{k} = \vec{k}_1 + \vec{k}_2$ is zero) as P_y. As follows from the invariants (2*a*) the polarization along the y axis may appear only when the y component of magnetic order is nonzero together with either the x or z component. This is the case of the **AF2** phase as is found in experiments. Neither the **AF1** phase nor the **AF3** one possesses the ferroelectric order along the b axis since the corresponding invariants are zeros. However, provided that $\eta_\alpha\xi_\alpha(\eta_\alpha^2 - \xi_\alpha^2) \neq 0$, the polarization along the a and c axes may exist in all of the magnetically ordered phases, as can be inferred from the last two invariants (2*d*). The polarization along the a axis has been found in experiments [13] although this effect should be smaller due to the fact that the corresponding invariants are of the fourth order with respect to the magnetic order parameter. The highest measured values of P_a are indeed about six times smaller than those of P_b [13].

3. Thermodynamic potential

We now construct the thermodynamic potential in terms of the order parameters (η_x, ξ_x), (η_y, ξ_y) and $P = P_y$. In order to qualitatively describe the phase transition sequence we do not consider the z component of the magnetic order parameters as well as we consider the dependence of the order parameters only on x for simplicity. The expansion of the thermodynamic potential up to the fourth order in $(\eta_\alpha, \xi_\alpha)$ and up to the second order in P takes the form

$$\begin{aligned}\Phi = \int \Bigg[& \frac{A_x}{2}(\eta_x^2+\xi_x^2) + \frac{B_{1x}}{4}(\eta_x^4+\xi_x^4) + \frac{B_{2x}}{4}(\eta_x^2+\xi_x^2)^2 \\ & + \sigma_x\left(\eta_x\frac{\partial\xi_x}{\partial x} - \xi_x\frac{\partial\eta_x}{\partial x}\right) + \delta_x\left(\left(\frac{\partial\eta_x}{\partial x}\right)^2 + \left(\frac{\partial\xi_x}{\partial x}\right)^2\right) \\ & + \frac{A_y}{2}(\eta_y^2+\xi_y^2) + \frac{B_{1y}}{4}(\eta_y^4+\xi_y^4) + \frac{B_{2y}}{4}(\eta_y^2+\xi_y^2)^2 \\ & + \sigma_y\left(\eta_y\frac{\partial\xi_y}{\partial x} - \xi_y\frac{\partial\eta_y}{\partial x}\right) + \delta_y\left(\left(\frac{\partial\eta_y}{\partial x}\right)^2 + \left(\frac{\partial\xi_y}{\partial x}\right)^2\right) \\ & + \kappa P(\eta_x\eta_y + \xi_x\xi_y) + \frac{a}{2}P^2 + \delta_p\left(\frac{\partial P}{\partial x}\right)^2\Bigg]\mathrm{d}x, \end{aligned} \tag{3}$$

where A_α, $B_{1\alpha}$, $B_{2\alpha}$, σ_α, δ_α, κ, a and δ_p are phenomenological constants ($\alpha = x, y$). The temperature dependence of A_α can be assumed to be $A_\alpha = A_{\alpha 0}(T - T_{\alpha 0})$, where $T_{\alpha 0}$ is the temperature at which A_α changes sign and $A_{\alpha 0}$ is a constant, which can be dependent on pressure. We assume that the polarization P consists of the homogeneous p_0 and inhomogeneous $p(x)$ parts ($P = p_0 + p(x)$).

Variation of the functional (3) with respect to the order parameters gives a system of ordinary differential equations. The linear part of these equations has the solution in the form

$$\begin{aligned} \eta_x &= \frac{2k\sigma_x(A_y + 2k^2\delta_y)g_x - 2kp_0\kappa\sigma_y g_y}{(A_x + 2k^2\delta_x)(A_y + 2k^2\delta_y) - \kappa^2 p_0^2}\sin kx \\ \xi_x &= g_x\cos kx \\ \eta_y &= \frac{2k\sigma_y(A_x + 2k^2\delta_x)g_y - 2kp_0\kappa\sigma_x g_x}{(A_x + 2k^2\delta_x)(A_y + 2k^2\delta_y) - \kappa^2 p_0^2}\sin kx \\ \xi_y &= g_y\cos kx \qquad p = g_p\cos 2kx, \end{aligned} \tag{4}$$

where g_x, g_y and g_p are amplitudes and k is the long-wavelength modulation vector. The solutions for the order parameters (η_x, ξ_x) and (η_y, ξ_y) are chosen in such a way that the relative phase shift between them is zero, which maximizes the magnetoelectric interaction (2*a*). For simplicity in the potential (3) we do not consider the interaction between the order parameters (η_x, ξ_x) and (η_y, ξ_y), which may lead to nonzero phase shift between them. The nonzero phase shift leads to the appearance of ferroelectric polarization along the x and z axes, as can be inferred from the invariants (2*b*) and (2*c*). This effect should be smaller, though, due to the fact that the corresponding invariants are of higher order with respect to the magnetic order parameters than the magnetoelectric interaction (2*a*). Equations (4) give the structure of the low symmetry modulated phases only in the vicinity of the high symmetry phase where the linear approximation is valid.

It should be noted that the modulation vector of the modulated part of the polarization is doubled with respect to the one of the magnetic order parameters. Such a choice provides the highest possible magnetoelectric interaction (2*a*).

It can be shown that $p_0 \sim g_x g_y$ and that the possible phases are

(I) $g_x \neq 0$; $g_y, g_p, p_0 = 0$
(II) $g_y \neq 0$; $g_x, g_p, p_0 = 0$
(III) $g_x, g_y, g_p, p_0 \neq 0$.

The appearance of nonzero homogeneous polarization p_0 may be explained in the following way. As can be seen from the form of the solutions (4) substituting them into the expression $\eta_x\eta_y + \xi_x\xi_y$ in the magnetoelectric interaction (2*a*) leads to an expression with homogeneous ($\sim g_x g_y$) and inhomogeneous ($\sim g_x g_y \sin^2 kx$) parts. Therefore, the former favors the appearance of nonzero homogeneous polarization p_0, which reduces the thermodynamic potential (3), whereas the latter induces spatially modulated polarization with the modulation vector $2k$. It has to be noted that P_y can only be induced by simultaneous condensation of both IRs G_1 and G_2, whereas when only a single IR is condensed, either G_1 or G_2, P_x and P_z may appear.

Phase I is characterized by nonzero and spatially modulated values of (η_x, ξ_x), which corresponds to the phase **AF3** in $MnWO_4$. In phase II the y component (η_y, ξ_y) of the magnetic order parameter is nonzero and spatially modulated. Finally, in phase III spatially modulated (η_x, ξ_x) and (η_y, ξ_y) simultaneously appear as well as improper ferroelectricity. This phase corresponds to the polar **AF2** phase. Note that the homogeneous polarization p_0 appears together with the modulated part g_p at the same phase transition.

The second-order phase transition to phase I occurs at $A_x = \sigma_x^2/(2\delta_x)$, whereas the phase transition to phase II takes place at $A_y = \sigma_y^2/(2\delta_y)$.

A schematic phase diagram is shown in figure 2. According to the basic principles of the phenomenological theory of phase transitions in the vicinity of a phase transition the coefficients at the thermodynamic potential terms with degrees higher than 2 are assumed to be weakly dependent on external thermodynamic parameters (e.g. temperature and pressure), whereas those at the quadratic terms are functions of the external thermodynamic parameters vanishing at the transition point. The temperature and pressure dependence of A_x and A_y can be assumed in the form (we retain only the linear terms in the expansion with respect to $(T - T_{c\alpha})/T_{c\alpha}$ and $(P - P_{c\alpha})/P_{c\alpha}$)

$$\begin{aligned} A_x &= A_{xT}\frac{T - T_{cx}}{T_{cx}} + A_{xP}\frac{P - P_{cx}}{P_{cx}}, \\ A_y &= A_{yT}\frac{T - T_{cy}}{T_{cy}} + A_{yP}\frac{P - P_{cy}}{P_{cy}}, \end{aligned}$$

where $A_{\alpha T}$ and $A_{\alpha P}$ are coefficients of the expansion, and $T_{c\alpha}$ and $P_{c\alpha}$ are the temperature and pressure at which the respective coefficient A_α vanishes. Considering this expansion as a linear transformation one may redraw the phase diagram of figure 2 in the T–P coordinates. Alternatively, on the assumption of P = const (the condition usually met in

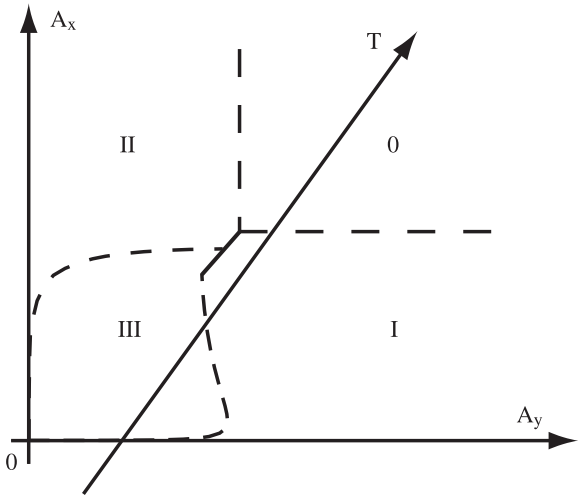

Figure 2. Schematic phase diagram. Solid line is the first-order phase transition line and the dashed lines are the second-order ones. Numbers give the corresponding phases. Phase 0 corresponds to the high symmetry phase. A possible temperature axis T is shown.

experiments) one may put the T axis on to the diagram of figure 2 as shown in the picture.

Assuming $(T_{c\alpha} - T)/T_{c\alpha}$ and $(P_{c\alpha} - P)/P_{c\alpha}$ small the phase diagram of figure 2 should have the same topological structure as that in T–P coordinates. However, due to a large number of phenomenological coefficients it is impossible to set scales of A_x and A_y. Besides, since the phase transitions in $MnWO_4$ occur at sufficiently low temperatures ($T_c \sim 10$ K) the region of validity of the linear expansion with respect to $(T_{c\alpha} - T)/T_{c\alpha}$ is very narrow and nonlinear terms quickly come into play upon moving away from the **PM–AF3** phase transition. Therefore, any quantitative description is hardly feasible.

A possible thermodynamic path T which can be relevant to $MnWO_4$ is shown in figure 2. Thus, the phase transition sequence observed in $MnWO_4$ can be described by the suggested model. As can be inferred from the diagram, the phase transition sequence 0–I–III of two second-order phase transitions corresponds to the **PM–AF3–AF2** sequence of $MnWO_4$. At the second-order phase transition I–III ferroelectricity is induced in an improper way by the magnetic order. The induced polarization possesses a homogeneous as well as a long-wavelength modulated part.

It has to be noted that the linear approximation (4) used for minimizing the functional (3) is valid only in the vicinity of the lines $A_x = \sigma_x^2/(2\delta_x)$ and $A_y = \sigma_y^2/(2\delta_y)$. Therefore, within this approximation it is not possible to describe the first-order phase transition from phase III to the commensurate phase $(\eta_x, \xi_x) \neq 0$. Moreover, the behavior of the phase transition lines far from $A_x = \sigma_x^2/(2\delta_x)$ and $A_y = \sigma_y^2/(2\delta_y)$ may be an artifact of the approximation used.

At the second-order phase transition from phase I to phase III the dielectric susceptibility diverges. In phase I the dielectric susceptibility diverges as

$$\epsilon \sim \frac{1}{T - T_2},$$

whereas in phase III it is as

$$\epsilon \sim \frac{1}{2(T_2 - T)},$$

where T_2 is the temperature of the phase transition from phase I to phase III. Far from the phase transition the susceptibility has the value $1/a$ in both phases. It has to be noted that the phase transition from phase I to phase III is, in fact, a quasi-proper phase transition. Indeed, it follows from the form of the invariants (2*a*) that the order parameters η_y, ξ_y and P_y have the same symmetry in phase I.

The specific heat jump at the phase transition from the nonmagnetic phase to phase I has the form

$$\Delta c_p = \frac{T_N \sigma_x^4}{2(3B_{1x} + 4B_{2x})(T_N - T_{\alpha 0})^2 \delta_x^2},$$

where we assumed that $A_{x0}(T_N - T_{\alpha 0}) = \sigma_x^2/(2\delta_x)$.

4. Discussion

In this section we discuss the influence of external magnetic fields on the phase transitions. For this purpose it is possible to consider the magnetic phase transitions in $MnWO_4$ starting from the orthorhombic structure of the crystal instead of the monoclinic one. It can be shown [22] that the monoclinic structure $P2/c$ of $MnWO_4$ may be considered as a slightly distorted orthorhombic one described by the space group $Pmcm$ (D_{2h}^5). By a small displacement of the oxygen ions to the nearest sites of higher symmetry one can obtain a crystal structure of orthorhombic symmetry. The atoms in the orthorhombic unit cell obtain the positions Mn–2f(1/2, y_1, 1/4), W–2e(0, y_2, 1/4), O_I–4g(x_1, 0, 0) and O_{II}–4h(x_2, 1/2, 0).

The orthorhombic structure thus found can be thought of as a praphase for the monoclinic structure of $MnWO_4$. One can expect that, upon increasing the temperature above room temperature, the monoclinic structure may transform to an orthorhombic one. This is justified by the closeness of the two structures but, in general, decomposition or melting of the sample may happen before such a phase transition takes place.

The orthorhombic structure transforms into the monoclinic one via a ferrodistortive phase transition at which the U_{xz} component of the deformation tensor appears, which is described by the irreducible representation GM^{2+} of the parent orthorhombic space group.

The main advantage of this approach is that the (1/4; 1/2; 1/2) modulation direction persists in the orthorhombic structure and that the magnetic representation of the Mn^{2+} ions in this point of the Brillouin zone contains three times the four-dimensional irreducible representation P_1 of the $Pmcm$ space group, i.e. the four quantities $M_{i\alpha}^{\vec{k}_j}$ for every direction α transform according to P_1. Thus, the two order parameters (η_x, ξ_x) and (η_y, ξ_y) merge into one four-dimensional order parameter, which we denote $(\eta_x, \xi_x, \eta_y, \xi_y)$.

Thorough analysis assuming the orthorhombic praphase will be presented elsewhere can be found in reference [22], whereas here we briefly discuss the results. Such an

approach results in a significant reduction of the number of phenomenological coefficients or in the closeness of some of them and in the appearance of new important invariants. Apart from the usual isotropic invariant $\eta_x^2+\xi_x^2+\eta_y^2+\xi_y^2$ there appears another invariant

$$U_{xz}(\eta_x^2+\xi_x^2-\eta_y^2-\xi_y^2). \tag{5}$$

Thus, the sign of U_{xz} determines which part of the order parameter, (η_x, ξ_x) or (η_y, ξ_y), condenses first upon lowering the temperature, while the value of U_{xz} determines the difference between A_x and A_y. Since monoclinic distortion is small this difference is also small, which supports the choice of the temperature axis in figure 2.

Application of an external magnetic field results in renormalization of the phenomenological coefficients and, which is more important, in the appearance of new invariants:

$$H_xH_z(\eta_x^2+\xi_x^2-\eta_y^2-\xi_y^2), \tag{6a}$$

$$H_yH_z(\eta_x\xi_y-\xi_x\eta_y). \tag{6b}$$

The invariant (6*a*) is responsible for the phase transition behavior in magnetic fields parallel to the easy axis ($H_xH_z \neq 0$). When the applied magnetic field decreases, in absolute values, the term proportional to $(\eta_x^2+\xi_x^2-\eta_y^2-\xi_y^2)$ in the thermodynamic potential the splitting between the two order parameters (η_x, ξ_x) and (η_y, ξ_y) is reduced. It results in a decrease of the stability region of the **AF3** phase due to a decrease, which is proportional to H_xH_z, of T_N. Furthermore, it can be shown that reduction of the splitting also lowers in temperature the region of the **AF1** phase stability and stabilizes the **AF2** phase. These effects are also proportional to H_xH_z, i.e. quadratic in magnetic field. In accordance with the experiments this is the case of the magnetic field applied parallel to the easy axis [15, 16].

Further increase of the field strength results in growth of the term proportional to $(\eta_x^2+\xi_x^2-\eta_y^2-\xi_y^2)$ in absolute values but with an opposite sign. This results in reduction of the stability region of the **AF2** phase and appearance of the high field **HF** phase, which is characterized by the order parameter $(0, 0, 0, \xi)$ in contrast to the phase **AF1** for which it has the form $(0, \xi, 0, 0)$. Magnetic representation analysis shows that the $(0, 0, 0, \xi)$ state is characterized by the same relative spin arrangement as in **AF1** but the magnetic moments are switched perpendicular to their direction in **AF1** within the *ac* plane, which is supported by the neutron diffraction experiments [17]. Moreover, the **AF3′** phase (see below) should appear in the phase diagram with further increase of the field strength, which is not observed experimentally. Different behavior should be observed when the magnetic field is applied perpendicular to the easy axis within the *ac* plane (i.e. H_xH_z has opposite sign) [16]. As follows from (6*b*) and the invariant $(\eta_x\eta_y+\xi_x\xi_y)P_y$ the magnetic field applied in such a way that $H_yH_z \neq 0$ should decrease P_y (i.e. the stability region of **AF2** shrinks).

Considering the phase transitions starting from the orthorhombic praphase the invariant $(\eta_x\eta_y+\xi_x\xi_y)P_y$ naturally involves only one magnetic order parameter. Therefore, it can be stated that the magnetic phase transitions observed in $MnWO_4$ are due to a single instability with respect to the irreducible representation P_1 of the orthorhombic space group $Pmcm$ ((1/4; 1/2; 1/2) point of the Brillouin zone).

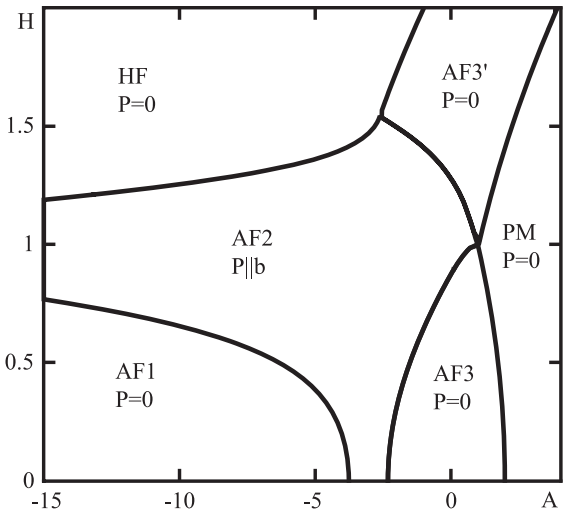

Figure 3. H–A phase diagram with the magnetic field applied along the easy axis. The order parameters in the phases are **AF1**—$(0, \xi_x, 0, 0)$, **AF2**—$(\eta_x(x), \xi_x(x), \eta_y(x), \xi_y(x))$, **AF3**—$(\eta_x(x), \xi_x(x), 0, 0)$, **AF3′**—$(0, 0, \eta_y(x), \xi_y(x))$ and **HF**—$(0, 0, 0, \xi_y)$.

In order to compare the obtained results we have numerically minimized the thermodynamic potential, which can be written as follows (assuming that $(\eta_x, \xi_x, \eta_y, \xi_y)$ depend on x):

$$\Phi = \int\left[\frac{A}{2}I_1+\frac{B_1}{4}I_2+\frac{B_2}{4}I_1^2+B_3I_3+\frac{B_4}{2}I_4+\frac{B_5}{2}I_5 + \frac{B_6}{6}I_1^3+f_1I_u+f_2I_H+\sigma I_L+\frac{\delta}{2}I_\delta\right]\mathrm{d}x, \tag{7}$$

where the invariants are $I_1 = c_1^2+c_2^2+c_3^2+c_4^2$, $I_2 = c_1^4+c_2^4+c_3^4+c_4^4$, $I_3 = c_1c_2c_3c_4$, $I_4 = c_1^2c_2^2+c_3^2c_4^2$, $I_5 = c_1^2c_3^2+c_2^2c_4^2$, $I_u = U_{xz}(c_1c_3+c_2c_4)$, $I_H = H_xH_z(c_1c_3+c_2c_4)$, $I_L = c_1\partial c_4/\partial x - c_4\partial c_1/\partial x + c_3\partial c_2/\partial x - c_2\partial c_3/\partial x$ and $I_\delta = (\partial c_1/\partial x)^2+(\partial c_2/\partial x)^2+(\partial c_3/\partial x)^2+(\partial c_4/\partial x)^2$ and where we used the linear transformation $c_1 = -\eta_x+\xi_x+\eta_y+\xi_y$, $c_2 = \eta_x+\xi_x-\eta_y+\xi_y$, $c_3 = -\eta_x+\xi_x-\eta_y-\xi_y$, $c_4 = \eta_x+\xi_x+\eta_y-\xi_y$.

Figure 3 shows the H–A phase diagram, where the magnetic field H is applied along the easy axis. The phenomenological coefficients take the values $B_1 = 7$, $B_2 = 1$, $B_3 = -1$, $B_4 = -6$, $B_5 = 1$, $B_6 = 1$, $\sigma = 1$, $\delta = 1$, $f_1 = 1$, $f_2 = 2.128$ and $U_{xz} = -1$. The H–A phase diagram is topologically equivalent to the H–T one since $A \sim (T-T_N)$. The phase diagram is in good correspondence with the experimental one [15, 16], but shows additional features. The numerical solution reveals the existence of the **AF3′** phase, which is characterized by the long-wavelength modulation of the magnetic moment component along the b axis, whereas in the **AF3** phase the magnetic moments are confined to the *ac* plane. Heretofore the **AF3′** phase was not experimentally observed.

It has been reported [11] that a strong magnetic field along the b axis induces the **X** phase with polarization $P \parallel a$. It can be accounted for by carrying out the expansion (7) to higher order and taking into consideration the invariants

$$(\eta_x\xi_x(\eta_x^2-\xi_x^2-3\eta_y^2+3\xi_y^2)+\eta_y\xi_y(\eta_y^2-\xi_y^2-3\eta_x^2+3\xi_x^2))P_x,$$

$$(\eta_x\xi_x(\eta_x^2-\xi_x^2+3\eta_y^2-3\xi_y^2)-\eta_y\xi_y(\eta_y^2-\xi_y^2+3\eta_x^2-3\xi_x^2))P_z.$$

These invariants imply that some of the magnetically ordered phases induced by the order parameter $(\eta_x, \xi_x, \eta_y, \xi_y)$ have nonzero P_a and P_c.

5. Conclusions

In summary, we have built a phenomenological theory of phase transitions in $MnWO_4$. The magnetic structure is described by the order parameters $(\eta_\alpha, \xi_\alpha)$ $(\alpha = x, y, z)$ belonging to the $(1/4; 1/2; 1/2)$ point of the Brillouin zone. It is shown that Lifshitz invariants allowed by the symmetry are responsible for the appearance of magnetically ordered phases **AF3** and **AF2** incommensurately modulated along the x and z directions as observed in experiments. Invariants responsible for the magnetoelectric interaction are established. It is found that incommensurability of the magnetic ordering is not essential for polarization induction. The ferroelectric polarization along the y axis appears in an improper way provided that the y component of magnetic order is nonzero together with either the x or z component, which corresponds to the **AF2** phase of $MnWO_4$ according to neutron diffraction experiments [10]. The induced polarization P_y consists of homogeneous as well as modulated parts which appear at the same phase transition. Ferroelectric order along the a and c axes can also be induced by the magnetic order, although it should be smaller than along the b axis due to the higher order of the respective invariants with respect to the magnetic order parameters. Introduction of the orthorhombic praphase allows us to describe the phase transitions in $MnWO_4$ using a single four-dimensional order parameter, which significantly simplifies the thermodynamic potential and results in the appearance of new important invariants. The approach used is a general one and was recently applied [23] to orthorhombic magnetoelectrics including the rare-earth manganites RMn_2O_5.

References

[1] Fiebig M 2005 *J. Phys. D: Appl. Phys.* **38** R123
[2] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 *Nature* **426** 55
[3] Tokura Y 2007 *J. Magn. Magn. Mater.* **310** 1145
[4] Scott J F 2007 *Nat. Mater.* **6** 256
[5] Gajek M, Bibes M, Fusil S, Bouzehouane K, Fontcuberta J, Barthélémy A and Fert A 2007 *Nat. Mater.* **6** 296
[6] Harris A B and Lawes G 2005 Ferroelectricity in incommensurate magnets arXiv:cond-mat/0508617v1
[7] Mostovoy M 2006 *Phys. Rev. Lett.* **96** 067601
[8] Kimura T, Lawes G, Goto T, Tokura Y and Ramirez A P 2005 *Phys. Rev.* B **71** 224425
[9] Kimura H, Kobayashi S, Wakimoto S, Noda Y and Kohn K 2007 *Ferroelectrics* **354** 77
[10] Lautenschläger G, Weitzel H, Vogt T, Hock R, Böhm A, Bonnet M and Fuess H 1993 *Phys. Rev.* B **48** 6087
[11] Taniguchi K, Abe N, Takenobu T, Iwasa Y and Arima T 2006 *Phys. Rev. Lett.* **97** 097203
[12] Arkenbout A H, Palstra T T M, Siegrist T and Kimura T 2006 *Phys. Rev.* B **74** 184431
[13] Heyer O, Hollmann N, Klassen I, Jodlauk S, Bohatý L, Becker P, Mydosh J A, Lorenz T and Khomskii D 2006 *J. Phys.: Condens. Matter* **18** L471
[14] Dachs H, Stoll E and Weitzel H 1967 *Z. Kristallogr.* **125** 120–9
[15] Taniguchi K, Abe N, Sagayama H, Ohtani S, Takenobu T, Iwasa Y and Arima T 2008 *Phys. Rev.* B **77** 064408
[16] Ehrenberg H, Weitzel H, Heid C, Fuess H, Wltschek G, Kroener T, van Tol J and Bonnet M 1997 *J. Phys.: Condens. Matter* **9** 3189
[17] Ehrenberg H, Weitzel H, Theissmann R, Fuess H, Rodriguez-Martinez L M and Welzel S 2000 *Physica* B **276–278** 644
[18] dela Cruz C R, Lorenz B, Sun Y Y, Wang Y, Park S, Cheong S-W, Gospodinov M M and Chu C W 2007 *Phys. Rev.* B **76** 174106
[19] Aliouane N, Argyriou D N, Strempfer J, Zegkinoglou I, Landsgesell S and Zimmermann M v 2006 *Phys. Rev.* B **73** 020102(R)
[20] Arima T, Goto T, Yamasaki Y, Miyasaka S, Ishii K, Tsubota M, Inami T, Murakami Y and Tokura Y 2005 *Phys. Rev.* B **72** 100102(R)
[21] Harris A B 2007 *Phys. Rev.* B **76** 054447
[22] Ter-Oganessian N V and Sakhnenko V P 2010 *Crystallogr. Rep.* submitted
[23] Sakhnenko V P and Ter-Oganessian N V 2010 *Ferroelectrics* at press