Magnetoelectricity and weak ferromagnetism in the antiferromagnet $KNiPO_4$

E. A. Turov

Institute of Metal Physics, Russian Academy of Sciences, 620219 Ekaterinburg, Russia
(Submitted 30 August 1995)
Zh. Éksp. Teor. Fiz. **110**, 202–217 (July 1996)

A tentative explanation is given of the coexistence of weak ferromagnetism with the magnetoelectric effect in the orthorhombic antiferromagnet $KNiPO_4$. Its magnetic group $mm2$, obtained from neutron scattering studies and confirmed by magnetoelectric measurements, does not allow weak ferromagnetism, but experiment gives it. The idea of the explanation is that an orientational phase transition takes place during magnetization to the state with the magnetic group $m'm2'$ for $\mathbf{H}\|\mathbf{b}$ and to the state with magnetic symmetry $m'm'2$ for $\mathbf{H}\|\mathbf{c}$. In these states weak ferromagnetism can already exist, and its presence is revealed by extra polating to $\mathbf{H}=0$, and also as the manifestation of the metastable state obtained by the corresponding annealing in a magnetic field. Other possible mechanisms of spontaneous magnetization are also indicated. The experimental results already available are discussed as well as whether it would be desirable to carry out additional experiments to obtain a definitive solution of the problem. © *1996 American Institute of Physics.*
[S1063-7761(96)01607-1]

1. INTRODUCTION

The orthorhombic crystal $KNiPO_4$ belongs to the spatial group $Pna2_1$ which does not contain a $\bar{1}$ symmetry center and, as a consequence, is a pyroelectric with spontaneous polarization $\mathbf{P}\|2_1\|\mathbf{Z}$. The magnetic Ni^{2+} ions occupy the $4(a)$ position:

$$1(x,y,z),\quad 2(-x,-,1/2+z),\quad 3(1/2+x,1/2-y,z),$$

$$4(1/2-x,1/2+y,1/2=z).$$

Its unit cell projected onto the XY plane is depicted in Fig. 1. Besides the positions of the magnetic ions, the figure also shows the symmetry elements—the n_x slip plane perpendicular to the $\mathbf{X}\|\mathbf{a}$ axis, and the a_y slip plane perpendicular to the $\mathbf{Y}\|\mathbf{b}$ axis, and also the second-order screw axis $2_{1z}\|\mathbf{Z}$. Only two of them (any two) are independent. At temperatures below $T_N\approx 25$ K antiferromagnetic ordering takes place with preservation of the unit cell. Thus, the antiferromagnetic structure can be described in terms of four magnetic sublattices with magnetizations $\mathbf{M}_n$ $(n=1,2,3,4)$. According to neutron scattering data[1] and magnetoelectric measurements,[2] it has been concluded that magnetic ordering preserves both the spatial group and the point symmetry group $mm2$.

All of the aforementioned information was taken from Refs. 1 and 2. In Ref. 2 a special detailed study of the magnetoelectric effect was undertaken, which showed that only the α_{12} and α_{21} components of the magnetoelectric susceptibility are nonzero. The tensor α_{ij} defines the linear coupling between the electric polarization $\mathbf{P}$ and the magnetic field $\mathbf{H}$ (the $(ME)_H$ effect):

$$P_i=\alpha_{ij}H_j, \tag{1a}$$

and also the inverse effect (the $(ME)_E$ effect):

$$M_j=\alpha_{ij}E_i \tag{1b}$$

(E is the electric field). This result, it would seem, confirms the magnetic structure with symmetry $mm2$ and eliminates two other possible magnetic structures with four magnetic sublattices: $m'm2'$ (for which α_{23} and α_{32} are nonzero) and $m'm'2$ (for which $\alpha_{ii}\neq 0, i=1,2,3$). But the problem is that for the structure with symmetry $mm2$ weak ferromagnetism should not exist. Indeed, it is easy to show that the set of elements m_x, m_y, and 2_z does not leave invariant even one of the components of the vector $\mathbf{M}$ invariant. But at the same time, the spontaneous magnetic moment $M_s\neq 0$ in $KNiPO_4$ is quite confidently observed. It was even observed in the first paper[3] on the magnetic properties of $KNiPO_4$, but the measurements reported in this paper were in powders of small single crystals, and in the more recent work,[2] in single crystals. Most of the present paper represents an attempt to resolve this contradiction.

A weak point in the interpretation of the experiment in Refs. 1 and 2, and also in a number of other works in Refs. 4 and 5, is the implicit assumption that the magnetic structure with symmetry $mm2$ is preserved in the magnetization process (or even thermomagnetic treatment), i.e., no orientational phase transitions take place. The rejection of this assumption is the basis of the present work. Magnetic and, generally speaking, electric fields can produce a rotation of the antiferromagnetic ordering axis (i.e., the antiferromagnetism vector $\mathbf{L}$). Here it is worthwhile to discuss the properties of such materials not in terms of their magnetic point symmetry, but in terms of their crystallochemical spatial symmetry (the Fedorov group $Pna2_1$, augmented by time inversion $1'$), in which due to the coincidence of the crystallochemical and magnetic unit cells, translations (by a whole period) can be assumed to be an identity element.

As already mentioned, the crystallochemical group of $KNiPO_4$ does not contain spatial inversion (a symmetry center). In this case, the coexistence of weak ferromagnetism

 1063-7761/96/070108-08$10.00

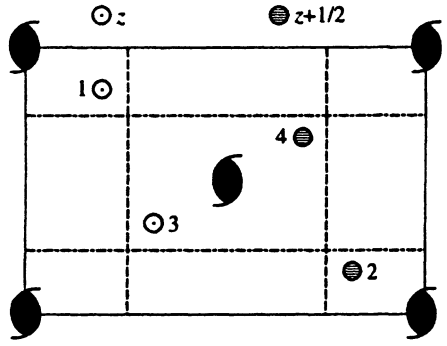

FIG. 1. Unit cell of the lattice of $KNiPO_4$ projected onto the XY plane. Only the positions of magnetic Ni^{2+} ions and the symmetry elements—the slip planes $n \perp X$ and $a \perp Y$ and the screw axis $2_{1z}=na$—are shown.

and the magnetoelectric effect is possible.[6] And although weak ferromagnetism is indeed lacking the orientational state corresponding to the point magnetic group $mm2$, when the magnetic moments are ordered along the $\mathbf{X}\|\mathbf{a}$ ($\mathbf{L}\|\mathbf{X}$) axis, it can show up in the magnetization process if rotation of the antiferromagnetism vector takes place.

Going over to a crystallochemical description means that the tensor α_{ij} in Eqs. (1) should be represented as an expansion in the vector $\mathbf{L}$—an expansion that is invariant with respect to the crystallochemical symmetry group.

Reference 2 presents results of a study of the angular dependence of the electric polarizability P_x in a magnetic field $\mathbf{H} \perp \mathbf{X}$ that are also very informative for theory. Unfortunately, a theoretical explanation of these results is hindered (although I undertake such an effort) by a lack of information about the orientational state of the vector $\mathbf{L}$ in an external magnetic field.

To conclude this paper, I advance some proposals for additional experimental studies motivated by the present work.

2. POSSIBLE COLLINEAR EXCHANGE MAGNETIC STRUCTURES AND THEIR CLASSIFICATION FORMULAS AND VECTOR ORDER PARAMETERS

The mutual orientation of the magnetic moments (the magnetizations of the sublattices) is called the exchange magnetic structure. I will refer to their orientation relative to the crystallographic axes associated with magnetic anisotropy in an external magnetic field (and under other circumstances; see below) as the orientational state.

As usual,[6,7] we first carry out a symmetry classification of the exchange magnetic structures in terms of the crystallochemical group G_F1'. By virtue of the fact that the crystallochemical and magnetic unit cells coincide, it is sufficient to consider only the symmetry elements g_F indicated in Fig. 1—the slip planes n and a, and the screw axis 2_1. Since only two of them (ignoring $1'$) are independent, we take n and a as those two ($2_1=na$). The first column of Table I indicates possible combinations of parity of the exchange magnetic structures[6] relative to these elements, and the second gives the classification formulas of possible collinear exchange magnetic structures. Three of them, a, b, and c, are antiferromagnetic, and the fourth, f, is ferromagnetic. The last column gives the corresponding vector order parameters, and Fig. 2 shows diagrams of these same exchange magnetic structures. The plus and minus signs indicate only the mutual directions of the magnetic moment irrespective of their orientation to the crystallographic axes.

TABLE I.

	n	a	Classification number of the exchange magnetic structure	Vector order parameter
a	+	−	$m_x(+)m_y(-)$	$\mathbf{L}_a=\mathbf{M}_1-\mathbf{M}_2-\mathbf{M}_3+\mathbf{M}_4$
b	−	+	$m_x(-)m_y(+)$	$\mathbf{L}_b=\mathbf{M}_1-\mathbf{M}_2+\mathbf{M}_3-\mathbf{M}_4$
c	−	−	$m_x(-)m_y(-)$	$\mathbf{L}_c=\mathbf{M}_1+\mathbf{M}_2-\mathbf{M}_3-\mathbf{M}_4$
f	+	+	$m_x(+)m_y(+)$	$\mathbf{M}=\mathbf{M}_1+\mathbf{M}_2+\mathbf{M}_3+\mathbf{M}_4$

Note that the exchange magnetic structure classification number (Table I and Fig. 2) already contain the symbols of the point symmetry elements; in particular, m_x and m_y denote the mirror planes normal to the X and Y axes. The spatial character of g_F is taken into account by the indication of the parity of the exchange magnetic structure ("+" or "−") relative to it. Recalling the transformation rules,[6]

$$g(\pm)\mathbf{L}=\pm g\mathbf{L}, \quad g(\pm)\mathbf{M}=g\mathbf{M} \quad g(\pm)\mathbf{P}=g\mathbf{P}. \tag{2}$$

Note that the fields $\mathbf{E}$ and $\mathbf{H}$ transform analogously to $\mathbf{P}$ and $\mathbf{M}$.

The information contained in the exchange magnetic structure classification number (together with inversion $1'$) is all that is needed for a symmetry-based treatment of the properties of a collinear (or weakly non-collinear) antiferromagnet in terms of its crystallochemical symmetry.

3. TRANSFORMATION OF DYNAMICAL VARIABLES; ENERGY INVARIANTS

Relations (2) allow us to write down invariant expansions in $\mathbf{L}$, $\mathbf{M}$, $\mathbf{P}$, and other dynamical variables in thermodynamics, kinetics, optics, acoustics, etc. We reiterate that

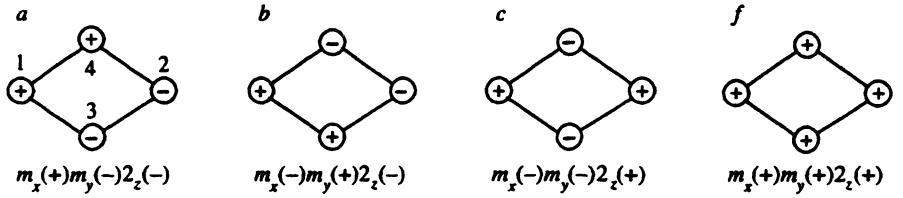

FIG. 2. Possible collinear antiferromagnetic structures a, b, and c, and the ferromagnetic structure f.

TABLE II.

	P_x	P_y	P_z	M_x	M_y	M_z	L_{ax}	L_{ay}	L_{az}	L_{bx}	L_{by}	L_{bz}	L_{cx}	L_{cy}	L_{cx}
n_x	−	+	+	+	−	−	+	−	−	−	+	+	−	+	+
a_y	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+
$m_{x'}$	−	+	+	−	+	+	−	+	+	+	−	−	+	−	−
$m_{y'}$	+	−	+	+	−	+	−	+	−	+	−	+	−	+	−
2_z	−	−	+	−	−	+	+	+	−	+	+	−	−	−	+

$mm2$
$m'm2$
$m'm'2$

the coefficients of these expansions (the form and symmetry of the corresponding tensors) derive from the required invariance of the latter with respect to the crystallochemical symmetry elements entering into the classification formula of the exchange magnetic structures with allowance for their parity.

For example, for the contributions of weak ferromagnetism and the magnetoelectric effect to the thermodynamic potential, it is necessary to write invariant expressions of the form

$$F_{WF}=-D_{ij}M_iL_j, \tag{3}$$

$$F_{ME}=-\gamma_{ijk}P_iM_jL_k/L. \tag{4}$$

For $\mathbf{L}$ here we choose the vector $\mathbf{L}_n$ ($n=a$, b, or c) from Table I for the exchange magnetic structure of interest. To find the explicit form of the tensors D and γ that ensures invariance of these expressions, we construct a table of transformations (Table II) for the dynamical variables $\mathbf{P}$, $\mathbf{M}$, and $\mathbf{L}_n$ relative to n_x and a_y, or (what amounts to the same thing) relative to the point elements m_x and m_y with allowance for their parity in accordance with the classification formula of each exchange magnetic structure. The transformation rules are represented by (2), and depend on the classification formula of the exchange magnetic structure, i.e., they are different for different $\mathbf{L}_n$, as can be seen from Table II. The minus and plus signs in Table II indicate, respectively, that the variable (upper row of the table) being acted on by the symmetry operation (far left column) changes sign (does not change sign). The lower part of Table II (below the line) gives the transformation rules for the variables being acted on by the primed elements $m'=m1'$, and also $2_x=m_xm_y=m'_xm'_y$. We will need this to determine the magnetic (point) groups.

The maximum program of the symmetric (crystallochemical) approach which we use here could consist in constructing a phenomenological theory of the magnetic and magnetoelectric properties of the antiferromagnetic crystal of interest with allowance for the possible orientational transitions for which the orientational state (and along with it the magnetic group) varies, but the exchange magnetic structure corresponding to its classification formula (Table I) remains invariant. Toward this end, it is necessary, along with the contributions of weak ferromagnetism (3) and the magnetoelectric effect (4) to the thermodynamic potential F, to also write down the magnetic contribution (exchange and magnetic anisotropy), and the electric and Zeeman contributions. Again we emphasize that they should be invariant relative to the crystallochemical spatial symmetry group $Pna2_1$, which if the magnetic and crystallochemical unit cells coincide reduces to the two elements n_x and a_y indicated in the upper part of Table II (disregarding 1 and $1'$). The complete expression for F will contain more than fifty terms with independent coefficients, and it is clear that at the present time a quantitative treatment on this basis is simply unrealistic. But all the same, writing out the indicated invariants (without the coefficients), we can still effect a qualitative treatment of the phenomena observed in Refs. 1–3, and make definite recommendations regarding the formulation of additional experiments.

From Table II, above all it is clear, that there is an invariant consisting of one cofactor of P_z, independent of the magnetic state of the crystal. This has to do with the fact that the latter is a pyroelectric with spontaneous polarization $\mathbf{P}_s\|2_1\|\mathbf{Z}$.

Those products of variables in Table II corresponding to a plus sign for both elements are also invariant (with respect to n and a). Here, to preserve invariance with respect to time inversion $1'$ we must consider only the products that are even in the magnetic vectors $\mathbf{L}$ and $\mathbf{M}$ As a result, we have

1) magnetic invariants:

$$M^2,L_a^2,L_b^2,L_c^2 \quad \text{(exchange)},$$

$$L_{ax}^2,L_{ay}^2,L_{az}^2,L_{bx}^2,L_{by}^2,L_{bz}^2,L_{cx}^2,L_{cy}^2,L_{cz}^2,$$

$$L_{ax}L_{by},L_{ax}L_{cz},L_{ay}L_{bx},L_{az}L_{cx},L_{by}L_{cz},L_{bz}L_{cy},$$

$$L_{ay}M_z,L_{az}M_y,L_{bx}M_z,L_{bz}M_x,L_{cx}M_y,L_{cy}M_x$$

(anisotropy); (5)

2) magnetoelectric invariants: all invariants with $\mathbf{M}$ from Eq. (5), multiplied by P_z, and also

$$P_xM_xL_{ay},P_xM_xL_{bx},P_xM_yL_{ax},P_xM_yL_{by},P_xM_yL_{cz},$$

$$P_xM_zL_{bz},P_xM_zL_{cy},P_yM_xL_{ax},P_yM_xL_{by},P_yM_xL_{cz},$$

$$P_yM_yL_{ay},P_yM_yL_{bx},P_yM_zL_{az},P_yM_zL_{cx}; \tag{6}$$

3) antiferromagnetic invariants: all invariants from Eq. (5) quadratic in $\mathbf{L}$, multiplied by P_z, and also

$$P_xL_{ax}L_{az},P_xL_{ax}L_{cx},P_xL_{ay}L_{bz},P_xL_{ay}L_{cy},P_xL_{az}L_{by},$$

$$P_xL_{az}L_{cz},P_xL_{bx}L_{bz},P_xL_{bx}L_{cy},P_xL_{by}L_{cx},P_yL_{ax}L_{bz},$$

$$P_yL_{ay}L_{az},P_yL_{ax}L_{cy},P_yL_{ay}L_{cx},P_yL_{az}L_{bz},P_yL_{az}L_{cy},$$

$$P_yL_{by}L_{bz},P_yL_{cy}L_{cz},P_yL_{bx}L_{cx},P_yL_{by}L_{cy},P_yL_{bz}L_{cz}. \tag{7}$$

Regarding invariants (6) and (7), we note that it is possible to combine them to form nonrelativistic invariants. For (6) these are

$$P_x(\mathbf{ML}_b), \quad P_y(\mathbf{ML}_a), \tag{8}$$

and for (7)

$$P_x(\mathbf{L}_a\mathbf{L}_c), \quad P_y(\mathbf{L}_b\mathbf{L}_c). \tag{9}$$

They can give, generally speaking, a significantly greater contribution to the energy than the analogous relativistic terms. It is necessary to bear this in mind when constructing a quantitative theory of thermodynamics or dynamics (a theory of excitations). Induction of the exchange interaction by the electric field (by the polarization **P**) for other antiferromagnets was predicted in my earlier paper.[6]

Note also that for certain directions of the vectors $\mathbf{L}_n$ (those not coincident with the crystallographic axes **X**∥**a**, **Y**∥**b**, **Z**∥**c**) invariants of the form (7) can lead to spontaneous electric polarization **P**∥**X** or **P**∥**Y** associated with antiferromagnetic ordering. In particular, we take note of the first invariant in the first row and the first invariant in the third row of (7). They correspond to the exchange magnetic structure of type *a* (see Tables I and II), which, according to Refs. 1 and 2, are realized in $KNiPO_4$. More will be said about this below.

4. SUPERPOSITION OF VARIOUS EXCHANGE MAGNETIC STRUCTURES AND MAGNETIC SYMMETRY

According to Table II, in the quadratic approximation in M and L_a the exchange energy can be represented in the form

$$F_{ex}=\frac{1}{2}\,(J_0M^2+J_1L_a^2+J_2L_b^2+J_3L_c^2). \tag{10}$$

In the paramagnetic region all the exchange constants J are greater than zero, which corresponds to $\mathbf{M}=\mathbf{L}_a=\mathbf{L}_b=\mathbf{L}_c=\mathbf{0}$. As the temperature is lowered, in the presence of magnetic ordering, that one of the four possible exchange magnetic structures (Fig. 2) is realized for which one of the exchange constants in Eq. (10) changes sign. According to Refs. 1 and 2, this is J_1, so that a collinear exchange magnetic structure with $\mathbf{L}_a\neq\mathbf{0}$ is realized. In this case, $\mathbf{M}=\mathbf{L}_b=\mathbf{L}_c=\mathbf{0}$, whence it follows that $\mathbf{M}_1=\mathbf{M}_4$ and $\mathbf{M}_2=\mathbf{M}_3$. The orientation of $\mathbf{L}_a$ is determined by the anisotropy constants K_{ai} for $i=x, y, z$ (and, generally speaking, by the constants for other anisotropy invariants from (5)–(7)). It is well known from Ref. 2 that $\mathbf{L}_a\|\mathbf{X}$, and this occurs for $K_{ax}<K_{ay}, K_{az}$.

It is clear from Table II that the orientational state with $\mathbf{L}_a\|\mathbf{X}$ for the structure *a* does indeed correspond to the magnetic group $mm2$. It is specifically under this group that the component L_{ax} is invariant. But the components L_{by} and L_{cz} of the antiferromagnetism vectors of the exchange magnetic structures *b* and *c* are invariant under this same group, which leads to the terms

$$L_{ax}L_{by}, L_{ax}L_{cz}, L_{by}L_{cz} \tag{11}$$

in the magnetic anisotropy energy (third line in (5)). This means that a "three-dimensional cross" (see Ref. 8, Ch. 10) will be a more accurate magnetic structure with allowance for a relativistic interaction like that of (11). Here, the y and z components of the magnetic moments should be small in comparison with the x component. Specifically such an antiferromagnetic structure has been proposed on the basis of neutron scattering data.[1]

For this magnetic structure with nonzero components

$$L_{ax}, L_{by}, L_{cz} \tag{12}$$

according to (6) (the third, fourth, fifth, and eighth, ninth, and tenth invariants) the components α_{12} and α_{21} of the magnetoelectric susceptibility tensor should be nonzero. This also agrees with experiment.[2]

However, for the magnetic group $mm2$ according to Table II, invariant components of the vector **M** are absent, which indicates a lack of weak ferromagnetism. The same conclusion follows from the lack in (5) of crystallochemical invariants in which the components of **M** are mixed with the components of (12). It would seem that this in itself contradicts the experiments which found weak ferromagnetism with the vector $\mathbf{M}_s$ parallel to the Y and Z axes.

Let us consider, however, other orientational states corresponding to the main antiferromagnetism vector $\mathbf{L}_a$, all the while requiring that it be aligned with one of the crystallographic axes. Besides the case considered above ($\mathbf{L}_a\|\mathbf{a}\|\mathbf{X}$), these can be $\mathbf{L}_a\|\mathbf{b}\|\mathbf{Y}$ and $\mathbf{L}_a\|\mathbf{c}\|\mathbf{Z}$.

The first of these cases, according to Table II, corresponds to the magnetic symmetry group $m'm'2$. Besides L_{ay}, the components L_{bx} and M_z are invariants of this group. An indication of the energy coupling of this triple of variables

$$L_{ay}, L_{bx} \quad \text{and} \quad M_z \tag{13}$$

is given by the corresponding crystallochemical invariants in (5):

$$L_{ay}L_{bx}, L_{ay}M_z, L_{bx}M_z. \tag{14}$$

This means that when the exchange magnetic structure of type *a* arises in this orientational state with $\mathbf{L}_a\|\mathbf{Y}$ due to exchange forces, the structures $\mathbf{L}_b\|\mathbf{X}$ and $\mathbf{M}\|\mathbf{Z}$ also arise, automatically, due to the relativistic forces.

Finally, according to Table II, the orientational state with $\mathbf{L}_a\|\mathbf{Z}$ corresponds to the magnetic group $m'm2'$, for which the variables

$$L_{az}, L_{cx}, M_y, \tag{15}$$

interacting via the energy invariants

$$L_{az}L_{cx}, L_{az}M_y, L_{cx}M_y. \tag{14'}$$

are themselves invariants. This is the weakly ferromagnetic state with $\mathbf{M}_s\|\mathbf{Y}$.

Note also that for the orientational state (13), as follows from (5) and (6), the components of the magnetoelectric susceptibility α_{ii} ($i=1,2,3$) are nonzero, and for (15) it is the components α_{23} and α_{32}.

Next it must be noted that besides the orientational states (12), (13), and (15), considered above, which correspond to the point magnetic groups $mm2$, $m'm'2$, and $m'm2'$, generally speaking, other less symmetric states can occur.

Reasons for this can be a higher-order anisotropy and, as we will see below, terms of the form (3) and (7), and finally, a magnetic field. As can be seen from Table II, this state can be

1) the state with $\mathbf{L}_a \perp \mathbf{Y}$, $\mathbf{L}_b \| \mathbf{Y}$, and $\mathbf{L}_c \perp \mathbf{Y}$, for $M_y \neq 0$ and $P_x \neq 0$ ($P_z \neq 0$ is always the case, even for $T > T_N$), the magnetic symmetry group m_y;

2) the state with $\mathbf{L}_a \perp \mathbf{X}$, $\mathbf{L}_b \| \mathbf{X}$, and $\mathbf{L}_c \perp \mathbf{X}$, for $M_{y,z} \neq 0$ and $P_y \neq 0$, the magnetic symmetry group m'_x;

3) the state with $\mathbf{L}_a \perp \mathbf{X}$, $\mathbf{L}_b \| \mathbf{Z}$, and $\mathbf{L}_c \perp \mathbf{Y}$, for $M_z \neq 0$, the magnetic symmetry group 2_z.

It will become clear from energy considerations to follow (in a simplified model) that the first two such states, for certain relations of the parameters, can be stable even in the absence of an external magnetic field, and the third, only in a field $\mathbf{H} \| \mathbf{Z}$.

5. FEASIBLE ORIENTATIONAL STATES AND THEIR STABILITY

In the simplified model, setting $\mathbf{L}_b = \mathbf{L}_c = \mathbf{0}$ and $L_a^2 = L^2 = \text{const}$, we find the possible orientational states and their stability conditions, first in the absence of an external magnetic field ($\mathbf{H} = \mathbf{0}$). Here, according to (5)–(7), the density of the thermodynamic potential can be written in the form

$$F = \frac{1}{2}\chi_\perp^{-1} M_\perp^2 + \frac{1}{2}\chi_\|^{-1} M_\|^2 + \frac{1}{2}K_2 L_y^2 + \frac{1}{2}K_3 L_z^2 - D_{23} M_y L_z - D_{32} M_z L_y - (\gamma_1 P_x M_y L_x + \gamma_2 P_y M_x L_x) L^{-1} - (\delta_1 P_x L_x L_z + \delta_2 P_y L_y L_z) L^{-1} + \frac{1}{2}\kappa^{-1}(P_x^2 + P_y^2). \quad (16)$$

Here the exchange energy (the first two terms) is written in such a way that along with the transverse (to the vector $\mathbf{L}$) magnetic susceptibility $\chi_\perp$ it is also possible to take account of the longitudinal susceptibility $\chi_\| \neq 0$ (κ is the electric susceptibility). It is understood that $\mathbf{M}_\| = (\mathbf{ML})\mathbf{L}/L^2$ and $\mathbf{M}_\perp = \mathbf{M} - \mathbf{M}_\|$. Also, in the present paper, in the interest of further simplification of a problem that is, in general, quite complex, we will assume that $\chi_\perp \gg \chi_\| \approx 0$, which corresponds to the low-temperature region $T \ll T_N$, as is the case for most of the experimental measurements in Ref. 2 of interest to us (for $T = 4.38$ K). In this case, the second term on the right-hand side in Eq. (16) vanishes despite the fact that $\chi_\|$ stands in the denominator, since under these conditions $\mathbf{M}_\| = \mathbf{0}$. The remaining constants in Eq. (16) (K, D, γ, and δ) are chosen in such a way that they are dimensionless.

Under the condition that $L^2 = \text{const}$ there are seven independent variables in the system: two angles—the polar angle θ and the azimuthal angle φ,—defining the direction $\mathbf{L}$, and the five components M_x, M_y, M_z, P_x, and P_y. The component P_z is assumed to be given and to a first approximation does not depend on the magnetic state.

Minimizing F (16) over the indicated variables gives the following possible orientational states (angles θ and φ) and their stability conditions.

The state "x" ($\mathbf{L} \| \mathbf{X}$, $\sin^2 \theta_x = 1$, $\sin \varphi_x = 0$) with energy

$$F_x = 0 \quad (17)$$

and magnetic symmetry $mm2$, stable for

$$k_3 > r_1, \quad k_2 > 0. \quad (18)$$

Here and below we use the abbreviated notation

$$k_2 = K_2 - D_{32}^2 \chi_\perp, \quad k_3 = K_3 - D_{23}^2 \chi_\perp,$$

$$r_1 = \delta_1^2 \kappa, \quad r_2 = \delta_2^2 \kappa.$$

In this state $\mathbf{M} = \mathbf{0}$ and $P_x = P_y = 0$.

The state "y" ($\mathbf{L} \| \mathbf{Y}$, $\sin^2 \theta_y = 1$, $\cos \varphi_y = 0$) with energy

$$F_y = (k_2/2)L^2 \quad (19)$$

and magnetic symmetry $m'm'2$, stable for

$$k_2 < 0, \quad k_3 - k_2 > r_2. \quad (20)$$

In this state $M_x = M_y = P_x = P_y = 0$ and $M_z = \chi_\perp D_{32} L$.

The state "z" ($\mathbf{L} \| \mathbf{Z}$, $\sin \theta_z = 0$) with energy

$$F_z = (k_3/2)L^2 \quad (21)$$

and magnetic symmetry $m'm2'$, stable for

$$k_3 + r_1 < 0, \quad k_2 - k_3 > r_2. \quad (22)$$

Here

$$M_x = M_z = 0, \quad M_y = \chi_\perp D_{23} L, \quad P_x = P_y = 0.$$

The state "xz" ($\mathbf{L} \| \mathbf{Y}$, $\sin \varphi_{xz} = 0$), where

$$\sin^2 \theta_{xz} = (k_3 + r_1)/2r_1, \quad (23)$$

with energy

$$F_{xz} = \frac{1}{2}(k_3 - r_1 \sin^4 \theta_{xz})L^2 \quad (24)$$

and magnetic symmetry m_y, stable for

$$-r_1 < k_3 < r_1,$$

$$r_1 k_2 > (r_1 - r_2)(k_3 - r_1). \quad (25)$$

Here

$$M_x = M_z = P_y = 0, \quad M_y = \chi_\perp D_{23} L \cos \theta_{xz},$$

$$P_x = \frac{1}{2}\kappa \delta_1 L \sin(2\theta_{xz}). \quad (26)$$

The state "yz" ($(\mathbf{L} \| \mathbf{X}$, $\sin \varphi_{yz} = 0$), where

$$\sin^2 \theta_{yz} = (k_3 - k_2 + r_1)/2r_2, \quad (27)$$

with energy

$$F_{yz} = \frac{1}{2}(k_3 - r_2 \sin^4 \theta_{yz})L^2 \quad (28)$$

and magnetic symmetry m'_x stable for

$$-r_2 < k_3 - k_2 < r_2,$$

$$k_2(r_1 + r_2) < (r_1 - r_2)(k_3 - r_2). \quad (29)$$

Here

$$M_x = P_x = 0,$$

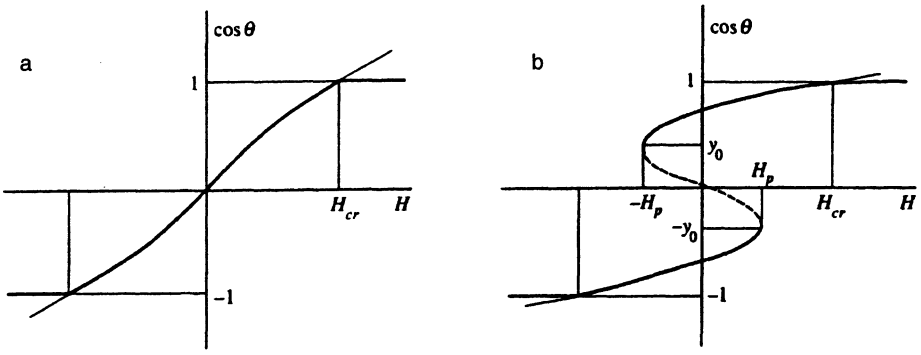

FIG. 3. Solutions of Eq. (38) for cos θ (schematically) for magnetization from the state "x" (a) and the state "xz" (b).

$$M_y=\chi_\perp D_{23}L\cos\theta_{yz},\quad M_z=\chi_\perp D_{32}L\sin\theta_{yz},$$

$$P_y=\frac{1}{2}\kappa\delta_2 L\sin^2\theta_{yz}. \tag{30}$$

According to Refs. 1 and 2, the state "x" corresponding to stability conditions (18) and energy (17), is realized in $KNiPO_4$. However, attention must be given to the state "xz" described by Eqs. (23)–(26). In fact, for this case there are two equivalent states with

$$\cos\theta_{xz}=\pm\left|\frac{r_1-k_3}{2r_1}\right|^{1/2}\equiv\pm y_1. \tag{31}$$

Let y_1 be a comparatively small quantity (≈ 0.1) and let the volumes of the domains corresponding to these two states (each with symmetry m_y) be roughly equal. The question arises, can such a system with $L_x\equiv L_{ax}\approx L$, $L_z=\pm Ly_1$, and $M_y=\pm\chi_\perp D_{23}Ly_1$ be perceived as the above-mentioned "cross" with $L_{ax}, L_{by}, L_{cz}\neq 0$, which, it would seem, corresponds to the neutron scattering experiment by Fisher *et al.*[1]

The point here is that it is not entirely clear how they obtained the transverse (to the x axis) components of the atomic moments: $\mu_y=\pm 0.06\ \mu_B$/atom and $\mu_z=\pm 0.21\ \mu_B$/atom (respectively, 2% and 7% of $\mu_x\approx\pm 3\ \mu_B$/atom). It is necessary to bear in mind that the total macrosymmetry of the domain structure under consideration, in which the domains transform one into the other via the operation m_x, coincides with the symmetry of the "x" state (and the "cross"), i.e., $mm2$. The values $M=P_x=P_y$ are also zero in both models.

Thus, what is taken to be the "x" structure (or "cross" structure) is quite possibly the "xz" structure with the indicated type of domains.

Let us now turn our attention to the existence in the "xz" and "yz" states of spontaneous polarizability (in the limit $\mathbf{H}\to\mathbf{0}$) of antiferromagnetic origin, as defined by expressions (26) and (30). Here, of course, we refer to the case in which the volumes of the domains, in contrast to the situation considered above, are not equal. It is convenient to call this effect antiferroelectric.

Note the lack of a type "xy" state (for $\mathbf{H}=\mathbf{0}$), analogous to the "xz" and "yz" states.

6. MAGNETIZATION CURVES

Further discussion of the experiment is impossible without studying the behavior of the system in an external magnetic field. Let us first consider the directions in which weak ferromagnetism (along the Y or Z axis) is possible, taking the "x" state ($\mathbf{L}\|\mathbf{X}$) as the initial state.

Then for $\mathbf{H}\|\mathbf{Z}$ we have $\cos\theta=0$ and

$$M_z=\chi_\perp(|D_{32}L\sin\varphi|+H_z),\quad P_x=P_y=0, \tag{32}$$

where

$$|\sin\varphi|=|D_{32}|\chi_\perp H/k_2L \tag{33}$$

for

$$H_z<H_{cr,z}=|k_2/D_{32}\chi_\perp|L \tag{34}$$

and $|\sin\varphi|=1$ for $H_z>H_{cr,z}$. In the region $0<H_z<H_{cr,z}$ we have $M_z=\tilde{\chi}_\perp H_z$, where

$$\tilde{\chi}_\perp=\chi_\perp(1+D_{32}^2\chi_\perp/k_2), \tag{35}$$

and for $H>H_{cr,z}$

$$M_z=M_{sz}+\chi_\perp H_z, \tag{36}$$

where $M_{sz}=\chi_\perp|D_{32}|L$ is the spontaneous magnetization along the Z axis, obtained by extrapolating M_z to $H_z=0$. Here $P_z=P+y=0$ (for arbitrary H_z).

Thus, for $\mathbf{H}\|\mathbf{Z}$ the field induces the "xy" state with symmetry 2_z transforming in the presence of the field $H_{cr,z}$ (34) to the "y" state with symmetry $m'm'2$.

Next, for $\mathbf{H}\|\mathbf{Y}$ we obtain $\sin\varphi=0$ and

$$M_y=\chi_\perp(D_{23}L\cos\theta+H_y),$$

$$P_x=\kappa(\delta_1 L\cos\theta+\gamma_1 M_y)\sin\theta, \tag{37}$$

where $\cos\theta\equiv y$ is determined by the equation

$$2r_1y^3+(k_3-r_1)y=D_{23}\chi_\perp H_y/L. \tag{38}$$

For definiteness, let $D_{23}>0$. In this case, the solution is suitable both for magnetization from the state "x" ($k_3>r_1$) and from the state "xz" ($k_3<r_1$). Rotation of the vector $\mathbf{L}$ in the XZ plane (symmetry m_y) ceases ($|\cos\theta|=1$, symmetry $m'm2'$) at the critical field

$$H_{cr,y}=(k_3+r_1)L/D_{23}\chi_\perp. \tag{39}$$

The curves of $\cos\theta$ as a function of H_y, which together with Eq. (37) define the magnetization curves, have the form

shown in Figs. 3a and b. for these two cases. The regions of stability are depicted by the solid curves, and the region of instability—by the dashed curve. As can be seen from Fig. 3b, hysteresis is possible in the case of magnetization from the state "xz". In the initial sample, let the domains with $\cos\theta>0$ and $\cos\theta<0$ be equal in size, so that for $H_y=0$ the total magnetization (37) is zero. Then for magnetization in fields $H_y>H_p$, where

$$H_p=\frac{L}{3}\sqrt{\frac{2(r_1-k_3)^3}{3r_1}}, \tag{40}$$

when

$$\cos\theta=y_0=\sqrt{\frac{r_1-k_3}{6r_1}},$$

a discontinuous remagnetization of the second domain takes place. As a result, when the field is removed, a residual magnetization arises, found by solving Eq. (38) for $H_y=0$, see Eq. (23) or (31). In this case

$$M_y=\chi_\perp LD_{23}\cos\theta_{xz}\equiv M_{sy}. \tag{41}$$

We emphasize once again that the indicated situation can arise when the initial stable state (for $\mathbf{H}=\mathbf{0}$) is the "xz" state. In this case, to obtain nonzero residual magnetization M_{sy} for $H_y=0$ it is not necessary to reach the critical field (39): $H_p<H_{cr,y}$. Simultaneously, a residual (spontaneous) polarization

$$P_x=\kappa L(\delta_1+\gamma_1\chi_\perp D_{23})\sin 2\theta. \tag{42}$$

should appear.

Note here that in the previous case ($\mathbf{H}\|\mathbf{Z}$) we considered only the solution corresponding to magnetization from the "x" state. The solution corresponding to the initial state being the "xz" state was not investigated. In the given case this would require a numerical treatment, which, not knowing the parameters used in the theory, is not advisable. Besides, as follows from Sec. 5, there are no other solutions, apart from (32), that would give $M_{sz}\neq 0$ in the limit $H_z\to 0$. This latter result has to do with the lack of a stable "xy" state (for $\mathbf{H}=\mathbf{0}$) mentioned at the end of the given section. For the same reason, the y-projection of μ is due not to a deflection of $\mathbf{L}$ in the XY plane (in contrast to the z-projection, which is due to a deflection of the vector $\mathbf{L}$ in the XZ plane), but to weak ferromagnetism (41) in the presence of the indicated domain structure, and, of course, there remains as before the possibility of non-collinearity associated with the admixture of the $\mathbf{L}_b\|\mathbf{Y}$ state with the $\mathbf{L}_a\|\mathbf{X}$ state.

For $\mathbf{H}\|\mathbf{X}$ for magnetization from the state "x" at first, for small fields, $M_x=0$ (or, more accurately, $M_x=\chi_\| H_x$), and then, with an increase in the field, a spin-flop transition to one of the states "y," "z," and "yz" takes place, depending on which of these transitions corresponds to the smaller critical field. After the transition, $M_x=\chi_\perp H_x$. It is important to note that for the first two transitions $P_x=P_y=0$, and after the transition to the "yz" state, a nonzero polarization P_y appears, as given by Eq. (30). (Do not forget the possible existence of antiferromagnetic domains with opposite signs of θ_{yz}!).

7. DISCUSSION OF RESULTS

This study shows that the observation of weak ferromagnetism in the oriented magnetic state $mm2$ (with $\mathbf{L}\|\mathbf{X}$) may be due not only to an orientational phase transition from this state during the magnetization process, but also (in any event for $\mathbf{H}\|\mathbf{Y}$) to the fact that in reality the initial state is the "xz" state with minor deviation of the vector $\mathbf{L}$ from the X axis. Then, taking the antiferromagnetic domain structure into account, this latter state, in its properties and even in its macrosymmetry, can to some extent imitate the "x" state, however, with the difference that for the "xz" state, in contrast to the "x" state, weak ferromagnetism prevails after destruction of the domain structure.

This study, dealing as it does with samples having a homogeneous magnetoelectric structure, does not provide a unique explanation of the detailed mechanism of the observed weak ferromagnetism. Additional experiments are required to refine the theory. Some suggestions are given below.

Above all, it would be desirable, to the extent possible, to get rid of inhomogeneities in the sample in order to work with a true single crystal. These inhomogeneities can be not only the reason for new unstable states, but should lead directly to the appearance of local magnetization. According to Table II (allowing for the fact that the spatial derivatives transform like the components of the vector $\mathbf{P}$), such an effect can give, for example, invariants of the form $(\partial P_z/\partial x)M_yL_{ax}$ or $(1+cP_z)M_y(\partial L_{ax}/\partial x)$ (where c is a constant), etc. Elastic deformations e_{ij} associated, for example, with mounting of the sample, etc., can also be a source of local magnetization. Such deformations generate magnetization associated with piezomagnetism:

$$M_i=\Pi_{ijk}\epsilon_{ijk}L_{ax}e_{jk},$$

where P_{ijk} is the piezomagnetic tensor and ε_{ijk} is the antisymmetric unit tensor (the Levi–Civita tensor).

But what especially complicates the description and interpretation of the experiment, in my opinion, is the presence of pyroelectric domains, which in fact are twinning phenomena. First of all, the constants γ in Eq. (16) (and after them the components of the tensor α_{ij}), as well as the constants δ, reckoned in the same coordinate system for the domains with value of P_z opposite in sign, have opposite signs (in addition to Ref. 2, also see Ref. 9). Therefore, in the presence of such domains the experiment does not give the true value of these constants (for a single-domain sample), only the value associated with the uncompensated total magnitude of P_z over the sample. Moreover, since the component P_z is itself invariant (see Table II), we need to add the same values to all the other terms in F (16), but with the additional factor P_z.

As a result, it turns out that experiments on multiple-domain (in P_z) samples, generally speaking, should give results dependent on the domain structure, for the weak ferromagnetism and the anisotropy constants and even the magnetic susceptibility. If the experiment confirms this situation (on samples grown in different regimes with subsequent inspection of the domain structure), then a quantitative description of the experiment becomes essentially impos-

sible, and the problem of growing samples that are single-domain in P_z becomes of paramount importance. It was for this reason that I did not determine the values of the parameters D_{23} and D_{32}, although from the experimental data[2] this, in truth, can be done.

We may mention some other things we may desire of the experimental measurements whose results would allow further development of the theory and also check some of the above desiderata.

1) If we are dealing with magnetic measurements, then it would be desirable above all to have the true magnetization curves (along the principal axes of the crystal **a**, **b**, and **c**). For large enough fields (tens of kOe?), do these curves approach the theoretical dependence

$$M(H)=M_s+\chi_\perp H, \tag{43}$$

where $M_s=0$ for $\mathbf{H}\|\mathbf{X}$ and $M_s\neq 0$ (and differ) for $\mathbf{H}\|\mathbf{Y}$ and $\mathbf{H}\|\mathbf{Y}$? What is the temperature dependence of M_s and χ?

2) Of course, direct neutron scattering experiments in a strong enough magnetic field would be of decisive significance as a check on the inferred occurrence of weakly ferromagnetic magnetization as a result of field-induced rotation of the vector **L** in the direction of the Z or Y axis. To the extent possible, the field strength should reach values above critical, (34) or (39), where departure from a dependence of the form (43) can serve as an indication of the attainment of such fields.

Neutron scattering in a magnetic field can probably also help us choose between two possible mechanisms behind the existence of y and z components of the atomic magnetic moments: as a consequence of domains with the magnitude of $\cos\theta$ determined by Eq. (31), or as a result of relativistic mixing of exchange magnetic structures due to the invariants (11).

3) Turning to magnetoelectric phenomena, here it seems to me that of greatest interest is the experimental detection of the effect which earlier in this paper I named the antiferroelectric effect, and which is due to the terms in F (16) containing the constants $\delta_{1,2}$. Note that it is only by way of these terms that the "xz" and "yz" states, which are stable at $H=0$, become feasible. And it is precisely in these states, whether spontaneous or caused by a field H, that the antiferroelectric effect should show up. This corresponds to Eq. (26) (or its more complete form (42), allowing for the usual $(ME)_H$ effect associated with weak ferromagnetism) for P_x in the "xz" state, or Eq. (30) for P_y in the "yz" state. For magnetization by a field $\mathbf{H}\|\mathbf{X}$, the occurrence of polarization $P_y\neq 0$ given by Eq. (30) would indicate that an orientational phase transition to the state "yz," and not the state "y" or "z," had occurred.

If these experimental investigations could be successfully undertaken, the mechanism of weak ferromagnetism in a situation in which, at first glance, it should be absent would be uniquely solved. The values of the constants χ, K, D, δ, and γ obtained in this way, that is, all or at least some of them, would make it possible to develop a quantitative theory of magnetoelectric phenomena in $KNiPO_4$, and would also make it possible to more completely describe how the orientational state (the direction of the vector **L**) varies as a function of the magnitude and direction of the magnetic field **H**. We could even see what influence the application of an external electric field **E** might have on this orientational state (where again antiferroelectric terms—the terms containing $\delta_{1,2}$ in the energy (16)—should appear).

Here it is fitting to note that due to my lack of knowledge of the values of the necessary parameters I did not make an effort to describe one more concrete result of Ref. 2. I have in mind the measurement of P_x as a function of θ_H reckoned from the Z axis, when **H** rotates in the YZ plane. The experiment is described by the formula $P_x\propto\sin\theta_H$. The calculations carried out in Sec. 6 for special cases ($\theta_H=0$ and $\theta_H=\pi/2$) agree with this dependence (see, respectively, Eqs. (32) and (37)). However, consideration of the more general case again requires numerical calculation, which would be unfruitful without a knowledge of specific values of the parameters.

In conclusion, I would again like to note the extraordinary relevance of further experimental study of the interesting object that the $KNiPO_4$ crystal has turned out to be, where weak ferromagnetism and piezomagnetism, and pyroelectricity and magnetoelectricity coexist.

ACKNOWLEDGMENTS

I would like to express my deep appreciation to my colleagues at the University of Geneva, M. Lujan and H. Schmid, who instigated the present work, for sending Refs. 1 and 2 prior to publication and for subsequent discussion. I am also very grateful to A. V. Kolchanov for his part in the calculations and to M. I. Kurkin for his helpful critiques.

This work was partially supported by the Russian Fund for Fundamental Research (Project No. 93-2-14026).

[1] F. Fisher, M. Lujan, F. Kubel, and H. Schmid, Ferroelectrics **162**, 37 (1994).
[2] M. Lujan, J.-P. Rivera, S. Kizhaev *et al.*, Ferroelectrics **161**, 77 (1994).
[3] S. A. Kizhaev and G. A. Smolenskiĭ, Fiz. Tverd. Tela **22**, 1573 (1980) [Sov. Phys. Solid State **22**, 922 (1980)].
[4] A. J. Freeman and H. Schmid (eds.), *Magnetoelectric Interaction Phenomena in Crystals*, Gordon and Breach, London (1975).
[5] Ferroelectrics **161–162**, *Proceedings of MEIPIC-2* (1994).
[6] E. A. Turov, Usp. Fiz. Nauk **164**, 325 (1994) [Phys.-Usp. **37**, p. (1994)].
[7] E. A. Turov, *Kinetic, Optical, and Acoustic Properties of Antiferromagnetics* [in Russian], Nauka, Moscow (1990).
[8] M. I. Kurkin and E. A. Turov, *NMR in Magnetically Ordered Materials and Its Applications* [in Russian], Nauka, Moscow (1990).
[9] D. V. Litvin, V. Janovec, and S. Y. Litvin, Ferroelectrics **162**, 275 (1994).

Translated by Paul F. Schippnick