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Can the magnetoelectric effect coexist with weak piezomagnetism and ferromagnetism?

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Contents

Abstract. A new approach to the study of antiferromagnetic phenomena in terms of the exchange magnetic structure code is examined. If the positions of the magnetic ions are known this code could play the same role in the symmetric description as the international symbol for the crystallographic space group plays in the description of the properties of nonmagnetic crystals.

1. Introduction

Antiferromagnetics are the largest class of magnetically ordered substances. At present the number of antiferromagnetic (AFM) compounds, alloys, etc. is counted in thousands. It can be said that "God loves antiferromagnetism". Nevertheless there are no modern monographs (or, at least, detailed reviews) devoted specifically to the properties of antiferromagnetics. In the new edition of the Physical Encyclopedia [1] the compilers of various articles on antiferromagnetism have to refer to publications up to 30 years old†.

In recent years we have witnessed a marked increase in the study of antiferromagnetics. This is due on the one hand to the fact that antiferromagnetism exists in oxides used as a basis for the synthesis of HTSC, and on the other hand to the fact that its most important applications lie in the field of multilayer magnetic systems ('large magnetoresistance', etc.), which are attracting wide interest at the moment.

The need to compile the present review became clear to me while I was preparing the contributions submitted to the Second International Conference on Magnetic Interaction Phenomena in Crystals (MEIPIC-2, Ascona, Switzerland, 13 – 18 September 1993) and during the conference itself. The proceedings will be published in 1994 in the journal *Ferroelectrics*. Unfortunately, this field of research includes many erroneous theoretical studies and many (apparently) incorrect assertions arising from the absence of a single language (i.e. of a universally adopted terminology).

Under these conditions it seems very desirable to formulate accurate crystal physical propositions which allow characteristic properties of antiferromagnetics (weak ferromagnetism, piezomagnetism, magnetoelectricity, and other properties due to the AFM order [2]) to be examined as simply as possible, as well as their interdependence and the possibility of their coexistence. The problem chosen as a title for this review is only a symbolic representation of problems of this type.

In the present discussion I shall analyse specific articles and name their authors, whom I hold in great respect. Antagonists will be identified as an abstract person: Dr N. Full references are given (unfortunately, rather uncritically) in a well known review [3] and in a more recent book [4].

In order not to appear to 'explain the inexplicable' I shall confine the discussion to colinear and weakly noncolinear magnetic structures, such as those produced by magnetoanisotropic and relativistic interactions. We shall also assume that the magnetic and the chemical unit cells coincide (which is usually a necessary condition for the appearance of these effects). We shall use the term *exchange*

†Of course, there is a new, small, book by the present writer [2], but it is not familiar to a wide circle of readers because it was produced by the Metal Physical Institute of the Urals Branch of the Russian Academy of Sciences (Ekaterinburg) and it has not been put on the market through the booksellers' network. Nevertheless interested readers can still order the book (cash on delivery) from the Metal Physics Institute.

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magnetic structure to define the mutual directions of the magnetic moments (induced by the magnetic interaction), and their direction (usually, in the case of antiferromagnetics, the direction of the antiferromagnetism vector $\boldsymbol{L}$) relative to the crystallographic axes will be called the magnetic state. Of course, this division of two concepts is not always legitimate, but it is justified in the situation discussed below, when the magnetoanisotropic interactions are small in comparison with the exchange interactions.

2. Magnetic and crystal chemical symmetries

Let us examine some of the symmetry aspects of the crystal physics of magnetically ordered (and, in particular, AFM) substances. To make the discussion specific we shall demonstrate the above statements for individual examples of AFM structures having tetragonal crystals with $P4_2/mnm\ (D_{4h}^{14})$ symmetry. These include the trirutiles (a group of compounds of the type of Fe_2TeO_6, Cr_2WO_6, V_2WO_5, etc.) [5]. The trirutile unit cell shown in Fig. 1 indicates only the four-fold position of the magnetic ions (Fe^{3+}, Cr^{3+}, etc.) in the coordinates

$$(4e)\colon 1(0,\ 0,\ z),\ \ 2(0,\ 0,\ 1-z),\ \ 3\left(\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2}+z\right),$$
$$4\left(\frac{1}{2},\ \frac{1}{2},\ \frac{1}{2}-z\right).$$

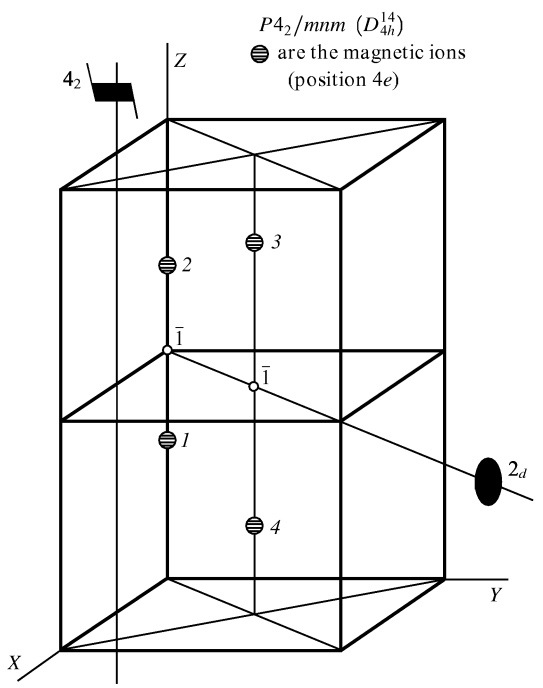
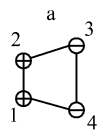
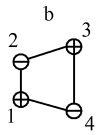
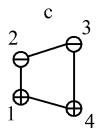
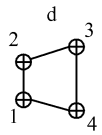


Figure 1. Unit cell of the trirutile.

Fig. 1 also shows the position in space of some symmetry elements of this group: a centre of symmetry ($\bar{1}$), a tetrad screw axis (4_2), and a diad axis of rotation (2_d).

This is a particularly convenient example to consider because different AFM structures and states can be realised in trirutiles. Furthermore putting $z = 0$ gives the double position $2a\,(1 \equiv 2,\ 3 \equiv 4)$, characteristic of another large group of crystals with AFM ordering and the same symmetry $P4_2/mnm$. These are the fluorides of the transition metals, which have the rutile structure.

Table 1.

Exchange magnetic structure	Code	Vectorial order parameter
	$\bar{1}(+)4_z(-)2_d(+)$	$L_1 = M_1 + M_2 - M_3 - M_4$
	$\bar{1}(-)4_z(+)2_d(-)$	$L_2 = M_1 - M_2 + M_3 - M_4$
	$\bar{1}(-)4_z(-)2_d(-)$	$L_3 = M_1 - M_2 - M_3 + M_4$
	$\bar{1}(+)4_z(+)2_d(+)$	$M = M_1 + M_2 + M_3 + M_4$

Three different colinear exchange magnetic structures available for trirutiles are shown in Table 1 (first column). The symbols $\oplus$ and $\ominus$ denote mutually antiparallel magnetic moments, irrespective of their orientation with respect to the crystallographic axes. By additionally determining these directions we fix the magnetic states for these structures. The magnetic states most often found in uniaxial crystals (trigonal, tetragonal, and hexagonal) are states of the 'easy axis' (EA) type, in which the magnetic moments are oriented along or against the principal axis of symmetry (i.e. the 4_2 axis in Fig. 1), or of the 'easy plane' (EP) type, in which the magnetic moments lie in a plane at right angles to this axis.

The true symmetry, which allows not only for the ordering in space of the atoms or ions of which the crystal is composed but also for periodic ordering of their magnetic moments, is described by the magnetic (Shubnikov) space groups. In other words, the magnetic symmetry is a parameter which combines the exchange magnetic structure with the magnetic state (though this combination is often simply called the magnetic structure).

However, the initial symmetry of the crystal chemical ordering of microparticles (i.e. the symmetry not allowing for their magnetic moments), described by the Fedorov space groups G_F, may be of even greater importance in the symmetry description of magnetically ordered crystals (magnetics). I refer not only to the fact that the magnetic state often becomes labile and easily changed: when planes of easy anisotropy are present in the magnetic substance a magnetic field of a fraction of an oersted is often sufficient to change the direction of the magnetic moments (i.e. the

magnetic state and the magnetic symmetry) while retaining the crystal symmetry.

In fact, if we wish to describe the behaviour of a magnetic in external magnetic fields, in orientational and (in general) structural magnetic phase transitions, and also its dynamics, we should start from the crystal chemical symmetry, which provides a background upon which all the phenomena listed above can take place. One should stress the fact that in this discussion the term crystal chemical symmetry refers to a Fedorov space group complemented by the time inversion, $R \equiv 1'(t \to -t)$. Thus, if the magnetic and the chemical cells coincide, we can use the contracted G_F' group, in which all the translations (by a whole period) are considered to be the same element as compared with G_F.

3. Energy invariants in the context of magnetic and crystal chemical symmetries

Two variants of the symmetry description of the properties of a magnetic material are generally used. The first consists in the invariant description of the material equations linking the observed macroscopic quantities, or of the material tensors describing this link. This approach directly establishes the possibility and the symmetry conditions for the existence of the effect of interest. The second variant, which is more compatible with the objects of the present study, is based on the symmetry description of the corresponding contribution to the energy (thermodynamic potential) responsible for the effect. But two alternative approaches are again possible: from the standpoint of magnetic or of crystal chemical symmetry.

We shall demonstrate the state of affairs by considering a magnetoelectric (ME) effect linear with respect to a field $\boldsymbol{E}$. If we are considering a specific exchange AFM structure and a specific magnetic state, corresponding to a fully determined (in general) magnetic symmetry space group, the existence of the ME effect is due to the presence in the thermodynamic potential of a term of the form [6]

$$F_{\mathrm{ME}} = -\hat{\alpha}\boldsymbol{HE} \equiv -\alpha_{ij}H_iE_j \,, \tag{1}$$

where $\hat{\alpha}$ is the ME susceptibility tensor. The form of $\hat{\alpha}$ is determined by the condition of invariance of Eqn (1) with respect to the transformations of the magnetic (i.e. the true) symmetry. In these circumstances it is sufficient, in accordance with the fundamental law of crystal physics (see, for example, §25 of Ref. [7]), to consider only the elements of the magnetic *point* group [5]. For example, for Fe_2TeO_6 this is $4/m'm'm'$, and the above invariance requirement gives only the following nonzero components of the tensor $\hat{\alpha}$:

$$\alpha_{11} = \alpha_{22} \equiv \alpha_\perp \,, \ \alpha_{33} \,. \tag{2}$$

We note that the symmetry element written with a prime is $g' = gR$. Since $4^2 = 2$, we can write $2/m' = \bar{1}R \equiv \bar{1}'$, i.e. we have an antisymmetry centre (ASC). This is the necessary (but not, in general, the sufficient!) condition for the existence of a linear ME effect in the centresymmetric (CS) antiferromagnetics (in the crystal chemical sense) to which the discussion to follow is applicable.

Thus, the information provided by the magnetic symmetry effectively explains the presence of nonzero components of the tensor $\hat{\alpha}$ and identifies these components, i.e. it gives the geometric conditions under which the effect can be observed under known concrete values of the exchange magnetic structure and of the magnetic state. In the present case, by using Eqns (1) and (2) and allowing for

$$M_i = -\frac{\partial F_{\mathrm{ME}}}{\partial H_i} \,, \quad P_i = -\frac{\partial F_{\mathrm{ME}}}{\partial E_i}$$

we obtain

$$M_x = \alpha_\perp E_x \,, \quad M_y = \alpha_\perp E_y \,, \quad M_z = \alpha_{33}E_z \,,$$
$$P_x = \alpha_\perp H_x \,, \quad P_y = \alpha_\perp H_y \,, \quad P_z = \alpha_{33}H_z \,. \tag{3}$$

(These linking equations can also be obtained by the first variant of the symmetric treatment mentioned above.)

However, if we are concerned with a wider circle of phenomena associated with the EM effect in an antiferromagnetic material with a given AFM exchange structure, beginning with the thermodynamics and magnetic transitions and ending with the dynamics (spectrum, wave propagation, etc.), we must start (as was mentioned above) with the crystal chemical symmetry. Under these conditions the ME interaction is most effectively expressed as an expansion over all the dynamic variables which tend to perturb this symmetry. In our case, in addition to the local magnetisation $\boldsymbol{M} = \boldsymbol{M}_1 + \boldsymbol{M}_2$ and the polarisability $\boldsymbol{P}$, this will include a vectorial AFM order parameter $\boldsymbol{L} = \boldsymbol{M}_1 - \boldsymbol{M}_2$, and if allowance is made for the elastic subsystem it will also include the deformation tensor $e_{ij} = \frac{1}{2}(\partial u_i/\partial x_j + \partial u_j/\partial x_i)$, where $\boldsymbol{u}$ is a displacement vector. Here the vectors $\boldsymbol{M}$ and $\boldsymbol{L}$ are expressed in the model of two magnetic sublattices. However, the conclusions outlined below will apply also to the great majority of sublattices with colinear or slightly noncolinear magnetisations.

To express the energy densities responsible for the linear ME effect Eqn (1) must be replaced by an expression of the following form:

$$F_{\mathrm{ME}} = \gamma_{ijk}L_iM_jP_k \,. \tag{4}$$

We should again underline the fact that since all the 'perturbers' of the crystal chemical symmetry ($\boldsymbol{L}$, $\boldsymbol{M}$, and $\boldsymbol{P}$) appear explicitly in Eqn (4) the form of the tensor $\hat{\gamma}$ should be determined from the requirement of invariance of (4) relative to transformations of the crystal chemical symmetry.

However, we now find a very important difference from the previous case. From the standpoint of the magnetic symmetry the invariant of (1) could be determined simply from the elements of the point group, whereas from the standpoint of the crystal chemical symmetry allowance for the space character of this symmetry is needed to determine the invariants of (4). In practice, without going into the details of symmetry theory, this can be ascribed to the dependence of the transformation properties of the vector $\boldsymbol{L}$, which reflects the sublattice structure of the antiferromagnetic, upon the distribution in space of the symmetry elements relatively to the magnetic atoms (or ions) which compose the magnetic sublattices.† In the colinear AFM structures (with which we are not concerned) if all the magnetic sites belong to the same crystallographic position (as in the trirutiles, position 4e) we have two possibilities: either the symmetry element $g_s \equiv g(+)$ of the space group G_F' interconverts the magnetic sites with the same magnetic sublattice (or in a different sublattice, but with equally oriented magnetisations), or $g_s \equiv g(-)$ correlates the

†A more detailed definition of the magnetic sublattice concept is given in §2.2 of Ref. [8].

magnetic moments of sublattices with oppositely oriented magnetisations. In the first case the element g_s has exactly the same effect on $\boldsymbol{L}$ as the corresponding element of the point group g (even when g_s is a screw axis or a glide plane), and in the second case $\boldsymbol{L}$ additionally changes sign, so that

$$g(\pm)\boldsymbol{L} = \pm g\boldsymbol{L} . \tag{5}$$

For the other vectors ($\boldsymbol{M}$ and $\boldsymbol{P}$) the action of g(+) and g(−) does not differ from the same action for the elements of the point group:

$$g(\pm)\boldsymbol{M} = g\boldsymbol{M} \quad \text{and} \quad g(\pm)\boldsymbol{P} = g\boldsymbol{P} .$$

In the author's monograph [9] in which these concepts were first formulated, and in some later books [2, 8, 10], the symbol $g^{\pm}$ was used in place of g(±), and the elements were called even (+) and odd (−) respectively. It is not clear whether this terminology is successful: the only indisputable fact is that all the crystal chemical symmetry elements should be classified into two types (in the above sense) according to their distribution in space relative to the magnetic sublattices.

4. Code of the exchange magnetic structure

Since we are discussing antiferomagnetism in a system of magnetic sites belonging to the same crystallographic position there will be at least one among the elements of the group G_F' which relates any two arbitrarily chosen sites of this position in the unit cell. (It should not be forgotten that sites at a mutual distance equal to the translation period of the lattice are effectively the same site.) For example, sites 1 and 2 (or 3 and 4) in Fig. 1 are related by the centre of symmetry $\bar{1}$ and by the axis 2_d, whereas the site 4 is obtained from 1 by the consecutive action of 4_2 and $\bar{1}$, i.e. by the transformation equal to the product of these elements. It follows that in this antiferromagnetic at least one odd element g(−) should be found among other independent elements of the group G_F' (group generators).

In order to underline the fact that g(+) and g(−) are the same element of crystal chemical symmetry depending on its position in space we shall in what follows apply the term even or odd with respect to g to the magnetic structure itself.

If the elements G_F' include a space inversion $\bar{1}$ (as in the CS crystals with which we are concerned) it is important to specify whether the magnetic structure becomes even or odd after ordering. Thus, in Table 1 the structure (a) corresponds to $\bar{1}(+)$, and the structures (b) and (c) to $\bar{1}(-)$. From the point of view of the magnetic symmetry in the magnetic group in the first case we have, as in the crystal chemical case, a centre of symmetry $\bar{1}$, and in the second case we have a centre of antisymmetry $\bar{1}'$ (CS and CAS antiferromagnetics).

It should be noted that $\bar{1}(-)$ cannot coincide with $\bar{1}'$, since $\bar{1}(-)$ is an element of crystal chemical symmetry (the index '−' bears only the essential information on its distribution in space), and $\bar{1}'$ is a magnetic symmetry element. Even with respect to their action on the vectors $\boldsymbol{L}$ and $\boldsymbol{M}$ the two elements are markedly different:

$$\bar{1}(-)\boldsymbol{M} = \boldsymbol{M} , \quad \bar{1}(-)\boldsymbol{L} = -\boldsymbol{L} ,$$
$$\bar{1}'\boldsymbol{M} = -\boldsymbol{M} , \quad \bar{1}'\boldsymbol{L} = \boldsymbol{L} . \tag{7}$$

Furthermore, in order to characterise the exchange magnetic structure fully it is sufficient to establish its parity with respect to other elements taken as group generators. This is done in the second column of Table 1. If necessary, the parity of the structure can be obtained against all the other elements of the group by using the rules

$$g_1(\pm)\,g_2(\pm) = g_3(+) , \quad g_1(\pm)\,g_2(\mp) = g_3(-) .$$

As a result, by writing the group generators G_F' with an indication of their parity we obtain a notation which can be called the code of the exchange magnetic structure.† In Table 1 we show the codes of all four possible colinear structures (three AFM and one ferromagnetic) in the crystal of interest.

Generally speaking, the order in which the discussion is carried out differs from the example given above. First of all, all possible combinations of parities for the elements $\bar{1}$, 4_2, and 2_d are selected (by inspection) from Fig. 1. It must be remembered that the parities of the elements $\bar{1}$ and 2_d can only be equal, because in this case they express identical rearrangements of the sites in the position of interest (4*e*). Only the four combinations of parities which appear in the codes in the second column of Table 1 are obtained in this way.

We should stress once again that the spatial character of the symmetry elements included in a code is defined by indicating their parity: once this is done there is no longer any need to state whether simple or screw axes are involved, and whether the planes are mirror or glide planes. They act as symmetry elements of the point type, additionally accounting for (5). The subscript defines the direction of the axis of symmetry (or of the normal to the plane of symmetry).

5. Code and properties

The information contained in the code is fully sufficient for a symmetry treatment of a wide range of properties in the thermodynamics, kinetics, optics, acoustooptics, etc. of antiferromagnetics [2]. If the code is given, the type of exchange magnetic structure can be obtained immediately from it: this requires treating as parallel the magnetic moments related by even symmetry elements and as antiparallel those related by odd elements. Thus, the structures shown in Table 1 (first column) can be obtained independently from their codes (second column). Furthermore, this information is necessary and sufficient for writing the corresponding invariants in the thermodynamic (terms in the thermodynamic potential), antiferromagnetic (i.e. depending on the vector $\boldsymbol{L}$) terms in the electric resistance or the dielectric permittivity, or corresponding elastic moduli in kinetics, optics, or acoustics [2]. However, if Dr N, when writing out the thermodynamic potential required for his calculation, were to indicate each time the code of the AFM (exchange) structure being considered it would be a simple matter for each reader to satisfy himself of the invariance of this potential. Thus, if we are

†The number of generators is usually not more than three, but for centred lattices the centring translations (which do not affect the nominal size of the unit cell) may also appear. Under AFM ordering they may be converted into antitranslations, as in La_2CuO_4, for example (see appendix 2 of Ref. [2]).

studying the ME effect due to invariants of type (4) it is clear that these invariants are possible only in the ASC of antiferromagnetics, for example in the structures (b) and (c) of Table 1. According to (7) applying $\bar{1}(-)$ to these structures changes the sign of the vector $\boldsymbol{L}(\equiv \boldsymbol{L}_b$ or $\boldsymbol{L}_c)$, but it also changes the sign of $\boldsymbol{P}$ as a polar vector†. (Throughout this article $\boldsymbol{L}_{a,b,c} \equiv \boldsymbol{L}_{1,2,3}$.),

At the same time there is no ME interaction of type (4) in the CS antiferromagnetics $[(\bar{1} \equiv \bar{1}(+)]$, for example, in the structure (a) in Table 1. The vectors $\boldsymbol{L} \equiv \boldsymbol{L}_a$ and $\boldsymbol{M}$ do not vary, and the vector $\boldsymbol{P}$ changes sign under the influence of $\bar{1}(+)$. Then in antiferromagnetics of this type (which include the fluorides mentioned above) we find a weak ferromagnetism (WF) and piezomagnetism (PM), described respectively by the invariants

$$F_{\mathrm{WF}} = D_{ij} L_i M_j \tag{8}$$

and

$$F_{\mathrm{PM}} = \Pi_{ijkn} L_i M_j e_{kn} \ . \tag{9}$$

[In this case both vectors as well as the tensor e_{kn} are invariant with respect to $\bar{1}(+)$.]

Thus we seem to have answered the question formulated in the title of this paper: the ME effect exists in the CAS antiferromagnetics, whereas the WF and PM effects exist in the CS antiferromagnets, so that the first and the second effect are mutually exclusive.

However, this conclusion calls for some important stipulations. First, all these remarks relate to centrosymmetric crystal groups. Otherwise neither $\bar{1}(+)$ nor $\bar{1}(-)$ will appear after the magnetic ordering.

Second, we had been considering the antiferromagnetism in a system of magnetic sites belonging to a single crystallographic position, as in the case of the trirutiles quoted above as an example (see Fig. 1).

A different situation arises when the magnetic ions are arranged in two (or more) different crystallographic positions (no symmetry transformations able to convert the system from one position into another should be available to the system). Under these conditions in one position the magnetic moments can become ordered so that $\bar{1} \equiv \bar{1}(+)$, and in the other position for $\bar{1} \equiv \bar{1}(-)$. In this case antiferromagnetism is compatible with WF and PM in the first subsystem, and with the ME effect in the second. In this way the two can coexist. A real example is provided by the rare-earth orthoferrites and orthochromites, in which the iron (or chromium) ions are ordered centrosymmetrically while their magnetic moments can be distributed centro-antisymmetrically [2]. But this situation is trivial, and a theoretically more interesting case of 'coexistence' is provided by the superposition of two (or more) structures in a system of magnetic sites from a single position.

6. Structure superposition caused by the electric field (polarisability)

Let us go back to the third column of Table 1, which lists the corresponding antiferromagnetism vectors (or ferromagnetism vectors, for structure f). So far we have effectively assumed that one of the three (a, b, c) AFM structures is realised: the structure for which the exchange parameter J_1, J_2, or J_3 in the exchange energy

$$F_{\mathrm{ex}} = \tfrac{1}{2} J_1 |\boldsymbol{L}_a|^2 + \tfrac{1}{2} J_2 |\boldsymbol{L}_b|^2 + \tfrac{1}{2} J_3 |\boldsymbol{L}_c|^2 + \tfrac{1}{2} J_4 |\boldsymbol{M}|^2 \tag{10}$$

become negative upon lowering the temperature (all the $J_n > 0$ in the paramagnetic region). It was assumed, effectively, that the other two $\boldsymbol{L}_i$ fall to zero and that the problem reduces to its two-sublattice modifications. For example, for $L_a \neq 0$, $L_b = L_c = 0$ we find that

$$\boldsymbol{M}_1 = \boldsymbol{M}_2 \equiv \tfrac{1}{2}\boldsymbol{M}_{\mathrm{I}} \ , \quad \boldsymbol{M}_3 = \boldsymbol{M}_4 \equiv \tfrac{1}{2}\boldsymbol{M}_{\mathrm{II}} \ ,$$
$$\boldsymbol{L}_a \equiv \boldsymbol{L} = \boldsymbol{M}_{\mathrm{I}} - \boldsymbol{M}_{\mathrm{II}} \quad \text{and} \quad \boldsymbol{M} = \boldsymbol{M}_{\mathrm{I}} + \boldsymbol{M}_{\mathrm{II}} \ .$$

However, allowing for the relativistic (magnetically anisotropic) interaction shows that the vectors $\boldsymbol{L}_n (n = 1, 2, 3)$ and $\boldsymbol{M}$ are no longer mutually independent, and that the appearance of one of them (as a result of the exchange interaction) during the phase transition can spontaneously introduce a small impurity of the other to satisfy the symmetry requirements. Generally speaking the WF induced by the interaction (8) is at the same time a manifestation of the admixture of one structure ($\boldsymbol{M}$) with another ($\boldsymbol{L} \equiv \boldsymbol{L}_a$). For the AFM compounds the structure $(a)\bar{1}(+)4_z(-)2_d(+)$ the expression (8) takes the specific form

$$D_{12}(L_{ax} M_y + L_{ay} M_x) \ , \tag{11}$$

which also accounts for the appearance of WF for this structure.

The fact that both the structures $(a)(\boldsymbol{L}_a)$ and $(f)(\boldsymbol{M})$ are odd with respect to $\bar{1}$ has a strong relevance upon the existence of invariants of the type of (8) [or (11)]. By making use of their codes (given in Table 1) the reader can easily confirm whether a mixed code of the form

$$L_{bx} L_{cy} + L_{by} L_{cx} \tag{12}$$

can exist in these systems. In this calculation it should be remembered that the vectors $\boldsymbol{L}_b$ and $\boldsymbol{L}_c$ are interconverted in accordance with the code of their structure.

Invariants of the type of (12), responsible for the addition (relativistically small, in our case) of one AFM structure to another, give a resulting structure of the 'cross' type. (These structures and the NMR studies which have been reported on them are discussed in detail in §3.8 of Ref. [8].)

It should also be stressed that mixing of the structures can also occur as a result of antiferromagnetically elastic invariants of the type

$$L_{bi} L_{cj} e_{kn} \ ,$$

whose role has not yet been investigated as far as the writer knows. The effect is to some extent analogous to the piezomagnetic interaction (9), the only exception being that here two AFM structures of identical parity with respect to $\bar{1}$ are mixed instead of $\boldsymbol{L}$ and $\boldsymbol{M}$.

However, we are at present interested in the mixing of CS structures $[\bar{1} \equiv \bar{1}(+)]$ with CAS structures $[\bar{1} \equiv \bar{1}(-)]$. A direct link between them could be given by invariants of the type $c_{ij} L_{ai} L_{bj}$, but for reasons which are now well understood these invariants do not exist [as can be shown by using the expression (5) in $\bar{1}$]. Then the application of an electric field $\boldsymbol{E}$ and/or the presence of a spontaneous

†The explicit form of the invariants (4) for rhombohedral and for tetragonal crystals with respect to other symmetry elements in the code is given in Refs [11–14].

polarisability $\boldsymbol{P}$ for the vectors $\boldsymbol{L}_a$ and $\boldsymbol{L}_b$ produce the invariants

$$f_1(L_{ax}L_{by}+L_{ay}L_{bx})P_z+f_2(L_{ax}P_y+L_{ay}P_x)L_{bz} +f_3(L_{bx}P_y+L_{by}P_x)L_{az}\ . \tag{13}$$

Thus if we have, for example, an AFM structure with $\boldsymbol{L}_a \neq 0$ [for $J_1 < 0$ in (10)], which allows WF, a vector $\boldsymbol{L}_b \neq 0$ is induced by an interaction of the form of (13), i.e. we observe an additional structure displaying the ME effect.

In order to make the problem more precise we should note that since the induced vector $\boldsymbol{L}_b \sim P\boldsymbol{L}_a$ the replacement of $\boldsymbol{L}$ by $\boldsymbol{L}_b$ in (4) gives an expression proportional to P^2, i.e. this ME effect is quadratic with respect to P rather than linear. Thus we have identified one possible mechanism of this latter effect.

In a similar way we can identify from $\boldsymbol{L}_a$ and $\boldsymbol{L}_c$ the variants associated with $\boldsymbol{P}$. Although the structure corresponding to $\boldsymbol{L}_c$ differs from that corresponding to $\boldsymbol{L}_b$ only by the parity of the 4_z axis (see Table 1) these invariants differ very markedly from (13). We shall not list them all, but only refer to the one responsible for this difference in principle:

$$fP_z(\boldsymbol{L}_a\cdot\boldsymbol{L}_c)\ . \tag{14}$$

This is a nonrelativistic invariant, given as the exchange interaction induced by the polarisation $\boldsymbol{P}$ (electric field $\boldsymbol{E}$), which must be added to the exchange energy (10) (quadratic in $\boldsymbol{L}_n$). If this interaction is large enough, which can be established either experimentally or from the microscopic theory, it should manifest itself in the appropriate magnetoelectric properties and also in all the other physical properties of an antiferromagnetic: its kinetics, its optics, its acoustics, etc.

I have not seen any publications in which allowance is made for these interactions in one-position AFM structures induced by an electric field $\boldsymbol{E}$ (or by a polarisability $\boldsymbol{P}$): neither of the magnetically anisotropic type (13) nor of the exchange type (14)†. Because this paper appears under the heading "Methodological Notes" I shall not discuss the physical consequences of applying this approach. This is the object of a special investigation. The topic of this section emerged during the writing of the paper, offering new opportunities of demonstrating the usefulness of this approach by using the parities of the AFM structure (or the symmetry of the elements indicated in the code).

7. About noninvariant 'invariants'

And now I shall demonstrate in the present section the depth of misunderstanding reached in the forgetting by Dr N of the basic propositions of crystal physics which were mentioned above. I do not mean to rely on the concrete approach (with parity structures etc.) which is used above, but I do rely on the basic propositions themselves, which were first formulated almost 35 years ago in Dzyaloshinskii's earlier papers [16–18]. Dr N must be either so old that he has forgotten them or so young that he has not yet read them. We shall once again briefly summarise these propositions.

(1) Invariant expressions for the energy, material equations (linking equations), and others, presented as an expansion over the dynamic variables which are known to perturb the crystal chemical symmetry ($\boldsymbol{L}$, $\boldsymbol{M}$, $\boldsymbol{P}$, e_{ij}, etc.) i.e. the parameters identified from the requirements of invariance of this crystal chemical (spatial) symmetry.

(2) The essential feature of the system is that the same elements of symmetry when in different positions in space relative to the magnetic sites (the magnetic sublattice) may lead to entirely different (and even mutually exclusive) properties.

This is specially true of the centre of symmetry, if such a centre is present in the crystal chemical group, and divides all the one-position antiferromagnetics into two principally different groups: centrosymmetric $[\bar{1} \equiv \bar{1}(+)]$ and centro-antisymmetric $[\bar{1} \equiv \bar{1}(-)]$. As was pointed out in Section 5 WF and PM are possible for the former, and the linear ME effect is impossible; whereas for the latter the linear ME effect is possible and the WF and PM are excluded.

This description of the exchange AFM structure with the help of a code containing all the information required for a symmetric description of the properties of an antiferromagnetic offers only a moderately helpful formalisation of the above statements. If the positions of the magnetic sites are known, the form of the exchange magnetic structure can be calculated from the code, producing all the invariants needed to describe the properties of the ferromagnetic under study.

All these spatial considerations of the exchange AFM structure are so elementary as to raise doubts in the writer's mind of the wisdom of publishing it. However, there is no alternative but to go ahead, because Dr N's papers are published and they are exerting a confusing influence on the work of experimenters and, to some extent, on the work of some theoreticians. Their results and conclusions are being constantly quoted even in the most recent publications. Someone should take upon himself the thankless task of attempting to evaluate them.

First of all, let us look again at the invariants which happen not to be invariant.

(1) In many reports the thermodynamic potential for an antiferromagnetic with a CS crystal chemical structure described by a single vector $\boldsymbol{L}$ is described simultaneously by singe invariants of the type (4), responsible for the ME effect, and invariants of the type (8) and (9), responsible for WF and PM respectively. (Similar attempts were made at the recent MEIPIC-2 Conference.) However, as was pointed out above, the first and the second attempts were mutually exclusive.

(2) We can expect, in CS crystals in both cases of $\bar{1}(+)$ and $\bar{1}(-)$, that invariants of the following form cannot exist, though some are found in Dr N's publications:

$$P_iL_jL_k\ . \tag{15}$$

(3) In discussions of the ME properties of antiferromagnetics, when $\bar{1} \equiv \bar{1}(-)$, 'simplified' or 'general' invariants of type (4) can be written: for example

$$\boldsymbol{P}(\boldsymbol{M}_1\times\boldsymbol{M}_2) \equiv \tfrac{1}{2}\boldsymbol{P}(\boldsymbol{L}\times\boldsymbol{M})\ , \tag{16}$$

or

$$P_z(\boldsymbol{M}_1\times\boldsymbol{M}_2)_z \equiv \tfrac{1}{2}P_z(\boldsymbol{L}\times\boldsymbol{M})_z\ . \tag{17}$$

†For the case in which the interacting vectors $\boldsymbol{L}_n$ belong to different crystalline positions [as in the orthoferrites, discussed at the end of Section (5)] invariants of the type (13) and (14) are discussed by Stefanovskii and Yablonskii [15].

These would seem to be consistent with any symmetry in the case of (16) and with all uniaxial crystals in the case of (17).

And, of course, with respect to $\bar{1}(-)$ they are invariant, so that all is in order for the triclinic group $\bar{1}$. The invariance is retained also for the monoclinic group $2/m$ if $2 \equiv 2_z \equiv 2(+)$, and $m \equiv m_z \equiv m(-)$. But for the reciprocal parities $2_z \equiv 2(-)$ and $m_z \equiv m(+)$ the invariances (16) and (17) are perturbed with respect to both these elements. However, these elements cannot have identical parities because their product is $2_z m_z = \bar{1}(-)$. And, in general, for any given plane of symmetry $m(+)$ or any axis of symmetry $N(-)$ invariants of the type (16) or (17) do not exist. They can be formed only when all the other elements in the code complementary to $\bar{1}(-)$ are either even axes or odd planes of symmetry. In any case, the expressions (16) and (17) are not general invariants. There are no such invariants even for the best known ME, which has the structure $\bar{1}(-)3_z(+)2_x(-)$. And generally speaking there are no officially reported antiferromagnetics which comply with the conditions mentioned above for the existence of the invariants (16) and (17).

8. Is there an exchange-increased band in the spin wave spectrum due to the ME interaction?

The assertion by Dr N that in ME antiferromagnetics there exits an ME band for magnons (MEIs), increased by exchange and completely analogous to a magnetoelastic (MU) band, is widely quoted in publications [3, 4].

Let us first consider the analogy aspects. The magnetoelastic band exists by virtue of the fact that the elastic (ionic) subsystem is slower than the spin subsystem. Thus the oscillations of the spins (vectors $\boldsymbol{L}$ and $\boldsymbol{M}$) are controlled by the 'frozen lattice' model [19], according to which the 'frozen' deformations e^0_{kn} generate an effective anisotropy field through an MU energy of the type

$$B_{ijkn} L_i L_j e^0_{kn}$$

for the vector $\boldsymbol{L}$ (and it must be $\boldsymbol{L}$!). The latter determines the MU band, increased by exchange, because the contribution to the frequency of uniform magnons (wave vector $\boldsymbol{k} = \boldsymbol{0}$) after magnetic ordering all lie in two different groups in the form $\omega_0 \propto (2H_{\mathrm{E}} H_{\mathrm{MU}})^{1/2}$, where H_{E} is the exchange field. It is important to note that the MU band is observed even in a fully isotropic antiferromagnetic.

For the ME interaction the situation is just the reverse. The polarisability $\boldsymbol{P}$ (the optical part of the frequency region) is a faster subsystem than the spin subsystem, so that at antiferromagnetic resonance frequencies corresponding to the magnon bands, $\boldsymbol{P}$ follows the oscillations of the spins in a quasiequilibrium way. And if $\boldsymbol{P}$ were not retained by the anisotropy (for ferroelectrics) or by the electric field there would be (in general) no magnetoelectric effect of the band with the magnons. Thus, everything is just the other way round even from the point of view of analogy.

Let us now examine the linear magnetoelectric effect of the type of (4). In the presence of a constant polarisability $\boldsymbol{P}$ (spontaneous, or induced by the external field E) we can effectively include it into the constant $\hat{\gamma}$ and produce an expression of the type of (8), characteristic of WF. And, though this interaction produces a contribution to the magnon band [9], the magnetisation $\boldsymbol{M}$ remains inversely proportional to the change in the exchange field H_{E}, whether monitored in static or in dynamic experiments.

A different state of affairs is found for the interaction in quadratic (with respect to $\boldsymbol{P}$ or $\boldsymbol{E}$) magnetoelectric effects of the type

$$P_i P_j L_k L_n \ .$$

For this the constant vector $\boldsymbol{P}$ (once again, spontaneous, or induced by the field $\boldsymbol{E}$) generates an effective anisotropy for $\boldsymbol{L}$, and this can lead to an ME band that is actually increased by exchange interaction.

Lastly, if the crystal and its crystal chemical group do not contain a CS even after separation of the 'disturbing factors' $\boldsymbol{L}$, $\boldsymbol{M}$, and $\boldsymbol{P}$, invariants of the type (15) can give an exchange-increased magnon band, linear in $\boldsymbol{P}$ (or $\boldsymbol{E}$) and having an ME origin.

9. Conclusions

This paper offers a critique and a discussion of some inconsistent assertions and conclusions in our field of physics (especially with relation to ME crystals). It is undeniably biased, in the present troubled atmosphere, in favour of the methodological approach to the discussion of AFM phenomena proposed above in terms of the exchange magnetic structure code. When the position of the magnetic ions is known, this code for the exchange AFM can play the same role in the symmetrical description of these phenomena as does the international symbol for the crystallographic space group (again with a statement of the crystallographic position). Furthermore, a well defined terminology associated with this code allows scientists not sufficiently aware of the apparatus of abstract group theory to find a common language. For the same reason the writer did not use the representational analysis methods, and started from simple notions of symmetry transformations, invariance, etc.

It should be emphasised that the main object of the article was to deal with the electromagnetic thermodynamics of antiferromagnetics. But one can use the same approach to the kinetics, optics, acoustics, etc [2] in conjunction with the AFM structure code to obtain the same benefits. This makes it possible to formalise simply and easily (up to automation if required) the description of the appropriate properties. The same is true of the symmetrical description of the frequency spectrum of the NMR frequencies in antiferromagnetics [8].

Remark. Readers interested in the effect of the induction by an electric field of the exchange interaction of type (14) between the antiferromagnetism vectors $\boldsymbol{L}_a$ and $\boldsymbol{L}_c$ (even and odd respectively) should note that the effect is seen also in rhombohedral crystals with an $R3c(D^{16}_{3d})$ symmetry. The magnetic structures $(a)\bar{1}(+)3_z(+)2_x(-)(\alpha\text{-}Fe_2O_3)$ and $(c)\bar{1}(-)3_z(+)2_x(-)(Cr_2O_3)$ (see p. 13 of Ref. [2]) can exist for them. An interaction of the type (14) should take place between the appropriate vectors $\boldsymbol{L}_a$ and $\boldsymbol{L}_c$.

In conclusion we note that the colinearity of the AFM exchange structures proposed in this review is due to the fact that in our case all the J_i constants are different, and only one of them changes sign upon going through the NeOtel point. The difference in J_i is attributed to the absence in group G'_{F} of elements capable of converting into each

other different $\boldsymbol{L}_i$. If such elelments existed (as is the case, for example, in neodymium cuprate [21]) the corresponding J_i constants would be equal, possibly leading to an exchange superposition of different $\boldsymbol{L}_i$, capable of giving an exchange non-colinear AFM structure [21].

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