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Mechanism Leading to Ferroelectricity Induced in Centrosymmetric Crystals by Antiferromagnetic Transitions

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The appearance of ferroelectricity in conjunction with a paramagnetic-to-antiferromagnetic transition in centrosymmetric crystals is considered. Ferroelectricity is forbidden in centrosymmetric crystals. As a result of a magnetic transition such crystals may lose their center of symmetry. Hence, ferroelectricity, which is forbidden in the paramagnetic phase, may appear in the magnetically ordered one. To illustrate this effect from a symmetry point of view, an antiferromagnetic transition in a structure belonging to the space group *Pmma* is discussed in detail. An estimation of the ferroelectric moment in a model crystal with some "reasonably real" properties yields a moment of 10^{-8} C/cm^2. It is also shown that a discontinuity in the dielectric constant may occur at the transition point, due to the ferroelectric moment. This discontinuous change is expected to be $\Delta\epsilon/\epsilon \approx 10^{-6}$.

I. INTRODUCTION

The reduction of symmetry which accompanies a magnetic transition results in the appearance of effects which vanish in the paramagnetic phase. Such effects may be classified, according to Birss,[1] as "permissible" and "forbidden". Permissible effects are described by tensors which are invariant under time reversal while forbidden effects are described by tensors which change sign under this operation. Piezoelectricity, ferroelectricity, and magnetic susceptibility are examples of the first kind; Faraday effect, piezomagnetism, and magnetoelectricity are examples of the second kind. In the present paper we consider effects of the first (permissible) type. In particular, we are interested in centrosymmetric crystals which lose the inversion during a magnetic transition while retaining the time reversal in the point symmetry. In such cases the appearance of ferroelectricity and piezoelectricity may be expected.[2] Some compounds which exhibit magnetic transition of this kind are listed in Table I.[3-5] These compounds have the point symmetry $mmm1'$ in the paramagnetic phase. They undergo an antiferromagnetic transition which doubles the unit cell leading to a noncentrosymmetric point group. It is, therefore, expected that ferroelectricity and piezoelectricity will be induced by the magnetic transition in these compounds.

II. SYMMETRY CONSIDERATIONS

In order to gain some insight into transitions of the type discussed above from a microscopic point of view, we consider a centrosymmetric crystal having the space symmetry $Pmma(D_{2h}^5)$. Unlike the experimental examples (Table I), which have four or more magnetic ions per unit cell, the crystal considered subsequently will have only two magnetic ions at the sites $(2a)$ [6]:

$$(1)\ 000, \qquad (2)\ \tfrac{1}{2}00.$$

There are two main reasons for which we choose to consider this structure: (a) It is simple from the symmetry point of view. (b) The ferroelectric moment induced by a magnetic transition is easy to estimate.

As in the experimental examples mentioned above we consider an antiferromagnetic transition which doubles the unit cell, say in the x direction, $[\mathbf{k}=(\frac{1}{2},0,0)]$. The resulting magnetic cell consists of two chemical cells. The equilibrium spin structure in the magnetically ordered phase resulting from a second-order phase transition belongs to a basis of an irreducible representation of the paramagnetic group.[7] There are two bidimensional irreducible representations of this group associated with $\mathbf{k}=(\frac{1}{2},0,0)$.[8] These representations are listed in Table II. Upon reducing the transformation matrices of the group which operate in the product space of atomic coordinates and spins, we find that $\Gamma^{(1)}$ appears once and $\Gamma^{(2)}$ twice in the transformation matrices. Let us define two vectors:

$$\mathbf{F}=\mathbf{S}_1+\mathbf{S}_2,$$
$$\mathbf{A}=\mathbf{S}_1-\mathbf{S}_2, \tag{1}$$

where $\mathbf{S}_i$ is the spin of the ion in the ith position. The subscripts 1, 2 correspond to sites $(2a)$ of the chemical cell. Invariant subspaces of the product space of atomic coordinates and spins are listed in Table III, in terms of the components of $\mathbf{F}$ and $\mathbf{A}$. The actual spin structure resulting from the magnetic transition belongs to the representation which minimizes the Hamiltonian. The Hamiltonian of order two in the spin coordinates has the following form:

$$H=a(A_z^2+F_z^2)+b(F_x^2+A_x^2)+c(A_zF_x+F_zA_x)+d(A_y^2+F_y^2), \tag{2}$$

and it is invariant under the paramagnetic group of the crystal. The parameters a, b, c, d determine the energy associated with each subspace.

TABLE I. Compounds reported to have lost a center of symmetry in the transition from paramagnetic to magnetically ordered state.

Compound	Ordering temperature (°K)	Crystal space group	Propagation vector **k**	Magnetic space group	Point symmetry in paramagnetic state	Point symmetry in magnetic state	Possible direction of ferro-electricity	Reference
$BiMn_2O_5$	46	$Pbam\text{-}D_{2h}^9$	$(\frac{1}{2}, 0, \frac{1}{2})$	P_Bb2_1m	$mmm1'$	$m2m1'$	[0, 1, 0]	3, 4
$TbCrO_3$	3.05[a]	$Pbnm\text{-}D_{2h}^{16}$	$(0, \frac{1}{2}, 0)$	$P_{2b}2_1'nm'$	$mmm1'$	$2mm1'$	[1, 0, 0]	5

[a] Ordering temperature of the Tb^{3+} ions.

In order to find the structures which minimize this Hamiltonian, certain assumptions should be made concerning the coefficients a, b, c, d. Landau's theory[9] stipulates that the transition occurs according to a single representation, and we shall assume this representation to be $\Gamma^{(2)}$. This means that one of the coefficients $a(T, P)$ or $b(T, P)$ changes its sign from positive to negative when T decreases through T_c while the other coefficients remain positive in the neighborhood of T_c. Let us find the equilibrium structures of this Hamiltonian subject to the following constraint:

$$\mathbf{S}_1^2+\mathbf{S}_2^2=\tfrac{1}{2}(\mathbf{A}^2+\mathbf{F}^2)=S^2,$$

where S^2 is a nonzero constant. This constraint is added to the formulation in order to avoid the trivial solution $\mathbf{S}_i=0$.

The following solution is obtained using the method of Lagrange multipliers:

$$F_x=-2\frac{a+\lambda}{c}A_z, \qquad A_x=-2\frac{a+\lambda}{c}F_z,$$

$$A_y=F_y=0, \tag{3}$$

where λ satisfies the quadratic equation

$$4\lambda^2+4(a+b)\lambda+4ab-c^2=0. \tag{4}$$

This solution contains one degree of freedom: Linear combinations of A_x and F_x are all degenerate solutions. The mixture of A_x and F_x, however, results in magnetic structures with magnetic moments of different magnitude at sites $(2a)$. The degeneracy is removed by adding terms of higher order to the Hamiltonian, such as $e(F_x^2-A_x^2)^2$. Equations (3) show that the components appear in pairs (F_x, A_z) and (F_z, A_x). These pairs ("pure states") by contrast, do not result in magnetic moments of different magnitude at sites $(2a)$. This is not true in general. In Appendix A we discuss an example of antiferromagnetic transition in a crystal having the symmetry $Pnma$ in which even a transition into pure state leads to magnetic moments of different magnitudes. In that case, sites which were equivalent before the transition become nonequivalent subsequently. It is then expected that nuclei at these sites will "see" different magnetic fields. In this case, splitting may appear in the NMR lines, indicating that sites are indeed nonequivalent. It is worth while to note here that some interesting phenomena, such as resonant absorption due to spin flip induced in nuclei inside domain walls by electrical fields, may occur below the transition in the crystal considered above. This is discussed in detail in Appendix B.

Let us assume that in our example the spin structure resulting from the magnetic transition is a mixture of A_z and F_x. The magnetic group corresponding to this structure is $P_{2a}m'm'2$ and it allows ferroelectricity in the z direction. The structures A_z, F_z and the corresponding symmetry elements are shown in Fig. 1.

By examining the allowed displacements of the ions during the transition, it can be shown that the allowed direction of ferroelectricity is [001] in accordance with the symmetry group $P_{2a}m'm'2$. The atoms which occupied the sites $(2a)$ of the group $Pmma$ in the paramagnetic state will be found at the site $(2e)$ of the group $Pmm2$ in the magnetically ordered state. (See

TABLE II. Irreducible representations of $Pmma$, $\mathbf{k}=(\frac{1}{2}, 0, 0)$.[a]

	1	m_x	m_y	a_z	2_{1x}	2_y	2_z	$\bar{1}$
$\Gamma^{(1)}$	$\begin{bmatrix}1 & \\ & 1\end{bmatrix}$	$\begin{bmatrix}1 & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix}1 & \\ & 1\end{bmatrix}$	$\begin{bmatrix} & \bar{1}\\ 1 & \end{bmatrix}$	$\begin{bmatrix} & \bar{1}\\ 1 & \end{bmatrix}$	$\begin{bmatrix} & \bar{1}\\ \bar{1} & \end{bmatrix}$	$\begin{bmatrix}1 & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix} & \bar{1}\\ \bar{1} & \end{bmatrix}$
$\Gamma^{(2)}$	$\begin{bmatrix}1 & \\ & 1\end{bmatrix}$	$\begin{bmatrix}1 & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix}\bar{1} & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix} & \bar{1}\\ 1 & \end{bmatrix}$	$\begin{bmatrix} & 1\\ \bar{1} & \end{bmatrix}$	$\begin{bmatrix} & \bar{1}\\ \bar{1} & \end{bmatrix}$	$\begin{bmatrix}\bar{1} & \\ & 1\end{bmatrix}$	$\begin{bmatrix} & 1\\ 1 & \end{bmatrix}$

[a] m_x and m_y are mirror planes perpendicular to the x and y axes, respectively; a_z is a mirror plane perpendicular to z axis followed by a translation $(\frac{1}{2}, 0, 0)$; 2_1 is a twofold screw axis.

footnote of Table IV). The sites (2*a*) coincide in the paramagnetic state with the sites (2*e*) with $(x_0, z_0) = (\frac{1}{4}, 0)$. In the ordered state the parameters may have values of the form

$$x = x_0 + \delta x, \qquad z = z_0 + \delta z, \tag{5}$$

where δx, δz are small displacements. The sum of displacements of the ions in a unit cell is 0, 0 and $2\delta z$ in the x, y and z directions, respectively; hence ferroelectricity is allowed only in the z direction.

III. ESTIMATION OF ELECTRIC MOMENT INDUCED BY MAGNETIC TRANSITION

We shall estimate the displacements of the magnetic ions due to the magnetic interaction in the example of the preceding section, namely, the transition $Pmma \rightarrow P_{2a}m'm'2$. A Hamiltonian of second order in the space and spin coordinates is constructed in such a way as to produce a ferroelectric moment in the z direction and to be minimized by the A_z structure (Fig. 1). This is done under the following assumptions which are compatible with the symmetry required by *Pmma* with magnetic ions at (2*a*).

1. The interaction between neighbors in y and z directions is of the ferromagnetic type. It is therefore sufficient to specify the Hamiltonian for a chain of ions in the x direction.
2. In the x direction there is an interaction of the antiferromagnetic type between second nearest neighbors ($J_2 < 0$) and of ferromagnetic type between nearest neighbors ($J_1 > 0$). The ferromagnetic interaction depends linearly on the displacements of ions from their equilibrium position: $J_1(1 + \alpha(x_{i+1} - x_i))$. Here α is a constant and x_i is the displacement of the ith ion from its equilibrium position.
3. The antiferromagnetic interaction is dominant, i.e., $|J_2| \gg |J_1|$.
4. The elastic energy related to the displacement of atom i is

$$\tfrac{1}{2}\beta(x_i - z_i)^2 + \tfrac{1}{2}\gamma(x_i - z_i)^2 + \tfrac{1}{2}\delta y_i^2, \tag{6a}$$

while for atom $i+1$ this energy is

$$\tfrac{1}{2}\beta(x_{i+1} - z_{i+1})^2 + \tfrac{1}{2}\gamma(x_{i+1} + z_{i+1})^2 + \tfrac{1}{2}\delta y_{i+1}^2. \tag{6b}$$

In these expressions $\mathbf{r}_i = (x_i, y_i, z_i)$ is the displacement of the ith ion from its equilibrium position. These expressions are related by a twofold axis in the z direction which interchanges the atoms.

Table III. Basis vectors of the irreducible representations of *Pmma*, $\mathbf{k} = (\frac{1}{2}, 0, 0)$, in the spin space of (2*a*).

Component	Representations $\Gamma^{(1)}$	$\Gamma^{(2)}$
ψ_1	$-A_y$	$F_x\ A_z$
ψ_2	F_y	$A_x\ F_z$

Table IV. Sites (2*a*) and (2*e*) in *Pmma* and *Pmm*2, respectively.[a]

Space group	*Pmma*	*Pmm*2
Site	(2*a*)	(2*e*)
Coordinates	0, 0, 0	$x - \frac{1}{4}, 0, z$
	$\frac{1}{2}, 0, 0$	$\frac{3}{4} - x, 0, z$

[a] The origin of *Pmm*2 as appeared in the International Tables is shifted by $(\frac{1}{4}, 0, 0)$ in order to bring it into coincidence with the origin of *Pmma*.

5. An anisotropy term of the form

$$-KS_z^2, \qquad \text{where } K > 0, \text{ is present.}$$

6. The magnetic moments lie in the yz plane, which means that the magnetic moment of the ith atom has one degree of freedom: the angle ψ_i with respect to the z axis.

With these assumptions, the second-order classical Hamiltonian with respect to spin and space coordinates will be of the following form[10]:

$$\begin{aligned} H = -S^2 \sum_n \{ & J_1[1 + \alpha(x_{n+1} - x_n)] \cos(\psi_{n+1} - \psi_n) \\ & + J_2 \cos(\psi_{n+2} - \psi_n)\} - KS^2 \sum_n \cos^2\psi_n \\ & + \sum_n \{[\tfrac{1}{2}\beta(x_{2n} + z_{2n})^2 + \tfrac{1}{2}\gamma(x_{2n} - z_{2n})^2 + \tfrac{1}{2}\delta y_{2n}^2] \\ & + [\tfrac{1}{2}\beta(x_{2n+1} - z_{2n+1})^2 + \tfrac{1}{2}\gamma(x_{2n+1} + z_{2n+1})^2 + \tfrac{1}{2}\delta y_{2n+1}^2]\}. \end{aligned} \tag{7}$$

The structure which minimizes this Hamiltonian is determined in Appendix C. It is found that this structure is A_z, where

$$\begin{gathered} x = x_{2n} = -x_{2n+1} = -\tfrac{1}{2}\alpha S^2 J_1(1/\beta + 1/\gamma), \\ z_n = (\beta - \gamma)/(\beta + \gamma)\ |x_n|, \qquad y_n = 0, \end{gathered} \tag{8}$$

and the corresponding energy per atom is

$$E = -2\alpha x J_1 S^2 + J_2 S^2 - KS^2 + [2\beta\gamma/(\beta + \gamma)]x^2. \tag{9}$$

Enz[11] considered a simplified Hamiltonian of this type and determined its minimum under the following assumptions: the ions are fixed in space, and the Hamiltonian is therefore independent of $\mathbf{r}_i$; furthermore, the anisotropy term vanishes. He obtained a helicoidal structure in which the angle θ between the magnetic moments of two adjacent ions is given by

$$\cos\theta = -J_1/4J_2,$$

while the corresponding energy per ion is

$$E = S^2 J_2 + J_1^2 S^2 / 8J_2.$$

If we perturb this structure by introducing the anisotropy term $-KS_z^2$, assumed small compared to the exchange energy, as is generally the case,[12] the follow-

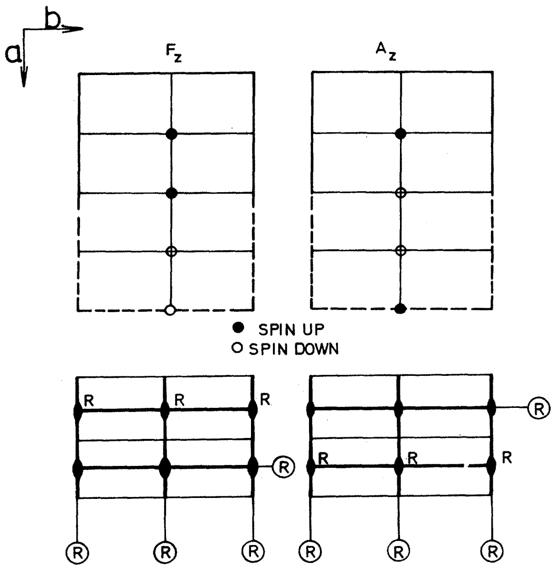

FIG. 1. Magnetic structures A_z and F_z (basis vectors) of the representation $\Gamma^{(2)}$ of *Pmma* (Table III) leading to $P_{2a}m'm'2$. *R* associated with an element means that this element is multiplied by time reversal.

ing energy per ion is obtained:

$$E = S^2J_2 + J_1^2S^2/8J_2 - \tfrac{1}{2}KS^2. \qquad (10)$$

Let us examine the possibility of appearance of structure A_z. We require that the energy corresponding to structure A_z be lower than the energy of the helicoidal structure,

$$S^2(J_2-K) + [2\beta\gamma/(\beta+\gamma)]x^2 - 2\alpha x J_1 S^2 < S^2[J_2 - \tfrac{1}{2}K + (J_1^2/8J_2)].$$

Neglecting the terms $[2\beta\gamma/(\beta+\gamma)]x^2$, $-2\alpha x J_1 S^2$, which will be shown to be small, we obtain

$$S^2(J_2-K) < S^2[J_2 - \tfrac{1}{2}K + (J_1^2/8J_2)],$$

or

$$K > -J_1^2/4J_2 = |J_1^2/4J_2|;$$

using J_1 and J_2 given in the following section, a K of order of magnitude of 10^{-5} eV is obtained. Anisotropy energies of this order of magnitude, and even larger, were found experimentally.[12]

We shall now make an estimate of the magnitude of the displacements z_i. The constants γ and δ are a measure of the microscopic elasticity. If we assume that the microscopic and macroscopic elasticities are of the same order of magnitude we then have $\gamma \sim y/N$, where y is Young's modulus and N is the number of atoms per unit volume. We may take[13] $y \sim 5\times10^{11}$ dyn/cm^2 and $N \sim 4\times10^{22}$ cm^{-3}. A Curie temperature of 100°K will lead to $J_2 \sim 10^{-3}$ eV. J_1 is smaller than J_2 and we shall take it as 10^{-4} eV. Finally using $\alpha = -10/3$, found[14] for rare-earth iron garnets, one obtains

$$|x| = \tfrac{1}{2}J_1\alpha S^2(\beta^{-1}+\gamma^{-1}) \simeq \frac{2\times4\times10^{22}\times10^{-16}\times10}{5\times2\times10^{11}\times3} \simeq 10^{-4}$$

and the displacement in the z direction decreases by the factor $(\beta-\gamma)/(\beta+\gamma)$. As long as the magnitudes of β and γ are not close, x and z will be of the same order of magnitude. Now, the "ionic" charge per cm^3 for a compound with four cations per (8 Å)^3 is

$$q = \frac{4}{(8\times10^{-8})^3}\,1.6\times10^{-19} \sim 10^3 \text{ C/cm}^3.$$

Hence with displacement of 10^{-5} of the cell dimension we obtain the ferroelectric moment

$$P \sim 10^3 \times 8 \times 10^{-12} \sim 10^{-8} \text{ C/cm}^2,$$

which is measurable.[15] Note, however, that in order to observe the ferroelectricity, the crystals or powders[16] may have to be cooled in an electric field in order to eliminate domain effects.

One can estimate the magnitude of the electric moment in somewhat different way. Let us write the free energy F to the fourth order in the magnetization $\mathbf{M}$ and to the second order in the polarization $\mathbf{P}$, as follows:

$$F(M,P) = \tfrac{1}{2}aM^2 + \tfrac{1}{4}bM^4 + \tfrac{1}{2}cPM^2 + \tfrac{1}{2}dP^2 - EP, \qquad (11)$$

where E is an external electric field. Minimizing this with respect to P and M one obtains

$$P = (ac/2b)(d - c^2/2b)^{-1} + (d - c^2/2b)^{-1}E, \qquad (12)$$

$$M^2 = -(c/b)P - a/b. \qquad (13)$$

That is, the spontaneous electric polarization (in the absence of external field) is given by

$$P_s = (ac/2b)(d - c^2/2b)^{-1}, \qquad (14)$$

and the electric susceptibility by

$$\chi_e = (d - c^2/2b)^{-1}. \qquad (15)$$

Above the transition, the electric susceptibility is given by

$$\chi_{e0} = 1/d. \qquad (16)$$

Hence, a discontinuous change in the electric susceptibility is expected, given by

$$\frac{\Delta\chi_e}{\chi_{e0}} = \frac{\chi_e - \chi_{e0}}{\chi_{e0}} = \frac{c^2/2b}{d - c^2/2b}. \qquad (17)$$

To a first approximation we may neglect the ferroelectric effects in the derivation of the magnetization. Hence one obtains

$$M_0^2 = -a/b. \qquad (18)$$

Following Landau's theory[9] we set

$$a(T) = a_0(T - T_c),$$

where a_0 is a constant and T_c is the Curie temperature.

For $T > T_c$ the magnetic susceptibility χ_m is given by

$$\chi_m = M/H = 1/a(T) = 1/a_0(T - T_c).$$

Comparing this with the Curie-Weiss law, $\chi_m = C_w/(T - T_c)$, one obtains $a_0 = 1/C_w$.
Hence,

$$a(0) = -T_c/C_w$$

and

$$M_0^2 = -a/b = T_c/bC_w.$$

Using this, one obtains the following expressions for the spontaneous polarization and the discontinuous change in the electric susceptibility:

$$P_s = \tfrac{1}{2}M_0^2 c(1/\chi_{e0} - c^2 M_0^2 C_w/2T_c)^{-1}, \tag{19}$$

$$\Delta\chi_e/\chi_{e0} = (1/\chi_{e0} - c^2 M_0^2 C_w/2T_c)^{-1}(c^2 M_0^2 C_w/2T_c). \tag{20}$$

Let us estimate these quantities, taking $\chi_{e0} \simeq 1$ [12] for a crystal having an interatomic distance of 2×10^{-8} cm and magnetic ions with magnetic moment of $1\mu_B$,

$$M_0 \simeq 0.4 \times 10^{-6}\ \mathrm{C/cm^2}$$

and[12]

$$C_w = Ng^2 S(S+1)\mu_B^2/3k_B = 0.05°\mathrm{K}. \tag{21}$$

Here N is the number of ions per cm^3, g is the g factor ($\simeq 2$), S is the magnetic moment of the ion in Bohr magneton ($=1$), and k_B is the Boltzmann constant.

In order to estimate c let us consider the magnetoelastic term in the Hamiltonian written above,

$$J_1 \alpha x S^2 = (J_1\alpha/ea)xeaS^2, \tag{22}$$

where a is the interatomic distance. The magnetoelastic energy per unit volume is

$$\begin{aligned}(J_1\alpha/ea)xeaNS^2 &= (J_1\alpha/eaN^2\mu_B^2)(xeaN)(S^2\mu_B^2N^2) \\ &= (J_1\alpha/eaN^2\mu_B^2)PM^2. \end{aligned} \tag{23}$$

Hence

$$\tfrac{1}{2}c = J_1\alpha/eaN^2\mu_B^2, \tag{24}$$

taking as in the previous section

$$T_c \simeq 100°\mathrm{K}, \qquad \alpha \simeq 10/3, \qquad J_1 \simeq 10^{-4}\ \mathrm{eV},$$

one obtains

$$c = 2 \times 10^5\ (\mathrm{C/cm^2})^{-1}.$$

Using these quantities, it is found that

$$P_s \simeq 10^{-8}\ \mathrm{C/cm^2} \quad \text{and} \quad \Delta\chi_e/\chi_{e0} \simeq 10^{-6}.$$

Such a change in the electric susceptibility is too small to be measured.

The temperature dependence near the transition temperature T_c, of the electric polarization induced by the antiferromagnetic transition, is expected to be different from that in simple ferroelectrics. As shown in Appendix D, the electric polarization behaves as the square of the sublattice magnetization, while the sublattice magnetization behaves nearly as the electric polarization in simple ferroelectrics.

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APPENDIX A: EXAMPLE WHERE EQUIVALENT SITES TURN NONEQUIVALENT

We shall consider an example where equivalent sites turn nonequivalent upon a transition into a pure state. Such a transition may lead to magnetic moments of different magnitudes in sites which were equivalent in the paramagnetic phase.

Consider a crystal having the space symmetry $Pnma(D_{2h}^{16})$ in which the magnetic ions occupy the sites $(4c)$[6]:

1. $x\frac{1}{4}z$,   3. $\frac{1}{2}-x, \frac{\bar{1}}{4}, \frac{1}{2}+z$,
2. $\bar{x}\frac{1}{4}\bar{z}$,   4. $\frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z$.

We assume that this crystal undergoes an antiferromagnetic transition which doubles the unit cell in the x direction $[\mathbf{k} = (\frac{1}{2}, 0, 0)]$. The corresponding irreducible representations are given in Table V. In reducing the transformation matrices of the group in the product space of atomic coordinates and spins, we find that $\Gamma^{(1)}$ appears four times and $\Gamma^{(2)}$ twice. Let us define four vectors:

$$\mathbf{F} = (\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4),$$

$$\mathbf{G} = (\mathbf{S}_1 - \mathbf{S}_2 + \mathbf{S}_3 - \mathbf{S}_4),$$

$$\mathbf{A} = (\mathbf{S}_1 - \mathbf{S}_2 - \mathbf{S}_3 + \mathbf{S}_4),$$

$$\mathbf{C} = (\mathbf{S}_1 + \mathbf{S}_2 - \mathbf{S}_3 - \mathbf{S}_4),$$

where the indicies 1–4 correspond to the sites $(4c)$ of the chemical cell.

The basis vectors of the invariant subspaces of the product space of atomic coordinates and spins in terms of **F**, **G**, **C**, **A** are listed in Table VI. The structures F_z, C_z and the corresponding symmetry elements are given in Fig. 2. The magnetic groups according to which the basis vectors of $\Gamma^{(1)}$ and $\Gamma^{(2)}$ transform are $P_{2a}n'm'2_1$ and $P_{2a}nm2_1$, respectively, which are the groups $P_{2b}m'n'2_1$ and $P_{2b}mn2_1$ in the setting of Opechowski and Guccione.[17] This decrease in symmetry is sufficient to break up the equivalence of the $(4c)$ sites into pairs 1, 3 and 2, 4 which make up the $(2a)$ sites of $Pnm2_1$.

APPENDIX B: NMR ABSORPTION IN DOMAIN WALLS

In the case that the magnetic transition takes place without the presence of external electric field, a multidomain crystal is obtained. In our example two neighboring domains may have magnetic structures of F_z and A_z type with opposite electric polarization. Bloch walls will separate these domains. A possible structure of such a wall is shown in Fig. 3. This structure is

TABLE V. The irreducible representations of *Pnma* with $\mathbf{k}=(\frac{1}{2},0,0)$.

	1	n_x	m_y	a_z	2_{1x}	2_{1y}	2_{1z}	$\bar{1}$
$\Gamma^{(1)}$	$\begin{bmatrix}1 & \\ & 1\end{bmatrix}$	$\begin{bmatrix}\bar{1} & \\ & 1\end{bmatrix}$	$\begin{bmatrix}\bar{1} & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix} & \bar{1} \\ 1 & \end{bmatrix}$	$\begin{bmatrix} & 1 \\ \bar{1} & \end{bmatrix}$	$\begin{bmatrix} & 1 \\ 1 & \end{bmatrix}$	$\begin{bmatrix}1 & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix} & \bar{1} \\ \bar{1} & \end{bmatrix}$
$\Gamma^{(2)}$	$\begin{bmatrix}1 & \\ & 1\end{bmatrix}$	$\begin{bmatrix}1 & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix}1 & \\ & 1\end{bmatrix}$	$\begin{bmatrix} & 1 \\ \bar{1} & \end{bmatrix}$	$\begin{bmatrix} & 1 \\ \bar{1} & \end{bmatrix}$	$\begin{bmatrix} & 1 \\ 1 & \end{bmatrix}$	$\begin{bmatrix}1 & \\ & \bar{1}\end{bmatrix}$	$\begin{bmatrix} & 1 \\ 1 & \end{bmatrix}$

consistent with our assumption of antiferromagnetic interaction between second neighbors in the x direction. An alternating electric field in the z direction will make the wall move back and forth, inducing alternating magnetic field on the nuclei populating the wall. In the resonance frequency of these nuclei, one may observe a strong absorption. On the other hand, if the transition takes place in a constant electric field, a single phase will emerge due to the electric interaction. No absorption in the resonance frequency mentioned above will occur in this case. These considerations are merely qualitative, and the effect may be too small to be observed.

APPENDIX C: MINIMIZATION OF HAMILTONIAN

In order to show that A_z is the equilibrium state of the Hamiltonian, we first replace ψ_n and $\mathbf{r}_n$ by more convenient parameters. Define

$$\bar{x}_n=\begin{cases} x_n & \text{for } n=2k \\ -x_n & \text{for } n=2k+1, \end{cases} \tag{C1}$$

$$\bar{\psi}_n=\begin{cases} \psi_n & \text{for } n=4k,\ 4k+3 \\ \pi+\psi_n & \text{for } n=4k+1,\ 4k+2 \end{cases} \tag{C2}$$

$$\bar{z}_n=z_n, \tag{C3}$$

$$\bar{y}_n=y_n. \tag{C4}$$

The Hamiltonian is given in this notation by

$$\begin{aligned} H=-J_1S^2\sum_n \{&[1-\alpha(\bar{x}_{2n+1}+\bar{x}_{2n})]\cos(\bar{\psi}_{2n+1}-\bar{\psi}_{2n}) \\ &-[1+\alpha(\bar{x}_{2n+2}+\bar{x}_{2n+1})]\cos(\bar{\psi}_{2n+2}-\bar{\psi}_{2n+1})\} \\ &+J_2S^2\sum_n \cos(\bar{\psi}_{n+2}-\bar{\psi}_n)-(KS^2\sum_n \cos^2\bar{\psi}_n) \\ &+\tfrac{1}{2}\sum_n [\beta(\bar{x}_n+\bar{z}_n)^2+\gamma(\bar{x}_n-\bar{z}_n)^2+\delta\bar{y}_n{}^2]. \end{aligned} \tag{C5}$$

TABLE VI. Basis vectors of the irreducible representations of *Pnma* with $\mathbf{k}=(\frac{1}{2},0,0)$ in the spin space of (4*c*).

	$\Gamma^{(1)}$	$\Gamma^{(2)}$
ψ_1	$F_z\,G_z\,C_x\,A_x$	$A_y\,C_y$
ψ_2	$-C_z\,A_z\,-F_x\,G_x$	$-G_y\,F_y$

Let us define the parameter $u=n\cdot a$, where a is the distance between two adjacent ions. We replace in the Hamiltonian the summation by integration using the following approximations:

$$\bar{x}_{2n+1}+\bar{x}_{2n}=2\bar{x}-a\dot{\bar{x}},$$

$$\bar{x}_{2n+2}+\bar{x}_{2n+1}=2\bar{x}+a\dot{\bar{x}},$$

$$\bar{\psi}_{2n+1}-\bar{\psi}_{2n}=-a\dot{\bar{\psi}},$$

$$\bar{\psi}_{2n+2}-\bar{\psi}_{2n+1}=a\dot{\bar{\psi}},$$

$$\bar{\psi}_{n+2}-\bar{\psi}_n=2a\dot{\bar{\psi}},$$

where

$$\dot{\bar{x}}=d\bar{x}/du, \qquad \dot{\bar{\psi}}=d\bar{\psi}/du.$$

Using these approximations the Hamiltonian will have

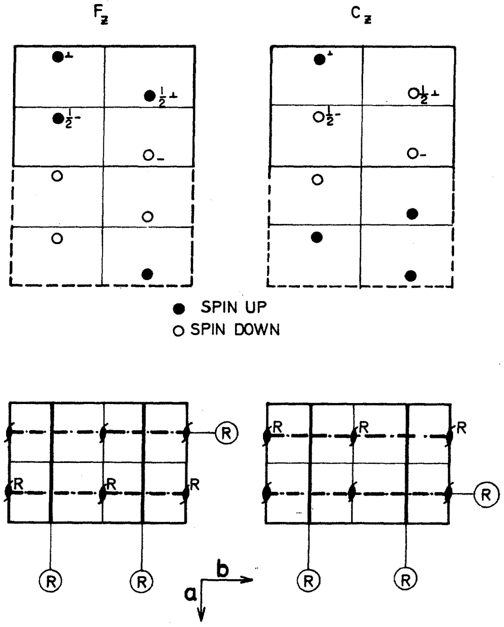

FIG. 2. Magnetic structures C_z and F_z (basis vectors) of the representation $\Gamma^{(1)}$ of *Pnma* (Table VI) leading to $P_{2a}n'm'2_1$. *R* associated with an element means that this element is multiplied by time reversal.

the form

$$H=S^2\int[J_1 2\alpha\bar{x}\cos a\dot{\bar{\psi}}+J_2\cos 2a\dot{\bar{\psi}}-K\cos^2\bar{\psi}]du$$
$$+\tfrac{1}{2}\int[\beta(\bar{x}-\bar{z})^2+\gamma(\bar{x}+\bar{z})^2+\delta\bar{y}^2]du. \quad \text{(C6)}$$

Using variational methods one finds that the structure

$$\bar{\psi}=0,\qquad \bar{x}=-\tfrac{1}{2}\alpha S^2 J_1(1/\beta+1/\gamma),$$
$$\bar{z}=(\beta-\gamma)/(\beta+\gamma)\bar{x},\qquad \bar{y}=0,$$

minimizes the Hamiltonian. The displacements of the atoms from their equilibrium position will then be

$$x_n=(-)^{n+1}\tfrac{1}{2}\alpha S^2 J_1(1/\beta+1/\gamma), \quad \text{(C7)}$$
$$z_n=(\beta-\gamma)/(\beta+\gamma)\,|\,x_n\,|. \quad \text{(C8)}$$

APPENDIX D: RELATION BETWEEN MAGNETIZATION AND ELECTRIC POLARIZATION NEAR T_c

We use the above example of a crystal having the space group $D_{2h}{}^5$-*Pmma* with magnetic ions at sites (2*a*) in order to show that the electric polarization near the Néel temperature is proportional to the square of the sublattice magnetization. Let us expand the free energy of the crystal in powers of the magnetization **M** and electric polarization **P**, up to order 4 in **M** and order 2 in **P**.

All terms must be invariant under the operations of the paramagnetic group. Examples of such terms which correspond to $\Gamma^{(2)}$ (Table III) are

$$(A_z{}^2+F_z{}^2),\quad (A_xF_z+F_xA_z),\quad (A_z{}^2-F_z{}^2)^2,$$
$$P_z{}^2,\quad (A_xF_z-F_xA_z)P_z,\quad (A_z{}^2-F_z{}^2)P_z.$$

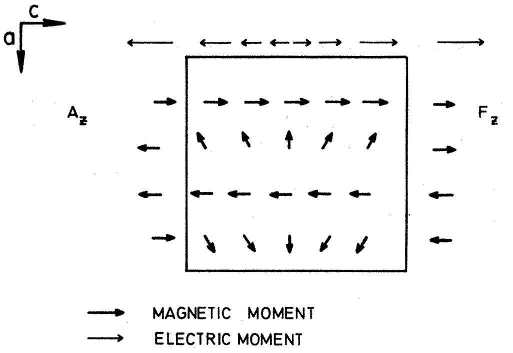

FIG. 3. Schematic magnetic and electric structures of Bloch walls between domains of A_z and F_z type.

That is, the thermodynamic potential will have the form

$$F(M,P)=aM^2+bM^4+cP^2+dM^2P$$

and the minimum is obtained at

$$P=-(d/2c)M^2.$$

Hence, near the transition temperature the electric polarization behaves as the square of the sublattice magnetization. This magnetization behaves nearly as in a simple antiferromagnetic transition, because the magnetic interactions are dominant here. That is,[18]

$$M\sim(T_c-T)^\beta,\qquad P\sim(T_c-T)^{2\beta},$$

where $\beta=\frac{1}{3}$.

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[10] This Hamiltonian is more general than the one appearing in the preceding section. Here we do not assume that the magnetic unit cell is twice as large as the chemical cell; furthermore, additional degrees of freedom $\mathbf{r}_i$ are included in this Hamiltonian which are not present in the previous one.

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