Are antiferroelectricity and other physical properties 'hidden' in spinel compounds?

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Abstract. The piezoelectric switching of antiferroelectric domains by the simultaneous application of an electric field E_i and mechanical stress T_{jk} is proposed as a direct method for examining whether some spinel compositions do have point symmetry $\bar{4}3m$ and concomitant antiferroelectric ordering as proposed by Grimes.

For piezoelectric antiferroelectrics, the switching energy is $\Delta g = 2d_{ijk}E_iT_{jk}$ (d_{ijk} = piezoelectric coefficient). For point symmetry $\bar{4}3m$, various possible switching procedures have been described in detail. The smallest coercive product of electric field and stress $(E_iT_{jk})_c$ is required for switching when the electric field is chosen along cubic [001], and directional stress along [110] or [1$\bar{1}$0]. For particular directions, for example [111], the colinear application of electric field and stress also leads to switching.

If the assumed prototype with space group $F\bar{4}3m$ —the symmetry proposed by Grimes— is supposed to undergo a phase transition leading to ferrimagnetism, the possible symmetries of the ferrimagnetic domains are given by the magnetic groups $I4m'2'$, $Im'm2'$ and $R3m'$, which are M-maximal subgroups of the prototype magnetic group $F\bar{4}3m1'$. All three ferrimagnetic phases permit piezoelectricity, piezomagnetism and the linear and second-order magneto-electric effect. The tetragonal phase ($I\bar{4}m'2'$) remains antiferroelectric as the prototype is supposed to be, whereas the orthorhombic ($Im'm2'$) and trigonal ($R3m'$) phases become ferro-electric. The full lattice of subgroups of $F\bar{4}3m1'$ is presented.

1. Introduction

It is the intention, in this paper, to propose crucial experiments with a view to examining the validity of the proposition made by Grimes (1973) that the correct space group of certain spinel compositions, for example, $MgCr_2O_4$, would be $F\bar{4}3m$ instead of $Fd3m$, as hitherto generally admitted for the cubic phase of spinels. A large number of experimental facts, reviewed by Grimes (1971, 1972, 1973), appear to support the proposal of the lower symmetry of certain spinel compositions: off-centre displacements along [111] of the octahedrally coordinated metal ions (for example Cr^{3+}) were inferred from x-ray Debye–Waller-factor measurements (Grimes and Hilleard 1970), infrared spectra (Grimes and Collett 1971), electron spin resonance (Stahl-Broda and Low 1959) and optical spectra (Lou and Ballentyne 1968). The optical spectra can only be interpreted by admitting point symmetry $3m$ for the octahedrally coordinated Cr^{3+} position; a fact which is incompatible with space group $Fd3m$, but a strong argument for $F\bar{4}3m$. All these data suggest metal-ion displacements within the cubic phase of spinels off the centre of the

ideal octahedral site, but do not prove a long-range ordering of these ionic shifts. Such long-range ordering would, however, be required if the ionic displacements should lead to antiferroelectricity. This property is permitted by class $\bar{4}3m$ (see for example, Schmid 1973), and hence necessarily by space group $F\bar{4}3m$, as pointed out by Grimes (1973). Electron diffraction patterns of polycrystalline films of $MnFe_2O_4$ (Hulscher *et al* 1972) and $MgFe_2O_4$ (Walters and Wirtz 1972), as well as transmission electron-diffraction patterns of single crystalline $MgAl_2O_4$ and $MgFe_2O_4$, showed weak reflections for $h + k = 4n + 2$, which are forbidden for space group $Fd3m$, requiring a lower symmetry. These reflections are consistent with, but do not prove, space group $F\bar{4}3m$. If these extra reflections were caused by the above-mentioned ionic shifts, they would represent the first experimental indication of their long-range ordering and, thereby, a strong argument for finding antiferroelectricity.

One might be tempted to infer the occurrence of antiferroelectricity in spinels from the high low-frequency dielectric constant observed in certain compositions (reviewed by Grimes 1972). One has, however, to be careful about such interpretation, because high dielectric constants can be simulated in various ways (von Hippel 1967), for example, by the stacking of insulating and conducting layers (Koops 1951). Moreover, antiferroelectrics are not necessarily materials with high dielectric constant, just like many ferroelectrics are known to have very low dielectric constants of the order of 10 to 20 (for example $REMnO_3$, RE $\equiv$ rare earth, Peuzin (1965); boracites, Ascher *et al* (1964)). Therefore, the occurrence of antiferroelectricity in spinels would not necessarily be linked to compositions with high dielectric constant.

At first glance, it would appear easy to demonstrate, by determination of the x-ray extinction rules, that a spinel with inferred off-centre octahedral site ions, for example $MgCr_2O_4$, really belongs to space group $F\bar{4}3m$. However, because of the small magnitude of the ionic displacements involved, the difference in diffraction pattern may escape observation. A further difficulty arises in the particular case of ferrites: the space group $F\bar{4}3m$, proposed by Grimes (1973, figure 1), is an equi-translation subgroup of $Fd3m$; therefore, no increase of the unit cell relative to the ideal spinel symmetry $Fd3m$, permitting a distinction from the $F\bar{4}3m$ phase, need occur. Another problem is that the Debye–Waller factors (Grimes and Hilleard 1970), from which metal-ion shifts have been inferred, are not unusually large, so that normal thermal motion cannot be excluded unambiguously. There also remains the possibility that spinels exist which show only a short-range ordering of the cited ionic shifts. Such short-range ordering has been considered, for example, by van Santen (1950), for the cubic phase of the spinel Fe_3O_4. With a view to the clarification of this point, it would be rewarding to undertake x-ray diffuse-scattering and electron-diffraction experiments. Short-range ordering has been inferred from x-ray diffuse scattering for silicon, quartz, the cubic phase, and certain ferroelectric phases of perovskites (Comès *et al* 1970) and for boracites (Félix *et al* 1973). In general, the short-range ordered phase would be expected to undergo a transition to one or more completely ordered phases. It is, however, noteworthy to recall that the 'short-range ordering interpretation' of the observed x-ray diffuse scattering, mentioned above, is not generally accepted; possibly a lattice vibrational explanation may turn out to be the correct one.

The aforesaid shows that we need a reliable direct method in order to verify the supposed occurrence of antiferroelectricity of point symmetry $\bar{4}3m$ in spinels. Because the inferred symmetry is non-centrosymmetric, the piezoelectric effect, the Pockels effect and nonlinear optical effects, such as frequency multiplication, etc should be permitted and detectable, and we would thereby have a direct sensitive method. In reality the

situation is not this simple, because, for a macroscopic crystal in an antiferroelectric phase with $\bar{4}3m$ symmetry, the piezoelectric and linear electro-optic effect would usually cancel out owing to the presence of antiferroelectric domains. Then, only the centrosymmetric symmetry $m3m$ of cubic spinels which *has* been reported, would be apparent. In particular, when the various possible domain orientation states are small and equally distributed, the effects mentioned would escape observation entirely. If this were the case in certain cubic spinel compositions, it would explain why, to the best of our knowledge, piezoelectricity has not been reported for such compounds. A further important consequence of lower crystallographic symmetry in spinels would be that some magnetically ordered phases of ferrites would, in reality, have lower magnetic symmetry (see below) than that mimicked by the superposition of antiferroelectric/ferrimagnetic domains. This might lead to the discovery that certain ferrites have, in reality, magnetic symmetries, some of which would permit, among other things, the linear magnetoelectric effect. Because high Curie temperatures are common among ferrites, it is possible that magnetoelectrics of technical interest may thus be found.

2. Proposal for an experiment with a view to demonstrating the potential presence of antiferroelectricity with point symmetry $\bar{4}3m$ in spinels

2.1. The antiferroelectric species

The number, mutual orientation and switching behaviour of domains always depend on both the high (prototypic) and low temperature symmetry group (Ascher 1967 unpublished and Ascher 1970). This is valid quite generally, that is, for ferromagnetic, ferroelectric, ferroelastic, antiferromagnetic, antiferroelectric, magnetoelectric etc domains. If we postulate, in the sense of Grimes (1973), the existence of an antiferroelectric spinel phase with point group $\bar{4}3m$, then the prototype group for the antiferroelectric transition would be $m3m$, and in the general case, a phase transition of the prototype to an electrically ordered phase would be expected. However, by analogy with
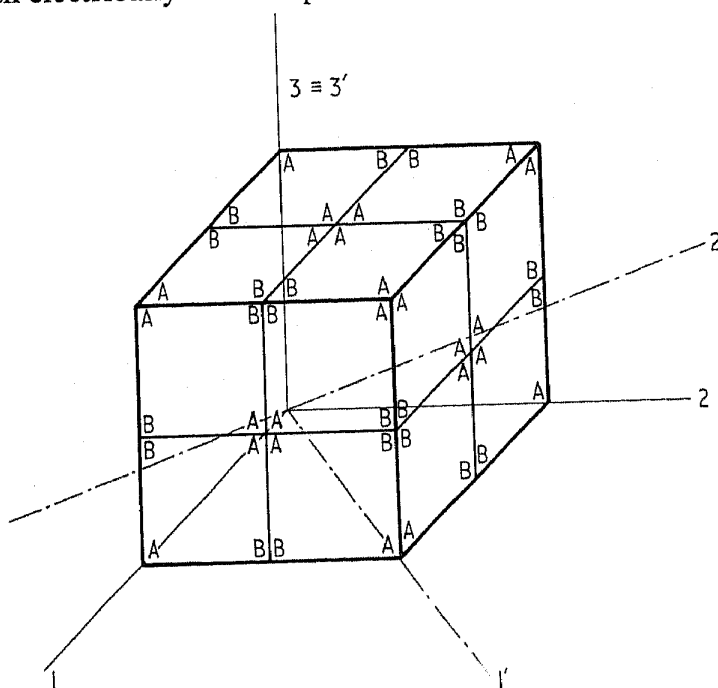

Figure 1. Antiferroelectric polydomain crystal of point symmetry $\bar{4}3m$ (schematic). The domain walls are arbitrarily assumed parallel to (100) planes.

certain ferroelectrics that do *not* undergo a transition up to the melting point at atmospheric pressure, ferrites might also be found that remain antiferroelectric up to the melting point. In the latter case, the relevant prototype, *m3m*, would be hypothetical. In either case, the *Aizu species* (Aizu 1970) in Shubnikov notation would be $m3m1'F\bar{4}3m1'$ and would permit *two kinds* of domain in the antiferroelectric phase. The situation is schematically represented in figure 1. The mutual orientation of the domains is related, for example, by a mirror plane parallel to $(100)_{cubic}$; that is, by one of the symmetry elements lost during the transition from the high temperature (*m3m*) to the low temperature ($\bar{4}3m$) phase. A crystal cooled through a hypothetical antiferroelectric Néel temperature, or grown below that temperature, would be expected to display such a polydomain pattern. Only in the case of very high potential barriers for the antiferroelectric ionic shifts, might a single-crystal nucleus be expected to continue growing into a large single-domain state. This is a situation which probably does not pertain to spinels.

2.2. Piezoelectric switching of antiferroelectric domains

It has been proposed elsewhere (Schmid 1973) that 'piezoelectric switching' of piezoelectric antiferroelectric domains should be possible. If antiferroelectricity with point group $\bar{4}3m$ really does occur among some spinels, then these would be excellent examples to demonstrate the predicted effect. Piezoelectric switching is based on the fact that every piezoelectric material permits terms in the Taylor expansion of the density of 'stored free enthalpy' *g*, which are linear in the electric field E_i and linear in the components of the stress tensor T_{jk}:

$$-g = \ldots + d_{ijk}E_iT_{jk} + \ldots . \tag{1}$$

Here d_{ijk} stands for the piezoelectric coefficient.

If we consider an antiferroelectric domain alternatively submitted to an electric field of opposite sign, $\pm E_i$, at fixed sign of stress T_{jk}, or vice versa, then the energy stored in that domain will be different by Δg for these two situations:

$$
\begin{aligned}
-g\,(\text{domain}') &= + d_{ijk}E_iT_{jk} + \cdots \\
-g\,(\text{domain}'') &= - d_{ijk}E_iT_{jk} + \cdots \\
\hline
\Delta g &= 2d_{ijk}E_iT_{jk}
\end{aligned}
\tag{2}
$$

For the case when the energy supplied, $2d_{ijk}E_iT_{jk}$, reaches the critical switching energy Δg_c, the antiferroelectric domain will switch into the more stable orientation state. The switching energy would be expected to be of the same order of magnitude as that necessary for reversing or reorienting ferroelectric domains.

In the case of symmetry $\bar{4}3m$, the tensor d_{ijk} has the following matrix form (the symmetric pair of indices *jk* has been replaced, as usual, by α single index running from 1 to 6):

$$
d_{i\alpha} =
\begin{bmatrix}
0 & 0 & 0 & d_{14} & 0 & 0 \\
0 & 0 & 0 & 0 & d_{14} & 0 \\
0 & 0 & 0 & 0 & 0 & d_{14}
\end{bmatrix} .
\tag{3}
$$

We see that only the piezoelectric shear-stress moduli d_{14} appear. For the convenience of experiment, it is useful to transform to orthorhombic coordinates by rotating the cubic 1 and 2 axes by 45° around a cubic [001] direction parallel to 3.

This is reasonable because application either of an electric field along a cubic [100] direction or of directional stress along a cubic [110] direction induces orthorhombic symmetry, the principal axes of which coincide with the new (primed) coordinate axes. For that orthorhombic description of the cubic $\bar{4}3m$ phase, the piezoelectric matrix takes the following form (see for example, Cady 1946):

$$d_{i'\alpha'} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{14} & 0 \\ 0 & 0 & 0 & -d_{14} & 0 & 0 \\ -\frac{1}{2}d_{14} & \frac{1}{2}d_{14} & 0 & 0 & 0 & 0 \end{bmatrix}. \tag{4}$$

From (4) we recognize that there exist two equivalent, experimentally straightforward, ways of realizing the switching of the antiferroelectric domains. This involves the simultaneous application of either *directional stress* along 1' and an electric field along 3', or stress along 2' and electric field along 3', respectively, The switching energies are identical for the two cases:

$$\Delta g = |\Delta g_1| = |\Delta g_2| = |d_{14}E_{3'}T_{1'}| = |-d_{14}E_{3'}T_{2'}|. \tag{5}$$

Whereas (5) requires mutual perpendicular electric field and stress, symmetry $\bar{4}3m$ also permits antiferroelectric domain switching by colinear application of electric field and directional stress. Two special cases become clear by rotating the primed coordinate system around the 2' direction ($\|$cubic [110]) by $\theta = \cos^{-1}(1/\sqrt{3})$: that is, in such a way that the new axes 1'' and 3'' coincide with the cubic [112] and [$\bar{1}\bar{1}1$] directions, respectively, 2' being parallel to 2''. Then the piezoelectric matrix takes the following form:

$$d_{i''\alpha''} = \begin{bmatrix} -d_{14}/\sqrt{6} & d_{14}/\sqrt{6} & 0 & 0 & d_{14}/\sqrt{3} & 0 \\ 0 & 0 & 0 & -d_{14}/\sqrt{3} & 0 & \sqrt{\frac{2}{3}}d_{14} \\ -d_{14}/\sqrt{6} & -\frac{1}{2}d_{14}/\sqrt{3} & d_{14}/\sqrt{3} & 0 & 0 & 0 \end{bmatrix}. \tag{6}$$

From (6) one can easily see two special cases for which the switching of the antiferroelectric domains is realizable with colinear electric field and mechanical stress:

$$\Delta g = |-\sqrt{\tfrac{2}{3}}d_{14}E_{1''}T_{1''}| \tag{7}$$

and

$$\Delta g = |-d_{14}E_{3''}T_{3''}/\sqrt{3}|. \tag{8}$$

Moreover, (6) shows up two further special cases of switching with mutually perpendicular electric field and stress:

$$\Delta g = |\sqrt{\tfrac{2}{3}}d_{14}E_{1''}T_{2''}| \tag{9}$$

and

$$\Delta g = |-\sqrt{\tfrac{2}{3}}d_{14}E_{3''}T_{1''}|. \tag{10}$$

Among the switching processes listed (see equations (5), (7), (8), (9) and (10)), the one represented by (5) requires the smallest product of the constraints, E_iT_{jk}. Hence, it appears recommendable for experimental use and will be discussed in detail in the following.
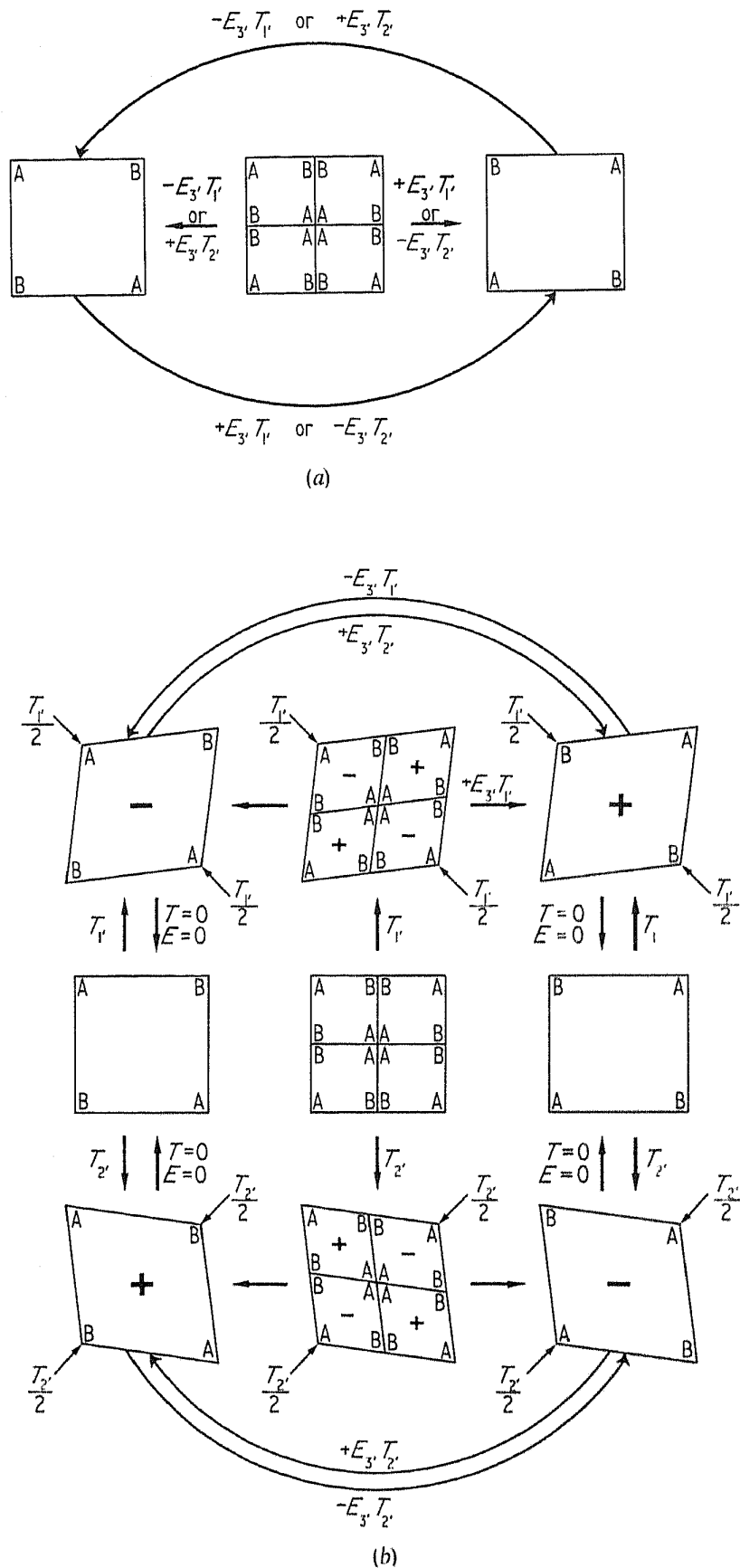
Figure 2. Schematic 'poling' and switching pathways for an antiferroelectric with point symmetry $\bar{4}3m$. The primed indices of the fields to be applied pertain to orthorhombic coordinates. (a) pathways showing only starting and end situations for the electric field applied along a [100] direction; (b) pathways and intermediate situations for pressure and pressure plus electric field applied consecutively.

In figures 2(*a*) and 2(*b*) we have schematically represented the 'poling' and switching pathways for an antiferroelectric with point symmetry $\bar{4}3m$, founded on the relation (5). In figure 2(*a*), the overall possibilities are shown for the case in which the electric field is applied along *one* out of the three cubic [100] directions; there exist, however, three more possibilities if all permutations are taken into account.

For the sake of a better understanding of the switching procedure, some intermediate situations have been represented schematically in figure 2(*b*) for the case of pressure and electric field plus pressure being applied consecutively. We can start by applying pressure alone on the polydomain crystal, either along the 1′ or along the 2′ direction. We then see that in either case both kinds of antiferroelectric domain become orthorhombically deformed, but the different states develop opposite piezoelectrically induced polarization charges on the orthorhombic (001) facets. The antiferroelectric crystal behaves like a ferroelectric as long as the above-mentioned pressure is applied (quasiferroelectricity). It is then plausible that the subsequent application of an electric field along 3′—simultaneously with the pressure along 1′ or 2′—will lead to the 'poling' of the pressure induced quasiferroelectric domains. After lifting the electric field and stress, a large antiferroelectric single domain would result under ideal experimental circumstances. By cooling the crystal under simultaneous electric field and stress through the antiferroelectric Néel temperature, an analogous result would be obtained.

An alternative way of splitting the switching procedure into plausible steps would be to start by applying an electric field alone in the 3′ direction of the polydomain crystal. Then one would notice that opposite shear is produced within the orthorhombic (001) plane of the antiferroelectric domains of different orientation. The action of the subsequently applied stress can then be understood as a ferroelastic poling. The antiferroelectric crystal behaves like a ferroelastic as long as the above-mentioned electric field is applied (quasiferroelasticity).

If antiferroelectricity with point group $\bar{4}3m$ really did exist in some spinel compositions, the described 'poling' procedure should be applicable. Verification of the degree of 'poling' might be performed by piezoelectric measurements or by visual observation under a microscope using the Pockels effect.

3. Ferrimagnetism

Suppose a spinel with antiferroelectric domain symmetry $F\bar{4}3m$ undergoes a phase transition that leads to ferrimagnetism (and no further structural transition, such as that from $Fd3m$ to $F\bar{4}3m$, occurs). What, then, are the possible symmetries of ferrimagnetic domains?

They are given by the *M*-maximal subgroups of $F\bar{4}3m$, the prototype group for the ferrimagnetic transition. *M*-maximal subgroups are subgroups leaving a magnetization vector *M* invariant, but which are not contained in any other subgroup having this property. Those of $F\bar{4}3m$ are $I\bar{4}$, Bm and $R3$, the directions of easy magnetization being [100], [110], and [111], respectively. Such results can be obtained from (i) a knowledge of the *M*-maximal subgroups of the point groups (Ascher 1965) and (ii) the lattices of subgroups of the space groups (Ascher 1968a). In figure 3 we show the lattice of subgroups of $F\bar{4}3m$. Numbers on lines connecting two groups indicate the number of times the lower one is contained in the upper one (the number one always being omitted). The *M*-maximal subgroups of $F\bar{4}3m$ are placed in a box.

If we want to know the magnetic symmetry of these phases, we have to remember that
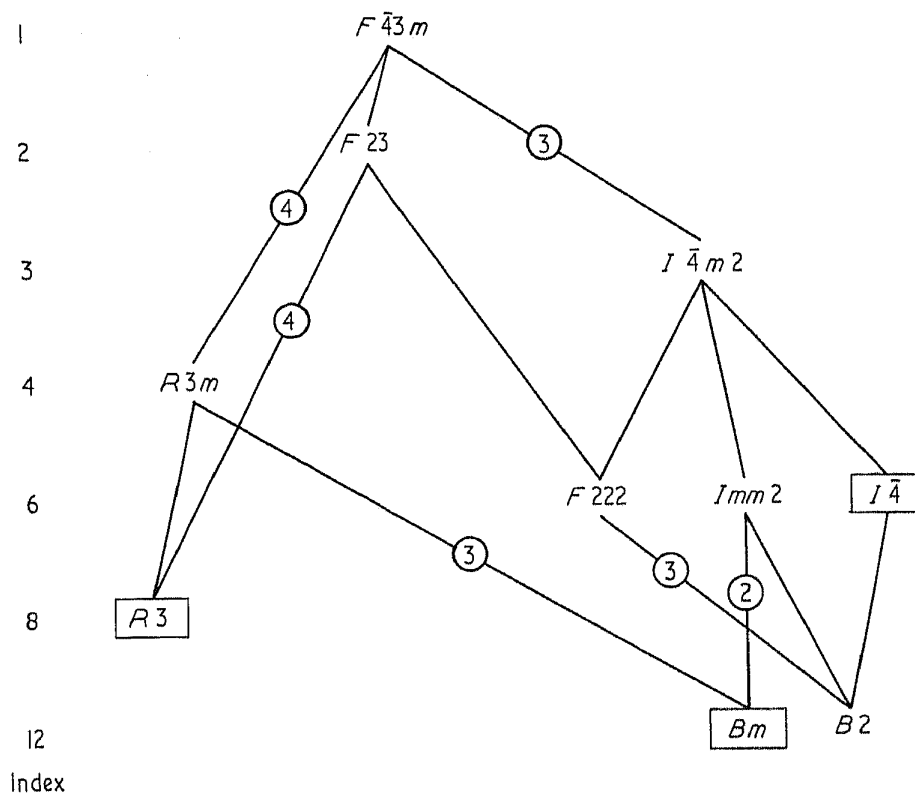
Figure 3. Lattice of subgroups of $F\bar{4}3m$. The M-maximal subgroups are placed in a box.

the groups we have found above are subgroups, H, of index 2 of the respective magnetic groups G, and that all elements of G that are not in H, comprise time reversal. Let us write $G(H)$ for such a group. Then by inspection of figure 4, we find that the magnetic groups we are looking for are:

$$I\bar{4}m2(I\bar{4}) \qquad Imm2(Bm) \qquad R3m(R3).$$

From this we deduce the international notation for these groups:

$$I\bar{4}m'2' \qquad Im'm2' \qquad R3m'.$$

This can also be found in Koptsik's table of two-term symbols for Shubnikov groups (Koptsik 1966). These groups are M-maximal subgroups of $F\bar{4}3m1'$ and are underlined in the lattice of subgroups of this group (figure 4). Notice that this lattice, of course, contains the lattice shown in figure 3 as a sublattice (the latter is drawn with heavy lines).

Besides being ferrimagnetic, all these phases inherit piezoelectricity from the cubic phase; however, only the tetragonal phase ($I\bar{4}m'2'$) remains antiferroelectric as the cubic one is supposed to be. The orthorhombic ($Im'm2'$) and the trigonal phase ($R3m'$) become ferroelectric. Furthermore, all three phases would be magnetoelectric and piezomagnetic and would exhibit the higher-order magnetoelectric effects corresponding to the coefficients α_{ijk} and β_{ijk} (Ascher 1968b). It should, however, be kept in mind that, for a fixed direction of magnetization, there are two antiferroelectric domains. The average properties of these two unresolved domains are those given by the higher symmetry of the M-maximal subgroups of $Fd3m$. Thus the above-mentioned new properties can be observed only if, by an appropriate 'poling' procedure, we are able to produce (simultaneous magnetic *and* electric) single domains.

In contrast to these findings it is useful to remember that none of the tetragonal

$(I4_1/am'd')$, orthorhombic $(Im'm'a)$ or trigonal phases $(R\bar{3}m')$ of spinels, with the usual cubic prototype symmetry $Fd3m$, is ferroelectric, magnetoelectric or piezoelectric. Therefore, it would be worthwhile to look for ferrimagnetism in spinels with cubic symmetry $F\bar{4}3m$.
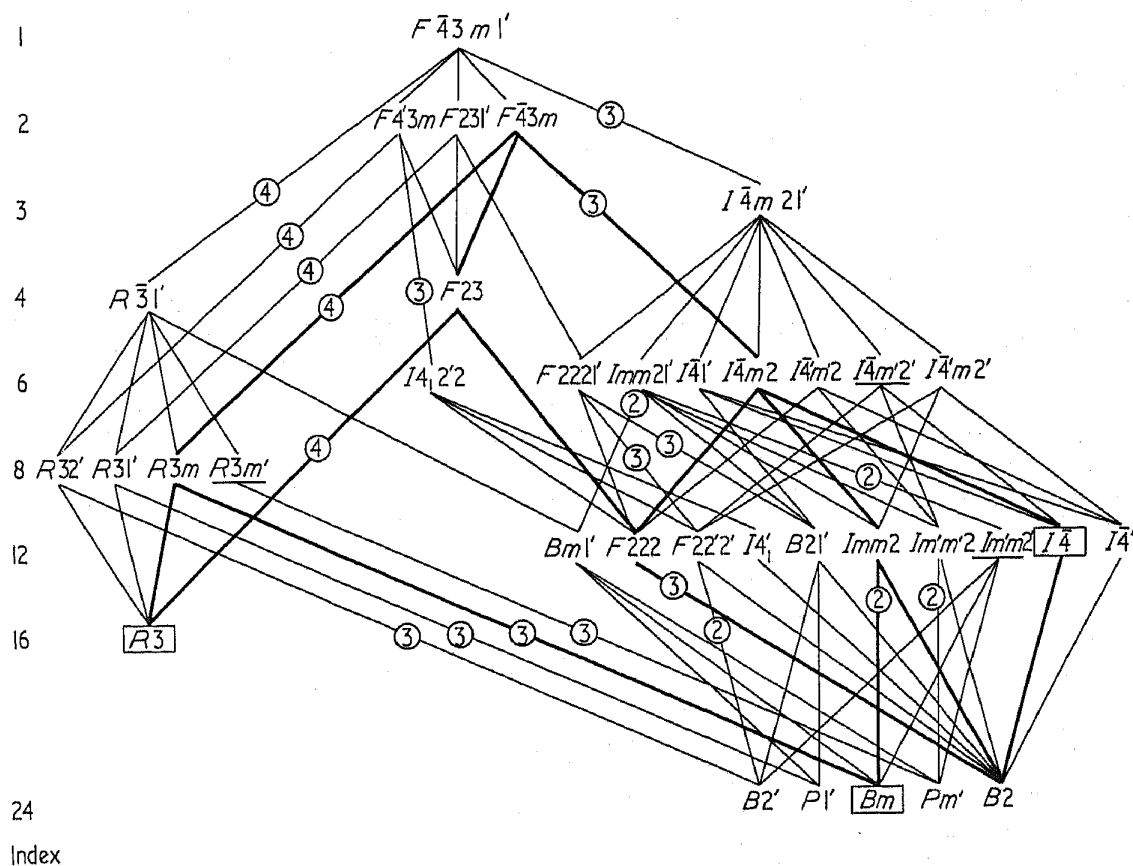

Figure 4. Lattice of subgroups of $F\bar{4}3m1'$. The M-maximal subgroups are placed in a box. The sublattice of subgroups of $F\bar{4}3m$ is drawn with heavy lines and the M-maximal subgroups of this group are underlined.

Good candidates for finding magnetoelectric phases in ferrimagnetic spinels would be $MgFe_2O_4$ and $MnFe_2O_4$. Antiferroelectricity may possibly be found in $MgFe_2O_4$, $MnFe_2O_4$ and $MgAl_2O_4$; these three compositions show the reflections $h + k = 4n + 2$. The success of the proposed experiments would of course depend on the possibility of producing highly insulating compositions to allow the application of the necessary electric fields. Some candidates for the simultaneous occurrence of ferroelectricity and ferrimagnetism among hausmannite type compounds (distorted spinels) were tabulated by Cox (1974).

Though an enormous effort on the technological development of many ferrimagnetic spinel compositions has been made in the past, it is astonishing that reliable data on their magnetic space groups are only very scanty (see, for example, Kucab 1972). This is certainly due, in part, to the limitations of the neutron-diffraction technique which were pointed out by Cox (1974). It is expected that much progress in this field will be made if the virtues of neutron. *and* x-ray, *and* electron diffraction, *and* those of magnetoelectric, piezoelectric etc measurements are combined for experiments on samples being electrically *and* magnetically *and* mechanically true single domains.

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