

(v) Classes 622 , $6mm$, $\bar{6}2m$, $6/mmm$

$$d_{ijk} = d[v_{3k}(v_{1i}v_{2j} - v_{2i}v_{1j}) + v_{3j}(v_{1i}v_{2k} - v_{2i}v_{1k})]. \quad (43)$$

Cubic system

(i) Classes 23 , $m\bar{3}$, $\bar{4}3m$, $m\bar{3}m$

$$d_{ijk} = d(v_{1i}v_{2j}v_{3k} + v_{1i}v_{3j}v_{2k} + v_{2i}v_{3j}v_{1k} + v_{2i}v_{1j}v_{3k} + v_{3i}v_{1j}v_{2k} + v_{3i}v_{2j}v_{1k}). \quad (44)$$

The form-invariant expressions for β_{ij} and d_{ijk} obtained in the case of various magnetic crystal classes are referred to a Cartesian coordinate system with respect to which the triad v_1, v_2, v_3 has an arbitrary orientation. However, when conventional choice (Bhagavantam, 1966) of the Cartesian system is made, the form-invariant expression furnished above gives the appropriate number of non-vanishing components d_{ijk} , as demonstrated in the case of (30). A similar check can be made in the case of expressions for β_{ij} and d_{ijk} corresponding to other classes.

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Shubnikov Point Groups and the Property of 'Ferroelasticity'

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Previously the concept of ferroelasticity, introduced by Aizu, has only been studied in connexion with classical point groups. In this paper the use of this concept is extended to the Shubnikov point groups; this is important in connexion with ferroelectric phase transitions and various kinds of magnetic phase transition. Tables are given which enable all ferroelastic species to be identified.

1. Introduction

The concept of a 'ferroelastic' crystal was introduced by Aizu (1969) and it is relevant to the discussion of displacive phase transitions. By the term 'displacive' phase transition we mean a phase transition which does not involve any major structural rearrangement of the atomic positions in a crystal, but involves only rather small displacements of the equilibrium positions of the atoms. These displacements will generally be accompanied by a reduction in the symmetry of the crystal and displacive phase transitions may also be ferroelectric transitions but need not necessarily be so. The concept of ferroelasticity, its relationship to the phenomenon of ferroelectricity, and the examination of the symmetries of ferroelastic crystals described by Aizu (1969) was restricted to materials with the symmetry of one of the 32 classical point groups. It

seemed to be desirable to extend Aizu's work to the Shubnikov point groups for two reasons. First, there are many possible ferroelectric symmetries which are described by Shubnikov point groups (Neronova & Belov, 1959; Ascher, 1970; Schelkens, 1970; Zheludev, 1971). Secondly, it would seem to be profitable to extend the use of the concept of 'ferroelasticity' in connexion with magnetic phase transitions, which would also involve the use of Shubnikov point groups.

In many magnetic crystals the onset of magnetic ordering is accompanied by a magnetostrictive distortion of the crystal structure, with a consequent reduction in the symmetry of the crystal. There may be several possible choices of direction for the preferred orientation associated with the magnetic ordering, with the resultant occurrence of magnetic domains even within a crystal that was a single crystal in its non-magnetic phase. The relevance of the concept of ferro-

elasticity to magnetic phase transitions can be seen from the fact that the application of mechanical stress to a single-crystal specimen, while it undergoes the transition from the non-magnetic state to the magnetically ordered state, is one of the ways of attempting to produce single-domain single-crystal specimens of magnetic materials. If a magnetic phase transition only involved an ordering of the magnetic moments of the atoms in a crystal, without any associated magnetostrictive distortion, the concept of ferroelasticity would not be relevant to magnetic phase transitions. It is common to regard most magnetic phase transitions as continuous (*i.e.* second-order) phase transitions, or at least approximately continuous phase transitions. There are, however, a number of examples of magnetic phase transitions which are actually discontinuous (*i.e.* first-order) phase transitions and which are accompanied by significant magnetostrictive distortions [see for example the tables given by Grazhdankina (1968) and Pál (1969)]; it is in connexion with this type of magnetic phase transition that the concept of ferroelasticity can also be expected to be useful.

2. The determination of the possible symmetries of ferroelastic crystals

There is an analogy between the property of ferroelasticity and the properties of ferroelectricity and of ferromagnetism. It is common to regard a ferroelectric crystal as a crystal in which there exists a spontaneous electric polarization \mathbf{P} in the absence of an external electric field. Using the well known theory of the symmetries of the tensor properties of crystalline materials (Nye, 1957; Birss, 1966) it is possible to show that for a large number of the Shubnikov point groups a polar i -vector, such as \mathbf{P} , must be null. Of all the 122 Shubnikov point groups there are only 31 in which ferroelectricity is possible (Neronova & Belov, 1959) and the list of these groups is reproduced in Table 1(a).

Table 1. *Ferroelectric and ferromagnetic point groups*

(a) Ferroelectric

Type I	Type II	Type III
1	1'	
2	21'	2'
m	$m1'$	m'
$mm2$	$mm21'$	$m'm2' m'm'2'$
4	41'	4'
$4mm$	$4mm1'$	$4'mm' 4m'm'$
3	31'	
$3m$	$3m1'$	$3m'$
6	61'	6'
$6mm$	$6mm1'$	$6'm'm 6m'm'$

(b) Ferromagnetic.

Type I	Type III
1 $\bar{1}$	
2 m $2/m$	$2' m' 2'/m' 2'2'2' m'm'2' m'm'2' m'm'm'$
3 $\bar{3}$	$32' 3m' \bar{3}m'$
4 $\bar{4}$ $4/m$	$42'2' 4m'm' \bar{4}2'm' 4/mn'm'$
6 $\bar{6}$ $6/m$	$62'2' 6m'm' \bar{6}m'2' 6/mn'm'$

In a similar manner it is possible to show that there are also 31 Shubnikov point groups which describe structures in which ferromagnetism is possible, see Table 1(b); these are the point groups in which \mathbf{M} , the magnetization, which is represented by an axial c -vector need not necessarily vanish.

In connexion with Table 1(a) it is perhaps worth mentioning that in the literature there are two different ways of interpreting the operation of anti-symmetry when using the Shubnikov groups to describe ferroelectric crystals. One possibility, which is the one used in Table 1(a), is to use the operation of antisymmetry with the same meaning that is commonly assigned to it in connexion with the description of magnetic symmetries, that is, the operation of antisymmetry is taken as being θ , the operation of time inversion. In the alternative interpretation, which is used by a number of authors (Neronova & Belov, 1959; Zheludev, 1971), when the operation of antisymmetry is used in connexion with ferroelectric crystals it is used to mean the operation of reversing the electric dipole moment \mathbf{P} . In this interpretation the symbols of many of the 31 ferroelectric point groups will be different from the symbols given in Table 1(a). Our reason for using the convention adopted is connected with the fact that to obtain a satisfactory explanation of some physical phenomenon, in microscopic terms, one almost inevitably becomes involved in the use of wave functions at some stage in the discussion. Therefore, in the case of ferroelectricity, the advantage of retaining the same meaning for the operation of antisymmetry as θ , the operation of time inversion, which is commonly used in the description of magnetic symmetry, is that the effect of θ on wave functions is well known and can easily be determined [see, for example, Bradley & Cracknell (1972)].

The consideration of the property of ferroelasticity from the viewpoint of symmetry studies differs from ferroelectricity and ferromagnetism in one rather important respect. The question of the possibility of the existence of ferroelectricity or of ferromagnetism in a crystal with the symmetry of some given point group is determined by the transformation properties of certain tensors of rank one under the operations of that point group. The possibility of the existence of ferroelectricity or of ferromagnetism in any given point group \mathbf{G} is therefore a property of that point group \mathbf{G} itself and is independent of the point group which describes the symmetry of the paraelectric or paramagnetic phase of the crystal and which, generally, is some supergroup of \mathbf{G} . Therefore in connexion with Table 1 which lists the possible symmetries of ferroelectric and ferromagnetic crystals, there is no consideration given to the symmetry of the crystal in the high-temperature phase. However, in the case of ferroelasticity the symmetry restrictions on the existence of ferroelasticity do not simply consist of determining the form of a certain tensor in a given point group. Neither is the property of ferroelasticity a property of a point

group G on its own, but rather it is a property of G considered in relation to some given prototypic group which is a supergroup of G . To clarify this we recall the explanation of the concept of ferroelasticity, as developed by Aizu (1969).

Instead of regarding a ferroelectric or ferromagnetic crystal as a crystal in which there is a non-zero vector, P or M , there is an alternative approach which is more illuminating in connexion with the introduction of the concept of ferroelasticity. If a certain specimen is ferroelectric it can be regarded as being capable of existing in either of two 'orientation states', with polarizations P and $-P$ in the absence of an external electric field. It is then possible to 'flip' the polarization of the specimen from P to $-P$ (or from $-P$ to P) by the application and subsequent removal of an appropriate external electric field. Similarly, a ferromagnetic crystal can be regarded as a crystal which is capable of existing in either of two states with magnetization M and $-M$, where the magnetization of the specimen can be flipped from one value to the other by a suitable external magnetic field. In the case of ferroelasticity the polarization P or the magnetization M is replaced by the mechanical strain which is a tensor of rank two. Similarly the external electric field, or magnetic field, which can be used to 'flip' a specimen between the two orientation states $\pm P$, or $\pm M$, is replaced by an external mechanical stress, which is also a tensor of rank two. In the definition of *ferroelasticity* (Aizu, 1969): 'A crystal is said to be *ferroelastic* when it has two or more orientation states in the absence of mechanical stress, or of other external fields, and can be made to change from one to another of these states by a mechanical stress.' Thus, suppose that a certain cubic material undergoes a displacive phase transition to a tetragonal structure with c/a very close to unity, as occurs, for example, in V_3Si at a temperature of about $20.5^\circ K$. If one starts with a single-crystal specimen of the cubic phase there will be three possible choices of direction for the fourfold axis of the tetragonal phase and, therefore, also the possibility of the existence of 'domains'. However, suppose that the whole crystal has been induced to produce a single crystal of the tetragonal phase with the four-fold axis along the x axis of the cubic phase. Then if it is possible, by the application of an external mechanical stress, to 'flip' the specimen's distortion so that the fourfold axis is now along either the y axis or the z axis of the cubic phase the material would provide an example of ferroelasticity. This demonstrates that ferroelasticity is not just a property of the point group G of the tetragonal phase, but of the fact that this point-group symmetry arises in this particular example in a material which is only very slightly distorted from a structure with a higher symmetry. Thus in constructing a table of point groups in which ferroelasticity may exist it is, therefore, necessary to specify the appropriate supergroup; this is done for the classical point groups in Table 2 of Aizu (1969).

3. Tabulation of results

Suppose that a certain point group G describes the symmetry of a specimen of a crystal which can be regarded as obtained by only a small distortion of a structure that possesses the symmetry of another point group G_p , which is a supergroup of G and which is described as the 'prototypic point group' of G in this structure. Suppose also that one orientation state of a given ferroelastic crystal is labelled as S_1 ; then each of the operations of the supergroup G_p either regenerates S_1 or generates one of a number of other orientation states S_2, S_3, \dots . Ferroelasticity will be forbidden if the form of the tensor representing elastic strain is identical for the various orientation states S_1, S_2, S_3, \dots . An alternative but equivalent approach would be to say that ferroelasticity is forbidden unless the tensor representing elastic strain takes a simpler form in G_p than in G . By 'taking a simpler form' we mean that there are some components which are required by symmetry to vanish or to be equal to other components.

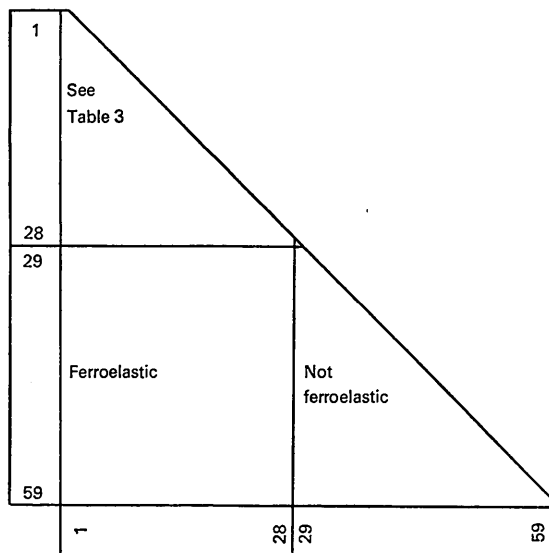
These conditions were applied to the classical point groups and the results were tabulated in Table 2 of the paper by Aizu (1969). We have now extended the use of these conditions to determine similar tables for all the Shubnikov point groups. In this connexion we have made extensive use of the subgroup tables given by Ascher & Janner (1965). We also note, of course, that the elastic strain is represented by a symmetric polar i -tensor of rank 2 and that, therefore, the form of the elastic strain tensor for any given Shubnikov point group can easily be obtained by using Table 7 of the book by Birss (1966). It can be seen from Table 7 of Birss (1966) that the form taken by a symmetric polar i -tensor of rank 2 is the same for all the Shubnikov point groups in any given crystal system (see Table 2). The condition for the possibility of the existence of ferroelasticity is that the species G_pFG will have the possibility of being ferroelastic if G is a subgroup of G_p and if G and G_p belong to different crys-

Table 2. *General forms of symmetric second-rank polar i -tensors in each of the Shubnikov point groups*

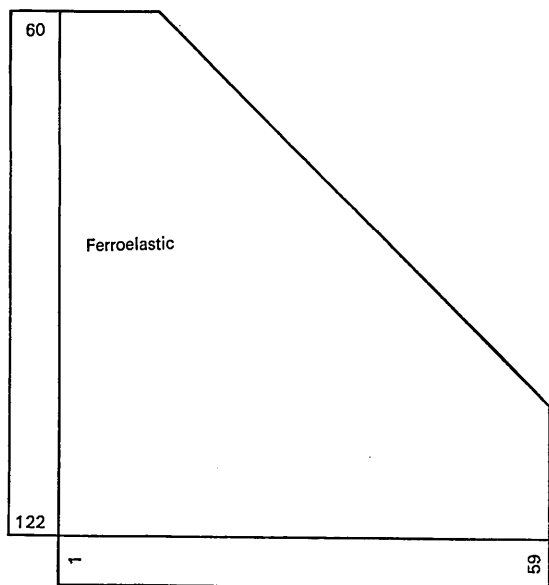
Crystal system	ϵ_{ij}
Triclinic	$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{12} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{13} & \epsilon_{23} & \epsilon_{33} \end{pmatrix}$
Monoclinic	$\begin{pmatrix} \epsilon_{11} & \epsilon_{12} & 0 \\ \epsilon_{12} & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$
Orthorhombic	$\begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$
Trigonal, tetragonal, hexagonal	$\begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{33} \end{pmatrix}$
Cubic	$\begin{pmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{11} \end{pmatrix}$

on the view that a species G_PFG is not able to be ferroelastic if there exists any F-operation [that is any operation of the set $(G_P - G)$] which leaves the strain tensor of an orientation state S_1 unchanged. We take the alternative, and not necessarily equivalent, view that

Table 4. Identification of ferroelastic species for groups 29 to 122

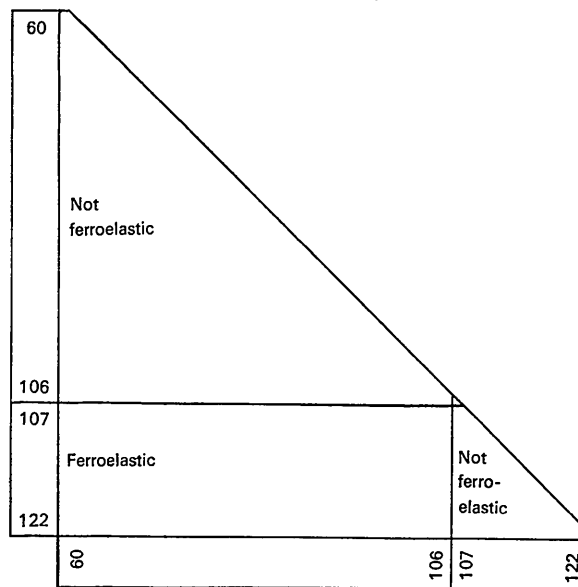


(a)



(b)

Table 4 (cont.)



(c)

Tables 4(a), 4(b) and 4(c) are to be regarded as superimposed on Tables 3(a), 3(b) and 3(c) of Ascher & Janner (1965). For a species G_PFG to be ferroelastic (i) G must be a subgroup of G_P , and (ii) the entry in the row and column labelled by G_P and G respectively, must occur in one of the blocks indicated above as ferroelastic.

a species G_PFG is not able to be ferroelastic if all the F-operations [that is all the operations of the set $(G_P - G)$] leave the form of the strain tensor of an orientation state S_1 unchanged.

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