Higher-order Magneto-electric Effects

By Edgar Ascher
Battelle Institute, Advanced Studies Center,
Geneva, Switzerland

[Received 11 September 1967]

Abstract

Effects related to the terms $\alpha_{ijk}H_iE_jE_k$ and $\beta_{ijk}E_iH_jH_k$ in the Gibbs function are discussed, especially in relation to the measurement by O'Dell, of a magneto-electric effect induced by an electric field. It is pointed out that it would be interesting to establish (**H**, T) phase diagrams.

---

§ 1. Introduction

Recently O'Dell (1967) has confirmed the existence of rather strong higher magneto-electric effects in a ferrimagnetic material that shows no ordinary magneto-electric effect. This result was presented in the above paper as induced magneto-electric effect, i.e. as a lowering of the symmetry of a magnetic crystal by the application of a (strong) electric field. We want to show that it is more convenient to consider the effect as higher-order magneto-electric effect; it is thus possible to give more precise expressions for the measured quantities, to compare the quantities measured under different conditions, and to relate the effect to other effects. It then also becomes clear in which crystal classes the symmetry can be forced into one of 58 magneto-electric crystal classes and what strong electric field would mean within this context.

§ 2. Higher-order Magneto-electric Effects in Y.I.G.

Consider the Gibbs function. The magneto-electric effect proper corresponds to terms:

$$\alpha_{ij}E_iH_j. \qquad (1)$$

(Here and elsewhere, the summation convention applies to indices appearing in two different positions.) The succeeding mixed terms have the form:

$$\tfrac{1}{2}\alpha_{ijk}H_iE_jE_k. \qquad (2)$$

and

$$\tfrac{1}{2}\beta_{ijk}E_iH_jH_k. \qquad (3)$$

The tensor α_{ijk} has components different from zero in all crystal classes that permit piezo-magnetism, whereas the tensor β_{ijk} is different from zero in all piezo-electric crystal classes.

Thus in the case of Y.I.G., β_{ijk} is zero, but α_{ijk} may have components different from zero. More generally there exists a magneto-electric effect induced by an electric field in all ferri or ferromagnetic crystals. Similarly in all ferro-electric crystals, the application of a magnetic field will produce an induced magneto-electric effect. In an appendix to this paper the tensors characterizing both kinds of induced magneto-electric effect are given. Here we want to discuss in detail only the induced magneto-electric effect in Y.I.G.

The point group of ferrimagnetic Y.I.G. is $\bar{3}$m′. (The space group is R$\bar{3}$c′.) The relevant invariants are:

$$H_3E_3^2,\ H_3(E_1^2+E_2^2),\ H_2(E_2^2-E_1^2)-2H_1E_1E_2,\ H_2E_2E_3+H_1E_1E_3. \quad (4)$$

The formula giving the electrical polarization due to these terms is then:

$$P_i=\bar{\alpha}_{ik}H_k. \quad (5)$$

and the corresponding contribution to the Gibbs function may be written $\bar{\alpha}_{ik}E_iH_k$ so as to exhibit explicitly the induced magneto-electric tensor $\bar{\alpha}_{ik}$. It is easily found that the tensor has the following form:

$$\bar{\alpha}_{ik}=\begin{bmatrix} -\alpha_{222}E_2+\frac{1}{2}\alpha_{113}E_3 & -\alpha_{222}E_1 & \alpha_{311}E_1 \\ -\alpha_{222}E_1 & \alpha_{222}E_2+\frac{1}{2}\alpha_{113}E_3 & \alpha_{311}E_2 \\ \frac{1}{2}\alpha_{113}E_1 & \frac{1}{2}\alpha_{113}E_2 & \alpha_{333}E \end{bmatrix}. \quad (6)$$

The x_3-axis is that of the three-fold axis (one of the body diagonals of the cube), the x_1-axis is perpendicular to one of the three elements m′ (one of the face diagonals of the cube), and the x_2-axis is chosen so as to make, together with the two former, a right-handed coordinate system. For all domains having the symmetry $\bar{3}$m′ we shall use such a coordinate system.

In O'Dell's experiments, the electric field is always applied along the cubic [110] direction. Then three possibilities arise for the angle between the electric field and the domain magnetization; two possibilities will be discussed in this section, the third in the next one.

(i) *The domain is magnetized along the* [1$\bar{1}$1] *or along the* [1$\bar{1}\bar{1}$] *direction.* The electric field is then perpendicular to the magnetization and has (in the coordinate system we have chosen above) the components:

$$E_1=E,\quad E_2=E_3=0. \quad (7)$$

The polarization due to this field is parallel to it:

$$P_1=\epsilon_{11}E_1,\quad P_2=P_3=0. \quad (8)$$

and the Shubnikov point group of the crystal with that polarization is indeed 2′ (as stated by O'Dell). The induced magneto-electric tensor is:

$$\bar{\alpha}_{ik}=E\begin{bmatrix} 0 & -\alpha_{222} & \alpha_{311} \\ -\alpha_{222} & 0 & 0 \\ \frac{1}{2}\alpha_{113} & 0 & 0 \end{bmatrix}. \quad (9)$$

For a magnetic field parallel to the electric field, the polarization resulting. from (5) is then:

$$P_1 = P_2 = P_3 = 0. \quad \ldots \quad (10)$$

(ii) *The domain is magnetized along the* [111] *or along the* [11$\bar{1}$] *direction.* The electric field is then not perpendicular to the magnetization (but makes an angle arc tg $1/\sqrt{2} \approx 35°$ with [110]). The electric field thus has the components:

$$E_1 = 0, \quad E_2 = \frac{1}{\sqrt{3}} E, \quad E_3 = \sqrt{\tfrac{2}{3}} E = \sqrt{2} E_2. \quad \ldots \quad (11)$$

The polarization due to this field is not parallel to it:

$$P_1 = 0, \quad P_2 = \frac{1}{\sqrt{3}} \epsilon_{22} E, \quad P_3 = \sqrt{\tfrac{2}{3}} \epsilon_{33} E = \sqrt{2} \frac{\epsilon_{33}}{\epsilon_{22}} P_2, \quad (12)$$

because generally $\epsilon_{33} \neq \epsilon_{22}$ for the point group $\bar{3}$m′. Thus the crystal does not become polarized along [110], and the Shubnikov point group of the crystal with the polarization is not m′ (compare O'Dell 1967). The induced magneto-electric tensor is now:

$$\bar{\alpha}_{ik} = \frac{1}{\sqrt{3}} E \begin{bmatrix} -\alpha_{222} + \frac{\sqrt{2}}{2} \alpha_{113} & 0 & 0 \\ 0 & \alpha_{222} + \frac{\sqrt{2}}{2} \alpha_{113} & \alpha_{311} \\ 0 & \frac{1}{2} \alpha_{113} & \sqrt{2} \alpha_{333} \end{bmatrix} \quad (13)$$

For a magnetic field parallel to the electric field, the polarization resulting from (5) is:

$$\left. \begin{aligned} P_1 &= 0, \\ P_2 &= \bar{\alpha}_{22} H_2 + \bar{\alpha}_{23} H_3 = \tfrac{1}{3} E H \left(\sqrt{2} \alpha_{311} + \frac{\sqrt{2}}{2} \alpha_{113} + \alpha_{222} \right), \\ P_3 &= \bar{\alpha}_{32} H_2 + \bar{\alpha}_{33} H_3 = \tfrac{1}{3} E H (2 \alpha_{333} + \tfrac{1}{2} \alpha_{113}), \end{aligned} \right\} \quad (14)$$

so that the magneto-electric polarization is not parallel to the applied magnetic field.

The peak polarization in O'Dell's experiments is given by:

$$\frac{1}{E} (P_2 E_2 + P_3 E_3) = \frac{1}{3\sqrt{3}} E H [2\sqrt{2} \alpha_{333} + \sqrt{2} (\alpha_{311} + \alpha_{113})]. \quad . \quad (15)$$

A similar experiment performed on a (111) platelet would yield a peak value depending on a single coefficient, probably the largest, viz.

$$P_3 = \alpha_{333} E H, \quad \ldots \quad (16)$$

and an application of high biasing magnetic fields would not decrease the measured polarization.

In the original experiment, the signal does decrease to zero in sufficiently high biasing fields. An adequate explanation of this finding probably cannot be given without performing further experiments. The questions involved seem to be most interesting and have not been gone into for too long.

§ 3. The (**H**, T) Phase Diagram

By applying a sufficiently high magnetic field, the magnetization of the specimen in O'Dell's experiments is along the [110] direction, parallel to the applied electric field. It is not possible, however, to say *a priori* what the symmetry of the domain is under these circumstances. There are two possible cases.

One case arises when the applied magnetic field induces a phase transition from m3ml′ (the Shubnikov point group of paramagnetic Y.I.G.) to m′m′m, a maximal **M**-subgroup of the former. The latter symmetry permits a magnetization in a [110] direction. If now an electric field is applied along the same [110] direction, a polarization ($\epsilon_{33}E_3$) arises that is parallel to the electric field, and the symmetry of the magnetically and electrically polarized domain is m′m′2 (as indicated by O'Dell 1967), a maximal **P**–subgroup of m′m′m. But then the magnetization is not rotated against the anisotropy from [110] towards [110], because [110] is the direction of easy magnetization for the symmetry m′m′m (and m′m′2) and because the [111] direction is a quite general direction for these symmetries and no relative minimum of the anisotropy energy is associated with it. The relevant symmetry for the electrically induced magneto-electric effect is m′m′m. For this symmetry, the tensor α_{ijk} has all components zero, so that the measured signal and the induced magneto-electric tensor are both strictly zero.

If, in the other case, the magnetization *is* rotated against the anisotropy, this means that in the [111] direction there is still a relative minimum of the anisotropy energy and that the intrinsic symmetry of the domain is still $\bar{3}$m′; then the symmetry of the domain with the magnetization in the [110] direction is $\bar{1}$. The superposition of an electrical field parallel to the magnetization will reduce the symmetry to 1, but the polarization is not necessarily parallel to the magnetization. The symmetry $\bar{1}$ imposes no symmetry restrictions on the tensor α_{ijk}. The components of the induced magneto-electric tensor $\bar{\alpha}_{ik}$ are given by:

$$\bar{\alpha}_{ij}=\tfrac{1}{2}\tilde{\alpha}_{ijk}E_k, \qquad (17)$$

where

$$\tilde{\alpha}_{ijk}=\left\{\begin{matrix}\alpha_{ijk}, & k\neq j\\ 2\alpha_{ijk}, & k\neq j\end{matrix}\right\}. \qquad (18)$$

Taking the x_3-axis parallel to [110], the measured polarization will be:

$$P_3=\bar{\alpha}_{33}H=\alpha_{333}EH. \qquad (19)$$

The coefficient α_{333} appearing should not be confused with that in relation (16). The symmetry of the crystal and the coordinate system are different. There the effect is probably large, here it is probably very small if not quite negligible.

Thus the two cases discussed in this section presumably cannot be distinguished on the basis of the measurement of the induced magneto-electric effect. From the above discussion there results moreover that a measurement of the anisotropy energy would allow this distinction to be made. If there is no relative minimum in the [111] direction, a magnetic field applied along the [110] direction induces a (first-order) phase transition from $\bar{3}m'$ to $m'm'm$; if a relative minimum is found in the [111] direction, no phase transition is induced by the applied magnetic field.

More generally, and in a more fruitful way, the problem should be dealt with on its own merits and amounts exactly to the determination of the relevant $(\mathbf{H}, T)$ phase diagrams. Here the magnetic field replaces the pressure of the usual phase diagram. A separate phase diagram should be established for each crystallographically significant direction of the magnetic field $\mathbf{H}$. These phase diagrams (and the analogous ones for ferro-electric and supraconductive transitions) have not received as yet sufficient attention.

§ 4. Other Effects Depending on the Coefficients α_{ijk} and β_{ijk}

The following effects depend (obviously) on the coefficients α_{ijk} and hence provide alternative means of measuring these coefficients.

(i) The existence of terms in the electric susceptibility tensor that depend linearly on an applied magnetic field. In the case of Y.I.G. with the symmetry $\bar{3}m'$, these terms are:

$$\kappa_{ik} = \begin{bmatrix} -\alpha_{222}H_2 + \alpha_{311}H_3 & -\alpha_{222}H_1 & \tfrac{1}{2}\alpha_{113}H_1 \\ -\alpha_{222}H_1 & \alpha_{222}H_2 + \alpha_{311}H_3 & \tfrac{1}{2}\alpha_{113}H_2 \\ \tfrac{1}{2}\alpha_{113}H_1 & \tfrac{1}{2}\alpha_{113}H_2 & \alpha_{333}H_3 \end{bmatrix},$$

whereas the ordinary electric susceptibility has only the terms κ_{33} and $\kappa_{11} = \kappa_{22}$ different from zero.

(ii) The quadratic magneto-electric effect given by:

$$M = \tfrac{1}{2}\alpha_{ijk}E_jE_k.$$

Similarly, the following effects depend on the coefficients β_{ijk}.

(iii) The existence of terms in the magnetic susceptibility that depend linearly on an applied electric field.

(iv) The quadratic magneto-electric effect given by:

$$P_i = \tfrac{1}{2}\beta_{ijk}H_jH_k.$$

Without going into any details we shall mention one more effect.

(v) Harmonic generation and optical rectification. The electric field and the magnetic field of a linearly polarized electromagnetic wave interact through α_{ijk} to yield second-harmonic generation and electric optical rectification, whereas the existence of a tensor β_{ijk} gives rise to second-harmonic generation and magnetic optical generation. Thus in a single-domain crystal of Y.I.G. (with symmetry $\bar{3}$m′), an electromagnetic wave propagating in the x_1 directions and having the electric field in the x_2 direction (the magnetic field being in the x_3 direction) would give:

$$P_2(0) = \tfrac{1}{2}\alpha_{311}E_2H_3, \quad P_2(2\omega) = \tfrac{1}{2}\alpha_{311}E_2H_3\cos 2\omega t.$$

The effect should be very sensitive to the orientation of the linearly polarized electromagnetic wave.

APPENDIX

Survey of the Induced Magneto-electric Tensors

Here we give a survey of the electrically induced ($\bar{\alpha}_{ik}$) and of the magnetically induced ($\bar{\beta}_{ik}$) magneto-electric tensors for the Shubnikov crystal classes. Since to each crystal class admitting a given $\bar{\alpha}_{ik}$ there corresponds a crystal class that admits a tensor $\bar{\beta}_{ik}$ having the same form, a single listing is sufficient. The inducing field will be denoted by F, the tensors by $\bar{\zeta}_{ik}$ and ζ_{ijk}. In the case (α), this will mean:

$$F = E, \quad \bar{\zeta}_{ik} = \alpha_{ik}, \quad \zeta_{ijk} = \alpha_{ijk}$$

and

$$P = \bar{\alpha}_{ik}H_k,$$

whereas in the case (β), the meaning is:

$$F = H_1, \quad \bar{\zeta}_{ik} = \beta_{ik}, \quad \zeta_{ijk} = \beta_{ijk}$$

and

$$M = \bar{\beta}_{ik}E_k.$$

Among the listed twice 66 groups, twice 27 do not permit the ordinary magneto-electric effect. These are:

(α): $\bar{1}$, 2/m, 2′/m′, mmm, m′m′m, 4/m, $\bar{6}$, 6/m, 4′/m
4/mmm, $\bar{6}$m2, 6/mmm, 4′/mmm, 4/mmm, $\bar{6}$m′2′
6/mm′m′, $\bar{3}$, $\bar{3}$m, $\bar{3}$m′, 6′, 6′/m′, 6′2′2, 6′m′m
6/m′m′m, m3, 4′32′, m3m

(β): 1′, 21′, m1′, 2221′, mm21′, 41′, 6′, 61′, 41′
4221′, 6′2′2, 6224′, $\bar{4}$2m1′, 4mm1′, 6′mm′
6mm1′, 31′, 321′, 3m1′, $\bar{6}$, $\bar{6}$1′, $\bar{6}$m2, $\bar{6}$′m′2′
$\bar{6}$m21′, 231′, $\bar{4}$3m, $\bar{4}$3m1′

1. (α): 1, $\bar{1}$; (β): 1, 1′

$$\bar{\zeta}_{ik}=\tfrac{1}{2}\tilde{\zeta}_{ijk}E_k \quad \tilde{\zeta}_{ijk}=\begin{cases}\zeta_{ijk}, & k\neq j\\ 2\zeta_{ijk}, & k=j\end{cases}$$

2. (α): 2, m, 2/m; (β): 2, 2′, 21′

$$\begin{bmatrix}\tfrac{1}{2}\zeta_{112}F_2 & \zeta_{211}F_1+\tfrac{1}{2}\zeta_{231}F_3 & \tfrac{1}{2}\zeta_{312}F_2\\ \tfrac{1}{2}\zeta_{112}F_1+\zeta_{123}F_3 & \zeta_{222}F_2 & \tfrac{1}{2}\zeta_{312}F_1+\zeta_{332}F_3\\ \tfrac{1}{2}\zeta_{123}F_2 & \tfrac{1}{2}\zeta_{231}F_1+\zeta_{233}F_3 & \tfrac{1}{2}\zeta_{332}F_2\end{bmatrix}$$

3. (α): 2′, m′, 2′/m′; (β): m, m′, m1′

$$\begin{bmatrix}\zeta_{111}F_1+\tfrac{1}{2}\zeta_{113}F_3 & \tfrac{1}{2}\zeta_{221}F_2 & \zeta_{331}F_1+\tfrac{1}{2}\zeta_{331}F_3\\ \zeta_{122}F_2 & \tfrac{1}{2}\zeta_{221}F_1+\zeta_{223}F_3 & \zeta_{332}F_2\\ \zeta_{133}F_3+\tfrac{1}{2}\zeta_{112}F_1 & \tfrac{1}{2}\zeta_{223}F_2 & \tfrac{1}{2}\zeta_{331}F_1+\zeta_{333}F_3\end{bmatrix}$$

4. (α): 222, mm2, mmm; (β): 222, 2′2′2, 2221′

$$\begin{bmatrix}0 & \tfrac{1}{2}\zeta_{231}F_3 & \tfrac{1}{2}\zeta_{312}F_2\\ \tfrac{1}{2}\zeta_{123}F_3 & 0 & \tfrac{1}{2}\zeta_{312}F_1\\ \tfrac{1}{2}\zeta_{123}F_2 & \tfrac{1}{2}\zeta_{231}F_1 & 0\end{bmatrix}$$

5. (α): 2′2′2, m′m′2, m′m2′, mm′m′;
(β): mm2, m′m′2, m′m2′, mm21′

$$\begin{bmatrix}\tfrac{1}{2}\zeta_{113}F_3 & 0 & \zeta_{311}F_1\\ 0 & \tfrac{1}{2}\zeta_{223}F_3 & \zeta_{322}F_2\\ \tfrac{1}{2}\zeta_{113}F_1 & \tfrac{1}{2}\zeta_{223}F_2 & \zeta_{333}F_3\end{bmatrix}$$

6. (α): 4, $\bar{4}$, 4/m, 6, $\bar{6}$, 6/m; (β): 4, 4′, 41′, 6, 6′, 61′

$$\begin{bmatrix}\tfrac{1}{2}\zeta_{113}F_3 & -\tfrac{1}{2}\zeta_{123}F_3 & \zeta_{311}F_1\\ \tfrac{1}{2}\zeta_{123}F_3 & \tfrac{1}{2}\zeta_{113}F_3 & \zeta_{311}F_2\\ \tfrac{1}{2}\zeta_{113}F_1+\tfrac{1}{2}\zeta_{123}F_2 & -\tfrac{1}{2}\zeta_{123}F_1+\tfrac{1}{2}\zeta_{113}F_2 & \zeta_{333}F_3\end{bmatrix}$$

7. (α): 4′, $\bar{4}'$, 4′/m; (β) $\bar{4}$, $\bar{4}'$, 41′

$$\begin{bmatrix}\tfrac{1}{2}\zeta_{113}F_3 & \tfrac{1}{2}\zeta_{123}F_3 & \zeta_{311}F_1+\tfrac{1}{2}\zeta_{321}F_2\\ \tfrac{1}{2}\zeta_{123}F_3 & -\tfrac{1}{2}\zeta_{113}F_3 & \tfrac{1}{2}\zeta_{321}F_1-\zeta_{311}F_2\\ \tfrac{1}{2}\zeta_{113}F_1+\tfrac{1}{2}{}_{123}\zeta F_2 & \tfrac{1}{2}\zeta_{123}F_1-\tfrac{1}{2}\zeta_{113}F_2 & 0\end{bmatrix}$$

8. (α): 422, 4mm, $\bar{4}$2m, 4/mmm, 622, 6mm, $\bar{6}$m2, 6/mmm
(β): 422, 42′2′, 4′22′, 4221′, 622, 62′2′, 6′2′2, 6221′

$$\begin{bmatrix}0 & -\tfrac{1}{2}\zeta_{123}F_3 & 0\\ \tfrac{1}{2}\zeta_{123}F_3 & 0 & 0\\ \tfrac{1}{2}\zeta_{123}F_2 & -\tfrac{1}{2}\zeta_{123}F_1 & 0\end{bmatrix}$$

9. (α): 4′22′, 4′mm′, $\bar{4}$′2m′, $\bar{4}$′2′m, 4′/mmm

(β): $\bar{4}$2m, $\bar{4}$2′m′, $\bar{4}$′2m′, $\bar{4}$′2′m, $\bar{4}$2m1′

$$\begin{bmatrix} 0 & \frac{1}{2}\zeta_{123}F_3 & \frac{1}{2}\zeta_{321}F_2 \\ \frac{1}{2}\zeta_{123}F_3 & 0 & \frac{1}{2}\zeta_{321}F_1 \\ \frac{1}{2}\zeta_{123}F_2 & \frac{1}{2}\zeta_{123}F_1 & 0 \end{bmatrix}$$

10. (α): 42′2′, 4m′m′, $\bar{4}$2′m′, 4/mmm, 62′2′, 6m′m′, $\bar{6}$m′2′, 6/mm′m′

(β): 4mm, 4m′m′, 4′mm′, 4mm1′, 6mm, 6m′m′, 6′mm′, 6mm1′

$$\begin{bmatrix} \frac{1}{2}\zeta_{113}F_3 & 0 & \zeta_{311}F_1 \\ 0 & \frac{1}{2}\zeta_{113}F_3 & \zeta_{311}F_2 \\ \frac{1}{2}\zeta_{113}F_1 & \frac{1}{2}\zeta_{113}F_2 & \zeta_{333}F_3 \end{bmatrix}$$

11. (α): 3, $\bar{3}$; (β): 3, 31′

$$\begin{bmatrix} \zeta_{111}F_1 - \zeta_{222}F_2 + \frac{1}{2}\zeta_{113}F_3 & -\zeta_{222}F_1 - \zeta_{111}F_2 - \frac{1}{2}\zeta_{123}F_3 & \zeta_{311}F_1 \\ -\zeta_{222}F_1 - \zeta_{111}F_2 + \frac{1}{2}\zeta_{123}F_3 & -\zeta_{111}F_1 + \zeta_{222}F_2 + \frac{1}{2}\zeta_{113}F_3 & \zeta_{311}F_2 \\ \frac{1}{2}\zeta_{113}F_1 - \frac{1}{2}\zeta_{123}F_2 & -\frac{1}{2}\zeta_{123}F_1 + \frac{1}{2}\zeta_{113}F_2 & \zeta_{333}F_3 \end{bmatrix}$$

12. (α): 32, 3m, $\bar{3}$m; (β): 32, 32′, 321′

$$\begin{bmatrix} \zeta_{111}F_1 & -\zeta_{111}F_2 - \frac{1}{2}\zeta_{123}F_3 & 0 \\ -\zeta_{111}F_2 + \frac{1}{2}\zeta_{123}F_3 & -\zeta_{111}F_1 & 0 \\ \frac{1}{2}\zeta_{123}F_2 & -\frac{1}{2}\zeta_{123}F_1 & 0 \end{bmatrix}$$

13. (α): 32′, 3m′, $\bar{3}$m′; (β): 3m, 3m′, 3m1′

$$\begin{bmatrix} -\zeta_{222}F_2 + \frac{1}{2}\zeta_{113}F_3 & -\zeta_{222}F_1 & \zeta_{311}F_1 \\ -\zeta_{222}F_1 & \zeta_{222}F_2 + \frac{1}{2}\zeta_{113}F_3 & \zeta_{311}F_2 \\ \frac{1}{2}\zeta_{113}F_1 & \frac{1}{2}\zeta_{113}F_2 & \zeta_{333}F_3 \end{bmatrix}$$

14. (α): 6′, $\bar{6}$′, 6′/m′; (β): $\bar{6}$, $\bar{6}$′, $\bar{6}$1′

$$\begin{bmatrix} \zeta_{111}F_1 - \zeta_{222}F_2 & -\zeta_{222}F_1 - \zeta_{111}F_2 & 0 \\ -\zeta_{222}F_1 - \zeta_{111}F_2 & -\zeta_{111}F_1 + \zeta_{222}F_2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

15. (α): 6′2′2, 6′mm′, $\bar{6}$′m′2, $\bar{6}$′m2′, 6/m′m′m

(β): $\bar{6}$m2, $\bar{6}$m′2′, $\bar{6}$′m′2, $\bar{6}$m2′, $\bar{6}$m21′

$$\begin{bmatrix} -\zeta_{222}F_2 & -\zeta_{222}F_1 & 0 \\ -\zeta_{222}F_1 & \zeta_{222}F_2 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

16. (α): 23, m3, 4′32′, $\bar{4}$′3m′, m3m′

(β): 23, 231′, $\bar{4}$3m, $\bar{4}$′3m′, $\bar{4}$3m1′

$$\begin{bmatrix} 0 & \frac{1}{2}\zeta_{123}F_3 & \frac{1}{2}\zeta_{123}F_2 \\ \frac{1}{2}\zeta_{123}F_3 & 0 & \frac{1}{2}\zeta_{123}F_1 \\ \frac{1}{2}\zeta_{123}F_2 & \frac{1}{2}\zeta_{123}F_1 & 0 \end{bmatrix}$$

Reference

O'Dell, T. H., 1967, *Phil. Mag.*, **16**, 487.