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Second-Order Piezomagnetism in Polychromatic Crystals

By K. Rama Mohana Rao*

Department of Applied Mathematics, AUPG Extension Centre, Nuzvid 521201, *Andhra Pradesh, India*

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Abstract

The group-theoretical method established for obtaining the non-vanishing independent number of constants required to describe a magnetic/physical property in respect of the 18 polychromatic crystal classes [Rama Mohana Rao (1987). *J. Phys. A*, **20**, 47-57] has been explored to enumerate the second-order piezomagnetic coefficients (n_i') for the same classes. The advantage of Jahn's method [Jahn (1949). *Acta Cryst.* **2**, 30-33] is appreciated in obtaining these n_i' through the reduction of a representation. The different group-theoretical methods are illustrated with the help of the point group 4. The results obtained for all 18 classes are tabulated and briefly discussed.

1. Introduction

The non-vanishing independent first-order piezomagnetic constants (n_i) for the 90 magnetic classes [32 conventional point groups (G_k) and 58 double colour point groups (G_k')] were studied in detail by Bhagavantam (1966) and Bhagavantam & Suryanarayana (1949) using the character method (Bhagavantam, 1942) based on the computation of characters for deriving the number of independent constants for the description of various magnetic/physical properties. Jahn (1949), employing a general method also based on group theory, provided an alternative procedure for deriving these constants using the reduction of a representation corresponding to the physical property considered. The representation in each case was obtained in terms of the representation $\mathbf{V}_a$ or $\mathbf{V}_p$ of an axial or polar vector, depending on the nature of the physical property under question. Subsequently, Krishnamurty & Gopala Krishna Murty (1969) extended Jahn's method to find the second-order piezomagnetic coefficients for the 90 magnetic classes.

The non-vanishing first-order piezomagnetic constants (n_i) for the applicationally important polychromatic crystal classes $G_k^{(p)}$, $p = 3$, 4 or 6 (Indenbom, Belov & Neronova, 1960; Rama Mohana Rao, 1985), have already been derived in an earlier paper by the present author (Rama Mohana Rao, 1987). With the group-theoretical method (Rama Mohana Rao, 1987), the second-order piezomagnetic coefficients (n_i') are enumerated for these classes in this paper by computing the character for the 10 crystallographic point groups G_k that generate the 18 polychromatic classes $G_k^{(p)}$, $p = 3, 4$ or 6. To appreciate the advantage of Jahn's method, the non-vanishing second-order piezomagnetic coefficients are rederived in § 3 by the method of reduction of a representation and the results obtained through the former (character) method are compared. The different group-theoretical procedures are illustrated here, with the help of the point group 4 that induces the polychromatic class $4^{(4)}$. The results obtained for the rest of the 17 classes are tabulated in Table 1 and a brief discussion of the results is provided in § 4. The nomenclature adopted in this paper for the point groups is that of Hermann-Mauguin (International) and the notation for the polychromatic classes is that of Indenbom, Belov & Neronova (1960).

Table 1. *Second-order piezomagnetic coefficients needed by the* 18 *polychromatic crystal classes*

	Polychromatic class	Second-order piezomagnetic coefficients needed
1	$6^{(6)}$	12
2	$\bar{3}^{(6)}$	0
3	$3^{(3)}/m'$	12
4	$6^{(3)}$	9
5	$\bar{3}^{(3)}$	21
6	$3^{(3)}/m$	9
7	$6^{(6)}/m$	0
8	$6^{(3)}/m$	9
9	$6^{(6)}/m'$	12
10	$6^{(3)}/m'$	0
11	$3^{(3)}$	21
12	$4^{(4)}$	17
13	$\bar{4}^{(4)}$	17
14	$4^{(4)}/m$	0
15	$4^{(4)}/m'$	17
16	$3^{(3)}/2$	4
17	$\bar{6}^{(3)}/2$	4
18	$\bar{6}^{(6)}/2$	0

2. Second-order piezomagnetic coefficients of the polychromatic classes

Piezomagnetism is the appearance of a magnetic moment $\mathbf{M}$ (M_i, $i = 1, 2, 3$) on the application of stress σ. The occurrence of this phenomenon has already

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* Junior Associate Member at the International Centre for Theoretical Physics, Trieste, Italy.

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been verified and measured by Borovik-Romanov (1959) in the fluorides of cobalt and manganese in the anti-ferromagnetic state. The first-order piezomagnetic constants C_{ijk} are studied from the relation

$$M_i = \sum_j \sum_k C_{ijk} \sigma_{jk} \quad (i, j, k = 1, 2, 3), \tag{2.1}$$

where **M**, the magnetic moment, is an axial vector and σ is a second-rank symmetric polar tensor. The character $\chi^{(\Gamma)}(R_\varphi)$ corresponding to a symmetry operation R_φ, as given by Bhagavantam (1966), is

$$\chi^{(\Gamma)}(R_\varphi) = (4 \cos^2 \varphi \pm 2 \cos \varphi)(1 \pm 2 \cos \varphi) \tag{2.2}$$

with the usual convention for + or − signs, according as the symmetry operation is a pure rotation or a rotation-reflection.

The orientation of the magnetic moments of those magnetic structures that correspond to the piezomagnetic crystal classes have already been described by Koptsik (1966). It was actually shown that only 66 out of the 90 magnetic classes were piezomagnetic.* However, in respect of second-order piezomagnetism, Krishnamurty & Gopala Krishna Murty (1969) observed that 69 out of the 90 magnetic classes exhibit this phenomenon.

The non-vanishing independent first-order piezomagnetic coefficients in respect of the 18 polychromatic crystal classes have been obtained by Rama Mohana Rao (1987) and 13 of these classes were shown to be piezomagnetic. The second-order piezomagnetic coefficients for these 18 classes are enumerated in this section for the first time, using the character method, by considering the irreducible representation (IR) of the appropriate factor group G_k/H with the 10 crystallographic point groups (G_k) containing one-dimensional (1D) complex IRs.

It can be seen that second-order piezomagnetism represents a relation between the axial vector and a quadratic combination of stresses (symmetrized stress). The constants for the second-order piezomagnetic effect can be studied from the governing relation

$$\mu_i = \sum_j \sum_k \sum_l \sum_m C_{ijklm} \sigma_{jk} \sigma_{lm}, \tag{2.3}$$

with the indices taking the values as per the usual convention. Since the character of the axial vector is given by $(1 \pm 2 \cos \varphi)$ and that of the character of symmetrized stress can be given by $(16 \cos^4 \varphi \pm 8 \cos^3 \varphi - 4 \cos^2 \varphi + 1)$, the compound character for second-order piezomagnetism, expressed as the product of the characters of the quantities involved, is given by

$$\chi^{(\Gamma)}(R_\varphi) = (1 \pm 2 \cos \varphi)(16 \cos^4 \varphi \pm 8 \cos^3 \varphi - 4 \cos^2 \varphi + 1) \tag{2.4}$$

with the understanding as before about the alternative signs when they occur.

The enumeration of the desired coefficients is made in this section by utilizing (*a*) the 1D complex IR of the appropriate factor group G/H, (*b*) the definition of the character of a coset (Krishnamurty, Appalanarasimham & Rama Mohana Rao, 1977), (*c*) the expression for $\chi_\rho^{(\Gamma)}$ in respect of second-order piezomagnetism as provided by (2.4) and (*d*) the known formula (Bhagavantam & Venkatarayudu, 1951)

$$n_i' = (1/g) \sum_\rho h_\rho \chi_\rho^{(\Gamma)} \bar{\chi}_\rho^{(\Gamma_i)} \tag{2.5}$$

with the usual notation. The actual procedure is now illustrated with the help of the point group 4 that induces the class $4^{(4)}$.

It can be seen that the point group 4 contains one pair of 1D complex IRs ^1E and ^2E and either of these two IRs induces the polychromatic class $4^{(4)}$ (Indenbom, Belov & Neronova, 1960; Rama Mohana Rao, 1985). The character table of the appropriate factor group $4/1 \cong 4$ is given by

$4/1$	E	C_{4z}^+	C_{2z}	C_{4z}^-	n_i'
A_1	1	1	1	1	17
B_1	1	−1	1	−1	
^1E	1	$-i$	−1	i	
^2E	1	i	−1	$-i$	
$\chi_\rho^{(\Gamma)}$	63	1	−5	1	

Following theorem 3 of Rama Mohana Rao (1987), it can be inferred that the polychromatic class $4^{(4)}$ requires 17 second-order piezomagnetic coefficients. This method, when extended to the rest of the nine point groups containing 1D complex IRs, yields the desired coefficients n_i' for the remaining 17 polychromatic variants. The results obtained through this group-theoretical procedure are provided in Table 1.

3. Jahn's method

To appreciate the advantage of Jahn's method, the coefficients n_i' are recalculated in this section through the idea of reduction of a representation. The procedure is illustrated here with the help of the same point group, 4.

If $[\mathbf{V}_a^2]$ represents the symmetrical product (Tisza, 1933) of $\mathbf{V}_a$ (the representation of an axial vector) with itself, the form of the representation corresponding to piezomagnetism has already been computed (Krishnamurty & Gopala Krishna Murty 1969) and

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* The number of piezomagnetic coefficients for the 32 crystallographic point groups (G_k) and the 58 piezomagnetic groups (G_k') are provided in the classic work by Koptsik (1966). They are also dealt with in the book by Sirotin & Shaskolskaya (1982). However, for the 18 groups $G_k^{(p)}$, $p = 3$, 4 or 6, the numbers of *c*'s given in this paper are reported for the first time.

is given by

$$\mathbf{V}_a[\mathbf{V}_a^2] = 2D_1^g + D_2^g + D_3^g, \qquad (3.1)$$

where D_L^g stands for the representation of dimension $(2l+1)$ of the group R_∞^i which is even with respect to inversion. Now the corresponding form of the representation for the second-order piezomagnetism can be obtained either from (2.3) or from (2.1) by including the symmetrized square (quadratic combination) of the polar second-rank stress tensor σ. The appropriate axial tensor is then of rank 5 and will necessarily be magnetic. Then the representation pertaining to the second-order piezomagnetic effect can be given by $\mathbf{V}_a[[\mathbf{V}_p^2]^2]$ and, when reduced, its value is given by

$$\mathbf{V}_a[[\mathbf{V}_p^2]^2] = 4D_1^g + 2D_2^g + 3D_3^g + D_4^g + D_5^g. \qquad (3.2)$$

The values of the various D_L^g obtained for the point group 4 can be seen to be

$$\begin{aligned} D_1^g &= A_1 + E \\ D_2^g &= A_1 + 2B_1 + E \\ D_3^g &= A_1 + 2B_1 + 2E \qquad (3.3) \\ D_4^g &= 3A_1 + 2B_1 + 2E \\ D_5^g &= 3A_1 + 2B_1 + 3E. \end{aligned}$$

The above reductions of D_L^g provided by (3.3) when substituted in the RHS of (3.2) yield

$$\mathbf{V}_a[[\mathbf{V}_p^2]^2] = 15A_1 + 14B_1 + 17E, \qquad (3.4)$$

which is the reduced form of the representation for the point group 4 for second-order piezomagnetism. Since any one of the 1D complex IRs E of the point group 4 induces the variant $4^{(4)}$, the numerical coefficient 17 of E in the reduced form (3.4) gives the number of second-order piezomagnetic coefficients needed by $4^{(4)}$.

Results obtained through Jahn's method for the polychromatic class $4^{(4)}$ illustrated here, as well as for the rest of the 17 polychromatic classes, are in complete agreement with those obtained through the alternative (character) method described in § 2.

4. Discussion

It is interesting to note that in respect of piezomagnetism, the 18 polychromatic crystal classes divide themselves into two categories: (a) those classes which do not need any piezomagnetic coefficients (there are 5 such classes: $\bar{6}^{(6)}/2$, $\bar{3}^{(6)}$, $6^{(6)}/m$, $6^{(3)}/m'$ and $4^{(4)}/m$) and (b) those groups which need piezomagnetic coefficients but with varying number for the first and second orders under consideration (a total of 13 classes). The five polychromatic classes given in category (a) and which are induced by the 1D complex IRs of the crystallographic point groups – $m3$, $\bar{3}$, $6/m$, $6/m$ and $4/m$ respectively – did not require any piezomagnetic coefficients (either of first order or of second order), since piezomagnetism is a centrosymmetric property and the centre of inversion (i) in the inducing 1D complex IR of the generating point groups has the character -1.

The 13 polychromatic classes under category (b) which exhibit piezomagnetism and belong to hexagonal, trigonal, tetragonal and cubic syngonies divide themselves into three types. It can be observed that the six classes with hexagonal symmetry split themselves into two sets requiring different numbers of coefficients. Whereas the three groups $6^{(6)}$; $3^{(3)}/m'$; $6^{(6)}/m'$ require 12 second-order piezomagnetic coefficients, the others $6^{(3)}$; $3^{(3)}/m$; $6^{(3)}/m$ require nine such coefficients. The two polychromatic classes with trigonal symmetry [$\bar{3}^{(3)}$ and $3^{(3)}$] need 21 second-order piezomagnetic coefficients. The three classes belonging to the tetragonal class of symmetry [$4^{(4)}$; $\bar{4}^{(4)}$; $4^{(4)}/m'$] need 17 second-order piezomagnetic coefficients and the two classes with cubic symmetry [$3^{(3)}/2$; $\bar{6}^{(3)}/2$] require four such coefficients.

It has already been shown (Koptsik, 1966) that, in the absence of magnetic and mechanical stresses, there exist 353 magnetic structures when the first-order piezomagnetic effects are alone considered. The appearance of non-vanishing second-order piezomagnetic coefficients in respect of the point groups $\bar{4}3m$, 432 and $m3m$ (Krishnamurty & Gopala Krishna Murty, 1969) of the cubic system (for which the first-order piezomagnetic coefficients do not survive); and the appearance of non-vanishing first- and second-order piezomagnetic coefficients in respect of the 13 polychromatic crystal classes [an outcome of the study already made by this author (Rama Mohana Rao, 1987) and through study during the present work] may give rise to an increased number of magnetic structures. The theoretical studies made by this author show positive evidence for such an extension of the magnetic structures.

It can be observed that Jahn's method of reduction of a representation employed for the enumeration of magnetic coefficients here is in conformity with the physical significance of the derived constants (n_i), established earlier by this author (Rama Mohana Rao, 1987) while studying the magnetic properties of polychromatic crystals, and it fits closely with the construction of polychromatic groups (Indenbom, Belov & Neronova, 1960; Rama Mohana Rao, 1985). The results obtained here through Jahn's method are in complete agreement with those of the n_i' obtained *via* the character method.

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Homometrism in Close-Packed Structures

BY S. MARDIX

University of Rhode Island, Department of Electrical Engineering, Kingston, Rhode Island 02881, *USA*

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Abstract

Homometric structures are non-congruent structures having identical X-ray intensity distributions. It has so far been assumed that such structures, while theoretically interesting, would not be realized in practice. Homometrism in close-packed structures is shown to be a realistic possibility. Some general rules applicable to homometric pairs are presented; it is shown that an infinite number of them can be derived from one-dimensional homometric pairs. An exhaustive search of close-packed structures with periods of up to 26 reveals that the smallest period of a homometric pair is 15 and that their number increases rapidly with the period. Homometrism in polytypic structures is further discussed.

Introduction

The term 'homometric pair' was introduced by Patterson (1939, 1944) to denote two non-congruent structures having the same set of distances $\mathbf{r}_i-\mathbf{r}_j$ $(i, j = 1, \ldots, N)$, where N is the number of atoms in the unit cell and $\mathbf{r}_i$ is the coordinate vector of the ith atom. As X-ray intensities depend on the distance $\mathbf{r}_i-\mathbf{r}_j$ and not on the individual $\mathbf{r}_i$'s, the two members of a homometric pair will have the same set of intensities even though they are not congruent structures. Two structures are considered to be congruent if they can be brought into coincidence by a combination of translation, rotation and reflection operations. Patterson (1944) discusses in some detail the characteristics of homometric structures consisting of one type of atom in one, two and three dimensions and gives a large number of examples of such structures. Patterson's work made it clear that the information included in X-ray intensity sets is not sufficient in all cases to determine a structure uniquely. As a consequence, X-ray structure determination must be followed by an examination of possible homometric structures and, if found, other methods must be utilized for a unique structure determination.

In the years following Patterson's publication, the importance of the possible ambiguities associated with X-ray structure determination was played down. Lipson & Cochran (1966) quote Robertson's conclusion that the chance of finding homometric pairs is small and, even if discovered, it would be unlikely that both would present structures that are chemically possible. Stout & Jensen (1968) referring to homometric sets state: 'Although of theoretical interest, these are exceedingly unlikely to appear in practice and do not pose a real difficulty'.

In their discussion of homometric pairs in close-packed structures, Jain & Trigunayat (1977) point out that, in structures based on the closest packing of spheres where each sphere is replaced by more than one atom, two identical stacking sequences may under certain conditions constitute a homometric pair. This type of homometrism cannot exist in close-packed structures of only one kind of atom.

In the above case of homometrism, the two members of the pair are simply related to one another and both have the same stacking sequence of layers, a property important for many investigations in

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