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Least-squares refinement of centrosymmetric trial structures in non-centrosymmetric space groups. A warning.

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It is impossible to distinguish by means of a least-squares analysis between a centrosymmetric structure and a corresponding non-centrosymmetric one by simple expansion of the set of parameters over the questionable inversion centre.

In many cases the space group of a crystal is not uniquely defined by the systematically absent reflexions. In solving the structure of such a crystal from X-ray diffraction data it is often convenient to start from the simplifying assumption that the structure is centrosymmetric, but once a reasonable trial structure has been found on this basis the question arises as to whether the actual structure is centrosymmetric or not. If one wishes to answer this question by least-squares analysis of the diffraction data, one might decide to simply expand the trial set of parameters over the questionable inversion centre and carry out the least-squares refinement in the corresponding non-centrosymmetric space group. This procedure is easily shown to be invalid.

Since the structure factor derivatives with respect to pairs of centrosymmetrically related positional parameters are equal in magnitude and have opposite sign, while derivatives with respect to corresponding pairs of temperature factor parameters are equal, the normal equations are identical in pairs and the resulting normal equations matrix becomes singular. In such a case, full-matrix refinement would lead to catastrophic results, while diagonal or block-diagonal refinement is clearly equivalent to refinement in the originally assumed centrosymmetric space group. Small, random shifts may be applied to the centrosymmetric set of parameters so as to make it only approximately centrosymmetric, but then the occurrence of an ill-conditioned set of normal equations has to be reckoned with. Diamond (1958) has shown how an eigenvalue–eigenvector technique may be applied to obtain the maximum amount of information in similar cases.

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Magnetic symmetry and transport properties of crystals.

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The generalized Onsager relations applicable to transport property tensors for magnetic and non-magnetic crystals in the presence or absence of an external magnetic field were given by Kleiner. In this paper it is shown that the symmetry-restricted forms of the thermogalvanomagnetic property tensors conforming to Kleiner's prescription can be obtained from the forms of the polar and axial tensors appropriate to the 32 classical point groups, making use of the rules given by Birss for the equilibrium magnetic property tensors.

We consider the effect of magnetic symmetry of a crystal on its thermogalvanomagnetic (TGM) properties. The electric current density J_i, the heat current density q_i, the electric field E_i and the negative temperature gradient G_i in a crystal are related as shown in the phenomenological equations (1). The usual summation convention has been adopted throughout this paper.

$$\begin{aligned} E_i &= \varrho_{ij}J_j + \alpha_{ij}G_j\,, \\ q_i - J_i\frac{\xi}{e} &= -\beta_{ij}J_j + \kappa_{ij}G_j\,. \end{aligned} \tag{1}$$

ξ is the chemical potential of the electrons, e is the electronic charge, ϱ_{ij} is the electrical resistivity, κ_{ij} the thermal conductivity, α_{ij} the thermoelectric power and β_{ij} the property inverse to α_{ij}.

In the presence of an external magnetic field, the tensors ϱ_{ij}, α_{ij}, β_{ij} and κ_{ij} can be expanded as power series in the field components H_i as in (2).

$$\varrho_{ij}(\mathbf{H}) = \varrho_{ij} + \varrho_{ijk}H_k + \varrho_{ijkl}H_kH_l + \ldots \tag{2}$$

The tensors of various ranks on the right-hand side of (2) define the TGM tensors. H_i is an axial vector whereas J_i, q_i, E_i and G_i are polar vectors. Consequently the TGM tensors of even rank are polar while those of an odd rank are axial.

According to Kleiner (1966) the space-time symmetry of a crystal, in which these properties are observed, imposes the relations (3) and (4) between the corresponding tensor components. These relations which take account of the space-time symmetry of the crystal are the appropriate generalizations of the classical Onsager relations.

A pure rotation in space is represented by a 3×3 orthogonal matrix $||R_{ij}||$. The space-time operation of a pure rotation followed by time-invariance is denoted by R, and that followed by time-reversal by R. A rotation-inversion followed by time-invariance is denoted by R while that followed by time-reversal is denoted by R.

$$\text{For } R \text{ or } R: \varrho_{ijkl\ldots} = R_{im}R_{jn}R_{kp}R_{lq}\ldots\varrho_{mnpq}\,. \tag{3a}$$

For $\underline{R}$ or $\underline{\bar{R}}$: $\varrho_{ijkl}\ldots=(-1)^{n-2}R_{im}R_{jn}R_{kp}R_{lq}\ldots\varrho_{nmpq}$. (3b)

For R or $\bar{R}$: $\alpha_{ijkl}\ldots=R_{im}R_{jn}R_{kp}R_{lq}\ldots\alpha_{mnpq}$. (4a)

For $\underline{R}$ or $\underline{\bar{R}}$: $\alpha_{ijkl}\ldots=(-1)^{n-2}R_{im}R_{jn}R_{kp}R_{lq}\ldots\beta_{nmpq}$. (4b)

The relations are given for a tensor of general rank n. Equations (3a) and (3b) are applicable to the diagonal ϱ and κ tensors; (4a) and (4b) hold for the non-diagonal α and β tensors.

We take up first the diagonal ϱ and κ tensors. Considering a ϱ tensor, it is convenient to express this as the sum of its symmetric (ϱ^s) and anti-symmetric (ϱ^a) parts with respect to the first two indices as in (5) (Kleiner, 1966). The tensor is symmetric with regard to all permutations of the rest of the indices.

$$\begin{aligned}\varrho_{ijkl}\ldots&=\tfrac{1}{2}(\varrho_{ijkl}\ldots+\varrho_{jikl}\ldots)+\tfrac{1}{2}(\varrho_{ijkl}\ldots-\varrho_{jikl}\ldots)\\&=\varrho^s+\varrho^a\,.\end{aligned}\tag{5}$$

For n odd, (3b) takes the form (6).

$$\begin{aligned}\varrho^s_{ijk}\ldots&=-R_{im}R_{jn}R_{kp}\ldots\varrho^s_{nmp}\\&=-R_{im}R_{jn}R_{kp}\ldots\varrho^s_{mnp}\\\varrho^a_{ijk}\ldots&=-R_{im}R_{jn}R_{kp}\ldots\varrho^a_{nmp}\\&=R_{im}R_{jn}R_{kp}\ldots\varrho^a_{mnp}\,.\end{aligned}\tag{6}$$

For n even, (3b) takes the form (7).

$$\begin{aligned}\varrho^s_{ijkl}\ldots&=R_{im}R_{jn}R_{kp}R_{lq}\ldots\varrho^a_{nmpq}\\&=R_{im}R_{jn}R_{kp}R_{lq}\ldots\varrho^a_{mnpq}\\\varrho^a_{ijkl}\ldots&=R_{im}R_{jn}R_{kp}R_{lq}\ldots\varrho^a_{nmpq}\\&=-R_{im}R_{jn}R_{kp}R_{lq}\ldots\varrho^a_{mnpq}\,.\end{aligned}\tag{7}$$

From (6), we find that the symmetric part of the odd rank, axial, transport property tensor transforms like the corresponding equilibrium, magnetic property tensor (C tensor). Birss (1962) established that the form of such an axial C tensor of odd rank, appropriate to a double colour magnetic (M) group, is the same as that of the corresponding polar, equilibrium, non-magnetic property tensor (I tensor) appropriate to an associated classical group of the B type. The general rule given by Birss is: in a magnetic (M) group the forms of a polar C tensor of even rank and an axial C tensor of odd rank are the same as those of an axial I tensor of even rank and polar I tensor of odd rank respectively, in an associated classical group of the B type. Birss has given the list of A and B groups associated with the M groups.

Again, from (6), we find that the anti-symmetric part of the odd rank, axial transport property tensor transforms under an R or $\bar{R}$ in the same manner as under the corresponding $\underline{R}$ or $\underline{\bar{R}}$. It follows that the anti-symmetric part is unaffected by the magnetic structure of the crystal. Its form in a magnetic group is the same as that of a corresponding equilibrium property I tensor appropriate to the classical group obtained by replacing the $\underline{R}$ and $\underline{\bar{R}}$ with the corresponding R and $\bar{R}$ in the group.

From (7), we find that the symmetric part of an even rank transport property tensor is unaffected by the magnetic structure of the crystal. Its form in a magnetic crystal is the same as that of the corresponding equilibrium I tensor appropriate to the classical group obtained from the magnetic group by replacing $\underline{R}$ and $\underline{\bar{R}}$ with the corresponding R and $\bar{R}$.

Again from (7), we find that the antisymmetric part of an even rank transport property tensor transforms like the corresponding equilibrium property C tensor. From Birss's rule stated above, it follows that the form of such a tensor in a magnetic group is the same as that of an equilibrium property axial I tensor of the same rank appropriate to the associated classical B type group.

The above discussion applies to the κ tensor as well.

The forms of the general I tensors, axial or polar, up to the sixth rank, have been obtained by Fumi (1951, 1952) and Fieschi & Fumi (1953). The forms of the tensors up to the fourth rank have been reproduced in Birss (1962). The necessary intrinsic symmetry with respect to the indices can be imposed on these general forms.

The symmetry-restricted forms of an α or β tensor appropriate to a magnetic group are obtained by applying only the operations of the type R and $\bar{R}$, *i.e.* relations (4a). Relations (4b) are used only to obtain the form of an α tensor from the known form of the corresponding β tensor or *vice versa*. It follows that the forms of an α or β transport property tensor appropriate to a magnetic group is the same as that of an equilibrium property I tensor appropriate to the sub-group of R and $\bar{R}$ operations contained in the magnetic group.

The splitting of the ϱ tensor into symmetric and anti-symmetric parts is physically significant. The latter describes the Hall effect and does not give rise to Joule heat. The former describes the magnetoresistance. In the non-magnetic crystals, the anti-symmetric part is an odd function in the H_i components while the symmetric part is an even function. The transition into a magnetic state does not affect the anti-symmetric part of the odd function, *i.e.* the symmetry of the Hall effect does not change. Similarly, the symmetry of the magnetoresistance does not change. The transition into a magnetic state gives rise to a symmetric part in the odd function, which is a different kind of magnetoresistance which depends on the direction of the external magnetic field and an anti-symmetric part in the even function which is a different kind of Hall effect that is unaffected by the direction of the magnetic field.

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