

General Relations for Transport Properties in Magnetically Ordered Crystals

BY HANS GRIMMER

Labor für Neutronenstreuung, Paul Scherrer Institut, Würenlingen and Villigen, 5232 Villigen PSI, Switzerland

(Received 5 March 1993; accepted 15 April 1993)

Abstract

In a previous paper [Grimmer (1991). *Acta Cryst.* A47, 226–232], general connections were given between the forms of tensors describing equilibrium properties in materials with point-group symmetry described by any of the 122 crystallographic Shubnikov point groups. In the present paper, it is shown how the results must be modified to include transport properties also. At least six different prescriptions for the treatment of transport properties in magnetically ordered crystals have been proposed in the literature. It is shown that the one due to Shtrikman & Thomas [*Solid State Commun.* (1965), 3, 147–150; erratum (1965), 3, civ] leads to a straightforward generalization of the results for equilibrium properties that seems to agree with experiment. Tensors describing transport properties generally consist of two contributions, $T = T^i + T^s$. The tensor T^i is invariant under time reversal $1'$, whereas T^s changes sign under $1'$ and therefore vanishes for dia- and paramagnetic crystals, which are invariant under $1'$. The form of the tensors describing electric and thermal conductivity, the thermoelectric Seebeck and Peltier effects and the Hall, Righi–Leduc, Nernst & Ettingshausen effect are given explicitly for all the 122 crystallographic and 21 limiting point groups.

1. Introduction

The application of space–time symmetry to the transport properties of magnetically ordered crystals has been the subject of considerable controversy. Consider, as an example, the linear relation between the Cartesian components of the electric field \mathbf{E} and the current density \mathbf{j} ,

$$j_i = \sigma_{ik} E_k.$$

Birss (1964) was the first to propose a prescription that gives the forms of tensors describing transport properties in magnetically ordered crystals. He argued that σ_{ik} changes sign under time reversal $1'$ because \mathbf{E} is invariant and \mathbf{j} changes sign under $1'$. A dia- or paramagnet is left invariant under $1'$ and so σ_{ik} is also invariant under $1'$, according to the Neumann principle. It follows that the electric con-

ductivity σ_{ik} must vanish for dia- and paramagnets, in contrast to experimental evidence. Birss, therefore, restricted the validity of the Neumann principle for transport properties to the unitary operations in the Shubnikov point group, *i.e.* those conserving the direction of time.

Expressing \mathbf{E} as a function of \mathbf{j} , we can write

$$E_i = \rho_{ik}(\mathbf{H}) j_k$$

if an external magnetic field \mathbf{H} is applied. Using the Onsager relations in the form $\rho_{ik}(\mathbf{H}) = \rho_{ki}(-\mathbf{H})$, Birss (1964) showed that the part of ρ_{ik} that is symmetric in i and k is an even function of \mathbf{H} and that the antisymmetric part is an odd function of \mathbf{H} . The component of \mathbf{E} determined by the antisymmetric part is perpendicular to \mathbf{j} and, therefore, causes no energy loss, whereas the component determined by the symmetric part does contribute to energy dissipation. If ρ is expanded into a power series with respect to \mathbf{H} , the constant term describes (electrical) resistance, the linear term the ordinary Hall effect and the quadratic term magneto-resistance. The coefficients of odd powers of \mathbf{H} describe the generalized Hall effect and the coefficients of even powers describe generalized magneto-resistance according to Birss. This implies that the Hall effect should vanish at $\mathbf{H} = 0$.

The Birss (1964) prescription was criticized by many authors. An early criticism was published by Shtrikman & Thomas (1965), who do not limit the validity of Neumann's principle and who consider the behaviour of ρ_{ik} under time reversal to be determined by applying $1'$ not to the constitutive equation but to the Onsager relations, which give $\rho_{ik}(\mathbf{S}, \mathbf{H}) = \rho_{ki}(-\mathbf{S}, -\mathbf{H})$, where \mathbf{S} denotes the spin arrangement of a magnetically ordered material. The two prescriptions give the same result for materials with grey point groups (diamagnets, paramagnets and those antiferromagnets that are invariant under antitranslations). They differ in that the Shtrikman–Thomas prescription allows an extraordinary Hall effect (*i.e.* for $\mathbf{H} = 0$) in all crystal classes compatible with ferromagnetism and a linear magneto-resistance in all classes compatible with piezomagnetism. Shtrikman & Thomas also discuss the experimental evidence in favour of their view.

Unfortunately, the concise paper of Shtrikman & Thomas (1965) was given much less attention than a series of papers by Kleiner (1966, 1967, 1969) published in the influential *Physical Review*. Kleiner uses a point group \mathcal{K} that either is equal to the Shubnikov point group \mathcal{S} of the crystal or has twice as many elements. Whereas \mathcal{S} leaves the Hamiltonian $\mathcal{H}(\mathbf{H})$ invariant, the elements of \mathcal{K} map it into $\mathcal{K}(\pm\mathbf{H})$. Kleiner uses the Neumann principle for the unitary elements of \mathcal{K} and a modified principle for the antiunitary elements. This modified principle is that of 'generalized Onsager relations' and replaces the usual Onsager relations.

Cracknell (1973) criticizes both Birss and Kleiner and proposes prescriptions that supplement those of Birss with a modified Neumann principle for the antiunitary elements of the point group.

Pourghazi, Saunders & Akgöz (1976) and Birss & Fletcher (1980) criticized all preceding prescriptions [except that of Shtrikman & Thomas (1965), which they ignored] and proposed new ones. Finally, Butzal & Birss (1982) and Malinowski (1986) advocated prescriptions that are equivalent to those of Shtrikman & Thomas (1965), but did so without mentioning their paper.

The controversy also concerned the question of whether time reversal $1'$ should be replaced by magnetic reversal $\underline{1}$ in the discussion of transport properties. The operator $\underline{1}$ reverses the signs of all magnetic moments in the material as well as the signs of external magnetic fields, whereas $1'$ is, in addition assumed to reverse the sign of any current.

The argument given at the beginning of this section, which led Birss to restrict the validity of the Neumann principle, led Pourghazi *et al.* (1976) and Pourghazi & Saunders (1977) to apply $\underline{1}$ instead of $1'$ to $j_i = \sigma_{ik}E_k$; they obtained $\underline{1}\sigma_{ij}(\mathbf{B}) = \sigma_{ij}(-\mathbf{B})$ because $\underline{1}$ leaves \mathbf{j} and \mathbf{E} invariant.

Butzal & Birss (1982) also rejected the use of $1'$, but included a theoretical justification of the fact that $1'$ may be applied to constitutive equations defining equilibrium properties but not to those defining transport properties. They also avoided applying $\underline{1}$ to $j_i = \sigma_{ik}E_k$ and assumed instead that the effect of $\underline{1}$ on σ_{ik} is given by the Onsager relations. The result is the same as that obtained 17 years earlier by Shtrikman & Thomas (1965). These authors had already shown that the flows in constitutive equations describing transport properties do not simply change sign under $1'$ because of the irreversible nature of transport processes. Therefore, the transformation law under $1'$ of transport properties does not follow in a simple way from the constitutive equations but is given by the Onsager relations.

We conclude that it does not matter whether we speak of magnetic or of time reversal as long as the behaviour of the tensors describing transport properties is taken from the Onsager relations. It follows

from these relations that the transport flows in the constitutive equations for transport properties can be split into two parts, one that is invariant and another that changes sign under $1'$ or $\underline{1}$. It is interesting that to Butzal & Birss (1982) such behaviour seemed acceptable for $\underline{1}$ but not for $1'$, whereas Shtrikman & Thomas (1965) accepted it for $1'$.

It seems to the present author that the use of 'magnetic reversal' in connection with transport properties expresses the physical meaning more clearly than 'time reversal'. The term 'magnetic reversal' instead of 'time reversal' could also be employed in connection with equilibrium properties. The simultaneous use of two different operators $\underline{1}$ and $1'$ leads to unnecessary complications. The symbol $1'$ and the term 'time reversal' will be employed in the following in accordance with usual practice.

It thus took about 20 years for the Shtrikman-Thomas prescription to gain widespread acceptance. It is the purpose of the present paper to apply this prescription to transport properties involving temperature and concentration gradients and electric and magnetic fields in crystals that may have magnetic order and to show that it leads to a formalism of beautiful simplicity.

Interest in such transport properties has increased considerably in recent years because it has been found that thermoelectric and thermomagnetic effects attain considerable values in the mixed states of many high- T_c superconductors. [See, for example, Varlamov & Livanov (1991), Huebener (1990), Kober, Ri, Gross, Koelle, Huebener & Gupta (1991), Freimuth, Hohn & Galffy (1991), Zavaritsky, Samoilov & Yurgens (1991) and references mentioned in these papers.]

2. Thermoelectric phenomena

2.1. Basic equations and Onsager relations

Nye (1985) gives a careful presentation of the concepts of thermoelectricity, which may be summarized for cubic materials as follows:

$$\begin{aligned} \mathbf{j} &= -\sigma \text{grad } \bar{\varphi} - \beta' T^{-1} \text{grad } T \\ \mathbf{h} &= -\beta'' \text{grad } \bar{\varphi} - \gamma T^{-1} \text{grad } T. \end{aligned} \quad (1)$$

These equations give the densities of electric current \mathbf{j} and heat current \mathbf{h} as functions of the gradients of temperature T and of the electrochemical potential $\bar{\varphi} = \varphi - \mu/e$, where φ is the electric potential, μ is the chemical potential and $-e$ is the charge of the electron. The Onsager theorem states that $\beta' = \beta''$ for dia- or paramagnetic materials in the absence of magnetic fields \mathbf{H} . The isotropy of the thermoelectric effects described by (1) is a consequence of the cubic symmetry that has been assumed.

If the crystal under consideration does not have cubic symmetry, (1) must be replaced by

$$\begin{aligned} j_i &= -\sigma_{ik}(\partial\bar{\varphi}/\partial x_k) - \beta'_{ik}T^{-1}(\partial T/\partial x_k) \\ h_i &= -\beta''_{ik}(\partial\bar{\varphi}/\partial x_k) - \gamma_{ik}T^{-1}(\partial T/\partial x_k), \end{aligned} \quad (2)$$

where a Cartesian coordinate system is used. For dia- or paramagnetic materials in the absence of magnetic fields, the Onsager theorem states that γ and the electric conductivity tensor σ are symmetric ($\gamma_{ik} = \gamma_{ki}$ and $\sigma_{ik} = \sigma_{ki}$) and that β'' is the transpose of β' ($\beta'' = \beta'^t$ or $\beta''_{ik} = \beta'_{ki}$). It follows that the 6×6 matrix

$$\Gamma = \begin{bmatrix} \sigma & \beta' \\ \beta'' & \gamma \end{bmatrix} \quad (3)$$

is symmetric, *i.e.* $\Gamma^t = \Gamma$ or $\Gamma_{\nu\mu} = \Gamma_{\mu\nu}$, where $\mu, \nu = 1, \dots, 6$.

In the following, we take \mathbf{j} and $\text{grad } T$ as independent variables in accordance with the usual experimental conditions. This will allow us to connect β' and γ with more frequently used quantities. It follows from (2) that

$$\begin{aligned} (\partial\bar{\varphi}/\partial x_i) &= -\rho_{ik}j_k - \Sigma'_{ik}(\partial T/\partial x_k) \\ h_i &= T\Sigma''_{ik}j_k - k_{ik}(\partial T/\partial x_k), \end{aligned} \quad (4)$$

where

$$\rho_{ik} = (\sigma^{-1})_{ik} \quad (5)$$

$$k_{ik} = -T^{-1}(\beta'_{ij}\rho_{jl}\beta'_{ik} - \gamma_{ik}) \quad (6)$$

$$\Sigma'_{ik} = T^{-1}\rho_{ij}\beta'_{jk} \quad (7)$$

$$\Sigma''_{ik} = T^{-1}\beta'_{ij}\rho_{jk}. \quad (8)$$

The property tensor ρ_{ik} describes electrical resistivity, k_{ik} describes the thermal conductivity at $\mathbf{j} = 0$, Σ'_{ik} is responsible for the Seebeck effect and $T\Sigma''_{ik}$ is responsible for the Peltier effect. If Γ is symmetric then ρ and k are also symmetric and $\Sigma'' = \Sigma'^t$, *i.e.* the 6×6 matrix

$$K = \begin{bmatrix} \rho & \Sigma' \\ \Sigma'' & k \end{bmatrix} \quad (9)$$

is symmetric.

Dia- and paramagnets are invariant under time reversal $1'$; the point groups of such crystals are 'grey', *i.e.* they are direct products of the ordinary 'black' point groups with $1'$. Neumann's principle, which will be discussed below in more detail, then gives the usual restrictions for the forms of symmetric second-rank tensors σ , γ , ρ and k and general second-rank tensors β' and Σ' . These restrictions are given, for example, by Nye (1985) in Table 3 on p. 23 and Table 14 on p. 227 of his book. They are also contained in Table 1 of the present paper, as explained below.

Let us now consider magnetically ordered crystals; for example, ferromagnets or ferrimagnets, which possess nonvanishing magnetic moments, and antiferromagnets, which consist of two or more sublattices with magnetic moments, the vector sum of which vanishes. Let \mathbf{S} symbolize the spin arrangement in the crystal and $-\mathbf{S}$ the arrangement in the magnetic companion with all spins reversed; an external magnetic field \mathbf{H} may also be applied to the crystal. The Onsager relations then can be written as (*cf.* Shtrikman & Thomas, 1965)

$$\sigma_{ij}(-\mathbf{S}, -\mathbf{H}) = \sigma_{ji}(\mathbf{S}, \mathbf{H}) \quad (10)$$

and

$$\beta''_{ij}(-\mathbf{S}, -\mathbf{H}) = \beta'_{ji}(\mathbf{S}, \mathbf{H}). \quad (11)$$

Relations similar to (10) also hold for γ , ρ and k ; relations similar to (11) also connect Σ'' and Σ' .

The Neumann principle states that the form of a property tensor such as σ is such that the tensor remains invariant under the point group of the material under consideration. Each element of a point group is of one of four possible types R , $R1'$ ($=R'$), $R\bar{1}$ ($=\bar{R}$) or $R\bar{1}'$ ($=\bar{R}'$), where R denotes rotation, $1'$ time inversion, $\bar{1}$ space inversion and $\bar{1}'$ ($=\bar{1}1'$) combined space and time inversion. Notice that the identity 1 is a special case of a rotation.

Temperature T and the potential $\bar{\varphi}$ are invariant whereas $\partial T/\partial x_k$, $\partial\bar{\varphi}/\partial x_k$, \mathbf{j} and \mathbf{h} change sign under space inversion $\bar{1}$. It follows then from (2), (3), (4) and (9) that Γ and K are always invariant under $\bar{1}$ [*i.e.* Γ and K must be of type i or s in the terminology of Grimmer (1991)]. In order to evaluate the restrictions on Γ and K that follow from Neumann's principle, we may therefore replace the elements \bar{R}_1 in the point group of the material by R_1 and \bar{R}_2 by R'_2 . Therefore, it is sufficient to consider amongst the 122 crystallographic and 21 limiting Shubnikov point groups the 32 crystallographic and seven limiting ones that only contain elements of types R and R' . These point groups are referred to as 'proper' groups because they contain only proper rotations (with $\det R = 1$), not roto-inversions \bar{R} (with $\det \bar{R} = -1$).

2.2. Magnetic crystals in the absence of an external magnetic field

The equation

$$\sigma'_{ij}(\mathbf{S}) = R_{ik}^{-1}R_{jl}^{-1}\sigma_{kl}(\mathbf{S}) = R_{ki}R_{lj}\sigma_{kl}(\mathbf{S}) = \sigma_{ij}(R * \mathbf{S}) \quad (12)$$

may be interpreted passively as describing the electric conductivity of the present physical system in a new (primed) Cartesian coordinate system obtained by a rotation R^{-1} or actively as the description (in the former coordinate system) of a new physical system obtained by a rotation R , which transforms the spin arrangement \mathbf{S} into $R * \mathbf{S}$. Similarly, R' transforms \mathbf{S}

Table 1. The forms of tensors of the second and third ranks describing tensor properties

	S	G	A	s-type	S	G	A	s-type	S	G	A	s-type
anorthic				1				2				2'
	monoclinic y									m		
monoclinic z					2				222			
				(m)				mm2				m'm'2
				(2/m)				mmm				m'm'm
								(m2m)				m'2'm
orthorhombic				(2')				(2'22')				(2'2'2')
				(m')				(m'2m')				(2m'm')
				(2'/m')				(m'mm')				(mm'm')
								(2'mm')				(m2'm')
tetragonal				4				422				42'2'
				4				4mm				4m'm'
				4/m				4/mmm				4/mm'm'
								42m				42'm'
								(4m2)				(4m'2')
				4'				4'22'				(4'2'2)
				4'				4'2m'				(4'm'2)
				4'/m				4'/mmm'				(4'/mm'm)
							4'm2'				(4'2'm)	
							4'mm'				(4'm'm)	

into $R' * S = -R * S$ and $\sigma_{ij}(S)$ into

$$\begin{aligned} \sigma_{ij}(R' * S) &= \sigma_{ij}(-R * S) = R_{ki}R_{lj}\sigma_{kl}(-S) \\ &= R_{ki}R_{lj}\sigma_{lk}(S), \end{aligned} \quad (13)$$

where (10) has been used. If R (or \bar{R}) is an element of the point group of the material, then (12) becomes

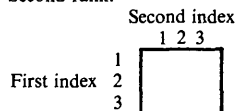
$$\sigma_{ij}(S) = R_{ki}R_{lj}\sigma_{kl}(S); \quad (14)$$

Table 1 (cont.)

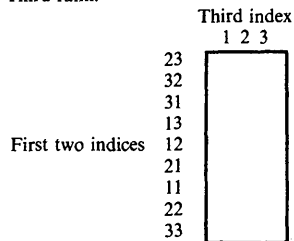
	S	G	A	s-type	S	G	A	s-type	S	G	A	s-type
tri-gonal				$\boxed{3}$				$\boxed{32}$				$32'$
				$\bar{3}$				$3m$ $\bar{3}m$				$3m'$ $\bar{3}m'$
cyclic and hexa-gonal				∞				$\infty 2$ ∞m ∞/m				$\infty 2'$ $\infty m'$ ∞/mm'
				∞/m								
				$\boxed{6}$ $\bar{6}$ $6/m$				$\boxed{622}$ $6mm$ $6/mmm$ $\bar{6}2m$ $(\bar{6}m2)$				$62'2'$ $6m'm'$ $6/m'm'm'$ $\bar{6}2'm'$ $(\bar{6}m'2')$
				$6'$				$6'22'$				$(6'2'2)$
				$\bar{6}'$ $6'/m'$				$\bar{6}'2m'$ $6'/m'mm'$ $\bar{6}'m2'$ $6'mm'$				$(\bar{6}'m'2)$ $(6'/m'm'm)$ $(\bar{6}'2'm)$ $(6'm'm)$
iso-tropic and cubic								$\infty\infty\infty$ $\infty\infty m$				
				$\boxed{23}$				$\boxed{432}$ $\bar{4}3m$ $m\bar{3}m$				$4'32'$ $\bar{4}'3m'$ $m\bar{3}m'$
				$m\bar{3}$								

Arrangement of tensor elements:

Second rank:



Third rank:



Key to graphic symbols:

- Nonvanishing element,
- Equal elements,
- Elements equal in modulus but with opposite sign.

if R' (or \bar{R}') is an element of the point group of the material, then (13) becomes

$$\sigma_{ij}(\mathbf{S}) = R_{ki}R_{lj}\sigma_{lk}(\mathbf{S}). \quad (15)$$

We define

$$\sigma^i_{ij}(\mathbf{S}) = \frac{1}{2}[\sigma_{ij}(\mathbf{S}) + \sigma_{ji}(\mathbf{S})] \quad (16)$$

and

$$\sigma^s_{ij}(\mathbf{S}) = \frac{1}{2}[\sigma_{ij}(\mathbf{S}) - \sigma_{ji}(\mathbf{S})]. \quad (17)$$

It follows from these definitions that σ^i is symmetric and σ^s antisymmetric, $\sigma^s_{ji} = -\sigma^s_{ij}$. Putting $R' = 1'$ in (13), one obtains $\sigma_{ij}(-\mathbf{S}) = \sigma_{ji}(\mathbf{S})$, from which it follows that $\sigma^i_{ij}(-\mathbf{S}) = \sigma^i_{ij}(\mathbf{S})$ and $\sigma^s_{ij}(-\mathbf{S}) = -\sigma^s_{ij}(\mathbf{S})$. The tensor σ^i is therefore invariant under $\bar{1}$, $1'$ and $\bar{1}'$, whereas σ^s is invariant under $\bar{1}$ and changes sign under $1'$ and $\bar{1}'$. Such tensors are referred to as inversion-invariant or i tensors and space-inversion-invariant or s tensors, respectively (cf. Grimmer, 1991). We conclude that σ can be written as

$$\sigma_{ij} = \sigma^i_{ij} + \sigma^s_{ij}, \quad (18)$$

where σ^i is a symmetric i tensor and σ^s an antisymmetric s tensor.

Table 1 gives the forms of these tensors and also of tensors of the third rank. It follows from Neumann's principle that tensors of type s vanish for materials with point groups containing $1'$ or $\bar{1}'$. Table 1 lists in the 's-type' columns all crystallographic and limiting Shubnikov point groups that contain neither $1'$ nor $\bar{1}'$. These point groups are denoted by their Hermann-Mauguin symbols. The monoclinic point groups are listed twice, for monoclinic axes parallel to y and z . (x , y and z are the axes of the Cartesian coordinate system used to describe the tensor.) Also, many other crystallographic point groups appear several times in different orientations, distinguished by the order in which generating elements are listed in the Hermann-Mauguin symbol. A symbol in parentheses refers to a point group that has already been met in a different orientation when the table is read as usual from left to right and top to bottom. The connection between the position in the Hermann-Mauguin symbol and the orientation of the generating element with respect to the Cartesian coordinate system follows the usual conventions. These are stated in detail in Grimmer (1991). The point groups* listed in a box in an 's-type' column give the same restrictions for s tensors of any given rank and intrinsic symmetry. These are stated in Table 1 for tensors of the second rank in the upper 3×3 fields and for tensors of the third rank in the lower 9×3 fields. The 'G' columns refer to general tensors, *i.e.* tensors without intrinsic symmetry, the 'S' columns to tensors symmetric in their first two

indices and the 'A' columns to tensors antisymmetric in these indices.

The forms of the i tensors can also be read from Table 1. Because these tensors are invariant under inversions, the Neumann principle gives the same restrictions for the point group G and for the Laue group obtained from G by taking $\bar{1}$ and $1'$ as additional generators. All the point groups with the same Laue group form a Laue class; the restrictions on i tensors depend only on the Laue class to which the point group of the crystal belongs. Each Laue class contains exactly one group consisting of pure rotations only. Such groups are in boxes in Table 1. For pure rotation groups, Neumann's principle leads to the same restrictions for i and s tensors (of given rank and intrinsic symmetry) because the behaviour of the tensor under inversion is irrelevant for pure rotation groups. We conclude that the forms given for one of the framed groups are valid also for i tensors and all crystals with point groups in the corresponding Laue class. Only the forms in the heavier-rule boxes therefore appear for i tensors.

Returning to (18), we notice that an antisymmetric s tensor of the second rank is equivalent to an s vector,

$$\begin{bmatrix} 0 & \sigma^s_{12} & -\sigma^s_{31} \\ -\sigma^s_{12} & 0 & \sigma^s_{23} \\ \sigma^s_{31} & -\sigma^s_{23} & 0 \end{bmatrix} \sim \begin{bmatrix} \sigma^s_{23} \\ \sigma^s_{31} \\ \sigma^s_{12} \end{bmatrix}. \quad (19)$$

The magnetization M is also an s vector, from which it follows that σ^s may be different from zero for all point groups that are compatible with spontaneous magnetization, *i.e.* with ferro- or ferrimagnetism.

Consider as an example cobalt with point group $62'2'$.* Table 1 gives the form of the antisymmetric s tensor σ^s in column A of the field $62'2'$ and the form of the symmetric i tensor σ^i in column S of the field $\boxed{622}$, *i.e.*

$$\sigma = \begin{bmatrix} \sigma^i_{11} & \sigma^s_{12} & 0 \\ -\sigma^s_{12} & \sigma^i_{11} & 0 \\ 0 & 0 & \sigma^i_{33} \end{bmatrix}. \quad (20)$$

If an electric field \mathbf{E} is applied parallel to the x axis, we find for the current density

$$\begin{bmatrix} j_1 \\ j_2 \\ j_3 \end{bmatrix} = \begin{bmatrix} \sigma^i_{11} & \sigma^s_{12} & 0 \\ -\sigma^s_{12} & \sigma^i_{11} & 0 \\ 0 & 0 & \sigma^i_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} \sigma^i_{11}E_1 \\ -\sigma^s_{12}E_1 \\ 0 \end{bmatrix}. \quad (21)$$

The second component of \mathbf{j} is a result of the extraordinary Hall effect. It is also called the spontaneous Hall effect and we have shown that it may appear in

* The conventions state that the z axis of the Cartesian coordinate system is parallel to the symmetry axis 6 and that x and y are parallel to two of the symmetry axes $2'$.

* The proper point group has always been listed first.

exactly those crystals the symmetry of which allows for spontaneous magnetization \mathbf{M}_0 . An early measurement of the spontaneous Hall effect, *i.e.* the Hall effect in the absence of an external magnetic field \mathbf{H} , was made by Cheremushkina & Vasil'eva (1966), who found it in cobalt.

Notice that the form (20) for σ is valid not only for $62'2'$. In fact, Table 1 shows that σ^i and σ^s have, for the groups

		$2'2'2$	$m'm'2$	$m'2'm$	$m'm'm$
4	$\bar{4}$	$4/m$	$42'2'$	$4m'm'$	$\bar{4}2'm'$
3	$\bar{3}$	$32'$	$3m'$	$3m'$	$\bar{3}m'$
6	$\bar{6}$	$6/m$	$62'2'$	$6m'm'$	$\bar{6}2'm'$
∞	∞/m	$\infty 2'$	$\infty m'$	$\infty m'$	∞/mm'

the same form as for $62'2'$. For all these groups, the spontaneous magnetization \mathbf{M}_0 must be parallel to the third orthogonal axis and the spontaneous Hall coefficient will be the same for any direction of \mathbf{E} perpendicular to \mathbf{M}_0 .

Generally, one can say that the tensor σ of electrical conductivity splits into a tensor σ^i , which may be different from zero for any crystal symmetry and which describes electrical conductivity in its narrow (energy-dissipative) sense, and a tensor σ^s , which may be different from zero only for crystal symmetries permitting spontaneous magnetization and which describes the (lossless) spontaneous (or extraordinary) Hall effect. The tensor σ in its broader sense is, in general, neither purely of type i nor purely of type s , *i.e.* it does not transform according to an irreducible representation of the group $\{1, \bar{1}, 1', \bar{1}'\}$, in contrast to the tensors describing equilibrium properties. However, σ can be split into two tensors, σ^i and σ^s , that not only have a definite type but also a higher intrinsic symmetry and a clear physical interpretation. The current density \mathbf{j} also, in general, neither is invariant nor simply changes sign under time reversal $1'$.

Malinowski (1986) discusses whether the Onsager theorem predicts tensor symmetries that do not depend on the point group of the material, *i.e.* intrinsic symmetries, as thermodynamic arguments do for equilibrium properties [*cf.* Nye, 1985, chapter X] or whether it gives restrictions depending on the point group of the material, as Neumann's principle does. It has been shown above that, for σ , the answer is that Onsager's theorem predicts the splitting into two tensors with different intrinsic symmetry and different behaviour under $1'$.

Obviously, relations (12)–(18) remain valid if σ is replaced by γ , ρ or k .

Whereas in (12) and (14) σ may be replaced by Σ^i or Σ^s , it must be replaced by Σ^i on one side of the equality sign and by Σ^s on the other in (13) and (15) because the Onsager relations

$$\Sigma_{ij}'(-\mathbf{S}) = \Sigma_{ji}'(\mathbf{S}) \quad (22)$$

are used in their derivation. It follows that

$$\begin{aligned} \Sigma_{ij}'(\mathbf{S}) &= R_{ki} R_{lj} \Sigma_{kl}'(\mathbf{S}) \\ \Sigma_{ij}''(\mathbf{S}) &= R_{ki} R_{lj} \Sigma_{kl}''(\mathbf{S}) \end{aligned} \quad (23)$$

if R (or \bar{R}) belongs to the point group of the material and

$$\begin{aligned} \Sigma_{ij}''(\mathbf{S}) &= R_{ki} R_{lj} \Sigma_{lk}'(\mathbf{S}) \\ \Sigma_{ij}'(\mathbf{S}) &= R_{ki} R_{lj} \Sigma_{lk}''(\mathbf{S}) \end{aligned} \quad (24)$$

if R' (or \bar{R}') belongs to the point group. Arguments similar to those leading to (18) show also that Σ^i and Σ^s can be written as sums of two contributions

$$\begin{aligned} \Sigma_{ij}^i &= \Sigma_{ij}^i + \Sigma_{ij}^s \\ \Sigma_{ji}^s &= \Sigma_{ij}^i - \Sigma_{ij}^s, \end{aligned} \quad (25)$$

where the tensors Σ^i and Σ^s are second-rank tensors without intrinsic symmetry; Σ^i is of type i and Σ^s of type s . If $\Sigma^s = 0$, as is the case for, for example, diamagnets and paramagnets, then $\Sigma''(\mathbf{S})$ is determined completely by $\Sigma^i(\mathbf{S})$. The 3×3 matrix describing Σ'' is then the transpose of the matrix describing Σ^i , $\Sigma'' = \Sigma^i$. This is no longer true if $\Sigma^s \neq 0$. In fact, if the point group of the crystal is black, then Neumann's principle will give the same restrictions for Σ^i and Σ^s , *i.e.* no connection between $\Sigma^i(\mathbf{S})$ and $\Sigma^s(\mathbf{S})$, whereas, for black and white point groups (which contain $1'$ only in combination with rotations), the restrictions on Σ^s are usually stronger than those on Σ^i , according to Table 1. The effect giving rise to Σ^s in magnetically ordered crystals may be called the spontaneous or extraordinary Nernst–Ettingshausen effect. This effect also has been measured in cobalt by Cheremushkina & Vasil'eva (1966). Further references to measurements of the spontaneous Hall and Nernst–Ettingshausen effects are given by Campbell (1979). Results analogous to (22)–(25) connect β^i and β^s .

2.3. Crystals in an external magnetic field

Assume that an external magnetic field is applied to a crystal with or without magnetic order. If we restrict our attention to terms linear in \mathbf{H} , we may use (4) with

$$\begin{aligned} \rho_{ij}(\mathbf{S}, \mathbf{H}) &= \rho_{ij}^0(\mathbf{S}) + \rho_{ijk}^1(\mathbf{S}) H_k \\ k_{ij}(\mathbf{S}, \mathbf{H}) &= k_{ij}^0(\mathbf{S}) + k_{ijk}^1(\mathbf{S}) H_k \\ \Sigma_{ij}'(\mathbf{S}, \mathbf{H}) &= \Sigma_{ij}'^0(\mathbf{S}) + \Sigma_{ijk}'^1(\mathbf{S}) H_k \\ \Sigma_{ij}''(\mathbf{S}, \mathbf{H}) &= \Sigma_{ij}''^0(\mathbf{S}) + \Sigma_{ijk}''^1(\mathbf{S}) H_k, \end{aligned} \quad (26)$$

where ρ^1 describes the (ordinary) Hall effect, k^1 the Righi–Leduc effect, Σ'^1 the Nernst effect and $T\Sigma''^1$ the Ettingshausen effect.

An arbitrary rotation transforms the spin arrangement \mathbf{S} into $R * \mathbf{S}$, the magnetic field \mathbf{H} into $R * \mathbf{H}$,

where $(R * \mathbf{H})_k = R_{qk}H_q$, and $\rho_{ij}(\mathbf{S}, \mathbf{H})$ into

$$\rho_{ij}(R * \mathbf{S}, R * \mathbf{H}) = R_{mi}R_{nj}\rho_{mn}(\mathbf{S}, \mathbf{H}). \quad (27)$$

$$\rho_{ij}(R * \mathbf{S}, R * \mathbf{H}) = \rho_{ij}^0(R * \mathbf{S}) + \rho_{ijk}^1(R * \mathbf{S})R_{qk}H_q; \quad (28)$$

$$\begin{aligned} R_{mi}R_{nj}\rho_{mn}(\mathbf{S}, \mathbf{H}) &= R_{mi}R_{nj}[\rho_{mn}^0(\mathbf{S}) + \rho_{mnq}^1(\mathbf{S})H_q] \\ &= R_{mi}R_{nj}[\rho_{mn}^0(\mathbf{S}) + R_{pk}R_{qk}\rho_{mnp}^1(\mathbf{S})H_q], \end{aligned} \quad (29)$$

where $R_{pk}R_{qk} = \delta_{pq}$ has been used. It follows from (27)–(29) that

$$\rho_{ij}^0(R * \mathbf{S}) = R_{mi}R_{nj}\rho_{mn}^0(\mathbf{S}) \quad (30)$$

and

$$\rho_{ijk}^1(R * \mathbf{S}) = R_{mi}R_{nj}R_{pk}\rho_{mnp}^1(\mathbf{S}). \quad (31)$$

R' transforms \mathbf{S} into $R' * \mathbf{S} = -R * \mathbf{S}$, \mathbf{H} into $R' * \mathbf{H} = -R * \mathbf{H}$ and $\rho_{ij}(\mathbf{S}, \mathbf{H})$ into

$$\begin{aligned} \rho_{ij}(R' * \mathbf{S}, R' * \mathbf{H}) &= \rho_{ij}(-R * \mathbf{S}, -R * \mathbf{H}) \\ &= R_{mi}R_{nj}\rho_{mn}(-\mathbf{S}, -\mathbf{H}). \end{aligned} \quad (32)$$

$$\rho_{ij}(R' * \mathbf{S}, R' * \mathbf{H}) = \rho_{ij}^0(R' * \mathbf{S}) - \rho_{ijk}^1(R' * \mathbf{S})R_{qk}H_q. \quad (33)$$

Using the Onsager relations, we obtain

$$\begin{aligned} R_{mi}R_{nj}\rho_{mn}(-\mathbf{S}, -\mathbf{H}) &= R_{mi}R_{nj}\rho_{nm}(\mathbf{S}, \mathbf{H}) \\ &= R_{mi}R_{nj}[\rho_{nm}^0(\mathbf{S}) + R_{pk}R_{qk}\rho_{nmp}^1(\mathbf{S})H_q]. \end{aligned} \quad (34)$$

It follows from (32)–(34) that

$$\rho_{ij}^0(R' * \mathbf{S}) = R_{mi}R_{nj}\rho_{nm}^0(\mathbf{S}) \quad (35)$$

and

$$\rho_{ijk}^1(R' * \mathbf{S}) = -R_{mi}R_{nj}R_{pk}\rho_{nmp}^1(\mathbf{S}). \quad (36)$$

The form of ρ^0 (and of the other tensors with superscript zero) has been discussed in the previous section.

Both the electric resistivity ρ and the magnetic field \mathbf{H} are invariant under $\bar{1}$, irrespective of the symmetry of the crystal. It follows then from (26) that ρ^1 is also invariant under $\bar{1}$. If the point group of the crystal contains R (or \bar{R}), it follows from (31) that

$$\rho_{ijk}^1(\mathbf{S}) = R_{mi}R_{nj}R_{pk}\rho_{mnp}^1(\mathbf{S}); \quad (37)$$

if it contains R' (or \bar{R}'), it follows from (36) that

$$\rho_{ijk}^1(\mathbf{S}) = -R_{mi}R_{nj}R_{pk}\rho_{nmp}^1(\mathbf{S}). \quad (38)$$

Arguments similar to those leading to (18) show that the third-rank tensor ρ^1 can be split according

to

$$\rho_{ijk}^1 = \rho_{ijk}^{1i} + \rho_{ijk}^{1s} \quad (39)$$

into an i tensor ρ_{ijk}^{1i} , antisymmetric in its first two indices, and an s tensor ρ_{ijk}^{1s} , symmetric in these indices.

The *ordinary Hall effect*, *i.e.* the Hall effect due to an external magnetic field, is described in its narrow sense by ρ^{1i} , whereas ρ^{1s} gives the influence of magnetic order on this effect. The ordinary Hall effect in its narrow sense may appear in any point group. It describes a Hall voltage perpendicular to the current density (owing to the antisymmetry of ρ^{1i}), which, for cubic and isotropic crystals, is also perpendicular to \mathbf{H} . The Hall voltage determined by ρ^{1s} need not be perpendicular to the current density. The tensor ρ^{1s} vanishes for all point groups containing $1'$ or $\bar{1}'$, in particular for the point groups of dia- and paramagnetic crystals, which are grey, *i.e.* contain $1'$; the point groups of antiferromagnets with black and white Bravais classes* are also grey (*cf.* Thomas, 1965). On the other hand, ρ^{1s} may be different from zero not only for ferro- and ferrimagnets but also for many antiferromagnets.

The *Righi–Leduc* tensor k^1 can formally be treated in complete analogy with ρ^1 , *i.e.*

$$k_{ijk}^1 = k_{ijk}^{1i} + k_{ijk}^{1s}, \quad (40)$$

where k^{1i} is an i tensor antisymmetric in its first two indices and k^{1s} an s tensor symmetric in its first two indices. The tensor k^{1s} describes the influence of magnetic order on the Righi–Leduc effect.

The *Nernst* and *Ettingshausen* tensors Σ'^1 and $T\Sigma'^1$ are related by the Onsager relation $\Sigma'_{ij}(-\mathbf{S}, -\mathbf{H}) = \Sigma'_{ji}(\mathbf{S}, \mathbf{H})$, from which it follows that

$$\Sigma'_{ijk}{}'^1(-\mathbf{S}) = -\Sigma'_{jik}(\mathbf{S}). \quad (41)$$

An argument similar to the derivation of (37) and (38) gives

$$\begin{aligned} \Sigma'_{ijk}{}'^1(\mathbf{S}) &= R_{li}R_{mj}R_{nk}\Sigma'_{lmn}{}'^1(\mathbf{S}) \\ \Sigma'_{ijk}{}'^1(\mathbf{S}) &= R_{li}R_{mj}R_{nk}\Sigma'_{lmn}{}'^1(\mathbf{S}) \end{aligned} \quad (42)$$

if the point group of the crystal contains R (or \bar{R}) and

$$\begin{aligned} \Sigma'_{ijk}{}'^1(\mathbf{S}) &= -R_{li}R_{mj}R_{nk}\Sigma'_{mln}{}'^1(\mathbf{S}) \\ \Sigma'_{ijk}{}'^1(\mathbf{S}) &= -R_{li}R_{mj}R_{nk}\Sigma'_{mln}{}'^1(\mathbf{S}) \end{aligned} \quad (43)$$

if it contains R' (or \bar{R}'). In particular, if it contains $1'$ (or $\bar{1}'$) then

$$\Sigma'_{ijk}{}'^1 = -\Sigma'_{jik}. \quad (44)$$

In this case, $\Sigma'{}^1$ is completely determined by Σ'^1 according to (44). Both are general i tensors of the third rank. Generally speaking, the tensor Σ'^1 can be

**I.e.* antiferromagnets with antitranslations in their Shubnikov space group.

split as

$$\Sigma_{ijk}^{\prime\prime 1} = \Sigma_{ijk}^{1i} + \Sigma_{ijk}^{1s} \quad (45)$$

into an i tensor Σ^{1i} and an s tensor Σ^{1s} , both of which are third-rank tensors without intrinsic symmetry. $\Sigma^{\prime\prime 1}$ can be expressed in terms of these tensors as

$$\Sigma_{jik}^{\prime\prime 1} = -\Sigma_{ijk}^{1i} + \Sigma_{ijk}^{1s}. \quad (46)$$

3. Discussion

In contrast to tensors describing equilibrium properties, tensors describing transport properties generally split into two components behaving differently under $1'$ if the point group is not grey. If one of the two components is symmetric under the exchange of the two indices that do not refer to \mathbf{H} , the other will be antisymmetric in these indices.

Some authors (Cracknell, 1973; Birss & Fletcher, 1980; Malinowski, 1986) let \mathbf{H} include internal magnetic fields generated by the magnetic structure in addition to the externally applied magnetic field. Although both types of magnetic field behave in the same way under time reversal, there are essential differences, which require separate treatment in order to avoid confusion. Externally applied magnetic fields may be chosen to be arbitrarily small so that an extension into powers of \mathbf{H} does make sense, which is not the case for internal fields, e.g. in a magnetic domain of a single crystal of ferromagnetic material. The internal field of such a domain is invariant under the symmetry group of the domain whereas \mathbf{H} may have any direction.

Our treatment of transport properties is compatible with the treatment of magneto-optic effects in magnetically ordered crystals by Eremenko & Kharchenko (1984). The optical properties also differ essentially from equilibrium properties because of the high frequencies that are involved.

The author is very grateful to Professors H. Schmid and J. Brandmüller for drawing his attention to transport properties in magnetically ordered crystals, for guiding him to relevant literature and for their constructive criticism of an earlier version of this paper.

References

- BIRSS, R. R. (1964). *Symmetry and Magnetism*. Amsterdam: North-Holland.
- BIRSS, R. R. & FLETCHER, D. (1980). *J. Magn. Magn. Mater.* **15-18**, 915-916.
- BUTZAL, H.-D. & BIRSS, R. R. (1982). *Physica (Utrecht)*, **A114**, 518-521.
- CAMPBELL, I. A. (1979). *J. Magn. Magn. Mater.* **12**, 31-33.
- CHEREMUSHKINA, A. V. & VASIL'eva, R. P. (1966). *Fiz. Tverd. Tela (Leningrad)*, **8**, 822-825; Engl. transl: (1966). *Sov. Phys. Solid State*, **8**, 659-661.
- CRACKNELL, W. H. (1973). *Phys. Rev. B*, **7**, 2145-2154.
- EREMENKO, V. V. & KHARCHENKO, N. F. (1984). *Sov. Sci. Rev. A*, **5**, 1-97.
- FREIMUTH, A., HOHN, C. & GALFFY, M. (1991). *Phys. Rev. B*, **44**, 10396-10399.
- GRIMMER, H. (1991). *Acta Cryst.* **A47**, 226-232.
- HUEBENER, R. P. (1990). *Physica (Utrecht)*, **C168**, 605-608.
- KLEINER, W. H. (1966). *Phys. Rev.* **142**, 318-326.
- KLEINER, W. H. (1967). *Phys. Rev.* **153**, 726-727.
- KLEINER, W. H. (1969). *Phys. Rev.* **182**, 705-709.
- KOBER, F., RI, H.-C., GROSS, R., KOELLE, D., HUEBENER, R. P. & GUPTA, A. (1991). *Phys. Rev. B*, **44**, 11951-11959.
- MALINOWSKI, S. (1986). *Acta Phys. Pol. A*, **69**, 33-43.
- NYE, J. F. (1985). *Physical Properties of Crystals*, 2nd ed. Oxford: Clarendon.
- POURGHAZI, A. & SAUNDERS, G. A. (1977). *Phys. Lett. A*, **62**, 521-522.
- POURGHAZI, A., SAUNDERS, G. A. & AKGÖZ, Y. C. (1976). *Philos. Mag.* **33**, 781-784.
- SHTRIKMAN, S. & THOMAS, H. (1965). *Solid State Commun.* **3**, 147-150; erratum (1965), **3**, civ.
- THOMAS, H. (1965). *Z. Angew. Phys.* **18**, 404-414.
- VARLAMOV, A. A. & LIVANOV, D. V. (1991). *Zh. Eksp. Teor. Fiz.* **99**, 1816-1826; Engl. transl: (1991). *Sov. Phys. JETP*, **72**, 1016-1022.
- ZAVARITSKY, N. V., SAMOILOV, A. V. & YURGENS, A. A. (1991). *Physica (Utrecht)*, **C180**, 417-425.

Acta Cryst. (1993). **A49**, 771-781

X-ray Scattering from Systems in Early Stages of Precipitation

BY C. R. HOUSKA

Department of Materials Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

(Received 12 January 1993; accepted 15 April 1993)

Abstract

Certain age-hardenable alloy systems can produce zones of large matrix distortion about precipitates

having a size misfit with the surrounding matrix. These zones grow with ageing and give diffraction effects that are challenging to interpret. This paper describes such a model, based upon the random