Space-Time Symmetry of Transport Coefficients

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The symmetry properties of linear transport coefficients are derived treating time inversion and spatial transformations on the same footing. The possible presence of a uniform external magnetic field is taken into account. The method used can be applied more generally—to nonlinear transport coefficients, for example. It is shown that the usual Onsager reciprocity relations do not in general apply in practice to magnetic crystals; appropriate generalized Onsager relations are given. The 1651 3-dimensional space groups which exist when time inversion is taken into account fall into three categories: (a) 230 which contain time inversion as an element, (b) 230 which do not involve time inversion, and (c) 1191 which contain time inversion only in combination with spatial transformations; (a) refers to nonmagnetic crystals and (b) and (c) refer to magnetic crystals. Onsager's relations are shown to apply in their usual form to crystals in category (a), not at all to crystals in category (b), and in general only in a modified form to crystals in category (c). As an application, the equations derived which determine the symmetry restrictions are used to obtain symmetry-restricted matrices for the thermogalvanomagnetic coefficients for each of the 1651 space-group symmetries, and the results are tabulated.

1. INTRODUCTION

SYMMETRY properties of magnetic crystals have been actively investigated in recent years.[1–7] Symmetry restrictions on equilibrium-property tensors have been examined for magnetic as well as nonmagnetic crystals treating spatial and time-inversion transformations on the same footing.[2,3,8] For transport properties, on the other hand, earlier investigations have treated the spatial symmetry and time-inversion symmetry separately, the latter leading to restrictions consisting of the usual Onsager relations. In the present paper, symmetry restrictions on transport-property tensors are examined treating spatial and time-inversion symmetry on the same footing.

The electric current density $\mathbf{j}$ and the heat current density $\mathbf{q}$ in a crystal are related to the gradients of the electrochemical potential $\mu=\zeta-e\phi$ and the temperature T by[9]

$$\begin{aligned}\mathbf{j}&=\mathbf{S}^{(1)}(\mathbf{H})\cdot\left(\mathbf{E}+\frac{T}{e}\nabla\xi\right)+\mathbf{S}^{(2)}(\mathbf{H})\cdot\frac{1}{T}\nabla T,\\ \mathbf{q}&=-\mathbf{S}^{(3)}(\mathbf{H})\cdot\left(\mathbf{E}+\frac{T}{e}\nabla\xi\right)-\mathbf{S}^{(4)}(\mathbf{H})\cdot\frac{1}{T}\nabla T,\end{aligned}\tag{1.1}$$

where $-e$ is the electron charge, $\mathbf{E}$ is the electric field, $\xi=\zeta/T$, and $\mathbf{H}$ is the external magnetic field. The usual Onsager reciprocity relations among the coefficients can be expressed in this case as

$$S_{\mu\nu}^{(1)}(\mathbf{H})=S_{\nu\mu}^{(1)}(-\mathbf{H}),\quad S_{\mu\nu}^{(4)}(\mathbf{H})=S_{\nu\mu}^{(4)}(-\mathbf{H}),\quad S_{\mu\nu}^{(2)}(\mathbf{H})=S_{\nu\mu}^{(3)}(-\mathbf{H}).\tag{1.2}$$

These are equivalent to the Onsager relations

$$\rho_{\mu\nu}(\mathbf{H})=\rho_{\nu\mu}(-\mathbf{H}),\quad \kappa_{\mu\nu}(\mathbf{H})=\kappa_{\nu\mu}(-\mathbf{H}),\quad \pi_{\mu\nu}(\mathbf{H})=T\alpha_{\nu\mu}(-\mathbf{H})\tag{1.3}$$

for the electrical resistivity $\boldsymbol{\rho}$, thermal conductivity $\boldsymbol{\kappa}$, Peltier coefficient $\boldsymbol{\pi}$, and thermoelectric (or Seebeck) coefficient $\boldsymbol{\alpha}$, which enter in the form of equations[1,10,11] describing thermogalvanomagnetic effects convenient for application to experiment. Equations (1.2) and (1.3) hold for nonmagnetic crystals.

In Sec. 2 a derivation is given of *generalized Onsager relations* which hold in the presence or in the absence of an external magnetic field, for magnetic as well as nonmagnetic crystals, and which incorporate modifications of the usual Onsager relations required for the symmetry of some magnetic crystals. The relations derived in Sec. 2 are applied in Sec. 3 to obtain symmetry restricted matrices for the thermogalvanomagnetic coefficients for each of the 1651 space-group symmetries. Corresponding restrictions for $\boldsymbol{\rho}$, $\boldsymbol{\kappa}$, $\boldsymbol{\pi}$, and $\boldsymbol{\alpha}$ follow immediately.

2. SPACE-TIME SYMMETRY RESTRICTIONS

We derive generalized Onsager relations in a slightly more general form than is necessary for the specific Eqs. (1.1). We introduce the transport coefficients[12,13]

$$\tau_{B_\mu A_\nu}(\omega,\mathbf{H})=\int_0^\infty dt\, e^{-i\omega t}\int_0^\beta d\lambda\, \mathrm{Tr}\rho(\mathbf{H})A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})\tag{2.1}$$

* Operated with support from the U. S. Air Force.

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[13] R. Kubo, *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I, p. 120.

which depend on the angular frequency ω as well as on the magnetic field $\mathbf{H}$. Derivations and applications of expressions of this type for linear transport coefficients have been reviewed recently.[13a] In (2.1),

$$B_\mu(t;\mathbf{H})\equiv\exp\{[i\mathcal{H}(\mathbf{H})t/\hbar]\}B_\mu \times\exp\{-[i\mathcal{H}(\mathbf{H})t/\hbar]\} \quad (2.2)$$

is the operator B_μ in the Heisenberg picture, with $\mathcal{H}(\mathbf{H})$ the Hamiltonian, and

$$\rho(\mathbf{H})\equiv\exp\{-\beta\mathcal{H}(\mathbf{H})\}/\mathrm{Tr}\exp\{-\beta\mathcal{H}(\mathbf{H})\} \quad (2.3)$$

is the density operator for the canonical ensemble; $\beta=1/kT$ and k is the Boltzmann constant. The trace in (2.1) represents the thermal average $\langle A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})\rangle$, the average of the operator product $A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})$ with respect to the canonical distribution.

If we identify A and B with the electrical and heat current density operators $\mathbf{j}$ and $\mathbf{q}$ and set $\omega=0$, (2.1) gives the following expressions[9] for the coefficients in (1.1)

$$\begin{aligned} S_{\mu\nu}^{(1)}(\mathbf{H})&=\int_0^\infty dt\int_0^\beta d\lambda\langle j_\nu j_\mu(t+i\hbar\lambda;\mathbf{H})\rangle\,,\\ S_{\mu\nu}^{(2)}(\mathbf{H})&=\int_0^\infty dt\int_0^\beta d\lambda\langle q_\nu j_\mu(t+i\hbar\lambda;\mathbf{H})\rangle\,,\\ S_{\mu\nu}^{(3)}(\mathbf{H})&=\int_0^\infty dt\int_0^\beta d\lambda\langle j_\nu q_\mu(t+i\hbar\lambda;\mathbf{H})\rangle\,,\\ S_{\mu\nu}^{(4)}(\mathbf{H})&=\int_0^\infty dt\int_0^\beta d\lambda\langle q_\nu q_\mu(t+i\hbar\lambda;\mathbf{H})\rangle\,. \end{aligned} \quad (2.4)$$

The symmetry properties of these coefficients depend on the transformation properties of $\mathbf{j}$ and $\mathbf{q}$. They would be unaffected, for example, if $\mathbf{j}$ and $\mathbf{q}$ were multiplied by real constants. Consequently, we need not be concerned here with a precise definition of the operators $\mathbf{j}$ and $\mathbf{q}$. For similar reasons, symmetry restrictions obtained using (2.1) or (2.4) as a starting point can be expected to be valid under conditions at least as general as those assumed in deriving these equations.

A. Symmetry Groups

As an aid in deriving and discussing symmetry restrictions we consider the group $\mathcal{K}=\mathcal{K}(\mathbf{H})$ of quantum-mechanical operators corresponding to space-time symmetry transformations[14,15,4] with the property that an element of $\mathcal{K}$ leaves the Hamiltonian $\mathcal{H}(\mathbf{H})$ invariant or changes $\mathcal{H}(\mathbf{H})$ to $\mathcal{H}(-\mathbf{H})$.[16] Time transformations are here restricted to time inversion. $\mathcal{K}$ consists of unitary operators u and antiunitary operators[17] $a=v\theta$, where v is unitary and θ is the time-inversion operator. We assume that $\mathcal{K}(\mathbf{H})$ is a subgroup of $\mathcal{K}(0)$, the group in the absence of a field, an assumption which one can ordinarily expect to be satisfied in practice.

A group $\mathcal{K}$ falls into one of three *categories*. It (a) contains the time-inversion operator θ as an element, (b) does not involve θ, or (c) contains θ only in combination with a spatial operator. These categories provide a convenient classification of the groups $\mathcal{K}$. The space group of a nonmagnetic crystal is one of 230 in category (a). The space group of a magnetic crystal is one of 230 in category (b) or one of 1191 in category (c). The derivation in Sec. 2B is, however, not limited to these 1651 groups and their subgroups.

Associated with $\mathcal{K}$ are the groups $\mathcal{K}_L$, $\mathcal{K}_C$, and $\mathcal{G}$. $\mathcal{K}_L$ is the subgroup of $\mathcal{K}$ of linear operators u. The group $\mathcal{K}_L$ has index 1 or 2 in $\mathcal{K}$ and is therefore an invariant subgroup of $\mathcal{K}$. If $\mathcal{K}$ contains antiunitary operators, it consists of $\mathcal{K}_L$ and the coset $\mathcal{K}_L a$, where a can be any element of the coset: $\mathcal{K}=\mathcal{K}_L+\mathcal{K}_L a$. $\mathcal{K}_C$ is the group of linear operators generated by $\mathcal{K}_L$ and any $v=a\theta^{-1}$: $\mathcal{K}_C=\mathcal{K}_L+\mathcal{K}_L v$. $\mathcal{G}$ is the subgroup of $\mathcal{K}$ which leaves $\mathcal{H}(\mathbf{H})$ invariant: $\mathcal{K}=\mathcal{G}+\mathcal{G}b$, where b is an element of $\mathcal{K}$ (if any) which changes $\mathcal{H}(\mathbf{H})$ to $\mathcal{H}(-\mathbf{H})$. Related groups $\mathcal{G}_L$ and $\mathcal{G}_C$, defined in an obvious way, can also be considered.

When $\mathbf{H}\neq0$ it is convenient to classify a group $\mathcal{K}$ also according to the index of $\mathcal{G}$ in $\mathcal{K}$, the index of $\mathcal{G}_L$ in $\mathcal{G}$, and the index of $\mathcal{K}_L$ in $\mathcal{K}$. The five possible *cases* are indicated in Table I. The case determines the category, as shown. In cases (i) and (ii) $\mathcal{K}=\mathcal{G}$ and $\mathcal{H}(\mathbf{H})$ is invariant; antiunitary operators occur in case (ii) but not in case (i). In cases (iii), (iv), and (v) $\mathcal{K}$ contains elements which reverse the direction of $\mathbf{H}$; in case (iii) these elements are unitary, in case (iv) they are antiunitary, and in case (v) half of these elements are unitary and half are antiunitary.

TABLE I. Classification of symmetry groups for $H\neq0$.

Case	Category	$\mathcal{K}/\mathcal{G}$	$\mathcal{G}/\mathcal{G}_L$	$\mathcal{K}/\mathcal{K}_L$
(i)	(b)	1	1	1
(ii)	(c)	1	2	2
(iii)	(b)	2	1	1
(iv)	(a)	2	1	2
(v)	(a)	2	2	2

B. Derivation

We proceed by transforming (2.1) using the elements of the group $\mathcal{K}(0)$. The operators A_ν and B_μ are assumed

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[14] E. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959).

[15] A. Messiah, *Quantum Mechanics* II (Interscience Publishers, Inc., New York, 1963).

[16] The selection of $\mathcal{H}(\mathbf{H})$ is discussed briefly after (2.29).

[17] Here *unitary* means linear and unitary, while *antiunitary* means antilinear and unitary. For a particularly pertinent discussion of properties of antilinear operators, see Ref. 4.

to have the transformation properties

$$uA_\nu u^{-1}=\sum_\lambda A_\lambda D^{(A)}(u)_{\lambda\nu}, \quad (2.5)$$

$$aA_\nu a^{-1}=\sum_\lambda A_\lambda D^{(A)}(a)_{\lambda\nu}, \quad (2.6)$$

$$uB_\mu u^{-1}=\sum_\kappa B_\kappa D^{(B)}(u)_{\kappa\mu}, \quad (2.7)$$

$$aB_\mu a^{-1}=\sum_\kappa B_\kappa D^{(B)}(a)_{\kappa\mu}. \quad (2.8)$$

The group properties of $\mathcal{K}(0)$ are reflected in the equations[18]

$$D(uu')=D(u)D(u'), \quad D(ua)=D(u)D(a),$$
$$D(au)=D(a)D(u)^*, \quad D(aa')=D(a)D(a')^*, \quad (2.9)$$

satisfied by the co-representation matrices $D(u)$ and $D(a)$.

We first transform the trace in (2.1) using a unitary operator of $\mathcal{K}(0)$. We make use of the identity

$$\mathrm{Tr}LL'=\mathrm{Tr}L'L \quad (2.10)$$

which holds for linear operators L and L', together with $\mathrm{Tr}L=\mathrm{Tr}(u^{-1}u)L(u^{-1}u)=\mathrm{Tr}u^{-1}(uLu^{-1})u$, to obtain

$$\mathrm{Tr}L=\mathrm{Tr}uLu^{-1}. \quad (2.11)$$

On using (2.11) and inserting $u^{-1}u$ between adjacent operator factors in L on the right-hand side we obtain

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})$$
$$=\mathrm{Tr}\{u\exp[-\beta\mathcal{H}(\mathbf{H})]u^{-1}\}[uA_\nu u^{-1}]$$
$$\times[uB_\mu(t+i\hbar\lambda;\mathbf{H})u^{-1}]. \quad (2.12)$$

For u in $\mathcal{K}(0)$

$$u\mathcal{H}(\mathbf{H})u^{-1}=\mathcal{H}(\mathbf{H}_u), \quad (2.13)$$

where $\mathbf{H}_u$ is a transformed field which will be specified later. Consequently, using the definition (2.2) for $B(t;\mathbf{H})$ together with (2.13) and (2.7) gives

$$uB_\mu(t+i\hbar\lambda;\mathbf{H})u^{-1}$$
$$=\sum_\kappa B_\kappa(t+i\hbar\lambda;\mathbf{H}_u)D^{(B)}(u)_{\kappa\mu}. \quad (2.14)$$

On using (2.13), (2.5), and (2.14), (2.12) becomes

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})$$
$$=\sum_{\kappa\lambda}\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H}_u)]A_\lambda B_\kappa(t+i\hbar\lambda;\mathbf{H}_u)$$
$$\times D^{(A)}(u)_{\lambda\nu}D^{(B)}(u)_{\kappa\mu}. \quad (2.15)$$

By letting A_ν and B_μ be the identity operator, we obtain from (2.15) the special case

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]=\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H}_u)]. \quad (2.16)$$

Introducing (2.15) and (2.16) into (2.1) we obtain for every u in $\mathcal{K}(0)$ the linear homogeneous equations

$$\tau_{B_\mu A_\nu}(\omega,\mathbf{H})=\sum_{\kappa\lambda}\tau_{B_\kappa A_\lambda}(\omega,\mathbf{H}_u)D^{(B)}(u)_{\kappa\mu}D^{(A)}(u)_{\lambda\nu} \quad (2.17)$$

for the transport coefficients.

We next use a similar procedure to transform the trace in (2.1) using an antiunitary operator of $\mathcal{K}(0)$. The analog of (2.10) for two antiunitary operators a and a' is

$$\mathrm{Tr}(aa')=[\mathrm{Tr}(a'a)]^*, \quad (2.18)$$

which leads to the analog

$$\mathrm{Tr}L=[\mathrm{Tr}(aLa^{-1})]^* \quad (2.19)$$

of (2.11). The analogs of (2.12), (2.13), and (2.14) are then

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})$$
$$=\{\mathrm{Tr}[a\exp[-\beta\mathcal{H}(\mathbf{H})]a^{-1}][aA_\nu a^{-1}]$$
$$\times[aB_\mu(t+i\hbar\lambda;\mathbf{H})a^{-1}]\}^*, \quad (2.20)$$

$$a\mathcal{H}(\mathbf{H})a^{-1}=\mathcal{H}(\mathbf{H}_a), \quad (2.21)$$

and

$$aB_\mu(t+i\hbar\lambda;\mathbf{H})a^{-1}$$
$$=\sum_\kappa B_\kappa(-t+i\hbar\lambda;\mathbf{H}_a)D^{(B)}(a)_{\kappa\mu}. \quad (2.22)$$

Substituting (2.21), (2.6), and (2.22) into (2.20) gives for the analog of (2.15)

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})$$
$$=\sum_{\kappa\lambda}\{\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H}_a)]A_\lambda B_\kappa(-t+i\hbar\lambda;\mathbf{H}_a)\}^*$$
$$\times D^{(A)}(a)_{\lambda\nu}{}^*D^{(B)}(a)_{\kappa\mu}{}^*. \quad (2.23)$$

By making use of the identity

$$(\mathrm{Tr}L)^*=\mathrm{Tr}L^\dagger \quad (2.24)$$

for the linear operator L, the identity (2.10), and the identity

$$\mathrm{Tr}\exp(-\beta\mathcal{H})B(\tau)A=\mathrm{Tr}\exp(-\beta\mathcal{H})BA(-\tau), \quad (2.25)$$

we transform (2.23) into

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]A_\nu B_\mu(t+i\hbar\lambda;\mathbf{H})$$
$$=\sum_{\kappa\lambda}\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H}_a)]B_\kappa{}^\dagger A_\lambda{}^\dagger(t+i\hbar\lambda;\mathbf{H}_a)$$
$$\times D^{(B)}(a)_{\kappa\mu}{}^*D^{(A)}(a)_{\lambda\nu}{}^*. \quad (2.26)$$

On putting $A_\nu=B_\mu=1$ in (2.26), we find

$$\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H})]=\mathrm{Tr}\exp[-\beta\mathcal{H}(\mathbf{H}_a)] \quad (2.27)$$

the analog of (2.16). On substituting (2.26) and (2.27) into (2.1) we obtain finally the analog of (2.17): For every antiunitary operator a of $\mathcal{K}(0)$ the transport coefficients satisfy the linear relations

$$\tau_{B_\mu A_\nu}(\omega,\mathbf{H})=\sum_{\kappa\lambda}\tau_{A_\lambda{}^\dagger B_\kappa{}^\dagger}(\omega,\mathbf{H}_a)D^{(B)}(a)_{\kappa\mu}{}^*D^{(A)}(a)_{\lambda\nu}{}^*. \quad (2.28)$$

The basic equations are (2.17) and (2.28). The former determine the spatial symmetry restrictions, while the latter determine the symmetry restrictions involving time inversion.

[18] Reference 14, Eq. (26.21).

C. Discussion

To obtain the restrictions imposed on a property tensor by a symmetry group it suffices to use the restrictions determined by a set of elements which generate the group[19,2,3] This is a consequence of the fact that if the property tensor satisfies the restrictions determined by two elements of the group, it also satisfies the restrictions determined by the product of these two elements. In the case of $\tau_{B_\mu A_\nu}(\omega,\mathbf{H})$ this fact can be proved directly by using (2.17) and (2.28) together with the properties (2.9) of the transformation matrices.

The *generalized Onsager relations* result from (2.28) when $\mathcal{K}(\mathbf{H})$ is the group of operators under consideration. Recall that in this case $\mathbf{H}_a=\mathbf{H}$ if a is in $\mathcal{J}(\mathbf{H})$, and $\mathbf{H}_a=-\mathbf{H}$ if not.

If $\mathcal{K}(\mathbf{H})$ is in category (a) of Table I we can take $a=\theta$. Then, $v=1$, $\mathbf{H}_a=-\mathbf{H}$. We assume now that θ either commutes or anticommutes with A_ν and with B_μ, so that $D^{(A)}(\theta)=\pm 1$ and $D^{(B)}(\theta)=\pm 1$. This assumption is satisfied by many operators of practical interest. Then (2.28) reduces to

$$\tau_{B_\mu A_\nu}(\omega,\mathbf{H})=D^{(A)}(\theta)D^{(B)}(\theta)\tau_{A_\nu{}^\dagger B_\mu{}^\dagger}(\omega,-\mathbf{H}), \quad (2.29)$$

the usual form of the Onsager reciprocity relations. For the thermogalvanomagnetic coefficients (2.4), $D^{(j)}(\theta)=D^{(q)}(\theta)=-1$, so that (2.29) reduces to (1.2).

If $\mathcal{K}(\mathbf{H})$ is in category (b) there is no antiunitary operator in $\mathcal{K}(\mathbf{H})$, so that (2.28) cannot be applied, and there is consequently no Onsager reciprocity relation.

If $\mathcal{K}(\mathbf{H})$ is in category (c), (2.28) can be applied only with v not the identity, so that in general (2.28) does not reduce to (2.29). The implications of (2.28) for thermogalvanomagnetic coefficients are examined in more detail in Sec. 3.

The group $\mathcal{K}(H)$ is by definition determined by the Hamiltonian $\mathcal{H}(H)$. In applications the selection of an appropriate $\mathcal{H}(H)$ for use in (2.1) can involve subtle questions which are common to calculations of equilibrium properties and are beyond the scope of the present paper. For example, by adopting a sufficiently fundamental approach, $\mathcal{H}(H)$ can always be chosen for any system so that $\mathcal{K}(H)$ is in category (a) and the usual Onsager reciprocity relations (2.29) hold. This is analogous to the statement that the symmetry group of the Hamiltonian of a crystal includes all spatial transformations and not simply space-group transformations when nuclear motion is taken into account on the same footing as electronic motion (see also Ref. 6, p. 108 and Ref. 3, Chap. 5, Sec. 1). Here we assume that an adequate description of the system can be found using a Hamiltonian $\mathcal{H}(H)$ with symmetry appropriate to the observed symmetry, or with symmetry otherwise prescribed. As a more concrete illustration of a possible application, to calculate the conductivity tensor $S^{(1)}$ in (2.4) for a magnetic crystal with localized magnetic moments (rare-earth ions, say) $\mathcal{H}(0)$ might be taken to describe the motion of conduction electrons in the field of the fixed localized moments; the symmetry of this field would determine the group $\mathcal{K}(0)$.

The procedure used in this section can also be used to determine implications of spatial symmetry and time-inversion symmetry for other physical properties, including microscopic properties. In particular, this procedure can be applied to nonlinear transport coefficients, for example, nonlinear conductivity and susceptibility coefficients.[20,21] In this case, the procedure is applied to a thermal average of r operators where, in contrast to (2.1), $r>2$.

The procedure used here can also be extended to take account of other external fields, such as an electric field and a strain field. This extension can be approached along lines used[22] earlier in connection with spatial symmetry only.

[19] H. Jagodzinski, edited by S. Flügge *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1955), Vol. 7/1, p. 1.

3. APPLICATION TO THERMOGALVANOMAGNETIC COEFFICIENTS

A. Simplification of the Symmetry Restrictions

Let us now apply the results (2.17) and (2.28) of Sec. 2 to the case of thermogalvanomagnetic coefficients. In this case A_ν and B_μ are both components of translationally invariant polar vectors which change sign under time reversal. We shall take A_ν and B_μ to be rectangular components. Consequently, for the space-group operator[4] $u=\{\sigma|t\}$, where σ is an operator representing a point-group transformation and t is an operator representing a translation,

$$D^{(A)}(u)=D^{(B)}(u)=D(\sigma) \quad (3.1)$$

is a real orthogonal 3×3 matrix.

It is convenient to introduce the proper counterpart P_σ of σ. If σ is an improper rotation operator we can write $\sigma=IP_\sigma=P_\sigma I$, where P_σ is a proper (or pure) rotation operator and I is the spatial inversion operator. Then $P_\sigma=I\sigma$ and $D(\sigma)=-D(P_\sigma)$. If σ is a proper rotation operator, $\sigma=P_\sigma$. Consequently, $D^{(B)}(u)_{\kappa\mu}D^{(A)}(u)_{\lambda\nu}$ in (2.17) can be replaced by $D(P_\sigma)_{\kappa\mu}D(P_\sigma)_{\lambda\nu}$, so that (2.17) simplifies to

$$\tau_{B_\mu A_\nu}(\mathbf{H})=\sum_{\kappa\lambda}\tau_{B_\kappa A_\lambda}(\mathbf{H}_u)D(P_\sigma)_{\kappa\mu}D(P_\sigma)_{\lambda\nu}, \quad (3.2)$$

where we have suppressed the dependence on ω. Similarly, if $v=\{\rho|t'\}$, (2.28) simplifies to

$$\tau_{B_\mu A_\nu}(\mathbf{H})=\sum_{\kappa\lambda}\tau_{A_\lambda B_\kappa}(\mathbf{H}_a)D(P_\rho)_{\kappa\mu}D(P_\rho)_{\lambda\nu}. \quad (3.3)$$

In (3.2), $\mathbf{H}_u$ is given by

$$H_{u\alpha}=\sum_\beta D(P_\sigma)_{\alpha\beta}H_\beta \quad (3.4)$$

and in (3.3), $\mathbf{H}_a$ is given by

$$H_{a\alpha}=-\sum_\beta D(P_\rho)_{\alpha\beta}H_\beta. \quad (3.5)$$

In (3.4) and (3.5) account has been taken of the fact

[20] P. N. Butcher and T. P. McLean, Proc. Phys. Soc. (London) **83**, 579 (1964).

[21] P. S. Pershan, Phys. Rev. **130**, 919 (1963).

[22] L. Grabner and J. A. Swanson, J. Math. Phys. **3**, 1050 (1962).

that the magnetic field $\mathbf{H}$ is an axial vector which changes sign under time reversal.

Alternative forms for (3.2) and (3.3) often found convenient in applications can be obtained by replacing D by $\tilde{R}=R^{-1}=D$ and $\mathbf{H}$ by $\mathbf{H}_{u^{-1}}=\mathbf{H}_{\sigma^{-1}}$ in (3.2) and $\mathbf{H}_{a^{-1}}=-\mathbf{H}_{\rho^{-1}}$ in (3.3). Then (3.2) and (3.3) become

$$\tau_{B_\mu A_\nu}[\mathbf{H}(\sigma)]=\sum_{\kappa\lambda} R(P_\sigma)_{\mu\kappa}R(P_\sigma)_{\nu\lambda}\tau_{B_\kappa A_\lambda}(\mathbf{H}), \quad (3.6)$$

and

$$\tau_{B_\mu A_\nu}[-\mathbf{H}(\rho)]=\sum_{\kappa\lambda} R(P_\rho)_{\mu\kappa}R(P_\rho)_{\nu\lambda}\tau_{A_\lambda B_\kappa}(\mathbf{H}), \quad (3.7)$$

where

$$H(\sigma)_\mu=H_{u^{-1}\mu}=H_\mu'=\sum\nolimits_\nu R_{\mu\nu}(P_\sigma)H_\nu \quad (3.8)$$

and the corresponding coordinate transformation is

$$x(\sigma)_\mu=x_\mu'=\sum\nolimits_\nu R_{\mu\nu}(\sigma)x_\nu. \quad (3.9)$$

The usual method[19,22–24,2,3] for deriving spatial symmetry restrictions on property tensors, based on tensor transformations [such as (3.9)], leads directly to (3.7).

B. Laue Groups

The group $\mathcal{K}(0)$ in the present application is a group of quantum-mechanical operators representing one of the 1651 3-dimensional space groups of symmetry transformations which exist when time inversion is taken into account.[5,4] We see from (3.2) and (3.3) or (3.6) and (3.7) that the symmetry restrictions imposed by one of these groups are the same as those imposed by its Laue group (enantiomorphous group). The *Laue group* of a group is defined here as the group obtained from the given group by [1] replacing every translation by the identity, and [2] replacing every improper rotation by its proper counterpart. The operation [1] replaces a space group by its point group, while [2] replaces a space group by a space group containing no improper elements. We denote by a superscript L the result of applying operations [1] and [2]; thus, the Laue group of $\mathcal{K}$ is $\mathcal{K}^L$. $\mathcal{K}^L$ is a point group involving spatial operators only in the form of pure rotation operators. Every space group and every point group has a unique Laue group.

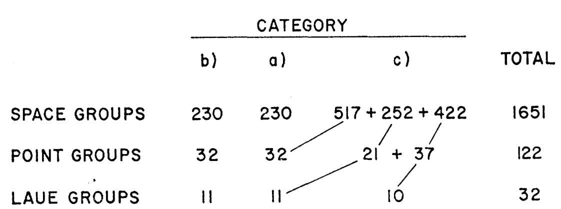

FIG. 1. Number of space groups, point groups, and Laue groups in each of the categories (a), (b), and (c).

[23] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1960).

[24] C. S. Smith, *Solid State Physics*, edited by F. Seitz and G. Turnbull (Academic Press Inc., New York, 1958), Vol. 6, p. 175.

TABLE II. Classification of the crystallographic point groups according to their Laue groups. International symbols are used to denote the groups (see Ref. 25, p. 28, Ref. 5, p. xiii, and Ref. 8). The prime denotes that the spatial point operation is combined with time inversion. The Laue group is given for each of the point groups of category (b) and category (c). The point groups of category (a) are omitted from the table, since the Laue group of a point group of category (a) is obtained simply by appending 1′ to the Laue group of the corresponding point group of category (b). Table II corresponds to an extension to include time inversion of Table 3.8.1 of Ref. 25.

Point groups	Laue groups
(b)	(b)
$1, \bar{1}$	1
$2, m, 2/m$	2
$222, mm2, mmm$	222
$4, \bar{4}, 4/m$	4
$422, 4mm, \bar{4}2m, 4/mmm$	422
$3, \bar{3}$	3
$32, 3m, \bar{3}m$	32
$6, \bar{6}, 6/m$	6
$622, 6mm, \bar{6}m2, 6/mmm$	622
$23, m3$	23
$432, \bar{4}3m, m3m$	432
(c)	(a)
$\bar{1}'$	$1'$
$2/m', 2'/m$	$21'$
$m'm'm', mmm'$	$2221'$
$4/m', 4'/m'$	$41'$
$4/m'm'm', 4/m'mm, 4'/m'm'm$	$4221'$
$\bar{3}'$	$3'$
$\bar{3}'m', \bar{3}'m$	$3'2$
$6/m', 6'/m$	$61'$
$6/m'm'm', 6/m'mm, 6'/mmm'$	$6221'$
$m'3$	$23'$
$m'3m', m'3m$	$43'2$
	(c)
$2', m', 2'/m'$	$2'$
$2'2'2, m'm'2, 2'm'm, m'm'm$	$2'2'2$
$4', \bar{4}', 4'/m$	$4'$
$4'22', 4'mm', \bar{4}'2m', \bar{4}'m2', 4'/mmm$	$4'22'$
$42'2', 4m'm', \bar{4}2'm', 4/mm'm'$	$42'2'$
$32', 3m', \bar{3}m'$	$32'$
$6', \bar{6}', 6'/m'$	$6'$
$6'22', 6'mm', \bar{6}'2m', \bar{6}'m2', 6'/m'mm'$	$6'22'$
$62'2', 6m'm', \bar{6}m'2', 6/mm'm'$	$62'2'$
$4'32', \bar{4}'3m', m3m'$	$4'32'$

Figure 1 shows the number of space groups, point groups, and Laue groups in each of the categories (a), (b), and (c) defined in Sec. 2A. The lines indicate the genealogy of the groups with respect to the operations [1] and [2], and are based on the effect of these operations applied in succession on $\{\sigma|t\}$:

$$\{\sigma|t\}\underset{[1]}{\longrightarrow}\sigma\underset{[2]}{\longrightarrow}P_\sigma. \quad (3.10)$$

Category (c) space groups are further classified into three mutually exclusive subcategories (c.1) ,(c.2), and (c.3) of which there are 517, 252, and 422, respectively. A category (c) space group is of subcategory (c.1) if it contains an element of the form $\{E|t\}\theta$, where t is nonprimitive and E is the identity operator. Otherwise, it is either of subcategory (c.2) if it contains an element of the form $\{I|t\}\theta$ with t nonprimitive, or else it is of subcategory (c.3) if it does not. A point group of category (c) is one of 21 groups if it contains $I\theta$ as an element;

TABLE III. Classification of the crystallographic and limiting Laue groups. Category and case refer to Table I. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for various classifications are given in the tables indicated.

	Category	Case	Table	Groups
$H=0$	(b)		4	$\mathcal{K}^L=\mathcal{K}_L{}^L=\mathcal{K}_C{}^L$: all 11 crystallographic groups; ∞, $\infty 2$, $\infty\infty$
	(a)		5	$\mathcal{K}^L=\mathcal{K}_L{}^L+\mathcal{K}_L{}^L\theta$: all 11 crystallographic groups; $\infty 1'$, $\infty 21'$, $\infty\infty 1'$
	(c)		6	$\mathcal{K}^L=\mathcal{K}_L{}^L+\mathcal{K}_L{}^La^L$: all 10 crystallographic groups; $\infty 2'$
$H\neq 0$	(b)	(i)	4	$\mathcal{K}^L=\mathcal{G}_L{}^L=\mathcal{G}_C{}^L$: 1, 2, 3, 4, 6; ∞
		(iii)	7	$\mathcal{K}^L=\mathcal{K}_L{}^L=\mathcal{G}_L{}^L+\mathcal{G}_L{}^Lb_L{}^L\neq\mathcal{G}_L{}^L$: 2, 222, 32, 422, 622; $\infty 2$
	(a)	(iv)	8	$\mathcal{K}^L=\mathcal{G}_L{}^L+\mathcal{G}_L{}^L\theta$: 1′, 21′, 3′, 41′, 61′; $\infty 1'$
		(v)	9	$\mathcal{K}^L=\mathcal{K}_L{}^L+\mathcal{K}_L{}^L\theta$, $\mathcal{K}_L{}^L=\mathcal{G}_L{}^L+\mathcal{G}_L{}^Lb_L{}^L\neq\mathcal{G}_L{}^L$: 21′, 2221′, 3′2, 4221′, 6221′; $\infty 21'$
	(c)	(ii)	6	$\mathcal{K}^L=\mathcal{G}^L=\mathcal{G}_L{}^L+\mathcal{G}_L{}^La^L\neq\mathcal{G}_L{}^L$: 2′, 22′2′, 32′, 42′2′, 62′2′; $\infty 2'$

otherwise it is one of 37. From Fig. 1 we observe that although a space group of category (a) has a Laue group of category (a) and a space group of category (b) has a Laue group of category (b), a space group of category (c) can have a Laue group of either category (a) or category (c).

The correspondence between point groups and Laue groups indicated in Fig. 1 is detailed in Table II. International symbols[25,5,8] are used to denote the groups. Determining the subcategory of a category (c) space group from a table[5–7] of space groups is facilitated by use of Table II.

For polycrystalline samples it is useful to consider groups with infinite-fold axes (*limiting*[26] groups). A limiting group arises as the limit as $n\to\infty$ of a sequence of groups with an n-fold axis. Different sequences may lead to limiting groups which are indistinguishable, at least insofar as they imply the same symmetry restrictions. Whether ∞' and $\infty 1'$ are regarded as identical or not,[27] the symmetry restrictions for ∞' are the same as for $\infty 1'$, since an infinitesimal rotation approaches the identity in the limit. Consequently, we make the identifications $\infty'=\infty 1'$, $\infty'2=\infty 21'=\infty'2'$, and $\infty'\infty=\infty\infty 1'=\infty'\infty'$. Our considerations of limiting groups are restricted in what follows to limiting Laue groups.

The 32 crystallographic Laue groups and 7 limiting Laue groups are classified in Table III for $\mathbf{H}=0$ and $\mathbf{H}\neq 0$ according to the three categories. For $\mathbf{H}\neq 0$ they are further classified according to the five cases of Table I.

C. Symmetry-Restricted Matrices of Thermogalvanomagnetic Coefficients

The symmetry restrictions (3.6) and (3.7) constitute a system of linear homogeneous equations. To obtain all the symmetry restrictions for given $\mathbf{H}$ it suffices to use only equations determined by a set of elements which generate the Laue group $\mathcal{K}^L(\mathbf{H})$. The relations among the transport coefficients which result from solving these equations are conveniently expressed in matrix form. Such *symmetry-restricted matrices* are listed in Tables IV–IX. The effect of the symmetry restric-

TABLE IV. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for $H=0$, (b).

Laue group	$\boldsymbol{\tau}$
1	$\begin{pmatrix}\tau_{xx} & \tau_{xy} & \tau_{xz}\\ \tau_{yx} & \tau_{yy} & \tau_{yz}\\ \tau_{zx} & \tau_{zy} & \tau_{zz}\end{pmatrix}$
2	$\begin{pmatrix}\tau_{xx} & \tau_{xy} & 0\\ \tau_{yx} & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$
222	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$
3, 4, 6; ∞	$\begin{pmatrix}\tau_{xx} & \tau_{xy} & 0\\ -\tau_{xy} & \tau_{xx} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$
32, 422, 622; $\infty 2$	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{xx} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$
23, 432; $\infty\infty$	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{xx} & 0\\ 0 & 0 & \tau_{xx}\end{pmatrix}$

TABLE V. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for $H=0$, (a).

Laue group	$\boldsymbol{\tau}'$	$\boldsymbol{\sigma}$
1′	$\begin{pmatrix}\tau_{xx} & \tau_{yx} & \tau_{zx}\\ \tau_{xy} & \tau_{yy} & \tau_{zy}\\ \tau_{xz} & \tau_{yz} & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & \sigma_{xy} & \sigma_{xz}\\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz}\\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz}\end{pmatrix}$
21′	$\begin{pmatrix}\tau_{xx} & \tau_{yx} & 0\\ \tau_{xy} & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & \sigma_{xy} & 0\\ \sigma_{xy} & \sigma_{yy} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$
2221′	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & 0 & 0\\ 0 & \sigma_{yy} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$
3′, 41′, 61′ 3′2, 4221′, 6221′; $\infty 1'$, $\infty 21'$	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{xx} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & 0 & 0\\ 0 & \sigma_{xx} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$
23′, 43′2; $\infty\infty 1'$	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{xx} & 0\\ 0 & 0 & \tau_{xx}\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & 0 & 0\\ 0 & \sigma_{xx} & 0\\ 0 & 0 & \sigma_{xx}\end{pmatrix}$

[25] *International Tables for X-ray Crystallography I* (Kynoch Press, Birmingham, England, 1952).
[26] Reference 5, pp. 75, 161.
[27] Reference 5, p. 116.

TABLE VI. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for $H=0$, (c).

Laue group	$\boldsymbol{\tau}'$	$\boldsymbol{\sigma}$
$2'$	$\begin{pmatrix} \tau_{xx} & \tau_{yx} & -\tau_{zx} \\ \tau_{xy} & \tau_{yy} & -\tau_{zy} \\ -\tau_{xz} & -\tau_{yz} & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ -\sigma_{xz} & -\sigma_{yz} & \sigma_{zz} \end{pmatrix}$
$2'2'2$	$\begin{pmatrix} \tau_{xx} & -\tau_{yx} & 0 \\ -\tau_{xy} & \tau_{yy} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
$32'$, $42'2'$ $62'2'$; $\infty 2'$	$\begin{pmatrix} \tau_{xx} & \tau_{xy} & 0 \\ -\tau_{xy} & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
$4'$	$\begin{pmatrix} \tau_{yy} & -\tau_{xy} & 0 \\ -\tau_{yx} & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
$4'22'$	$\begin{pmatrix} \tau_{yy} & 0 & 0 \\ 0 & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
$6'$	$\begin{pmatrix} \tau_{xx} & -\tau_{xy} & 0 \\ \tau_{xy} & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
$6'22'$	$\begin{pmatrix} \tau_{xx} & 0 & 0 \\ 0 & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
$4'32'$	$\begin{pmatrix} \tau_{xx} & 0 & 0 \\ 0 & \tau_{xx} & 0 \\ 0 & 0 & \tau_{xx} \end{pmatrix}$	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{xx} \end{pmatrix}$

tions for all 32 crystallographic and 7 limiting Laue groups can be determined from these tables by inspection. These results are classified according to Table III, as shown in the "Table" column. Although the results in Tables IV, V, VIII, and IX are not entirely new,[28] all results are included since it is useful to have them presented together for comparison and for reference.

The abbreviations $\tau_{\mu\nu}=\tau_{A_\mu B_\nu}$, $\tau_{\mu\nu}'=\tau_{B_\mu A_\nu}$, $\sigma_{\mu\nu}=\tau_{A_\mu A_\nu}$ are used, where we can choose $A=j$, $B=q$ or $A=q$, $B=j$.

TABLE VII. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for $H\neq 0$, (b.iii).

Laue group	$\boldsymbol{\tau}^e(H)$	$\boldsymbol{\tau}^o(H)$
2	$\begin{pmatrix} \tau_{xx} & \tau_{xy} & 0 \\ \tau_{yx} & \tau_{yy} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \tau_{xz} \\ 0 & 0 & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & 0 \end{pmatrix}$
222	$\begin{pmatrix} \tau_{xx} & 0 & 0 \\ 0 & \tau_{yy} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} 0 & \tau_{xy} & 0 \\ \tau_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$
32, 422, 622; $\infty 2$	$\begin{pmatrix} \tau_{xx} & 0 & 0 \\ 0 & \tau_{xx} & 0 \\ 0 & 0 & \tau_{zz} \end{pmatrix}$	$\begin{pmatrix} 0 & \tau_{xy} & 0 \\ -\tau_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$

[28] The results in Table IV are given in Ref. 2, Table 2(d), in Ref. 3, Table 4d, and, in a different but convenient form, in Ref. 23, p. 227. The matrices for $\boldsymbol{\sigma}$ in Table V are given in Ref. 23 p. 23 and in Ref. 24, p. 215. Some of the matrices for $\boldsymbol{\sigma}$ in Tables VIII and IX occur in Ref. 22, Eqs. (25)–(27).

Thus, $\boldsymbol{\tau}$ and $\boldsymbol{\tau}'$ represent $\mathbf{S}^{(2)}$ and $\mathbf{S}^{(3)}$ or $\mathbf{S}^{(3)}$ and $\mathbf{S}^{(2)}$ in (2.4), while $\boldsymbol{\sigma}$ represents $\mathbf{S}^{(1)}$ and $\mathbf{S}^{(4)}$.

In the remainder of this subsection each of the classifications in Table III is discussed briefly.

$\mathbf{H}=0$

When $\mathbf{H}=0$, $\mathcal{K}=\mathcal{G}$.

(b) In this case the symmetry-restricted matrices result from application of (3.6). The matrices for $\boldsymbol{\tau}$ are listed in Table IV; $\boldsymbol{\tau}'$ and $\boldsymbol{\sigma}$ have the same form as $\boldsymbol{\tau}$.

(a) In this case $\theta=1'$ is an element of the Laue group and (3.7) implies the usual Onsager relations: $\tau_{\mu\nu}'=\tau_{\mu\nu}$ and $\sigma_{\mu\nu}=\sigma_{\nu\mu}$. These are to be imposed on the symmetry-restricted matrix of $\boldsymbol{\tau}$ for $\mathcal{K}_L{}^L$ given in Table IV. The resulting symmetry-restricted matrices are given in Table V.

(c) The symmetry-restricted matrices for $\boldsymbol{\tau}'$ and $\boldsymbol{\sigma}$ are given in Table VI for this case. These are obtained by imposing on the symmetry-restricted matrix for $\mathcal{K}_L{}^L$, as given in Table IV, any additional restrictions arising from using an element of $\mathcal{K}_L{}^L a^L$ in (3.7).

$\mathbf{H}\neq 0$

For $\mathbf{H}\neq 0$ it is convenient to represent the results in terms of the parts of $\boldsymbol{\tau}$, $\boldsymbol{\tau}'$, and $\boldsymbol{\sigma}$ even and odd with respect to reversal of the direction of $\mathbf{H}$.

$$\boldsymbol{\tau}^e(\mathbf{H})\equiv\tfrac{1}{2}[\boldsymbol{\tau}(\mathbf{H})+\boldsymbol{\tau}(-\mathbf{H})], \qquad (3.11a)$$

$$\boldsymbol{\tau}^o(\mathbf{H})\equiv\tfrac{1}{2}[\boldsymbol{\tau}(\mathbf{H})-\boldsymbol{\tau}(-\mathbf{H})]. \qquad (3.11b)$$

In terms of these quantities, (3.6) takes the form

$$\tau^e[H(\sigma)]_{\mu\nu}=\sum_{\kappa\lambda} R(P_\sigma)_{\mu\kappa}R(P_\sigma)_{\nu\lambda}\tau^e(\mathbf{H})_{\kappa\lambda}, \qquad (3.12a)$$

$$\tau^o[H(\sigma)]_{\mu\nu}=\sum_{\kappa\lambda} R(P_\sigma)_{\mu\kappa}R(P_\sigma)_{\nu\lambda}\tau^o(\mathbf{H})_{\kappa\lambda}, \qquad (3.12b)$$

and (3.7) takes the form

$$\tau'^e[H(\rho)]_{\mu\nu}=\sum_{\kappa\lambda} R(P_\rho)_{\mu\kappa}R(P_\rho)_{\nu\lambda}\tau^e(\mathbf{H})_{\lambda\kappa}, \qquad (3.13a)$$

$$-\tau'^o[H(\rho)]_{\mu\nu}=\sum_{\kappa\lambda} R(P_\rho)_{\mu\kappa}R(P_\rho)_{\nu\lambda}\tau^o(\mathbf{H})_{\lambda\kappa}. \qquad (3.13b)$$

For complete symmetry information the same groups are involved as for $\mathbf{H}=0$, but for determining the symmetry-restricted matrices of $\boldsymbol{\tau}$, $\boldsymbol{\tau}'$, and $\boldsymbol{\sigma}$ for given $\mathbf{H}$ only the subgroups $\mathcal{G}(\mathbf{H})$ and $\mathcal{K}(\mathbf{H})$ enter. Each operator group $\mathcal{G}(\mathbf{H})$ represents the intersection of a space group with the group of space-time transformations which leave $\mathbf{H}$ invariant, while each operator group $\mathcal{K}(\mathbf{H})$ represents the intersection of a space group with the group of space-time transformations an element of which either leaves $\mathbf{H}$ invariant or reverses its direction. Corresponding statements hold for the point group and for the Laue group of a group $\mathcal{G}(\mathbf{H})$ and of a group $\mathcal{K}(\mathbf{H})$. The Laue group which leaves $\mathbf{H}$ invariant is $\infty 2'$; the Laue group an element of which either leaves $\mathbf{H}$ invariant or reverses its direction is $\infty 21'$.

TABLE VIII. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for $H\neq0$, (a.iv).

Laue group $\mathcal{K}_L{}^L=\mathcal{G}_L{}^L$	$\boldsymbol{\tau}'^e(H)$	$\boldsymbol{\tau}'^o(H)$	$\boldsymbol{\sigma}^e(H)$	$\boldsymbol{\sigma}^o(H)$
$1'$	$\begin{pmatrix}\tau_{xx} & \tau_{yx} & \tau_{zx}\\ \tau_{xy} & \tau_{yy} & \tau_{zy}\\ \tau_{xz} & \tau_{yz} & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & -\tau_{yx} & -\tau_{zx}\\ -\tau_{xy} & 0 & -\tau_{zy}\\ -\tau_{xz} & -\tau_{yz} & 0\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & \sigma_{xy} & \sigma_{xz}\\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz}\\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \sigma_{xy} & \sigma_{xz}\\ -\sigma_{xy} & 0 & \sigma_{yz}\\ -\sigma_{xz} & -\sigma_{yz} & 0\end{pmatrix}$
$21'$	$\begin{pmatrix}\tau_{xx} & \tau_{yx} & 0\\ \tau_{xy} & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & -\tau_{yx} & 0\\ -\tau_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & \sigma_{xy} & 0\\ \sigma_{xy} & \sigma_{yy} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \sigma_{xy} & 0\\ -\sigma_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$
$3'$, $41'$, $61'$; $\infty 1'$	$\begin{pmatrix}\tau_{xx} & -\tau_{xy} & 0\\ \tau_{xy} & \tau_{xx} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \tau_{xy} & 0\\ -\tau_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & 0 & 0\\ 0 & \sigma_{xx} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \sigma_{xy} & 0\\ -\sigma_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$

TABLE IX. Symmetry-restricted matrices of thermogalvanomagnetic coefficients for $H\neq0$, (a.v).

Laue group $\mathcal{K}_L{}^L\neq\mathcal{G}_L{}^L$	$\boldsymbol{\tau}'^e(H)$	$\boldsymbol{\tau}'^o(H)$	$\boldsymbol{\sigma}^e(H)$	$\boldsymbol{\sigma}^o(H)$
$21'$	$\begin{pmatrix}\tau_{xx} & \tau_{yx} & 0\\ \tau_{xy} & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & 0 & -\tau_{zx}\\ 0 & 0 & -\tau_{zy}\\ -\tau_{xz} & -\tau_{yz} & 0\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & \sigma_{xy} & 0\\ \sigma_{xy} & \sigma_{yy} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & 0 & \sigma_{xz}\\ 0 & 0 & \sigma_{yz}\\ -\sigma_{xz} & -\sigma_{yz} & 0\end{pmatrix}$
$2221'$	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{yy} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & -\tau_{yx} & 0\\ -\tau_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & 0 & 0\\ 0 & \sigma_{yy} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \sigma_{xy} & 0\\ -\sigma_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$
$3'2$, $4221'$, $6221'$; $\infty 21'$	$\begin{pmatrix}\tau_{xx} & 0 & 0\\ 0 & \tau_{xx} & 0\\ 0 & 0 & \tau_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \tau_{xy} & 0\\ -\tau_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$	$\begin{pmatrix}\sigma_{xx} & 0 & 0\\ 0 & \sigma_{xx} & 0\\ 0 & 0 & \sigma_{zz}\end{pmatrix}$	$\begin{pmatrix}0 & \sigma_{xy} & 0\\ -\sigma_{xy} & 0 & 0\\ 0 & 0 & 0\end{pmatrix}$

It is important to bear in mind that the coordinate axes of the Laue groups listed in Table III may not coincide with crystal coordinate axes. The symmetry-restricted matrices of $\boldsymbol{\tau}$, $\boldsymbol{\tau}'$, and $\boldsymbol{\sigma}$ referred to crystal coordinates are then obtained from the tabulated matrices by a rotation of coordinates. Concomitantly, a different choice of the independent parameters of $\boldsymbol{\tau}$, $\boldsymbol{\tau}'$, and $\boldsymbol{\sigma}$ may be convenient.

(b.i) In this case $\mathcal{K}^L$ does not involve θ and it leaves $\mathbf{H}$ invariant. It is therefore a point group which is a subgroup of the group ∞. The symmetry-restricted matrix is the same for $\boldsymbol{\tau}^e$ and $\boldsymbol{\tau}^o$, and is given in Table IV for each of the crystallographic and limiting Laue groups; $\boldsymbol{\tau}'$ and $\boldsymbol{\sigma}$ have the same form as $\boldsymbol{\tau}$.

(b.iii) The elements of $\mathcal{G}_L{}^L$ leave $\mathbf{H}$ invariant. The elements of $\mathcal{K}_L{}^L-\mathcal{G}_L{}^L$ reverse the direction of $\mathbf{H}$ and are therefore twofold rotations perpendicular to $\mathbf{H}$. The Laue group $\mathcal{K}^L$ is consequently one of the subgroups of $\infty 2$ obtained by augmenting those for (b.i) with a twofold rotation perpendicular to $\mathbf{H}$. The symmetry-restricted matrix of $\boldsymbol{\tau}$ is obtained correspondingly from that for $\mathcal{G}_L{}^L$, given in Table IV, by imposing the restrictions (3.6) for one of the elements of $\mathcal{K}_L{}^L-\mathcal{G}_L{}^L$. If the element is 2_x, then $R_{xx}=-R_{yy}=-R_{zz}=1$, $R_{\mu\nu}=0$, $\mu\neq\nu$. This restriction takes the form

$$\tau(-\mathbf{H})_{\mu\nu}=R(2_x)_{\mu\mu}R(2_x)_{\nu\nu}\tau(\mathbf{H})_{\mu\nu}, \qquad (3.14)$$

or, from (3.12),

$$\tau^e(\mathbf{H})_{\mu\nu}=R(2_x)_{\mu\mu}R(2_x)_{\nu\nu}\tau^e(\mathbf{H})_{\mu\nu}, \qquad (3.15a)$$

$$-\tau^o(\mathbf{H})_{\mu\nu}=R(2_x)_{\mu\mu}R(2_x)_{\nu\nu}\tau^o(\mathbf{H})_{\mu\nu}. \qquad (3.15b)$$

The resulting symmetry-restricted matrices for $\boldsymbol{\tau}$ are given in Table VII. Notice that those for $\boldsymbol{\tau}^e$ are the same as in Table IV. The symmetry-restricted matrices for $\boldsymbol{\tau}'$ and $\boldsymbol{\sigma}$ are the same as for $\boldsymbol{\tau}$.

(a.iv, a.v) These groups can be obtained by appending $\theta=1'$ to the groups of category (b). When θ is used as a group element (3.7) reduces to the usual Onsager relations

$$\tau'(\mathbf{H})_{\mu\nu}=\tau(-\mathbf{H})_{\nu\mu}, \qquad (3.16)$$

$$\sigma(\mathbf{H})_{\mu\nu}=\sigma(-\mathbf{H})_{\nu\mu}, \qquad (3.17)$$

or, according to (3.13),

$$\tau'^e(\mathbf{H})_{\mu\nu}=\tau^e(\mathbf{H})_{\nu\mu}, \quad \tau'^o(\mathbf{H})_{\mu\nu}=-\tau^o(\mathbf{H})_{\nu\mu}, \qquad (3.18)$$

$$\sigma^e(\mathbf{H})_{\mu\nu}=\sigma^e(\mathbf{H})_{\nu\mu}, \quad \sigma^o(\mathbf{H})_{\mu\nu}=-\sigma^o(\mathbf{H})_{\nu\mu}. \qquad (3.19)$$

These restrictions are to be imposed on the symmetry-restricted matrices for $\mathcal{K}_L{}^L$, given in Table IV in case $\mathcal{K}_L{}^L=\mathcal{G}_L{}^L$ and in Table VII in case $\mathcal{K}_L{}^L\neq\mathcal{G}_L{}^L$. The resulting symmetry-restricted matrices are given in Tables VIII and IX.

(c.ii) Each group in this case is formed by appending to a group $\mathcal{G}_L{}^L$ an antibinary rotation $a^L=2'$ with axis perpendicular to **H**. Notice that no Laue groups $\mathcal{K}^L(\mathbf{H})$ in category (c) contain elements which reverse the direction of **H**. This is in contrast to the groups which yield the ordinary Onsager relations (2.29); the latter groups are in category (a) and always have $\mathcal{K}^L \neq \mathcal{G}^L$.

The symmetry-restricted matrices are obtained in this case from those of $\mathcal{G}_L{}^L$, given in Table IV, by applying (3.7) using an element of $\mathcal{G}_L{}^L a^L$. For the element $a^L=2'$, (3.7) reduces to

$$\tau'(\mathbf{H})_{\mu\nu}=\sum_{\kappa\lambda} R(2)_{\mu\kappa}R(2)_{\nu\lambda}\tau(\mathbf{H})_{\lambda\kappa} \qquad (3.20)$$

which has the same form as when $\mathbf{H}=0$. The resulting symmetry-restricted matrices for $\boldsymbol{\tau}'(\mathbf{H})$ and $\boldsymbol{\sigma}(\mathbf{H})$ are given in Table VI. Equation (3.20) also relates $\boldsymbol{\tau}'^e$ to $\boldsymbol{\tau}^e$ and $\boldsymbol{\tau}'^o$ to $\boldsymbol{\tau}^o$, so that Table VI applies as well for $\boldsymbol{\tau}'^e$, $\boldsymbol{\sigma}^e$ and $\boldsymbol{\tau}'^o$, $\boldsymbol{\sigma}^o$.

Inspection of the tables shows that as the Laue symmetry increases, transformations involving time inversion tend, roughly speaking, to have a smaller additional effect on the form of the symmetry-restricted matrices.

To illustrate the difference between the symmetry-restricted matrices given here and those given earlier by Birss[2,3] we consider the $\mathbf{H}=0$ electrical conductivity $\boldsymbol{\sigma}$ for an orthorhombic crystal with Laue group $2'2'2$. The symmetry restricted matrix is given in Table VI, according to the present theory. On the other hand, according to Birss, the symmetry restrictions are determined by the maximal subgroup of $2'2'2$ which does not involve time inversion, namely, the group 2, together with the restrictions imposed by the usual Onsager relations, namely, that $\boldsymbol{\sigma}$ be symmetric. The symmetry-restricted conductivity matrix for $2'2'2$ predicted by Birss is thus the same as that given in Table V for $21'$. It is symmetric and clearly different from the one given in Table VI, which is antisymmetric.

It appears that Birss' prescription for symmetry-restricted matrices is inconsistent with the existence of the extraordinary Hall effect in ferromagnets.

D. Symmetry-Restricted Matrices of the Isothermal Magnetic Susceptibility

With regard to symmetry restrictions the implications of time inversion for equilibrium properties are in general different from the implications of time inversion for transport properties. To illustrate this consider the isothermal magnetic susceptibility $\boldsymbol{\chi}$, an equilibrium property. The magnetic susceptibility and the thermogalvanomagnetic coefficients are both second-rank polar tensors, and therefore transform the same way under spatial transformations. Time inversion has no effect on the isothermal magnetic susceptibility, in contrast to its effect on the thermogalvanomagnetic coefficients. There are, however, *intrinsic symmetry*[29–31] restrictions which are separate from the space-time symmetry restrictions. Intrinsic symmetry requires the isothermal magnetic susceptibility to be symmetric in its tensor indices. This is evident from the definition, $\chi_{\mu\nu}\equiv-\partial^2F/\partial H_\mu\partial H_\nu$, where F is the appropriate free energy.

It follows that, aside from the intrinsic symmetry, the symmetry-restricted matrices for the isothermal magnetic susceptibility are the same as for the electrical conductivity except that the Laue group $\mathcal{K}_C{}^L$ is used instead of the Laue group $\mathcal{K}^L$. ($\mathcal{K}_C{}^L$ is obtained from $\mathcal{K}^L$ by replacing time inversion wherever it occurs by the identity.)

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