

## Space-Time Symmetry Restrictions on Transport Coefficients. II. Two Theories Compared

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(Received 9 February 1966)

The space-time symmetry restrictions on transport coefficients given by two recent theories are compared and the differences are exhibited in detail for the zero-magnetic-field electrical conductivity. The symmetry restrictions of one of the theories are shown to be inconsistent with the existence of the extraordinary Hall effect in ferromagnets.

THE theory of symmetry of properties of crystals has a long history. The implications of spatial symmetry for macroscopic properties of crystals were developed exhaustively by Voigt.<sup>1</sup> Other restrictions were introduced by Onsager<sup>2,3</sup> for transport coefficients. The Onsager reciprocity relations are a consequence of time-inversion symmetry. These developments, which have been reviewed by many authors,<sup>4-6</sup> dealt with crystals which are *nonmagnetic* (diamagnetic, paramagnetic).

The effect of spatial symmetry and time-inversion symmetry on properties of *magnetic* as well as nonmagnetic systems was discussed initially in 1951 by Landau and Lifshitz,<sup>7,8</sup> was developed for equilibrium properties by Le Corre<sup>9</sup> and Birss<sup>10</sup> and for linear transport properties by Birss,<sup>10</sup> and has been reviewed at length recently.<sup>10,11</sup> Le Corre did not distinguish between equilibrium and transport properties. Birss, in an example following his basic discussion<sup>12</sup> of the symmetry of transport coefficients, discusses the application of symmetry restrictions to a (nonpyromagnetic) antiferromagnet. He employs, essentially, the following prescription (*prescription A*) for the symmetry restrictions on transport coefficients: *combine the symmetry restrictions arising from all spatial symmetry operations with the restrictions embodied by the usual Onsager reciprocity relations.* From Birss's subsequent discussion<sup>13</sup>

of saturated ferromagnets it appears, however, that he does not regard this prescription as being appropriate to all types of magnetic crystals. More recently symmetry restrictions on transport properties of crystals have been derived by Kleiner<sup>14,15</sup> treating time inversion and spatial transformations on the same footing. This results in a different prescription (*prescription B*) for symmetry restrictions on transport coefficients. The spatial symmetry restrictions are the same as those of prescription A, but for restrictions related to time inversion, *generalized Onsager relations* replace the usual ones. In the present paper the symmetry restrictions resulting from these two prescriptions are contrasted and are confronted by experiment with particular regard to thermogalvanomagnetic coefficients.

The space-time symmetry restrictions on the thermogalvanomagnetic coefficients of a crystal are determined by its Laue group,<sup>15,16</sup> since spatial translations and spatial inversion do not affect these coefficients. Symmetry-restricted matrices of the thermogalvanomagnetic coefficients have been tabulated<sup>15</sup> by Kleiner for each of the Laue groups according to prescription B. The corresponding symmetry-restricted matrices according to prescription A can be read from the same tables by using an "effective" Laue group instead of the actual one. The "effective" Laue group is obtained from the actual one by prescription A and is a Laue group in category<sup>15</sup> (a). It is the group generated by adjoining time inversion as an element to the purely spatial subgroup of the actual Laue group.

The symmetry-restricted matrices resulting from the two prescriptions are in general different, although they are the same for nonmagnetic crystals. To illustrate the difference, Table I exhibits the zero-magnetic-field

netization or spin distribution is determined solely by the applied magnetic field. The magnetization distribution can then be regarded simply as an external influence acting on an effectively nonmagnetic crystal, a situation in which the ordinary Onsager relations apply. With this treatment Birss finds (in agreement with experiment and in contrast to the result when prescription A is used) that the extraordinary Hall effect in ferromagnets is not ruled out by symmetry (Ref. 11, pp. 231, 235).

<sup>14</sup> W. H. Kleiner, Bull. Am. Phys. Soc. **10**, 1101 (1965).

<sup>15</sup> W. H. Kleiner, Phys. Rev. **142**, 318 (1966).

<sup>16</sup> The Laue (or enantiomorphous) group of a given group is defined here as the group obtained from the given group by replacing every spatial translation by the identity translation and every improper rotation by its proper counterpart. There are 32 crystallographic Laue groups, 11 of which characterize nonmagnetic crystals.

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

<sup>1</sup> W. Voigt, in *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1928), 2nd ed.

<sup>2</sup> L. Onsager, Phys. Rev. **37**, 405 (1931).

<sup>3</sup> L. Onsager, Phys. Rev. **38**, 2265 (1931).

<sup>4</sup> H. Jagodzinski, in *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7/1, p. 1.

<sup>5</sup> J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, London, 1960).

<sup>6</sup> C. S. Smith, Solid State Phys. **6**, 175 (1958).

<sup>7</sup> L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958).

<sup>8</sup> W. Opechowski and R. Guccione, *Magnetism IIA*, edited by Rado and Suhl (Academic Press Inc., New York, 1965), p. 105.

<sup>9</sup> Y. Le Corre, J. Phys. Radium **19**, 750 (1958).

<sup>10</sup> R. R. Birss, Rept. Progr. Phys. **26**, 307 (1963).

<sup>11</sup> R. R. Birss, *Symmetry and Magnetism* (John Wiley & Sons, Inc., New York, 1964).

<sup>12</sup> Reference 10, pp. 348-349 and Ref. 11, pp. 99-101 and 110-113.

<sup>13</sup> Birss does not adhere to prescription A in his subsequent discussion of transport properties of magnetic crystals (Ref. 11, pp. 149, 153, 226-236) which is confined largely to ferromagnets and ferrimagnets magnetized to saturation. These systems are represented by a model (Ref. 11, pp. 150, 153) in which the mag-

TABLE I. Symmetry-restricted conductivity matrices for  $\mathbf{H}=0$  according to two theories.

Laue group	Kleiner	"Effective" Laue group	Birss
	$\sigma$		$\sigma$
1	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix}$	1'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{yz} & \sigma_{zz} \end{pmatrix}$
2	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{yx} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$	21'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
3	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$	3'	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
4		41'	
6		61'	
$\infty$		$\infty 1'$	
2'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ -\sigma_{xz} & -\sigma_{yz} & \sigma_{zz} \end{pmatrix}$	1'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{xy} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{xz} & \sigma_{yz} & \sigma_{zz} \end{pmatrix}$
2'2'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$	21'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
32'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ -\sigma_{xy} & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$	3'	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
42'2'		41'	
62'2'		61'	
$\infty 2'$		$\infty 1'$	
4'	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$	21'	$\begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$
4'22'	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{xx} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$	2221'	$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$

symmetry-restricted electrical conductivity matrices<sup>17</sup> of the two theories for the 12 crystallographic and 2 textural<sup>18</sup> Laue groups for which they differ. This table can be used in designing a comparative experimental test of the two theories. Notice that for some Laue groups the matrices are more highly restricted according to one prescription, but for other Laue groups the other prescription gives more highly restricted matrices. All the Laue groups in Table I are consistent with the presence of a magnetic moment, and therefore describe ferromagnets, except 4' and 4'22'. One can expect that for more complicated properties than conductivity the difference between the symmetry-restricted transport coefficients of the two theories will tend to increase.

Prescription A for symmetry-restricted matrices appears to be inconsistent with the existence of the extraordinary Hall effect in ferromagnets. This conclusion is based on the usual interpretation of Hall-effect data taken on a ferromagnet,<sup>19,20</sup> in which the electrical resistivity component  $\rho_{yx}(\mathbf{H})$  is assumed to be pro-

portional to  $R_0H + R_1M$ . Here  $\mathbf{H} = H\hat{\mathbf{H}}$  is the magnetic field,  $M$  is the magnitude of the magnetization ( $\mathbf{M} = M\hat{\mathbf{M}}$ ),  $R_0$  is the ordinary Hall coefficient, and  $R_1$  is the extraordinary Hall coefficient. Consider the ferromagnetic metal Co, for example. It has the hcp structure and the easy direction of magnetization is along the principal axis. The domain magnetization is either  $M_0\hat{\mathbf{z}}$  or  $-M_0\hat{\mathbf{z}}$ , where  $M_0$  is the saturation magnetization and  $\hat{\mathbf{z}}$  is a unit vector along the principal axis. Consequently,  $M = (f_{\uparrow} - f_{\downarrow})M_0$ , where  $f_{\uparrow}$  and  $f_{\downarrow}$  are, respectively, the fractions of domain volume with  $\hat{\mathbf{M}}$  along  $\hat{\mathbf{z}}$  and  $-\hat{\mathbf{z}}$ . It then follows that  $\rho_{yx}(0) \sim R_1M$ , and that  $\rho_{yx}(0) \neq 0$  if there is an extraordinary Hall effect ( $R_1 \neq 0$ ) and a remanent magnetization ( $M \neq 0$ ), as in Co. To compare this experimental result with the symmetry-restricted matrices<sup>17</sup> determined by theory, we note that the Laue group for a single-crystal single-domain sample of Co is 62'2'. It follows from Table I that, according to prescription A,  $\rho_{yx}(0) = \rho_{xy}(0) = 0$ , in contradiction to  $R_1 \neq 0$ . The same is true for a multi-domain single-crystal sample, where  $\rho_{yx}(0)$  is an average over the domains.<sup>13</sup> On the other hand, prescription B requires only that  $\rho_{yx}(0) = -\rho_{xy}(0)$ , which is consistent with  $R_1 \neq 0$  and with the observed effect of exchanging the subscripts  $x$  and  $y$  or reversing the magnetization.

Antiferromagnetic structures for which the two prescriptions predict different symmetry-restricted conductivity matrices, as given in Table I, are exemplified by  $\text{MnF}_2$ ,  $\text{FeF}_2$ , and  $\text{CoF}_2$ . The space group of these crystals is  $P4'_2/mnm'$  and the Laue group is 4'22'. On the other hand, the array of magnetic ions<sup>21</sup> alone has the Laue group<sup>22</sup> of higher symmetry 4221', for which the two prescriptions predict the same form for symmetry-restricted thermogalvanomagnetic coefficients. Thus, the lowering of the magnetic symmetry due to the presence of the anions is essential in order that the two theories give different predictions for the symmetry-restricted conductivity. Because of the low electrical conductivity of  $\text{MnF}_2$ ,  $\text{FeF}_2$ , and  $\text{CoF}_2$ , it may be that an experimental test can be more readily accomplished by measurement of a thermogalvanomagnetic coefficient matrix different from electrical resistivity, or possibly by a photoconductivity experiment.

*Note added in proof.* Shtrikman and Thomas<sup>23</sup> point out that prescription A for symmetry restrictions on transport coefficients excludes an extraordinary Hall effect, in agreement with a conclusion of the present paper, and they point out in addition that a magnetoconductivity with a component linear in  $H$  is also excluded by prescription A.

<sup>17</sup> The symmetry-restricted matrices for electrical conductivity, electrical resistivity, thermal conductivity, and thermal resistivity all have the same form.

<sup>18</sup> A. V. Shubnikov, *et al.*, in *Colored Symmetry*, edited by W. J. Hosler (The Macmillan Company, New York, 1964).

<sup>19</sup> E. M. Pugh and N. Rostoker, *Rev. Mod. Phys.* **25**, 151 (1953).

<sup>20</sup> S. Foner, F. E. Allison, and E. M. Pugh, *Phys. Rev.* **109**, 1129 (1958).

<sup>21</sup> R. A. Erickson, *Phys. Rev.* **90**, 779 (1953).

<sup>22</sup> The magnetic cations lie on a body-centered tetragonal lattice with magnetic moments along the tetragonal axis, in opposite directions on the two primitive tetragonal sublattices (according to Ref. 19). The space group of the magnetic-ion array is  $P4_1/mnc$  according to Ref. 9, and the Laue group is 4221'.

<sup>23</sup> S. Shtrikman and H. Thomas, *Solid State Commun.* **3**, 147 (1965); *Solid State Commun.* **3**, No. 9 (1965). The author is indebted to R. R. Birss for apprising him of this reference.