CRYSTAL SYMMETRY AND PHYSICAL PROPERTIES: APPLICATION OF GROUP THEORY

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1. Introduction

The subject of the relation between the symmetry of crystals and their physical properties has been dealt with by a number of authors from time to time. In all such studies, the physical properties of a material system are regarded as tensors which express the relation between two physical quantities—the action and the effect—which are also represented by tensors of appropriate rank and kind. This view enables a broad classification of all physical properties. Since a given symmetry has the same effect on all physical properties represented by the same tensor irrespective of the physical nature of each one of them, such a classification provides a powerful tool for studying the effect of symmetry on physical properties.

Several years ago, one of us (Bhagavantam, 1942) indicated the possibility of such a general study and outlined a group theoretical method to obtain in particular, the number of independent non-vanishing constants of a physical property tensor subject to a point group symmetry. Tables showing the numbers of independent components of various tensors in each of the 32 classes were subsequently given, citing several examples of actual physical properties corresponding to each tensor (Bhagavantam and Suryanarayana, 1949).

Experience has shown that a knowledge of the number of independent non-vanishing components derived by such a direct and simple method serves as a valuable check on the schemes of independent components of various tensors obtained by the longer methods involving application of symmetry transformations to them. Moreover, even the mere knowledge of numbers of independent tensor components has been found to be of considerable help in the study of properties of crystal systems of high symmetry.

It is proposed to extend such work here to the galvanomagnetic and thermomagnetic effects and piezo-galvanomagnetic effects in single crystals, the study of which is gaining importance in semi-conductor physics. Some studies have already been made in that direction. The earliest were those by Kohler (1934). Okada (1955) derived the schemes of non-vanishing independent components of galvanomagnetic tensors up to the third power in H. Juretschke (1955) pointed out the need for studying the galvanomagnetic effects up to the fourth power in H and made a detailed study for only the point group 3 m. We will present here a comprehensive picture of the effect of symmetry on the galvanomagnetic and thermomagnetic phenomena of all orders in H up to the fourth, giving the numbers of independent components in each of the 32 classes.

Of the piezo-galvanomagnetic effects, the piezo-resistance has been investigated earlier by Smith (1958) who gave the schemes of independent non-vanishing components in all the 32 classes. We are giving here the numbers of non-vanishing independent components of piezo-Hall effect tensor and piezo-magneto-resistance tensor.

It will be noticed that some of the physical properties that are now being studied are represented by tensors already included in the previous work mentioned. In such cases, it is in fact only necessary to show that the particular physical property under consideration is represented by a tensor of a particular rank and kind which was already studied and the number of constants under each point group symmetry computed. The physical properties numbered 1, 2, 4, 5 in Table II are such. The numbers of independent constants for these are included in Table III only for the sake of completeness.

2. THE METHOD

Since the method of finding the number of independent non-vanishing tensor components under a crystallographic point group symmetry has already been described (Bhagavantam and Suryanarayana, 1949) in detail, we give here the outline only. n, the number of non-vanishing independent components of a tensor, is given by the formula

$$n = \frac{1}{N} \sum_{\rho} h_\rho \chi_\rho (R)$$

where N is the order of the point group under consideration, h_ρ is the number of elements in the ρth class, χ_ρ (R) is the character of the element R belonging to the ρth class in the representation of the group formed by the tensor components as basis. χ_ρ (R) for tensors of higher ranks is found by interpreting the representation formed by the tensor as a direct product representation of lower rank tensors in which the characters are known, and making use of the result that the character in a direct product representation is the product of characters in the factor representations. A more elegant way would be to adopt the method given by Lyubarskii (1960). The general form of characters in the representations formed by various tensors under consideration is given in column 3 of Table II.

3. The Galvanomagnetic and Thermomagnetic Effects

The galvanomagnetic and thermomagnetic effects occur when an electric current flows in a crystal in the simultaneous presence of an electric field, a magnetic field and a temperature gradient. The phenomenological description of the effect in anisotropic media is given by a set of simultaneous tensor equations which express the electric field E and heat current density q, as linear functions of electric current density j and negative temperature gradient G. These equations are same as those which govern the thermoelectric phenomena in anisotropic media, except that the coefficient tensors are now functions of the magnetic field H. The equations are written in the following form adopting the usual summation convention:

$$\left.\begin{aligned} E_i &= \rho_{ik} j_k + \alpha_{ik} G_k \\ q_i - \frac{\xi}{e} j_i &= -\beta_{ik} j_k + K_{ik} G_k \end{aligned}\right\} \tag{1}$$

In (1), ξ is the chemical potential of the electrons and e is electron charge. On the application of Onsager's principle to equations (1), the following symmetry relations for the coefficient tensors may be obtained (Landau and Lifshitz, 1960).

$$\rho_{ik}\ (H) = \rho_{ki}\ (-H) \tag{2}$$

$$K_{ik}\ (H) = K_{ki}\ (-H) \tag{3}$$

$$\beta_{ik}\ (H) = T\alpha_{ki}\ (-H). \tag{4}$$

T is the absolute temperature and all the tensors may be developed in power series in H to obtain the effects of various orders of magnitude in H. We may, therefore, write

$$\begin{aligned} \rho_{ik}\ (H) &= \rho_{ik}^{\circ} + \rho_{ikl}H_l + \rho_{iklm}H_lH_m + \rho_{iklmn}H_lH_mH_n \\ &\quad + \rho_{iklmnp}H_lH_mH_nH_p + \dots \\ K_{ik}\ (H) &= K_{ik}^{\circ} + K_{ikl}H_l + K_{iklm}H_lH_m + K_{iklmn}H_lH_mH_n \\ &\quad + K_{iklmnp}H_lH_mH_nH_p + \dots \\ \alpha_{ik}\ (H) &= \alpha_{ik}^{\circ} + \alpha_{ikl}H_l + \alpha_{iklm}H_lH_m + \alpha_{iklmn}H_lH_mH_n \\ &\quad + \alpha_{iklmnp}H_lH_mH_nH_p + \dots \\ \beta_{ik}\ (H) &= \beta_{ik}^{\circ} + \beta_{ikl}H_l + \beta_{iklm}H_lH_m + \beta_{iklmn}H_lH_mH_n \\ &\quad + \beta_{iklmnp}H_lH_mH_nH_p + \dots \end{aligned}$$

We shall consider the galvanomagnetic and thermomagnetic effects up to fourth power in H, and therefore limit the development of the tensors to terms of fourth power in H. The coefficient of a particular power in H in the development of a tensor gives that particular order effect of magnetic field on the physical property represented by the tensor. For example, the first term ρ_{ik}° in the development of ρ_{ik} (H) in powers of H is independent of H and represents the electrical resistivity in the absence of H. The coefficient ρ_{ikl} in the second terms gives the first order effect of H on electrical resistivity. Thus ρ_{ikl} tensor represents the physical property which is the interaction of the magnetic field to the first power and electrical resistivity.

The quantities ρ_{ik}°, ρ_{ikl}, ρ_{iklm}, ρ_{iklmn}, ... and β_{ik}°, β_{ikl}, β_{iklm}, β_{iklmn}, ... are called galvanomagnetic coefficients. The quantities K_{ik}°, K_{ikl}, K_{iklm}, K_{iklmn}, ... and α_{ik}°, α_{ikl}, α_{iklm}, α_{iklmn}, ... are called thermomagnetic coefficients. It can be seen from relations (2), (3) and (4) that ρ and K coefficients of corresponding order are tensors of same rank and kind. Similarly, the α and β coefficients of corresponding order are tensors of same rank and kind. Moreover α and β are not independent of each other. We shall investigate the effect of symmetry on these tensors of increasing rank in succession.

Zero order effects and tensors of second rank.—The Onsager reciprocity relations (2) and (3) show that ρ_{ik} (H) and K_{ik} (H) are not symmetric in *i* and *k*. Each one of them can be expressed as the sum of a symmetric tensor and an antisymmetric tensor of second rank. From relations (2) and (3), it further follows that the symmetric parts of these tensors are even functions of H while the antisymmetric parts are odd functions of H (Landau and Lifshitz, 1960). In the power series exapansion, the symmetric part is given by the terms of even powers of H and antisymmetric part by the terms of odd powers of H. Therefore, it can be concluded that ρ_{ik}° and K_{ik}° are symmetric in suffixes *i*, *k*, which result must also follow from the fact that ρ_{ik}° and K_{ik}° are electrical resistivity and thermal conductivity respectively in the absence of a magnetic field which are known to be symmetric second rank tensors, again from Onsager's principle.

In the case of α_{ik} (H) and β_{ik} (H) it does not follow that α_{ik}° and β_{ik}° are symmetric in *i*, *k*. They are thus second rank general tensors. α_{ik}° is the thermoelectric power in the absence of a magnetic field. β_{ik}° similarly represents an effect independent of a magnetic field but it appears that no agreed name has so far been assigned to it.

First order effects and tensors of third rank.—Let us consider ρ_{ikl} which may be called the Hall tensor. From (2) it follows that

$$\rho_{ikl}H_l = -\rho_{kil}H_l; \qquad \therefore \ \rho_{ikl} = -\rho_{kil}.$$

Thus ρ_{ikl} relates an antisymmetric tensor of second rank (which is equivalent to an axial vector) and an axial vector (H) and is equivalent to a second rank general tensor. Same considerations hold for K_{ikl} which may be called the Leduc-Righi tensor.

Regarding α_{ikl} and β_{ikl}, which may be called the Nernst tensor and Ettingshausen tensor respectively, the relation (4) does not impose any kind of symmetry on the suffixes *i*, *k*. They are therefore third rank tensors which relate a second rank general tensor and an axial vector. The character of a general symmetry element in the representation formed by such a tensor is given in Table II and numbers of independent components in various classes in Table III.

Second order effects and tensors of fourth rank.—ρ_{iklm} is the magneto-resistance tensor. It is symmetric in suffixes *i* and *k* because from (2) it follows that $\rho_{iklm}H_lH_m = \rho_{kilm}(-H_l)\ (-H_m)$. It is also symmetric in suffixes *l* and *m* because the order in which H_l and H_m are multiplied does not matter. Thus ρ_{iklm} (also K_{iklm}) is a fourth rank tensor which relates two second rank symmetric tensors. K_{iklm} is the magneto-thermal conductivity tensor.

α_{iklm} and β_{iklm} on the other hand are not symmetric in *i* and *k*. They relate a second rank general tensor with a second rank symmetric tensor. They give the second order effect of magnetic field on the thermoelectric power and on the effect described by $\beta_{ik}{}^{\circ}$ to which we have not assigned a name.

Third order effects and tensors of fifth rank.—ρ_{iklmn} which represents the third order effect of the magnetic field on electrical resistivity can be regarded as second order Hall effect. Similarly K_{iklmn} can be regarded as second order Leduc-Righi effect. These tensors are antisymmetric in *i*, *k* and totally symmetric in *lmn*. They relate an antisymmetric tensor of second rank to a totally symmetric third rank tensor.

α_{iklmn} and β_{iklmn} on the other hand relate a second rank general tensor with a totally symmetric third rank tensor. They can be regarded as second order Nernst effect and second order Ettingshausen effect respectively.

Fourth order effects and tensors of sixth rank.—ρ_{iklmnp} represents the second order magneto-resistance. Similarly K_{iklmnp} represents the second order magneto-thermal conductivity. They both relate a second rank symmetric tensor with a fourth rank totally symmetric tensor (totally symmetric in suffixes *lmnp*).

TABLE I

	Composite tensor	Zero order component	First order component	Second order component	Third order component	Fourth order component
Galvanomagnetic effects	$\rho_{ik}(H)$	Electrical resistivity ρ_{ik}°	Hall effect ρ_{ikl}	Magneto-resistance ρ_{iklm}	Second order Hall effect ρ_{iklmn}	Second order Magneto-resistance ρ_{iklmnp}
	$\beta_{ik}(H)$	No name β_{ik}°	Ettingshausen effect β_{ikl}	No name β_{iklm}	Second order Ettingshausen effect β_{iklmn}	No name β_{iklmnp}
Thermomagnetic effects	$K_{ik}(H)$	Thermal conductivity K_{ik}°	Leduc-righi effect K_{ikl}	Magneto-thermal conductivity K_{iklm}	Second order Leduc-Righi effect K_{iklmn}	Second order Magneto-thermal conductivity K_{iklmnp}
	$\alpha_{ik}(H)$	Thermo-electric power α_{ik}°	Nernst effect α_{ikl}	Magneto-thermo-electric power α_{iklm}	Second order Nernst effect α_{iklmn}	Second order Magneto-thermoelectric power α_{iklmnp}

α_{iklmnp} and β_{iklmnp} relate a second rank general tensor with a fourth rank totally symmetric tensor.

In Table I are given the galvanomagnetic and thermomagnetic coefficients, conveniently tabulated under columns and giving properties of increasing order effects in H.

4. Piezo-Galvanomagnetic Effects

The effects of elastic stress on the electrical resistivity in the presence of a magnetic field may be called piezo-galvanomagnetic effects. From the point of view we have been adopting here, it amounts to the study of elastic stress on the various coefficient tensors in the expansion of ρ_{ik} (H) in power series in H.

The zero order term or the coefficient independent of H is ρ_{ik}° which is the ordinary electrical resistivity. The effect of elastic stress S_{ik} on ρ_{ik}° is called piezo-resistance and, as mentioned earlier, has been studied in some detail by Smith (1958). S_{ik} and ρ_{ik}° are both second rank symmetric tensors. Piezo-Hall effect relates a general second rank tensor to which Hall tensor ρ_{ikl} reduces and the elastic stress S_{ik}. The numbers of independent components of such tensors have already been given in the papers referred to earlier and are reproduced in columns numbered 4 and 5 in Table III for the sake of completeness. Piezo-magneto-resistance relates the magneto-resistance tensor ρ_{iklm} with elastic stress S_{ik}. The character of a general symmetry element in the representation formed by such a tensor and the numbers of independent components are shown in Tables II and III against No. 10.

5. Results and Conclusions

Results in respect of the ten types of physical properties as classified in Table II are given in Table III for all the 32 crystal classes. The number at the head of each column in Table III corresponds to the number in the first column of Table II, each number representing one type of properties. One can now pick out any physical property and study it in detail in respect of a particular crystal class. It is interesting to note that in respect of all the properties studied in this paper, the 32 classes divide themselves into eleven groups.

TABLE II

Classification of Physical Properties

No.	Physical property represents relation between	Character χ_p (R) $c = \cos\phi$	Maximum no. of constants	Physical property
1	Vector and Vector ($\rho_{ik}{}^{\circ} = \rho_{ki}{}^{\circ}$)	$4c^2 \pm 2c$	6	Electrical resistivity, Thermal conductivity.
2	Second rank antisymmetric tensor and axial vector same as axial vector and axial vector ($\rho_{ikl} = -\rho_{kil}$)	$4c^2 \pm 4c + 1$	9	Hall effect, Leduc-Righi effect.
3	Second rank general tensor and axial vector ..	$(4c^2 \pm 4c + 1)(1 \pm 2c)$	27	Nernst effect, Ettingshausen effect.
4	Second rank symmetric tensor and second rank symmetric tensor	$(4c^2 \pm 2c)(4c^2 \pm 2c)$	36	Magneto-resistance, Magneto-thermal conductivity, Piezo-resistance.
5	Second rank general tensor and second rank symmetric tensor	$(4c^2 \pm 4c + 1)(4c^2 \pm 2c)$	54	Magneto-thermoelectric power, Piezo-Hall effect.
6	Axial vector and totally symmetric third rank tensor ($\rho_{iklmn} = -\rho_{kilmn}$ for all permutations of lmn)	$(1 \pm 2c)(\pm 8c^3 + 4c^2 \mp 2c)$	30	Second order Hall effect, Second order Leduc-Righi effect.
7	Second rank symmetric tensor and a totally symmetric fourth rank tensor ($\rho_{iklmnp} = \rho_{kilmnp}$ for all permutations of $lmnp$)	$(4c^2 \pm 2c) \times (16c^4 \pm 8c^3 - 8c^2 \mp 2c + 1)$	90	Second order magneto-resistance, Second order magneto-thermal conductivity.
8	Second rank general tensor and a totally symmetric third rank tensor (ρ_{iklmn} remains the same for all permutations of lmn)	$(4c^2 \pm 4c + 1) \times (\pm 8c^3 + 4c^2 \mp 2c)$	90	Second order Nernst effect, Second order Ettingshausen effect.
9	Second rank general tensor and a totally symmetric fourth rank tensor (ρ_{iklmnp} remains the same for all permutations of $lmnp$)	$(4c^2 \pm 4c + 1) \times (16c^4 \pm 8c^3 - 8c^2 \mp 2c + 1)$	135	Second order magneto-thermoelectric power
10	Second rank symmetric tensor and a fourth rank tensor of the type No. 4	$(4c^2 \pm 2c) \times (16c^4 \pm 16c^3 + 4c^2)$	216	Piezo-magneto-resistance.

TABLE III

Number of coefficients in each of the 32 crystal classes

Class symbols \ Property No.	1	2	3	4	5	6	7	8	9	10
1, $\bar{1}$	6	9	27	36	54	30	90	90	135	216
m, 2, 2/m	4	5	13	20	28	16	48	44	69	112
2 m m, 2 2 2, 2/m 2/m 2/m	3	3	6	12	15	9	27	21	36	60
4, $\bar{4}$, 4/m	2	3	7	10	14	8	24	22	35	56
4 m m, $\bar{4}$ 2 m, 4 2 2, 4/m 2/m 2/m	2	2	3	7	8	5	15	10	19	32
3, $\bar{3}$	2	3	9	12	18	10	30	30	45	72
3 m, 32, $\bar{3}$ 2/m ..	2	2	4	8	10	6	18	14	24	40
3/m, 6, 6/m	2	3	7	8	12	6	16	16	23	40
$\bar{6}$ 2 m, 6 m m, 6 2 2, 6/m 2/m 2/m	2	2	3	6	7	4	11	7	13	24
2 3, 2/m $\bar{3}$	1	1	2	4	5	3	9	7	12	20
$\bar{4}$ 3 m, 4 3 2, 4/m $\bar{3}$ 2/m	1	1	1	3	3	2	6	4	7	12

6. SUMMARY

A group theoretical method given by one of us in earlier publications for studying the effect of crystal symmetry on physical properties is now extended to cover the galvanomagnetic, thermomagnetic and piezo-galvano-magnetic effects in single crystals. These effects have gained importance in semi-conductor physics and such studies are therefore of current interest and may be expected to yield valuable new information.

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