On the theory of kinetic phenomena in axially symmetric and low-symmetry crystals

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(Submitted 23 January 1979)
Zh. Eksp. Teor. Fiz. 77, 250–256 (July 1976)

It is shown that the Hall effect and the thermoelectric phenomenon should possess the following peculiar anomalies in crystals in which a pseudovector can exist: a) the Hall field should be inclined at an angle to the magnetic field **H** even if **H** and the current density **j** are aligned in the principal directions and b) an effect similar to the Nernst effect should be observed at $\mathbf{H}=0$. The reflection of a wave from a low-symmetry crystal is considered.

PACS numbers: 72.15.Gd, 72.15.Jf

1. INTRODUCTION

Crystals of certain classes possess a preferred axis, $\mathbf{z}_0$, along which an axial vector (a pseudovector) can be aligned. For this purpose, this axis should not intersect a D axis (a two-fold symmetry axis) and, furthermore, it should not lie in a symmetry plane (i.e., in a v plane). Let us emphasize that crystals of these classes can possess a center of inversion. In Table I we have written out some of the classes in question, and give examples of intermetallic compounds[1)] for each class. In the last column we indicate papers in which the symmetry of the crystals is determined.

The object of the present paper is to show that, in crystals of these classes (they are called crystals with axial symmetry), certain macroscopic kinetic phenomena described by second-rank tensors should possess a number of specific anomalies. In the majority of cases the second-rank tensors that describe the macroscopic properties of solids are symmetric under interchange of the indices. The symmetry of the tensors is either a consequence of the Onsager relations (see Ref. 10, § 120; for example, the conductivity tensor $\sigma_{ik}=\sigma_{ki}$), or a consequence of the fact that the tensor is a mixed derivative of a scalar function (for example, the static magnetic susceptibility tensor $\mu_{ik}=-\partial^2F/\partial H_i\partial H_k$, where **H** is the magnetic field and F is the free energy). There is, however, no symmetry requirement in certain cases. In these cases, whether the tensor does or does not possess an antisymmetric part is determined solely by the class symmetry of the crystal. Since the antisymmetric part of a second-rank tensor can be associated with a dual pseudovector, it is clear that the tensor can possess an antisymmetric part if the symmetry admits of the existence of a pseudovector, i.e., if the crystal in question possesses axial symmetry.

For the demonstration of the anomalies of the kinetic phenomena in crystals with axial symmetry, we chose the Hall effect and the thermoelectric phenomena.

2. THE "STRANGE" HALL EFFECT

If a conductor is placed in a constant, uniform magnetic field, then the relation expressing the electric-field intensity **E** in terms of the current density **j** has the form [see Ref. 11, § 21, formula (21.10)]:

$$E_i=\rho_{ik}^{(s)}(\mathbf{H})j_k+[\mathbf{j}\times\mathbf{b}]_i,\quad \rho_{ik}^{(s)}(\mathbf{H})=\rho_{ki}^{(s)}(\mathbf{H})=\rho_{ik}^{(s)}(-\mathbf{H}),\quad b_i(\mathbf{H})=-b_i(-\mathbf{H}). \tag{1}$$

The second term in the first expression describes the Hall effect. If the magnetic field can be considered to be weak, then the vector **b** depends linearly on the magnetic field:

$$b_i=R_{ik}H_k. \tag{2}$$

No restrictions have been imposed on the symmetry of the tensor R_{ik}. If $R_{ik}-R_{ki}\neq 0$, then we can introduce the pseudovector, **R**, that is the dual of the antisymmetric tensor $R_{ik}^{(a)}=\frac{1}{2}(R_{ik}-R_{ki})$:

$$R_i={}^1/_2\varepsilon_{ikl}R_{kl}^{(a)}, \tag{3}$$

where ε_{ikl} is the completely antisymmetric tensor of the third rank. Then the Hall field, $\mathbf{E}_{\text{Hall}}$, acquires the "strange" form:

$$\mathbf{E}_{\text{Hall}}=[\mathbf{j},\times\hat{R}_s\mathbf{H}]+[\mathbf{j}\times[\mathbf{R}\times\mathbf{H}]],\quad R_{ik}^{(s)}={}^1/_2(R_{ik}+R_{ki}), \tag{4}$$

from which it follows that, even in the case when the magnetic field and the current density are oriented along the principal directions of the tensor $R_{ik}^{(s)}$, the Hall field is not perpendicular to **H**. In Fig. 1 the vectors **R** and **j** are parallel to one of the principal directions of the tensor $R_{ik}^{(s)}$, **H** is parallel to another, and the components

TABLE I.

System	Class	Substance	Reference
Triclinic	–	$Al_{11}Mn_4$	[1]
Monoclinic	–	Al_4W, β-Pu	[2], [3]
Rhombohedral	C_3	AgZn	[4]
Tetragonal	S_4	Al_2Te_4Zn	[5]
	C_{4h}	$MoNi_4$	[6]
Hexagonal	C_6	Al_5Mo	[7]
	C_{6h}	$Rh_{20}Si_{13}$	[8]
	C_{3h}	Al_3Hf_4	[9]

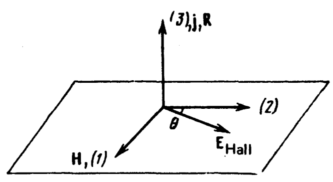

FIG. 1.

0038-5646/79/070128-04$02.40

of the Hall field are respectively equal to

$$E_2^{\text{Hall}} = R_2^{(s)} jH, \quad E_1^{\text{Hall}} = -RHj, \quad \operatorname{tg}\theta = -R/R_2^{(s)}; \tag{5}$$

θ is the angle between $\mathbf{E}_{\text{Hall}}$ and $\mathbf{H}$; and $\mathbf{R}_2^{(s)}$ is one of the principal values of the tensor $R_{ik}^{(s)}$.

To elucidate the nature of the strange Hall effect, let us first express the vector **b** in terms of the components of the conductivity tensor $\sigma_{ik}(\mathbf{H}) = \rho_{ik}^{-1}(\mathbf{H})$ (see the problem of 21 in Ref. 11):

$$b_i = -\frac{1}{|\sigma|} s_{ik} a_k, \quad a_i = \frac{1}{2}\varepsilon_{ikl} a_{kl}, \quad a_{ik} = \frac{1}{2}(\sigma_{ik}(\mathbf{H}) - \sigma_{ki}(\mathbf{H})),$$
$$s_{ik} = {}^1/_2(\sigma_{ik}(\mathbf{H}) + \sigma_{ki}(\mathbf{H})), \tag{6}$$

with $|\sigma| = |s| + s_{ik} a_i a_k$, where $|s|$ is the determinant composed of the elements of the matrix s_{ik}. In the case of weak fields the vector **a** depends linearly on the magnetic field:

$$a_i = Q_{ik} H_k, \tag{7}$$

and it follows from (6) that

$$R_{ik} = -\frac{1}{|\sigma_0|}\sigma_{il} Q_{lk}. \tag{8}$$

Here σ_{ik} is the conductivity tensor for $H = 0$ and $|\sigma_0|$ is the determinant composed of its components. The tensor σ_{ik}, as we have said, is a symmetric tensor. This restriction does not extend to the tensor Q_{ik} if the crystal possesses axial symmetry.[2)] The antisymmetry of the tensor Q_{ik} naturally leads to the antisymmetry of the tensor R_{ik}, and

$$\mathbf{R} = -\frac{1}{|\sigma_0|}\{\operatorname{Sp}\hat{\sigma}\mathbf{Q} - \hat{\sigma}\mathbf{Q}\}. \tag{9}$$

Here $\operatorname{Sp}\hat{\sigma} = \sigma_{ii}$, $\mathbf{a}(\hat{\sigma}\mathbf{Q})_i = \sigma_{ik} Q_k$; $Q_i = \frac{1}{2}\varepsilon_{ikl} Q_{kl}^{(a)}$, $Q_{ik}^{(a)} = \frac{1}{2}(Q_{ik} - Q_{ki})$.

The use of a formal solution to the kinetic equation in a weak magnetic field (Ref. 12, §§ 22 and 27) allows us to find an expression for the vector **Q**. The tensor $\sigma_{ik}(\mathbf{H})$ can be represented in the form

$$\sigma_{ik}(\mathbf{H}) = -\frac{2e^2}{(2\pi\hbar)^3}\int \frac{\partial f_F}{\partial \varepsilon} v_i \psi_k d^3p, \tag{10}$$

where the vector ψ is the solution to the integrodifferential equation

$$\frac{e}{c}\left([\mathbf{v}\times\mathbf{H}]\frac{\partial}{\partial \mathbf{p}}\right)\boldsymbol{\psi} + \hat{W}_{\mathbf{p}}\{\boldsymbol{\psi}\} = \mathbf{v}, \quad \mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}}, \tag{11}$$

and $\hat{W}_{\mathbf{p}}$ is the linearized collision operator [into its definition enters the derivative, $\partial f_F/\partial\varepsilon$, of the Fermi function (see Ref. 12, §22)].

In weak fields

$$\boldsymbol{\psi} \approx \hat{W}_{\mathbf{p}}^{-1}\{\mathbf{v}\} - \frac{e}{c}\hat{W}_{\mathbf{p}}^{-1}\left\{\left([\mathbf{v}\times\mathbf{H}]\frac{\partial}{\partial \mathbf{p}}\right)\hat{W}_{\mathbf{p}}^{-1}\{\mathbf{v}\}\right\}. \tag{12}$$

The term proportional to the magnetic field determines the antisymmetric Hall part of the electrical-conductivity tensor:

$$\sigma_{ik}^{\text{Hall}} = \frac{2e^3}{(2\pi\hbar)^3 c}\int d^3p \frac{\partial f_F}{\partial \varepsilon} v_i \hat{W}_{\mathbf{p}}^{-1}\left\{\left([\mathbf{v}\times\mathbf{H}]\frac{\partial}{\partial \mathbf{p}}\right)\hat{W}_{\mathbf{p}}^{-1}\{v_k\}\right\}, \tag{13}$$

the antisymmetry of the tensor $\sigma_{ik}^{\text{Hall}}$ ensuring that the differential operator $[\mathbf{v}\times\mathbf{H}]\partial/\partial\mathbf{p}$ will be anti-Hermitian and the collision operator, $\hat{W}_{\mathbf{p}}$, Hermitian (see Ref. 12, § 23, as well as Ref. 13).

Let us introduce the notation

$$\mathbf{l} = \hat{W}_{\mathbf{p}}^{-1}\{\mathbf{v}\}. \tag{14}$$

In the τ-approximation $\mathbf{l} = l\mathbf{n}$, where $\mathbf{n} = \mathbf{v}/v$; thus, $\mathbf{l}$ is the mean-free-path vector. From (13) and (14) we have

$$\sigma_{ik}^{\text{Hall}} = \frac{2e^3}{(2\pi\hbar)^3 c}\int \frac{\partial f_F}{\partial \varepsilon} l_i [\mathbf{v}\times\mathbf{H}]\frac{\partial l_k}{\partial \mathbf{p}} d^3p$$
$$= \frac{2e^3}{(2\pi\hbar)^3 c}\int \frac{\partial f_F}{\partial \varepsilon} l_i \left[\frac{\partial l_k}{\partial \mathbf{p}}, \times\mathbf{v}\right]_l d^3p H_l.$$

Hence

$$a_i = \frac{1}{2}\varepsilon_{ikl}\int \frac{\partial f_F}{\partial \varepsilon} l_k \left[\frac{\partial l_l}{\partial \mathbf{p}}, \times\mathbf{v}\right]_m d\Gamma' H_m, \quad d\Gamma' = \frac{2e^3}{(2\pi\hbar)^3 c} d^3p, \tag{15}$$

or, according to (7)

$$Q_{ik} = \frac{1}{2}\varepsilon_{imn}\int \frac{\partial f_F}{\partial \varepsilon} l_m \left[\frac{\partial l_n}{\partial \mathbf{p}}, \times\mathbf{v}\right]_k d\Gamma'. \tag{16}$$

Separating out the antisymmetric part, and going over to the dual vector **Q**, we have after simple transformations the expression

$$Q_i = \frac{1}{4}\int \frac{\partial f_F}{\partial \varepsilon}\left[\left(l_k\frac{\partial l_i}{\partial \mathbf{p}} - l_i\frac{\partial l_k}{\partial \mathbf{p}}\right), \times\mathbf{v}\right]_k d\Gamma'. \tag{17}$$

Noting that $(\partial f_F/\partial\varepsilon)\mathbf{v} = \partial f_F/\partial\mathbf{p}$, and integrating by parts, we can transform the last expression into the compact form:

$$Q_i = \frac{1}{2}\int f_F \left[\frac{\partial l_k}{\partial \mathbf{p}}, \times\frac{\partial l_i}{\partial \mathbf{p}}\right]_k d\Gamma'. \tag{18}$$

It can be seen from the formulas (17) and (18) that the value of **Q** essentially depends on the characteristics of the scattering, it being necessary for the existence of the strange Hall effect that the antisymmetry be present at the microscopic level. Let us introduce the differential mobility tensor $u_{ik}(u_{ik} = \partial l_i/\partial p_k)$. The expression (18) can be written in terms of this tensor:

$$Q_i = \int f_F u_{im} u_m d\Gamma', \tag{19}$$

where **u** is the vector dual of the antisymmetric part of the u_{ik} tensor. Since l_i is a solution to the integral equation with the kernel $W_{\mathbf{p},\mathbf{p}'}$, which is proportional to the probability of transition from the state $|\mathbf{p}\rangle$ into the state $|\mathbf{p}'\rangle$:

$$\int W_{\mathbf{p},\mathbf{p}'} l_i(\mathbf{p}') d^3p' = v_i,$$

while $\partial v_i/\partial p_k = \partial^2\varepsilon/\partial p_i \partial p_k$, it is clear that u_{ik} does not have an antisymmetric part only if $W_{\mathbf{p},\mathbf{p}'}$ is a function of the difference $\mathbf{p} - \mathbf{p}'$. In the general case this is, naturally, not so. It is difficult to find a sufficiently simple expression for the dependence $\mathbf{l}(\mathbf{p})$ that would allow us to estimate the value of **Q**. The point is that, in the τ-approximation [for $\mathbf{l} = \tau(\varepsilon)\mathbf{v}$ and for $\mathbf{l} = l(\varepsilon)\mathbf{p}/p$], the strange Hall-effect vector $\mathbf{Q} = 0$, a fact which can be directly verified. If we assume that

$$\left|\left[\frac{\partial l_i}{\partial \mathbf{p}}, \times\frac{\partial l_k}{\partial \mathbf{p}}\right]_k\right| \approx \frac{l^2}{p_F^2},$$

then, accooding to (18) and (19), $|R| \approx 1/nec$ (n is the number of electrons in a unit volume) and, consequently, the constant of the strange Hall effect is of the same order of magnitude as the normal Hall constant.

3. THE THERMOELECTRIC TENSOR

The electric-field intensity $\mathbf{E} = -\nabla\varphi$ and the temperature gradient ∇T are connected with the current density $\mathbf{j}$ and the thermal flux $\mathbf{q} - \varphi\mathbf{j}$ in the case of crystals of arbitrary symmetry by relations of the following form:

$$E_i = \sigma_{ik}^{-1} j_k + \alpha_{ik}(\partial T/\partial x_k),$$
$$q_i - \varphi j_i = T\alpha_{ki} j_k - \varkappa_{ik}(\partial T/\partial x_k) \tag{20}$$

(in Landau and Lifshitz's notation[11]). As we have said, σ_{ik} is a symmetric tensor. The thermal-conductivity tensor $\varkappa_{ik}$ is also symmetric, but the "thermoelectric tensor α_{ik} is nonsymmetric in the general case" (Ref. 11, p. 145). Since the antisymmetric part of the tensor α_{ik} can be associated with a dual vector $\mathbf{A}$, it is clear that the tensor α_{ik} can have an antisymmetric part only in crystals possessing axial symmetry (see above). For $\mathbf{A} \neq 0$ the relations (20) can be written as follows:

$$\mathbf{E} = \hat{\sigma}^{-1}\mathbf{j} + \hat{\alpha}_s \nabla T + [\mathbf{A}\times\nabla T],$$
$$\mathbf{q} - \varphi\mathbf{j} = T\hat{\alpha}_s \mathbf{j} - \hat{\varkappa}\nabla T - T[\mathbf{A}\times\mathbf{j}]. \tag{21}$$

It is clear from these relations that effects similar to the Nernst-Ettingshausen effects should be observed in crystals with axial symmetry when $H = 0$ (naturally, there should not be effects of the Hall and Leduc-Righi types because of the symmetry of the tensors σ_{ik} and $\varkappa_{ik}$).

The microscopic nature of the antisymmetry of the tensor α_{ik} has not been investigated by us. Therefore, we note only the following circumstance. In a calculation the tensor α_{ik} is expressed in the form of a product of two second-rank tensors. For example, for the degenerate electron gas [see Ref. 12, 25, formula (25.23)]

$$\alpha_{ik} = (\pi^2/3e) T \psi_{im}^{-1}(\varepsilon_F)(d\varphi_{mk}/d\varepsilon)_{\varepsilon=\varepsilon_F}. \tag{22}$$

The tensors $\psi_{ik}(\varepsilon)$ and $\varphi_{ik}(\varepsilon)$ are respectively equal to

$$\psi_{ik}(\varepsilon) = \frac{2}{(2\pi\hbar)^3} \oint_{\varepsilon(\mathbf{p})=\varepsilon} \frac{1}{v} v_i l_k \, dS,$$
$$\varphi_{ik}(\varepsilon) = \frac{2}{(2\pi\hbar)^3} \oint_{\varepsilon(\mathbf{p})=\varepsilon} \frac{1}{v} v_i l_k^{(\varepsilon)} \, dS, \tag{23}$$

and $\mathbf{l}^{(\varepsilon)}$ is the solution to the kinetic equation

$$\hat{W}_\varepsilon\{\mathbf{l}\} = \mathbf{v}, \tag{24}$$

$\hat{W}_\varepsilon$ differing from $\hat{W}_\mathbf{p}$ (see above) only in the case when the electrons undergo inelastic collisions [into the definition of the operator $\hat{W}_\varepsilon$ enters not $\partial f_F/\partial\varepsilon$, but $\partial f_F/\partial T$; see Ref. 12, 23, the formulas (23.13) and (23.14)]. The electrical- and thermal-conductivity tensors can be expressed in terms of $\psi_{ik}(\varepsilon_F)$ and $\varphi_{ik}(\varepsilon_F)$:

$$\sigma_{ik} = e^2 \psi_{ik}(\varepsilon_F), \quad \varkappa_{ik} = (\pi^2 T/3)\varphi_{ik}(\varepsilon_F). \tag{25}$$

The Hermitian nature of the operators $\hat{W}_\mathbf{p}$ and $\hat{W}_\varepsilon$ guarantees the symmetry of σ_{ik} and $\varkappa_{ik}$. This very same property of the collision operator most likely leads to the symmetry of the tensor $[d\varphi_{ik}/d\varepsilon]_{\varepsilon=\varepsilon_F}$ [otherwise it is difficult to explain the symmetry of the tensor $\varkappa_{ik}$ at an arbitrary temperature; the symmetry of $\varphi_{ik}(\varepsilon)$ has, as far as we know, not been analyzed in detail]. Even if both tensors (ψ_{ik} and $d\varphi_{ik}/d\varepsilon$) are symmetric, the tensor α_{ik} is symmetric only in the case when the principal axes of the tensors ψ_{ik} and $d\varphi_{ik}/d\varepsilon$ coincide. If the crystal possesses so low a symmetry that there are not three preferred, mutually perpendicular directions in it (crystals of the triclinic and monoclinic classes), then there is no reason whatsoever to expect the two different tensors to have coincident principal directions. In this cases the tensor σ_{ik} will certainly have an antisymmetric part.

In metals, in which the thermal conductivity of the electrons, as a rule, significantly exceeds the thermal conductivity of the lattice, the tensors ψ_{ik} and φ_{ik} can coincide with each other, owing to the Wiedemann-Franz law, and this should apparently lead to a decrease in the antisymmetric part of the thermoelectric tensor α_{ik}; therefore, it is desirable that the detection of the antisymmetric part be carried out in that temperature region where inelastic collisions are important and the Wiedemann-Franz law is not obeyed. Notice that in low-symmetry crystals the deviation from the Wiedemann-Franz law is manifested, in particular, in the fact that the principal directions of the tensors σ_{ik} and $\varkappa_{ik}$ will not coincide.

4. PROPERTIES OF LOW-SYMMETRY CRYSTALS

The absence of three preferred, mutually perpendicular directions in crystals with triclinic and monoclinic lattices should lead to a number of distinctive anomalies in the kinetic properties of these crystals. First of all, notice that the strange Hall effect should be observed in them even if the tensor Q_{ik} does not have an antisymmetric part (see footnote 2), since there is no reason to expect that the principal directions of the tensors Q_{ik} and σ_{ik} will coincide.

The fact that in low-symmetry crystals each symmetric second-rank tensor "selects" its own set of principal directions may have an effect on the optical properties of these crystals. Owing to the dependence of the components of the permittivity tensor ε_{ik} on the frequency ω, the principal directions of ε_{ik} should also be frequency dependent. Furthermore, there is no reason to expect that the imaginary, ε''_{ik}, and real, ε'_{ik}, parts of the tensor $\varepsilon_{ik} = \varepsilon'_{ik} + i\varepsilon''_{ik}$ will have common principal directions. Because of this, the propagation of electromagnetic waves in such crystals will differ from the propagation of the waves in crystals with a higher symmetry. For example, let us consider the reflection of an electromagnetic wave normally incident on the surface $z = 0$ of a low-symmetry crystal. We shall characterize the crystal by the surface impedance $\zeta_{\alpha\beta} = r_{\alpha\beta} + ix_{\alpha\beta}$ ($\alpha, \beta = x, y$), the principal directions of the tensors $r_{\alpha\beta}$ and $x_{\alpha\beta}$ being different (they are rotated with respect to each other through an angle

φ):

$$r_{\alpha\beta}=\begin{pmatrix} r_1 & 0 \\ 0 & r_2 \end{pmatrix},$$

$$x_{\alpha\beta}=\begin{pmatrix} x_1\cos^2\varphi+x_2\sin^2\varphi & (x_1-x_2)\sin\varphi\cos\varphi \\ (x_1-x_2)\sin\varphi\cos\varphi & x_1\sin^2\varphi+x_2\cos^2\varphi \end{pmatrix}. \tag{26}$$

Let (for definiteness) the incident wave be polarized along the axis 1. Let us denote its amplitude by E_{in}. The reflected wave will turn out to be elliptically polarized, with the axes of the ellipse turned through some angle with respect to the axis 1. The value of the ellipticity and the angle of rotation of the plane of polarization can easily be determined from the values of the components of the electric-field intensity, $\mathbf{E}_{ref}$, in the reflected wave along the axes 1 and 2:

$$\frac{E_1^{ref}}{E_{inc}}=-\frac{(1-\zeta_1)(1+\zeta_2)-\zeta_{12}^2}{(1+\zeta_1)(1+\zeta_2)-\zeta_{12}^2},\quad \frac{E_2^{ref}}{E_{inc}}=\frac{2i\zeta_{12}\zeta_1}{(1+\zeta_1)(1+\zeta_2)-\zeta_{12}^2}; \tag{27}$$

$$\zeta_1=r_1+i(x_1\cos^2\varphi+x_2\sin^2\varphi),\quad \zeta_2=r_2+i(x_1\sin^2\varphi+x_2\cos^2\varphi),$$
$$\zeta_{12}=i(x_1-x_2)\sin\varphi\cos\varphi.$$

CONCLUSION

It is now fashionable to investigate noncrystalline solids (disordered alloys, amorphous solids, glassy substances), or two-dimensional and one-dimensional structures, i.e., solids deprived of the "usual" symmetry elements. In this paper we have attempted to ascertain the phenomena to which the loss by a crystal of a certain number of point-group symmetry elements will lead. Of course, the analyzed examples by no means exhaust the range of possible unusual properties of low-symmetry crystals and crystals with axial symmetry.

I take the opportunity to thank N. R. Serebryanaya for her help in the solution of the crystallographic problems and for selecting the examples (see Table I). Furthermore, I am grateful to A. F. Andreev and I. M. Lifshitz for useful discussions.

1) We have found only one suitable simple metal: β-Pu.

2) Below we shall discuss the "accidental" symmetry of the tensor Q_{ik}.

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Translated by A. K. Agyei