vectors **a**, **b** is a tensor

$$T = \mathbf{ab}, \quad \text{components:} \quad T_{ik} = a_i b_k. \quad (89)$$

The divergence of a tensor and the gradient of a vector are written as

$$\text{Div} T, \quad \text{components:} \quad (\text{Div} T)_i = \sum_k (\partial/\partial x_k) T_{ki}, \quad (90)$$

$$\text{Grad} \mathbf{a}, \quad \text{components:} \quad (\text{Grad} \mathbf{a})_{ik} = (\partial/\partial x_i) a_k. \quad (91)$$

The interior products between a tensor and a vector

are denoted by

$$\mathbf{T} \cdot \mathbf{a}, \quad \text{components:} \quad (\mathbf{T} \cdot \mathbf{a})_i = \sum_k T_{ik} a_k, \quad (92)$$

$$\mathbf{a} \cdot \mathbf{T}, \quad \text{components:} \quad (\mathbf{a} \cdot \mathbf{T})_i = \sum_k a_k T_{ki}. \quad (93)$$

Finally,

$$\mathbf{T} : \mathbf{U} = \sum_{i,k} T_{ik} U_{ki} \quad (94)$$

is the interior product of two tensors, $\mathbf{T}$ and $\mathbf{U}$, contracted twice.

Extension of Onsager's Theory of Reciprocal Relations. II

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(Received December 7, 1953)

The extension of Onsager's theory of reciprocal relations between irreversible processes, developed previously by the authors, is applied to electric conduction in anisotropic crystals, and the symmetry properties of the conduction tensor are derived.

1. INTRODUCTION

IN a previous paper[1] the authors have extended Onsager's theory for reciprocal relations between irreversible processes in such a way that it could be directly applied to vectorial and tensorial phenomena (see I, Sec. 1). Results were obtained for heat conduction, diffusion, viscosity, and cross effects. It was assumed that external forces, taken into account, were conservative. Thus electromagnetic irreversible phenomena were not treated. It is the purpose of this paper to apply the general theory outlined in I, Secs. 2 and 3 to electromagnetic processes. We shall consider the case of electric conduction in anisotropic crystals at uniform temperature. In Secs. 2 and 3 the macroscopic phenomenological theory of electric conduction is developed. In Sec. 4 we then derive an expression for the entropy production in an energetically insulated crystal in terms of local fluctuations of state variables, as required for the application in Secs. 5–7 of the formalism from I, Secs. 2 and 3. In such a way the symmetry properties of the conduction tensor are derived.

2. ENTROPY PRODUCTION IN LOCAL FORM

Let us consider a system, consisting of a rigid ion lattice and of electrons, in an electromagnetic field. The entropy production can be calculated as follows:

Charge conservation is expressed by

$$\partial \rho_e / \partial t = -\text{div} \mathbf{i}, \quad (1)$$

where ρ_e is the electrical charge density, and $\mathbf{i}$ the electric current.

Conservation of energy can be written as

$$\partial e_v / \partial t = -\text{div} \mathbf{J}_e, \quad (2)$$

where e_v is the density of total energy and $\mathbf{J}_e$ the energy flow. These are given by

$$e_v = u_v + \tfrac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2), \quad (3)$$

$$\mathbf{J}_e = \mathbf{J}_q + c\mathbf{E} \times \mathbf{B}, \quad (4)$$

with u_v the density of internal energy, $\tfrac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2)$ the density of electromagnetic energy (**E** is the electric and **B** the magnetic field), and $c\mathbf{E} \times \mathbf{B}$ the Poynting vector. Relation (4) defines the heat flow $\mathbf{J}_q$. Subtracting Poynting's theorem

$$\tfrac{1}{2}\partial(\mathbf{E}^2 + \mathbf{B}^2)/\partial t = -\text{div} c\mathbf{E} \times \mathbf{B} + \mathbf{i} \cdot \mathbf{E}, \quad (5)$$

from (2) one obtains the equation for the internal energy

$$\partial u_v / \partial t = -\text{div} \mathbf{J}_q + \mathbf{i} \cdot \mathbf{E}. \quad (6)$$

Furthermore, we need the Gibbs' equation

$$T ds_v / dt = du_v / dt - \sum_k \mu_k d\rho_k / dt, \quad (7)$$

where T is the temperature, s_v the density of entropy, μ_k and ρ_k the chemical potential per unit mass and the density of component k (ions or electrons). The time derivatives in this equation are substantial derivatives with respect to the center of mass motion. Taking the velocity of the ion lattice zero we can neglect the center of mass motion, because the ions are heavy as compared

[1] S. R. de Groot and P. Mazur, preceding paper [Phys. Rev. 94, 218 (1954)], referred to in the following as I.

to the electrons. We have then instead of (7):

$$T\partial s_v/\partial t = \partial u_v/\partial t - (\mu/e)\partial\rho_e/\partial t, \qquad (8)$$

where μ is the chemical potential and e the charge per unit mass of the electrons. We have taken into account the fact that the density of the ions is constant (ρ_e is the electrical charge density due to both electrons and ions).

In accordance with the approximation made above no equation of motion is needed, whilst no convection terms occur in (4).

From (1), (6) and (8) the entropy balance equation can be derived

$$\partial s_v/\partial t = -\mathrm{div}\mathbf{J}_s + \sigma, \qquad (9)$$

with the entropy flow

$$\mathbf{J}_s = (\mathbf{J}_q - \mathbf{i}\mu/e)/T, \qquad (10)$$

and the entropy source σ from

$$T\sigma = -\mathbf{J}_q\cdot(\mathrm{grad}T)/T + \mathbf{i}\cdot\{\mathbf{E} - T\,\mathrm{grad}(\mu/Te)\}$$
$$= -\mathbf{J}_s\cdot\mathrm{grad}T + \mathbf{i}\cdot\{\mathbf{E} - \mathrm{grad}(\mu/e)\} \geqslant 0. \qquad (11)$$

At uniform temperature (11) reduces to

$$T\sigma = \mathbf{i}\cdot\{\mathbf{E} - \mathrm{grad}(\mu/e)\} \geqslant 0. \qquad (12)$$

Expressing $\mathbf{E}$ in the electromagnetic potentials φ and $\mathbf{A}$

$$E = -\mathrm{grad}\varphi - c^{-1}\partial\mathbf{A}/\partial t, \qquad (13)$$

(12) becomes

$$T\sigma = -\mathbf{i}\cdot\{\mathrm{grad}(\bar{\mu}/e) + c^{-1}\partial\mathbf{A}/\partial t\} \geqslant 0, \qquad (14)$$

where

$$\bar{\mu} = \mu + e\varphi \qquad (15)$$

is called the electrochemical potential of the electrons.

3. THE PHENOMENOLOGICAL EQUATION

With the flux and the force occurring in (14) we can establish the linear relationship

$$\mathbf{i} = -L(\mathbf{B})\cdot\{\mathrm{grad}(\bar{\mu}/e) + c^{-1}\partial\mathbf{A}/\partial t\}, \qquad (16)$$

which is Ohm's law. Here $L(\mathbf{B})$ is the electrical conductivity tensor which can be a function of the magnetic field strength $\mathbf{B}$. This equation can alternatively be written as

$$c^{-1}\partial\mathbf{A}/\partial t = -\mathrm{grad}(\bar{\mu}/e) - R(\mathbf{B})\cdot\mathbf{i}, \qquad (17)$$

where $R(\mathbf{B}) \equiv L^{-1}(\mathbf{B})$ is the resistivity tensor.

4. ENTROPY PRODUCTION IN TERMS OF FLUCTUATIONS

The entropy production d_iS/dt of the whole system, kept at uniform temperature, can be found by inte-

grating (14) over the volume of the system,

$$d_iS/dt = -T^{-1}\int_V \mathbf{i}\cdot\{\mathrm{grad}(\bar{\mu}/e) + c^{-1}\partial\mathbf{A}/\partial t\}dV$$

$$= -T^{-1}\int_V \{(\bar{\mu}/e)\partial\rho_e/\partial t + \mathbf{i}\cdot c^{-1}\partial\mathbf{A}/\partial t\}dV$$

$$\qquad -T^{-1}\int_\Omega (\bar{\mu}\mathbf{i}/e)\cdot d\mathbf{\Omega}, \qquad (18)$$

where (1) has been used and Gauss' theorem applied. The last term, which is an integral over the surface $\mathbf{\Omega}$, vanishes when the system is materially insulated ($\mathbf{i}$ vanishes at the surface).

If furthermore the system is also insulated for heat, it follows from the volume integral of (9) with (10), and from (18) that the change in the entropy of the whole system with time is

$$dS/dt = -T^{-1}\int_V \{(\bar{\mu}/e)\partial\rho_e/\partial t + \mathbf{i}\cdot c^{-1}\partial\mathbf{A}/\partial t\}dV, \qquad (19)$$

or, taking into account that at equilibrium $\bar{\mu}$ is uniform, $\mathbf{i}$ vanishes and all variables are constant in time,

$$d\Delta S/dt = -T^{-1}\int_V \{(\Delta\bar{\mu}/e)\partial\Delta\rho_e/\partial t$$
$$\qquad + \Delta\mathbf{i}\cdot c^{-1}\partial\Delta\mathbf{A}/\partial t\}dV, \qquad (20)$$

where conservation of charge has been applied, and where the symbol Δ indicates the difference of a quantity and its equilibrium value. We have obtained the change of entropy as a function of fluctuations of local state variables. It has the form (I, 15) required for the application of the formalism derived in I, Secs. 2 and 3. However, this formalism is based on the consideration of an *energetically* insulated system. It is therefore necessary to investigate whether such a condition leaves expression (20) unmodified. For this purpose let us write down the law of conservation of energy for the whole system which follows from (2), (3), and (4):

$$(d/dt)\int_V u_v dV + (d/dt)\int_V \tfrac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2)dV$$

$$= -\int_\Omega \mathbf{J}_q\cdot d\mathbf{\Omega} - c\int_\Omega (\mathbf{E}\times\mathbf{B})\cdot d\mathbf{\Omega}. \qquad (21)$$

Energetic insulation means that no energy fluxes enter through the limiting surface, i.e., both terms on the right-hand side of (21) vanish. The fact that the heat flow $\mathbf{J}_q$ must vanish at the boundary has been used already as a sufficient condition to obtain formula (20). On the other hand electromagnetic insulation of the system, i.e., vanishing of the last term of (21), is impossible since varying charges and currents give rise to energy changes in free space. Therefore, energetic

insulation must imply here the constancy of a quantity

$$\int_V u_v dV + \int_\infty \tfrac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2) dV, \qquad (22)$$

where the first integral is taken over the material system, and the second is to be extended over the whole of space. Of course the material system must contain all relevant sources of electromagnetic fields. If now the fields vanish sufficiently rapidly at infinity

$$c\int_\infty (\mathbf{E}\times\mathbf{B})\cdot d\mathbf{\Omega}$$

vanishes and constancy of (22) is achieved.

5. FLUCTUATIONS

In formula (20) we have the variables $\Delta\rho_e(\mathbf{r})$ of the α type, whereas the components of $\Delta\mathbf{A}(\mathbf{r})$ are of β-type variables (see I, Sec. 2). They are continuous function of space coordinates $\mathbf{r}$. The quantities $\Delta(\bar{\mu}/e)$, and the components of $\Delta\mathbf{i}$ are the corresponding X- and Y-type variables. The variables $\Delta\mathbf{i}$ and $\Delta\rho_e$ are connected by Eq. (1).

The relation (I, 11) and (I, 12) read for these variables

$$\left.\begin{array}{c}\langle\Delta\rho_e(\mathbf{r})\Omega(\mathbf{r}')\Delta\bar{\mu}(\mathbf{r}')/e\rangle_{Av}=kT\Omega(\mathbf{r}')\delta(\mathbf{r}-\mathbf{r}'),\\[4pt]\langle\Delta\rho_e(\mathbf{r})\Omega(\mathbf{r}')\Delta i_i(\mathbf{r}')\rangle_{Av}=0,\quad(i=1,2,3)\end{array}\right\}\quad(23)$$

$$\left.\begin{array}{c}\langle\Delta A_i(\mathbf{r})\Omega(\mathbf{r}')\Delta i_j(\mathbf{r}')\rangle_{Av}=kT\Omega(\mathbf{r}')\delta_{ij}\delta(\mathbf{r}-\mathbf{r}'),\\[4pt](i,j=1,2,3)\\[4pt]\langle\Delta A_i(\mathbf{r})\Omega(\mathbf{r}')\Delta\bar{\mu}(\mathbf{r}')/e\rangle_{Av}=0,\quad(i=1,2,3)\end{array}\right\}\quad(24)$$

where i and j indicate the Cartesian coordinates.

6. MICROSCOPIC REVERSIBILITY

Microscopic reversibility can be expressed as follows

$$\langle\Delta\rho_e(\mathbf{r})(\partial/\partial t)\Delta\rho_e(\mathbf{r}')\rangle_{Av}\{\mathbf{B},\mathbf{B}'\}$$
$$=\langle\Delta\rho_e(\mathbf{r}')(\partial/\partial t)\Delta\rho_e(\mathbf{r})\rangle_{Av}\{-\mathbf{B},-\mathbf{B}'\},\quad(25)$$

$$\langle\Delta\rho_e(\mathbf{r})(\partial/\partial t)\Delta A_i(\mathbf{r}')\rangle_{Av}\{\mathbf{B},\mathbf{B}^1\}$$
$$=-\langle\Delta A_i(\mathbf{r}')(\partial/\partial t)\Delta\rho_e(\mathbf{r})\rangle_{Av}\{-\mathbf{B},-\mathbf{B}'\},\quad(26)$$

$$\langle\Delta A_i(\mathbf{r})(\partial/\partial t)\Delta A_j(\mathbf{r}')\rangle_{Av}\{\mathbf{B},\mathbf{B}'\}$$
$$=\langle\Delta A_j(\mathbf{r}')(\partial/\partial t)\Delta A_i(\mathbf{r})\rangle_{Av}\{-\mathbf{B},-\mathbf{B}'\},\quad(27)$$

which are examples of (I, 19), (I, 20), and (I, 21) respectively. With time reversal, i.e., all particles retracing their path, the magnetic field reverses its direction everywhere. In formulas (25)–(27), $\mathbf{B}$ and $\mathbf{B}'$

indicate the magnetic field strengths at the positions $\mathbf{r}$ and $\mathbf{r}'$, where the averages are performed.

7. RECIPROCAL RELATIONS FOR ELECTRIC CONDUCTION

In order to derive reciprocal relations for electric conduction in anisotropic crystals, we insert the law of conservation of charge (1) and the phenomenological equation (17) into the expressions for the microscopic reversibility (25)–(27),

$$\langle\Delta\rho_e \,\mathrm{div}'\Delta\mathbf{i}'\rangle_{Av}=\langle\Delta\rho_e'\,\mathrm{div}\Delta\mathbf{i}\rangle_{Av},\qquad(28)$$

$$\langle\Delta\rho_e\{(\partial/\partial x_i')\Delta\bar{\mu}/e+\textstyle\sum_j R_{ij}'(\mathbf{B}')\Delta i_j'\}\rangle_{Av}$$
$$=-\langle\Delta A_i'\textstyle\sum_j(\partial/\partial x_j)\Delta i_j\rangle_{Av},\quad(29)$$

$$\langle\Delta A_i\{(\partial/\partial x_j')\Delta\bar{\mu}/e+\textstyle\sum_k R_{jk}'(\mathbf{B}')\Delta i_k'\}\rangle_{Av}$$
$$=\langle\Delta A_j'\{(\partial/\partial x_i)\Delta\bar{\mu}/e+\textstyle\sum_k R_{ik}(-\mathbf{B})\Delta i_k\}\rangle_{Av}.\quad(30)$$

With the (23) and (24) we find that both members of (28) vanish, whereas (29) and (30) become

$$(\partial/\partial x_i')\delta(\mathbf{r}-\mathbf{r}')=-\textstyle\sum_j\delta_{ij}(\partial/\partial x_j)\delta(\mathbf{r}-\mathbf{r}'),\quad(31)$$

$$\textstyle\sum_k R_{jk}'(\mathbf{B}')\delta_{ik}\delta(\mathbf{r}-\mathbf{r}')=\sum_k R_{ik}(-\mathbf{B})\delta_{jk}\delta(\mathbf{r}-\mathbf{r}').\quad(32)$$

Eliminating the Kronecker δ's and the δ functions, (31) gives an identity whereas (32) yields the result

$$R_{ji}(\mathbf{B})=R_{ij}(-\mathbf{B}),\qquad(33)$$

or, in matrix notation

$$R(\mathbf{B})=R^\dagger(-\mathbf{B}),\qquad(34)$$

where the sign $\dagger$ indicates the transpose matrix. Formula (34) is the desired result for the symmetry properties of the electrical resistivity tensor.

We may remark that (25) did not lead to any result, since both terms became identically equal to zero [see (28)]. Such a behavior for a correlation between α-type variables, when β-type variables, related to the α's, are taken into consideration for the description of the system, was also found in I, Sec. 8 and was first noted by Machlup and Onsager.[2] We have also seen that (26) leads to no physical result [see (29) and (31)] since it is an identity. This means that a correlation between α variables and a related β variable is identically equal (but with opposite sign!) to the correlation between this β and this α. Or in other words, the property of microscopic reversibility is identically satisfied in this case. The complete result (34) is obtained from relation (27) alone.

The authors are indebted to Dr. R. Fieschi for some useful comments.

[2] S. Machlup and L. Onsager, Phys. Rev. **91**, 1512 (1953).