Mazur, P.
De Groot, S. R.
1953

Physica XIX
961-970

ON ONSAGER'S RELATIONS IN A MAGNETIC FIELD

by P. MAZUR and S. R. DE GROOT *)

Instituut voor theoretische natuurkunde, Universiteit van Utrecht, Nederland

Synopsis

Onsager's theory is extended to the case of systems with a magnetic field, which is a continuous function of space. The reciprocal relations between phenomenological coefficients are found to be

$$L_{ji}\,(\mathbf{r}', \mathbf{B}'; \mathbf{r}, \mathbf{B}) = L_{ij}(\mathbf{r}, -\mathbf{B}; \mathbf{r}', -\mathbf{B}'),$$

where i and j number state variables of various kinds (which are continuous functions of space and time), $\mathbf{r}'$ and $\mathbf{r}$ indicate space coordinates of two positions in the system, $\mathbf{B}'$ and $\mathbf{B}$ denote the magnetic fields at those positions.

The implications of these reciprocal relations on the symmetry properties of the electric and heat conduction tensors are derived.

For this purpose it was necessary to define insulation for systems, in which electromagnetic phenomena occur, from appropriate thermodynamic considerations.

§ 1. *Introduction*. Casimir [1]) has pointed out that the application of Onsager's reciprocal relations [2]) in the thermodynamics of irreversible processes [3]) [4]) requires special attention in many cases. As a matter of fact the phenomenological laws in "continuous systems" (*i.e.*, with state variables continuous functions of space and time coordinates) contain three-dimensional flows (heat flow, diffusion flow, electric current, etc.) which are not properly time derivatives of state variables, as was required in Onsager's original treatment.

Casimir has elaborated this idea for heat conduction in anisotropic crystals by reducing the problem in such a way that Onsager's theory can be applied. This is achieved by starting from the consideration of an infinite number of local temperature fluctuations in a closed system. However, for the case of electric conduction Casimir

*) Actual address: Instituut voor theoretische natuurkunde, Universiteit van Leiden, Nederland.

prefers to choose an entirely different method, the relation of which with the framework of the Onsager theory is less apparent.

One of the objectives of this paper is to treat the electrical case in a manner analogous to Casimir's treatment of heat conduction. This leads to some specific complications, also encountered by Casimir. Actually one must consider energetically insulated systems in order to comply with the Onsager scheme. This is difficult for electromagnetic phenomena in so far as the fields vary also outside the material system. The thermodynamics of this case, and the proper definition of insulation, is developed in § 3.

Another objective of this paper is the consideration of the influence of a magnetic field on the phenomena studied. The magnetic field may be a continuous function of space. Onsager and Casimir considered only external uniform fields. For a continuously varying magnetic field, the derivation of the Onsager relations must be reexamined. This is done in § 2.

The theory outlined above is applied to electrical conduction (§ 4) and heat conduction (§ 5) in anisotropic crystals The different results obtained for these examples are finally discussed in § 6.

§ 2. *The Onsager relations for systems with electromagnetic fields.* *a.* Theory of fluctuations. Consider an adiabatically insulated system. The variables $A_1, A_2, \ldots, A_n$ which describe the thermodynamical state of the system are continuous functions of time and space coordinates. For convenience we shall divide the system into a number cells of volume V^μ, in which the variables A_1, $A_2, \ldots, A_n$ may be considered as uniform (here μ numbers the cells). The deviations of the state variables from their equilibrium values are denoted by

$$\alpha_i^\mu \equiv A_i^\mu - (A_i^\mu)_{equ}. \quad (i = 1, 2, \ldots, n) \tag{1}$$

The deviation of the entropy of the system from its equilibrium value is given by the quadratic form

$$\Delta S = -\tfrac{1}{2} \Sigma_{\mu,\nu} V^\mu V^\nu \Sigma_{i,k} g_{ik}^{\mu\nu} \alpha_i^\mu \alpha_k^\nu. \tag{2}$$

The probability distribution for the α_i^μ is expressed by

$$P\Pi_{\mu,i} \, d\alpha_i^\mu = \frac{\exp(\Delta S/k) \, \Pi_{\mu,i} \, d\alpha_i^\mu}{\int \ldots \int \exp(\Delta S/k) \, \Pi_{\mu,i} \, d\alpha_i^\mu} \, . \tag{3}$$

We introduce the following linear combinations of parameters

$$X_i^\mu = (V^\mu)^{-1}\, \partial \Delta S / \partial \alpha_i^\mu = -\, \Sigma_\nu\, V^\nu\, \Sigma_k\, g_{ik}^{\mu\nu}\, \alpha_k^\nu. \tag{4}$$

The following average is easily found with (3) and (4)

$$\overline{\alpha_i^\mu\, X_j^\nu} = -\, k\delta^{ij}\, \delta^{\mu\nu}\, (V^\mu)^{-1}. \tag{5}$$

Passing to the limit of continuous variables, we can replace μ and ν, which indicate the cells, by $\mathbf{r}$ and $\mathbf{r}'$, which denote space coordinates, whereas the last two factors of (5) combine into a Heaviside-Dirac-δ-function. Consequently (5) becomes

$$\overline{\alpha_i(\mathbf{r}) X_j(\mathbf{r}')} = -\, k\delta^{ij}\delta(\mathbf{r} - \mathbf{r}'). \tag{6}$$

(Of course the average is performed by taking $\alpha_i(\mathbf{r})$ and $X_j(\mathbf{r}')$ at the same time t). This result will be used in the derivation of the Onsager relations.

Remark. We note that with (4) the time derivative of (2) (or entropy production per unit time) can be written as

$$\Delta^{\boldsymbol{\cdot}} S = \Sigma_\mu\, V^\mu\, \Sigma_i\, \dot{\alpha}_i^\mu\, X_i^\mu, \tag{7}$$

or,

$$\Delta^{\boldsymbol{\cdot}} S = \int \Sigma_i\, \dot{\alpha}_i\, (\mathbf{r})\, X_i\, (\mathbf{r})\, \mathrm{d}\mathbf{r} \tag{8}$$

in the limit of infinitely small cells.

b. Microscopic time reversal invariance. The property of time reversal invariance ("microscopic reversibility") of the equations of motion of individual particles in the presence of a magnetic field $\mathbf{B}$ can be written as

$$\overline{\alpha_i(\mathbf{r}, t)\, \alpha_j(\mathbf{r}', t + \tau)}\, \{\mathbf{B}, \mathbf{B}'\} = \overline{\alpha_i(\mathbf{r}, t)\, \alpha_j(\mathbf{r}', t - \tau)}\, \{-\mathbf{B}, -\mathbf{B}'\}. \tag{9}$$

We have taken a field $\mathbf{B}$ which is a continuous function of space coordinates. With time reversal, i.e., all particles retracing their paths, the field $\mathbf{B}(\mathbf{r})$ reverses everywhere its direction. But since in formula (9) the quantities refer only to the positions $\mathbf{r}$ and $\mathbf{r}'$, they depend exclusively on the values $\mathbf{B}$ and $\mathbf{B}'$ of the magnetic field at these positions. Shifting the time axis at the right-hand side of (9), this formula becomes

$$\overline{\alpha_i(\mathbf{r}, t)\, \alpha_j\, (\mathbf{r}', t + \tau)}\, \{\mathbf{B}, \mathbf{B}'\} = \overline{\alpha_i(\mathbf{r}, t + \tau)\, \alpha_j(\mathbf{r}', t)}\, \{-\, \mathbf{B}, -\, \mathbf{B}'\}. \tag{10}$$

The averaging can be performed in an alternative way, *viz.* by taking first fixed values of all parameters at the time t and averaging the quantities belonging to the time $t + \tau$, and subsequently by averaging over the hitherto fixed parameters

$$\overline{(a_i(\mathbf{r},t)\,\overline{[a_j(\mathbf{r}',t+\tau)}_t\{\mathbf{B}'\}])}\,\{\mathbf{B},\mathbf{B}'\} = \overline{(a_j(\mathbf{r}',t)\,\overline{[a_i(\mathbf{r},t+\tau)}_t\{-\mathbf{B}\}])}\{-\mathbf{B},-\mathbf{B}'\}. \quad (11)$$

Here the suffix t indicates that all parameters $a_i(\mathbf{r}, t)$ for all values of i and $\mathbf{r}$ have fixed values at the time t. The averaged quantities denoted by the lower bar are now functions of the fields at one single position, whereas the averages denoted by the upper bar are still functions of the fields at both positions $\mathbf{r}$ and $\mathbf{r}'$. We now subtract a constant quantity from both sides of (11). This gives

$$\begin{aligned}\overline{a_i(\mathbf{r}, t)\,[\overline{\{a_j(\mathbf{r}', t + \tau) - a_j(\mathbf{r}', t)\}}_t\,\{\mathbf{B}'\}]}\,\{\mathbf{B}, \mathbf{B}'\} &= \\ = \overline{a_j(\mathbf{r}', t)\,[\overline{\{a_i(\mathbf{r}, t + \tau) - a_i(\mathbf{r}, t)\}}_t\,\{-\mathbf{B}\}]}\,\{-\mathbf{B}, -\mathbf{B}'\}&, \quad (12)\end{aligned}$$

a formula, which will be used in the following.

c. Regression of fluctuations. In the linear approximation the average decay of the fluctuations can be described by the phenomenological laws, expressing that the time derivatives of the parameters $a_i(\mathbf{r}, t)$ are linear functions of these parameters themselves. Instead of the latter we use the linear combinations $X_i(\mathbf{r}, t)$ from (4).

$$\begin{aligned}J_i(\mathbf{r}, t, \mathbf{B}) \equiv \frac{\overline{\{a_i(\mathbf{r}, t + \tau) - a_i(\mathbf{r}, t)\}_t\,\{\mathbf{B}\}}}{\tau} &= \\ = \int \Sigma_k\, L_{ik}(\mathbf{r}, \mathbf{B}; \mathbf{r}'', \mathbf{B}'')\, X_k(\mathbf{r}'', t)\, \mathrm{d}\mathbf{r}''&. \quad (13)\end{aligned}$$

Thus one extablishes relations between the quantities which occur in the entropy production (8). The "phenomenological coëfficients" $L_{ik}(\mathbf{r}, \mathbf{B}; \mathbf{r}'', \mathbf{B}'')$ depend on the positions $\mathbf{r}$ and $\mathbf{r}''$ and the fields $\mathbf{B}$ and $\mathbf{B}''$ there.

d. Derivation of the Onsager relations. With the help of the three preceding results, the derivation of the Onsager relations is straight-forward. Introducing (13) into (12), and applying (6) yields

$$\begin{aligned}\int \Sigma_k\, L_{jk}(\mathbf{r}', \mathbf{B}'; \mathbf{r}'', \mathbf{B}'')\, \delta^{ik}\delta(\mathbf{r} - \mathbf{r}'')\, \mathrm{d}\mathbf{r}'' &= \\ = \int \Sigma_k\, L_{jk}(\mathbf{r}, -\mathbf{B}; \mathbf{r}'', -\mathbf{B}'')\, \delta^{jk}\delta(\mathbf{r}' - \mathbf{r}'')\, \mathrm{d}\mathbf{r}''&. \quad (14)\end{aligned}$$

This gives immediately

$$L_{ji}(\mathbf{r}', \mathbf{B}'; \mathbf{r}, \mathbf{B}) = L_{ij}(\mathbf{r}, -\mathbf{B}; \mathbf{r}', -\mathbf{B}'), \qquad (15)$$

which is the general form of the Onsager relations, i.e., the macroscopic counterpart of time reversal invariance, for systems described by parameters, which are continuous functions of space and time.

For a uniform system (15) reduces to

$$L_{ji}(\mathbf{B}) = L_{ij}(-\mathbf{B}), \tag{16}$$

where $\mathbf{B}$ is the (uniform) field.

It is rather unsatisfactory to base a reasoning on properties of non-uniform systems on formula (16). As a matter of fact it will be shown in the following that the general formula (15) is necessary for a rigorous derivation of observable relations.

§ 3. *Thermodynamics of insulated electromagnetic system.* The Onsager relations are proved for decay of quantities J_i (formula (13)) in an insulated system. When electromagnetic phenomena occur the problem arises of giving a proper definition of an insulated system. In the framework of the Onsager theory as exposed here, by insulation we have to understand that the system should be energetically closed in order to be able to use formula (3) which is valid for a microcanonical ensemble.

From energy conservation it follows that the change of total energy of a system with constant volume V and surface Ω is

$$(\mathrm{d}/\mathrm{d}t) \int_V u_v \,\mathrm{d}V + (\mathrm{d}/\mathrm{d}t) \int_V \tfrac{1}{2}(E^2 + B^2)\,\mathrm{d}V = \\ = -\int_\Omega \mathbf{J}_q . \mathrm{d}\boldsymbol{\Omega} - c \int_\Omega (\mathbf{E} \wedge \mathbf{B}) . \mathrm{d}\boldsymbol{\Omega}, \tag{17}$$

where u_v is the internal energy per unit volume, $\frac{1}{2}(E^2 + B^2)$ the electromagnetic energy per unit volume, $\mathbf{J}_q$ the heat flow and $\mathbf{E} \wedge \mathbf{B}$ the Poynting vector. Energetic insulation means that no energy fluxes enter through a limiting surface, *i.e.*, both terms at the right-hand side vanish. This cannot be achieved by the separate vanishing of both terms at the left-hand side owing to the possible exchange of internal and electromagnetic energy. Moreover electromagnetic insulation of the system with volume V and surface Ω *i.e.*, vanishing last term of (17*a*), is impossible since varying charges and currents give rise to energy changes in free space. Therefore insulation must imply here the constancy of a quantity

$$\bar{U} = \int_V u_v \,\mathrm{d}V + \int_\infty \tfrac{1}{2}(E^2 + B^2)\,\mathrm{d}V, \tag{17a}$$

where the first integral is extended 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. For simplicity's sake we have not considered electric and magnetic polarization of the matter here.

The entropy change of the whole system must now be written as a function of the above defined energy $\overline{U}$ (17). For this purpose we must start from the Gibbs equation

$$\mathrm{d}u_v/\mathrm{d}t = T\,\mathrm{d}s_v/\mathrm{d}t + \Sigma_\gamma\,\mu_\gamma\,\mathrm{d}\varrho_\gamma/\mathrm{d}t, \tag{18}$$

where s_v is the entropy per unit volume, μ_γ the chemical potential (per unit mass) of component γ, and ϱ_γ the density of γ. The time derivatives are substantial derivatives with respect to the centre of mass motion. For convenience we take a system consisting of a rigid ion lattice and of electrons. With the charge density $\varrho_e = e_1\varrho_1 + e_2\varrho_2$, were $e_1 = e$ and ϱ_1 are the specific charge and the density of the electrons, and e_2 and ϱ_2 the specific charge and the (constant) density of the ions, formula (18) becomes

$$\mathrm{d}u_v/\mathrm{d}t = T\,\mathrm{d}s_v/\mathrm{d}t + (\mu/e)\,\mathrm{d}\varrho_e/\mathrm{d}t, \tag{19}$$

where μ is the chemical potential of the electrons (per unit mass). Taking the velocity of ion lattice as zero, we can neglect the centre of mass velocity, because the ions are heavy as compared with the electrons. We then have from (19)

$$\partial u_v/\partial t = T\,\partial s_v/\partial t + (\mu/e)\,\partial\varrho_e/\partial t. \tag{20}$$

We now take the time derivative of (17a)

$$\mathrm{d}\overline{U}/\mathrm{d}t = \textstyle\int_V \partial u_v/\partial t\,\mathrm{d}V + \int_\infty (\mathbf{E}\,.\,\partial\mathbf{E}/\partial t + \mathbf{B}\,.\,\partial\mathbf{B}/\partial t)\,\mathrm{d}V. \tag{21}$$

On introducing (20) and applying Poynting's theorem we have

$$\mathrm{d}\overline{U}/\mathrm{d}t = \textstyle\int_V (T\,\partial s_v/\partial t + (\mu/e)\,\partial\varrho_e/\partial t)\,\mathrm{d}V - c\int_\infty \operatorname{div}\mathbf{E}\wedge\mathbf{B}\,\mathrm{d}V - \int_V \mathbf{i}\,.\mathbf{E}\,\mathrm{d}V. \tag{22}$$

With
$$\mathbf{E} = -\operatorname{grad}\varphi - c^{-1}\,\partial\mathbf{A}/\partial t, \tag{23}$$

we obtain, performing a partial integration, and applying Gauss' theorem

$$\frac{\mathrm{d}\overline{U}}{\mathrm{d}t} = \int_V T\,\frac{\partial s_v}{\partial t}\,\mathrm{d}V + \int_V \left(\frac{\tilde{\mu}}{e}\,\frac{\partial\varrho_e}{\partial t} + \mathbf{i}\,.\,\frac{1}{c}\,\frac{\partial\mathbf{A}}{\partial t}\right)\mathrm{d}V - c\int_\infty \mathbf{E}\wedge\mathbf{B}\,\mathrm{d}\Omega, \tag{24}$$

where the "electrochemical potential"

$$\tilde{\mu} = \mu + e\varphi, \tag{25}$$

and charge conservation

$$\partial\varrho_e/\partial t = -\operatorname{div}\mathbf{i} \tag{26}$$

have been used. We shall suppose that the fields vanish sufficiently rapidly at infinity, restrict ourselves to uniform temperature, and introduce the total entropy S. Then (24) reads

$$T\,\mathrm{d}S/\mathrm{d}t = \mathrm{d}\overline{U}/\mathrm{d}t - \int_V ((\tilde{\mu}/e)\,\partial\varrho_e/\partial t + \mathbf{i}.c^{-1}\,\partial\mathbf{A}/\partial t)\,\mathrm{d}V. \tag{27}$$

For the irrotational case this formula (*i.e.* without the last term) has been derived before [5]). From (27) we find the entropy production for an insulated system, *i.e.*, constant $\overline{U}$

$$T\,\mathrm{d}S/\mathrm{d}t = -\int_V ((\tilde{\mu}/e)\,\partial\varrho_e/\partial t + \mathbf{i}.c^{-1}\,\partial\mathbf{A}/\partial t)\,\mathrm{d}V. \tag{28}$$

Using (26) and the condition

$$\int \operatorname{div}\mathbf{i}\,\mathrm{d}V = 0, \tag{29}$$

valid for the system under consideration, we can bring equation (28) immediately into the required form (8)

$$T\,\mathrm{d}S/\mathrm{d}t = -\int_V ((\Delta\tilde{\mu}/e)\,\partial\varrho_e/\partial t + \mathbf{i}.c^{-1}\partial\mathbf{A}/\partial t)\,\mathrm{d}V, \tag{30}$$

where

$$\Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_{equ} \tag{31}$$

with $\tilde{\mu}_{equ}$ the uniform equilibrium value of $\tilde{\mu}$. (Of course the uniformity of $\tilde{\mu}$ and the vanishing of $\mathbf{i}$ at equilibrium can immediately be concluded from the equilibrium conditions).

§ 4. *The symmetry properties of the electric conduction tensor.* Formula (30), being of the form (8), can be used as a basis for the derivation of the implications of the Onsager relations (15) for the symmetry properties of the electric conduction tensor.

The phenomenological equations (13) for the fluxes and forces in (30) read, with $i, j = 1, 2, 3$ for the Cartesian components,

$$\partial\varrho_e/\partial t = -\int\{K(\mathbf{r},\mathbf{B};\mathbf{r}',\mathbf{B}')\Delta\tilde{\mu}'/e + \Sigma_i M_i(\mathbf{r},\mathbf{B};\mathbf{r}',\mathbf{B}')\,c^{-1}\partial A_i'/\partial t\}\mathrm{d}\mathbf{r}', \tag{32}$$

$$i_i = -\int\{N_i(\mathbf{r},\mathbf{B};\mathbf{r}',\mathbf{B}')\,\Delta\tilde{\mu}'/e + \Sigma_j\,Q_{ij}(\mathbf{r},\mathbf{B};\mathbf{r}',\mathbf{B}')\,c^{-1}\,\partial A_j'/\partial t\}\,\mathrm{d}\mathbf{r}', \tag{33}$$

where the dashes indicate dependence on position $\mathbf{r}'$.

The Onsager relations (15) read here

$$K(\mathbf{r},\mathbf{B};\mathbf{r}',\mathbf{B}') = K(\mathbf{r}',-\mathbf{B}';\mathbf{r},-\mathbf{B}), \tag{34}$$

$$M_i(\mathbf{r},\mathbf{B};\mathbf{r}',-\mathbf{B}') = N_i(\mathbf{r}',-\mathbf{B}';\mathbf{r},-\mathbf{B}),\quad (i = 1, 2, 3) \tag{35}$$

$$Q_{ij}(\mathbf{r},\mathbf{B};\mathbf{r}',\mathbf{B}') = Q_{ji}(\mathbf{r}',-\mathbf{B}';\mathbf{r},-\mathbf{B}).\quad (i, j = 1, 2, 3) \tag{36}$$

Our final task is now to find the influence of these Onsager relations on the electric conduction tensor $\boldsymbol{\sigma}$ of Ohm's law for anisotropic matter

$$\mathbf{i} = \boldsymbol{\sigma}(\mathbf{B}) \cdot (\mathbf{E} - \operatorname{grad}(\Delta\mu/e)), \tag{37}$$

or with (23) and in components

$$i_j = \Sigma_i\, \sigma_{ji}(\mathbf{B})\, (-\nabla_i\, \Delta\tilde{\mu}/e - c^{-1}\, \partial A_i/\partial t). \quad (j = 1, 2, 3) \tag{38}$$

From this formula and (26) it follows

$$\partial\varrho_e/\partial t = \Sigma_{i,j}\, \nabla_i\, \{\sigma_{ij}(\mathbf{B})\, (\nabla_j\, \Delta\tilde{\mu}/e + c^{-1}\, \partial A_j/\partial t)\}. \tag{39}$$

We must bring (39) and (38) in the required form (32) and (33). This is achieved by writing

$$\partial\varrho_e/\partial t = \int \delta(\mathbf{r} - \mathbf{r}')\, \Sigma_{i,j}\, \nabla_i'\, \{\sigma_{ij}'(\mathbf{B}')\, (\nabla_j'\, \Delta\tilde{\mu}'/e + c^{-1}\, \partial A_j'/\partial t)\}\, \mathrm{d}\mathbf{r}', \tag{40}$$

$$i_j = \int \partial(\mathbf{r} - \mathbf{r}')\, \Sigma_i\, \sigma_{ji}'(\mathbf{B}')\, (-\nabla_i'\, \Delta\tilde{\mu}'/e - c^{-1}\, \partial A_i'/\partial t)\, \mathrm{d}\mathbf{r}', \tag{41}$$

and by integrating by parts

$$\begin{aligned}\partial\varrho_e/\partial t = \int (\Sigma_{i,j}\, [\nabla_j'\, \{\sigma_{ij}'\, (\mathbf{B}')\, \nabla_i'\, \delta(\mathbf{r} - \mathbf{r}')\}]\, \Delta\tilde{\mu}'/e\, - \\ - \Sigma_{i,j}\, \{\sigma_{ij}'(\mathbf{B}')\, \nabla_i'\delta(\mathbf{r} - \mathbf{r}')\}\, c^{-1}\, \partial A_j'/\partial t)\, \mathrm{d}\mathbf{r}',\end{aligned} \tag{42}$$

$$i_j = \int (\Sigma_i [\nabla_i' \{\sigma_{ji}'(\mathbf{B}')\delta(\mathbf{r}-\mathbf{r}')\}]\, \Delta\tilde{\mu}'/e - \Sigma_i\, \sigma_{ji}'(\mathbf{B}')\delta(\mathbf{r}-\mathbf{r}')\, c^{-1} \partial A_i'/\partial t) \mathrm{d}\mathbf{r}'. \tag{43}$$

The Onsager relations (34), (35) and (36) for the coefficients in (42) and (43) thus become

$$\Sigma_{i,j} \nabla_j'\, \{\sigma_{ij}'(\mathbf{B}')\, \nabla_i'\delta\, (\mathbf{r} - \mathbf{r}')\} = \Sigma_{i,j}\, \nabla_j\, \{\sigma_{ij}(-\mathbf{B})\, \nabla_i\, \delta(\mathbf{r} - \mathbf{r}')\}, \tag{44}$$

$$\Sigma_i\, \sigma_{ij}'(\mathbf{B}')\, \nabla_i'\, \delta(\mathbf{r} - \mathbf{r}') = -\Sigma_i\, \nabla_i\, \{\sigma_{ji}(-\mathbf{B})\, \delta(\mathbf{r} - \mathbf{r}')\}, \tag{45}$$

$$\sigma_{ji}'(\mathbf{B}')\, \delta(\mathbf{r} - \mathbf{r}') = \sigma_{ij}\, (-\mathbf{B})\, \delta(\mathbf{r} - \mathbf{r}'). \tag{46}$$

We eliminate the δ-functions from these relations by multiplying with an arbitrary function $f(\mathbf{r}')$ and integrating over $\mathbf{r}'$

$$\Sigma_{i,j}\, \nabla_i\, \{\sigma_{ij}(\mathbf{B})\, \nabla_j\, f(\mathbf{r})\} = \Sigma_{i,j}\, \nabla_j\, \{\sigma_{ij}(-\mathbf{B})\, \nabla_i\, f(\mathbf{r})\}, \tag{47}$$

$$\Sigma_i\, \nabla_i\, \{\sigma_{ij}(\mathbf{B})\, f(\mathbf{r})\} = \Sigma_i\, \nabla_i\, \{\sigma_{ji}(-\mathbf{B})\, f(\mathbf{r})\}, \tag{48}$$

$$\sigma_{ji}\, (\mathbf{B})\, f(\mathbf{r}) = \sigma_{ij}\, (-\mathbf{B})\, f(\mathbf{r}). \tag{49}$$

Since the functions $f(\mathbf{r})$ are arbitrary the following set of relations is found from (47)

$$\sigma_{ij}^s\, (\mathbf{B}) = \sigma_{ij}^s(-\mathbf{B})\,;\ \Sigma_i\, \nabla_i\, \sigma_{ij}^a\, (\mathbf{B}) = -\Sigma_i\, \nabla_i\, \sigma_{ij}^a\, (-\mathbf{B}), \tag{50}$$

where s and a indicate the symmetric and antisymmetric parts of

σ_{ij}. Similarly, from (48) as well as from (49), it follows

$$\sigma_{ij}(\mathbf{B}) = \sigma_{ji}(-\mathbf{B}) \tag{51}$$

or

$$\sigma^s_{ij}(\mathbf{B}) = \sigma^s_{ij}(-\mathbf{B}),\ \ \sigma^a_{ij}(\mathbf{B}) = -\sigma^a_{ij}(-\mathbf{B}). \tag{52}$$

Of course (52) contains (50).

In this way the result (51) or (52), which has also been confirmed experimentally [6]), has been derived in a way consistent with the framework of the Onsager theorem.

§ 5. *The symmetry properties of the heat conduction tensor.* The theory of heat conduction of anisotropic crystals in a magnetic field can be developed along the same lines as the preceding derivation. For convenience we shall consider a one component system of constant density, containing no sources of the electromagnetic field. Thus, no exchange of internal and electromagnetic energy takes place. In contrast to the case of the preceding section, energy insulation can now be achieved by keeping the internal and the electromagnetic energies separately constant. This means that both terms at the left-hand side of (17) may vanish separately. Thus for an insulated system

$$\int_V (\partial u_v/\partial t)\,\mathrm{d}V = 0. \tag{53}$$

The entropy change of the insulated system

$$\mathrm{d}S/\mathrm{d}t = \int_V (\partial s_v/\partial t)\,\mathrm{d}V \tag{54}$$

is according to Gibbs relation equal to

$$\mathrm{d}S/\mathrm{d}t = \int_V T^{-1}(\partial u_v/\partial t)\,\mathrm{d}V \tag{55}$$

With (53) this expression can be brought into the required form (8)

$$\mathrm{d}S/\mathrm{d}t = \int_V (T^{-1} - T_0^{-1})(\partial u_v/\partial t)\,\mathrm{d}V = -\int_V (\Delta T/T_0^2)(\partial u_v/\partial t)\,\mathrm{d}V, \tag{56}$$

where $\Delta T = T - T_0$ is the deviation of the temperature T from its equilibrium value T_0.

The phenomenological equations (13) read for this case

$$\partial u_v/\partial t = -\int K(\mathbf{r}, \mathbf{B}; \mathbf{r}', \mathbf{B}')(\Delta T'/T_0^2)\,\mathrm{d}\mathbf{r}', \tag{57}$$

and the Onsager relations (15) are

$$K(\mathbf{r}, \mathbf{B}; \mathbf{r}', \mathbf{B}') = K(\mathbf{r}', -\mathbf{B}'; \mathbf{r}, -\mathbf{B}). \tag{58}$$

In order to find the influence of this relation on the heat conduction tensor, we write Fourier's law

$$\mathbf{J}_q = -\boldsymbol{\lambda}(\mathbf{B}).\mathrm{grad}\,\Delta T, \tag{59}$$

where $\mathbf{J}_q$ is the heat flow, and insert it into the energy balance

$$\partial u_v/\partial t = -\operatorname{div} \mathbf{J}_q = \operatorname{div} \{\boldsymbol{\lambda}(\mathbf{B}) . \operatorname{grad} \Delta T\}. \tag{60}$$

Applying the formalism of the preceding section (as from (39) on) one then finds analogous to (50)

$$\lambda_{ij}^s(\mathbf{B}) = \lambda_{ij}^s(-\mathbf{B}), \tag{61}$$

$$\Sigma_i \nabla_i \lambda_{ij}^a(\mathbf{B}) = -\Sigma_i \nabla_i \lambda_{ij}^a(-\mathbf{B}), \tag{62}$$

where s and a denote the symmetric and antisymmetric parts of λ_{ij}.

§ 6. *Concluding remarks.* It is perhaps useful to comment upon the difference between this result and the result (52) for the electric case. The results (61) and (62) can be understood by splitting the heat conduction tensor into its symmetric and antisymmetric part also in equation (60). This gives

$$\partial u_v/\partial t = -\operatorname{div} \mathbf{J}_q = \Sigma_{i,j} \nabla_i \{\lambda_{ij}^s(\mathbf{B}) \nabla_j T\} + \Sigma_{j,i} \nabla_j T \nabla_i \lambda_{ij}^a(\mathbf{B}). \tag{63}$$

Since only the devergence of the heat flow has physical meaning, it is clear from (63) that observable results can be obtained for the symmetric part itself, but only for the divergence of the antisymmetric part of the heat conduction tensor.

In the electrical case of § 4, on the other hand, the current $\mathbf{i}$ itself is observable. From (37) it can immediately be concluded that both the symmetric and the antisymmetric part of the electric conduction tensor have a physical meaning. As a matter of fact they both occur in (52) as such, *i.e.*, not preceded by a differential operator.

Received 14-8-53.

REFERENCES

1) Casimir, H. B. G., Rev. mod. Phys. **17** (1945) 343.
2) Onsager, L., Phys. Rev. **37** (1931) 405; **38** (1931) 2265.
3) Prigogine, I., Etude thermodynamique des phénomènes irréversibles, Éditions Desoer, Liège, 1947.
4) de Groot, S. R., Thermodynamics of irreversible processes, North Holland Publishing Company, Amsterdam and Interscience Publishers, New York, 1951.
5) Prigogine, I., Mazur, P. and Defay, R., J. Chim. phys. **50** (1953) 146.
6) Casimir, H. B. G. and Gerritsen, A. N., Physica **8** (1941) 1107.