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Irreversible Thermodynamics of Thermoelectric Effects in Inhomogeneous, Anisotropic Media*

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Beginning with the isotropic form of the thermoelectric equations of Onsager's irreversible thermodynamics as treated by Callen and deGroot, a direct transcription is made to the case of inhomogeneous and anisotropic media. The "emf" of Kelvin, Bridgman, Ehrenfest, and Rutgers is the gradient of the electrochemical potential and a general formula is given for this gradient in anisotropic media. Both the energy density vector and the electrochemical potential gradient are expressed in terms of a "transport entropy matrix" S_{ij}.* The theory leads in a natural and straightforward way to the postulated expression of Ehrenfest and Rutgers. The formulation is in a form easily adaptable to given experimental boundary conditions and, therefore, brings out the limited validity of the Kelvin symmetry relations, as first pointed out clearly by Kohler. Finally, the theory includes the irreversible effects of heat conduction and Joulean heating, as well as the reversible thermoelectric phenomena and is, therefore, more realistic and complete than the theory of Ehrenfest and Rutgers.

INTRODUCTION

THE Onsager theory of irreversible processes has recently been applied by Callen[1] to thermoelectric effects in isotropic media, and a more detailed discussion has been given by deGroot.[2] Ehrenfest and Rutgers[3] have given a brief treatment for anisotropic and inhomogeneous media, based on a postulated formulation which is simply a generalization of the basic equations found by Voigt.[4] Voigt, in turn, had attempted to generalize the theory of Kelvin,[5] but Voigt's theory has been shown to be incapable of predicting the "internal Peltier effect" discovered by Bridgman.[6] More recently other writers, notably Kohler and Meixner,[7] have treated thermoelectric anisotropy from the point of view of quantum kinetic theory. However, there has been no treatment of the problem of thermoelectric anisotropy on the basis of irreversible thermodynamics. Ehrenfest and Rutgers left out of account the irreversible thermal conduction and Joulean heat-generation effects. The treatment given here not only leads in a natural way to the postulated relations of Ehrenfest and Rutgers, but also includes these irreversible conduction and Joulean effects and thereby represents a more realistic and complete theory.

GENERAL EQUATIONS FOR INHOMOGENEOUS ISOTROPIC MEDIA

Let $\mathbf{J}^e$, $\mathbf{J}^s$, $\mathbf{W}$, and $\mathbf{Q}$ be, respectively, the particle current density, the entropy current density, the total energy current density, and the heat current density, and let $\bar{\mu}$ be the electrochemical potential (joules/particle) of an electron of charge $-e$ in the isotropic medium at a point which has absolute temperature T. It is known from the theory of irreversible thermodynamics[1,2] that these quantities are related as follows.

$$\mathbf{J}^e = -L_{ee}\nabla\bar{\mu} - L_{es}\nabla T, \tag{1}$$

$$\mathbf{J}^s = -L_{es}\nabla\bar{\mu} - L_{ss}\nabla T, \tag{2}$$

$$\mathbf{W} = \mathbf{Q} + \bar{\mu}\mathbf{J}^e, \quad \mathbf{Q} = T\mathbf{J}^s, \tag{3}$$

in which the so-called phenomenological coefficients L_{ee}, L_{es}, L_{ss} depend only on the temperature in the case of a homogeneous chemical phase and are related to physically measureable parameters by the expressions

$$L_{ee} = 1/(e^2\rho), \quad (T/L_{ee})(L_{ee}L_{ss} - L_{es}^2) = \kappa, \tag{4}$$
$$L_{es}/L_{ee} = S^* = -eS^{\text{abs}}.$$

Here ρ is the isothermal electrical resistivity, κ is the heat conductivity with no electrical current, and S^{abs} is the absolute thermoelectric power. S^* is the "transport entropy per particle" and plays a prominent role in the theory of irreversible thermodynamics. Throughout this paper we consider the charge carrier to be the electron, charge $-e$.

Substitution of Eqs. (4) into (1), (2), and (3) leads to the three fundamental relations:

$$\mathbf{J}^s = S^*\mathbf{J}^e - (\kappa/T)\nabla T, \tag{5}$$

$$\mathbf{W} = (TS^* + \bar{\mu})\mathbf{J}^e - \kappa\nabla T, \tag{6}$$

$$\nabla\bar{\mu} = -e^2\rho\mathbf{J}^e - S^*\nabla T. \tag{7}$$

Equation (6) states that at a point in an inhomogeneous

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[1] H. B. Callen, Phys. Rev. **73**, 1349 (1948).

[2] S. R. deGroot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, New York, (1951), Chap. 8.

[3] P. Ehrenfest and A. J. Rutgers, Proc. Acad. Sci. Amsterdam **32**, 698, 883 (1929).

[4] W. Voigt, *Kristallphysik* (Teubner, Leipzig, 1928).

[5] W. Thomson, Trans. Roy. Soc. (Edinburgh) **21**, 133 (1857).

[6] P. Bridgman, Proc. Am. Acad. Art. Sci. **61**, 101 (1926); and *Thermodynamics of Electrical Phenomena in Metals* (Macmillan and Company, Inc., New York, 1934), Chap. 6.

[7] M. Kohler, Ann. Physik **40**, 196 (1941); **27**, 201 (1936); W. Meissner, *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, Leipzig, 1935), Vol. 11, pt. 2. E. A. Uehling, Phys. Rev. **39**, 821 (1932); J. Meixner, Ann. Physik **35**, 701 (1939); **40**, 165 (1941).

isotropic medium at which there is electrical (particle) current flow as well as a temperature gradient, the total energy current density (watts per unit area) consists of three terms, *viz.*, an "entropy transport" term $TS^*\mathbf{J}^e$, an electrochemical potential term $\bar{\mu}\mathbf{J}^e$, and a thermal conduction term $-\kappa\nabla T$. Equation (7) may be called the "generalized Ohm's Law." The electrochemical potential $\bar{\mu}$ may be separated[1,2] into a chemical part and an electrical part, $\bar{\mu}=\mu-e\phi$. Thus, in an isothermal region of a chemically homogeneous phase with $\nabla T=0$, Eq. (7) gives the ordinary Ohm's Law, since the gradient $\nabla\mu$ of the chemical potential vanishes in this case. On the other hand, if no current flows, $\mathbf{J}^e=0$, Eq. (7) gives the "thermoelectric electrochemical potential gradient" $\nabla\bar{\mu}=-S^*\nabla T$.

GENERAL EQUATIONS FOR INHOMOGENEOUS ANISOTROPIC MEDIA

In setting up the general equations *we make the assumption that each component of the entropy current density J_i^s is a linear function of the components J_j^e of particle current density and of the components $\nabla_j T$ of the temperature gradient*, with i, $j=1, 2, 3$. The temperature T and the electrochemical potential $\bar{\mu}$ are considered as continuous and differentiable functions of position (x_1, x_2, x_3) within each separate phase. If an electrical current flows across a boundary between two media, there will be cases in which the electrochemical potential cannot be defined *within* the junction. In such cases, however, the finite *jump* in $\bar{\mu}$ across the junction can be defined, and one needs only to use the appropriate boundary conditions for $\bar{\mu}$; otherwise such cases introduce no particular difficulties. The relation (5) is thus replaced by the three equations:[8]

$$J_i^s=S_{ij}^*J_j^e-\frac{\kappa_{ij}}{T}\frac{\partial T}{\partial x_j},\quad (i,j=1,2,3) \tag{8}$$

in which the quantities S_{ij}^* are the "transport entropy matrix" and the κ_{ij} are the "heat conductivity matrix." We emphasize the fact that relations (8) are postulates, reasonable extensions of the isotropic formula (5). It follows from (8), (5), and (3) that the component W_i of the total energy current density can be written

$$W_i=TS_{ij}^*J_j^e+\bar{\mu}J_i^e-\kappa_{ij}\partial T/\partial x_j. \tag{9}$$

Next we require the anisotropic formulation of the relation (7) between electrochemical potential gradient, particle current density and temperature gradient. Equation (7) derives from the same basic relations (1) and (2) as do (5) and (6), and it is therefore clear that the required anisotropic form of (7) must be consistent with (8) and (9). It is seen that the only uncertainty in the direct transcription of (7) into anisotropic form lies in the order of subscripts in the transport entropy matrix S_{ij}^*. The matrices of electrical resistivity ρ_{ij} and of thermal conductivity κ_{ij} are already known to be symmetric.[9] In order to deduce the correct form of the anisotropic transcription of Eq. (7), we make use of the conjugation of the "fluxes" J_i^e and J_i^s and "forces" $\partial\bar{\mu}/\partial x_i$ and $\partial T/\partial x_i$ as expressed by the invariance of the sum:

$$T\zeta(s)=J_i^e(-\partial\bar{\mu}/\partial x_i)+J_i^s(-\partial T/\partial x_i). \tag{10}$$

According to the Onsager theory, the quantity $\zeta(s)$ is the time rate of *internal* entropy production per unit volume caused by irreversible processes, which in the present problem result from Joulean heat generation and heat conduction. Only the steady state need be considered for our purposes, so that the sum (10) is time independent as well as invariant with respect to transformations of the "fluxes" and "forces." If (8) is substituted into (10), one finds

$$\begin{aligned} T\zeta(s)&=-J_i^e\frac{\partial\bar{\mu}}{\partial x_i}-S_{ij}^*J_j^e\frac{\partial T}{\partial x_i}+\frac{\kappa_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i}\\ &=-J_i^e\left(\frac{\partial\bar{\mu}}{\partial x_i}+S_{ji}^*\frac{\partial T}{\partial x_j}\right)+\frac{\kappa_{ij}}{T}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_i}. \end{aligned} \tag{11}$$

The terms in κ_{ij} are the contribution of the irreversible heat conduction to the entropy source strength, and the terms in J_i^e represent the contribution of the irreversible Joule heating. The quantity $\zeta(s)$ is required by the Onsager theory to be positive, though not every individual term in $\zeta(s)$ need be positive. Now the entropy of the material contained within a given volume ΔV is a constant in the steady state, since this entropy is a single-valued function of characteristic parameters of the material in ΔV such as the internal energy ΔU, number of particle ΔN, and the volume ΔV. The internal entropy production $\zeta(s)$ resulting from irreversible processes within ΔV is carried out by the vector J^s at a rate, div J^s, just sufficient (in the steady state) to balance out $\zeta(s)$ so as to maintain a constant entropy within ΔV.

The Joule contribution to $T\zeta(s)$ can also be written

$$\rho_{ij}J_iJ_j=e^2\rho_{ij}J_i^eJ_j^e, \tag{12}$$

where $J_i=-eJ_i^e$ and $\rho_{ij}=\rho_{ji}$ is the resistivity matrix of the crystal at temperature T. If we equate (12) to the Joule contribution in (11), we have

$$\begin{aligned} -J_i^e\left(\frac{\partial\bar{\mu}}{\partial x_i}+S_{ji}^*\frac{\partial T}{\partial x_j}\right)&\equiv e^2\rho_{ij}J_i^eJ_j^e\\ &=-J_i^e(-e^2\rho_{ij}J_j^e), \end{aligned} \tag{13}$$

and since the particle (electrical) current density com-

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[8] The presence of two identical subscripts in a term indicates a summation.

[9] Reference 4, p. 345; reference 2, chap. 4. It has not yet been shown that for arbitrary crystal symmetry the matrix S_{ij}^* is symmetric. On the contrary, the work of Kohler[7] results in quantum-mechanical expressions for a matrix γ_{ij}, related to our S_{ij}^*, which are nonsymmetrical in the general case.

ponents are independently variable, (13) leads to

$$\partial\bar{\mu}/\partial x_i = -e^2\rho_{ij}J_j{}^e - S_{ji}{}^*\partial T/\partial x_j. \tag{14}$$

It is interesting to notice that the Joule heat is *not* correctly given in general by E_iJ_j, with $E_i = -\partial\phi/\partial x_i$. In fact, we can show that this is so even in an isotropic homogeneous phase, as follows. The correct Joule heat expression is, using (12) and (14),

$$\begin{aligned}\rho J\cdot J &= \frac{1}{e}\left(\frac{\partial\bar{\mu}}{\partial x}+S^*\frac{\partial T}{\partial x}\right)\cdot J = \frac{1}{e}\left(\frac{\partial\mu}{\partial x}-e\frac{\partial\phi}{\partial x}+S^*\frac{\partial T}{\partial x}\right)J\\ &= \frac{1}{e}\left(\frac{\partial\mu}{\partial T}+S^*\right)\frac{\partial T}{\partial x}\cdot J+E\cdot J,\end{aligned} \tag{15}$$

where we have written $\partial\mu/\partial x = (\partial\mu/\partial T)(\partial T/\partial x)$ and $E = -\partial\phi/\partial x$ Thus, we have $\rho J^2 = E\cdot J$ only for a phase at uniform temperature, when $\partial T/\partial x = 0$.

VOLUME AND SURFACE HEATING EFFECTS

The vector W_i in (9) gives the total energy current density at any point in the crystalline medium. In the steady state there can be no accumulation of energy within any infinitesimal volume element and the vector W_i must be divergenceless. Thus,

$$\begin{aligned}\frac{\partial W_i}{\partial x_i} \equiv 0 = T\frac{\partial(S_{ij}{}^*J_j{}^e)}{\partial x_i}+S_{ij}{}^*J_j{}^e\frac{\partial T}{\partial x_i}\\ +\bar{\mu}\frac{\partial J_i{}^e}{\partial x_i}+J_i{}^e\frac{\partial\bar{\mu}}{\partial x_i}-\frac{\partial}{\partial x_i}\left(\kappa_{ij}\frac{\partial T}{\partial x_j}\right).\end{aligned} \tag{16}$$

This relation and the following are thus valid for nonhomogeneous crystalline or crystalline-like media.[10] The third group of terms on the right-hand side of (16) vanish, since the particle current is divergenceless. Substitution of (14) into the fourth term on the right-hand side of (16) gives

$$\begin{aligned}J_i{}^e\partial\bar{\mu}/\partial x_i &= -e^2J_i{}^e\rho_{ij}J_j{}^e - J_i{}^eS_{ji}{}^*\partial T/\partial x_j\\ &= -e^2\rho_{ij}J_i{}^eJ_j{}^e - S_{ij}{}^*J_j{}^e\partial T/\partial x_i,\end{aligned} \tag{17}$$

the last term here cancelling the second on the right-hand side of (16). If we solve for the derivative $\partial(\kappa_{ij}\partial T/\partial x_j)/\partial x_i$, we find from (16):

$$\frac{\partial}{\partial x_i}\left(\kappa_{ij}\frac{\partial T}{\partial x_j}\right) = -e^2\rho_{ij}J_i{}^eJ_j{}^e+T\cdot\frac{\partial(S_{ij}{}^*J_j{}^e)}{\partial x_i}, \tag{18}$$

or, set $J_i{}^e = -(1/e)J_i$, where J_i is the electrical current density,

$$\frac{\partial}{\partial x_i}\left(\kappa_{ij}\frac{\partial T}{\partial x_j}\right) = -\rho_{ij}J_iJ_j-\frac{1}{e}T\cdot\frac{\partial(S_{ij}{}^*J_j)}{\partial x_i}. \tag{19}$$

Equation (19) is a general expression for the production of heat in an inhomogeneous, anisotropic medium, crystalline or otherwise.

In general the components $S_{ij}{}^*$ of the transport entropy matrix depend on temperature and on position in an inhomogeneous medium, so that the derivatives of $S_{ij}{}^*$ in (19) must include spatial as well as temperature variations. Thus, since in general $S_{ij}{}^* = S_{ij}{}^*(x_i, T)$, we must write

$$\frac{\partial S_{ij}{}^*}{\partial x_i} = \left(\frac{\partial S_{ij}{}^*}{\partial x_i}\right)_T+\left(\frac{\partial S_{ij}{}^*}{\partial T}\right)_{x_i}\cdot\frac{\partial T}{\partial x_i}, \tag{20}$$

and the last group of terms in (19) breaks down into the three groups:

$$\begin{aligned}-\frac{T}{e}\frac{\partial(S_{ij}{}^*J_j)}{\partial x_i} = -\frac{T}{e}J_j\left(\frac{\partial S_{ij}{}^*}{\partial x_i}\right)_T\\ -\frac{T}{e}J_j\left(\frac{\partial S_{ij}{}^*}{\partial T}\right)_{x_i}\frac{\partial T}{\partial x_i}-\frac{T}{e}S_{ij}{}^*\frac{\partial J_j}{\partial x_i}.\end{aligned} \tag{21}$$

Relation (21) is the starting point of the Ehrenfest-Rutgers theory. We shall use the following notation for the four separate groups of terms in (19) and (21):

$$\begin{array}{lll}\text{Joule:} & Q_J \equiv -\rho_{ij}J_iJ_j, & (22)\\ \text{Peltier:} & Q_P \equiv -\dfrac{1}{e}TJ_j\left(\dfrac{\partial S_{ij}{}^*}{\partial x_i}\right)_T, & (23)\\ \text{Thomson:} & Q_T \equiv -\dfrac{1}{e}TJ_j\left(\dfrac{\partial S_{ij}{}^*}{\partial T}\right)_{x_i}\dfrac{\partial T}{\partial x_i}, & (24)\\ \text{Bridgman:} & Q_B \equiv -\dfrac{1}{e}TS_{ij}{}^*\dfrac{\partial J_j}{\partial x_i}. & (25)\end{array}\left.\vphantom{\begin{array}{l}a\\a\\a\\a\\a\\a\\a\\a\end{array}}\right\}\text{(Volume effects)}$$

Each of the Q's represents a heat *absorbed* per unit volume per unit time. Our sign convention agrees with that of Bridgman, absorbed heat being taken as positive. Ehrenfest and Rutgers use the opposite convention. Equation (22) gives the Joule heat *evolved* and is therefore negative. If the medium is not homogeneous, there is a volume Peltier heating effect Q_P given by (23). Whether the medium is homogeneous or not, there is a Thomson heating effect given by (24). The last terms (25) describe an effect first predicted by Bridgman.[6]

We consider next the phenomena taking place when an electrical current crosses a boundary between two anisotropic media. The generalization to the anisotropic case follows directly from the formula (9) for total energy flow W_i. Consider a composite system consisting of two different anisotropic and inhomogeneous media X and R electrically and thermally jointed along some arbitrary surface AB, as shown in Fig. 1. The reference axes are x_1, x_2, x_3, and the principal crystallographic axes (or other characteristic axes) of each medium X and R may be oriented in any way whatever relative to these reference axes. As in the case of isotropic media,

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[10] An example of the latter kind of medium is a non-uniformly strained body in which the strains give rise to a crystalline-like anisotropy.

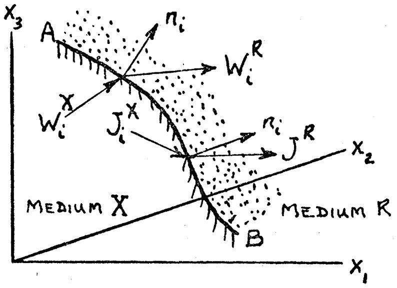

FIG. 1. The curve AB represents a junction between two anisotropic, inhomogeneous media X and R.

the joint or contact AB between X and R will, in general, be a very complex transition region of some finite thickness d. This thickness is, of course, somewhat indefinite, varying from place to place along the boundary and will depend upon the method used for joining the two media. Often the main bulk of the junction may consist primarily of some third material, for example, when two different crystals are cemented together with Wood's metal or with soft solder. In such cases the junction layer of solder may be several thousandths of an inch thick in many places. On the other hand, if the joining is done by electrical fusing of the two single crystals, the transition layer or sheath will probably be a physical mixture of polycrystals of X and R together with some alloy crystals, and so on. In almost all cases in which quantitative measurements are to be made on arbitrarily-oriented single crystals, the boundary AB will be a simple butt joint; in such cases some quantitative estimate can be made of the "contact resistance" or "sheath resistance" R_s, provided the resistance matrices ρ_{ij}^X and ρ_{ij}^R for the two crystals X and R are known. The procedure for determining R_s in the case of two crystals is essentially the same as that for isotropic phases, except for the added complications resulting from the crystalline nature of X and R. However, since these complications can be handled in a straightforward way having little to do with thermoelectricity, we shall not discuss the details.

If we return to formula (9) and the figure, we see that since in the steady state energy and charge cannot accumulate in the boundary region AB, the boundary conditions on total energy current density and electrical current density are

$$J_i^X n_i \equiv J_i^R n_i, \tag{26}$$

$$W_i^X n_i \equiv W_i^R n_i, \tag{27}$$

in which n_i are the three components of the unit normal vector which we agree always to point outward from medium X. The superscripts X and R refer to the medium in which the current flows. If we apply condition (27) to (9) and collect similar terms for the two media, we find

$$\begin{aligned} &e^{-1}T(S_{ij}{}^{*X}J_j{}^X n_i - S_{ij}{}^{*R}J_j{}^R n_i) \\ &\qquad + e^{-1}(\bar{\mu}^X J_i{}^X n_i - \bar{\mu}^R J_i{}^R n_i) \\ &\qquad + [\kappa_{ii}{}^X(\partial T/\partial x_i)^X n_i - \kappa_{ij}{}^R(\partial T/\partial x_j)^R n_i] \equiv 0. \end{aligned} \tag{28}$$

The bracketted groups of terms represent the energy flowing out of the boundary region (per unit area of the sheath) by ordinary heat conduction through media X and R. The middle group of terms give the Joule dissipation in the resistance R_s of the sheath; this can be seen as follows. If we write $J_i = -eJ_i{}^e$ in (14), we have

$$(\partial\bar{\mu}/\partial x_i)n_i = e\rho_{ij}J_j \cdot n_i - S_{ji}{}^*(\partial T/\partial x_j)n_i.$$

Now we assume the resistive sheath to be isotropic, so that $\rho_{ij}=0$ for $i\neq j$, $\rho_{ii}\equiv\rho_s$; and if we further assume that the second term on the right-hand side of this last equation is negligible compared with the first, we find in crossing the boundary

$$\begin{aligned} \Delta\bar{\mu} \equiv \bar{\mu}^R - \bar{\mu}^X = (\partial\bar{\mu}/\partial x_i)n_i d \\ = (\partial\bar{\mu}/\partial s)d \cong e\rho_s(J_i n_i)d, \end{aligned} \tag{29}$$

where s is distance along the normal n and d is the thickness of the resistive sheath. Because of (26), it makes no difference which current components, $J_i{}^X$ or $J_i{}^R$, are used in the last parentheses in (29), and we choose $J_i{}^R$.

$$\begin{aligned} e^{-1}(\bar{\mu}^X J_i{}^X n_i - \bar{\mu}^R J_i{}^R n_i) &= e^{-1}(\bar{\mu}^X - \bar{\mu}^R)J_i{}^R n_i \\ &= e^{-1}(-e\rho_s J_i{}^R n_i d)J_i{}^R n_i = -\rho_s d(J_i{}^R n_i)^2. \end{aligned} \tag{30}$$

We can now rewrite (28):

$$\begin{aligned} &[\kappa_{ij}{}^X(\partial T/\partial x_j)^X n_i - \kappa_{ij}{}^R(\partial T/\partial x_j)^R n_i] - \rho_s d(J_i{}^R n_i)^2 \\ &\qquad + e^{-1}T(S_{ij}{}^{*X}J_j{}^X n_i - S_{ij}{}^{*R}J_j{}^R n_i) = 0. \end{aligned} \tag{31}$$

Expression (31) describes the heat generation and transport at the boundary region between inhomogeneous, anisotropic media X and R and is the surface analog of the "volume" Eq. (19). We name the second and third sets of terms as follows:

$$\left.\begin{aligned} &\text{Joule:} \quad q_J \equiv -\rho_s d(J_i n_i)^2, &(32) \\ &\text{Peltier:} \; q_P \equiv e^{-1}(S_{ij}{}^{*X}J_j{}^X n_i - S_{ij}{}^{*R}J_j{}^R n_i). &(33) \end{aligned}\right\} \text{(Surface effects)}$$

Each of the "q" represents a heat *absorbed* per unit area per unit time.

We next set down the definitions:

$$\Pi_{ij} \equiv +\frac{1}{e}TS_{ij}{}^* \equiv \Pi_{ij}(T;\, x_1, x_2, x_3), \tag{34}$$

$$\tau_{ij} \equiv -e^{-1}T(\partial S_{ij}{}^*/\partial T)_{x_i} \equiv \tau_{ij}(T;\, x_1, x_2, x_3); \tag{35}$$

we call Π_{ij} the *Peltier coefficient matrix* and τ_{ij} the *Thomson coefficient matrix* for a given inhomogeneous, anisotropic medium at temperature T and at point x_1, x_2, x_3 within the medium, when referred to rectangular coordinate axes x_1, x_2, x_3. Relations (22) through (25) for the volume heating effects become, with i, $j=1, 2, 3$,

$$\left.\begin{aligned} &\text{Joule:} \quad Q_J \equiv -\rho_{ij}J_i J_j, &(36) \\ &\text{Peltier:} \quad Q_P \equiv -(\partial\Pi_{ij}/\partial x_i)J_j, &(37) \\ &\text{Thomson:} \; Q_T \equiv \tau_{ij}J_j \partial T/\partial x_i, &(38) \\ &\text{Bridgman:} \; Q_B \equiv -\Pi_{ij}\partial J_j/\partial x_i; &(39) \end{aligned}\right\} \text{(Volume effects)}$$

and (32) and (33) for the surface heating effects become

$$\left.\begin{aligned}&\text{Joule:}\quad q_J\equiv-\rho_s d(J_i n_i)^2, &(40)\\ &\text{Peltier:}\quad q_P\equiv-(\Pi_{ij}{}^R J_j{}^R-\Pi_{ij}{}^X J_j{}^X)n_i. &(41)\end{aligned}\right\}\text{(Surface effects)}$$

DISCUSSION

Starting with the isotropic theory of thermoelectricity we have postulated the fundamental relations (8) and from these have deduced without further assumptions the Ehrenfest-Rutgers equations (21). In addition, the irreversible effects of heat conduction and Joulean heat generation are included in the present theory in a natural way. Using our equations it is an easy matter to set down various boundary conditions appropriate to a given experimental arrangement, and thus one can easily derive the ordinary Kelvin symmetry relations which, as first shown clearly by Kohler,[7] are correct only for isothermal boundary conditions. If one applies adiabatic boundary conditions, he can derive more general relations which have been found by Kohler to give better agreement with experiment.

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Change of Electrical Conductivity of Sodium Chloride upon Bombardment with High-Energy Protons*

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The conductivity of NaCl in the region 125°C to 400°C is considerably decreased by bombardment at room temperature with 10^{15} protons/cm^2 of energy 350 Mev. There are several temperatures where part of the effect anneals. A small decrease in conductivity still remains after heating to as high as 470°C. No satisfactory explanation for the results is evident.

A new method of measuring conductivity is described.

THE generally accepted picture of electrical conductivity of alkali halides is a motion of ions associated with the presence of lattice defects. Since nuclear radiation is known to produce lattice defects, it is of interest to study the conductivity of irradiated crystals and the annealing of the changes at various temperatures.

Single crystals of sodium chloride (obtained from the Harshaw Chemical Company) were bombarded with 350-Mev protons in the Carnegie Institute of Technology synchrocyclotron. Crystals of the order of a millimeter thick and a few square centimeters area were placed inside the cyclotron's vacuum chamber in the direct path of the circulating proton beam. Aluminum foil mounted alongside the crystals was used to measure the amount of irradiation by means of the reaction $\mathrm{Al}^{27}(p,3pn)\mathrm{Na}^{24}$.[1] It is estimated that the temperature of the crystals probably did not get higher than about 50°C during irradiation. Most crystals had been annealed in a helium atmosphere at 650°C after cleaving and before irradiation.

The conductivity measuring apparatus is shown in Fig. 1. This circuit compares the resistance of the crystal with the input resistance of the oscilloscope. This particular arrangement allows one to observe any polarization effects and to eliminate trouble with dc amplifier drift, or the capacitance of the crystals. The conductivity was measured over the temperature range from about 125° to 470°C, the lower limit being determined by the sensitivity of the apparatus, and the upper limit by failure of the electrodes on the crystal. The crystal holder holds two specimens at the same temperature so that a bombarded crystal can be directly compared with a "control" crystal (cut from the same large crystal as the bombarded one) which has not been bombarded. This gives one confidence about the reproducibility of the data. The maximum resistance detectable with the apparatus as shown is 2×10^{11} ohms. Electrodes were either graphite ("Dag") or silver conducting paint (Dupont 4817).

RESULTS

Figure 2 shows typical results, expressed as the ratio of the conductivity of a control crystal to that of an irradiated crystal. The arrows indicate time, the sequence starting from top left. The figure shows that there are several ranges of temperature where healing

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[1] L. Marquez, Phys. Rev. **86**, 405 (1952).