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THERMOELECTRIC PHENOMENA IN CRYSTALS AND GENERAL ELECTRICAL CONCEPTS

By P. W. Bridgman

Abstract

It is shown that when an electric current passes across an interface where the crystal orientation changes there is a Peltier heat, but no corresponding jump of potential. This demands that we analyze the action of an impressed e.m.f. into two aspects. The following definitions are suggested: (1) energy per unit time delivered by the source when current i flows $= i \times$ "working" e.m.f.; (2) $i =$ ("driving" e.m.f. $-\Delta V)/\Delta R$. In ordinary isotropic materials this analysis is not necessary, but it is necessary in unequally heated materials in which thermal currents are flowing. In an unequally heated metal the "driving" e.m.f. between two points at a temperature difference $d\tau$ is $-d\tau \int_0^\tau \sigma d\tau/\tau$, and the "working" e.m.f. between the same two points is $\sigma d\tau$. It is shown that these expressions demand that the current convect with it the energy $\tau \int_0^\tau \sigma d\tau/\tau$, which must be described as thermal energy. We are able in these terms to give a thermodynamically consistent account of the energy transformations in all parts of a thermo-electric circuit. The theoretical significance of a thermal energy which depends on the direction of current flow is emphasized. The argument may be extended from crystals to ordinary isotropic substances. A number of questions peculiar to crystals are discussed. The existence of an internal Peltier heat when the direction of current flow changes is proved, and the importance of this effect for all theories of conduction is emphasized. Some fine structure seems demanded in a metal which is not ordinarily taken into account. Equipartition cannot hold, but the thermal energy of the electrons is of the same order of magnitude as that given by equipartition. Formulas are derived for the internal Peltier heat as a function of the direction of current flow, for the surface heats and for the two latent heats of evaporation of electrons. The possible existence of a Volta difference of potential between different faces of the same crystal is recognized. An argument is drawn from the connection with the photo-electric effect suggesting that this Volta difference may possibly vanish.

IN THIS paper I propose to discuss the bearing of various thermo-electric phenomena in crystals on the problem of understanding thermo-electric action, and the even broader problem of the electrical behavior of metallic conductors in general. These phenomena in crystals bear both on our idea of the underlying mechanism, and on the very concepts in terms of which such electric phenomena are described.

All the conclusions of this paper can be obtained by the use of simple thermodynamics, in conjunction with certain exceedingly simple physical assumptions, and the fundamental experimental fact that the thermo-electric properties of a single crystal are in general different in different directions.

Imagine a thermocouple, in which one branch is a straight rod cut from a single crystal in a definite orientation, and the second branch is some isotropic metal, such for example, as copper, as shown in Fig. 1. When the junctions are brought to different temperatures this couple functions exactly as any ordinary couple. A current flows in the circuit; the source of the energy which drives this current is heat, which flows into the circuit at the two junction points as Peltier heat, and into the parts of the circuit where there is a temperature gradient as Thomson heat. We assume these heats to be reversible, and thermodynamics to be applicable to the system, as in the ordinary analysis. Then if for the sake of definiteness we suppose the crystal rod cut parallel to the axis, we have the relations

$$P_{\|\mathrm{Cu}} = \tau dE_{\|\mathrm{Cu}}/d\tau$$

$$\sigma_{\mathrm{Cu}} - \sigma_{\|} = \tau d^2 E_{\|\mathrm{Cu}}/d\tau^2$$

for the Peltier and the Thomson heats respectively. $E_{\|\mathrm{Cu}}$ is the total e.m.f. of the couple, between a fixed lower and a variable upper temperature, directed from $\|$ to Cu at the hot junction.

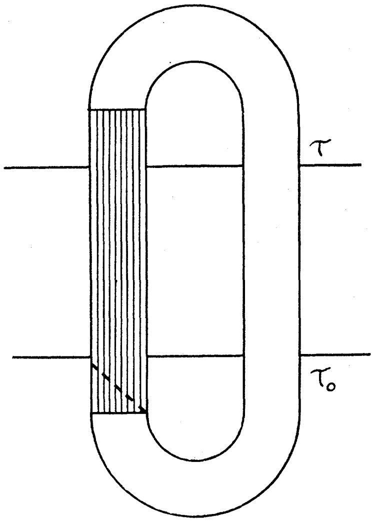

Fig. 1.

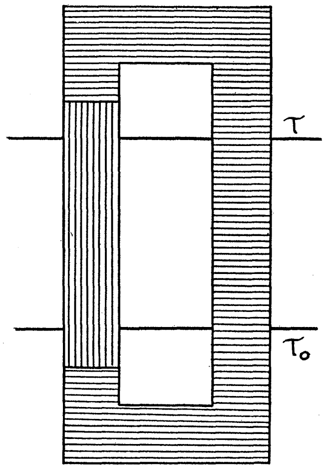

Fig. 2.

We may now construct another similar thermocouple, with the rod cut perpendicular to the axis, and obtain a similar set of formulas. Then by subtracting one set of formulas from the other, and using the relations $P_{\|\mathrm{Cu}} - P_{\perp\mathrm{Cu}} = P_{\|\perp}$ etc., which are valid for ordinary thermocouples, and are also valid here, since they follow immediately from the impossibility of obtaining work from a complete cycle at constant temperature, we have the equations:

$$P_{\|\perp} = \tau dE_{\|\perp}/d\tau \tag{I}$$

$$\sigma_{\perp} - \sigma_{\|} = \tau d^2 E_{\|\perp}/d\tau^2, \tag{II}$$

which apply to a couple, the two branches of which are cut from the same crystal, but have different orientations, as shown in Fig. 2. These formulas are in all respects like the formulas which apply to a couple composed of two different isotropic metals. It is furthermore obvious that similar formulas apply to rods cut from the crystal in any two directions.

There is, then, a Peltier heat when current flows across the surface separating two parts of the same crystal turned so as to have different orientations. As we have drawn it, the surface at which Peltier heat is absorbed is perpendicular to the direction of current flow, but there is no necessity in this restriction, for it is obvious in Fig. 1 that the surface of separation of the crystal from the copper might have been inclined at any angle to the direction of current flow, as shown by the dotted line, with no change in the total heat absorbed, because of the thermodynamic fact that no rearrangements of the parts of the circuit at constant temperature can have any net effect. The Peltier heat at the surface of a crystal depends, therefore, on the direction of flow of the current with respect to the crystal as it crosses the surface, and not on the orientation of the surface itself with respect to the crystal.

What physical account shall we now give of the nature of the action at the surface where this absorption of heat takes place? In the case of the ordinary thermocouple between isotropic metals there is more or less common consent as to the method of picturing the phenomenon. We recognize that there are two entirely different sorts of action at the surface. One of these is connected with the Volta difference of potential. This Volta difference, which as given by experiment is a difference between points outside the metals, may be divided in various ways between three surfaces, two separating the metals from surrounding empty space, and one separating the two metals from each other. There is not yet any agreement as to how this division should be made. But entirely apart from the Volta phenomenon, and of an order of magnitude only one one-hundredth as large, there are the surface effects responsible for the Peltier heat. We think of the surface of separation of the two metals as the seat of an impressed e.m.f., which functions in the two distinctly different ways that all ordinary e.m.f.'s do. The first function of the impressed e.m.f. is to deliver energy to the current as it flows across the junction in amount precisely equal to the Peltier heat. The second function is to tend to produce a motion of electricity, that is, to produce a current, precisely like an ordinary electric force. But now Ohm's law applies in the surface of separation, so that unless there is a finite resistance in an infinitesimal thickness at the surface, the impressed e.m.f. acting in this way would give an infinite current. This can be avoided only by supposing the development of a precisely equal opposing jump of electrostatic potential. But a jump of potential demands, by the ordinary laws of electrostatics, a double layer at the surface. The strength of this double layer must be equivalent to the Peltier heat. The electrostatic potential with which we are concerned here is the ordinary electrostatic potential of elementary macroscopic theory; it is a smooth point function, to be calculated by the law of the inverse first power from the position of distant electric charges. It is also to be noticed that we are restricting ourselves to steady systems.

The impressed e.m.f. which the conventional mode of representation employs to picture the action at a junction where there is a Peltier heat is exactly similar in its properties to the ordinary body forces of electrostatics, differing from such body forces only in the unknown nature of its origin. This impressed e.m.f. delivers energy when a current moves with it in amount equal to the product of current and e.m.f., and of itself tends to produce a current. The expression of Ohm's law in a substance where there is such action is: $i=(\text{e.m.f.}-\Delta V)/\Delta R$, where the e.m.f. of the equation is the total e.m.f. acting between two points whose difference of electrostatic potential is ΔV, and ΔR is the resistance between the same two points. This view of the nature of an impressed e.m.f. will be found explicitly stated, for example, in Abraham's treatment of the field equations.

Although this picture of an impressed e.m.f. functioning in these two ways (delivering energy and entering Ohm's law) is the usual one, it is by no means necessary, and in fact cases are already known in which this account of the nature of the action on a current in not broad enough to correspond to the physical phenomena. In particular, in an electron gas, in which there is an ordinary gas pressure, the conventional account of the situation fails. I have already discussed this matter at some length,[1] and from the fact that the ordinary account is demonstrably inadequate in an electron gas have drawn the conclusion that in general in a metal we must keep distinct these two possible aspects of the action on electricity. I insisted, in particular, that at a junction we could not equate Peltier heat, impressed e.m.f., and potential jump. I gave formulas in which these three things were explicitly recognized as different, but at the time was not able to go further in definitely splitting the action into its different aspects. One of the chief points of this paper is that phenomena in crystals give us a method of taking the next step, and of definitely specifying the relation between these different aspects of the action.

We are able to effect this analysis because we are able to show that in a crystal there can be no jump of potential at a surface where the orientation changes. Fig. 3 represents two pieces of the same crystal, differently oriented with the circuit completed by an isotropic metal. The system is at constant temperature, with no current flowing, and is therefore in equilbrium. Now describe the path indicated from A to B. There can be no changes of potential inside the homogenous metal, either crystal or isotropic, so that the only possibilities of a variation of potential in the path are at the two surfaces of discontinuity, at C and D. But these two surfaces of discontinuity are identical, so that if we make the simple and almost unavoidable assumption that any jump of potential at a surface of discontinuity is determined merely by local conditions at the surface, we see that any change of potential encountered at the surface C is wiped out at the surface D, which is traversed in the opposite direction, and therefore there can be no difference of potential A and B. The same conclusion is forced from an examination of the compound crystal shown in Fig. 4. If there can be no potential change inside the body of homogeneous metal and if the potential jump at a surface depends

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[1] P. W. Bridgman, Phys. Rev. **14,** 306–347 (1919).

only on the relative orientation of the abutting parts, then the potential at B exceeds that at A by the same amount that the potential at C exceeds that at D, and if the potential at B is equal to that at D, and that at A is equal to that at C the potential throughout the entire interior of the compound system must be the same, and there can be no jump at an interface.

We appear driven, therefore, to the conclusion that at a surface of discontinuity of orientation there can be no jump of potential, and therefore no double layer. *The impressed action at an interface is such as to deliver energy to the current, but it does not enter Ohm's law, and it does not tend to produce a current.*

Can we now extend these conclusions to the other parts of the circuit, and say that the action which we usually describe in terms of a Thomson e.m.f. involves only a transfer of energy to the current equal in amount to the Thomson heat, but that this action involves no tendency toward the production of current? It is evident that we cannot make this extension, because a current flows in the complete thermo-electric circuit, so that somewhere in the circuit there must be something tending to set the current in motion. Furthermore, the net effect around the circuit, or the line integral of the tendency, must be the same as that given by the conventional analysis, because the conventional analysis gives the correct total flow. But is this possible; is it possible to locate in the *body* of the metal a driving e.m.f. such as to satisfy the integral condition?

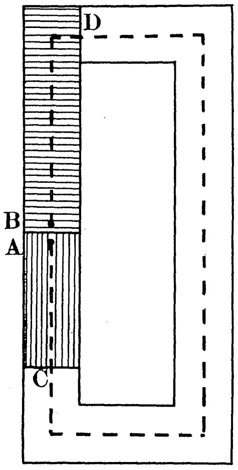

Fig. 3.

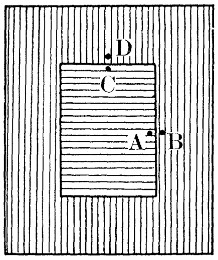

Fig. 4.

Before we carry this discussion further it will be convenient to invent a notation that explicitly recognizes the two aspects of impressed action. In lack of anything better, I shall speak of an impressed "working" e.m.f., $(\text{e.m.f.})_w$, and an impressed driving e.m.f., $(\text{e.m.f.})_d$. These two quantities are defined through the equations:

1. Energy* per unit time delivered by the source when current i flows $=$ $i \times (\text{e.m.f.})_w$

2. $$i=[(\text{e.m.f.})_d-\Delta V]/\Delta R \qquad \text{(Ohm's law)},$$

where ΔR is the resistance between two points whose difference of potential is ΔV.

We are now required so to locate a driving e.m.f. in the body of the metal that there is the proper net effect in the complete thermo-electric circuit. This may be accomplished by integrating the equations connecting the Thomson heat with the second derivative of the total e.m.f. We have

$$\frac{d^2E_{\|\perp}}{d\tau^2}=\frac{\sigma_\perp}{\tau}-\frac{\sigma_\|}{\tau}\,.$$

Integrating once,

$$\frac{dE_{\|\perp}}{d\tau}=\int_{\tau_0}^{\tau}\frac{\sigma_\perp}{\tau}d\tau-\int_{\tau_0}^{\tau}\frac{\sigma_\|}{\tau}d\tau+\text{const.}$$

In virtue of the condition on the Peltier heat

$$\text{const.}=(dE_{\|\perp}/d\tau)_{\tau=\tau_0}=(P_{\|\perp}/\tau)_{\tau=\tau_0}$$

Now if we put $\tau_0=0°$ Abs, $(P_{\|\perp}/\tau)_{\tau=0}=0$, in virtue of the third law, which states that there can be no entropy changes at 0° Abs. This gives

$$dE_{\|\perp}/d\tau=\int_0^\tau \sigma_\perp d\tau/\tau-\int_0^\tau \sigma_\| d\tau/\tau, \qquad \text{(III)}$$

and integrating again

$$E_{\|\perp}=\int_0^\tau d\tau\int_0^\tau \sigma_\perp d\tau/\tau-\int_0^\tau d\tau\int_0^\tau \sigma_\| d\tau/\tau. \qquad \text{(IV)}$$

The constant of integration is here zero, because the total e.m.f. of a couple whose two junctions are at 0° Abs is zero. Now the form of the expression just obtained for E shows at once that the total e.m.f. may be obtained by assigning to each element of length reaching from τ to $\tau+d\tau$ a driving e.m.f. of amount $-d\tau\int_0^\tau \sigma d\tau/\tau$, driving the current in the direction of increasing temperature.

The working e.m.f. at various parts of the circuit is given by the conventional description, since this accounts consistently for the energy absorbed as heat by the system in the local parts of the circuit.

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* In the following we do not speak of a current or an electron as having potential energy of position in the electric field, but when the mutual potential energy of the electron and the field changes we speak of a transfer of energy to the field by means of the Poynting vector. The electron or the current is from this point of view entirely neutral, constituting merely an intermediate link in a chain by which energy is transferred from some other agency to the field or vice versa. One can, if preferred, speak of the electron itself as having the potential energy, instead of the field; in this case the energy flow on the Poynting vector plays no part. These two points of view are really the same, and lead to the same formulas.

We now recapitulate the results found thus far. At a surface of discontinuity in the orientation there is an absorption of energy equal to the Peltier heat, and therefore by definition an equal working e.m.f., but there is no potential jump, no double layer, and no impressed driving e.m.f. In the body of the metal where there is a temperature gradient, there is an absorption of energy when current flows up the temperature gradient from τ to $\tau+d\tau$ of $\sigma d\tau$, that is, a working e.m.f. of $\sigma d\tau$, and there is furthermore between the same two points an impressed driving e.m.f. of $-d\tau\int_0^\tau \sigma d\tau/\tau$.

That we have been forced to recognize two different kinds of e.m.f. should not be disturbing, and in fact is to be expected as soon as we appreciate that the electronic structure of an electric current makes it in many respects like a current of an ordinary fluid. Consider, for example, an ordinary hot water circulating system. The source of the mechanical work used in overcoming the friction of the water against the pipes is thermal, but the current is *driven* by gravity, which can do no net work. The physical essence of our point of view is the recognition that there are other ways of imparting energy to electricity than by the action of a body force. This recognition is inevitable as soon as we discover the possibility of an electron gas which exerts a gas pressure and is the seat of thermal energy. That we have now been driven to recognize the existence of a similar situation inside a solid metal must be most significant for theories of metallic conduction.

Continuing with the argument, it is to be noted that the two e.m.f.'s which we have found in the body of the metal are, paradoxically, of opposite signs. It is evident, therefore, that this distribution of e.m.f.'s must involve a rather different description of the energy transformations in the circuit than the conventional one.

Before attempting a description of the energy transformations according to our new point of view, it will be well to have before us the conventional description of the situation. This description is suggested by Lord Kelvin's figurative ascription of a specific heat to the electric current. If we suppose that the current carries with it energy of amount $\sigma\tau$, or more generally $\int_0^\tau \sigma d\tau$, then we obviously have given a possible description of the absorption of Thomson heat. It is perhaps not generally recognized, however, that this method of associating thermal energy with the current is not consistent with the conventional views of the impressed e.m.f. We can see this in the following way. In an isotropic (non-crystalline) medium, in which a current is flowing, and in which there is a temperature gradient, consider the conditions of energy balance within any small closed surface. We can write the conditions of energy balance in two ways. First there is the geometrical condition on the closed surface, that no net energy cross the surface. Secondly, by regarding the current of electricity like a current of ordinary fluid, we have the condition that the energy carried by the current out of the region is equal to what it carries into the region, plus that acquired within. Suppose now that unit current convects with it the energy U. The first condition of energy balance, on the region, is

$$\operatorname{div}(iU)+\operatorname{div}(-k \operatorname{grad} \tau)+i\cdot\operatorname{grad} V=0 \qquad \text{(V)}$$

where the first term represents the net energy flowing out of the region carried by the current, the second term the energy flowing out as heat by conduction, and the third term the electromagnetic energy flowing out of the region on the Poynting vector. The second condition of energy balance, on the current, is

$$\operatorname{div}(iU) = i\cdot\sigma \operatorname{grad}\tau - i\cdot\operatorname{grad}V - i^2\rho, \qquad \text{(VI)}$$

where the first term on the right hand side is the reversible heat absorbed by the current as Thomson heat, the second term is the energy given by the current to the field by means of the Poynting vector, and the third term is the Joulean heat imparted by the current to the matter occupying the region. If now the impressed action enters Ohm's law in the conventional way, we have also

$$i = (\sigma \operatorname{grad}\tau - \operatorname{grad}V)/\rho$$

Multiply this equation by $i\rho$, and substitute back in VI, obtaining $\operatorname{div}(iU) = 0$. But since $\operatorname{div} i = 0$, we must have $U = \text{Const}$, which is not the conventional expression of Kelvin for the convected energy.

The conventional points of view therefore contain an inconsistency. It is to be noticed that this inconsistency does not react on the equations by which σ is determined experimentally, for on eliminating $\operatorname{div}(iU)$ between V and VI we get

$$i\cdot\sigma \operatorname{grad}\tau = i^2\rho + \operatorname{div}(k \operatorname{grad}\tau),$$

which is the usual equation by which σ is determined from the distribution of temperature in an unequally heated bar carrying a current. (See, for example, Borelius.[2])

To what account of the energy transformations are we now driven by accepting the expression $-d\tau\int_0^\tau \sigma d\tau/\tau$ for the driving e.m.f. in a crystal? We write down an equation analagous to Equation (VI), but in order to avoid complications from a resistance which is a function of direction, we apply the condition to an element of length of a long slender linear conductor cut from a crystal in a definite direction. Taking the x axis along the length gives

$$\frac{\partial}{\partial x}(iU) = i\sigma\frac{\partial\tau}{\partial x} - i\frac{dV}{\partial x} - i^2\rho,$$

Ohm's law becomes

$$i\rho = -\frac{\partial\tau}{\partial x}\int_0^\tau \frac{\sigma}{\tau}d\tau - \frac{\partial V}{\partial x}\cdot$$

Substituting back,

$$\frac{\partial}{\partial x}(iU) = i\frac{\partial U}{\partial x} = i\sigma\frac{\partial\tau}{\partial x} + i\frac{\partial\tau}{\partial x}\int_0^\tau \frac{\sigma}{\tau}d\tau = i\frac{\partial}{\partial x}\left[\tau\int_0^\tau \frac{\sigma}{\tau}d\tau\right].$$

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[2] G. Borelius, Ann. d. Physik **56,** 388 (1918).

Integration of this equation gives, except for a constant which has no physical significance, $U=\tau\int_0^\tau \sigma d\tau/\tau$. *The condition of energy balance demands, therefore, that the current convect with it the energy* $U=\tau\int_0^\tau \sigma d\tau/\tau$. Since σ is a function of direction, the energy convected is also a function of direction.

What account does our new expression for convected energy give of the phenomena at surfaces of discontinuity? Assume for the sake of definiteness that the current flows from $\|$ to $\perp$. Then on crossing the surface there must be an absorption of energy equal to the difference of convected energy on the two sides of the surface, or

$$\tau\left[\int_0^\tau \sigma_\perp d\tau/\tau - \int_0^\tau \sigma_\| d\tau/\tau\right].$$

But this is exactly equal to $P_{\|\perp}$, as we see at once from equations I and III, and is as it should be if our picture is consistent.

What shall we suppose is the nature of the convected energy? It is not difficult to see that we must formally describe the convected energy as *thermal* energy. This means that at the junction the current absorbs thermal energy from its surroundings, and convects this away with it, still in thermal form, like water in a heating system. This is demanded by the account we have given of the driving and the working e.m.f.'s at the surface. For if there is no potential jump, there is no Poynting flow, and hence no conversion of thermal to electro-magnetic energy, and if there is no driving e.m.f. there can be nothing corresponding to a non-electrical difference of potential on the two sides of the surface, such as has been sometimes assumed in postulating a non-electrical potential energy of position of the electron inside the metal. Furthermore, we are enabled to give a correct description of the energy transformations in the unequally heated parts of the circuit by describing the convected energy as thermal. The requirement is that the fraction $d\tau/\tau$ (equal to $\partial\tau/\tau\partial x$ for unit length) of the thermal energy entering the region at the higher temperature be converted into non-thermal energy. The energy converted in unit length is the energy which flows out on the Poynting vector ($i\partial V/\partial x$) plus the Joulean heat. Ohm's law already written, gives for the sum of these $i^2\rho+i\partial V/\partial x=-i(\partial\tau/\partial x)\int_0^\tau \sigma d\tau/\tau$. Now this is exactly equal to $(\partial\tau/\tau\partial x)$ $(-i\tau\int_0^\tau \sigma d\tau/\tau$, where the term in brackets is, to first order terms, equal to the energy convected into the region as heat by the current at the higher temperature, so that the thermodynamic requirement is completely met.

We have thus arrived at a consistent and definite method of describing the phenomena in a thermocouple consisting of two rods of the same crystal differently oriented, in which we have assigned definite and unequal values to working and driving e.m.f. at every point of the circuit, and have also found a unique value for the energy convected with the current, which we have had to describe as thermal energy. Can we not now give up the restriction that the results apply only to different orientations of the same crystal, and apply exactly similar expressions to couples composed of any two isotropic metals? It is at once evident that all the formulas do apply, if we are satisfied merely with a possible solution. We might question, however, whether there might not be other solutions in this case, because our entire argument rested on the fundamental fact that there can be no jump of potential across a crystal interface, and there is apparently no corresponding relation at an interface between different isotropic metals. A little consideration shows, however, that we can make the desired transition from crystalline to isotropic metals by way of the expression for the convected energy. For in an isotropic metal, that is, a metal crystallizing in the cubic system, we must still have for the convected energy $\tau\int_0^\tau \sigma d\tau/\tau$, and must still describe this energy as thermal, as we can see by starting with a non-cubic lattice, in which these results always hold, and continually deforming the lattice until it becomes cubic. It follows that at an interface between two isotropic metals all the Peltier heat goes to increasing the thermal energy of the current, and that there can be no Poynting flow, and therefore no potential jump, nor any change of non-electrical potential energy of position. It follows that all our arguments and our explicit formulas for crystals at once apply to any isotropic metal.

It is significant that we have been driven to ascribe a *thermal* energy to the current. This would seem to prove that a theory of metallic conduction such as Wien's, which does not allow the motion of the electrons which constitute the current to be affected by temperature, cannot be correct. Recognizing, however, that the energy of the current must be thermal in character, we are confronted with the problem of understanding how this energy may be negative in some metals, as experiment shows it to be. A possible explanation is that the electrons, when moving in such a way as to constitute the current, may have greater or less energy of haphazard agitation than when they are not so moving, and that what we have called the thermal energy of the current is merely the difference of these two energies. In any case it no longer seems possible to suppose that the electrons have equipartition energy, although doubtless their energy may be of the same order of magnitude as that demanded by equipartition. This question will be referred to again in connection with the internal Peltier heat.

It is to be carefully noted that our energy considerations give no hold whatever on any Volta jump at the surface of discontinuity, for all the energy transformations involved in the Volta jumps are entirely electromagnetic in character, and thermodynamics has nothing to say about them. In the case of crystals, the first argument used above does apply, however, and there can be neither Volta nor Peltier jump at a surface of discontinuity in the crystal orientation.

We now turn from these more general matters to consideration of several questions peculiar to crystals. First we must emphasize a most important crystalline phenomenon, which I have already mentioned in previous papers. Consider the two thermocouples shown in Fig. 5 composed of crystal and isotropic metal. The total e.m.f. of these two couples is the same, because the only difference between the two systems is in the regions at constant temperature. Hence the total heat absorbed when unit quantity flows around the circuit is the same in the two cases. Since the parts of the systems at temperature τ_0 are identical in the two cases, the heats absorbed in this part of the systems are the same. Hence the heat absorbed in the parts at τ must also be the same. Now in Fig. 5a, heat is absorbed at temperature τ only at the surface A. In Fig. 5b, heat is absorbed at A', but since the direction of current flow on leaving the surface A' is different from that at the surface A, this heat is not equal to that absorbed at A. Hence there must be some compensating absorption of heat somewhere else at temperature τ in Fig. 5b, and by the principle of sufficient reason, this can only be at the corner B where the direction of current flow changes. This I have called the internal Peltier heat. It is a heat per unit quantity of electricity, or per electron, and is therefore independent of the velocity with which the electron moves. The mere existence of this heat is a most significant thing. We have here an absorption of energy without change of position, and therefore without change of electrical potential, but merely a change of direction of motion. Since there is absorption of energy at the corner, we must recognize the existence of an impressed working e.m.f., but since there is no change of potential, there can be no impressed driving e.m.f., thus again showing the necessity of splitting our ordinary concept of impressed e.m.f. into these two aspects.

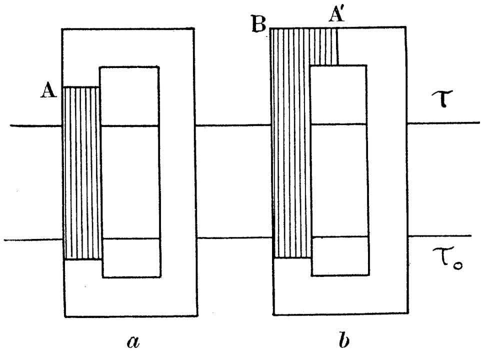

Fig. 5.

This fact, that there is no impressed driving e.m.f. at a bend in a crystal, I have verified by direct experiment, although protesting all the while that it was almost an insult to one's intelligence to make such an experiment. I made potentiometer measurements of the drop of potential between two points at opposite sides of a bend in a single crystal of bismuth (the crystal was cast with the bend in it), and verified that the potential drop is proportional to the current in the range of small currents and potential drops accessible to a high sensitivity galvanometer.

The physical explanation of the internal Peltier heat seems to demand the existence of some fine structure of which other phenomena give us little or no suggestion. There is no reason to think that this fine structure is confined to non-cubic crystals which have thermo-electric differences in different directions, but we must recognize its existence in cubic crystals as well, that is, in all ordinary metals. In ordinary cubic metals this fine structure has the same properties in all directions, and therefore does not force itself on our attention when the direction of current flow changes. It seems to me that the recognition of this structure or mechanism must revolutionize our attempts at a theory of metallic conduction. It was my former opinion that theories of conduction need have little or no regard for thermo-electric phenomena, since there seemed no simple connection between the two classes of phenomena, but the discovery of the internal Peltier heat entirely alters the situation, and demands that the two phenomena be treated inseparably in any theory.

By the same argument as that used in the first part of this paper, we must recognize that the energy absorbed by the current as internal Peltier heat when the direction of flow changes must still be classified as thermal energy after it has been absorbed by the current. This much restricts any mechanistic explanation that we can offer of the phenomenon. For instance, we cannot say that when the electron turns the corner it moves against an equivalent microscopic potential difference.

There is a possibility of explanation in terms of the same "grooves" that I have imagined in connection with other phenomena. There are a number of indications that the electron in a solid metal can move only along certain grooves; in this case the existence of an internal Peltier heat would demand that the thermal energy of an electron in a groove would depend on the direction of the groove. This evidently means that we must give up equipartition, at least in detail. This remark applies to my own theory of metallic conduction, as well as to others. From the fact that the internal Peltier heat in bismuth is of the same order of magnitude as the total energy of a degree of freedom, we may infer that in spite of the failure of equipartition, the thermal energy of the electrons is of the same order of magnitude as that demanded by equipartition. The effect may well be some sort of quantum effect, and depend on the fact that the characteristic frequency of the electrons in the different grooves is different. A physical basis for this variation of frequency with direction is evidently afforded by the different lattice spacings in different directions.

It is obvious that there is a simple connection between the internal Peltier heat when the direction of current flow changes from the angle α_1 with the axis to the angle α_2, and the difference of ordinary Peltier heat when the current emerges from the crystal in different directions. If we denote internal Peltier heat by Π, then obviously

$$\Pi_{\alpha_1\alpha_2}=P_{\alpha_1 x}-P_{\alpha_2 x}=P_{\alpha_1\alpha_2},$$

where the subscript x denotes any isotropic metal into which the current flows at the interface.

We are now in a position to consider certain other effects in crystals. We must first recognize the possibility of a Volta difference of potential between faces of different orientations. We have already seen that the jumps of potential which are involved in this Volta difference are situated entirely in the free faces of the crystal; there can be no jump at the interface in the metal. Of course in the case of ordinary metals there has long been difference of opinion as to the way in which the Volta difference should be divided between the two free surfaces and the interface. It is most interesting that we can here give definite proof that there can be no jump at the interface. It is tempting to extend this result to all metals, and to say that there can never be any Volta jump at an interface between two metals, but I can see no way of passing from the one case to the other. We may, however, draw the conclusion that the jump of potential at an interface between an isotropic metal and a crystal is independent of the orientation of the face of the crystal.

There is no experimental evidence of which I know bearing on the question of a crystalline Volta effect. It would not be easy to find it by experiments in vacuum, because of the extreme sensitiveness of the effect to slight variations in the surface conditions. There is one consideration which gives a certain plausibility to the expectation that the crystalline Volta effect may be zero. We have the photo-electric equation $\epsilon V_{AB}=h(\nu_{0A}-\nu_{0B})$ for the two metals A and B. This formula applies equally well to two different faces of the same crystal. Now it is not unreasonable to expect that the characteristic frequency ν_0 will be found to be independent of the orientation of the face, for the reason that it is known that in isotropic metals ν_0 is independent of the direction of polarization of the incident light. But until direct experimental proof is given, we must recognize the possible existence of this Volta effect. This effect means an intense field of force at the corners of a crystal. At temperatures high enough for the electron emission to be appreciable this means a different density of the electron atmosphere in equilibrium with the metal at different faces. This would lead us to expect also a different latent heat of evaporation at different faces. This difference of latent heats may, in fact, exist, whether or not there is a Volta difference.

The analysis of my former paper on the Volta and allied effects applies at once to many of the effects in crystals. In particular, I showed in that paper that there is a surface heat involved in charging a surface. In the crystal this surface heat is a function not only of the orientation of the surface, but also of the direction of motion of the charge in the crystal as it is brought up to the face. We must accordingly use a double subscript notation for this surface heat, one subscript to denote the orientation of the surface which receives the charge, and a second subscript to denote the direction of motion of the charge in the crystal. Thus $(P_s)_{\gamma\delta}$ means the heat absorbed when unit charge is added to a surface inclined at the angle δ with the principal axis of the crystal by being brought up to the surface along a direction inclined at the angle γ to the axis. It can now be shown at once, by carrying a charge around the two paths indicated in Fig. 6, that

$$(P_s)_{\alpha\gamma}-(P_s)_{\beta\gamma}=P_{\alpha\beta},$$

where $P_{\alpha\beta}$ is the ordinary Peltier heat at a crystalline interface, and is also, as we have shown, the internal Peltier heat when the direction of current flow inside the crystal changes from α to β.

We must now recognize that the latent heat of evaporation also depends on the orientation of the surface, and the direction in which the charge is brought up to the surface. Carry unit charge around the circuit shown in Fig. 7. The total heat absorbed in this circuit is zero, because it is described under equilibrium conditions at constant temperature. If the circuit is varied in any way that we please inside the region shown by the dotted circle, there is no change in the total heat, and therefore the heat absorbed in the dotted region is constant. First, carry charge across the surface at the angle β, and secondly, change the direction of motion, and carry across the surface at the angle α. On equating the heat absorbed in the two cases we obtain

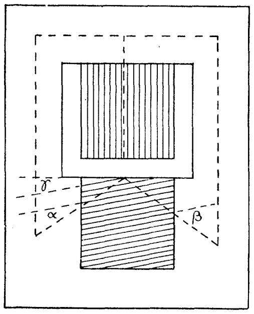

Fig. 6.

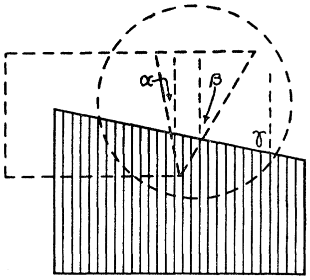

Fig. 7.

$$(\eta_p)_{\beta\gamma} - (\eta_p)_{\alpha\gamma} = P_{\beta\alpha},$$

where η_p denotes the latent heat at *constant* surface charge. It is this heat which is usually given directly by experiment, charge being brought up to the surface as fast as it evaporates.

We have now to distinguish another latent heat, when the electrons are allowed to evaporate from the insulated metal, leaving behind a charge on the surface. It is this latent heat which is given by the usual thermodynamic analysis, and which enters Clapeyron's equation. This latent heat I have called η, without the subscript. There is a connection between the two latent heats and the surface heat, namely $P_s + \eta = \eta_p$. Now apply this to the face of the crystal, the surface being inclined at the angle γ, and the charge being carried through the surface, first at the angle α, and then at the angle β.

$$(P_s)_{\alpha\gamma} + \eta_{\alpha\gamma} = (\eta_p)_{\alpha\gamma}$$
$$(P_s)_{\beta\gamma} + \eta_{\beta\gamma} = (\eta_p)_{\beta\gamma}.$$

Subtracting these two equations, and using the relations found above for η_p and P_s, we obtain

$$\eta_{\alpha\gamma} = \eta_{\beta\gamma},$$

or the latent heat of evaporation at variable charge is independent of the direction in which the charge is brought to the surface within the metal.

This is as it should be, because the thermodynamic analysis employed in deducing Clapeyron's equation is concerned only with the initial and final states, and not with the details of the process.

There are many other interesting questions connected with the thermoelectric behavior of crystals, which cannot, however, be discussed here. One of the most important of these concerns the nature of the symmetry of the Peltier heat. This I regard as a question for experiment to decide. Experimental examination of this question has been made both by Linder and myself. The last paper of Linder[3] takes issue with some of my conclusions, and seems to call for some comment from me. I can only say that at present I am satisfied with neither the measurements of Linder or myself, and that I am undertaking a fresh experimental examination of the question, which will, I hope, lead to more satisfactory conclusions.

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[3] E. G. Linder, Phys. Rev. **29**, 554 (1927).