

graphs  $\tau_a$ ,  $\tau_p$ ,  $\Delta\tau = \tau_p - \tau_a$ ,  $dh$ ,  $\Delta h$  and  $\Delta m$  being constructed as heretofore,  $dh$  and  $\Delta h$  referring to pressure on the air side. In the computations  $\Delta\tau$  and  $dh$  were reduced to zero at the beginning (0 minutes). One notes that the pronounced minimum in the temperature  $\tau_p$  of the phosphorus chamber coincides nearly with the minimum pressure ( $dh$ ) of the air chamber; i.e., with the maximum pressure on the phosphorus side, so that the emanation is produced with a *loss of heat*. This also is marked in the graph for  $\Delta\tau$  drawn in a larger scale and the two occurrences must therefore be correlative. After the lapse of 4 minutes, however, there is a collapse of the emanation, whereupon the temperature in the phosphorus side rises precipitately while the pressure rapidly falls owing to the gas absorption. After 12 minutes the temperature changes subside as do also the pressures, but more gradually. The corrected graph  $\Delta h$  which with its sign changed shows the actual loss of pressure due to the absorption of oxygen and the graph  $\Delta m$  which gives the mass of gas absorbed accentuate the same results. In different runs the final pressures,  $\Delta h$ , after 30 min. and the total amounts of gas absorbed,  $\Delta m$ , naturally differ somewhat, depending on how far the violent reactions at the beginning have been included,  $\Delta h$  from 0.7 to 0.9 cm. of Hg and  $\Delta m$  from 0.006 to 0.008 gram being fair averages. The possibility of measuring such relatively large pressures conveniently with the interferometer comes from the fact that  $\Delta h$  is from 20 to 40 times larger than  $dh$ .

\* Cf. Kay and Laby's Tables, p. 65.

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## RESISTANCE AND THERMO-ELECTRIC PHENOMENA IN METAL CRYSTALS

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In a recent number of the *Physical Review* I discussed the significance of some of the more important qualitative features of the thermo-electric behavior of metal crystals, but had to leave unsettled the precise nature of some of the experimental facts until the completion of an experimental investigation then in progress. This investigation has now been completed, and the results are being published in full detail in *Proc. Amer. Acad.*; a brief summary of these results is the purpose of this note. In the extended paper will also be found a rediscussion of a couple of rather important theoretical matters, with regard to which I had previously reached erroneous conclusions because of my failure to take due account

of the transverse thermal effect in crystals, a phenomenon at that time not known to me. A brief summary of these new conclusions is also given here.

An improved method of making single metal crystals has been developed by which it is possible to cast from the same melt a number of single crystal rods of a wide range of orientation. An apparatus has been constructed by which the thermal e.m.f. of 16 such rods may be measured simultaneously, so that the only variable factor in the results is the crystal orientation. The thermal e.m.f. between 20° and 88°C. of single crystal Zn, Cd, Sb, Sn and Bi against Cu has been measured, and from the results the thermal e.m.f., Peltier heat, and difference of Thomson heat between rods of the same metal in different orientations is calculated. The following results are found for thermal e.m.f.

$$\text{Zn: } (\text{t.e.m.f.})_{\parallel-\perp} = 1.800 \times 10^{-6} \times (\tau - 293.1) + 4.27 \times 10^{-9} \times (\tau - 293.1)^2$$

$$\text{Cd: } (\text{t.e.m.f.})_{\parallel-\perp} = 2.973 \times 10^{-6} \times (\tau - 293.1) + 10.82 \times 10^{-9} \times (\tau - 293.1)^2$$

$$\text{Sb: } (\text{t.e.m.f.})_{\parallel-\perp} = 26.7 \times 10^{-6} \times (\tau - 293.1) + 11.1 \times 10^{-9} \times (\tau - 293.1)^2$$

$$\text{Sn: } (\text{t.e.m.f.})_{\parallel-45^\circ} = -0.259 \times 10^{-6} \times (\tau - 293.1) + 0.85 \times 10^{-9} \times (\tau - 293.1)^2$$

$$(\text{t.e.m.f.})_{\parallel-\perp} = -0.657 \times 10^{-6} \times (\tau - 293.1) + 1.82 \times 10^{-9} \times (\tau - 293.1)^2$$

$$\text{Bi: } (\text{t.e.m.f.})_{\parallel-45^\circ} = 21.6 \times 10^{-6} \times (\tau - 293.1) - 38.1 \times 10^{-9} \times (\tau - 293.1)^2$$

$$(\text{t.e.m.f.})_{\parallel-\perp} = 51.2 \times 10^{-6} \times (\tau - 293.1) - 75.3 \times 10^{-9} \times (\tau - 293.1)^2$$

These formulas give the e.m.f. in volts in a thermocouple of two rods of the indicated orientations, one junction of which is maintained at 20°C. and the other junction of which is at the absolute temperature  $\tau$ . A positive sign for  $(\text{t.e.m.f.})_{\parallel-\perp}$  indicates that the positive current flows from the direction parallel to the crystal axis to the direction perpendicular to the axis at the hot junction.

It is emphasized that in the case of Sb and Bi the heat absorbed by an electron when its direction of motion changes from perpendicular to the axis to parallel to the axis is very large, being, respectively, 0.2 and 0.4 of the energy of a gas molecule at the same temperature. This is a difficult point for any theory like the recent one of Sommerfeld, in which that part of the energy of a conduction electron which varies with temperature is supposed small compared with the classical amount.

The Kelvin-Voigt law that thermal e.m.f. is a linear function of  $\cos^2\theta$ ,  $\theta$  being the angle between crystal axis and the length of the rod, is verified

for Zn, Cd and Sb, but there are deviations for Sn and Bi which seem distinctly greater than possible experimental error. It was this that made it necessary to give separate formulas above for the  $45^\circ$  and perpendicular directions of these two metals. It would appear in general, therefore, that the Kelvin-Voigt symmetry law for thermal e.m.f. is only an approximation. This is perhaps the most important result of the new experimental work. I had previously come to the same conclusion, but Linder<sup>2</sup> had questioned whether this conclusion was justified by the experimental accuracy, and thought that his own data indicated the opposite conclusion over my temperature range, although over a wider range he also found departures. I felt that both the work of Linder and myself was capable of considerable improvement experimentally, whence this new investigation. The new results bear out the conclusion of Linder with respect to zinc in the temperature range below  $100^\circ$ . The new data for Sn and Bi are, however, very much more complete than the former data for these metals, so that I believe that my original conclusion with regard to the approximate character of the Kelvin-Voigt symmetry law must stand. It is shown in the detailed paper that the failure of the symmetry relation is due to the Peltier heat, as distinguished from the Thomson heat.

In the case of Bi a special examination was made of the Kelvin-Voigt assumption that thermal e.m.f. has rotational symmetry about the crystal axis, and no appreciable deviation was found.

The specific resistance of these metals as a function of orientation was subjected to a more complete examination than has been made hitherto. The possible error arising from distortion of the crystal rod is so great in the case of Cd that a special method of measurement had to be used. The Kelvin-Voigt symmetry relation for resistance is satisfied within experimental error. Especial attention was given to the resistance of Bi, and my previous low value perpendicular to the cleavage plane verified. The pressure coefficient of resistance of Sb and Bi was redetermined, so that now this quantity is known over the entire range of orientation.

In the theoretical discussion is shown that the third law of thermodynamics gives considerable plausibility, although not complete certainty, to the thesis that the symmetry of the Peltier and the Thomson heat must be the same; this would mean that the apparent experimental difference in the symmetry of the two heats is merely an effect of the much greater error in the Thomson heat. It is shown that, contrary to statements previously made by me, Kelvin's axiom of the superposition of the thermal effects of currents is not internally inconsistent, so that his proof of the symmetry relations and of the existence of a transverse temperature effect\* are logically defensible. Experiment, however, seems opposed to the truth of the axiom. The revised discussion shows further that the local surface heat where a current leaves a metal crystal is a

function both of the direction of flow with respect to the crystal axis within the crystal and of the orientation of the surface, contrary to my former statement. It is also shown that these crystal phenomena no longer offer a basis for the proof that the electrons must move in the crystal along something analogous to fixed channels.

\* In *Proc. Nat. Acad.* for Jan., 1927, I announced the experimental detection of the transverse temperature effect, as I thought, for the first time. Recently, however, Dr. Borelius has called to my attention that this effect was experimentally established in a paper by Borelius and Lindh published during the war (*Ann. Phys.*, 53, 97, 1917). The effect has also been independently announced by Terada and Tsutsui in Japan (*Proc. Imp. Acad.*, 3, 132, 1927).

<sup>1</sup> P. W. Bridgman, *Phys. Rev.*, 31, 221, 1928.

<sup>2</sup> E. S. Linder, *Phys. Rev.*, 29, 554, 1927.

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## ANGULAR DISTRIBUTION OF INTENSITY OF RESONANCE RADIATION

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Spectrophotometric methods have recently been applied for the first time to the study of the solar chromosphere and prominences.<sup>1</sup> It is generally accepted that the line spectra emitted by such vapor is due to the scattering of incident light as fluorescent radiation. An atom situated in a beam of light absorbs a quantum, and the electronic configuration takes up a state of higher energy. The now excited atom after a normal interval of  $10^{-8}$  second re-emits the quantum in a random direction. That at any rate appears to be a widespread view of the process. Thus Milne in discussing an atom at the top of the chromosphere writes, "The atom will be exposed to radiation only on the side toward the sun... On the other hand emissions will be in a random direction, and consequently the recoil momentum acquired will on the average be zero."<sup>2</sup> And more recently, "for an atom these recoils give zero momentum since emissions are distributed at random in direction."<sup>3</sup>

We believe this assumption of random distribution of emission to be a mistake. No photometric measurements appear to have been made in the laboratory to compare the intensity of resonance radiation emitted at various angles from the incident beam. And in the absence of evidence the assumption of random emission would seem at first sight the most natural to make. Nevertheless we think that the interpretation of indirect evidence shows clearly not only that there is a variation with angle, but what is its magnitude.