

Experimental Verification of the Kelvin Relation of Thermoelectricity in a Magnetic Field

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The Seebeck coefficient (S) for a particular orientation of a bismuth single crystal at 78°K changes by 40% when a transverse magnetic field (B) of 10 000 Oe is reversed in direction ("Umkehrreffekt"). The Peltier coefficient (Π) also changes by the same proportion, but the field direction which gives the larger Seebeck effect, gives the smaller Peltier effect. This is a verification of the modified Kelvin relation, $\Pi(B) = TS(-B)$.

INTRODUCTION

THE Kelvin relation between the absolute Seebeck and Peltier tensors, S and Π , in the absence of a magnetic field is

$$\Pi = TS, \quad (1)$$

where T is the absolute temperature. This relation was first deduced from the first and second laws of thermodynamics, neglecting the irreversible processes which accompany these thermoelectric effects. The same relation follows from rigorous irreversible thermodynamics.¹ It is a particular example of the Onsager reciprocal relations

$$L_{ik} = L_{ki}, \quad (2)$$

where L_{ik} are the phenomenological coefficients which give the relationships between a properly chosen set of "fluxes" (e.g., energy flow and electrical current) and "forces" (e.g., temperature gradient divided by T^2 , and electrical potential gradient divided by T).

In the presence of a magnetic field, B , the classical argument remains unchanged and Eq. (1) should still be valid for the longitudinal Peltier and Seebeck effects. However, Eq. (2) is altered and becomes

$$L_{ik}(B) = L_{ki}(-B). \quad (3)$$

This result is a consequence of the principle of "microscopic reversibility." (With time reversal, charged particles will retrace their former paths only if the direction of the magnetic field is reversed as well.) The rigorous relation between Π and S in a magnetic field is, therefore,

$$\Pi(B) = TS(-B). \quad (4)$$

The diagonal components of the thermoelectric tensors Π and S are the normal Peltier and Seebeck effects measured in the direction of the current flow or applied temperature gradient. In most experiments, the changes in these effects with field are small or they do not depend on the sign of the magnetic field and it has not been possible to verify Eq. (4) for these diagonal components. However, in single crystals of bismuth² and bismuth-antimony alloys,³ a transverse magnetic

field gives rise to large increases in the Seebeck coefficient and a large "Umkehrreffekt"² has been observed, i.e., $S(B) \neq S(-B)$.

This inequality is not a violation of the Onsager reciprocal relations, which relate the components of the Seebeck tensor with those of the Peltier tensor but not among themselves. It is allowed by crystal symmetry if the direction of B is not parallel to a mirror plane of the crystal.⁴⁻⁶ In the present experiment, the "Umkehrreffekt" in the Seebeck and Peltier coefficients of bismuth were compared in order to verify the modified Kelvin relation, Eq. (4).

EXPERIMENTAL PROCEDURE AND RESULTS

Measurements were made on a specimen of bismuth cut from a pulled single crystal prepared from 99.9999% pure material. The length of the specimen was parallel to the trigonal axis of the crystal. The magnetic field was rotated in a plane perpendicular to this axis. One end of the specimen was soldered to the holder and a small resistive heater was soldered to the other end. Copper-constantan thermocouples were soldered on one edge of the specimen at distances far enough from the end contacts to avoid geometrical errors. The copper wires of these couples (0.003 in. in diameter) were used as voltage probes and similar wires soldered to the ends of the specimen served as current leads. The holder was evacuated to a pressure of about 5×10^{-6} mm Hg.

As the magnetic field was rotated, the magnetoresistance showed the expected sixfold symmetry. The maxima and minima in the magnetoresistance were used to determine the directions of the bisectrix and binary axes, respectively.⁷

The variation with field of Seebeck coefficient of bismuth vs copper is shown in Fig. 1. The average temperature was 78°K and a small temperature gradient was imposed parallel to the threefold symmetry axis. With B parallel to the bisectrix axis, no significant difference in the Seebeck coefficient was observed when the

Proceedings of the International Conference on Physics of Semiconductors, Exeter, 1962 (to be published).

⁴ C. Herring, T. H. Geballe, and J. E. Kunzler, *Phys. Rev.* **111**, 36 (1958).

⁵ J. Meixner, *Ann. Physik* **40**, 165 (1941).

⁶ J. Kohler, *Ann. Physik* **40**, 601 (1941).

⁷ B. Abeles and S. Meiboom, *Phys. Rev.* **101**, 544 (1956).

¹ S. R. deGroot, *Thermodynamics of Irreversible Processes*, (Interscience Publishers, Inc., New York, 1951).

² E. Gruneisen and J. Gielessen, *Ann. Physik* **27**, 243 (1936).

³ R. Wolfe and G. E. Smith, *Appl. Phys. Letters* **1**, 5 (1962);

TABLE I.

B	R_B/R_0	K_B/K_0	S_B/S_0	$\Delta V_B/\Delta V_0$
10 kOe	54	0.78	2.00	3.7
-10 kOe	55	0.77	1.42	3.7

direction of the field was reversed. However, with B parallel to a binary axis, large differences in S were observed, as shown in the lowest curve. In particular, in a field of 10 000 Oe, the Seebeck coefficient was increased by 42% for one direction of B and by 100% for the reverse direction.

Instead of a direct determination of the Peltier coefficient, the quantity which was actually measured was $S\Pi/K$, where K is the thermal conductance of the specimen between the probes. The method was the previously described transient modification⁸ of Harman's technique for measuring the thermoelectric "figure of merit," Z . This is essentially a determination of the difference between the adiabatic and isothermal resistivities.^{6,9} Under adiabatic conditions, when a current I , flows through the specimen, one end is heated and the other is cooled by the Peltier effect. The temperature difference between the probes is proportional to $\Pi I/K$ if the effects of Joule heating are negligible. The voltage between the probes is IR where R is the isothermal resistance, plus an extra voltage, ΔV , due to the temperature difference:

$$\Delta V = \Delta T \alpha S\Pi/K.$$

This extra voltage was measured by switching off the current and recording the decay of ΔV with time as the temperature gradient decays. Since the measured thermal conductivity does not change when the magnetic field is reversed (in agreement with the Onsager reciprocal relations), any change in ΔV when B is reversed gives a measure of the "Umkehrreffekt" in $S\Pi$ and, therefore, in Π .

The measurement of ΔV was made on the same bismuth specimen mounted in the holder as described above. This is certainly not an adiabatic arrangement since one end of the specimen is anchored to the holder. With current flow in one direction, the free end of the specimen is cooled by the Peltier effect and with the current reversed it is heated. In both cases there is some Joule heating which results in a nonlinear temperature distribution. The effects of Joule heating were eliminated by averaging the ΔV values for both directions of current and by using different current levels (between 10 and 100 mA). It is apparent that the average ΔV is proportional to $S\Pi/K$.¹⁰

Measurements of ΔV_B were made with a field of $\pm 10\,000$ Oe applied parallel to a binary axis. The results

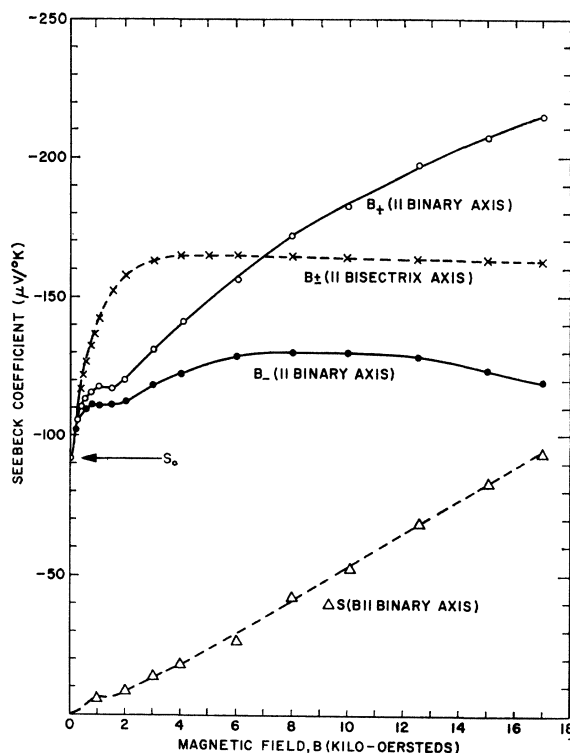


FIG. 1. Seebeck coefficient of bismuth parallel to the threefold axis in a transverse magnetic field at 78°K.

are compared with those obtained in zero field in the following Table:

If $\Delta V_B/\Delta V_0$ is calculated using Eq. (4) and the measured values of S_B/S_0 and K_B/K_0 , the value is 3.7, the same for both directions of magnetic field. This value is in excellent agreement with the experimental results. The calculated values based on Eq. (1) would be $\Delta V_B/\Delta V_0 = 5.2$ for $B = +10$ kOe and $\Delta V_B/\Delta V_0 = 2.6$ for $B = -10$ kOe.

DISCUSSION

Since $\Delta V_B/\Delta V_0$ is the same for both directions of magnetic field, the "Umkehrreffekt" in the Peltier coefficient is of the same magnitude as that in the Seebeck coefficient, but of opposite sign. The field direction which gives rise to the larger Seebeck coefficient is associated with the smaller Peltier coefficient, and the simple Kelvin relation of Eq. (1) does not apply in a magnetic field.

If we assume that $\Pi = TS$ does apply in zero field (this relation has been verified in many experiments), then the agreement between the measured value of $\Delta V_B/\Delta V_0$ and the value calculated using Eq. (4) is a quantitative verification (within the experimental error of $\pm 5\%$) of the modified Kelvin relation Eq. (4).

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⁸ G. E. Smith and R. Wolfe, J. Appl. Phys. **33**, 841 (1962).

⁹ P. Lenard, Ann. Physik Chem. **39**, 619 (1890).

¹⁰ N. Fuschillo and F. J. Donahoe, Advanced Energy Conversion **2**, 131 (1962).