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THE HALL EFFECT AND RESISTANCE IN SPUTTERED TELLURIUM FILMS

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Abstract

Effect of heat treatment on the Hall e.m.f. and resistance of sputtered tellurium films.—Aside from an ageing process the Hall e.m.f. was found to be directly proportional to the resistance both when the temperature coefficient of resistance was negative and when it was positive. The films were from 10^{-5} to 10^{-6} cm thick. *Heating the film in a gas* (air or hydrogen) when the film was not completely aged brought departures from the proportionality between Hall e.m.f. and resistance, while pumping out and cooling returned the film to its previous condition.

THE Hall effect in thin sputtered films of gold was found by Mackeown[1] to be independent of the resistance of the film when the latter decreased over a wide range during the process of ageing at room temperature. Various theories, including those of Lorentz,[2] Richardson,[3] Eldridge,[4] and Page,[5] give the Hall coefficient as dependent upon the resistivity. The resistance of a metal is a function of temperature, and the resistance of thin films depends on the previous heat treatment as well. Reynolds[6] has found that by suitable conditions of sputtering and by heat treatment both a negative and a positive temperature coefficient of resistance may be obtained in thin films of platinum. It was believed instructive therefore to find whether the Hall effect in sputtered films remains independent of resistance or varies with resistance when the changes are made by heating. Tellurium has, at room temperature, a positive and an extraordinarily large Hall coefficient and the effect reverses at moderately high temperatures. Sputtered films of tellurium offered many possibilities.

Apparatus and Procedure

In order to make measurements of the Hall e.m.f. and resistance without exposing the film to air, a small sputtering jar, three inches in diameter was built between the pole pieces of a large electromagnet.

The sputtering electrodes and the glass plate onto which the film was deposited were in vertical planes and the sputtering was horizontal. The plate was in the center and directly between the pole pieces and measurements could be made without moving the film. An inverted Pyrex beaker with the edge ground smooth was used for the sputtering jar, and a clean,

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[1] Mackeown, Phys. Rev. **23,** 85 (1924).

[2] Lorentz, Versl. Kon. Akad. Amst. (2), **19,** 217 (1884).

[3] Richardson, Electron Theory of Matter, p. 434.

[4] Eldridge, Phys. Rev. **21,** 131 (1923).

[5] Page, Phys. Rev. **24,** 283 (1924).

[6] Reynolds, Phys. Rev. **24,** 523 (1924).

soft rubber gasket used at the base. While the pumps maintained a fair vacuum, the seal was not sufficiently tight to insure that the initial residual gas, argon, remained in the jar throughout the sputtering of the film. It was found convenient frequently to sputter in a larger jar, then transfer the film to the beaker jar for measurement. A seal with de Khotinsky cement in place of the rubber gasket was very satisfactory and held a good vacuum but the cement was difficult to remove. The de Khotinsky was melted in place on the cold glass by a very fine hydrogen flame, which melted the cement without burning it.

The cathode was cast from tellurium powder which had been purified by distillation, by melting the powder in a stream of hydrogen, the molten tellurium flowing down a tube into a graphite mould. The tellurium was kept under hydrogen until cold. This is essentially the method used by Wold,[7] whose plates were found to be very pure.

The tellurium films, 5 cm square, were sputtered onto glass plates overlapping heavily sputtered gold terminals. The copper connecting wires were rigidly clamped to the gold sputtered terminals. Soft lead foil was placed between the copper wire and the gold to prevent the latter from becoming scratched. The difference in the reading of the voltage between the two Hall terminals, with the magnetic field off and with it on, gave the Hall e.m.f. It was at times necessary to use an auxilliary balancing potential.

The current through the film was regulated by minute variations of the filament current of a radio tube (grid connected to plate) placed in series with the film and a 45 (or 90) volt storage battery, so that the current through the film was independent, or nearly so, of its resistance. To correct for the drift of the galvanometer of the potentiometer, due mainly to slow changes in the film, the potential difference between the Hall terminals was read in sequence for the magnetic field, $H=0$, H direct, $H=0$, H reversed, $H=0$, H direct, $H=0$, H reversed, and $H=0$, at equal time intervals, usually about twenty seconds, as rapidly as settings could be made. The intermediate readings for $H=0$ were usually omitted, since they were unnecessary in taking the average. By this method readings could be taken while the resistance, temperature and Hall effect were changing, the values for temperature and resistance before and after being averaged. The current through the film was reversed and the above procedure was repeated as a check. The primary current was read on a suitably calibrated galvanometer. The magnetic field was calibrated by a bismuth spiral.

In order to measure the thickness of the film, or rather the mass per square centimeter, a small piece of mica placed directly beside the film during sputtering was weighed before and after deposition.

A thermocouple was placed near each Hall terminal and rough checks on the Ettingshausen effect indicated that it was small compared to the large Hall effect.

The temperature of the glass plates onto which the films were deposited was controlled by a flat electric heater placed in contact with and directly

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[7] Wold, Phys. Rev. **7**, 169 (1916).

behind the plate. The temperature ranged, in the various films, from room temperature to 100°C. In general, films sputtered onto cold plates came slowly and had a negative temperature coefficient of resistance, while those sputtered onto hot plates came much more quickly but were partly aged and had, or soon acquired on heating, the positive resistance-temperature coefficient.

RESULTS

Figs. 1 and 2 show the proportionality of the Hall e.m.f. to the primary current and to the magnetic field respectively. No good check was obtained on the variation of the Hall e.m.f. with thickness since the films were deposited at different temperatures and were treated differently so that it was impossible to find exactly corresponding conditions. However the data indicate, if anything, a proportionality to the reciprocal of thickness rather than independence of thickness.

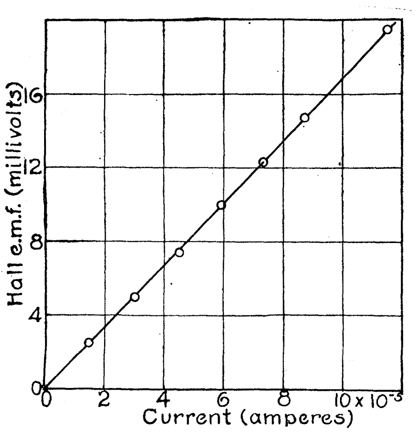

Fig. 1. Hall e.m.f. as a function of current.

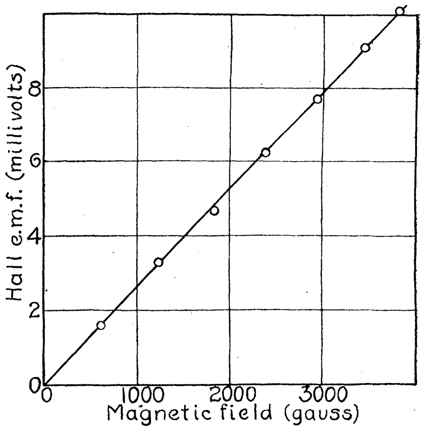

Fig. 2. Hall e.m.f. as a function of magnetic field.

The straight lines, *A* and *B* of Fig. 3, show that, aside from an ageing effect,[8] the Hall e.m.f. is directly proportional to the resistance of the film when the latter is changed by heating in vacuum. It is to be noted that after the rapid ageing by heat treatment (*a-f*), the Hall e.m.f. had the same value as before heating, five millivolts, although the resistance had decreased to one-sixth of its previous value. This fact and also the doubling of the resistance while the Hall e.m.f. remained constant (*f-g*), are consistent with the results obtained by Mackeown, who found that the Hall e.m.f. is independent of the change in resistance by ageing at room temperature. Continued treatment however brought changes in the film after which neither the Hall e.m.f. nor the resistance returned to the same value as before at room temperature. In contrast to the changes corresponding to the ageing

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[8] Ageing of the type observed by Mackeown.

process *a-b* and *d-e*, this latter ageing process[9] results in a change of Hall e.m.f. proportional to the resistance.

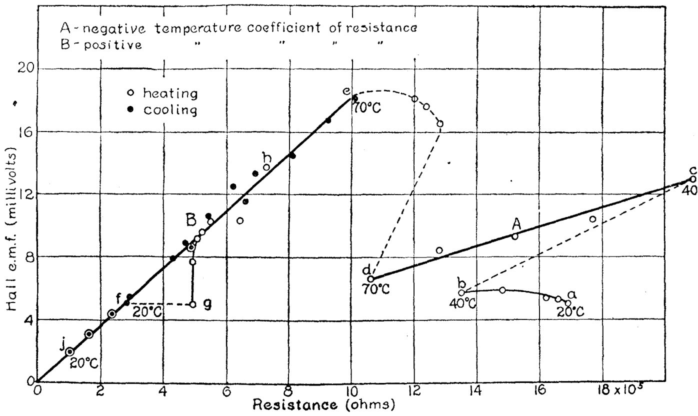

Fig. 3. Hall e.m.f. as a function of resistance: *a*, film heated slowly; *b*, air admitted (to pressure of 1 cm), temperature constant $\frac{1}{2}$ hour; *c*, air pumped out, heater turned on; *d*, heating discontinued since Hall e.m.f. began to increase rapidly; *d–e*, rapid ageing of film, reversal of temperature coefficient of resistance (negative to positive); *e*, slow cooling begun; *f*, air admitted at atmospheric pressure; *g*, air pumped out and heater turned on; *h*, data became erratic at 70°C, heater disconnected; *h–j*, data for second cooling shown by double circles. A subsequent heating and cooling gave points on same line *j–f–h*.

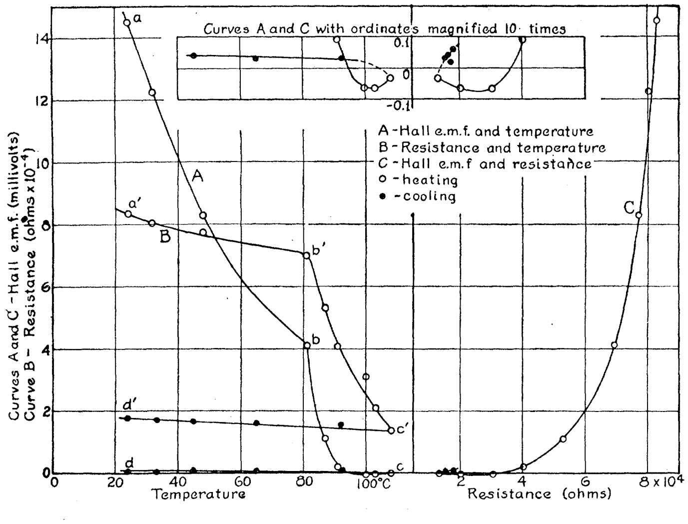

Fig. 4. Behavior of Hall e.m.f. and resistance when the film is heated to a temperature above that of annealing: *a–b–c*, *a′–b′–c′*, heating; *c–d*, *c′–d′*, cooling. Surface density of film $=1.2\times10^{-5}$ grams/sq. cm.

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[9] The permanent decrease in Hall e.m.f. and resistance proportionately (*f*—*j*), may be described by postulating a secondary ageing process closely allied to the reproducible direct proportionality between the Hall e.m.f. and the resistance. The ageing observed by Mackeown and also appearing in this film (*a*, *f*, *g*), which consists of a change in resistance while the Hall e.m.f. remains constant, is a process of a different kind.

Curve *B*, Fig. 4, shows the decrease in resistance in a film which was heated to a temperature above that at which it had previously been treated. Curve *A* shows the simultaneous decrease in the Hall effect. The rapid decrease in Hall e.m.f. and resistance above 80°C suggests a change in structure in the metal. The corresponding curve *C* shows that the Hall e.m.f., although not directly proportional to resistance, varies in a regular way with resistance even through the period of rapid ageing where the changes in the film are not reversible. The regularity of curves *A* and *C* during the reversal of the Hall e.m.f. (negative to positive) is seen more readily in the insert at the top, where the ordinate scale is magnified ten times.

The upper line, *a-b*, in Fig. 5, shows reproducible results in a film having a positive temperature coefficient of resistance (the same film as in Figs. 1 and 2). The lower lines show the effect in this fairly stable film of heating and cooling in hydrogen. The corresponding curve showing the positive (though not constant) temperature coefficient of resistance, is shown in Fig. 6. Plotting Hall e.m.f. against temperature gave a curve very similar to Fig. 6. The lag of Hall e.m.f. and resistance behind the temperature (*g-h*, *j-k*) indicating that the change in the metal is a slow process may be responsible for the shape of the curve in Fig. 6, it requiring a longer time for equilibrium to become established at 50°C to 60°C (a temperature above which the film had not previously been treated) than was allowed between readings.

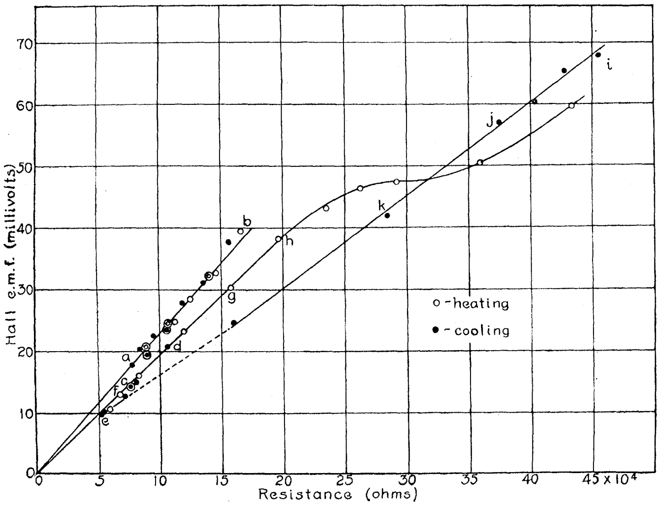

Fig. 5. Hall e.m.f.-resistance curve in a film having a positive temperature coefficient of resistance. Heating in hydrogen: *a–b–a′*, heating and cooling; *a′–b′–c*, second heating and cooling, data indicated by double circles; *c–d*, increase of resistance and Hall e.m.f. overnight by leakage into system of air (to a pressure of about $\frac{1}{2}$ cm); *d*, pumps turned on; *e*, hydrogen admitted cold at atmospheric pressure; *f*, heater turned on; *g–h*, temperature maintained constant at 37°C for 1 hour; *h*, heating resumed; *i–j*, cooling; *k*, after film had stood in hydrogen at room temperature overnight; *k–e*, pumping out hydrogen. Data for Hall e.m.f. above 80°C was erratic. Surface density of film $= 1.0 \times 10^{-5}$ grams/sq. cm.

The admission of oxygen to this film increased the Hall e.m.f. and resistance a small amount in the same ratio as was the case with hydrogen, and the heat and gas treatment in this more or less aged film was not continued.

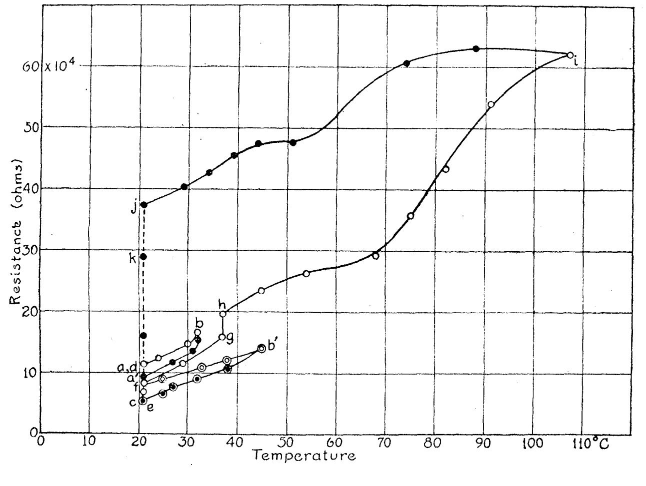

Fig. 6. Positive resistance-temperature coefficient for film of Fig. 5.

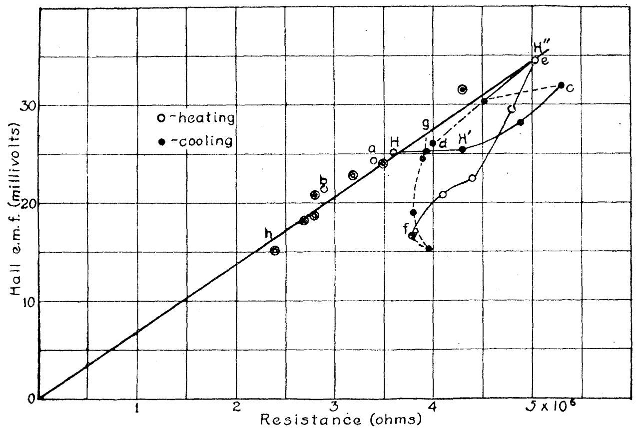

Fig. 7. Hall e.m.f.-resistance curve in a film having a negative temperature coefficient of resistance. Hydrogen and heat treatment: *a*, heater turned on; *b*, hydrogen admitted to pressure of ½ cm; *H*, hydrogen admitted to pressure of 3 cm; *H′*, heater disconnected; *c*, pumps started; *d*, hydrogen admitted cold; *e*, heater turned on; *f*, heater disconnected and pumps started; *g–h–e*, double circles indicate subsequent heating and cooling; *H*, *H′*, *H″*, points taken directly after the admissions of hydrogen.

It came as a surprise that the changes in the Hall e.m.f. followed those of resistance so well during the gas treatment, since in Fig. 3 the admission of air doubled the resistance without increasing the Hall e.m.f. at all. A possible explanation is that the adsorption of the gas, hydrogen or oxygen, when the film is aged and its structure stable, acts only to separate the molecules of tellurium, while in the less stable unaged film oxidation and other complications occur.

The effect of hydrogen and heating in an unaged film, one having a negative temperature coefficient of resistance, is shown in Fig. 7. The low precision is due to the high resistance of this film. The range of temperature through which the film could be varied without danger of rapid ageing was very limited. The important thing about this film is that after the excursions by gas and heat treatment the film returned to the previous condition, the Hall e.m.f. having the same proportionality to resistance as before.

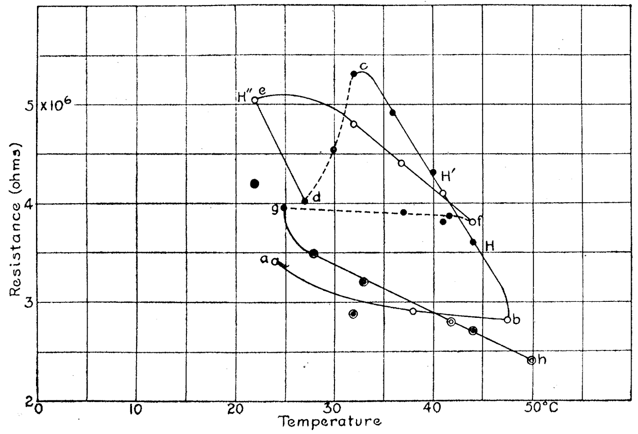

Fig. 8. Negative resistance-temperature coefficients for film of Fig. 7.

The Hall coefficient in the films here described was negative and somewhat less than the positive coefficient for the metal in bulk. Another film which was sputtered cold for a long time, and which was very thick and quite black showing the oxide, had a positive Hall e.m.f. and a negative temperature coefficient of resistance, the Hall e.m.f. being roughly proportional to the resistance. Whether the positive sign was due to the thickness or to the oxide was not evident. Most of the films were deposited hot. It is highly probable that the films were in the crystalline form that Wold[7] suggested for his negative Hall coefficient for tellurium between 30°–100°C and 245°C. Moreover the reversal shown in Fig. 4 checks very well with this assumption, the difference in temperature of the reversals being unimportant since the crystalline structure of the different films with their varied treatments may be widely different. Wold found the first reversal to vary widely with temperature and the negative coefficient nearly to disappear after successive heat treatment. Consistent with his observation, the Hall effect, during the cooling of this film, though definitely negative, was very small and therefore difficult to obtain accurately.

SUMMARY

In the sputtered films of tellurium studied, two results have been observed, at times simultaneously:

(1) The Hall effect has been found to be proportional to the resistance of the film, when the latter is changed by heating within a limited temperature range, a change which presumably does not involve a change in the crystal structure of the metal. *This proportionality holds both when the temperature coefficient of resistance is positive and when it is negative.* This is tantamount to saying that the temperature coefficient of resistance and the temperature coefficient of the Hall effect are proportional.

(2) There is also a process of ageing which can be hastened by heat treatment during which the Hall e.m.f. in a film is independent of resistance and has a definite value at a given temperature.

Effect (2) occurs more frequently in films having had little or no treatment and (1) maintains after treatment and appears in films sputtered onto hot plates.

Annealing the film at temperatures higher than that of its previous treatment brings about transformations which are not reversible, but even then the Hall effect and the resistance are closely linked together.

The admission of the gases, air, hydrogen and oxygen under certain conditions affected the Hall e.m.f. and the resistance alike, while gas and heating together brought about radical departures from the proportionality of the Hall e.m.f. to resistance, and cooling and removing the gas returned the Hall e.m.f. and resistance to their original relation.

The proportionality of the Hall e.m.f. to the resistance is consistent with the view that the negative temperature coefficient of resistance is due to the preponderance of the effect of the increase, as temperature rises, in the number of electrons separating from the atomic centers and taking part in the conduction of current. The less the atomic forces oppose the longitudinal motion of the electrons, the smaller is the resistance measured, and the less the atomic forces oppose the transverse motion of the electrons the smaller is the Hall e.m.f.

In conclusion, the writer wishes to express his appreciation of the interest shown in the problem and the valuable suggestions given by Professor F. K. Richtmyer, under whose direction this investigation was carried on.

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