Temperature Effects in Secondary Emission

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Measurements have been made on the effects of temperature changes on the emission of secondary electrons from iron, nickel, cobalt, and molybdenum. Abrupt changes of one or two percent were observed to accompany the $\alpha - \gamma$ transition of iron, while the hexagonal to face-centered cubic transformation of cobalt was accompanied by a change in secondary emission of only about 0.4 percent. The magnetic transformation was found to alter the secondary emission coefficient of nickel by less than 0.3 percent. The temperature coefficient of secondary emission, in the cases of nickel, cobalt, and molybdenum was found to be much less than the volume coefficient of expansion of the metal. The smallness of the temperature coefficient and the effect of the magnetic transformation are shown to lend support to the view that the secondary electrons are scattered or "absorbed" by an excitation process similar to that whereby they are originally produced.

THE nature of the dependence of secondary emission on temperature is of some theoretical importance. The work of Treloar and Landon[1] on iron, nickel and cobalt has shown that temperature plays no very great role, but their methods were incapable of detecting changes of less than about 5 percent in the secondary emission of their targets. This paper deals with more precise measurements of the effects of temperature on the secondary emission of iron, nickel, cobalt and molybdenum.

APPARATUS AND TECHNIQUE

There is one secondary emission datum that can be accurately determined more easily than any other. This is the bombarding voltage (V_1) for which the secondary emission coefficient (δ) is exactly unity. For, when $\delta = 1$, there is no net flow of current to or from the target; this is true regardless of what bombarding current is used. It is easy to devise a circuit[2] which will enable the observer to set the net flow of current to the target sufficiently near to zero that the accuracy of the determination of V_1 is limited by the precision with which the voltage can be read,— and the measured V_1 does not depend on the primary current.

In all the work to be described V_1 has been measured as a function of temperature. The data can easily be translated to variation in δ

at constant V provided that we know the slope of the δ *vs.* V curve near $\delta = 1$.

In the work done with iron, the target consisted of a 0.004" diameter wire, in a tube similar to that used by Treloar[3] in measurements on filaments. The target wire was heated by passing a current through it. The temperature was roughly determined by measurement of the resistance of the wire, supplemented by appropriate calculations of end cooling and radiation effects.

In all the rest of the work, the target consisted of a disk of thickness 0.015" to 0.020" and diameter 0.500". This disk was confronted by the open end of a molybdenum cylinder, which was maintained at a positive potential high enough to insure collection of all secondary electrons. The primary beam came through a mesh-covered hole in the opposite end of the cylinder and covered a spot of about $\frac{3}{16}$" diam. on the target. The target was heated by thermal radiation from a tungsten filament close behind the disk, and temperatures were measured by means of a thermocouple junction of fine Pt and Pt Rh wires welded to one edge of the target.

In all tubes, of course, pure, pre-glowed tungsten filaments were used as the source of primary current, and were operated at low enough temperatures to make evaporation of tungsten entirely negligible. The amount of metal used in the tubes was kept to a minimum. The parts were heat-treated before assembly,

[1] L. R. G. Treloar and D. H. Landon, Proc. Phys. Soc. **50**, 625 (1938).

[2] In the present work a one-stage d.c. amplifier was used.

[3] L. R. G. Treloar, Proc. Phys. Soc. **48**, 488 (1936).

and the designs were such that all metal parts could be heated in the assembled tubes by induction or bombardment. After the tube was baked and the elements glowed the target was heat-treated. Iron and molybdenum were outgassed by heating for a few minutes at an elevated temperature (1000° for iron, 1170° for molybdenum); nickel and cobalt targets were held at 850° for a few minutes, and then were kept at about 750° for twelve hours or more.

The resulting pressure, as measured with an ionization gauge, was always less than 10^{-7} mm Hg, which was also an upper limit for the pressures reached at any time during the subsequent measurements. The measurements were made on the pumps, but only in the case of molybdenum was there any indication of gaseous adsorption. In this case, measurements had to be made rapidly—an entire heating or cooling cycle lasting only a few minutes—in order to avoid difficulties with the adsorption of gas at the lower temperatures.

EXPERIMENTAL RESULTS

Iron

Figure 1 shows three typical V_1 vs. T curves plotted from measurements on a pure iron wire. The temperature scale is far from accurate in this work on filaments. Every plot of V_1 against filament heating current showed a break at a
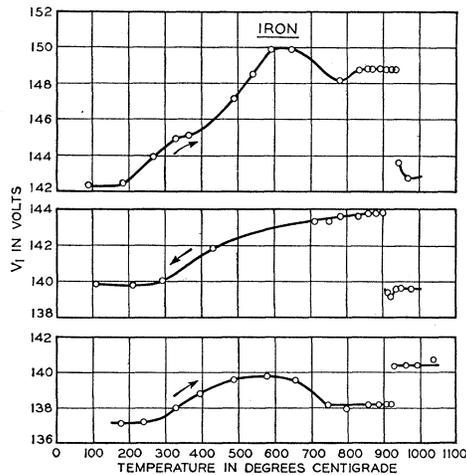

FIG. 1. Effect of crystal structure on the secondary emission from a small iron wire (one percent change in $V_1 = 0.6$ percent change in δ).

value of current which, from the calculations, had to be near 900°. Hence it was thought safe to assign to the average of these current values the temperature corresponding to the α to γ transition of iron—910°C. The remainder of the temperature scale undoubtedly decreases in accuracy as T varies away from this value.

In spite of the fact that all three curves of Fig. 1 correspond to measurements made in the same way on the same target, the results are
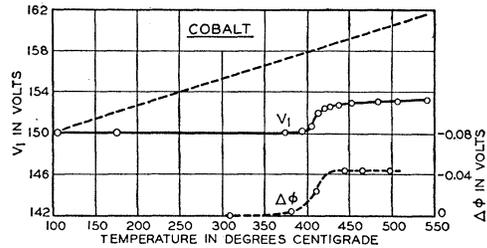

FIG. 2. Effect of crystal structure and temperature on the secondary emission parameter (V_1) and work function (ϕ) of a polycrystalline disk of cobalt (one percent change in $V_1 = 0.2$ percent change in δ), dotted line representing a temperature coefficient of secondary emission equal to the volume coefficient of expansion.

seen to be quite at variance with one another. The curves agree only in that, in every case, an abrupt change in V_1 occurs when the crystal form changes from body- to face-centered, or vice versa. The magnitude and even the direction of this change vary from run to run, as does the behavior of V_1 at lower temperatures. The explanation is probably about as follows. The heat treatment to which the iron wire was subjected resulted in the formation of long crystals, so that the small region in the center of the filament on which measurements were made consisted of only one or two single crystals of iron. (Subsequent photomicrographs of the iron filament have confirmed this.) Consequently each transition through 910° caused a particular crystal surface of α-iron to be replaced by some γ-iron surface configuration. It is not to be expected that exactly the same crystal orientation would be repeated on cooling and reheating. Thus the differences in the results of successive measurements correspond to differences in the crystal surfaces exposed to the primary bombardment. The large, continuous changes in V_1 at temperatures below 910° were probably due partly to continued recrystallization effects and partly
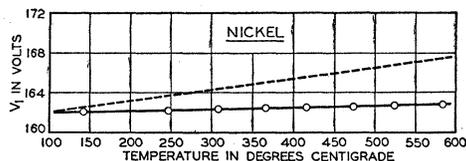
FIG. 3. Effect of magnetic state and temperature on the secondary emission from nickel (one percent change in $V_1 = 0.5$ percent change in δ), dotted line representing a temperature coefficient of secondary emission equal to the volume coefficient of expansion.
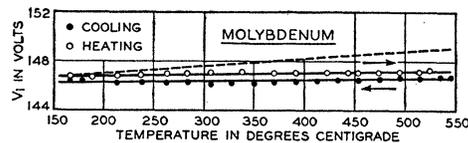

FIG. 4. Effect of temperature on the secondary emission from molybdenum (one percent change in $V_1 = 0.4$ percent change in δ), dotted line representing a temperature coefficient of secondary emission equal to the volume coefficient of expansion.

to shifting of the bombarding spot along the crystals of the target due to thermal expansion and contraction of the filament.

Thus the measurements on iron filaments tell us that the secondary emission coefficient of some surfaces of a body-centered iron crystal differs by at least one or two percent[4] from the secondary emission coefficient of some of the face-centered crystals, but that the variation from surface to surface of a body-centered crystal can be greater than this.

Cobalt

Figure 2 shows the results of measurements on a disk of pure[5] cobalt. In this, and all subsequently described work, the bombarded area was large enough to cover many crystals. There can be little doubt that the abrupt change in V_1 at 410° corresponds to the close-packed hexagonal to face-centered cubic crystal structure change which has been reported[6] to occur at a number of temperatures ranging between 400° and 490°C. The data of Fig. 2 were taken for ascending temperatures, and were thoroughly reproducible, only a few minutes being required to establish equilibrium even for a measurement around 410°. On cooling, the phase change appeared to occur much more slowly, however, and, unless a number of hours were consumed in making the measurements, the decrease in V_1 was distributed over 100° or more.

With this target the contact potential difference between the clean tungsten filament and the cobalt surface was measured simultaneously with the measurements of V_1. The variation in the work function of the cobalt is plotted as the

dotted curve of Fig. 2. Besides being too small, the change in work function is in the wrong direction to be directly responsible for the change in secondary emission that accompanies the phase change.

The broken line has the slope that the V_1 vs. T curve would have if δ varied with T as rapidly as the volume of the target metal changes with temperature. The slope of this line involves in an obvious way the coefficient of cubical expansion and the slope of the δ vs. V curve for cobalt near $\delta = 1$. The latter figure has been taken from measurements made by Treloar and Landon.[1]

Nickel

Figure 3 shows the dependence of the secondary emission of pure[7] nickel on temperature. It is notable that there is evident no influence produced by the magnetic transformation (Curie point $= 355°C$).

For the broken line showing the comparison with the volume expansion of the metal, the slope of the δ vs. V curve is taken from measurements made by the author on solid nickel.

Molybdenum

Figure 4 shows the dependence of the secondary emission of stock molybdenum on temperature. As has been mentioned earlier, the apparent ease with which molybdenum absorbs gas made it necessary for these measurements to be made very rapidly. The two sets of data of Fig. 4 were taken for successive cooling and heating, each set of data requiring about five minutes, with a similar interval elapsing between the cooling and the following heating run.

For the line showing the comparison with the volume expansion of the metal, the slope of the δ vs. V curve is taken from Warnecke.[8]

[4] For converting from variations in V_1 to equivalent changes in δ, the slope of the δ vs. V curve for iron was taken from R. Kollath, Physik. Zeits. **38**, 202 (1937).

[5] Impurities <0.1 percent.

[6] For a bibliography see L. Marick, Phys. Rev. **49**, 831 (1936).

[7] Impurities <0.2 percent.

[8] R. Warnecke, J. de phys. et rad. **7**, 270 (1936).

Theory and Discussion of Results

The theoretical considerations involved in a prediction of the effects of temperature on secondary emission are similar to those discussed in an earlier article.[9] In that paper particular attention was paid to the secondary electrons originating in the highest occupied energy band of the metal. The nearly quantitative agreement of some of the resulting predictions with experiment prompted the suggestion that excitation of electrons from the lower bands was perhaps not important. However, it can be shown that qualitatively similar results would be predicted by the same type of theory even though some of the lower bands do contribute to the process. Hence it will be of value to place the present considerations, if possible, on somewhat more general principles than some of those employed in the earlier work.

Even though the electrons dealt with are not nearly free, it can be shown (by a slight modification of the earlier theory) that the only probable interactions with primary particles of not too low energy are those which transfer the lattice electrons to levels in higher bands which have the same reduced wave vectors as the initially occupied levels. When the primary energy is not too low, the number of electrons per unit primary path length knocked from occupied levels of reduced wave vector $\sim \mathbf{k}$ in band B into corresponding, initially unoccupied, levels in band B' is

$$(dn/dx)_{\mathbf{k};\ B \to B'}$$

$$= 4\pi e^4 \rho_B(\mathbf{k}) |b_{\mathbf{k};\ B \to B'}|^2 / |\Delta E_{\mathbf{k};\ B \to B'}|^2. \quad (1)$$

$\rho_B(\mathbf{k})$ is the density of occupied levels of reduced wave vector $\sim \mathbf{k}$ in the lower band, $\Delta E_{\mathbf{k};\ B \to B'}$ is the energy difference between the initial and final states, while

$$|b_{\mathbf{k};\ B \to B'}|^2$$

$$= \frac{1}{\Omega^2} \left| \sum_{\mathbf{m}} \left\{ \left[\int \psi_{\mathbf{k};B}\ \exp\ [-i\mathbf{k}\cdot\mathbf{r} - i(2\pi\mathbf{m}/a)\cdot\mathbf{r}]d\tau_{\mathbf{r}} \right] \right. \right.$$

$$\left. \left. \times \left[\int \psi^*_{\mathbf{k};\ B'}\ \exp\ [i\mathbf{k}\cdot\mathbf{r} + i(2\pi\mathbf{m}/a)\cdot\mathbf{r}]d\tau_{\mathbf{r}} \right] \right\} \right|^2. \quad (2)$$

[9] D. E. Wooldridge, Phys. Rev. **56**, 562 (1939).

Here the two ψ's represent the probability amplitudes for the lattice electron in the initial and final states, normalized so that

$$\int \psi\psi^* d\tau_{\mathbf{r}} = \Omega. \quad (3)$$

Ω, of course, is the volume dealt with. The equation assumes a simple cubic lattice structure, of edge a, but the results are substantially the same for other structures. In terms of a simple cubic structure, $\mathbf{m}$ is to be summed over all vectors having integral components along each of the three cubic axes.

Equation (1) differs only slightly from Eq. (29) of the earlier paper, and is derived in practically the same way.

Temperature coefficient

The influence of temperature on secondary emission is partially determined by the volume dependence of $|b|^2$ and $|\Delta E|^2$. For a material in which the atoms are so far apart that the electrons are tightly bound, neither $|b|^2$ nor $|\Delta E|^2$ depends on a. For a material in which the electrons are nearly free, $|\Delta E|^2 \propto 1/a^4,$[9] whereas the volume dependence of $|b|^2$ varies with $\mathbf{k}$. For metals such as those we are concerned with in this paper, the average $|\Delta E|^2$ will probably depend on a somewhat less rapidly than through the fourth power, while the average $|b|^2$ will decrease with increasing volume at a rate not greater than three or four powers of a. In other words, the quotient $|b|^2/|\Delta E|^2$ will probably increase with a not much more rapidly than a^3, whereas the dependence may be considerably less than this.

The secondary emission coefficient of a target is proportional to the product of the number of secondaries produced per unit primary path, the reciprocal of the absorption or scattering coefficient of the secondaries, and a term which expresses the fraction of the secondaries which are initially directed so as to be able to leave the target surface, if not absorbed. In the nearly free electron case, this last term (within a numerical factor) is

$$[1 - \{(W_a)/(E_0 + E_F)\}^{\frac{1}{2}}],$$

where W_a is the height of the potential barrier

at the target surface, and $E_0 + E_F$ is the average kinetic energy with which the secondaries are produced. Both W_a and $E_0 + E_F$ should decrease with increasing a, at nearly enough the same rates that the temperature dependence of this term, which could not be large in any case, can be ignored. This should be true enough in the more general case also.

The volume dependence of the absorption coefficient of the secondaries, γ_s, depends upon the mechanism by which the secondaries are prevented from escaping. Two types of "absorption" may be important. They may best be discussed in connection with a concrete example. Consider the case of nickel, which possesses overlapping, incompletely filled $3d$ and $4s$ bands, with higher reaching unfilled $4p$ bands. The secondary electrons that escape probably are first excited into $4p$ levels. On their way to the target surface they may excite other electrons from $3d$ to unfilled $4s$ levels, losing large increments of energy in the process, or they may raise some of the electrons at the top of the filled portions of the $3d$ and $4s$ bands to slightly higher levels, losing small increments of energy in this process. The second type of energy loss has been shown[9] to be unimportant as regards the more energetic primary particles. If we assume the first process to be of controlling importance in slowing down the secondaries also, then the expression for γ_s must be similar in form to Eq. (1), involving, probably, nearly the same volume dependence. The net result would be a secondary emission coefficient nearly independent of temperature expansion.

If, on the other hand, the secondaries were scattered by small energy transfers to electrons in the upper levels of the occupied bands, the volume dependence of γ_s would probably not be the same as that of Eq. (1). The net result would be a secondary emission coefficient with a temperature dependence which might be as large as or larger than the cubical coefficient of expansion.

The observed smallness of the temperature coefficient of secondary emission therefore suggests that the mechanism which scatters the secondary electrons is an excitation process similar to that which originally produces them.

Magnetic transformation

The effect of the magnetic transformation should also be small. The influence on the secondary emission should probably be due principally to the change in the fractional occupancy of the $4s$ band and the shift in the energies of the occupied $3d$ and $4s$ levels, where the secondaries originate. Neither of these effects can be large; one can estimate (very roughly) that the resulting influence on the secondary emission would be of the order of several tenths of one percent. The experimental observations on nickel set an upper limit of 0.2 to 0.3 percent upon the effect on δ of the magnetic transformation. As in the case of the temperature coefficient of secondary emission, the experimental result seems lower than one would expect, but not enough lower to be conclusive. Once again, the low value is more easily understood if we assume the scattering of the secondaries to be altered by the magnetic transformation in much the same way that the creation of secondaries by the primaries is affected.

Crystal structure change

A change in the crystal structure of a target entails changes in $|b|^2$, $|\Delta E|^2$ and γ_s. In general, we would expect to observe differences of the same order of magnitude among the various faces of a single crystal. The measurements on iron bear this out. The values of δ measured on what we have inferred to be different crystalline surfaces of the iron wire differ among themselves by only two or three percent. The theory calls for the existence of crystalline directions along which the emission of secondaries is considerably higher than in other directions.[9] Even though γ_s depends on direction in much the same way, it seems unlikely that the two effects can compensate so well that all crystal surfaces have values of δ that agree this closely. It is probable that a complete set of measurements on all the crystal surfaces of iron would reveal values of δ involving differences of at least 10 percent—possibly more.

The effect of the crystal-structure change in cobalt was even less than in iron. In this case, however, microscopic examination of the target (after use, of course) showed that the grain size was so small that several thousand crystallites

had been included in the surface area on which measurements were made. If these crystals were randomly oriented, the result of a structure change would be dependent on changes in the mean values of $|b|^2$, $|\Delta E|^2$, and γ_s, appropriately averaged over all directions. For the cobalt transformation, changes in the physical properties are very slight, and it is likely that the average $b^2/|\Delta E|^2\gamma_s$, which determines δ, would

be only negligibly affected. If, however, as is often the case in sheet metal, preferred orientation existed in the target, we must suppose that it was preserved in the higher temperature phase in such a way as to leave nearly unaltered the average orientation of the directions of high emission.

Mr. C. D. Hartman has been of great assistance in making the measurements.

Scattering of Thermal Neutrons by Crystals

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The effect of crystal interference on the scattering coefficient for thermal neutrons was investigated under different conditions. Calcite shows a large interference effect, the effective molecular cross section for scattering by a single crystal being about three times smaller than for a microcrystalline aggregate. It is also shown that a single crystal becomes more transparent when the velocity of the neutrons is decreased. Scattering has also been measured for bismuth and lead, where the difference between a single crystal and the microcrystalline material is less pronounced. The scattering in the latter case is the same as found for the liquid. Cooling the crystal to liquid nitrogen temperature does not produce any considerable change in scattering. The cross section for 90 percent Pb^{206} was measured and found to be the same as for the ordinary isotope mixture.

INTRODUCTION

RECENT experiments have shown that the scattering coefficient of a substance for thermal neutrons is not generally equal to the product of the scattering cross section per nucleus by the number of nuclei per unit volume. Particularly in the case of crystalline substances,[1] interference between the neutron de Broglie waves scattered by the atoms in the lattice may give considerably large effects, mostly in the sense of making the total "effective" cross section for a molecule of a compound smaller than it would be expected by adding the cross sections of the component atoms.

The aim of the present investigation was to study these phenomena more systematically than it had hitherto been done, in order to establish the relative importance of different

factors which determine the interference effects. The main points taken into consideration were: comparison of scattering in the solid and liquid state; dependence of the scattering coefficient on the size and perfection of the crystal, on its temperature, and on the velocity of the neutrons.

EXPERIMENTAL PROCEDURE

The experimental set-up essentially consisted of a slow neutron source of the "howitzer" type, and a BF_3 ionization chamber connected to a linear amplifier.

The neutron source was a stainless steel tube, 14 mm in diameter and 25 mm in length, filled with a mixture of 250 mg Ra (as sulfate) and 1.25 g Be powder.[2]

The well in the paraffin "howitzer" had a

[1] M. D. Whitaker and H. G. Beyer, Phys. Rev. **55** 1101 (1939); **55**, 1124 (1939); M. D. Whitaker, W. C. Bright and E. J. Murphy, Phys. Rev. **57**, 551 (1940).