EFFECTS OF CRYSTALLOGRAPHIC TRANSFORMATIONS
ON THE PHOTOELECTRIC EMISSION FROM URANIUM

by

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INTRODUCTION

In 1905, (14) and 1906, (15) Einstein applied the quantum theory to photoelectricity, obtaining his famous equation,

$$E = h\nu - \phi,$$

where E = kinetic energy of emitted electron,

   h = Plank's constant,

   ν = frequency of radiation incident upon surface, and

   ϕ = work function of the emitting surface.

Einstein's equation supplied a direct connection between the photoelectric effect and the quantum theory of radiation.

However, Einstein's equation neglects the energy of the electrons within the metal. A more accurate equation would be

$$E = h\nu + E_e - \phi,$$

where E_e is the surface directed kinetic energy of the electron within the metal before its excitation by a photon. Thus, classically, an electron would be emitted photoelectrically if

$$h\nu + E_e - \phi > 0.$$

In 1928, Sommerfeld (18) derived, by use of quantum statistics, an expression for the energy distribution of unbound electrons in metals by assuming the electrons behaved as a highly degenerate Fermi gas. These unbound electrons were assumed to be free of the crystal lattice (except for the potential barrier at the surface of the metal) and exchanged energy with each other by elastic collision. Sommerfeld's theory has been highly successful in explaining various physical properties of metals associated with the unbound electrons.

Fowler (16), using Sommerfeld's theory as a basis, developed a graphical method by which the work function of a metal can be determined from photoelectric data. Fowler assumed:

(1) Unbound electrons in metals have an energy distribution given by the theory of Sommerfeld.

(2) The transmission coefficient of the potential barrier at the surface of the metal is unity for electrons with energy greater than the barrier height and zero for electrons with energy less than the barrier height.

(3) The probability that an electron with energy E will interact with a photon of frequency γ is constant for all electron energies and radiation frequencies near the threshold for emission.

With these assumptions the photoelectric current per unit light intensity is given by:

$$i = \propto \int_{h\nu_o - h\nu}^{\infty} P(E_e) \ dE_e,$$

where i = photocurrent per unit light intensity,

$P(E_e)$ = Sommerfeld's distribution function for the number of electrons with surface directed energy between E_e and $E_e + dE_e$,

$\propto$ = constant of proportionality,

$h\nu_o = \phi$ = work function of the metal,

h = Plank's constant, and

ν = frequency of the incident radiation.

By integration of the preceding equation, Fowler obtained

$$\log(i/T^2) = B + F(x), \text{ where}$$

$x = \dfrac{h\gamma - h\gamma_o}{kT}$, k being Boltzman's constant,

i = photocurrent per unit light intensity,

T = absolute temperature in degrees Kelvin,

B = a constant which depends upon the density of unbound
electrons within the metal and upon the probability
of interaction between photons and electrons, and

F(x) = a certain transcendental function.

With this result Fowler suggested a graphical method for
obtaining the work function of a metal from experimental data
of emission per unit light intensity at various wave lengths
near the threshold frequency taken at some constant temperature.
His suggestion was this: If $\log(i/T^2)$ is plotted versus $\dfrac{h\gamma}{kT}$,
the result should be a curve of the same shape as the theoret-
ical curve of F(x) versus x. If the ordinate of the experi-
mental curve is raised by an amount B, and its abcissa shifted
by $\dfrac{h\gamma_o}{kT}$, the experimental curve should coincide with the theo-
retical curve. The amount by which the abcissa of the exper-
imental curve is shifted to bring it into coincidence with the
theoretical curve would then be the photoelectric work function
of the metal divided by the product of Boltzman's constant and
the absolute temperature.

However, Cardwell (6), (7), (8), (9), (10), (11), (12),
and others, using the method of Fowler to analyze data taken on

carefully outgassed metals which undergo allotropic crystal-
lographic transformations have found that the photoelectric
properties of these metals change significantly at crystal-
lographic and/or magnetic transformation temperatures.

Uranium is a metal that undergoes allotropic crystallo-
graphic changes at about $665^{\circ}C$ and $770^{\circ}C$. Below $665^{\circ}C$ the
crystal lattice is orthorhombic; between $665^{\circ}C$ and $770^{\circ}C$, te-
tragonal; and above $770^{\circ}C$, body centered cubic (Duwez, 13).
This thesis is primarily concerned with the changes, if any,
in the photoelectric emission from uranium with change in crys-
tal structure at the two transformation temperatures.

The Fowler theory and method of analyzing photoelectric
emission from metals, based on Sommerfeld's theory, does not
account for this effect; However, the Sommerfeld model as-
sumes that the unbound electrons in metals do not interact
with the crystal lattice. It is indicated that, because of
the above mentioned anomolous behavior, the Sommerfeld theory
is only approximately correct and that a more accurate model
which includes the interaction of electrons with the crystal
lattice is needed to describe electronic behavior in metals.

A second purpose of this thesis is to report on the high-
vacuum techniques utilized in this experiment. High-vacuum
technique is a valuable experimental tool and especially so in
photoelectricity, as results are highly dependent upon whether
the metallic surface is free of occluded gas. The techniques
recently developed by Alpert and others (1), (2), (3), (4), will

enable the author and other investigators to make subsequent photoelectric studies on uranium and other metals at pressures on the order of 10^{-10} mm of mercury and perhaps lower.

EXPERIMENTAL APPARATUS

The measurements of photoelectric emission from uranium were made on an integrated system of apparatus, the components of which were mounted under and upon a metal and transite vacuum table which was specially constructed for this purpose. The fore pump and oil diffusion pump were under the table as were the transformers to supply the current to heat the uranium specimen. Upon the table was that part of the vacuum system which was baked out by means of ovens placed over the system. This part included the experimental tube, the ion gauge, the Alpert-type high-vacuum valve and the copper foil trap. Also on the table were the source of monochromatic light and the various meters. A description of some of these components follows.

Experimental Tube

The glass experimental tube contained the uranium specimen, which was a ribbon of normal uranium metal approximately 0.03 mm thick, 4 mm wide, and 12 cm long, suspended in a loop from the Kovar-tungsten leads to which the specimen was spot

welded. The several specimens used were supplied by the Atomic
Energy Commission.

A molybdenum collecting cylinder surrounded the uranium
strip to catch the photoelectrons which were accelerated from
the uranium by a potential difference between the collector and
specimen of -135 volts. After being collected by the cylinder,
the photoelectrons passed through a current measuring device to
ground.

Radiation from the monochromator was focused upon the spec-
imen through a quartz window in the experimental tube and an
opening in the collecting cylinder. A pyrex window was located
on the opposite side of the experimental tube for observing the
specimen with an optical pyrometer through another opening in
the collecting cylinder. The cylinder could be rotated by
means of an external magnet so that the openings in the cylin-
der were out of allignment with the windows in order to prevent
evaporation of the uranium onto the windows while heating the
specimen to high temperatures during outgassing.

A guard ring was placed above the collecting cylinder so
that only those electrons emitted by the lower part of the spec-
imen were collected by the cylinder. The tube was enclosed in
a metal box for electrostatic shielding.

High Vacuum System

Using techniques recently developed by Alpert, et. al.,
pressures on the order of 10^{-10} mm of mercury were obtained.

An oil diffusion pump of the type GF-25W, manufactured by Distilation Products, Inc., was backed by a Welch Duo-seal mechanical pump. Dow-Corning 705 pumping oil was used. Pressures of 2×10^{-8} mm of mercury were consistently attained, after thorough bake-out of the vacuum system by use of the diffusion pump only.

A copper foil trap developed by Alpert (2) was used between the oil diffusion pump and the system to be evacuated to prevent contamination of the system by the diffusion pump oil.

An Alpert-type metal high-vacuum valve (1), (2) manufactured by the Granville-Phillips Company, but of lower minimum conductance than the Alpert valve (Bills and Allen, 4), was used to seal the system off from the diffusion pump in order to allow the ion gauge to further reduce the pressure within the system after the diffusion pump had reached its equilibrium pressure.

An Alpert ion gauge was used to measure the low pressures and also, as mentioned above, to evacuate the system beyond the range of the diffusion pump (1), (3). Previous ion gauges had a lower limit to the pressure which they could measure due to a residual current produced by the release of photo-electrons from the ion collector by the soft x-rays which were produced by the electron bombardment of the grid. The Alpert gauge extended the lower limit of ion gauges by using a fine wire for the collector and enclosing it within the grid, thereby reducing the solid angle subtended by the collector at the grid for the interception of x-rays produced at the grid.

In conjunction with the ion gauge an ion gauge power supply, constructed from instructions and a circiut diagram developed and furnished to the author by P. Malmberg and A. McCoubrey of the Westinghouse Research Laboratories, was used to regulate the emission current of the ion gauge and to furnish power for out-gassing the ionization gauge electrodes by electron bombardment.

Radiation Source

The source of ultraviolet light was a high-pressure mercury arc. Light from the arc was focused by a quartz lens onto the entrance slit of the Bausch and Lomb grating monochromator. A second quartz lens focused the emergent beam upon the uranium sample through the quartz window in the experimental tube. The wave lengths used were chosen from characteristic lines produced by a mercury arc.

Current Measurement

Collector current of the ion gauge was of the order of 10^{-11} amperes and the photoelectric emission current was of the order of 10^{-12} amperes. To measure these small currents a Keithley model 410 $\mu\mu$ ammeter was used. This instrument is a high imped-ance vacuum tube voltmeter that measures the voltage across self-contained standard resistors. The scale reads current directly and the instrument is accurate to within three percent. Teflon

insulation and electrostatic shielding was used for all circuits carrying these minute currents.

OUTGASSING PROCESS

The system was baked out at 420°C by means of ovens placed over that part of system to be evacuated to ultra-high vacuum. This process was necessary in order to remove the gases from the inner surface of the glass parts of the system.

The uranium filament was outgassed with a conduction current which was slowly increased to seven amperes, at which current the specimen was at an extreme red heat. It has been found that excessive evaporation is prevented by outgassing for long periods of time at the lower temperatures and increasing the temperature slowly.

The collecting cylinder was outgassed by heating it to high temperatures with a high-frequency induction heater.

EXPERIMENTAL PROCEDURE

After the high vacuum had been attained and outgassing of the filament and the collecting cylinder of the experimental tube achieved, monochromatic light of a given wave length was focused upon the specimen. The emission current was then measured at various values of the uranium filament conduction current. These measurements were taken while increasing and decreasing the filament current to check on the reproducibility of the data. The

current due to photoelectric emission was obtained by subtracting
the thermionic emission current from the total emission current
readings. A graph was then made of photoemission versus fila-
ment current at constant wave length.

EXPERIMENTAL RESULTS

Measurements were made using half a dozen wave lengths, but
those made first were prior to the achievement of desirable out-
gassing conditions and these measurements were not reproducible,
although the curves obtained from such measurements had the same
general shape, i. e., changes in emission occured at the same
heating currents, as those taken during the latter stages of the
experiment.

Figure 1 is a graph of photoemission versus filament current
for the 2352 A° and the 2302 A° lines of the mercury spectrum.

It will be noted that:

      (1) The data is reproducible.

      (2) There is a hysteresis in the curves.[1]

      (3) Sharp changes in photoemission occur at two
           places in the emission current versus heater
           current curves.[2]

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[1] This effect can be explained as being due to both the time
lag of temperature change behind filament current change, and
the time lag of crystallographic change behind the temperature
change.

[2] The specimen temperatures at these two filament currents are
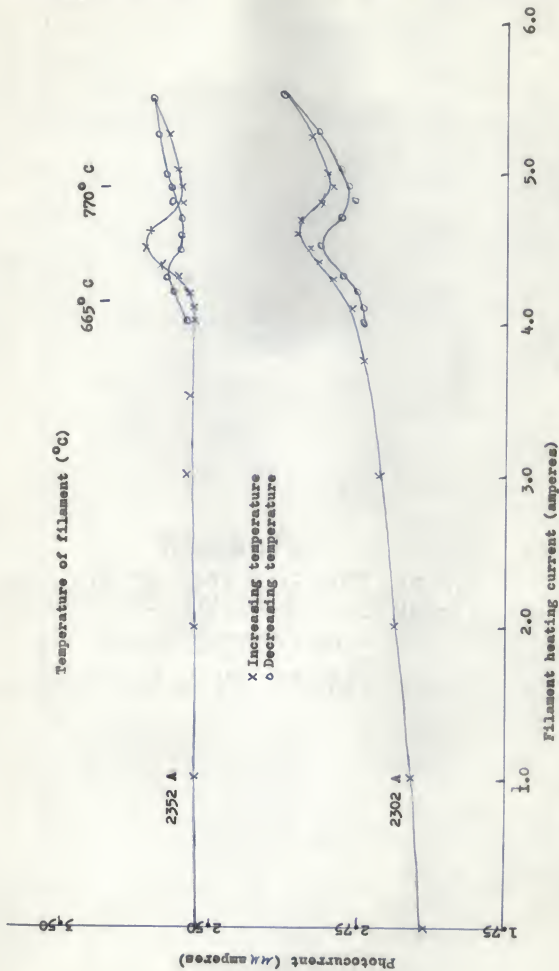indicated on the graph.

Figure 1. Photoemission from uranium as a function of temperature and filament current.

CONCLUSION

These measurements strongly indicate that the photoelectric emission from uranium changes markedly at the two transformation temperatures. The change in photocurrent with crystal structure could be due to a change in the work-function, a change in the reflectivity of the uranium, or a variation of the quantum efficiency with crystal structure, or some combination of all three.

Further experiment is needed to determine which of the three possibilities accounts for the phenomenon: Measurement of the reflectivity of uranium at various temperatures could be made; analysis of photoelectric data by the method of Fowler would ascertain whether the work function changes or whether there is a change in quantum efficiency with crystal structure, or both.

It was pointed out in the introduction to this thesis that taking into account the interaction of the electrons with the crystal lattice may be needed to explain this phenomenon. However, Callen (5) has indicated that electrostatic conditions at crystal surfaces is quite complicated due to the dependence on the crystal plane involved, exchange and correlation effects between the electrons, and impurities within the crystal lattice. How these affect photoemission is not well understood quantitatively. Further investigation is needed to resolve the problem.

ACKNOWLEDGMENT

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The theory of photoelectric emission from a metallic sur-
face is reviewed. It is pointed out that the theory due to
Einstein, Sommerfeld, Fowler, et. al., accounts for a smoothly
varying dependence upon temperature of photoemission from metals
and does not account for abrupt changes in photoemission exhib-
ited by various metals at crystallographic transformation temp-
eratures.

A description is given in some detail of the experimental
apparatus and the high-vacuum techniques employed.

Measurements were made of photoemission from uranium at
various temperatures at constant wave lengths. It was found
that photoemission changed markedly at approximately the two
temperatures at which uranium undergoes allotropic crystallo-
graphic transformations.

Possible effects causing the phenomenon are listed with
an indication of the subsequent experiments necessary to deter-
mine which effect is responsible. It is noted that taking into
account the interaction of the electrons with the crystal lat-
tice may be needed to explain changes in photoelectric emission
with crystallographic transformations.