

Photoelectric Properties of Natural Uranium and Changes Occurring at Crystallographic Transformations*

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Studies of the photoelectric properties of high-purity, carefully outgassed natural uranium were made through a wide temperature range, including the temperatures 938°K and 1043°K at which crystallographic transformations occur. Changes in the slope of the temperature-photoelectric current curves for various monochromatic radiations are presented. Analysis of the data at different temperatures by the method of Fowler indicates changes in both the surface work function and the combined number density of free electrons and transition probability factor at the allotropic transformation temperatures. The work function of "clean" uranium was found to be 3.47 ev, 3.52 ev, and 3.39 ev, respectively, for orthorhombic (below 938°K), tetragonal (938°K to 1043°K) and body-centered cubic (above 1043°K) uranium.

INTRODUCTION

ANOMALIES associated with crystallographic and/or magnetic transformation temperatures have been reported in the photoelectric properties of iron,^{1,2} tin,³ cobalt,^{4,5} and nickel.⁶ Analogous anomalies have been found to exist in the thermionic emission from iron,^{1,7} cobalt,^{4,5} and nickel.⁶ Attempts at a theoretical explanation of these anomalies⁸⁻¹³ make it obvious that data are needed on more of the nonmagnetic metals which undergo crystallographic transformations. This paper is concerned with the photoelectric properties on one such metal, natural uranium, at temperatures ranging from 300° to 1065°K and the changes exhibited in these properties at the two crystallographic transformation temperatures, 938° and 1043°K. Below 938°K the crystal structure of uranium is orthorhombic; between 938° and 1043°K, tetragonal; and above 1043°K, body-centered cubic.¹⁴⁻¹⁸

APPARATUS AND METHOD

The experimental tube consisted of a glass envelope enclosing a molybdenum collecting cylinder. The uranium specimen (purity 99.8% or higher) which, in

every case, was approximately 0.03 mm thick, 4 mm wide, and 7 cm long, was suspended in the form of a loop in the collecting cylinder. Iron tabs on the collecting cylinder made possible the rotation of the cylinder by means of an external magnet. Thus, evaporation of uranium onto the quartz window of the glass envelope could be prevented during the long outgassing periods.

Photoelectric currents were produced by the radiation from a quartz-enclosed mercury arc dispersed by a Bausch & Lomb grating monochromator. A quartz lens was used to focus the radiation, through a thin quartz window and a hole in the collecting cylinder, onto the uranium specimen. Relative intensities of the spectral lines were obtained by use of a vacuum thermopile designed for use with the Bausch & Lomb grating monochromator. Photoelectric currents were measured with a Keithley micromicroammeter. Proper electrostatic shielding was provided for the experimental tube and the circuit carrying the emission current.

Specimen temperatures were determined from a curve of temperature versus heating current through the particular specimen. To obtain data for this curve, a resistance versus specimen heating current curve was drawn. It was assumed that the marked changes in the slope of this curve occurred at the two known crystallographic transformation temperatures. These temperatures, along with room temperature, made available three points for a temperature versus specimen heating current curve from which temperatures could be read directly.

Before sealing the uranium sample in the experimental tube, the entire vacuum system, including the experimental tube, was filled with argon. This allowed the glass blowing to be done while the sample was in an argon atmosphere, and also allowed the sample to be in a predominantly argon atmosphere as the evacuation of the experimental tube proceeded.

The vacuum system used in connection with the experimental tube, consisted of a three-stage, silicone fluid, water-cooled diffusion pump, a copper-foil trap (in some cases this trap replaced by the liquid nitrogen trap), an Alpert ionization gage, an Alpert-type ultra-high vacuum valve, and a mechanical pump. With this

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¹ A. B. Cardwell, *Proc. Natl. Acad. Sci. U. S. A.* **14**, 439, 445 (1928).

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³ A. Goetz, *Phys. Rev.* **33**, 373, 385 (1929).

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⁵ A. B. Cardwell, *Phys. Rev.* **38**, 2033, 2040 (1931).

⁶ A. B. Cardwell, *Phys. Rev.* **76**, 125, 127 (1949).

⁷ H. B. Wahlen, *Phys. Rev.* **61**, 509, 512 (1942).

⁸ A. V. Sokolov and A. Z. Veksler, *Doklady Akad. Nauk SSSR* **81**, 27, 40 (1951).

⁹ A. V. Sokolov, *Zhur. Eksp. i. Teoret. Fiz.* **25**, 215, 224 (1953).

¹⁰ A. Z. Veksler, *Zhur. Eksp. i. Teoret. Fiz.* **29**, 201, 208 (1955).

¹¹ S. V. Vonsovskii, A. V. Sokolov, and A. Z. Veksler, *Uspekhi Fiz. Nauk* **56**, 477, 530 (1955).

¹² S. V. Vonsovskii and A. V. Sokolov, *Doklady Akad. Nauk SSSR* **76**, 197, 209 (1951).

¹³ E. Dayhoff, *Bull. Am. Phys. Soc.* **4**, 240 (1959).

¹⁴ J. Chipman, U. S. Atomic Energy Commission Publication MDDC (unpublished).

¹⁵ P. Duwez, *J. Appl. Phys.* **24**, 152, 156 (1953).

¹⁶ C. W. Jacob and B. E. Warren, *J. Am. Chem. Soc.* **59**, 2588, 2591 (1937).

¹⁷ C. W. Tucker, Jr., P. Senio, J. Thewlis, and N. Steeple, *Acta Cryst.* **9**, 472, 475 (1956).

¹⁸ A. S. Wilson and R. W. Rundle, *Acta Cryst.* **2**, 148, 150 (1949).

system, using the ion gauge as a pump, final pressures of the order of 10^{-10} (or better) mm of mercury were obtained.

The outgassing process consisted of the following steps: The Alpert valve, gage, copper-foil trap, and experimental tube were baked several times at 450°C in an electric oven. The molybdenum cylinder was heated by induction to red heat at intervals over a period of about two weeks. The heating current through the sample was slowly increased until the specimen was at about 1250°K . The total time in which current passed through the sample for the purpose of outgassing was about 1000 hr in every case. Heat treatment of this nature produced highly reflecting uranium samples which yielded stable, reproducible results. Further heat treatment, including flashing at higher temperatures, produced no change in photoelectric properties of the surface.

RESULTS

Figure 1 is a typical set of curves showing the variation of the photoelectric current per unit light intensity with temperatures for various wavelengths. Marked changes in the curve occur at the two transformation temperatures. In general, measurements were made over the entire temperature range (300 to 1065°K) with both increasing and decreasing temperature. No difference was detected between curves for increasing and decreasing temperatures. At the higher temperatures (above 950°K) the photoelectric currents were obtained by subtracting the thermionic currents from the total emission currents. Above 1065°K thermionic currents were so great that photocurrent measurements were masked. The interval of confidence, as indicated on the graph by the diameter of the circles, is an esti-

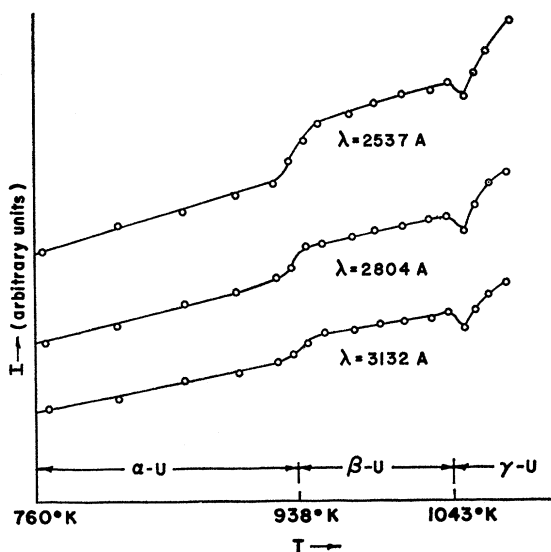


FIG. 1. Photoelectric current per unit light intensity as a function of temperature for various wavelengths.

mate based upon the significant figures to which the microammeter can be read.

Data were also taken for Fowler plots in order to determine the work functions(s). These measurements were made at 17 fairly uniformly spaced temperatures between 300° and 1065°K inclusive. Each determination consisted of measuring at a constant specimen temperature the photoelectric current per unit light intensity for each of the five chosen wavelengths. Fowler plots were then made from these data.

Figure 2 shows typical Fowler plots for each of the three crystalline forms, α , β , and γ . Table I shows the compiled results obtained from the Fowler plots on the specimens studied. Although the determinations were made throughout the temperature spectrum indicated, the vertical shifts and workfunctions of each crystal structure type showed no measurable variation within the temperature range of its existence, and hence the data in Table I are a compilation of the sixteen or so determinations made upon each crystal type. The interval of confidence given is the standard deviation of each group of determinations.

Since only changes in the vertical shifts of the origin of the curve are significant and since the vertical shifts resulting from the analysis of data from different samples are not in general the same, although the changes in the vertical shift for various specimens were the same, the vertical shift for the orthorhombic structure is arbitrarily taken as C . That of the other two structures then become C plus or minus the change in the vertical shift from that obtained for the orthorhombic crystal structure of the same specimen.

The analysis indicates changes in both the work function and the combined free-electron density and the intrinsic probability factor. Work is now being done on the Hall coefficient of uranium to determine if its value changes with crystal structure. This may shed some light on the magnitudes of the free electron density change in uranium at crystallographic transformation temperatures.

DISCUSSION OF RESULTS

These results give additional information on the complicated and interrelated changes which occur in

TABLE I. Work functions, vertical shifts, and changes in vertical shifts for uranium.

Crystal structure	Work function (electron volts)	Vertical shift in origin
Orthorhombic (300° to 938°K)	3.47 ± 0.01	C
Tetragonal (938° to 1043°K)	3.52 ± 0.01	$C + 0.12$
Body-centered cubic (1043° to 1065°K)	3.39 ± 0.01	$C - 0.08$

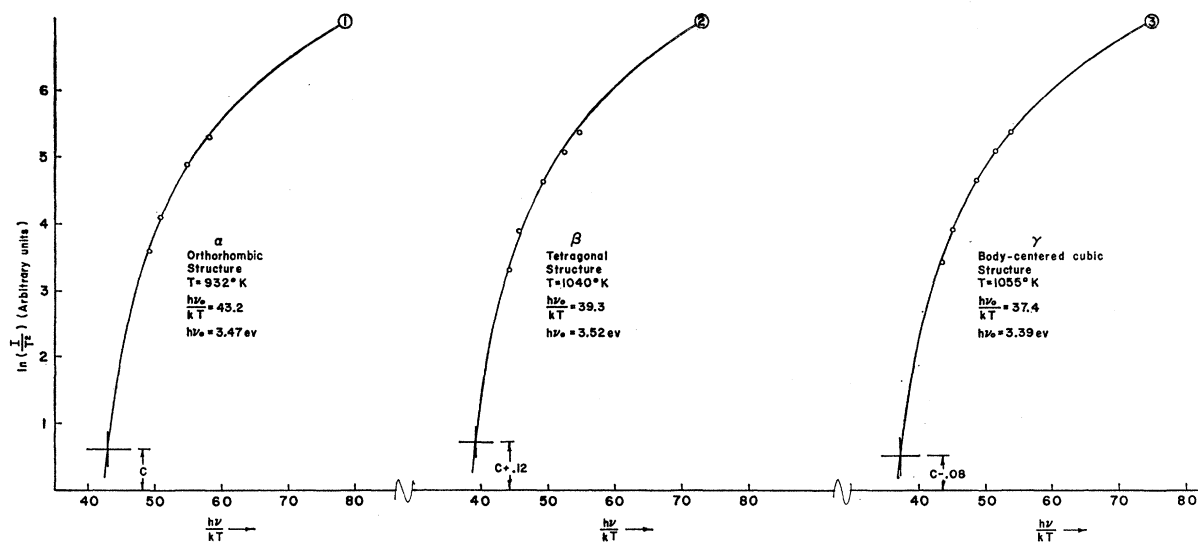


FIG. 2. Analysis of photoelectric observations by Fowler's method.

both the surface work function and the combined number density of free electrons and transition probability factor in metals as they pass through allotropic transformation temperatures.

The only photoelectric work on uranium, other than that reported in this article, is that done by Rentschler, Henry, and Smith¹⁹ who reported a value of 3.63 eV for the work function at temperatures which indicate that they worked with α uranium. This is to be compared with the value of 3.47 eV reported in this paper. Since their work was done under poor vacuum conditions using sputtered uranium on tungsten, it is not surprising that their reported work function is higher than the one given here. Their higher value, along with their poor vacuum conditions, suggests that their value is characteristic of a sample not well outgassed. In the present work it was found that as outgassing progressed, the work function decreased from near 4.0 eV to the final stable value of 3.47 eV for α uranium.

It is interesting to compare the values of the work function determined photoelectrically in this work with those obtained thermionically by others. Dushman,²⁰ Hole and Wright,²¹ and Rauh²² have made thermionic measurements on uranium, reporting 3.28, 3.27, and 3.47 eV, respectively, as the thermionic work function. Since, with the possible exception of the work of Hole and Wright, measurements were made above 1043°K, these values should be compared with the value of 3.39 eV for γ uranium in Table I.

Dushman's work was done on samples sputtered onto tungsten under relatively poor vacuum conditions.

Dushman states that he is not sure that the tungsten surface was "completely covered with a layer of one atom deep of the uranium." Because of this and serious doubt concerning the temperature scale used, little significance can be assigned to the value reported by Dushman.

The work of Hole and Wright was done in a vacuum with pressures more than 100 times greater than those used in the present work. Their outgassing processes were not as severe as those utilized in the present work. The value of the surface emissivity, 0.51, determined and used by them for optical pyrometer scale corrections is apparently too high and therefore may indicate the presence of an extraneous surface layer. Rauh, working under much better vacuum procedures, has given a value of 0.265 for the emissivity of clean uranium. However, Rauh's determination was made on a sputtered sample so thin as to be transparent. At any rate, the wide discrepancy in the emissivity values raises serious questions about the value of the work function given by Hole and Wright and indicates that it should be higher. It is interesting to note that Hole and Wright stated that some of their curves had two slopes. This suggests that they were at times working somewhat below the 1043°K transition temperature. Since neither data nor curves are published, this point cannot be checked easily.

Rauh's determinations were made on a layer of uranium, approximately 20 molecules in thickness, evaporated onto tungsten. In general, his vacuum and outgassing conditions were excellent. While his value is only 2.3% higher than that reported in this work, it is outside the range of experimental error. One possible explanation for the discrepancy might be a possible difference in the amount of impurities in the samples used by Rauh and those used in the present work. There

¹⁹ H. C. Rentschler, D. E. Henry, and K. O. Smith, *Rev. Sci. Instr.* **3**, 794, 802 (1932).

²⁰ S. Dushman, *Phys. Rev.* **21**, 623, 636 (1923).

²¹ W. L. Hole and R. W. Wright, *Phys. Rev.* **56**, 785, 787 (1939).

²² E. G. Rauh, Argonne National Laboratory Report ANL-5534 (unpublished).

also is the possibility that Rauh's method of deposition produced a preferred orientation in the sample as contrasted to a polycrystalline surface. A more reasonable explanation would be based on the assumption that the lattice spacing of the body-centered cubic uranium films deposited on the body-centered cubic tungsten is smaller than that for the natural uranium metal. This would be consistent with observations made on other metals. The lattice parameter, a , for body-centered cubic uranium is

3.55 Å²³; the same parameter for body-centered cubic tungsten is 3.16 Å. It therefore seems possible that Rauh's value, 3.47 eV, is the work function for clean body-centered cubic uranium with an artificially compressed lattice spacing, while the value of 3.39 eV reported here is the work function for clean, normal, body-centered cubic uranium.

²³ P. Chiotti, H. Klapfer, and W. White, *Am. Soc. Metals* **51**, 231, 236 (1958).

Superconducting Critical Field of Single-Crystal Mo₃Re

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Critical field measurements were performed on a cylindrical rod of single-crystal Mo₃Re. The isothermal, magnetic transitions were extremely sharp and reversible, indicating that the specimen was approaching nearly ideal properties. The principal data are: $T_c = 9.80^\circ\text{K}$, $H_0 = 530$ gauss, $(dH_c/dT)_{T=T_c} = -114$ gauss/deg. The deviation from parabolic behavior $D(t)$ indicated a positive maximum value of 0.065. On the basis of this present work, we suggest a possible correlation between the thermodynamic critical field and the "filamentary" critical field noted for the high-field superconducting materials.

THE superconductivity of the refractory metal alloy, Mo₃Re, was first reported by Hulm.¹ Subsequent work by Kunzler *et al.*² showed that this material could be drawn into wire suitable for fabricating superconducting solenoids. It was further shown that such wire, if cold worked as much as possible, remained superconducting in magnetic fields up to about 15 kilogauss. It is of considerable interest to inquire how this field for the destruction of supercurrents, which we suggest be called the Kunzler field H_K is related to the true thermodynamic critical field H_c . Since H_c values are not available for Mo₃Re, we decided to investigate these with the aid of single crystals.

Critical field measurements were performed on a cylindrical rod of single crystal Mo₃Re, 180 mm by 8 mm, prepared by electron beam melting and repeated zone refining. Magnetic induction versus magnetic field plots were taken at various temperatures using a ballistic induction technique.³ Temperatures were determined above 4.2°K with a constant-volume gas thermometer⁴ and below 4.2°K using the helium vapor pressure scale. The isothermal, magnetic transitions were extremely sharp and reversible, indicating that the specimen was approaching nearly ideal properties as is usually found only in high-purity, "soft" superconductors.

Figure 1 shows the threshold magnetic field H_c versus temperature representing the equilibrium boundary be-

tween the normal and superconducting states. The principal data are:

$$T_c = 9.80^\circ\text{K},$$

$$H_0 = 530 \text{ gauss } (T=0),$$

$$dH_c/dT = -114 \text{ gauss/deg } (T=T_c).$$

The deviation from parabolic behavior $D(t)$ calculated from the relation

$$D(t) = (H_c/H_0) - [1 - (T/T_c)^2],$$

indicated a positive maximum value of 0.065.

The coefficient of the electronic specific heat in the normal state, γ , can be approximately calculated from the relation

$$V(H_0)^2/8\pi = \frac{1}{2}\gamma T_c^2, \quad (1)$$

where V is the atomic volume. Using $V = 9.252 \text{ cm}^3/\text{mole}$ (private communication from A. Taylor), we obtain a γ value of 0.43 millijoules per mole deg². This value of γ is close to the values for either Mo or Re, and suggests that for Mo₃Re the density of states lies at a minimum in the d -band density of states versus energy curve. Possibly, in the above calculation, H_0 and subsequently γ should be adjusted as suggested by Goodman.⁵ Current calorimetric measurements, however, should indicate whether this correction is necessary.

In Table I, the thermodynamic, critical field value obtained for Mo₃Re in the present work is compared with the Kunzler field for this material. A similar

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³ J. K. Hulm and B. B. Goodman, *Phys. Rev.* **106**, 659 (1957).

⁴ J. K. Hulm and R. D. Blaugher, *Cryogenics* **1**, 229 (1961).

⁵ B. B. Goodman, *Phys. Rev. Letters* **6**, 597 (1961).