Emissive and Thermionic Characteristics of Uranium

W. L. HOLE* AND R. W. WRIGHT
University of Wisconsin, Madison, Wisconsin

(Received August 24, 1939)

Certain properties of clean uranium in vacuum have been investigated. The following values were found: for emissivity below the melting point ($\lambda=0.67\mu$), 0.51; for thermionic work function, 3.27 ± 0.05 volts, with a Richardson A of about 6; for melting point, 1700 ± 25°C; for average coefficient of linear expansion, 25°C to 1000°C, 4×10^{-5}.

INTRODUCTION

BY reason of its unique position in the periodic table of the elements, the physical properties of uranium are of peculiar interest. Enough of the element in metallic form was procured to permit observation of certain characteristics hitherto unreported.

A flat strip of uranium long enough to provide several filaments was obtained from A. D. Mackay. It was about 3 mm wide and 0.1 mm thick. These dimensions, however, were decidedly irregular. Another specimen, an oval rod about 16 cm long, was obtained through the kindness of Dr. H. C. Rentschler, of the Westinghouse Company. Its extreme diameters were 0.80 and 0.95 mm long, and its cross section was quite uniform. The degree of purity of neither sample is accurately known. The surfaces of both were initially covered with oxide, which readily forms when the metal is exposed to the atmosphere. Indeed, small pieces of uranium may be ignited by a match flame, burning brilliantly in air.

APPARATUS AND METHODS

Metallic uranium is rather hard and brittle at room temperature. Its high chemical activity precludes annealing in any of the common gases. Annealing in vacuum was found to improve its malleability only slightly. It was therefore necessary to make a blackbody for emissivity measurements of some other material. A hole 1/64-inch in diameter was drilled at the middle of a hollow columbium cylinder about 6 cm long and 3 mm in diameter. Above and below this opening patches of uranium about 1 mm square were spot-welded and filed thin. The cylinder, mounted in vacuum on a tungsten-Pyrex seal, was heated electrically. A Pyrex window for pyrometer observations was sealed in the tube. From the true temperature in the hole and the apparent temperature of the uranium patches the emissivity was calculated.

The thermionic tubes were of customary design. Filaments cut from the flat strip were hung by their ends as open loops. The oval rod, left straight, was mounted in a vertical position. Tungsten-Pyrex seals served as supports and heating current leads. Molybdenum collecting cylinders with insulated guard rings, outgassed before assembling the tubes, were afterward heated again by an induction furnace. Pyrometer windows in the cylinders were provided with magnetically operated shutters. Liquid-air traps were inserted between the tubes and any source of vapors. Outgassing periods up to 1000 hours gave final pressures of the order of 10^{-8} mm of Hg. Thermionic currents were measured with a high sensitivity Leeds and Northrup galvanometer.

In view of the uncertainties in published values[1] it was decided to make an approximate determination of the melting point. Curved segments were cut from the edges of a piece of the flat uranium strip so that the cross section at the thinnest point was about a third of its original value. In order to minimize gravitational effects a length of only 8 mm was supported horizontally on heavy vertical current leads. The strip was heated in vacuum until the thin portion melted. Its temperature was meanwhile followed continuously with a pyrometer.

The rough edges of one of the flat thermionic filaments were utilized for an approximate measurement of the coefficient of linear ex-

* Now at Elmhurst College, Elmhurst, Illinois.

[1] Cf. J. W. Mellor, *Treatise on Inorganic and Theoretical Chemistry* (Longmans, 1932), Vol. XII, p. 15.

pansion. Two notches were visible through the pyrometer window. The distance between them was measured with a comparator, at room temperature and at several temperatures in the pyrometer range. From these data the coefficient was calculated.

Discussion and Results

Clean uranium has a bright metallic luster similar to that of iron. This state was attained only when the vacuum system was thoroughly baked and flamed before the prolonged direct heating of the filament. The hot metal is reported to decompose water vapor. The presence of water from the flame used in sealing tubes together resulted in the appearance of a heavy oxide coating on samples initially bright, even at room temperature. Although no compound with hydrogen has been reported, uranium occludes considerable quantities of the gas. Heating in dry hydrogen was found to result in incomplete reduction of the oxide coating.

The non-uniformities of the flat specimens led at first to frequent hot spots and burning out of filaments. Rolling after annealing in vacuum improved the condition to some extent, although the edges cracked badly during rolling. It also became obvious that the melting point was somewhat lower than had been anticipated. Filaments always burned out near an end of the loop, appearing to soften at high temperatures and pull apart under their own weight. In many cases a sizable bead of metal formed on the lower lip of the melted aperture. No trace of vaporized metal was observable in any case.

Filaments warped, stretched and twisted in remarkable fashion during treatment, especially upon frequent heating and cooling. 12 cm of the oval rod stretched nearly 8 mm, or 6.5 percent, during thermionic study. The coefficient of linear expansion appears to have an abnormally high value (see below). The striking recalescence observed upon rapid heating or cooling has already been reported.[2] An x-ray study suggested by these phenomena is still in progress. It is hoped that a report may be published at a later date.

The temperature of the emissivity cylinder was increased, after preliminary outgassing, until one of the uranium patches softened and spread. This was done to insure good thermal contact and to minimize thermal gradient along the cylinder. To prevent further spread and possible alloying, readings were immediately taken on this patch at several lower temperatures. The average value found for the emissivity, at an effective wave-length of 0.67μ, was 0.51. This checks well with a value reported by Burgess and Waltenburg[3] for a similar method. Using a micro-sample fused on a Pt filament in hydrogen they obtained the value 0.55 at a wave-length of 0.65μ. They also indicate large changes with wave-length, and above the melting point.

Thermionic data were obtained from two flat filaments and from the oval rod. Currents of from 10^{-8} to 10^{-6} ampere were measured at temperatures between 950°K and 1300°K. During early stages of outgassing the curves of $\log I/T^2$ *vs.* $1/T$ often consisted of two portions with different slopes. This effect disappeared as heating was continued. Extreme values found for the work function during early stages were 3.15 and 3.60 volts. General progress with outgassing was from high to low values. The oval filament heated much more uniformly than the irregular flat filaments. It also exhibited satisfactory saturation at a much lower accelerating potential. Data from it have accordingly been more heavily weighted in arriving at the value, 3.27 ± 0.05 volts, for the thermionic work function of clean uranium. The value for the constant A of Richardson's equation also varied with the treatment of the specimen. Emitting areas were only roughly calculated. The final indicated value of about 6 is therefore only approximate.

In burning out the narrow strip for a melting point determination the final temperature rise, fuse-like, was uncontrollable and somewhat rapid. Fusion occurred just after the continuously variable pyrometer rheostat had reached the end of its range, and before a resetting could be made. Since the method is not one of precision, a repetition of the experiment was not considered worthwhile. However, our estimated value of 1700 ± 25°C for the melting point of uranium in

[2] W. L. Hole, R. Wright and H. B. Wahlin, Phys. Rev. **53**, 768 (1938).

[3] G. K. Burgess and R. G. Waltenburg, Bull. Nat. Bur. Stand. **11**, 591 (1915).

vacuum is considered more reliable than any value previously reported.

In measuring coefficient of linear expansion the total length observable with the comparator was only about 4 mm. Temperature measurements could be made only at room temperature and in the pyrometer range. Transition points, if they exist, lie between these limits. Repeated readings were not satisfactorily consistent. Doubtless the peculiar properties of uranium described at the beginning of this section partially account for the fact. The average value obtained for the coefficient of linear expansion over the range of 25°C to 1000°C is 4×10^{-5}, which is exceptionally large. No other value has appeared in the literature.

ACKNOWLEDGMENTS

Gladly is our indebtedness acknowledged to Dr. H. C. Rentschler, for providing one of the specimens; to the Wisconsin Alumni Research Foundation, for a grant in partial support of the project; and to Dr. H. B. Wahlin, for essential cooperation and assistance continued throughout the course of the experiments.

OCTOBER 15, 1939 PHYSICAL REVIEW VOLUME 56

Electronic Energy Bands in Metallic Tungsten[1]

MILLARD F. MANNING,* *University of Pittsburgh, Pittsburgh, Pennsylvania*

AND

MARVIN I. CHODOROW, *Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received June 21, 1939)

Calculations of the electronic energy bands in metallic tungsten are carried out by the Wigner-Seitz-Slater method. All numerical integrations were carried out on the M. I. T. differential analyzer. It is found that the *d* band is broken up into five sub-bands. Some of these *d* bands are found to be about fifteen electron volts in width. One is about two electron volts in width. The occupied energy range extends about five electron volts. The *s* band starts at a higher energy than the *d* bands and is occupied by much less than one electron per atom at the equilibrium interatomic distance. From the results of a previous paper, curves of E *vs.* k are plotted for the principal directions of propagation. From these, curves of the number of energy levels per unit energy range were determined by numerical and graphical methods which are described in an appendix. It is assumed that the $n(E)$ curve for tantalum is not greatly different from that for tungsten except that there is one less electron per atom. From the $n(E)$ curves the electronic contribution to the specific heat is calculated for the two metals and the results found to be in good agreement with the excess specific heat at high temperatures for both metals. The computed value does not agree with low temperature data on tantalum. There are no low temperature data for tungsten. Qualitative discussions of the differences in electrical resistance, temperature coefficient of resistance, and thermoelectric power of the two metals are given. The contribution of exchange effects to the paramagnetic susceptibility is treated by a rough model and it is shown that the assumption of the same value of the exchange integral for both metals gives satisfactory agreement with observed data.

CALCULATIONS of the electronic energy bands in solids have been carried out by either the Wigner-Seitz cellular method or by Slater's modification of that method for monovalent metals, for calcium, and for a number of insulators.[2,3] No calculations by either of these methods have been reported for any transition metals, although some general characteristics have been discussed by Mott[4,5,6] in a series of

[1] A preliminary report of this work was presented at the Washington Meeting of the American Physical Society in April, 1938. Phys. Rev. **53**, 673 (1938).

* This work was started at M. I. T. and some of the senior author's part was done while he was at the University of Toledo, Toledo, Ohio.

[2] Na: E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934). Cu: H. M. Kritter, Phys. Rev. **48**, 664 (1935). Li: F. Seitz, Phys. Rev. **47**, 400 (1935); J. Millman, Phys. Rev. **47**, 286 (1935). Ca: M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937). C: G. E. Kimball, J. Chem. Phys. **3**, 560 (1935); F. Hund, Physik. Zeits. **36**, 888 (1935). C *et al.*: F. Hund and B. Mrowka, Ber. d. Sachs. Akad. d. Wiss. **87**, 185, 325 (1935). LiF: D. H. Ewing and F. Seitz, Phys. Rev. **50**, 760 (1936). NaCl: W. Shockley, Phys. Rev. **50**, 754 (1936).

[3] J. C. Slater, Phys. Rev. **45**, 794 (1934).

[4] N. F. Mott, Proc. Phys. Soc. **47**, 571 (1935).

[5] N. F. Mott, Proc. Roy. Soc. **A153**, 699 (1936).

[6] N. F. Mott, Proc. Roy. Soc. **A156**, 368 (1936).