

Photoelectric Studies of Iron*

ALVIN B. CARDWELL
 Kansas State College, Manhattan, Kansas
 (Received June 15, 1953)

Studies of the photoelectric properties of spectroscopically pure, carefully outgassed iron were made through a wide temperature range, including the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformation points. Interesting changes in the slope of the temperature-photoelectric current curves for the various monochromatic radiations are shown. Analyses of the data by Fowler's method at different temperatures indicate that the change in photoelectric sensitivity, to be associated with the allotropic states of iron, is explainable more on a change in the number density of free electrons and the transition-probability factor than on a change in the surface work function. The work function of iron at room temperature was found to be 4.70 electron-volts. The variation of the work function for the three allotropic forms α , β , and γ is only 0.10 electron-volt.

I. INTRODUCTION

INTERESTING changes, associated with crystallographic and/or magnetic transformation temperatures, have been observed in the photoelectric and thermionic properties of several metals.¹⁻⁵ This paper is a report on the photoelectric properties of iron at temperatures ranging from 300°K to 1243°K. Thus, the changes associated with the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions are observed.

II. APPARATUS AND METHOD

The experimental tube was essentially like that used by the author in studies on tantalum⁶ and nickel.⁵ The spectroscopically pure iron from which the specimens were fabricated was obtained from Adam Hilgar. The specimen, which in every case was 0.03 millimeter thick, 4 millimeters wide, and 14 centimeters long, was suspended in the form of a loop in a molybdenum collecting cylinder. Iron tabs on the collecting cylinder made possible the rotation of the cylinder by means of an external magnetic field. Thus, the evaporation of iron onto the windows of the glass envelope could be prevented during long outgassing periods.

Photoelectric currents were produced by the radiation from a quartz-enclosed mercury arc dispersed by a Bausch and Lomb quartz monochromator. A quartz lens was used to focus the radiation, through a thin quartz window and a hole in the collecting cylinder, onto the iron specimen. Relative intensities of the spectral lines were determined by use of an eight-junction bismuth-silver vacuum thermopile.

Photoelectric currents were determined by measuring the potential drop across a fixed high resistor. A circuit utilizing a Western Electric D-96475 tube was used for this measurement. Proper electrostatic shielding was provided for the experimental and electrometer tubes.

* This work was generously supported by a Frederick Cottrell grant from the Research Corporation.

¹ Alvin B. Cardwell, Proc. Natl. Acad. Sci. U. S. 14, 438 (1928).

² A. Goetz, Phys. Rev. 33, 373 (1929).

³ Alvin B. Cardwell, Phys. Rev. 38, 2032 (1931).

⁴ H. B. Wahlin, Phys. Rev. 61, 509 (1942).

⁵ Alvin B. Cardwell, Phys. Rev. 76, 125 (1949).

⁶ Alvin B. Cardwell, Phys. Rev. 38, 2041 (1931).

Temperatures in the upper range were determined by an optical pyrometer of the disappearing filament type focused onto the specimen through a thin optically flat Pyrex window and a hole in the collecting cylinder. Temperature observations were corrected for emissivity according to the data of Wahlin and Wright.⁷ Lower temperatures were determined graphically by interpolation between room temperature and temperatures in the optical pyrometer range. A curve of temperature versus heating current through the specimen made this possible.

The vacuum system used in connection with the experimental tube consisted of a three-stage silicone fluid water-cooled diffusion pump, a liquid-air trap, a type VG-1A ionization manometer, and a mechanical pump. With this system final pressures of the order of 10^{-8} millimeter of mercury were obtained.

Each sample studied was subjected to essentially the same long tedious outgassing process. First, the entire tube and ionization manometer were baked at 500°C

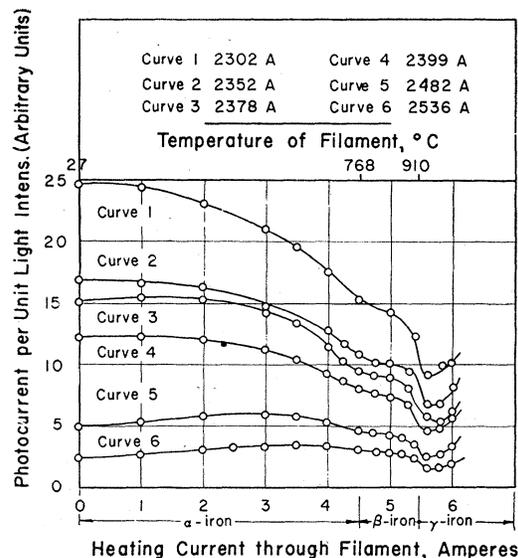


FIG. 1. Variation of photocurrent from iron with temperature.

⁷ H. B. Wahlin and R. Wright, J. Appl. Phys. 13, 40 (1942).

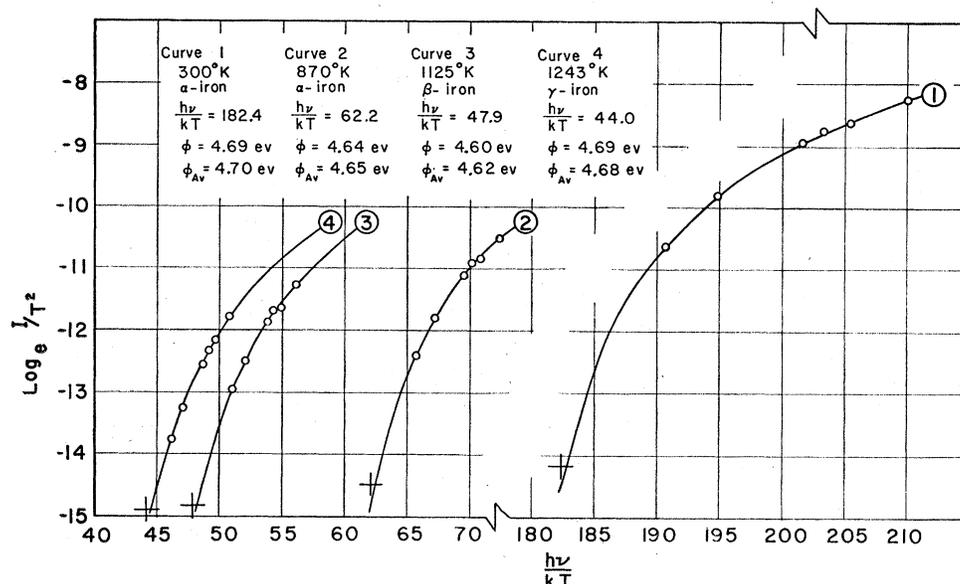


FIG. 2. Analysis of photoelectric observations by Fowler's method.

for several days. During the latter part of this period the specimen was heated by a conduction current to a temperature of approximately 800°C. Following this the iron sample was heated at temperatures which were slowly increased to 1200°C. Periodically the collecting cylinder was heated by high-frequency induction to a temperature of about 900°C. Heat treatment of this nature for 40 to 60 days produced iron samples which yielded stable reproducible results. It is therefore hoped that data presented below are characteristic of pure gas-free iron.

III. RESULTS

The variation of the photoelectric current per unit light intensity with temperature for various monochromatic wavelengths is shown in Fig. 1. As it was impossible to use the optical pyrometer for determining temperatures below 875°C, the photocurrent in Fig. 1 has been plotted as a function of the heating current through the iron specimen at the time the observation was made. The temperatures corresponding to three heating currents are indicated in the figure. Because of the large background thermionic emission, measurements of the photocurrent at temperatures higher than those indicated in the curves have not been made.

It is seen from Fig. 1 that the variation of the photocurrent with temperature for each of the monochromatic radiations is quite complex and does not follow the pattern required for a given metal by Fowler's theory.⁸ It seems natural to consider associating this unique variation in photoelectric sensitivity with the transition from α to β iron at 768°C (Curie temperature), which involves a slight increase in the edge of unit cube but no change in crystal form, and the change at 910°C,

⁸ R. H. Fowler, Phys. Rev. 38, 45 (1931).

where the crystal structure changes from a body-centered cubic to a face-centered cubic type. Such an association is reasonable in view of the discontinuities of electrical conductivity, thermal expansion, and secondary emission observed by Masumoto⁹ and Hayakawa¹⁰ at allotropic points in both nickel and iron. Changes analogous to those reported in this paper have been observed in the thermionic and/or photoelectric properties of tin,² cobalt,³ and nickel⁵ as these metals pass through temperatures at which allotropic changes occur.

Further interesting studies of these data may be made from their analysis by the Fowler method.⁸ For any fixed temperature one is justified in making Fowler plots, and such sample plots for four temperatures are shown in Fig. 2. The choice of these temperatures provides for comparison two curves for α iron, one for β iron, and one for γ iron. The origin of the theoretical curve required to bring the experimental curve into coincidence with the theoretical curve is indicated by the large plus sign in each case. The work functions Φ shown on the figure were computed from the horizontal shifts $h\nu/kT$ required to bring the experimental and theoretical curves into coincidence. The average value of the work function Φ_{Av} , determined from 32 runs at each temperature on 4 different samples, is also shown in each case.

The percentage change in the value of the work function for iron in the α , β , and γ forms is small and only partially accounts for the change in the photoelectric sensitivity. The value 4.70 ± 0.01 (standard deviation) electron volts for the photoelectric work function ob-

⁹ H. Masumoto, Sci. Repts. Tôhoku Univ. 15, 449 (1926).

¹⁰ K. Hayakawa, Sci. Repts. Tôhoku Univ. 22, 934 (1933).

tained at room temperature agrees well with the value 4.77 and 4.72 electron volts obtained by Glasoe¹¹ and Cardwell,¹ respectively, at room temperature. Wahlin's⁴ values 4.21 and 4.48 eV, determined thermionically for β and γ iron, respectively, do not agree with the corresponding values 4.62 and 4.68 eV reported in this work. No satisfactory explanation of this disagreement is evident.

As in the case of nickel,⁵ it should be noted that the magnitudes of the vertical shifts required to bring the experimental curves into coincidence with the theoretical curve are not the same for all temperatures. The photocurrent in each case was measured in the

¹¹ G. N. Glasoe, *Phys. Rev.* **38**, 1490 (1931).

same units. In a normal case with no allotropic change involved, no vertical shift occurs. According to Fowler's theory, such a shift indicates a change in the probability factor. Hence, the vertical shift in the case of iron indicates a change in both the number density of free electrons and the transition probability factor for these electrons. Whether the latter is characteristic of the metal itself or is produced by a changed equilibrium condition of a gaseous layer on the surface is a question which can be answered only when marked advances in present vacuum techniques are developed.

The writer wishes to express his indebtedness to Mr. Robert St. John whose services were valuable during the first year of the experimental work.

Solid-State Absorption Spectra of Mg and MgO †

JOHN R. TOWNSEND*

Department of Physics, Cornell University, Ithaca, New York

(Received June 24, 1953)

Linear absorption coefficients have been determined for Mg and MgO for wavelengths from 80A to 350A. The results for Mg have indicated values range from 1.8×10^4 to 12×10^4 cm⁻¹. These values are in reasonable agreement with those extrapolated from the region of the K absorption edge. Surface effects were eliminated by plotting transmission against foil thickness. MgO exhibits three absorption bands in this spectral region. These bands have been tentatively identified and discussed in relation to earlier emission data of O'Bryan and Skinner. A gap of about 4 eV is found to exist between the top filled level and the proposed conduction band.

INTRODUCTION

USING a method similar to that described by Tomboulian and Pell,¹ the photon absorption by magnesium and magnesium oxide has been studied experimentally in the wavelength region near the magnesium $L_{2,3}$ edges. The electronic configuration of Mg, which results in two 3s electrons, makes the distribution of electronic energy states in the metal of particular interest. This arises from the prediction based on a non-overlapping band structure that this metal should be an insulator. Since the energy band arising from the 3s atomic states is filled, no electronic conduction would be expected.

The absorption by the metal in this wavelength region (from 80A to 350A) has been measured by O'Bryan and Skinner.² Apparent trouble with surface contaminants, however, made absolute measurement of the absorption coefficients very difficult. The present work on Mg was therefore undertaken to eliminate or correct for surface effects and to seek absolute values

for the absorption coefficients. The work on MgO absorption was intended as a supplement to emission work done by O'Bryan and Skinner.³ Also it enabled a comparison to be made between the absorption spectrum for Mg when in a conductor and in an insulator. Since MgO contamination of the Mg films was anticipated, it was hoped a means of correcting for this would also come from the MgO study.

EXPERIMENTAL

The source of radiation was of the condensed spark discharge type described by Tomboulian and Pell.¹ A concave glass grating with a 1.5-meter radius of curvature was used at an angle of incidence of about 85°. Slit widths of 0.05 to 0.10 mm were used.

Absorber foils of Mg were formed by evaporation in a vacuum of less than 10^{-5} mm Hg as determined by a McLeod gauge. A liquid N₂ trap was used between the gauge and evaporation bell jar. A small disk of Mg was heated in an open graphite crucible on which was wound a tungsten heater coil. The evaporated Mg was condensed on a microscope slide coated with zapon plastic. To minimize the absorption effects of the zapon, the slide then was immersed in amyl acetate to free

† Based on the authors thesis presented in partial fulfillment of the requirements for the Ph.D. degree at Cornell University, September, 1951.

* Present address: Hanford Atomic Products Operation, General Electric Company, Richland, Washington.

¹ D. H. Tomboulian and E. M. Pell, *Phys. Rev.* **83**, 1196 (1951).

² H. M. O'Bryan and H. W. B. Skinner, *Proc. Roy. Soc. (London)* **A162**, 49 (1937).

³ H. M. O'Bryan and H. W. B. Skinner, *Proc. Roy. Soc. (London)* **A176**, 229 (1940).