

STUDIES ON THE SPECTRA OF CU I, CU II, AND  
MN II BY MEANS OF A VACUUM  
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(Received March 25, 1929)

## ABSTRACT

**New design of a high temperature vacuum tungsten or molybdenum furnace.**  
A high temperature vacuum tungsten furnace for the study of the spectra of elements having high boiling points is described.

**Absorption spectrum of Cu.**—All previously observed absorption lines of Cu in the range of the quartz spectrograph were observed and in addition six new lines from the  $3d^9 4s$  level as follows 2618.381, 2824.375, 2882.81, 2961.177, 3010.840, 3194.103. CuH bands were also observed in absorption.

**Excitation of Cu I spectrum by resonance absorption.**—Light from the furnace walls excited Cu atoms to the  $^2P$  state with the subsequent emission of 3247, 3274, 5106, 5700, 5782. With the walls somewhat cooler these lines were brought out when the vapor was exposed to intense radiation from the outside.

**Excitation of Cu II and Mn II spectra by collisions of second kind with rare gas ions.**—A-Cu mixtures at 25 volts failed to develop the Cu II spectrum. From Ne-Cu mixtures at 25 volts the lines from the  $3d^5 5s$  state were much stronger than those from  $3d^5 4p$ . Theory shows that in A-Mn, Ne-Mn, and He-Mn mixtures the spectrum of Mn II should be excited to the extent of 64800, 113400 and 138500 wave-numbers respectively. The strong  $(3d^5 4p)^1P - (3d^5 4d)^1D$  multiplet should be excited in Ne-Mn mixtures but not in A-Mn. This was verified experimentally. An analysis, similar to that of Russell, of the Mn II spectrum is given.

THE purpose of the work described here was to develop a high temperature vacuum furnace for the study of the atomic spectra of the elements having high boiling points and to demonstrate the adaptability of the furnace to these studies by using it to secure new information regarding such elements in a variety of ways.

In the analysis of the spectra of the elements, each group offers difficulties peculiar to itself and the chief difficulty with the more refractory elements is that of obtaining them in the vapor state under controllable conditions. From time to time various types of furnaces have been designed for this purpose. Thus King<sup>1</sup>, in 1907, described a furnace which consisted of a thin horizontal tube of graphite, heated by a current of about 1500 amperes and enclosed in a chamber which could be evacuated to a few millimeters of mercury. Zumstein<sup>2</sup> did considerable work on absorption spectra by using a horizontal tube of carbon mounted under a ventilating hood and heated by a blast from a large oxyacetylene blow-torch. He made no attempt at evacuation. The metal was vaporized in air at atmospheric pressure

<sup>1</sup> King, *Astrophys. J.* **28**, 300 (1908).

<sup>2</sup> Zumstein, *Phys. Rev.* **27**, 562 (1926).

unless the oxidation was too great, in which case a stream of nitrogen or hydrogen or illuminating gas was passed through the tube. McLennan and McLay<sup>3</sup> also worked on absorption spectra and used a furnace consisting of a horizontal carbon tube which acted as the upper electrode of a carbon arc, the lower electrode being touched to the center of the upper and an arc maintained between them.

Duffendack<sup>4</sup> used a tungsten furnace in studying the critical potentials of atomic hydrogen. A large percentage of dissociation of  $H_2$  was obtained thermally in such a furnace. It consisted of a thin horizontal tube of tungsten clamped between heavy water-cooled leads and heated by an electric current. It was enclosed in a vacuum chamber. A similar furnace has been used by Olmstead and Compton.<sup>5</sup> The furnace used in the present experiment was very similar to that used by Duffendack.

#### APPARATUS

A diagram of the apparatus is shown in Fig. 1. A sheet of tungsten or molybdenum about 0.001 inch thick was rolled into a cylinder about 2 cm in diameter and 9 cm long. This is shown as *C* in the drawing. It is clamped horizontally between two heavy water-cooled copper rods and heated by a large current from the low voltage transformer shown at the bottom of the

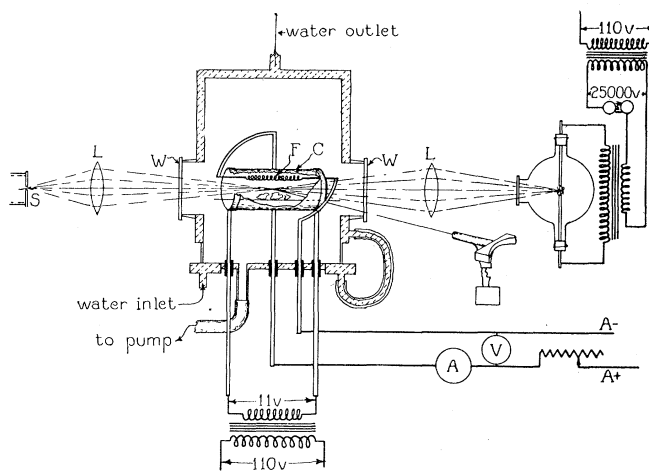


Fig. 1. Tungsten furnace mounted in a water-cooled vacuum chamber.

figure. The rods extend upward through collars in the base of the large chamber shown and are insulated from this base plate by thick collars of Pyrex tubing sealed on with deKhotinsky cement. The tungsten cylinder is so adjusted that its axis is in line with the centers of the two quartz windows *W*. These windows are sealed on with cement.

<sup>3</sup> McLennan and McLay, *Trans. Roy. Soc. Can. Sec. III*, 89 (1925).

<sup>4</sup> Duffendack, *Phys. Rev.* **20**, 665 (1922).

<sup>5</sup> Olmstead and Compton, *Phys. Rev.* **22**, 559 (1923).

Extending through the cylinder near the top is shown a tungsten filament of 12 mil wire with a few turns at the center. This filament serves as the hot cathode for the low voltage arc studies; electrons being accelerated from it to the trough which holds the metal. This trough is supported by two other water-cooled leads, insulated from the base, and of the same size as those supporting the furnace.

A water-cooled vacuum chamber surrounds the furnace and is sealed to the base plate with a laboratory wax known as "Picein." The inside of the water-cooled chamber is made of a tube of seamless cooper 6'' in diameter, 7'' high and 3/16'' thick. The bottom and top are of pure copper plate and the top is soldered on. The inside of the cylinder is heavily nickel-plated as an increased precaution against diffusion of gases and water vapor through the walls. The reason for using copper is that brass is porous to water vapor. The outer water jacket is made of brass. A circular hollow brass collar is soldered to the base plate just below the point at which the chamber is cemented to the base and cold water circulating through this prevents the Picein from softening.

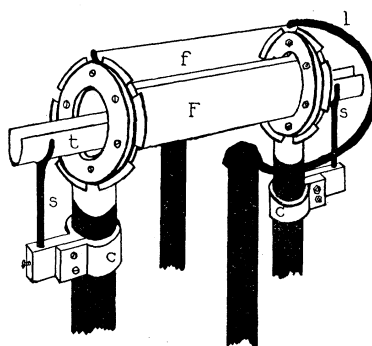


Fig. 2. Details of mounting of tungsten furnace.

Through the cylindrical furnace near the base may be seen a horizontal trough on which rests the metal to be studied. This trough is supported by insulated arms not shown in the figure and is grounded to the base plate. It is made of a strip of 5 mil molybdenum or tungsten about 1.5 cm wide and 10 cm long, bent into the shape of a trough. The details of this may be seen in Fig. 2. When the furnace is used for a low voltage arc discharge this trough is held at a positive potential with respect to the filament and serves as the anode.

In the absorption work on copper, a few grams of copper selected from Baker's Analyzed Chemicals were placed in the trough, the chamber was placed on and sealed and the system pumped out thoroughly. The furnace was then heated and the absorption spectrum taken in the usual manner.

The pumping system was of the usual type, consisting of a two-stage mercury vapor condensation pump backed by a Hyvac oil pump. A McLeod gauge was used to read the pressure and a pair of mercury cut-offs facilitated

letting in gases when desired. A small pressure of hydrogen was used to decrease the diffusion of metal vapor to the windows and helium, neon, and argon were used in the work of ionization and excitation by positive ions. Absorbable impurities in the helium and neon were removed by an activated coconut charcoal trap immersed in liquid air. To purify the argon a "getter" consisting of a bundle of sticks of misch metal was used.

The method of mounting the furnace tube is important. It is obvious from a glance at Fig. 2 how the ends of the cylinder of tungsten were split and flared into a fan shape so as to permit clamping with the soft steel clamps shown. Some trouble was experienced by the condensation of copper on these clamps. The current which flowed through this cylinder varied from 150 to 375 amperes, depending upon the temperature desired. When it was necessary to be very careful of the temperature it was measured with an optical pyrometer. Such was the case in the work on the excitation of the copper spectrum by photoelectric action. When the furnace cylinder burned or melted in two, about one hour's time was required for replacing it and getting the vacuum pumps into operation again.

The continuous light for the absorption experiments was furnished by a Tesla spark between tungsten electrodes in distilled water. This gave a beautiful continuous spectrum from the red to 2240Å.

#### ABSORPTION STUDIES ON COPPER

The first attempt at an adaptation of the furnace to a problem of atomic physics was in a study of the absorption spectrum of copper vapor. Copper was chosen because of its relatively high boiling point and because we could use it to compare the furnace with others which had been used in absorption studies on the same element. The classification of these lines by Shenstone<sup>6</sup> was used in the interpretation of the results.

The normal state of Cu I is a  $^2S$  state. Taking this as zero we find next metastable  $^2D_3$  and  $^2D_2$  states at 11202.5 and 13245.4  $\text{cm}^{-1}$  respectively while  $^2P$  levels come at 30543.1 and 30782.8  $\text{cm}^{-1}$ . The chief interest for our absorption work lies in the  $^2D$  levels. It should be remembered that in absorption by "cold" vapors only lines from the normal state are absorbed, since all of the atoms are in this state. If the temperature of the vapor is increased however, higher energy states will be occupied and absorption may be obtained from these states.

All the absorption lines of copper which have been observed from the normal state had been obtained previous to the work of Zumstein. He was able to obtain nine absorption lines from the  $(3d^94s)^2D$  state, using the temperature obtainable with the oxyacetylene blow-torch. He was also able to absorb the bands of copper-hydride by passing a stream of hydrogen through the vapor.

Using the tungsten furnace described here we were readily able to obtain all the previously observed absorbed lines within the range of a quartz spectrograph and in addition six new lines from the  $3d^94s$  level, as follows:—

<sup>6</sup> Shenstone, Phys. Rev. **28**, 449 (1928).

2618.381, 2824.375, 2882.81, 2961.177, 3010.840, 3194.103. There also appeared a nice absorption of the copper-hydride bands.

#### EXCITATION OF THE CU I SPECTRUM BY ABSORPTION OF RESONANCE RADIATION

We next attempted to excite the emission spectrum of Cu I by the absorption of resonance radiation. The necessity of attempting to excite the copper spectrum in this manner arose when we obtained certain Cu I lines in *emission* while trying to get the 5700, 5782 lines in absorption.

Since we were using a temperature close to the melting point of tungsten in order thermally to obtain a large number of metastable copper atoms, the furnace wall was emitting light whose short wave-length limit was about 2500Å. We were thus subjecting a large number of atoms to radiation of resonance wave-length. These atoms were thus excited to the  $^2P$ , state and any lines representing transitions from this state to the  $1^2S$  or  $^2D$  should appear in emission. We were thus able to obtain the lines 3247, 3274, 5106, 5700, 5782 in emission.

The fact that these lines appear thus in emission probably explains the difficulty encountered by Zumstein in absorbing the 5106, 5700, and 5782 lines, because there were probably as many electron transfers from  $^2P$  down to  $^2D$  as from the  $^2D$  up to  $^2P$ . With special effort he obtained 5106 as a narrow line but could not get 5700 and 5782. The line 5106 was obtained as a narrow, sharp absorption in our work, but the 5700 and 5782 lines failed to appear.

Reflections upon the theory of impacts of the second kind lead to interesting modifications which might be made in absorption experiments. For instance, it is theoretically possible that the hydrogen which we used to reduce the diffusion of the metal vapor inside of our furnace was able at the higher temperatures to increase the populations of the  $^2P$  levels by collisions in which the atomic hydrogen excited the copper to the  $^2P$  state. Such an action has been observed by Mohler<sup>7</sup> in the excitation of metallic spectra by atomic hydrogen. This would account for some of the radiation which registered as 5106, 5700 and 5782.

To return to the discussion of the present experiment—the walls of the furnace had been very hot during the absorption experiments and it was necessary to cool them so as to make sure that they were not emitting the resonance lines of copper while at the same time keeping them hot enough to furnish a supply of copper vapor. Maintaining them at such a temperature we photographed the spectrum emitted by the vapor when no resonance radiation was allowed to enter the vapor and on the same plate we took an exposure when an intense beam of continuous radiation entered the vapor from a direction at right angles to the optical axis of the collimator of the spectrograph. In the first case we obtained no evidence whatever of the emission of copper lines while in the second case there appeared strong lines at the wave-lengths mentioned above, 3247, 3274, 5106, 5700, 5782. Precau-

<sup>7</sup> Mohler, Phys. Rev. **29**, 419 (1927).

tions were taken to keep the total power input into the furnace slightly lower in the second case than in the first in order to be sure that the vapor which was not illuminated had fully as high a temperature as the illuminated, and for the same reason the temperature of the furnace as registered on an optical pyrometer was kept slightly lower in the second case.

#### EXCITATION OF THE CU II SPECTRUM BY POSITIVE RARE GAS IONS

We next applied the furnace in a test of simultaneous ionization and excitation by positive ions. It has recently been demonstrated by Smyth and Harnwell<sup>8</sup> and Hogness and Lunn<sup>9</sup> that a positive ion of one ionizing potential may, upon collision with a neutral atom or molecule, rob it of an electron, provided its ionization potential is lower. They used the method of Dempster's positive-ray analysis.

At the same time Duffendack and Smith<sup>10</sup> were performing an experiment which involved the ionization by contact with positive ions and which dealt with the disposal of the excess energy at such collisions. They showed that positive helium ions could, upon contact with CO molecules, ionize them, and spend the residual energy in exciting the ion formed. They were thus able to excite the bands of CO<sup>+</sup>. Their experiment differed from the others in that they were concerned with the excess energy at collision and showed that the excess energy after ionization went to excite the ion formed.

It was thought advisable to make a test of this type of energy transfer in metallic vapors, which are monatomic. Since the first spark spectrum of copper had been analyzed,<sup>11</sup> the method was tried in copper-helium, copper-neon and copper-argon mixtures.

The excess energy made available in the reaction

$$\text{He}^+ + \text{Cu} = \text{Cu}^+ + \text{He} \text{ is } 24.5 - 7.8 = 16.7 \text{ volts}$$

$$\text{Ne}^+ + \text{Cu} = \text{Cu}^+ + \text{Ne} \text{ is } 21.4 - 7.8 = 12.6 \text{ volts}$$

$$\text{A}^+ + \text{Cu} = \text{Cu}^+ + \text{A} \text{ is } 15.4 - 7.8 = 7.7 \text{ volts}$$

Reference to the energy levels of Cu II, Fig. 3, will show that helium ions should be able to excite any levels in the *Cu II* spectrum which are below 135270 wave-numbers. Neon ions should excite any levels below 110160 wave-numbers and should show the lines from the  $3d^94p$  configuration. Argon should, however, only be able to reach 61560 wave-numbers and the lines from the  $3d^94p$  levels should not be developed in this type of mixture. Such was found to be the case, and thus the conclusion of Duffendack and Smith that the excess energy went into excitation of the spark spectrum was confirmed in the case of monatomic molecules.

As for the experimental work, this consisted in outgassing the system and then introducing 3 millimeters of argon. The filament was next lighted

<sup>8</sup> Smyth and Harnwell, *Nature* Jan. 15, (1927).

<sup>9</sup> Hogness and Lunn, *Phys. Rev.* **30**, 26 (1927) See also a succeeding article in this journal.

<sup>10</sup> Duffendack and Smith, *Nature* **119**, 743 (1927).

<sup>11</sup> Shenstone, *Phys. Rev.* **29**, 380 (1927).

and then the furnace, so that after a few seconds a mixture of rare gas and copper vapor filled the furnace tube.

An accelerating potential difference of 25 volts was then applied between the trough and filament and the spectrum examined by means of a pocket spectroscope. When the currents had been adjusted for the desired intensity of the copper lines, a photograph was taken in a mixture of argon and copper. The system was again exhausted and outgassed and a photograph placed on the same plate, with the same conditions, except that neon and copper were used.

The argon-copper mixture failed to develop the lines of the Cu II spectrum while the neon-copper mixture showed a strong development of the spark lines.

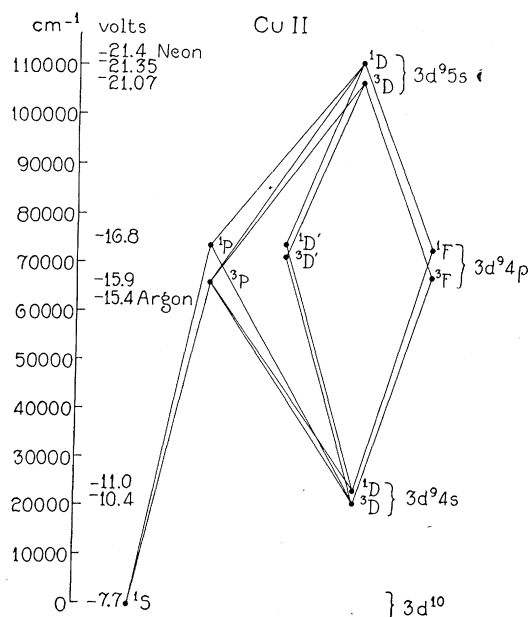


Fig. 3. Energy levels of Cu<sup>+</sup>

In the excitation of Cu II by neon ions the lines from the  $3d^9 5s$  state were relatively much stronger than those from the  $3d^9 4p$ . Reference to Fig. 3 will show that this  $3d^9 5s$  state is just below the ionizing potential of neon, while the  $3d^9 4p$  level is just below 16.7 volts, which is an important excited state of neon. The strong development of the lines from the  $3d^9 5s$  state can be attributed to the fact that this level is practically resonant with the normal ionized state of neon. The weakness of the lines from the  $3d^9 4p$  state which is resonant with the 16.6 volt excited state of neon is, however, somewhat unexpected, especially in the light of the work of Duffendack and Smith described in a succeeding paper. We had the opportunity to discuss this matter with Professor J. Franck, and he suggested that the weakness of these lines is probably due to the quenching action of hydrogen

on this state of neon. The ionizing potential of  $H_2$  is also practically resonant with this state of neon and Duffendack and Smith showed in their experiments that hydrogen does have a marked quenching action on this state of neon. Since the furnace chamber could not be outgassed and hydrocarbon vapors may be expected from the cements used, the presence of hydrogen in the neon can readily be explained.

#### EXCITATION OF THE SPECTRUM OF MN II

We next excited the spectrum of Mn II by the same method as was used on Cu II. The excess energy after contact ionizations by argon, neon and helium ions is 8, 14, 17.1 volts respectively and these are able therefore to excite the Mn II spectrum to the extent of 64800, 113400, 138500 wave numbers respectively. Reference to Fig. 4 will show that argon ions should

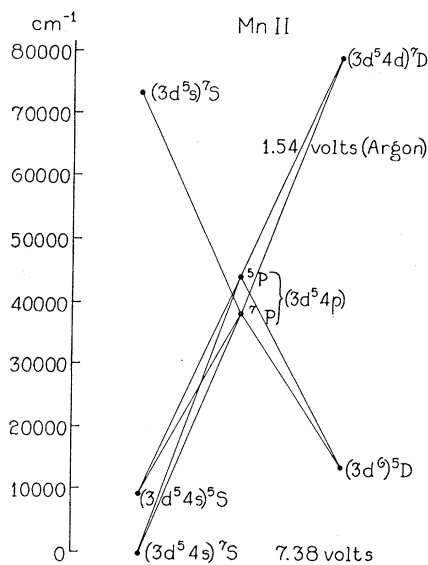


Fig. 4. Energy levels of Mn<sup>+</sup>.

develop the lower important terms, while neon ions should develop all the main terms in the spectrum while the second spark spectrum should be entirely absent. An interesting consequence of this is that the strong  $(3d^5 4p) ^7P - (3d^5 4d) ^7D$  multiplet should not be developed by argon ions, but should easily be developed by neon ions. This was tested by taking two successive exposures on the same plate, one using argon ions and the other neon. The neon ions gave a strong development of the nine lines but the argon failed to develop them.

In 1923 Catalan<sup>12</sup> discovered four multiplets in the spectrum of Mn II which we have recently identified<sup>13</sup> as the strongest multiplets of a septet

<sup>12</sup> Catalan, Phil. Trans. Roy. Soc. **223A** (1923).

<sup>13</sup> Black and Duffendack, Science **66**, 401 (1927).



and quintet system. The relative positions of the two systems were estimated from computations of convergences of two series in Mn I furnished us by Dr. O. Laporte, and intercombination lines which fixed the relative positions of the system were easily found.

The term scheme for the Mn II spectrum as far as we were able to analyze it is given graphically in Fig. 4. The same analysis was made independently by Russell.<sup>14</sup> Since he has published the classification of the lines, it is not necessary to reprint them here. He located a  $(3d^55s)^7S$  level at  $74555.98 \text{ cm}^{-1}$  and although the three lines which located it by combinations with  $(3d^54p)^7P$  fit excellently, we are inclined to doubt its correctness; for two of the lines, namely 2762.3 and 2796.3, were developed by argon ions whereas this  $^7S$  level is above the ionization potential of argon. In all other respects his analysis is identical with ours.

A considerable number of unclassified lines in Mn II in the region between 2600A and 3100A, 38500 and 32400 wave-numbers, are intensified in argon while many equally intense spark lines fail to appear in the spectrum excited in the argon-manganese vapor mixtures. It would seem that these lines are due to transitions between other terms of the configurations indicated in Fig. 4, and since the lines are excited in the argon mixture they must come from terms lying below 64800 wave-numbers from the normal state of the manganese ion. Therefore these lines are probably due to transitions from unknown terms of the  $3d^54p$  state to the terms of the  $3d^54s$  and  $3d^6$  states. It is hoped that a classification of these lines may be possible soon in order to check this hypothesis.

<sup>14</sup> H. N. Russell, *Astrophys. J.* **66**, 292 (1927).