

Soft X-Ray Absorption of Thin Films of Iron and Iron Oxide*

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The absorption of thin films of iron and of iron oxide has been studied in the wavelength region 170 to 340 angstroms. The absorption edge of iron was found to be at 225 angstroms, while that of iron oxide was at 218 angstroms.

I. INTRODUCTION

IT is possible, by irradiating a solid with radiation of the appropriate energy, to lift an electron from an inner level of an atom into the permitted empty states of the valence band. The absorption of this radiation is given as¹

$$\mu(E) \propto f(E)N(E),$$

where $\mu(E)$ is the absorption coefficient, $f(E)$ is a probability factor for the transition (the square of the dipole moment for the transition), and $N(E)$ is the density of unfilled energy levels in the valence band. It is thus possible to gain some information about $N(E)$ by studying the absorption of the radiation as a function of energy or wavelength.

As has been pointed out by Skinner,¹ the soft x-ray region above 100 angstroms has, in general, the greatest resolution for studying the structure of the valence bands. In our study of iron and iron oxide we used the $M_{2,3}$ level as the initial level. The approximate position of the $M_{2,3}$ absorption edge can be calculated from the data on the limiting frequencies of x-ray lines given in the International Critical Tables² or from the term values for the x-ray energy levels given by Bohr and Coster.³ These two sources give 218 and 228 angstroms, respectively.

II. DESCRIPTION OF SPECTROGRAPH

Because of the high absorption of soft x-rays by air, it was necessary to use a vacuum spectrograph. This was the same spectrograph described by Givens and Siegmund,⁴ altered to permit the transferral of films to it from a vacuum evaporator by means of a vacuum bottle.

A schematic diagram of the spectrograph is given in Fig. 1. The source was a copper spark operated in vacuum with a dc voltage of approximately 30 000 volts, as measured by a standard sphere gap in air. This gave a series of fairly evenly spaced lines from 100 to 400 angstroms. Both the spark gap and voltage were

adjustable. The sparking rate used was about 1000 sparks per hour. The number of sparks was counted by a pair of Cenco impulse counters fed by an amplifier with a loop which picked up the strong induction field produced by the spark.

The slit was composed of two adjustable jaws made of stellite. The slit had to be wide enough for reasonably short exposures, yet narrow enough for good resolution and for preventing the copper particles given off by the spark from breaking the absorbing films. A good compromise was found to be about 0.03 mm.

The absorbing films of iron or iron oxide on celluloid were mounted behind the slit for protection from the flying copper particles from the spark. It was found necessary to transfer the iron films from the vacuum evaporator to the spectrograph in a vacuum bottle to prevent their oxidation.

The two-meter grating was used at 5° from grazing incidence. The grating had 30 000 lines to the inch, the width of the ruled area being four inches.

The plates were mounted on a holder machined to the shape of the Rowland circle which would accommodate four 2×10 inch plates covering the range from about 100 to 1500 angstroms. Ilford Q plates were used in the early work, but later Kodak SWR plates were used. The plateholder could be moved up and down behind an occulting diaphragm, so that as many as four or five exposures could be made on one plate without disturbing the vacuum.

The entire system was evacuated by one fore pump and two oil diffusion pumps. One diffusion pump, a DPI MC-500, was connected directly to the plate chamber, and the other, a small glass diffusion pump, was connected to the source chamber. The fore vacuum for both of these was supplied by a Cenco Hypervac 20. The pressure could be reduced to less than 5×10^{-5} mm, as measured with an ion gauge.

III. FILMS

The films of iron were obtained by vacuum evaporation of chemically pure iron wire onto a supporting

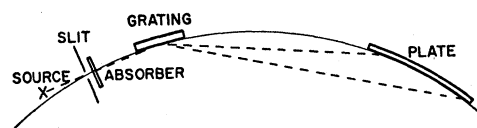


FIG. 1. Schematic diagram of grazing incidence spectrograph.

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¹ H. W. B. Skinner, Repts. Progr. in Phys. 5, 237 (1939).

² International Critical Tables (McGraw-Hill Book Company, Inc., New York, 1929), Vol. VI, p. 35.

³ N. Bohr and D. Coster, Z. Physik 12, 342 (1923).

⁴ M. P. Givens and W. P. Siegmund, Phys. Rev. 85, 313 (1952).

celluloid substrate. The celluloid films were made by placing a drop of collodion on the surface of a tray of distilled water. After the solvent (amyl acetate) had evaporated, the film was carefully lifted off on a holder. Celluloid was chosen for the supporting film because it had been shown to have no strong absorption bands in the wavelength region under investigation.⁵

At first the iron films were exposed to the air during the transfer from the vacuum evaporator to the spectrograph. Measurements of the electrical resistance of these films, however, established that the oxidation of the films was very rapid when the vacuum evaporator was opened to the atmosphere.

The first method that was tried to prevent this oxidation was to overcoat the iron films with silicon monoxide or magnesium fluoride before the vacuum evaporator was opened. Resistance measurements showed that while these coatings slowed the oxidation they did not prevent it.

The next method tried was to transfer the films from the vacuum evaporator to the spectrograph, which had already been pumped down, in a vacuum bottle. With this method measurements of resistance established that a thickness of less than 10 angstroms of the film would be oxidized, which was less than five percent of the thickness of the films used.

The iron oxide films were obtained by allowing the iron films to oxidize in the laboratory atmosphere for several days to insure that the oxidation was complete.

Thicknesses of films were determined by weighing a thin microscope glass cover slide before and after the evaporation of the iron. These films when weighed were, of course, iron oxide films. The weights of the iron films were obtained from the weight of the corresponding iron oxide films by multiplying by 112/160 (on the assumption that the oxidized film was Fe_2O_3). In order to avoid the tedious job of weighing each film separately, a plot of weight of film in micrograms per square centimeter *vs* optical density was made for several iron oxide films and the weights of subsequent films were determined by measuring the optical density.

The thickness of the films could be determined by dividing the weight per square centimeter by the density, if it was assumed that the density of the film was the same as the bulk density. A check on this assumption was made on an iron oxide film by measuring the thickness interferometrically by the method of Tolansky.⁶⁻⁸ The thickness of the film so determined was 440 angstroms. The thickness was also calculated by measuring the optical density, reading the weight from the graph *vs* optical density, and dividing the weight per square centimeter by the density of the bulk material. This gave 420 angstroms as the thickness. These data were interpreted to show

that the density of the films was substantially the same as the bulk density, and that calculations of the thickness from the weight based on this assumption were valid.

IV. PHOTOMETRY

The first step in determining the absorption of the films of iron or iron oxide was to determine the wavelengths of the spectral lines of the copper spark used as a source. Photographs and tables of the copper spark spectrum in the soft x-ray region were available,⁹ but it seemed advisable to make a preliminary wavelength calibration of the spectrographic plates by using a simpler spectrum. Accordingly, the plates were first calibrated for wavelength as a function of distance along the plate by the use of an aluminum spark spectrum, which gives a few quite dense, easily recognizable lines.¹⁰⁻¹² From this preliminary calibration and the available tables for the copper spark spectrum, it was then easy to determine the wavelengths of the lines of the copper spark spectrum.

It was also necessary to calibrate each plate individually in terms of density as a function of exposure in order to determine the absorption. To do this, three exposures of, for example, 4000, 2000, and 1000 sparks were made through the plain celluloid film of the same thickness as that on which the iron was deposited, and 8000 sparks through the iron on celluloid film. Since the spark was run at a constant voltage and at as nearly as possible a constant sparking rate, the exposure received by the plate was taken to be proportional to the number of sparks in the case of the plain film. The densities of various lines of the copper spark spectrum were determined for the three exposures through the plain celluloid film and for the one exposure through the iron film by a recording densitometer. The two exposures through the plain film nearest in density to the exposure through the iron film were used to calibrate the spectrographic plate for density as a function of exposure. Then, by comparing the density of a given line for the exposure through the iron film with the densities of that line for the two exposures through the plain film, it was possible to obtain the transmission of the iron film.

V. RESULTS AND DISCUSSION

Figure 2 is a graph of $\ln(I_0/I)$ as a function of wavelength for a thin film of iron, where I_0 is the intensity of the incident radiation and I is the intensity of the radiation transmitted. The ordinate was designated $\ln(I_0/I)$ rather than μx because there were undoubtedly some losses due to reflection and scattering, but, according to the results of Sabine,¹³ the losses due to

⁵ H. M. O'Bryan, *J. Opt. Soc. Am.* **22**, 739 (1932).

⁶ S. Tolansky, *Proc. Roy. Soc. (London)* **184**, 41 (1945).

⁷ S. Tolansky, *Proc. Roy. Soc. (London)* **186**, 261 (1946).

⁸ A. F. Gunn and R. A. Scott, *Nature* **158**, 621 (1946).

⁹ P. G. Kruger and F. S. Cooper, *Phys. Rev.* **44**, 826 (1933).

¹⁰ J. Soderquist, *Z. Physik* **79**, 634 (1932).

¹¹ E. Ekefors, *Z. Physik* **51**, 471 (1928).

¹² M. Siegbahn and T. Magnusson, *Z. Physik* **95**, 133 (1935).

¹³ G. B. Sabine, *Phys. Rev.* **55**, 1064 (1939).

reflection from the iron should be small. The weight of the iron film, determined as explained in Sec. III, was 17.7 micrograms per square centimeter, which would correspond to a thickness of 220 angstroms.

The chief characteristics of this curve are a marked absorption edge as the wavelength of the incident radiation is decreased, and a double-peaked band of absorption at shorter wavelengths. Since the absorption edge covers a wavelength range of several angstroms, it is difficult to specify any one wavelength as being the position of the edge. We have adopted the convention of Skinner and Johnston¹⁴ and have defined a mean absorption edge as being that point at which the absorption is one-half the sum of the maximum and minimum values of the absorption adjacent to the edge. The mean absorption edge of iron is at 225 angstroms or 54.9 electron volts. The width of the absorption band at half-maximum is 25 angstroms or 6.9 volts. The two peaks are at 216 and 210 angstroms, a separation of 6 angstroms of 1.6 volts.

The absorption is assumed to be due to transitions of electrons from the filled $M_{2,3}$ ($3p$) level of iron into the vacancies of the $M_{4,5}$ ($3d$) and N_1 ($4s$) bands. These two bands are the nearest bands with unfilled levels and transitions to them are permitted by the selection rules. The experimental results will be compared with those expected from these assumptions.

The value actually obtained for the position of the mean absorption edge for iron, 225 angstroms, compares favorably with the average of the two predicted values, 223 angstroms.

In the free atom the $M_{2,3}$ level is really not a single level but consists of two separate levels quite close together. The theoretical separation of these levels may be compared by the following formula¹⁵:

$$\frac{\Delta\bar{\nu}}{R} = \frac{M_2 - M_3}{R} = \frac{\alpha^2}{3^4} (Z-d)^4 \left[\frac{3}{2} + \frac{279}{32} \frac{\alpha^2}{3^2} (Z-d)^2 \right],$$

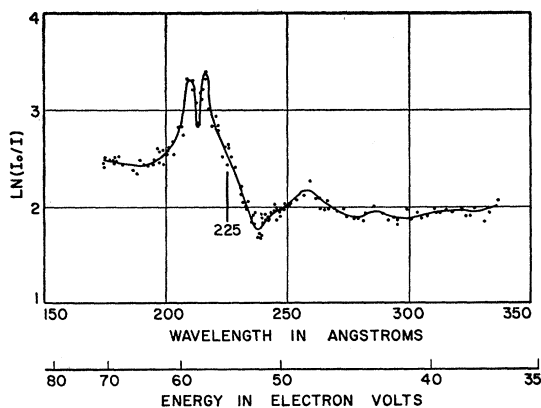


FIG. 2. Graph of $\ln(I_0/I)$ vs wavelength for a thin film of iron.

¹⁴ H. W. B. Skinner and J. E. Johnson, Proc. Roy. Soc. (London) **A161**, 420 (1937).

¹⁵ A. E. Ruark and H. C. Urey, *Atoms, Molecules, and Quanta* (McGraw-Hill Book Company, Inc., New York, 1930), p. 256.

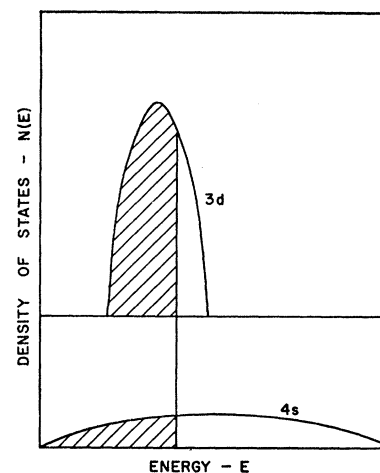


FIG. 3. Schematic plot of density of states vs energy for $3d$ and $4s$ bands of iron.

in which Z is the atomic number of the atom, d is the screening constant for the $M_{2,3}$ levels, α is the fine structure constant, R is the Rydberg constant, and $\bar{\nu}$ is the wave number. This formula gives the separation of the levels as 1.3 volts or 4.8 angstroms. These computations were for the free atom, but, since the $M_{2,3}$ levels are quite strongly bound, we should not expect them to be so broadened by interaction effects that they lose their doublet structure.

The observed separation of the peaks was 6 angstroms or 1.6 volts. In view of the uncertainty both in the experimental data and in the theoretical formula, it seems only natural to assume that the doubling of the absorption peaks is due to the doublet structure of the $M_{2,3}$ levels. (Skinner¹⁶ has reported a separation of 1.4 volts observed in emission work.)

It is generally assumed that the N_1 or $4s$ energy level of the iron atom is considerably broadened by the interactions of the atoms in the solid. The $M_{4,5}$ or $3d$ level should not be broadened nearly as much, since it is an inner level and the wave functions of the $3d$ electrons of one atom do not overlap those of the next atom appreciably. Thus the curve for $N(E)$ as a function of E is high and narrow for the $3d$ electrons and low and broad for the $4s$ electrons. It is further assumed that in the solid the energy bands of the $3d$ and $4s$ electrons of iron overlap. The $3d$ and $4s$ bands are filled up to the same level with the eight outer electrons of iron, and above the top of the filled portion there are unfilled states to which the electrons may go. This is represented very schematically in Fig. 3 (after Coster and Kiestra¹⁷).

The high absorption in the neighborhood of the edge is attributed to transitions into both the $3d$ and $4s$ bands. The height and narrowness of the peaks must be due to the shape of the unfilled part of the $N(E)$ distribution for the $3d$ electrons. The doubling of the peaks has already been explained by the fact that the

¹⁶ Skinner, Bullen, and Johnson, Phil. Mag. **45**, 1070 (1954).

¹⁷ D. Coster and S. Kiestra, Physica **14**, 175 (1948).

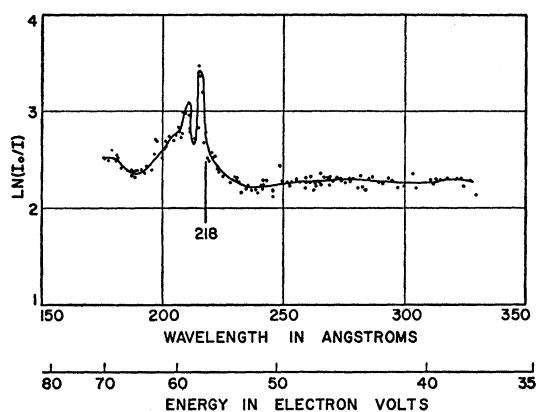


FIG. 4. Graph of $\ln(I_0/I)$ vs wavelength for a thin film of iron oxide.

initial level in the absorption transition, the $3p$, is really a double level. The absorption immediately to the left of the peaked structure is assumed to be due to the $4s$ band alone, as the empty levels of this band are pictured as extending some distance beyond those of the $3d$ band.

According to the view of energy bands filled to a certain level, we should expect the absorption edge to be quite sharp. Actually it is not sharp but diffuse, the absorption rising steadily over a considerable wavelength range. However, Skinner¹⁶ has found that the transition metals (including iron) do not have sharp emission edges as expected. Since if the emission edge of iron is not sharp the absorption edge would not be expected to be sharp either, our results for a diffuse edge are in accord with those of Skinner. A possible explanation of the diffuse edge suggested by Skinner is Auger transitions.

Figure 4 shows the graph of $\ln(I_0/I)$ as a function of wavelength for a thin film of iron oxide. The weight of the iron oxide was 14.5 micrograms per square centimeter, which would correspond to a thickness of 280 angstroms.

The curve for iron oxide is similar in general shape to that for iron but there are a few definite differences.

The mean absorption edge of iron oxide occurs at 218 angstroms or 56.6 volts. The width of the absorption band at half-maximum is 10 angstroms or 2.7 volts. The peaks are at 216 and 211 angstroms, a separation of 5 angstroms or 1.4 volts.

The two high narrow peaks are assumed to be due to transitions from the doublet $3p$ level to the unfilled $3d$ levels of the iron ion. The separation of the peaks for the iron oxide was found to be 5 angstroms as compared to 6 angstroms for the iron metal. The accuracy of the experiment was not sufficient to determine whether or not this was a real difference.

The absorption edge of the iron oxide occurred at a shorter wavelength or higher energy than that for the iron, the shift being 7 angstroms or 1.7 volts. This shift toward shorter wavelengths in the absorption edge of the metallic constituent as one goes from the metal to the oxide appears to be quite common and has been found by several other investigators working with other metals.¹⁸⁻²⁰

The width at half-maximum of the absorption edge for iron oxide was considerably narrower than that for iron. According to the band theory, the valence levels of the iron are broadened into bands by the interaction of the iron atoms or ions in the solid and the width of the bands is the greater the closer the spacing of the iron atoms or ions. In the iron oxide the iron ions are separated more than they are in the metal, the interaction is less, and so the energy levels associated with the iron ions are less broadened for the iron oxide than for the metal.

VI. ACKNOWLEDGMENTS

We would like to express our appreciation to Dr. Brian O'Brien for his suggestion of the problem and to the other members of the Institute of Optics for their assistance in various phases of the work.

¹⁸ International Critical Tables (McGraw-Hill Book Company, Inc., New York, 1929), Vol. VI, p. 44.

¹⁹ K. Das Gupta, *Indian J. Phys.* **29**, 226 (1946).

²⁰ D. E. Bedo and D. H. Tomboulian, *Phys. Rev.* **95**, 621(A) (1954).