Technical Report

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THE ABSORPTION OF IRON AND IRON OXIDE IN THE SOFT X-RAY REGION

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I. Introduction

In the process of x-ray absorption by solids the energy of the light quantum $h\nu$ is used to raise an electron from its initial energy state into another state which is both permitted and empty. The probability that an electron will absorb the energy of an incoming quantum and be raised to a vacant state of energy E is proportional to the density of permitted states with energy near E. This quantity is usually called N(E). The ultimate goal of most absorption measurements is to furnish information which may aid in the eventual determination of N(E) for the substance under study.

The soft x-ray region (or the extreme vacuum ultraviolet) is suitable for this work because the electrons involved are lifted into the outer bands from initial levels which are sufficiently narrow that their width may be ignored. At the same time the total energy involved in the transition is considerably less than 100 times the width of the upper energy band. For this reason the spectrometer need not have unusually high resolving power.

II. Experimental Procedure

Figure 1 is a simplified diagram of the equipment. The Rowland circle is one meter in radius. The plate holder follows the circle and the circle also passes through the slit. The grating of 30,000 lines per inch is tangent to the Rowland circle. The angle of incidence is 85°. The source used for this work was a vacuum spark between copper electrodes operated from a 50-kv power supply. The equipment is essentially the same as that used by Skinner and Johnston[1] and

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1 H.W.B. Skinner and J. E. Johnston, Proc. Roy. Soc. (London) A 161, 420 (1937)

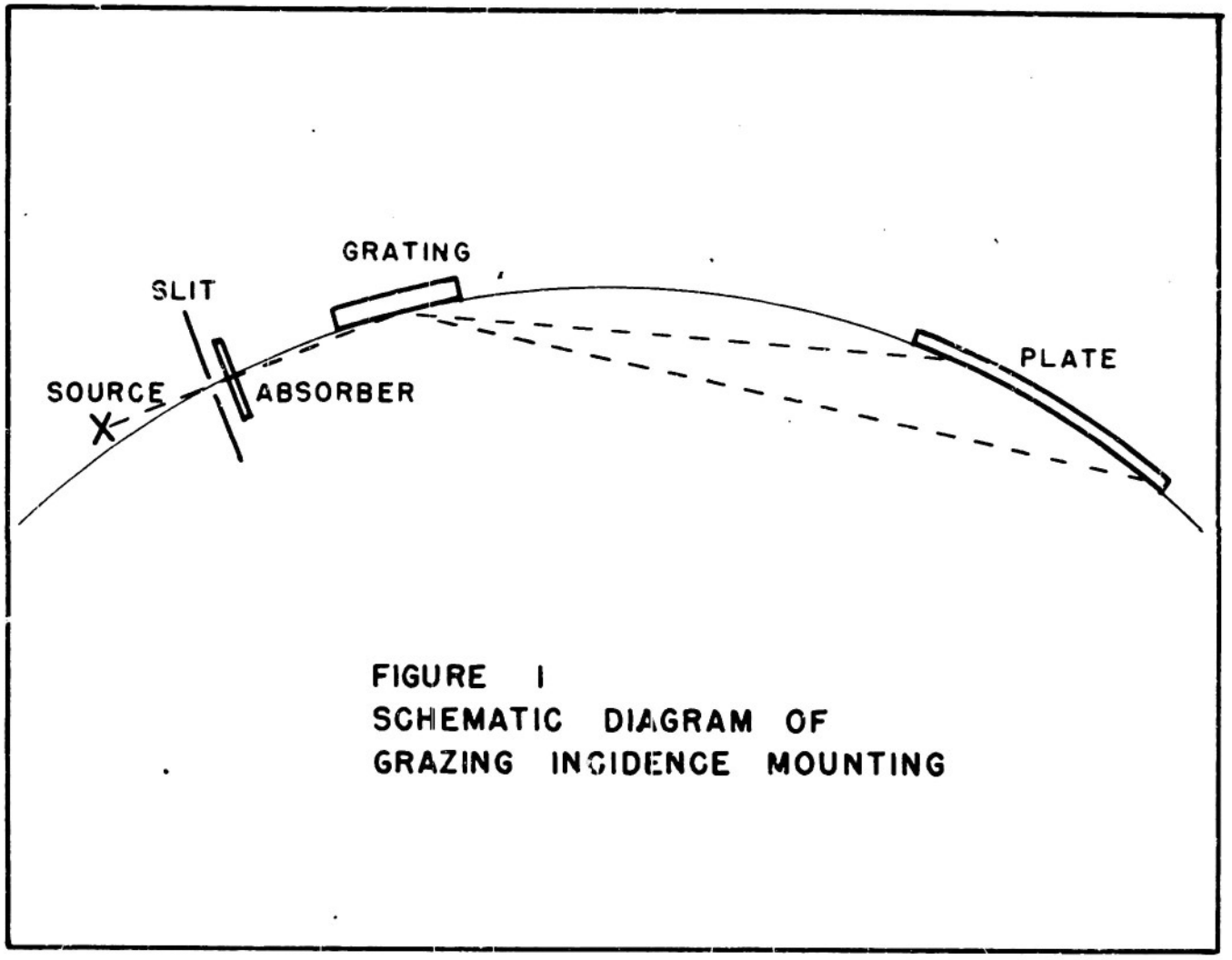

FIGURE 1
SCHEMATIC DIAGRAM OF
GRAZING INCIDENCE MOUNTING

by Sanner[2]. Wavelengths were determined from known lines[3] in the copper spectrum.

2 H. Sanner, Z. Physik 94, 523 (1935)

3 P. G. Kruger and F. S. Cooper, Phys. Rev. 44, 526 (1933)

The absorber was mounted on a small metal plate with a hole in it, and this plate was located just behind the slit.

The absorber consisted of a thin foil of the sample supported on celluloid. Iron foils were prepared by evaporation in vacuum; these upon exposure to air became iron oxide samples. Iron oxide prepared in this way is generally believed to be Fe_2O_3. In order to obtain the absorption due to the sample it is sufficient to compare the transmission through two absorbers, one bare celluloid and the other celluloid coated with the sample. The two pieces of celluloid were taken from the same floating so that the celluloid films would be as identical as possible.

The surface density of the sample in micrograms per square centimeter was determined by weighing. Each individual sample was not weighed, but samples of iron oxide prepared on microscope slide coverglasses were carefully weighed. The optical density of these weighed films was determined on an Ansco-Sweet densitometer. A plot was then made giving surface density versus optical density. For the foils actually used, the optical density was measured and converted to surface density by means of this graph.

The quantity of sample to be weighed was about one milligram. To obtain an accuracy of a per cent the weighings must be accurate to a few micrograms. In order to obtain this accuracy the methods established and recommended by the analytic chemists were followed carefully.

Since the weighing and optical density measurements were made in air they determine the surface density of iron oxide. To determine the surface

density of iron before oxidation the results must be multiplied by the ratio 112/160 which is the fraction by weight of iron in iron oxide.

Assuming that the density of the iron or iron oxide in the thin foil was the same as its density in bulk, then the thickness can be calculated from the surface density.

The thickness may also be measured directly by interferometric means. The techniques for this are well established[4,5,6] and need not be reviewed here.

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

5 Tolansky, S., Proc. Roy. Soc. 184, 41 (1945)

6 Tolansky, S., Proc. Roy. Soc. 186, 261 (1946)

This direct measurement differed from the previous indirect determination by less than 5% which is at least as good as could be expected. There is, therefore, no reason to believe that the density of iron oxide in the film differs from the bulk density. As a result of this comparison we were content to determine the thickness of the samples by the optical density method.

The iron sample had to be protected from the oxidising effects of the atmosphere at all times. In order to transfer it from the evaporator in which it was prepared to the vacuum spectrograph in which the absorption was measured, a special vacuum tight container was constructed. Using the vacuum container it was possible to transfer the sample in less than ten minutes, during which time the iron oxidised to a depth of less than 10 Angstroms. Once the sample was in the vacuum spectrograph the oxidation rate was too small to be measured. Since most of the samples were from 400 A to 500 A thick the oxidation of both sides would not convert as much as 5% of the iron to iron oxide.

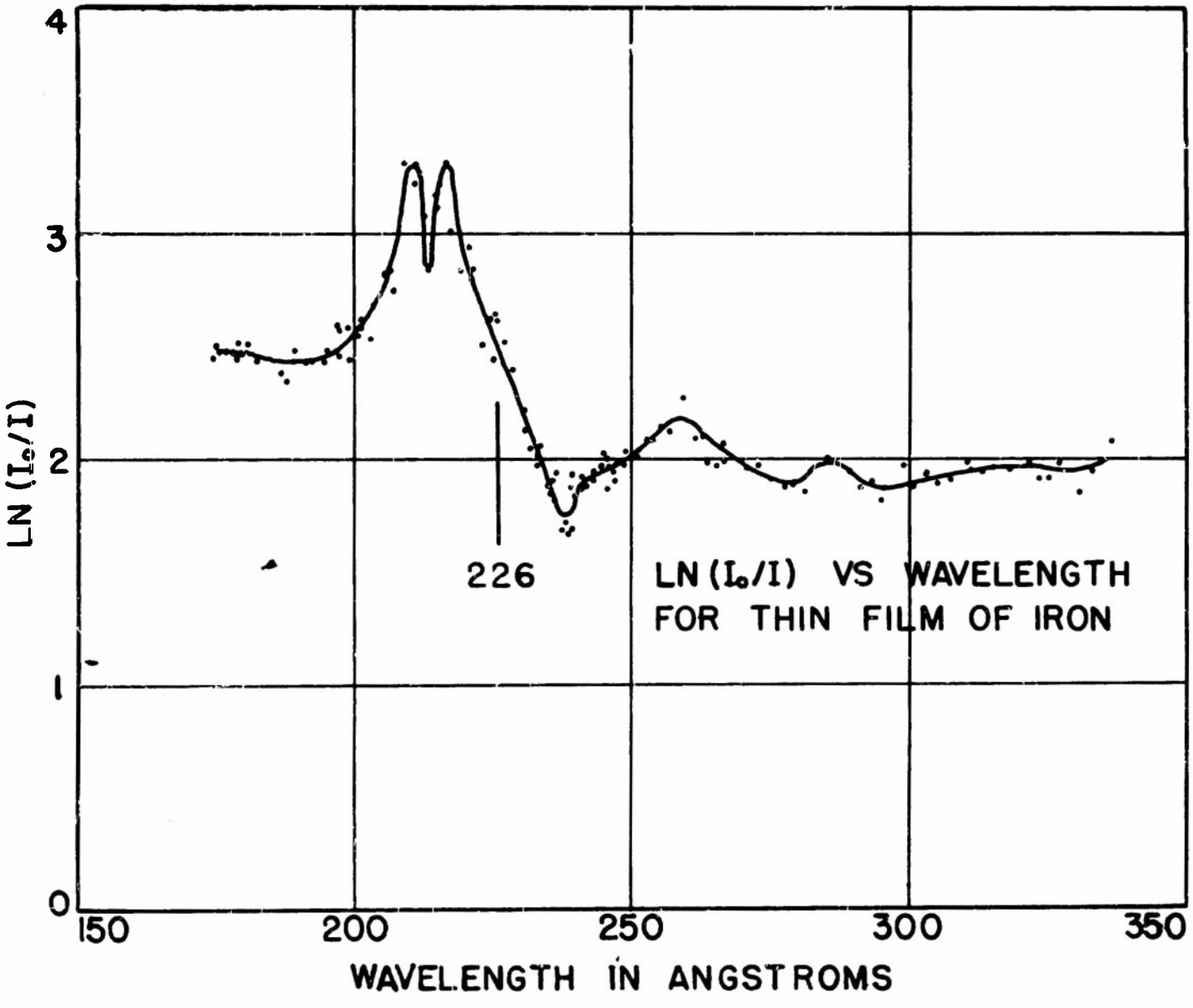
The photographic exposure was determined by counting the number of sparks produced by the source, and in a normal run four exposures were made on

the same photographic plate. Three of these were made through the plain celluloid film with the number of sparks in the ratio of 4:2:1. The fourth exposure was made through the film bearing the sample and usually made with twice the number of sparks as the longest exposure through the plain celluloid. Typical exposures were 3000, 1500, and 750 sparks through the plain film and 6000 sparks through the sample. The spark was operated at constant voltage and as nearly as possible at a constant sparking rate of one per second. The plate was developed with good agitation so that all four exposures received identical processing. Densitometer traces were then made from these spectra and measured in the usual manner. Kodak S. W. R. plates were used.

The first three exposures were used to determine the response curve of the photographic emulsion. At each wavelength there are three points on the curve, but the exposures are relative, not absolute. Using different wavelengths many such sets of points can be obtained, and these were fitted into a smooth response curve by matching exposures at overlapping densities. Finally the absorption is determined by comparing the fourth exposure with one of the other three using this response curve.

II. Results and Interpretation

The results of these investigations are shown in figures 2 and 3. The data for these curves were taken from the plates which showed the best internal consistency along with the absence of air lines in the spectrum. The ordinates are indicated as $\ln(I_o/I)$ where I_o/I is the ratio of the incident to the transmitted intensity. Except for the effects of reflection and scattering this would be the same as μx (absorption coefficient times thickness).


4
3
2
1
0
LN (I₀/I)
226
LN (I₀/I) VS WAVELENGTH
FOR THIN FILM OF IRON
150
200
250
300
350
WAVELENGTH IN ANGSTROMS

According to Sabine[7], who determined the reflectivity of iron in the vacuum

7 Sabine, G. S., Phys. Rev. 55, 1064 (1939)

ultraviolet, the losses due to reflection should be almost negligible. The losses due to scattering should be almost constant over the wavelength region used. The curves then should give a good indication of the selective absorption in this region.

The results for iron are shown in figure 2. These were obtained from a film 220 Angstroms thick (having a surface density of 17.7 micrograms per square centimeter). This curve has an absorption band which reaches half maximum at 225 A or 54.9 electron volts. The width of the absorption band at half maximum is 25 A or 6.8 ev. Ther are two peaks, one at 216 A, the other at 210 A, a separation of 6A or 1.7 ev.

We believe that the absorption is due to the transition of electrons from the filled $M_{2,3}$ level of iron into the vacancies in the $M_{4,5}$ and N_1 bands. These last two bands are the nearest bands to which transitions are permitted by the selection rules and which are also unfilled. On the basis of this assignment it is possible to predict the position of the absorption edge from data given in the International Critical Tables[8] on the limiting frequencies of

8 International Critical Tables, vol VI, page 35 (1929)

x-ray lines or from the term values of the x-ray energy levels given by Bohr and Coster[9] in their tables. These two sources predict the edge at 215 A and

9 Bohr, N. and Coster, D. Zeits. f. Phys. 12, 342 (1923)

225 A respectively. This compares favorably with the observed value of 2[illegible],

The theoretical separation of the $M_{2,3}$ levels may be calculated

from the following formula[10]

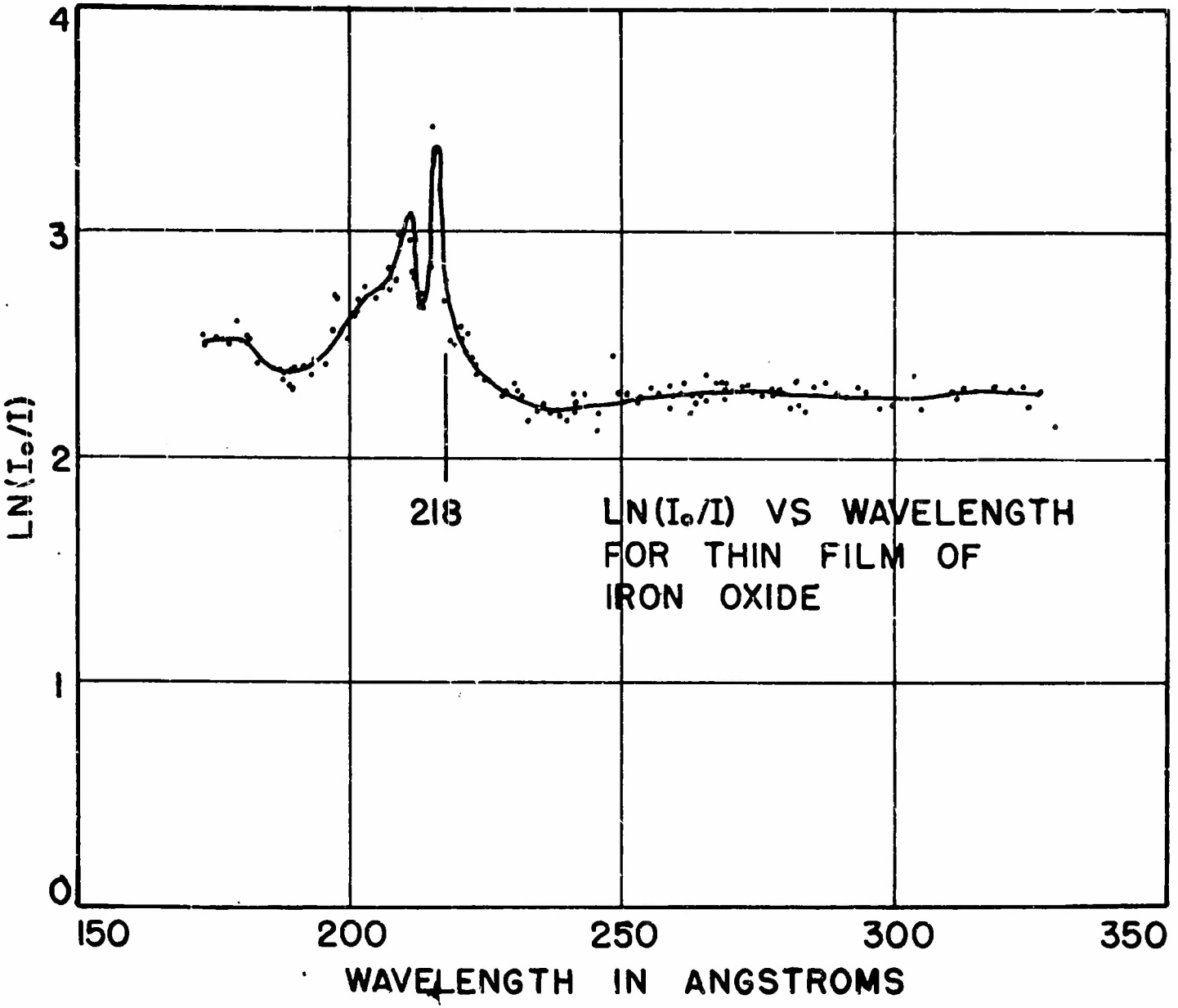
10 Rumark and Urey, Atoms, Molecules and Quanta, p 256, McGraw-Hill (1930)

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

where Z is atomic number, α is fine structure constant, R is the Rydberg constant, and d is the screening constant for $M_{2,3}$ levels. This formula gives 1.3 volts to compare with our experimental value of 1.7 volts. Since this agreement is comparable to that usually obtained from this formula we believe that the observed doubling of the absorption peak is due to the doublet structure of the $M_{2,3}$ level.

The results for iron oxide are shown in figure 3. These results were obtained from a film having 14.5 micrograms of the oxide per square centimeter, or a thickness of 280 A. The iron oxide curve is similar to the curve for iron, but there are a few definite differences. The peaks are at 216 and 211 A, a separation of 5A, instead of the 6A observed with iron; this difference is probably experimental error. The mean absorption edge for the oxide is at 218 A or 56.6 electron volts and the width of the band at half maximum is 10 A or 2 e.v. Thus the oxide has its absorption edge at shorter wavelengths than the iron and also a narrower band. These effects are too large to be experimental error.

We believe that we are dealing with the same electronic transitions in the oxide as were effective in the metal. Specifically, these are transitions from the $M_{2,3}$ (or 3p) levels of the iron atoms to the $M_{4,5}$ (or 3d) and the M_1 (or 4s) levels. The high narrow absorption peaks are due to transitions to the $M_{4,5}$ levels.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WAVELENGTH IN ANGSTROMS

Coster and Kiestra[11] have studied the K absorption of iron and its

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

oxides. Although their results cannot be compared directly with ours, since they were dealing with different electronic transitions, it is interesting to note that their curve for the oxide is quite similar in general shape to the one for the metal.

The absorption edge of the oxide is at 56.6 e.v. whereas the pure metal has its edge at 54.9 e.v., a change of 1.7 e.v. In their work on the K edge of these substances Coster and Kiestra observed a similar but larger shift. Das Gupta[12], also, studied the K absorption edges of a number of metals and

12 Das Gupta, K. Ind. J. Phys. 29, 226 (1946)

their oxides. He observed that in every case the edge was at higher energy for the oxide than for the metal.

The observation that the absorption bands are narrower for the oxide than for the iron is in keeping with the band theory of solids. According to this picture the valence levels are broadened into bands by the interaction of each iron atom with its neighbors, the band width increasing as the atoms are brought closer together. In the oxide the iron atoms (or ions) are more widely separated than in the metal and, hence, the bands are narrower. Das Gupta[13]

13 Das Gupta, K. Ind. J. Phys. 30, 129 (1947)

has made an extensive study of this effect in metalic chlorides and shown that the outermost levels associated with a given ion are broadened the most when the overlap of the wave functions of the electrons of these levels with those of the same type ion is the greatest.

It appears that the results for the $M_{2,3}$ absorption of iron and iron oxide as given in this report are consistent with the results of related experiments.