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THE FINE STRUCTURE OF CERTAIN X-RAY  
ABSORPTION EDGES

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ABSTRACT

**X-ray absorption edges for certain elements and compounds.**—In a recent paper Coster<sup>1</sup> reports a white line on the long wave-length side of the x-ray absorption edge of some metallic oxides. Evidence is here reported which shows that in each case the white line is the absorption edge for some of the material which had been reduced to the metal by the x-ray beam. Screens were prepared by covering black paper with a thin layer of finely divided metal weighing 2 to 3 mg per cm<sup>2</sup>. (1) *K absorption edges for Ti(22), V(23), Cr(24) and Mn(25)* were found at 2489.5, 2261.9, 2064.9 and 1891.4 x-units. (2) *L<sub>III</sub> absorption edges for Sn(50), Sb(51) Te(52) and I(53)* are 3146.9, 2291.5, 2847.1 (Coster) and 2712 (Coster). These values are all in good agreement (within less than 1 x-unit) with the positions of Coster's white lines. (3) *In the case of compounds of higher valence*, the white line Coster obtained is therefore due to reduced element. (4) *In the case of sulfides and sulfites*, the secondary absorption edge at 4988 x-units reported by Lindh<sup>3</sup> may likewise be due to traces of sulfate in the screen produced by the action of the x-rays.

**Chemical changes produced by x-rays.**—Chemical evidence of appreciable reduction of iodic acid and of potassium permanganate is presented, and also of the oxidation of sulfurous acid.

**Theory of changes of valence produced by absorption of radiation by elements 22-25 and 50-53 and of consequent chemical changes.**—It is proposed that the numerous electron transitions that follow the removal of an electron from its normal orbit by absorption of radiation may occasionally occur in such a way as to result in a change in the general electron configuration such that some of the valence electrons find stable positions farther in, thus resulting in a reduction of valence. Oxidation can also occur when the change in the electron configuration is such as to place an increased number of electrons in the valence group. What makes this proposal seem especially reasonable is that Ti(22), V(23), Cr(24) and Mn(25) occur in a portion of the periodic table in which inner groups are being filled in building new elements while Sn(50), Sb(51), Te(52) and I(53) are found very close to such a group. Bohr thus considers that configurations which place additional electrons in inner groups in this region are stable.

**I**N a recent article<sup>1</sup> Coster describes the K absorption edges of titanium, vanadium, chromium and manganese and the L<sub>III</sub> absorption edges of tin, antimony, tellurium and iodine, obtained when various compounds

<sup>1</sup> Coster, Zeits. f. Phys. (July 2, 1924).

were used in the absorbing screens. He found a complicated structure of the absorption edge in each case for the more highly oxidized compounds used. An important feature of the structure was a white line on the long wave-length side of the absorption edge about six or seven x-units from the main edge. It is the purpose of this investigation to inquire further into the significance of this white line. It is not found when the free element or a compound of low valence is used in the absorbing screen.

Coster's data which have to do with the present investigation are given in Tables I and II.

TABLE I  
*Coster's data for titanium to manganese.*

Element	Screen	K absorption edge	White line $K\alpha$	Valence
Titanium(22)	TiO <sub>2</sub>	2482.9x	2489.5x	4
	Ti metal	2484.0		
Vanadium(23)	V <sub>2</sub> O <sub>5</sub>	2256.4	2262.8	5
	V <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2256.7		3
Chromium(24)	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2059.5	2065.0	6
	K <sub>2</sub> CrO <sub>4</sub>	2059.1	2065.2	6
	Cr <sub>2</sub> O <sub>3</sub>	2060.6		3
	[Cr(NH <sub>3</sub> ) <sub>6</sub> ](NO <sub>3</sub> ) <sub>3</sub>	2063.8		3
	CrCl <sub>3</sub>	2063.0		3
Manganese(25)	KMnO <sub>4</sub>	1886.0	1891.3	7
	KMnO <sub>4</sub> (reduced)	1887.5		
	Mn <sub>3</sub> O <sub>4</sub>	1888.9		
	Manganic acetate	1887.8		3
	MnSO <sub>4</sub>	1889.2		2

TABLE II  
*Coster's data for tin to iodine.*

Element	Screen	L absorption edge	White line L <sub>IIIa</sub>	Valence
Tin(50)	SnO <sub>2</sub>	3140.6x	3147.5x	4
Antimony(51)	KSbO <sub>3</sub>	2984.1	2990.8	5
	Sb <sub>2</sub> O <sub>3</sub>	2985.1	2991.1	3
Tellurium(52)	H <sub>2</sub> TeO <sub>4</sub>	2840.6	2846.6	6
	H <sub>2</sub> TeO <sub>3</sub>	2842.2	2846.9	4
	Te metal	2847.1		
Iodine(53)	HIO <sub>4</sub>	2705.8	2711.3	7
	HIO <sub>3</sub>	2707.1	2711.5	5
	KI	2712.2		1
	I	2712		

It will be noted that the wave-length of the absorption edge increases slightly as compounds of lower valence are used in the absorbing screen; also that the white line is, in general, found only with compounds repre-

senting the higher valences and never with the free elements. Moreover, the values for the absorption edges of the free element in the case of both iodine and tellurium fall within a fraction of an x-unit of the white line reported for the oxidized states. This at once suggests that the white line may be the absorption edge of a portion of the material in the absorbing screen that has undergone reduction and that the x-ray beam is the reducing agent.

#### EXPERIMENTAL DETAILS

The present work was undertaken to investigate the hypothesis that x-rays might reduce part of the highly oxidized compound in passing through the absorbing screen and that the white line reported by Coster might be the simple absorption edge of the reduced portion. The resulting investigation took a two-fold course. In the first place, certain of the compounds used by Coster were exposed to x-rays for a number of hours in the effort to discover whether reduction of the highly oxidized compounds could be demonstrated chemically. In the second place, spectrograms were made of the  $L_{III}$  absorption edges of metallic antimony and tin and of the K edges of metallic titanium, vanadium, chromium and manganese to discover whether these would coincide as closely with the white lines obtained with the corresponding oxidized compounds as do the edges for iodine and tellurium in Coster's data.

For the chemical part, the procedure was as follows. Portions of a 25 percent solution of iodic acid in water were introduced into thin walled specimen tubes. These were filled about three fourths full and the neck of the tube rinsed carefully with distilled water before sealing off, to prevent possible reduction of any of the iodic acid by the heat of the blast lamp. One of these tubes also contained about 1 cc of carbon tetrachloride, another, the same amount of chloroform, a third, the same amount of carbon disulphide while several other tubes contained only iodic acid and were broken open and tested with the organic solvents after x-raying. The tubes were placed in a lead covered box containing a Coolidge tube and were exposed to x-rays for about 14 hr with a tension of 35000 volts, a current of 30 milli-amp., and a distance from target to specimen tube of about 5 inches (13 cm). Every sample gave indications of traces of free iodine by imparting a distinct pink coloration to the organic solvent.

The iodic acid was carefully tested with chloroform and found entirely free from iodine before exposure to the x-rays, a precaution that is quite necessary as iodine or iodide in traces frequently contaminate iodic acid. The carbon disulphide was of only technical grade and so not

above suspicion in regard to purity but the chloroform and the carbon tetrachloride had been especially purified for analytical work. Blanks treated exactly as were the other samples except that they were not exposed to the x-rays gave negative tests for iodine. The conclusion is, therefore, that traces of the iodic acid were reduced by the x-rays.

A solution of potassium permanganate, another of the compounds reported by Coster, was next used. This solution was so dilute that the permanganate imparted only a faint pink color to the water. It was placed in a glass stoppered Erlenmeyer flask and exposed to x-rays for two hours. By the end of that time the pink color had entirely disappeared, thus showing undoubted reduction of the permanganate ion.

The remainder of the investigation consisted in getting the  $L_{III}$  absorption for antimony and tin and the K absorption for titanium, vanadium, chromium and manganese, using the free metal in each case to make the absorbing screen. All of the spectrograms were made with a Siegbahn spectrograph similar to that used by Coster. The source of high potential was a small transformer giving a maximum potential of 20,000 volts. The potential was controlled by a rheostat in the primary circuit. The rough pump was a General Electric oil pump which was connected both to the x-ray tube and to the spectrograph chamber. A Gaede molecular pump was used as a finishing pump to produce a sufficiently high vacuum in the x-ray tube. Tungsten filaments were used throughout except for titanium when a molybdenum filament was used to prevent possible overlapping of the edge by tungsten lines in the second order.

In most cases the absorbing screens were made by grinding the metals as finely as possible in an agate mortar and then rubbing on pieces of the black paper which is placed by the Eastman Company between pieces of cut film to protect the sensitive emulsion. New screens were made for the duplicate plates in every case where there was any chance that the metal on the screen might have become oxidized by exposure to the air or changed in any other way.

Tin offered special difficulties because its malleability made it impossible to grind it fine, at least at ordinary temperatures. Moreover while it is brittle above 200°C, it proved impossible to get it ground to the necessary degree of fineness at that temperature. The thinnest tinfoil would make an absorbing screen many times as thick as was desired. The method finally used was to precipitate the tin from a slightly acid solution of stannous chloride by placing a sheet of zinc in it. The dark gray sludge thus deposited was scraped off and washed repeatedly with distilled water leaving the tin in flat particles having a metallic luster. The finer particles were separated by swirling in water until all the par-

ticles were in suspension, then allowing the heavier particles to settle out and removing the lighter particles by decantation. This was repeated several times. A Gooch crucible was next fitted with an alundum disk and a piece of the black paper, and a sufficient quantity of the suspension of tin particles in water was filtered through it to cover the black paper with a thin continuous layer of metallic tin. The paper and adhering tin were then dried over a Bunsen flame. In this way an absorbing screen was made which showed no uncovered portions and had a bright metallic luster. The total weight of tin was approximately 3 mg per cm<sup>2</sup>. The same method was followed in making one of the absorbing screens used for antimony. It would also have been possible with tellurium but not with chromium, vanadium, manganese or titanium, as these are not reduced to the free metal by zinc. These are, however, sufficiently brittle so that they can be ground to the necessary degree of fineness in an agate mortar and applied to the paper in the dry state.

The weight of absorbing metal was between 2 and 3 mg per cm<sup>2</sup> except one each of Mn and Ti which were 7.5 and 3.6 mg, respectively. In the case of iodine, iodic acid, pure or impure, was used.

Considerable variations in the amount of material on the absorbing screen apparently make little difference in the appearance of the edge. Thicker screens necessitate longer exposures which may have a tendency to obliterate detail by covering it with an excessive amount of secondary radiation. Thin screens are therefore preferable. It would also appear necessary to use samples of the metals that are as pure as possible. The first sample of metallic chromium used was not highly purified and contained a certain amount of slag. Absorbing screens made from this gave spectrograms showing an absorption edge that differed from Coster's white line by several x-units. When a purer sample of metallic chromium was obtained, however, the check was entirely satisfactory.

In certain cases, special precautions had to be taken because the absorption edge was obscured by an emission line. The L<sub>III</sub> edge of tin falls very close to the La lines of iodine. In spite of the fact that several plates had been made since any iodine compound had been placed in the tube, these lines both appeared, making the location of the edge somewhat uncertain. It was therefore necessary to scour the interior of the x-ray tube and the target with alundum polishing powder until all discoloration of the brass interior of the tube had been removed. A new focussing cylinder was also put around the filament. After this plates were secured that showed no sign of iodine lines. The titanium edge lies within a few x-units of the L<sub>β<sub>2</sub></sub> line of tungsten in the second order. The tube was

therefore cleaned again and a molybdenum filament used instead of tungsten.

It happened that suitable reference lines fell at convenient places on most plates because of the characteristic radiation of the metals in the x-ray tube. Chromium, manganese, vanadium or titanium salts were not used to obtain reference lines as the  $K\beta_2$  lines fall very close to the K absorption edges and there appeared to be danger that faint traces of these lines, if present, might be mistaken for the absorption edges. The only exception was in the case of manganese. Potassium permanganate solution was put on the target and reduced to manganese dioxide by evaporation to dryness in order to use the  $K\alpha_1$  line of manganese as a reference line to determine the chromium edge. It was not done, however, until after the manganese absorption had been completed so that there was no danger of obscuring the manganese edge from this source.

Table III gives the values for the white lines reported by Coster on the long wave-length side of the absorption edge for the compounds of higher valence and the simple absorption edges obtained by the writer for the free elements<sup>2</sup> and by Coster for tellurium and iodine.

TABLE III  
*Absorption edges of free elements.*

Element	Screen	White line (Coster)	Absorption edge of free element	Difference Line—edge
Ti	TiO <sub>2</sub>	2489.5x	2489.5x 2484.0(Coster)	0.0 (5.5)
V	V <sub>2</sub> O <sub>3</sub>	2262.8	2261.9	0.9
Cr	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2065.0	2064.9	0.1
Cr	K <sub>2</sub> CrO <sub>4</sub>	2065.2	2064.9	0.3
Sn	SnO <sub>2</sub>	3147.5	3146.9	0.6
Sb	KSbO <sub>3</sub>	2990.8	2991.5	-0.7
Sb	Sb <sub>2</sub> O <sub>3</sub>	2991.1	2991.5	-0.4
Mn	KMnO <sub>4</sub>	1891.3	1891.4	-0.1
Te	H <sub>2</sub> TeO <sub>4</sub>	2846.6	2847.1 (Coster)	-0.5
Te	H <sub>2</sub> TeO <sub>3</sub>	2846.9	2847.1 (Coster)	-0.2
I	HIO <sub>4</sub>	2711.3	2712 (Coster)	-0.7
I	HIO <sub>3</sub>	2711.5	2712 (Coster)	-0.5

In every case, with the exception of Coster's value for titanium, the absorption edge of the free element coincides within the limits of experimental error with the white line. Apparently, Coster's sample of titanium had become oxidized for Lindh reports a value for the titanium edge in

<sup>2</sup> The data for tellurium, iodine, antimony, and tin were reported together with the hypothesis proposed here, in *Nature*, October 4, 1924. Confirmatory data upon titanium, vanadium, chromium and manganese have appeared in an article by Lindh (*Zeits. f. Phys.*, February 11, 1925). His value for the absorption edge of metallic titanium is 2491.2 x-units.

substantial agreement with that of the present writer.<sup>2</sup> It would therefore seem conclusive that the spectrographic data for all eight elements concerned corroborate the chemical evidence of reduction obtained with iodic acid and potassium permanganate. One more piece of evidence in regard to the origin of the white lines can be offered here. Plates were made of the absorption with iodic acid using in one case a sample of the acid known to be free from the reduced forms of iodine and in the other, a sample that gave a test for contamination with traces of iodide or iodine. Both plates showed the white line but it was clearer on the plate made with the impure acid.

The evidence obtained would indicate that only traces of the material in the absorbing screen are reduced. Thus, we should expect the effect upon the photographic plate to be similar to that produced by a very thin absorbing screen. With such screens practically all the absorption is frequently confined to a very narrow band which gives the appearance of a white line on the plate such as Coster describes.

Certain evidence has been obtained that the x-ray beam can oxidize quadrivalent sulfur in sulfurous acid to the hexavalent form which would indicate that this is at least a contributing cause in the production of the secondary edges which Lindh reports in the neighborhood of 4988 x-units for the lower valence forms of sulfur.

The general plan was to make an acid solution of a soluble sulfite containing a small amount of barium chloride which, in the presence of sulfate, will precipitate barium sulfate, a very insoluble, dense, crystalline precipitate. It proved impossible to secure any sample of sodium sulfite prepared by the manufacturers of chemicals that was not contaminated with considerable quantities of sulfate. This is probably characteristic of all sulfites, and to a considerable extent of sulfides, that they will not be free from traces of sulfate unless special precautions are taken to prepare them in an atmosphere free from oxygen and to keep them from the oxygen of the air during use.

It was therefore decided to prepare a solution of sulfurous acid in water containing a small amount of barium chloride by saturating it with sulphur dioxide and to expose the solution thus formed to the x-ray beam to discover whether any of it would become oxidized to sulphate. The preparation of sulfurous acid free from all traces of sulfate proved rather difficult. The sulfur dioxide procurable in tanks contained sufficient oxygen to oxidize an appreciable amount of the sulphurous acid. The procedure finally adopted was as follows. Bulbs having a capacity of about 50 cc and a very thin wall were blown on one end of glass specimen tubes and the tubes were constricted above the bulb to facili-

tate sealing off after the specimen had been prepared. The whole was fitted with a two hole stopper, a delivery tube leading to the bottom of the bulb, and an outlet tube. Meanwhile, a sulfur dioxide generator had been set up containing about two hundred grams of acid sodium sulfite and about four hundred cubic centimeters of water. Concentrated sulfuric acid could be admitted as required through a dropping funnel. The generator was connected to a water trap, to insure that no sulfuric acid should be carried over, and then to the bulb. Before use, the generator was allowed to operate for some time to be certain that all air was removed. Meanwhile, one of the bulbs was filled with conductivity water, the purest distilled water obtainable, and boiled under a reflux condenser for about fifteen minutes to remove any oxygen that might be dissolved in the water. It was then connected as quickly as possible to the sulfur dioxide generator and sulfur dioxide passed in for about an hour and a half. By the end of this time, the contents of the bulb had cooled to room temperature and were saturated with the gas so the bulb was immediately sealed off in the flame of a blast lamp.

In this way two samples were prepared entirely free from turbidity. They were set aside for about ten hours as a precipitate is sometimes very slow in forming. When no precipitate had formed by the end of this time, however, it seemed conclusive that neither sulfate nor oxidizing agent capable of producing any was present in either bulb.

One was therefore set aside as a blank and the other exposed to the x-ray for about forty milli-ampere hours under a tension of a hundred and ten thousand volts. By the end of this time a small amount of barium sulfate had been precipitated thus demonstrating that traces of the material had become oxidized by the x-ray beam for the bulb that had not been x-rayed remained clear. Later, in order to make the test more conclusive, the other specimen was also exposed to the x-ray beam and a precipitate formed.

Lindh<sup>3</sup> has questioned the real existence of a secondary absorption edge in the case of quadrivalent sulfur because of the readiness with which it undergoes oxidation. The present writer would go a step farther and question whether any of the secondary edges reported by him at a wavelength in the neighborhood of 4988 x-units for divalent and quadrivalent compounds of sulfur are other than the simple absorption edges of hexavalent sulfur. Our experience here would indicate that the principal oxidizing agent is probably the oxygen of the air but the x-ray beam itself is quite evidently a contributing cause.

<sup>3</sup> Siegbahn, *Spektroskopie der Röntgenstrahlen*, p. 142.



## UNDERLYING THEORY OF THIS ABSORPTION

It will next be of interest to consider the bearing of these results upon the Bohr theory. While nothing definite has been said by Bohr regarding the valence electrons of these elements, the inference has always been that these are located in the electron groups of highest quantum number, i.e. in those groups representing electron orbits having the greatest major axes. Lewis,<sup>4</sup> Bury,<sup>5</sup> and J. J. Thomson<sup>6</sup> carry this a step farther and suggest that oxidation and reduction changes represent an increase or decrease in the number of electrons in the valence ring by a change in the number of electrons in inner groups. These outer electrons are the electrons that give rise to optical spectra, and require so little energy to eject them from their normal orbits to the periphery of the atom or beyond, that radiation of longer wave-length than that considered here will be required. Therefore, the way in which they are most likely to be removed by x-radiation is by what we may call the indirect method.

The mechanism of the process may be somewhat as follows. Below is the electron arrangement given by Bohr for titanium.

Group	K	L	M	N
Quantum numbers	1 <sub>1</sub>	2 <sub>1,2</sub>	3 <sub>1,3<sub>2</sub>,3<sub>3</sub></sub>	4 <sub>1</sub>
Number of electrons	2	4,4	4,4,2,	(2)

Since the atomic number of titanium is 22, only four groups of orbits, K, L, M and N, are possible. The energy level diagram shows one K level, three L levels, five M levels and one N level.

Suppose that radiation of the frequency required to eject an electron from the K orbit outside the atom is allowed to fall upon a titanium absorbing screen. The possible transitions, taking proper account of the Selection Principle, by means of which the vacant place may be filled again, are as follows. An electron might fall from the M<sub>3</sub> level to the K giving rise to radiation of the frequency designated as the Kβ<sub>1</sub> line. The vacant place in the M<sub>3</sub> level might then be filled by an electron from the N level and the electron originally ejected from the K to the periphery might fall back into the vacant place in the N. This is a typical case only, for a variety of transitions are possible, but the point is that any such phenomenon involves numerous transitions between the various electron orbits. It would therefore seem possible that, as a result of all these transitions, in certain cases a sufficient alteration of the atomic configuration might occur so that the possible number of electrons in groups of lower quantum number might increase, thus providing for more

<sup>4</sup> Lewis, Jour. Am. Chem. Soc. **38**, 770 (1916).

<sup>5</sup> Bury, Jour. Am. Chem. Soc. **43**, 1602 (1921).

<sup>6</sup> J. J. Thomson, The Electron in Chemistry, p. 96-99 (1923).

electrons in such groups and a corresponding reduction in the number of electrons in the valence group. This would seem to be a reasonable extension of Bohr's hypothesis regarding the formation of the rare earth group.

It will be recalled that he accounts for the formation of this group by the hypothesis that when electrons are added to compensate for the increased nuclear charge in passing from element to element, they are inserted into groups of lower quantum number. Thus, the most stable position open to the last added electron is at times in an electron group of lower quantum number than that available for those added just previously. In other words, at certain points in the up-building of the elements, electrons begin to be inserted again into groups of lower quantum number that had previously been in a state of temporary completion. If this occurs in the building up of new elements, it seems reasonable to inquire whether it might not occur also in a particular element when x-radiation falls upon it and produces numerous electron transitions in its atoms. Some of these transitions may produce a change in the configuration of certain orbits that would provide stable positions for part of the valence electrons in orbits of lower quantum number, thus resulting in a reduction of valence. Moreover, if some of the valence electrons were moved to positions in groups of lower quantum number, they would exert a shielding effect upon the outer electrons with a consequent slight reduction in the energy of these outer orbits. As a result, it would be expected that the different absorption edges would represent slightly less energy when the element exists in its lower valence forms; i.e., the wave-length of the edge would be slightly longer for a compound of low valence than for one of high. It will be noted that this is exactly what is found when the absorption edges are determined experimentally for the different valence forms of the same element.

If the mechanism of the process is as proposed here, oxidation as well as reduction by the x-ray beam may be considered possible. In fact, even if these changes of electron configuration occur only temporarily, they may be expected to produce an effect upon the absorption edge. Oxidation effects produced in this way would probably not be visible in many cases for the edge of the oxidized form would fall on the short wave-length side of the main edge; i.e. in that region in which absorption is already at a maximum, so that it would not be likely to be visible except in the case of those elements whose absorption edges for the various valence forms differ from each other by a number of x-units. Sulfur is an element whose absorption edges meet this requirement and

Lindh's data<sup>7</sup> showing multiple edges in the case of certain of its compounds exhibit rather greater agreement in wave-length between the secondary edges of lower valence compounds and the principal edges of those of higher valence than seems reasonable to attribute to chance. At least it seems reasonable to consider that the first secondary edge reported by Lindh<sup>3</sup> for various sulfides and sulfites is due to the presence of traces of hexavalent sulfur in the absorbing screens, as compounds of these kinds are slowly oxidized by exposure to the oxygen of the air. Moreover, sulfides and sulfites that are entirely free from traces of sulfate are almost unknown. It has also been shown that the x-ray beam itself can bring about oxidation of a portion of the material in the absorbing screen.

Attention might be called to the fact that titanium, vanadium, chromium, and manganese occur in a region in the periodic system in which Bohr proposes that the added electrons in building new elements are being inserted into inner groups. While it is true that the tin, antimony, tellurium, iodine group is built up by inserting electrons in the groups of highest quantum number rather than in inner positions, it seems significant to note that they come only three elements below the rare earth group and here, again, electrons begin to be inserted into inner groups. Thus, we find that both of these groups of elements that are capable of oxidation and reduction either fall in a portion of the periodic table in which electrons are being inserted into inner quantum groups or very close to such a portion. This would seem to make it extremely probable that electron shifts from outer to inner groups or vice versa may take place here in a particular element and that these shifts would result in a change of valence.

Exactly to what extent valence changes in the absorbing screen can account for the fine structure of absorption edges, it will be impossible to say until more data are available. Evidently, however, such changes must be taken into account in the interpretation of all absorption edges involving elements that are capable of oxidation and reduction and they may explain much that has previously been obscure regarding fine structure. Moreover, it may prove possible to reverse the process and interpret chemical valence in the light of the Bohr theory by a study of the absorption edges of elements that are capable of oxidation and reduction. Last, a systematic study of x-rays as an oxidizing or reducing agent for inorganic compounds may give the key to the solution of that vastly more difficult problem of what occurs in the human body when x-rays are used as a therapeutic agent.

<sup>7</sup> Lindh, Dissertation, Lund (1923).

In conclusion, I should like to express my thanks to Dr. George A. Lindsay, of the University of Michigan, for the use of a Siegbahn spectrograph and for valuable criticism during the progress of this work, to Mr. William Fink and Mr. James Kassner for helpful suggestions in regard to the chemical part of this investigation, and to Dr. Coster for his interest in my preliminary report and for the encouragement he offered to carry the work farther.

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