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THE DEPENDENCE OF X-RAY ABSORPTION SPECTRA UPON CHEMICAL AND PHYSICAL STATE

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Abstract

The x-ray absorption spectra of As, Se, Br, Zn, Hg, Xe, and Kr, and of compounds of some of these elements have been photographed for both the solid and the vapor states at a dispersion of about 5 X.U. per mm. The effect of the chemical and physical state of the absorbing atom upon the secondary structure which lies to the short wave-length side of the main absorption edge was investigated. It was found that: (1). The monatomic vapors Zn, Hg, Xe, and Kr exhibit no secondary structure at distance from the main edge greater than the ionization potential of the atom. (2). Polyatomic vapors usually, though not necessarily, have a secondary structure similar to that which is exhibited by the same molecule in the solid state. (3). For a polyatomic molecule in the solid state there is often an additional structure observed which is absent when the molecule is in the vapor state. (4). There is an additional structure in the secondary absorption of solid $NaBrO_3$ which is not observed in a solution of $NaBrO_3$. (5). Completed electron shells of atoms in the solid state do not necessarily mean the absence of secondary absorption edges as has been suggested. In order to account for this dependence of secondary absorption on molecular and physical state it is suggested that perhaps the secondary discontinuities correspond to the excitation energies of the structure electrons postulated by O. W. Richardson.

Introduction

A STUDY of the x-ray absorption spectrum of a substance shows that there are sharp discontinuities in the absorption at wave-lengths corresponding to the energies of the Bohr levels of the atom. These absorption discontinuities do not always have the same appearance for different elements. The absorption edge may be what is known as "simple," or there may be some absorption discontinuities of lesser magnitude associated with the principal absorption edge. Fig. 2 (a) and (b) illustrate respectively a simple edge and one with secondary absorption. This secondary absorption falls to the short wave-length side of the main edge and therefore means the absorption of quanta of greater energy than that which produces the main edge. In some cases the difference in energy between a secondary discontinuity and the main edge may be more than 300 volt electrons. Experiments show that the wave-length of the main edge and the type of the absorption are functions of the chemical state of the absorbing atom. Experiments also show that the chemical state of an atom affects the emission spectrum of the atom. These latter experiments are complicated by the fact that one can not be sure of the chemical state of atoms on the anode of an x-ray tube, so it seems that absorption experiments have an advantage in this respect. An excellent and

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complete presentation of the researches on the influence of chemical combination on the x-ray absorption and the x-ray emission spectra of an atom has been given by A. E. Lindh.[1] However, because of the complexity of the results, no unified picture of the work can be as yet formed.

There are two general questions, probably more or less related regarding absorption spectra to be considered. What are the factors which govern the position of the main edge; and, what is the origin or interpretation of the secondary absorption structure? The suggestions regarding the first question, as given by Wentzel, Coster, Stelling, Aoyama, Kimura and Nishina, are summarized by A. E. Lindh.[1] The latest work is that of Pauling[2] who was able to calculate quantitatively the shifts in the position of the K absorption edge in the alkali chloride series and in the potassium halide series. The answer to the second question as given by Coster,[3] Lindsay,[4] Ray,[5] and others, has been in terms of the simultaneous transitions of two or more electrons within the atom, due to the absorption of a single quantum. This suggestion does not give any idea as to why secondary absorption is a function of chemical state, though Coster and Wolf[6] have postulated that multiple jumps will be less probable in an atom which has completed electron shells. On the side of emission spectra, the suggestion of F. K. Richtmeyer[7] of simultaneous transitions of electrons to account for x-ray satellites seems to be the most acceptable at present in view of the recent experiments of Du Mond and Hoyt.[8,9] This fact no doubt makes the same hypothesis more probable as an explanation of secondary absorption. The writer simply wishes to bring out here that with the present knowledge regarding secondary absorption one can not make much use of the experimental data, whereas, because of its pene-

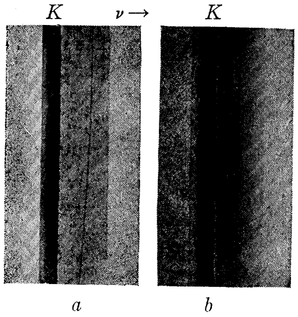

Fig. 1. (a) Simple edge. (b) Edge with secondary absorption.

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[1] Handbuch der Experimental Physik XXIV 2. Teil (1930).
[2] L. Pauling, Phys. Rev. **34,** 954 (1929).
[3] D. Coster, Zeits. f. Physik **25,** 83 (1924).
[4] G. A. Lindsay and H. R. Voorhees, Phil. Mag. **6,** 910 (1928).
[5] B. B. Ray, Nature **122,** 771 (1928).
[6] Coster and Wolf, Nature **124,** 652 (1929).
[7] F. K. Richtmyer, Journ. Frank. Inst. **208,** 325 (1929).
[8] Du Mond and Hoyt, Phys. Rev. **36,** 799 (1930).
[9] Du Mond, Phys. Rev. **36,** 1015 (1930).

trating power, it seems that the x-ray has the possibility of giving interesting information about the atom in the solid state. It was thought that a study of the x-ray absorption of vapors, where one is concerned with isolated atoms or molecules, would be of help to the problem.

Apparatus

In order to study absorption in vapors one must have a cell which will transmit the radiation, which will stand the requisite temperature to secure sufficient vapor pressure, and which will not react with the hot vapors. One is practically limited to a study of those vapors which have their characteristic x-ray absorption in the region from about one to two and one-half angstroms, since at shorter wave-lengths the energy dispersion becomes too small, and at longer wave-lengths nothing can be found to use for a cell. Fig. 2 shows the arrangement which was used. *S* is the slit, *C* is the calcite crystal, and *P* is the photographic plate. The furnace *B* is for controlling the vapor pressure, and the furnace *A* is for superheating the vapor. The furnace box is made of transite. The vapor cell *V* is made of Pyrex or of quartz, and the concave windows *W* may be drawn as thin as 0.005 mm in Pyrex,[10] and to 0.003 mm in quartz, and yet maintain a vacuum and stand temperatures to the melting points. In order to prevent any vapor condensation on the windows *W*, the openings in the ends of furnace *A* were covered with three sheets of Al foil or mica with air spaces between the sheets. *H* is a glass tube with gold-beater's skin windows. The air is flushed out with hydrogen simply to reduce the air path of the radiation. The dispersion of this spectrograph in the region worked varies from 4.9 to 5.3 X.U. per mm. The usual slit width was 0.05 mm, though for special cases it was narrowed to 0.025 mm or widened to 0.1 mm. The x-ray tube was an extra large size of the Siegbahn type. The current was usually about 30 m.a., and exposure times varied from 4 to 30 hours depending on the absorbing material.

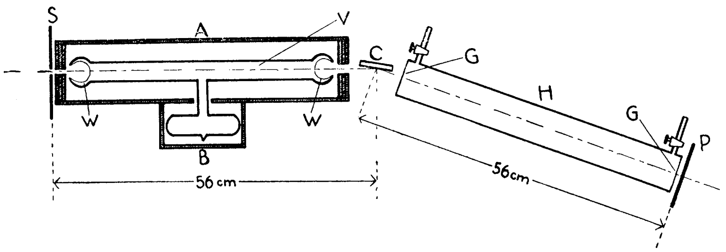

Fig. 2. Diagram of x-ray spectrograph.

Preparation of Materials

The substances which were investigated in this work were As, Se, Br, Zn, Hg, Xe, and Kr, and compounds of some of these elements. When it was possible, each substance was studied in both solid and vapor forms. In the solid form the absorption spectrum was secured for various thicknesses of screen, while in the vapor state all degrees of absorption could easily be se-

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[10] Slack, J.O.S.A. **18**, 123 (1929).

cured by regulating the vapor density through the temperature. After thorough cleaning and baking of the cell *V*, the material was inserted, and the cell sealed-off under high vacuum conditions. The cell was about 40 cm long. With this length of path a few cm pressure of vapor was usually sufficient to produce the maximum contrast in the absorption spectrum. The vapor was always superheated so that there would be no condensation on the ends of the tube. When studying Zn, the vapor was superheated to 950 degrees C, though all of the other vapors could be studied at temperatures much lower than this. Attention must be paid to the fact that polyatomic molecules dissociate at certain temperatures, so that this temperature must not be exceeded. The fact that the x-radiation itself decomposes some molecules did not cause any difficulty in this work since, for example with AsH_3, the As atoms froze on the walls of the cell and left only AsH_3 in the path of the radiation.

In studying solids, if it is possible, the simplest method is to soak cigarette paper in a solution of the material and let it dry. A metal like Zn may be rolled to a thin sheet. Thin sheets of metallic As were formed by passing AsH_3 through a Pyrex tube heated to 500 degrees C. The AsH_3 decomposes, depositing a silvery mirror of As which can be peeled off of the tube. Because of its surface tension, it is hard to get a thin sheet of Hg. A screen of finely divided Hg was formed by reducing mercurous nitrate by formic acid held in gelatine. This gives an emulsion containing very densely packed mercury globules of about 10μ diameter.[11] The compound $NaBrO_3$ can not be had in the vapor form so it was studied as a solid and in solution. Solutions varying from saturated to 1/3 normal were put in cells from 0.7 to 2.0 mm thick. These cells had thin mica windows.

EXPERIMENTAL RESULTS

Due to the character of secondary absorption, there has been no uniformity among different workers in the methods of recording measurements. The absorption regions may vary in width from the slit width of a few volts to as much as 40 volts. The tables in this paper record the distances of both sides of every absorption band, or the distance of the center of the absorption bands from the principal edge. The secondary discontinuities near to the principal edge are always sharper than those farther from the edge. This diffuseness of those farther out, makes it impossible to state their position to closer than about 10 volts.

B. B. Ray[12] has introduced two definitions which it will be convenient to use for purposes of classification and of discussion. Any absorption discontinuities which exist at energy distances from the principal edge of less than the ionization potential of the atom will be called "fine structure" while the term "secondary absorption" will be used to designate absorption discontinuities which occur at greater distances than this from the main edge.

An inspection of Table I shows the following facts: The secondary absorption of As in the solid and vapor states is radically different. $AsCl_3$ in the solid

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[11] M. Wolf, Zeits. f. Physik **53**, 72 (1929).

[12] B. B. Ray, Ind. Journ. Phys. **3**, 477 (1929).

form shows an additional structure near the main edge which does not occur for the vapor. The same statement applies to the spectra of As_2O_3 in solid and in vapor form. AsH_3 shows no secondary structure. In the vapor state, the principal edges agree within the experimental error, while in the solid state there are differences as great as 5.2 ± 1.5 volts.

The results of the study of Br_2 and its compounds are uncertain in a few cases because one can not get rid of the effect due to the AgBr in the photographic plate. All of the solids and the $NaBrO_3$ solution show an extensive secondary absorption structure. A comparison of the $NaBrO_3$ solid and the solution shows the same type of additional structure which appeared in the solid As compounds here occurring for the solid $NaBrO_3$. There are shifts in the positions of the main edges of as much as 6.9 ± 2.3 volts.

The positions of the main edges of the Se compounds were not determined. Se_8 vapor exhibits one very close fine structure line but no secondary absorption. Se solid has a white line absorption at the main edge and perhaps an indication of a fine line like that shown by the vapor. SeO_2 solid and vapor both show a secondary absorption, and, as in the cases of the As and Br compounds, there is an additional structure in the absorption spectrum of the solid which does not appear in that of the vapor.

TABLE I.

Substance	Temperature °C.#	Main Edge X.. U.	ΔV (volts)	Distances of both sides, or, of center of absorption bands from the main edge. (volts)
Solids				
As		1042.49	0	0–3.6, 10–12, 40–58, 75–92, 130–152, 168–?
$AsCl_3$		1042.41	0.9	0–7.6, 14–22, 33–38, 48–92, 145–?
As_2O_3		1042.22	3.1	0–5.1, 12–18, 55–97, 140–?
As_2O_5		1042.03	5.2	0–5.4, (54–30)*, 60–118, 150–?
Vapors				
	350			
As^4	270	1042.31	2.0	0–4.4, 57–102, 135–?
	95			
$AsCl_3$	35	1042.31	2.0	0–3.8, 57–82, 125–?
As_2O_3	320	1042.34	1.7	0–5.2, 55–93, 160–?
	260			
AsH_3	20	1042.43	0.7	0–3.0
Outer levels of Se atoms				12., 61., 160., 236.
Solids				
AgBr		918.23	4.1	0–6, 23.5, 52., 93., 129.
NaBr		918.04	6.9	0–9, 27.7, 60–?
$NaBrO_3$		918.09	6.1	0–7, 15–23, 35, 52–110, 180–?
Solution				
$NaBrO_3$		918.09	6.1	0–23, 55–110, 170–216
Vapors	20			
Br_2	−20	918.51	0	0–6
HBr	20	918.41	1.5	
	170			
$AsBr_3$	120	918.44	1.0	0–6.
Outer levels of Kr atom				13., 28., 96., 212., 295

TABLE I (*Cont'd.*)

Substance	Temperature°C	Main edge X.U.	ΔV (volts)	Distances of both sides, or, of center of absorption bands from the main edge. (volts)
Solids				
Se				0–4.
SeO_2				0–5.4, 12–18, 53–108, 159–?
Vapors				
Se_8	510			0–5.5, 10–12
	470			
SeO_2	330			0–32., 72–108, 159–?
	280			
Outer levels of Br atom				11., 23., 80., 183.
Solid				
Zn		1280.5	0.0	0–5.8, 9.7–16., 23., 28–43, 72–87, 113–145, 175–214, 252–280, 310–?
Vapor				
Zn	950	1280.7	−1.5	0–4, 5.8–9.
	750			
Outer levels of Ga Atom				10., 22., 106., 158.
Vapor				
Kr	20	863.72		
Vapor				
X.e	20	L_{III}2587.2		0–3.9
		L_{II} 2424.1		0–3.9
		L_I 2269.1		
Liquid		L_{III} edges		
Hg		1006.7	−2.5	
Solid				
$HgCl_2$		1006.4	+1.2	0–6, 18, 50, 115
HgO		1007.1	−7.4	0–8, 16–66, 80–?
Vapor				
Hg	250	1006.5	0.0	
	200			
$HgCl_2$	330	1006.9	−4.9	0–6, 18, 50, 115
	230			

* Faint absorption.

The upper temperature is the superheated vapor temperature, the lower is the temperature at which the vapor would be saturated.

No compounds of Zn were studied. The metal itself shows a very extended secondary absorption which is absent in the absorption spectrum of Zn vapor at 950°C. There is a very faint fine structure line at 5.8 volts from the main edge for Zn vapor. The data given on the secondary absorption of Zn are the results of observations on a number of different plates obtained under different conditions. Plates were taken using slit widths of 0.025, 0.05, and 0.1 mm. The fine structure close to the edge is just detectable with the narrowest slit, but with this slit the radiation is so faint that it would take too long a time to secure the secondary absorption farther from the edge. The $WL\beta_1$ line falls close to the K edge of Zn, so that some plates were taken using a Pt filament with a Mo, and also a Pt target to eliminate any uncertainties due to the presence of emission lines.

The K edge of Kr proves to be a simple edge without even a white line at the edge. The wave-length of the K edge of Kr is measured using Sr$K\alpha_1$ (873.37 X.U.) as a reference line.

The L edges of Xe show no secondary absorption, but at the L_{III} and L_{II} edges there is a white line absorption which is 3.9 volts in width. The positions of the L_{III}, L_{II}, and L_{I}, edges of Xe were measured from the W$L\beta_1$ (1279.17 X.U.), W$L\beta_2$ (1242.03 X.U.), and W$L\gamma_5$ (1129.2 X.U.) lines, respectively.

The data on mercury show that there is no secondary absorption for the liquid or the vapor, but there is for the Hg compounds. However, the structure is very faint and the values given are only approximate. The L_{II} edges of $HgCl_2$ solid and vapor also show a very faint secondary structure which has the same energy separations from the main edge as has that associated with the L_{III} edges. No secondary structure was found for any L_{I} edges. Noting the positions of the main edges, it is seen that $HgCl_2$ solid has the shortest, and HgO solid the longest wave-length. These edges can be determined to about 4 volts.

SUMMARY AND DISCUSSION

A consideration of the experimental results permits a number of generalizations to be made.

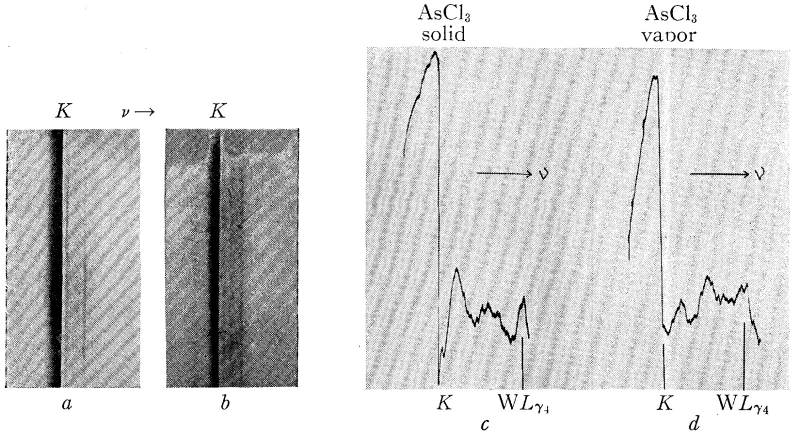

Fig. 3. $AsCl_3$ (a) solid; (b) vapor.

1. The secondary absorption of a polyatomic vapor usually has the same main characteristics as that of the solid, though the solid shows some additional structure, near the main edge, not found for the vapor. The examples of this are $AsCl_3$, As_2O_3, and SeO_2. Fig. 3 shows the data for $AsCl_3$. The microphotometer trace records clearly the dark line which splits the first white region, but it does not resolve the next dark region into the two close dark lines which can be seen on the original plate.*

* One may feel some assurance that statement No. 1. is a *bona fide* effect because of the fact that due to its perfect homogeneity the vapor makes as good, and probably a better absorbing screen for displaying secondary absorption than does the solid.

2. The Br secondary absorption shown by $NaBrO_3$ in the solid form has the same characteristics as that of $NaBrO_3$ in solution except that there is an additional structure near the main edge for the solid which is not observed for the solution. This same experiment has been performed by Meyer[13] for both $KBrO_3$ and $NaBrO_3$. He did not observe any additional structure in the absorption spectra for the solid state. Yost[14] found no detectable difference in the *K* absorption of manganous and chromate ions in crystals and in aqueous solutions.

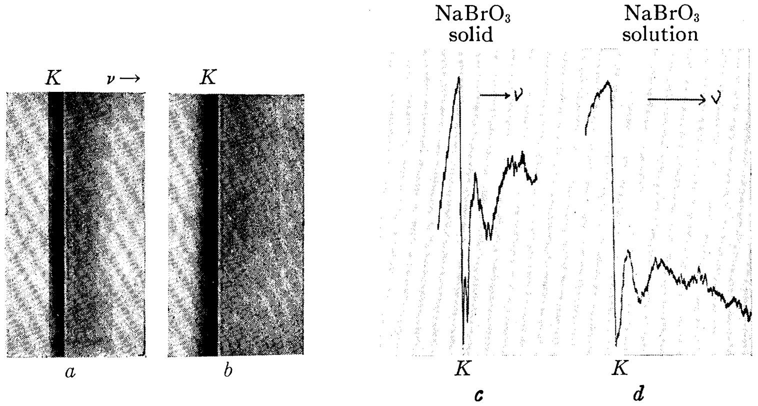

Fig. 4. $NaBrO_3$ (a) solid; (b) vapor.

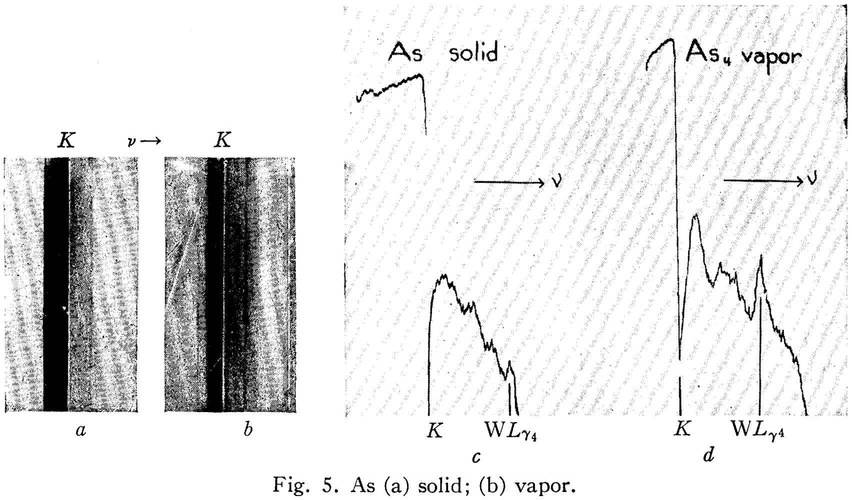

Fig. 5. As (a) solid; (b) vapor.

3. The secondary absorption of a polyatomic vapor may differ entirely from that of the solid. This effect is shown by As and illustrated in Fig. 5. As is tetratomic in the vapor state.

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[13] H. Th. Meyer, Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern **7,** 101 (1929).

[14] D. M. Yost, Phil. Mag. **8,** 845 (1929).

4. The secondary absorption of a compound may differ from that of the element. Every case investigated in this work corroborates this statement. Also, this effect is well known from previous work with the lighter elements, and has recently been shown by Lindh[15] for Cu and Ni.

5. Secondary absorption is not observed for any monatomic vapor. Hg vapor, Zn vapor, Xe, and Kr are the examples of this; and one may also include Coster's and Van derTuuk's[16] case of argon. Xe and Kr were not studied in the solid form. Liquid Hg showed no secondary absorption, but Zn in the solid state exhibited the extensive structure shown in Fig. 6.

6. A monatomic vapor may show a fine structure a few volts from the main edge. Zn vapor has a faint absorption at 5.8 volts from the principal edge, though it is too faint to be seen in Fig. 6. Coster and Van der Tuuk found an absorption line for A at 1.7 volts from the main edge. They interpreted this as due to the transitions of the electron to different virtual orbits of the A atom, since the 1.7 volts coincides exactly with the resonance potential of K which is the next higher atom in the periodic table. The 5.8 volts for zinc does not coincide with the resonance potential of Ga, which is only 3.06 volts and would not be resolved. However, the ionization potential of Ga is 5.97 volts. This might mean that the electron stops either at the first virtual orbit, causing the main edge, or travels entirely out of the atom causing the fine structure line.

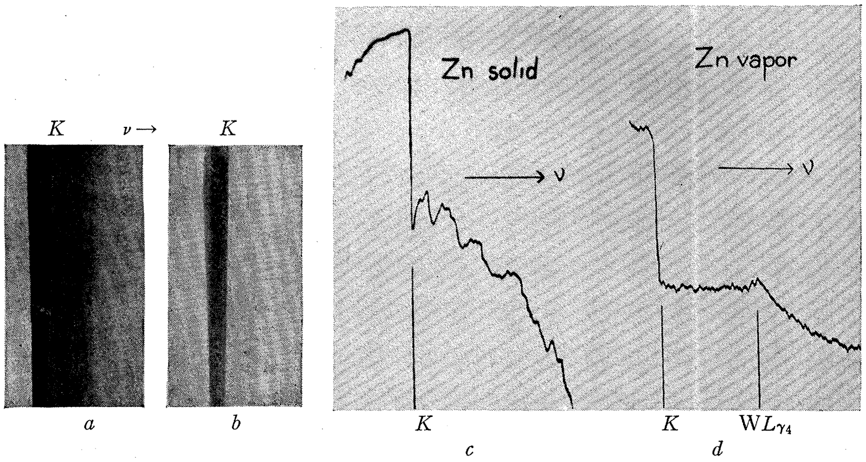

Fig. 6. Zn (a) solid; (b) vapor.

The L_{III} and L_{II} absorption edges of Xe showed a white line absorption at the main edges. The widths of these white lines were 3.9 volts. The short wavelengths edges were quite diffuse. Lepape and Dauvillier[17] have studied Xe and found a white line absorption only at the L_{III} edge. The width of their

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[15] A. E. Lindh, Zeits. f. Physik **63,** 106 (1930).

[16] Coster and Van der Tuuk, Zeits. f. Physik **37,** 367 (1926).

[17] Lepape and Dauvillier, Comp. Rend. **177,** 34 (1923).

white line was about 13 volts which they related to the ionization potential of Xe. (11.5 volts). However, with the [illegible] electron absent, the outer field of Xe should compare with the next higher atom which is Cs, and which has an ionization potential of 3.88 volts. The reason for there being no white line absorption at the L_{I} edge may be that according to the selection rule $\Delta l = \pm 1$, transitions to the first virtual orbit could take place from the L_{III} and L_{II} orbits, but not from the L_{I} orbit. The absorption edges of Hg and of Kr were 'simple' without the white line at the edge. However, this may simply be because the energy dispersion in this wave-length region is from 70 to 90 volts per mm. while in the Xe L region it is 9.7 volts per mm.

7. Secondary absorption is not exhibited by all polyatomic vapors. Se_8 vapor and AsH_3 are two examples of this.

8. Completed shells of the atom in the solid state need not necessarily be associated with the absence of secondary absorption. The Br absorption in both AgBr (in the photographic plate) and NaBr shows a secondary structure. Meyer[13] has reported that secondary absorption is absent for these compounds, and several people[6,18] have remarked that secondary absorption will not be exhibited by atoms with completed shells such as Br^-.

The points at which the results of these experiments differ from those of other workers can be attributed to higher dispersion and better resolution. The resolution is such that the $WL\gamma_4$ line, which is measured in Siegbahn's laboratory as 1025.8 X.U., is here separated into two components 15 mm apart. This is 0.79 X.U. and gives 0.68 ν/R units or 9.25 volts for the separation of the O_{II} and O_{III} levels of W. The results of Meyer,[13] for instance, that there is no structure in the K edge of Br in the photographic plate, and that the secondary absorption of $NaBrO_3$ solid and solution are identical, were gotten if the experiments were performed with an 18 cm radius Siegbahn spectrograph using a calcite 100 face (dispersion 16.6 X.U. per mm); or using a calcite 111 face (dispersion 7 X.U. per mm). This latter dispersion should be high enough to observe the additional structure but it is apparent from the pictures obtained that the 111 face does not allow the resolution which can be gotten with the 100 face.

It is not apparent as yet how successful the idea of multiple electron transitions will be in explaining the effects of physical and chemical state on secondary absorption. Several workers have quantitatively correlated the energies of the secondary discontinuities with the energies of certain chosen multiple electron jumps. In the table are shown the energies of *double* electron jumps simply calculated from the energy levels of the atom next higher in atomic number. There is an approximate agreement with at least one compound of each element. A more precise calculation such as that of Kievit and Lindsay[19] was not attempted because the discontinuities here measured could not be located more accurately than about 10 volts unless the discontinuities were close to the main edge, where they are always sharper. It seems that if

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[18] R. Swinne, Phys. Zeits. **30**, 523 (1929).

[19] Kievit and Lindsay, Phys. Rev. **36**, 648 (1930).

[20] G. Wentzel, Ann. d. Physik **66**, 437 (1921); **73**, 647 (1924).

secondary absorption is due to double electron transitions, then those discontinuities occurring more distant from the main edge represent transitions of electrons from deeper levels of the atom and so would be expected to be sharper, rather than more diffuse, than the discontinuities occurring close to the main edge and representing transitions of outer electrons.

The suggestion of transitions of electrons in multiply ionized atoms which has been made by Wentzel[20] to account for x-ray satellites, and applied also to absorption spectra[21,22] does not seem suited to explain secondary absorption, because the number of quanta of radiation of sufficient energy for ionization which are produced by the x-ray tube is so small that the number of ionized atoms in the absorbing screen at any time is a negligible fraction of the total number present.

The data as it appears in this work would seem to favor the idea of relating the secondary absorption to some characteristic of the structure of the molecule or solid. One might suppose that the secondary edges correspond to the energies of excitation of the vibrational states of "structure electrons" such as postulated by O. W. Richardson[23] to account for the facts observed in experiments both on the secondary electron emission of substances and the soft-x-ray production of substances. The relation between the secondary absorption discontinuities and the kinks in the secondary electron curves can not be carried very far at present because the sensitivity is so much less for the x-ray secondary absorption determinations of energies. However, there are some points of similarity between the observations made in the study of x-ray absorption spectra, and in the study of secondary electron emission.

The kinks in the secondary electron curves correspond to the Bohr energy levels of the atom when the experiment is done roughly, but with increased sensitivity many more kinks are discovered which can not be related to the Bohr levels of the atom. The range in which these kinks occur is from zero to about 500 volts. Above this range one finds only kinks which agree with Bohr levels. These facts are exactly paralleled by the study of x-ray absorption spectra. Also, the present experiments indicate a close relation between the occurrence of secondary absorption and the structure of the substance. Turning to the study of secondary electron emission, it is found that the number and positions of the kinks which are not related to Bohr levels are functions of the structure of the substances which the primary electron beam bombards. For example, the kinks obtained using a polycrystalline substance seem to be the sum of those from the faces of a single crystal of the substance studied separately. (This is presumably not a diffraction phenomenon.) There are enough of these kinks so that Richardson was able to see that they could all be included in tables like sets of bands, and this fact led to the idea of relating them to the excitation energies of the vibration levels of some oscillating system.

An obvious experiment to check the validity of such an idea to account for

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[21] E. C. Stover, Phil. Mag. **2,** 97 (1926).

[22] H. R. Robinson, Phil. Mag. **4,** 763 (1927).

[23] O. W. Richardson, Roy. Soc. Proc. **A128,** 63 (1930).

secondary absorption would be to study the absorption spectra of both elements of a chemical compound and see in how far the secondary absorption is a function of the individual elements and in how far a function of the compound. Satisfactory data for such a check do not exist at present.

In order to be certain that the absence of secondary absorption for zinc vapor at high temperature is not simply a temperature effect, experiments are now being carried out on the effect of high temperature on the secondary absorption exhibited by solids.

The writer wishes to express his warm appreciation for the excellent and ample facilities for research which have been available at the Department of Physics of the University of Michigan. He is particularly indebted to Professor G. A. Lindsay for much helpful advice, and to Mr. G. Kessler for his part in the difficult task of making the thin quartz windows.

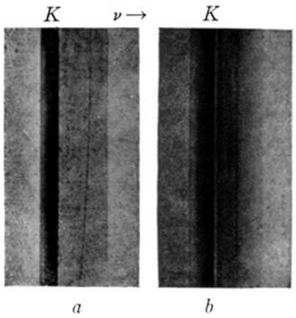

Fig. 1. (a) Simple edge. (b) Edge with secondary absorption.

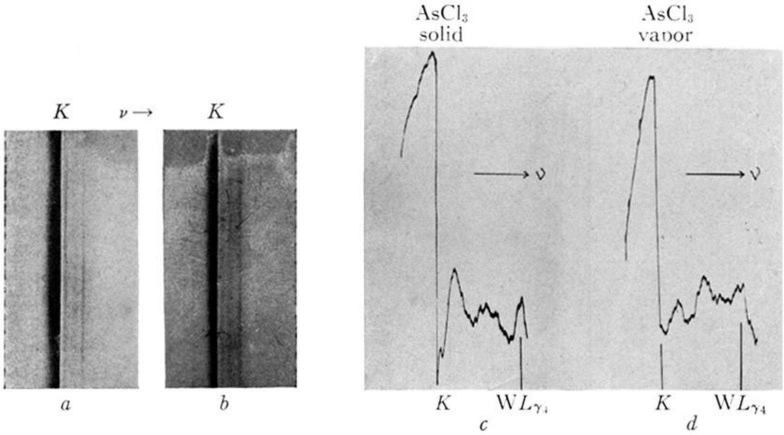

Fig. 3. $AsCl_3$ (a) solid; (b) vapor.

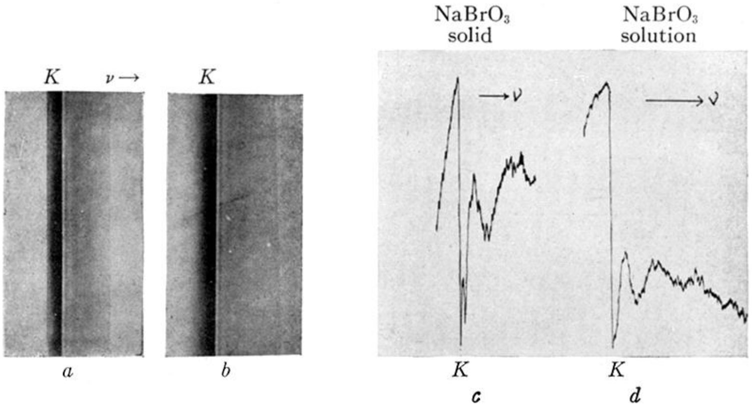

Fig. 4. NaBrO$_3$ (a) solid; (b) vapor.

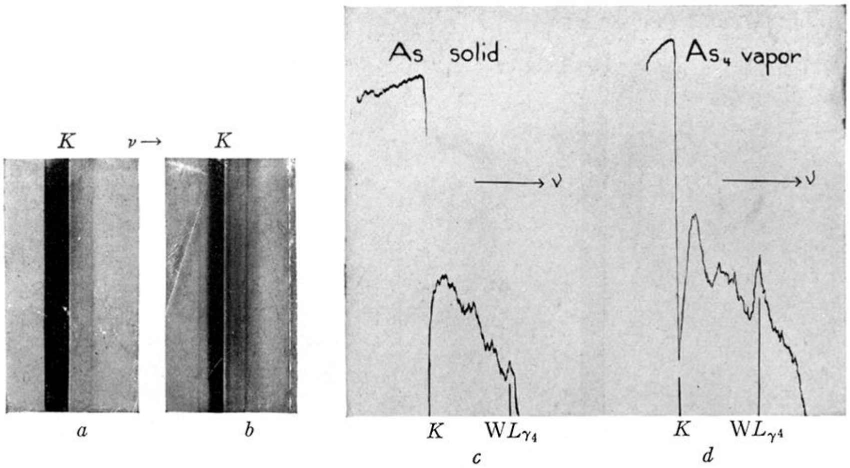

Fig. 5. As (a) solid; (b) vapor.

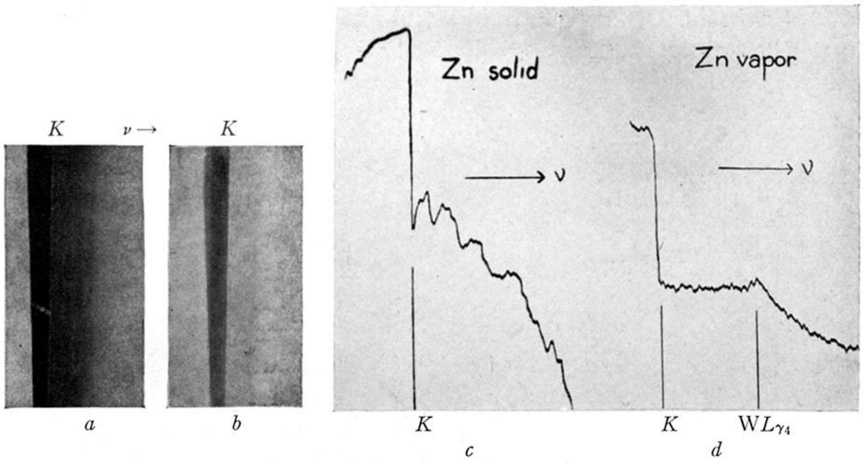

Fig. 6. Zn (a) solid; (b) vapor.