

The M -Series Absorption Spectrum of Metallic Bismuth

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(Received June 4, 1934)

With a vacuum spectrometer and sputtered bismuth films as absorbers, the five M -absorption edges were obtained. The large discrepancies between computed and observed wave-lengths of Bi M_{IV} and M_V were verified. The M_I , M_{II} and M_{III} discrepancies were found to be of the order of experimental error. To explain the M_{IV} and M_V discrepancies it is assumed that electrons from M_{IV} and M_V levels, in an absorption act, go to virtual lattice

levels above the filled conduction, or valence, levels of the crystal for the elements Ta73 to Th90. Data on, and Kronig's theory of, secondary x-ray absorption are shown to support this view. The application of the ordinary x-ray selection rule $\Delta l = \pm 1$, $\Delta j = \pm 1$ or 0 in M absorption, suggested by Siegbahn, is further discussed. That there is a definite selection rule operating in M absorption there is little room to doubt.

MEASUREMENTS on the M -series absorption spectra of Ta73 by Whitmer,¹ of W74 by Zumstein² and of Os76, Ir77, and Pt78 by Rogers³ show definite discrepancies between the observed and calculated ν/R values of the M_{IV} and M_V edges. The calculated values⁴ are based on L_{III} absorption and emission data, assuming that electrons from the M_{IV} , M_V , and L_{III} levels go out to the same level in an absorption act. Johnson⁵ showed, using metallic Pt films, that the M_I discrepancy is not due to chemical binding since the M_I absorption limit agrees with Roger's value obtained with Pt compounds. Lindberg⁶ repeated some of the work done in this laboratory and elsewhere^{7, 8} using the element in both the combined and uncombined state. He found no effect due to chemical state.

The data show possible discrepancies for the M_I and M_{II} limits, all of positive sign with the exception of Ir M_{II} . But these are in the range of the experimental error.

Not only are the data⁹ incomplete with reference to the M -absorption limits, but, as will later be explained, there has been presented no satisfactory explanation of the amply verified M_{IV} and M_V "discrepancies." The present work on Bi83 was undertaken to obtain measurements

especially on M_I and M_{II} , but on M_{III} , M_{IV} , and M_V as well, and to consider anew the most plausible explanation of the magnitude of the M_{IV} and M_V discrepancies.

RESULTS

The apparatus used is essentially that described by Whitmer¹ though with a few minor changes. The bismuth films used as absorbers were produced by sputtering in an atmosphere of spectroscopically pure hydrogen.

In Table I are tabulated the wave-lengths, ν/R and $(\nu/R)^{\frac{1}{2}}$ values of the M limits of bismuth obtained in this research and elsewhere. The emission lines¹⁰ used for reference are shown in Table II.

DISCUSSION

The M_I and M_{II} edges were obtained with the same absorption film. At both edges the visual contrast on the photographic plate was small relative to that at the M_{III} , M_{IV} , or M_V edge, as would be expected from the relatively low electron population of the M_I and M_{II} states.¹¹ The M_I limit was found more like a line absorption to be expected in transitions between two narrowly defined levels while the M_{II} limit was of the edge type.

The discrepancies found for the bismuth edges M_I , M_{II} , M_{III} , M_{IV} and M_V are, respectively, -8.2 , $+6.8$, $+2.7$, $+16.4$, $+19.1$ volts while the

¹ Whitmer, Phys. Rev. **38**, 1164 (1931).

² Zumstein, Phys. Rev. **25**, 747 (1925).

³ Rogers, Phys. Rev. **30**, 747 (1927).

⁴ Siegbahn, *Spectroscopy of X-Rays*, 1931 edition, pp. 336 and 346.

⁵ Johnson, Phys. Rev. **34**, 1106 (1929).

⁶ Lindberg, Zeits. f. Physik **50**, 91 (1928).

⁷ Stenström, Dissert. Lund. (1919).

⁸ Coster, Phys. Rev. **19**, 20 (1922).

⁹ M -absorption measurements have been made on Ta73, W74, Os76, Ir77, Pt78, Au79, Hg80, Tl81, Pb82, Bi83, Th90, and U92.

¹⁰ Siegbahn's *Spectroscopy of X-Rays*, 1931 edition, pp. 476-477.

¹¹ The number of electrons in the M_I , M_{II} , M_{III} , M_{IV} and M_V states are, respectively, 2, 2, 4, 4, 6. See Sidgwick's *Electronic Theory of Valency*, p. 50.

TABLE I. M limits of Bi83 obtained here and elsewhere.

Edge	Plate	λ	Reference lines	Average			Author
				λ	ν/R	$(\nu/R)^{\frac{1}{2}}$	
M_I	58	3.102A	Sb $L\alpha_1; \beta_1 \beta_2$				
M_I	59	3.099	Sb $L\alpha_1; \beta_1$				
M_I	60	3.098	Sb $L\alpha_1; \beta_1$				
M_I	65	3.101	Sb $L\beta_1; \beta_2$				
M_I	88	3.100	Sb $L\alpha_1; \beta_1$				
				3.100A	294.0	17.15	Phelps
M_{II}	58	3.343	Sb $L\alpha_1; \beta_1; \beta_2$				
M_{II}	59	3.341	Sb $L\alpha_1; \beta_1$				
M_{II}	63	3.345	Sb $L\alpha_1; \beta_1$				
M_{II}	88	3.340	Sb $L\alpha_1; \beta_1$				
				3.342	272.7	16.51	Phelps
M_{III}	106	3.887	K $K\alpha_1$				
M_{III}	112	3.890	K $K\alpha_1$				
M_{III}	118	3.889	K $K\alpha_1$				
M_{III}	119	3.890	K $K\alpha_1; Ag L\alpha_1; \beta_1$				
				3.889	234.3	15.31	Phelps
				3.893	234.1	15.30	Lindberg
				3.894			Coster
M_{IV}	101	4.573	Ag $L\alpha_1$				
M_{IV}	102	4.577	Bi $M\beta$				
M_{IV}	103	4.576	Bi $M\beta; Cl K\alpha_1$				
M_{IV}	104	4.571	Bi $M\beta; Cl K\alpha_1$				
				4.574	199.2	14.12	Phelps
				4.568	199.5	14.12	Lindberg
				4.569			Coster
M_V	102	4.765	Bi $M\beta; \alpha$				
M_V	103	4.763	Bi $M\beta; Cl K\alpha_1$				
M_V	104	4.761	Bi $M\beta; Cl K\alpha_1$				
				4.763	191.3	13.83	Phelps
				4.762	191.4	13.83	Lindberg
				4.762			Coster

maximum experimental error for each was estimated to be ± 5.1 , ± 4.4 , ± 3.2 , ± 2.4 , ± 2.2 volts, respectively. These discrepancies are of the order of magnitude to be expected from measurements on other elements.¹²

Different suggestions have been advanced to account for the relatively large discrepancies between the computed and observed ν/R values of the M_{IV} and M_V edges. In Table III these discrepancies are listed for the corresponding elements in columns 2 and 3. Sandström¹³ has shown experimentally that the ν/R values of the L_{II} and L_{III} edges for the elements Ta73 to Au79 are equal to the ν/R values of lines found by Idei¹⁴ and assigned as the transitions $O_{IV}L_{II}$ and

$O_{IV}, \nu L_{III}$, respectively, thus indicating that electrons from L_{II} and L_{III} go in an absorption act to the incompletely occupied O_{IV} and O_V levels for these elements. According to Siegbahn,¹⁵ Sandström's calculations explain the M_{IV} and M_V discrepancies, for, assuming the ordinary x-ray selection rule $\Delta l = \pm 1$, $\Delta j = \pm 1$ or 0 to apply in absorption as well as in emission, electrons from M_{IV} ¹⁶ and M_V are not allowed to go to the incomplete O_{IV} and O_V levels to which electrons from L_{II} and L_{III} go but must go to a different atomic level. In this manner he says the M_{IV} and M_V discrepancies come about, and there are no M_{II} and M_{III} discrepancies because the selection rule allows electrons from M_{II} , M_{III} and L_{III} to go to the same level. It should be pointed out here

¹² See Table III, columns 2 and 3 for M_{IV} and M_V discrepancies. See Siegbahn's *Spectroscopy of X-Rays*, 1931 edition, p. 278 and p. 346 for M_I , M_{II} and M_{III} discrepancies.

¹³ Sandström, *Zeits. f. Physik* **65**, 632 (1930).

¹⁴ Idei, Science Reports, Tohoku Imp. Univ. Series I, Vol. 19, No. 5,

¹⁵ Siegbahn, *Zeits. f. Physik* **67**, 567 (1931).

¹⁶ The l, j values of the levels L_{II} , L_{III} , M_I , M_{II} , M_{III} , M_{IV} , M_V , O_{IV} and O_V are, respectively, 1, 1/2; 1, 3/2; 0, 1/2; 1, 1/2; 1, 3/2; 2, 3/2; 2, 5/2, 2, 3/2; 2, 5/2. See Sidgwick's *Electronic Theory of Valency*, p. 50.

TABLE II. Wave-length of reference lines.

Sb $L\alpha_1$	3.432A	K $K\alpha_1$	3.734	Cl $K\alpha_1$	4.718
Sb $L\beta_1$	3.218	Bi $M\alpha$	5.108	Ag $L\alpha_1$	4.146
Sb $L\beta_2$	3.017	Bi $M\beta$	4.899	Ag $L\beta_1$	3.927

TABLE III. M_{IV} and M_V discrepancies in volts. W—Whitmer, S—Stenström, Z—Zumstein, J—Johnson, R—Rogers, C&V—Coster and Veldkamp, P—Phelps, H—Hanawalt, L—Lindberg, C—Coster, all cited in references.

Element	$M_{IV}' - L_{III}'$	$M_V' - L_{III}'$	*
Ta73	28.6 W	28.6 W	
W74	41.0 L		
W74	43.2 Z	41.0 Z	
Os76	46.4 R**	54.6 R**	
Ir77	41.0 R	41.0 R	
Pt78	45.1 R	47.8 R	55 C&V
Pt78	43.7 L	45.1 L	
Pt78	58.7 J	58.7 J	
Au79	35.5 L	32.8 L	40 C&V
Au79	45.1 J	38.2 J	
Hg80	28.6 L	28.6 L	29 H
Tl81	25.9 L	24.6 L	
Pb82	20.4 L	23.2 L	
Bi83	16.8 P	19.1 P	
Bi83	20.5 L	20.5 L	
Bi83	20.5 C	19.1 C	
Th90	15.0 L, S	15.0 L, S	
U92	-2.2 L, S	-2.7 L, S	

* Separation in volts of first secondary absorption band from main edge.

** Os M_{IV} and M_V computed from absorption data by Sandström¹⁸ and emission data from Siegbahn's *Spectroscopy of X-Rays*, 1931 edition, pp. 212 and 241.

that the selection rule, as applied by Siegbahn, also requires that electrons from M_I and L_{III} go to different levels while experimentally the M_I discrepancy is as questionable as that for M_{II} . To make this fact consistent with the selection rule explanation, it must be assumed that electrons from M_I and L_{III} go to levels close together. Of course the selection rule explanation alone can not indicate at all how many volts above the O_{IV} and O_V valence levels the M_{IV} and M_V electrons ought to go. Another objection is the assumption that the O_{IV} and O_V valence levels are atomic levels, whereas according to the quantum theory of conduction in metals,¹⁷ the valence electrons fill up the lower of the energy levels common to all the atoms of the crystal lattice. Hence the selection rule that holds between atomic levels may not hold between an atomic and a lattice level. But this objection does not prevent the selection rule from being correct in many cases, for an examination of Idei's¹⁴ careful measurements on the weaker emission lines of the L -

¹⁷ Bloch, *Zeits. f. Physik* **52**, 555 (1929).

group for the elements Ta73 to Bi83 shows that transitions connecting the conduction, or valence, levels with atomic levels in all cases appear to be obeying the ordinary x-ray selection rules. For Bi83, for example, the conduction electrons fall into the L_I level, corresponding to the transition $P_{II, III}L_I$ (allowed) for the isolated atom, but none fall into the L_{III} level (disallowed). For tungsten 74 occur the transitions $O_{IV, V}L_{III}$ and $O_{IV}L_{II}$ (allowed), but not the transition $O_{IV, V}L_I$ (disallowed). But for the elements Bi83, Pb82 and Tl81, the selection rule would permit the M_{IV} and M_V electrons to stop at the valence levels¹⁸ and would require the L_{III} electron to go above these levels thus making the M_{IV} and M_V discrepancies for these elements negative. Table III shows these discrepancies to be positive. Hence there is an objection to the application of the emission selection rule unless it can be shown from intensity considerations, or otherwise, that electron transitions from M_{IV} and M_V to the valence levels for bismuth,¹⁹ say, are relatively much less probable than transitions above the valence levels.

Pauling's²⁰ formula for the shift of the absorption edge of an ion in an ionic crystal gives good agreement with experiment for the halide crystals LiCl, NaCl, KCl and RbCl. However, it cannot account for the M_{IV} and M_V discrepancies since it treats electrons from M_I and M_V the same.

Before proposing an interpretation of the M_{IV} and M_V discrepancies based on secondary x-ray absorption data and other data, the two theories advanced to account for secondary structure will be briefly discussed. The theory of multiple transitions proposed by Ray,²¹ Coster,²² Lindsay and Voorhees²³ and Coster and Wolf²⁴ is able to account for the positions of the bands but other considerations throw considerable doubt on the correctness of the hypothesis of multiple transitions. For Hanawalt²⁵ finds no secondary struc-

¹⁸ The l, j values of the valence levels for Bi83, Pb82, and Tl81 are 1, 1/2 and 1, 3/2.

¹⁹ These transitions are $M_V P_{II, III}$ (2, 5/2 → 1, 1/2; 1, 3/2) and $M_{IV} P_{II}$ (2, 3/2 → 1, 1/2).

²⁰ Pauling, *Phys. Rev.* **34**, 954 (1929).

²¹ B. B. Ray, *Nature* **122**, 771 (1928).

²² Coster, *Zeits. f. Physik* **25**, 83 (1924).

²³ Lindsay and Voorhees, *Phil. Mag.* **6**, 910 (1928).

²⁴ Coster and Wolf, *Nature* **124**, 652 (1929).

²⁵ Hanawalt, *Phys. Rev.* **37**, 723 (1931).

ture in the absorption spectra of the monatomic gases Hg, Zn, Xe and Kr while mercury compounds and solid zinc show a definite structure. Also Hanawalt states that the bands near the main edge are always sharper than those farther out which fact is just the opposite of what would be expected on the multiple transitions theory.²⁶ Another significant objection to this theory is that it would not account for the M_{IV} and M_V absorption discrepancies.

According to Kronig's^{27, 28} theory secondary absorption bands are due to electrons being ejected, in an absorption act, from the x-ray level in question out to lattice levels of the crystal. The energy separation of the secondary absorption bands of a substance depends on its crystal system rather than on the particular atom in the substance. For different substances having the simple cubic structure the energy separation of their secondary absorption bands should be approximately equal when corrected to take account of the difference in the dimensions of the lattice cells. Two different atoms in a mixed crystal, such as a Cu²⁹-Au crystal, should give similar secondary absorption spectra. Coster's and Veldkamp's^{30, 31} data on the face-centered cubic crystals of Pt, Au, Cu²⁹ and Ca²⁹ verify the former conclusion, while their data on the mixed crystals Ni-Fe and Cu-Au very beautifully verify the latter. In addition Veldkamp³⁰ has examined the secondary absorption spectrum of the compounds³² NiF₂·2H₂O and CoF₂·2H₂O, the Debye-Sherrer photographs of which indicate the same crystal structure, and finds their absorption spectra to be exactly analogous. The failure of the monatomic gases Hg, Zn, Xe and Kr to show a secondary absorption structure

extending beyond the main edge more than the ionization potential of the atom, in disagreement with the theory of multiple transitions, is exactly in accord with the requirements of Kronig's theory. To Hanawalt's²⁵ data on the monatomic gases may be added that of Coster and Van der Tuuk³³ on argon.

Stephensen³⁴ concludes that his data on the secondary structure of Br in a KBr crystal agree with those of Lindsay³⁵ on the secondary structure of K also in a KBr crystal in accord with Kronig's theory.

Assuming the correctness of the view that secondary absorption bands are due to electron transitions to lattice levels of the crystal one may readily account for the M_{IV} and M_V discrepancies. Electrons from the M_{IV} and M_V levels go, in an absorption act giving rise to the M_{IV} and M_V edges, to the first lattice levels available to them above the valence, or filled conduction, levels for the elements Ta73 to Th90. The L_{III} edge is due to electron transitions from L_{III} to the valence levels for the elements Ta73 to Au79 as pointed out by Sandström.¹³ Although emission lines involving transitions from the valence levels of Hg80, Tl81 and Pb82 were not obtained by Idei,¹⁴ Sandström's¹³ comparison indicates that electrons from L_{III} go to the valence levels or nearby levels for the elements Hg, and Tl also. For Bi83 electrons from L_{III} go to a level close to the valence levels.

In Table III column 4 appears the voltage separation from the L_{III} edge of the first secondary absorption band for the solid substances Hg, Au and Pt. Comparing with the M_{IV} and M_V discrepancies the agreement is within experimental error. One may conclude that, for these elements, electrons from the M_{IV} and M_V levels and the L_{III} level either go to energy zones with the same quantum numbers or to overlapping zones with different quantum numbers.

In view of the fact that the valence, or conduction, levels appear to obey the ordinary x-ray selection rule in emission, it seems worth while to see wherein intensity considerations might help explain why electrons from the M_I level and the M_{IV} and M_V levels, though allowed by the

²⁶ On this theory the bands farther out from the main edge are due to electrons coming from inner and hence sharper levels.

²⁷ Kronig, Zeits. f. Physik **70**, 317 (1931).

²⁸ Kronig, Handb. d. Phys. **24** 1/2, 292 (1933).

²⁹ The first bands near the main edge in the absorption spectrum of Ca and Cu do not appear in that of Au and Pt. Their explanation is that these bands are due to levels characteristic of the atom and hence not common to the lattice.

³⁰ Veldkamp, Zeits. f. Physik **82**, 777 (1933).

³¹ Coster and Veldkamp, Zeits. f. Physik **74**, 203 (1932).

³² Brewington, Abstract in Bulletin of the American Physical Society, April, 1934. Brewington reports the secondary absorption spectra of the two elements in a KCl and a CaS compound to be dissimilar. Possibly better agreement may be obtained if secondary structure of ions of the same sign only in different compounds of the same crystal system were compared.

³³ Coster and Van der Tuuk, Zeits. f. Physik **37**, 367 (1926).

³⁴ Stephensen, Phys. Rev. **44**, 352 (1933).

³⁵ G. A. Lindsay, Zeits. f. Physik **71**, 735 (1931).

selection rule to do so, do not go to the same level in an absorption act. Applying the x-ray selection rule, $\Delta l = \pm 1$, $\Delta j = \pm 1$ or 0 to the five M levels and the L_{III} level, one readily finds the possible l, j values of the lattice levels to which electrons go, as allowed by this selection rule, in coming from the above x-ray levels in an absorption act. In Fig. 1 the possible l, j values of these experimentally determined levels for bismuth metal are indicated at the right. These levels, also indicated by primed letters at the left, together with the remaining figure constitute a Kronig²⁷ diagram of energy levels in a crystal (x-ray levels not shown).

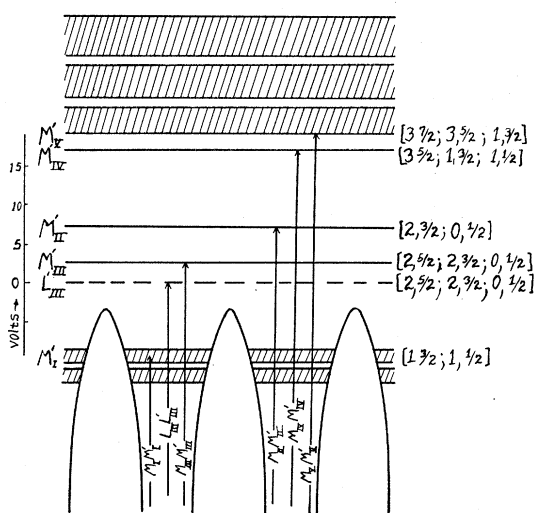


FIG. 1. Part of energy level diagram for bismuth metal (scale for primed levels only).

The separation of any one of the M' levels, which are drawn to scale, from the L'_{III} level gives the corresponding M discrepancy. Thus $M'_{IV} - L'_{III}$ gives the M_{IV} discrepancy in volts. The width of the primed levels is not shown, otherwise there would be overlapping for some levels. The upper and lower lattice levels, which are shown hatched, are not drawn to scale. The lowest zone is supposed to be filled with conduction electrons and the next one-half filled, since bismuth has a valence of three. M'_{I} is in the middle of the half filled zone.

In Fig. 1 one notes that some of the l, j values for M'_{IV} and M'_{V} appear also with M'_{I} although, as already stated, electrons from M_{IV} and M_{V} and M_{I} levels do not go to the same level. Before one

can hope to investigate the question of relative intensities of the possible transitions concerned from theoretical considerations more must be known about the wave functions representing the lattice states. Turning to emission data one notes that the strongest lines in the K, L and M series are those involving transitions of the type $l, j \rightarrow l-1, j-1$. For example $K\alpha_I$ is the $1, 3/2 \rightarrow 0, 1/2 (L_{III}K)$ transition, $L\alpha_I$ is the $2, 5/2 \rightarrow 1, 3/2 (M_V L_{III})$ transition, and $M\alpha_I$ is the $3, 7/2 \rightarrow 2, 5/2 (N_{VII} M_V)$ transition. For absorption these transitions correspond to the type $l, j \rightarrow l+1, j+1$. Corresponding to this rule, one would choose the l, j value to the extreme left in each bracket of Fig. 1 for the corresponding primed level. Of course, one may not be justified in extrapolating from the valence levels, which appear to have a definite l, j value as emission data indicate, in assigning l, j values to all or a part of these primed levels. This point cannot be investigated from emission data. Although the discrepancy $L'_{III} - M'_{I}$ is within experimental error, one would expect the L'_{III} level to lie above M'_{I} for bismuth since the selection rule allows electrons from M_{I} to stop at the valence levels but not electrons from L_{III} . Likewise for lead and thallium, M'_{I} may be expected to lie below L'_{III} .

The same type of diagram as Fig. 1 may be constructed for the elements Ta73 to Hg80 and Th90. U92 does not show M_{IV} and M_{V} discrepancies. According to the ordinary x-ray selection rule this fact indicates U92 then may have valence levels with quantum numbers 3, 5/2 and 3, 7/2. There is disagreement as to the assignment of quantum numbers to the valence levels of U92³⁶ and Th90.

In conclusion the large M_{IV} and M_{V} discrepancies are considered to be definite evidence for the existence of discrete energy levels 20 to 50 volts above the valence, or conduction, levels for the elements Ta73 to Th90. The M_{IV} and M_{V} edges are here interpreted to be due to electron transitions to virtual lattice levels of the crystal. Data on secondary x-ray absorption are cited in support of this view. The magnitude of the M_{IV} and M_{V} discrepancies would be greatly reduced for the atom in the monatomic gaseous state.

³⁶ Ruark and Urey, *Atoms, Molecules and Quanta*, p. 282 and Sidgwick, *The Electronic Theory of Valency*, pp. 46 and 50.

That there is a definite selection rule operating in M absorption there is little room to doubt. No attempt has been made to apply the above reasoning to include elements below Ta73 but if their valence levels obey the selection rule, one may expect to find M_{IV} and M_V discrepancies for Hf72 and Lu71 but none for elements Yb70 to Ce58.

The writer wishes to thank the staff members of the Department of Physics of the University of Iowa for their interest and cooperation. Thanks are especially due to Dr. G. W. Stewart who suggested and directed this research. He also wishes to express his appreciation of the skill and assistance of the instrument maker, Mr. J. G. Sentinella.

The Dependence of Secondary Structure in X-Ray Absorption on Crystal Form

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(Received July 6, 1934)

An examination of the Ca K absorption edge in the x-ray absorption spectra of different compounds shows clearly that the secondary structure is not the same in different compounds, and is not even the same in the two crystals calcite and aragonite, which are the same chemically, but of different crystalline form. These facts are in accord with Kronig's theory of the secondary structure.

In four other crystals, each of which contains two or more metals, the secondary structure was examined to see if it was the same for the two elements in the same crystal. There is a difference for the two elements, which indicates that the crystal form is not the sole factor in determining the secondary structure.

THE cause of secondary structure in x-ray absorption spectra near the characteristic absorption edges of the elements has been the subject of much investigation and discussion. The present paper considers some points suggested by the wave-mechanical theory of Kronig, which attributes the secondary structure to alternate permitted and forbidden zones in the continuous range of energy values for an electron passing through a crystal. A quantum of energy in the x-ray beam, great enough to remove the electron from the atom, or ion, of the absorbing material, and give it kinetic energy corresponding to one of the permitted zones, may be absorbed; if the kinetic energy corresponds to one of the forbidden zones it will not be absorbed.

The zones of possible absorption are given in Kronig's theory by the expression $W = n^2 h^2 / 8ma^2$, where W is the energy of the electron passing through the network of the crystal, a is the distance between atoms or ions in the direction of motion of the electron. h and m are as usual, Planck's constant, and the mass of the electron, respectively.

This result makes the secondary structure, as far as the limiting conditions of the theory may

be accepted, independent of the material of the absorber, and dependent only on the crystal structure. Several investigations have afforded results which give considerable support to the theory as advanced by Kronig.

A simple consequence of the theory is that if the same element occurs in two crystals of different type, then the secondary structure should be different, while two elements occurring in the same crystal should have similar structure in the absorption, because the electron ejected from the atom must pass through the same array of atoms whether it comes from the one element or the other. This last conclusion has been considered by Kronig and others to be invalid in a region near the absorption edge.

Two convenient crystals of different form, and not only containing the same element but consisting of *the same chemical compound* are calcite and aragonite. The formula is CaCO_3 and the K absorption edge of Ca, which lies at about 3060 x.u., has been observed for several calcium compounds. The secondary structure of the calcium edge has already been described.¹

¹G. A. Lindsay and G. D. Van Dyke, *Phys. Rev.* 30, 562 (1927).