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The Enhancement of Certain *L*- and *M*-Series X-Ray Satellite Lines by the Auger Effect

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Integrated relative energies for the satellites of $L\beta_1$ are measured by a photographic method. A marked change in relative intensity exists at $Z=40$, which is to be explained by enhancement of the $L\beta_1$ satellites due to the Auger effect. The enhancement of *M*-series satellites by the Auger effect is discussed. The theory explains the almost identical frequency separations and nearly equal intensities observed for the satellite groups of the $M\alpha_1$ and $M\beta$ lines of Bi(83). Some experimental evidence of an intensity anomaly due to the Auger effect, for the satellites of $M\alpha_1$, is presented.

A. THE ENHANCEMENT OF *L*-SERIES SATELLITES BY THE AUGER EFFECT

Introduction

IN 1922, D. Coster[1] published certain microphotometric curves which indicated that the satellites of the x-ray diagram line $L\alpha_1$ decreased markedly in intensity, relative to their parent line, in going from Rh(45) to In(49). In the same atomic number range, he did not observe a corresponding change for the satellites of $L\beta_1$.

A later study[2] of the $L\alpha_1$ satellites confirmed this rapid decrease in relative intensity (for cathode ray excitation), from $Z=45$ to $Z=47$, and indicated that there was a maximum relative intensity at $Z=45$.

A further study[3] shows that the $L\alpha_1$ satellites also "fade out"[4] near $Z=52$.

Another investigation,[5] made in the Cornell x-ray laboratory, showed that a similar maximum relative intensity existed for the satellites of $L\beta_2$ near $Z=47$.

The probability of the transition $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}$ with the emission of radiation, although the transition is permitted by "selection rules," is very small. Coster[1] reported a search for radiation corresponding to this transition, but failed to find such a line; however, Coster and Kronig[6] report that such a radiation has been observed.

Coster and Kronig[6] point out that the total amount of energy in the L_{I}-series of lines is smaller, compared to the energy in the L_{II}- and L_{III}-series, than would be expected from the radiative transition probability.

On the basis of these facts, Coster and Kronig[6] proposed their theory of a new Auger effect. This theory explains the $L\alpha_1$ and $L\beta_2$ satellite line groups as follows: the transition $L_{\mathrm{I}}\rightarrow L_{\mathrm{III}}$ is a radiationless transition which causes the simultaneous ejection of an $M_{\mathrm{IV,\,V}}$ electron. This is possible for atomic numbers less than $Z=50$; $(E_{L_{\mathrm{I}}}-E_{L_{\mathrm{III}}})_z<(E_{M\mathrm{IV,\,V}})_{z+1}$ for certain atomic numbers above $Z=50$. (E here stands for energy.)

[1] D. Coster, Phil. Mag. **43**, 1089 (1922).
[2] F. R. Hirsh, Jr. and F. K. Richtmyer, Phys. Rev. **44**, 955 (1933).
[3] F. R. Hirsh, Jr., Phys. Rev. **48**, 722 (1935).
[4] By "fade out" is meant that the satellite's relative intensity becomes too small to be measured photographically, although, as will be shown later in the present article, a microphotometric record may give positive evidence of the existence of such satellites.
[5] A. W. Pearsall, Phys. Rev. **46**, 694 (1934).
[6] D. Coster and R. de L. Kronig, Physica **2**, 13 (1935).

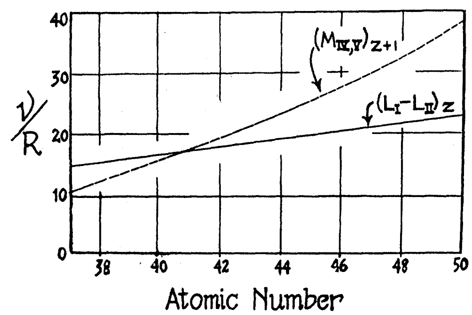

FIG. 1. The energy provided by the radiationless transition $L_I \rightarrow L_{II}$ and the energy required to eject an $M_{IV,\,V}$ electron, plotted against atomic number.

An atom is thus left doubly ionized, with L_{III} and $M_{IV,\,V}$ electrons missing, and therefore in the initial state, according to Druyvesteyn,[7] for the emission of the $L\alpha_1$ or $L\beta_2$ satellite groups. Single electron transitions, between these doubly ionized states, $L_{III}M_{IV,\,V} \rightarrow (M_{IV,\,V})^2$ or $L_{III}M_{IV,\,V} \rightarrow M_{IV,\,V}N_V$, cause the appearance of satellite lines. The single electron transitions $L_{III} \rightarrow M_V$ or $L_{III} \rightarrow N_V$ give rise to the parent $L\alpha_1$ or $L\beta_2$ lines.

If we admit that observed satellite intensity anomalies are partial evidence for the existence of the Auger effect, it follows that when it is known the Auger effect is possible and that it should enhance satellites over a given range of atomic numbers, we may similarly expect the existence of an intensity anomaly for these satellites.

Coster and Kronig[5] pointed out that for the satellites of $L\beta_1$ the Auger effect cannot exist if $Z>40$, for the radiationless transition $L_I \rightarrow L_{II}$ can no longer cause ionization of the $M_{IV,\,V}$ shell (see Fig. 1). It was later reported[8] that at $Z=40$ an intensity anomaly does exist for the satellites of $L\beta_1$. It is the purpose of the first part of the present paper to report more fully on this point.

Experimental

The $L\beta_1$ lines of the elements included between atomic numbers 30 and 48 (excited by 20 kv electrons) were photographed in a Siegbahn vacuum spectrograph using a gypsum (selenite) crystal. The radius of this instrument was 18.36 cm; a slit width of 0.1 mm was used. All lines of elements from $Z=30$ to $Z=40$ were photometered; the necessary constants were secured, and a density section through each line was plotted (see Fig. 2). These density plots are intensity plots for the x-ray lines. The range of wave-lengths studied in the present investigation (5.0 to 12.0A) is partly covered by the results of a previous study.[9] A linear region was found for density-exposure time curves of up to 5.4A in wave-length, overlapping the region of the present study. The region 6.0 to 12.0A has not been carefully studied[10] but, in view of the increasing extent with increasing wave-length of the region of linearity as found in the former investigation,[9] the density plots of Fig. 2 will be assumed to have their usual significance.

On these density plots, the short wave-length side of the parent line, i.e., the satellite background, was sketched in, and estimates of the integrated relative energy (total satellite energy divided by parent line energy) were made by planimetering areas (see Table I).

For the $L\beta_1$ lines of atomic numbers 41 through 48, no density sections were made. The microphotometric records are shown in Fig. 3. Satellites for these elements arise from double ionization by single electron impacts, and are extremely faint. For these elements, satellites which are present (see curve for Mo $L\beta_1$) would be completely masked by accidental irregularities (see Fig. 3). The satellite intensity, in all cases in Fig. 3, is estimated at less than one percent of the parent line intensity.

Fig. 4 shows a plot against atomic number, of the integrated relative energy of the satellites $L\beta_1'$ and $L\beta_1''$ of the x-ray diagram line $L\beta_1$. The estimates here show the existence of the satellite

TABLE I. *Values of the integrated relative energies of satellite and parent line.*

Element	Atomic Number	Integrated Relative Energy, (S/P)
Zn	30	0.100
Ga	31	0.100
Ge	32	0.107
As	33	0.099
Se	34	0.114
Br	35	0.122
Rb	37	0.200
Sr	38	0.327
Zr	40	0.143
$40<Z<49$, $(S/P)<0.01$		

[7] M. J. Druyvesteyn, Dissertation, Groningen (1928).
[8] F. R. Hirsh, Jr., Phys. Rev. **48**, 776 (1935).
[9] F. R. Hirsh, Jr., J. O. S. A. **25**, 229 (1935).
[10] It will be studied shortly.

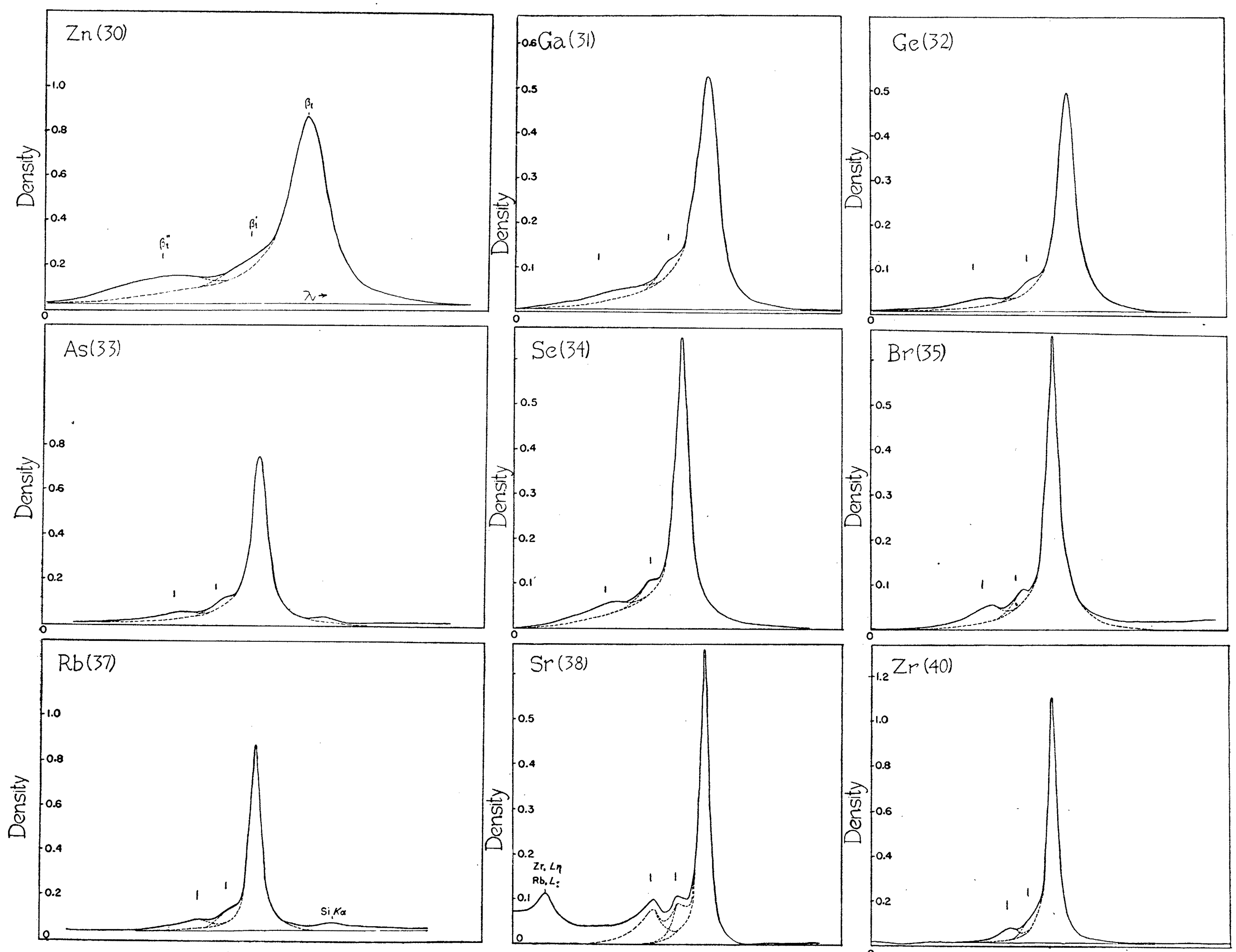

FIG. 2. Density, (intensity), plots of the $L\beta_1$ lines of the elements from Zn(30) through Zr(40) excited by 20 kv electrons. Vertical lines indicate positions at which satellites have been measured visually by Druyvesteyn, reference 7.

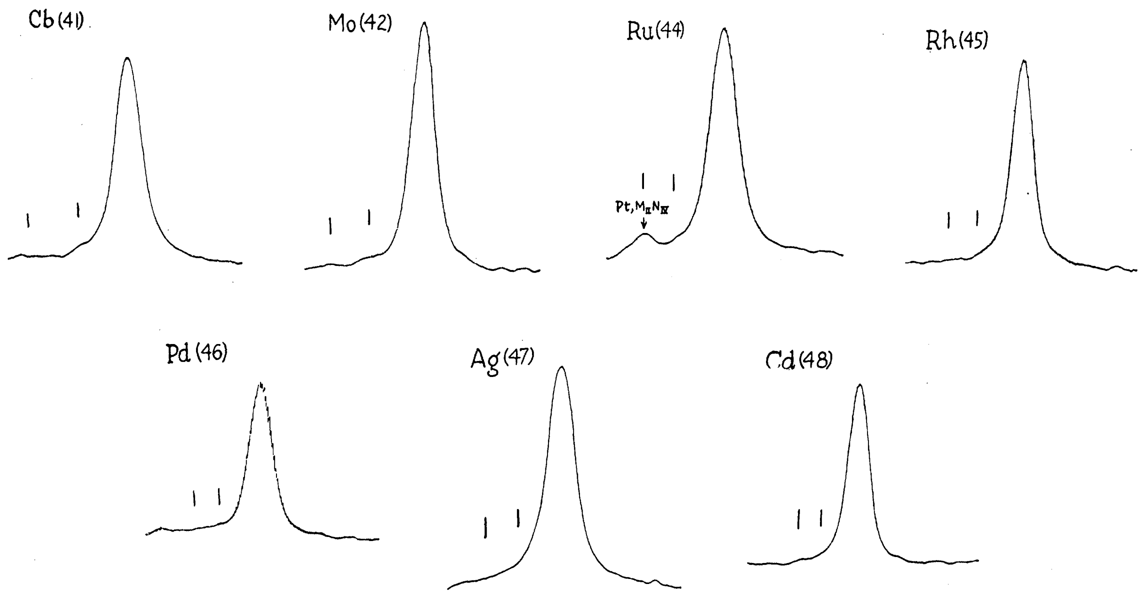

FIG. 3. Microphotometric records of the $L\beta_1$ lines of the elements from Cb(41) to Cd(48), excited by 20 kv electrons. Vertical lines indicate positions at which satellites have been measured visually by Druyvesteyn, reference 7.

intensity anomaly at $Z=40$. (This can also be seen in the density plots of Fig. 2.)

It must be emphasized here that these estimates involve a considerable error, chiefly due to the lack of resolving power of the single crystal spectrograph, and the consequent difficulty of drawing in a suitable satellite background. More careful studies in this field, with the use of the two crystal vacuum spectrometer, are clearly desirable.

B. Enhancement of M-Series Satellites by the Auger Effect

Introduction

In their paper[6] on the "new" Auger effect, Coster and Kronig remark in their summary, "it seems most reasonable to assume that in the M-region similar radiationless transitions occur with analogous results." Since the time when the present author studied M-series satellites,[11] no reasonable explanation of their origin has been advanced. As suggested by Coster and Kronig,[6] the theory of the Auger effect seems to hold promise of a solution of this problem.

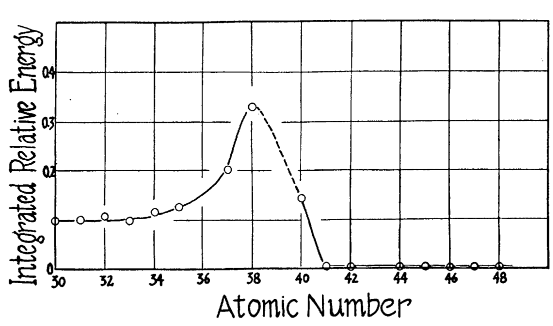

FIG. 4. The intensity anomaly for the satellites of $L\beta_1$.

Experimental considerations and results

The two strongest lines of the M-series, which are accompanied by satellites, are $M\alpha_1$, $(M_{\text{V}}N_{\text{VII}})$, and $M\beta$, $(M_{\text{IV}}N_{\text{VI}})$. A subsequent investigation of the plates previously obtained[11] shows that the greatest intensity of the satellites of $M\alpha_1$ and $M\beta$ is near $Z=83$. Another experimental fact appeared in the previous study: the semi-Moseley graphs for the $M\alpha_1$ and $M\beta$ satellite groups are remarkably similar (see p. 922, ref. 11). An explanation of the origin of these two satellite groups should involve two very similar initial doubly ionized states; since $M\alpha_1$ and $M\beta$ arise from two very similar transitions, the final doubly ionized states will also be similar. This would explain the similarity of the semi-Moseley diagrams for the $M\alpha_1$ and $M\beta$ satellite groups.

[11] F. R. Hirsh, Jr., Phys. Rev. **38**, 914 (1931).

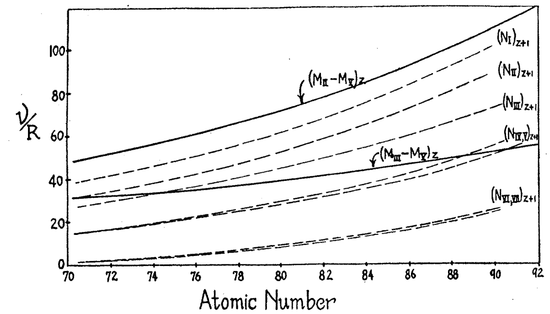

FIG. 5. The energy, in ν/R units, provided by the radiationless transitions $M_{II}\rightarrow M_V$ and $M_{III}\rightarrow M_V$, and the ionization energies, in ν/R units, of the N-shells, plotted against atomic number.

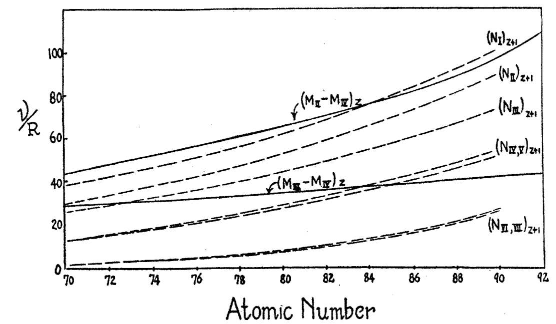

FIG. 6. The energy, in ν/R units, provided by the radiationless transitions $M_{II}\rightarrow M_{IV}$ and $M_{III}\rightarrow M_{IV}$, and the ionization energies in ν/R units, of the N-shells, plotted against atomic number.

Enhancement of the satellites of $M\alpha_1$ and $M\beta$ by the Auger effect must involve radiationless transitions leaving the M_V and M_{IV} shells respectively ionized, and, in addition, some N-shell (or shells).

In Fig. 5 are plotted the ionization energies of the N-shells (dashed lines) for $Z+1$ since an M shell will also be ionized,[12] and the energy, in ν/R units, provided by the radiationless transitions $M_{II}\rightarrow M_V$ and $M_{III}\rightarrow M_V$ (full curves).

If the energy provided by the radiationless transition is much greater than the ionization energy of any particular N-shell, the coupling between the electron involved in the radiationless transition and any electron in that N-shell is very weak; hence the Auger effect has small probability. Thus the radiationless transitions $M_I\rightarrow M_V$ and $M_{II}\rightarrow M_V$ (see Fig. 5) will not give rise to strong enhancement due to the Auger effect, in causing the ionization of M_V shell and some N-shell. Likewise the radiationless transition $M_{III}\rightarrow M_V$ can ionize the $N_{VI,\,VII}$ shells, but only with small probability.

However the curve for the energy difference M_{III}-M_V crosses the ionization energy curves for the $N_{IV,\,V}$ shells near $Z=89$. Because of strong coupling, the $N_{IV,\,V}$ shell will be left ionized as a result of the radiationless transition $M_{III}\rightarrow M_V$; the atom is left doubly ionized, M_V and $N_{IV,\,V}$ electrons missing, and therefore the atom is in an initial state for the emission of satellites. The radiationless transition $M_{IV}\rightarrow M_V$ is not considered, since, as may be seen from Fig. 5, the energy released is too small to cause the ionization of any N-shell.

[12] The use of $Z+1$ is, of course, merely an approximation, but it is sufficiently good for the purpose at hand.

Accounting for the enhancement of the $M\beta$ satellites, a similar plot, Fig. 6, shows the N-shell ionization energies and the curves for the energy differences M_{II}-M_{IV} and M_{III}-M_{IV}, corresponding to the radiationless transitions which leave the M_{IV} shell ionized.

For simplicity, let us disregard the energy difference curve M_{II}-M_{IV}. As it crosses the N_I shell at $Z=84$, it undoubtedly may be of some significance in causing satellite enhancement due to an M_{IV} and N_I double ionization for several atomic numbers below $Z=84$. However N_I is a single shell, while $N_{IV,\,V}$ is a double shell as in the case of the $L\alpha_1$ and $L\beta_2$ satellites, where $M_{IV,\,V}$, a double shell, is the second (outermost) ionized shell according to Coster and Kronig.[6] The coupling is enhanced as the probabilities of ionization of the two shells are here added, in the event of the ionization of this double shell as a result of a radiationless transition.

We see in Fig. 6 that the curve for the energy difference M_{III}-M_{IV} crosses and goes above the ionization energy curve for the $N_{IV,\,V}$ shell at about $Z=84$, and we therefore expect strong enhancement of the satellites of $M\beta$ for several atomic numbers below $Z=84$. The radiationless transition $M_{III}\rightarrow M_{IV}$ can cause the ionization of the $N_{IV,\,V}$ shell, and the atom may be left doubly ionized by the Auger effect because of the strong electron coupling. The energy released by the radiationless transition $M_{III}\rightarrow M_{IV}$ can also cause ionization of the $N_{VI,\,VII}$ shells throughout the entire atomic number range of Fig. 6, but this event is of small importance because of the weak

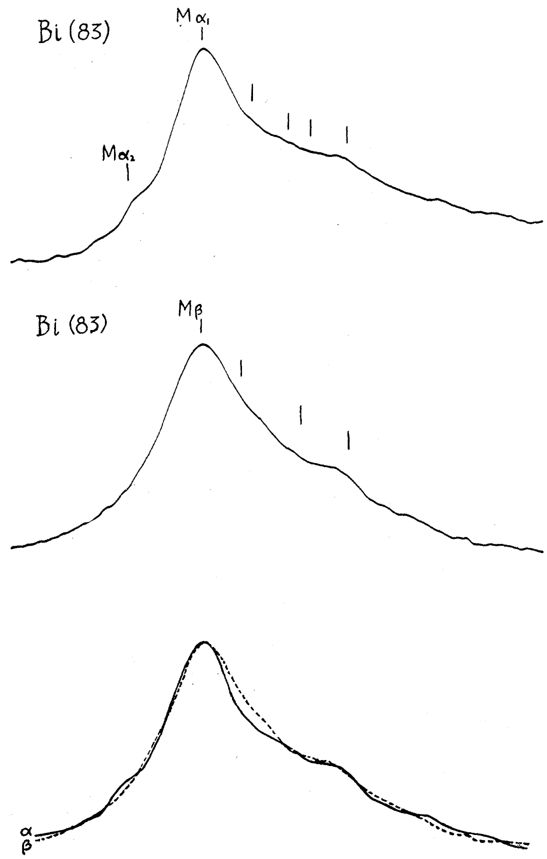

FIG. 7. Microphotometric records of the M-lines of Bi(83). Upper curve, $M\alpha_1$; middle curve, $M\beta$; lower curve, $M\alpha_1$ and $M\beta$ superimposed.

coupling between the electron involved in the radiationless transition and an $N_{VI,\ VII}$ electron. Likewise the radiationless transition $M_I \rightarrow M_{IV}$ is not considered because of weak coupling with the N-shells.

From the above discussion it is seen that we may have enhancement due to the Auger effect under very similar conditions for the satellites of the diagram lines $M\alpha_1$ and $M\beta$. Considering Fig. 5, we see that for the $M\alpha$ satellites the radiationless transition $M_{III} \rightarrow M_V$ will, with high probability for certain atomic numbers, cause ionization of the $N_{IV,\ V}$ shell, leaving the atom doubly ionized. Considering Fig. 6, we see that for the $M\beta$ satellites, ionization of the $N_{IV,\ V}$ shell may be caused, with high probability for certain atomic numbers, by the radiationless transition $M_{III} \rightarrow M_{IV}$. Thus we might expect that the satellites of $M\alpha_1$ and $M\beta$ would have approximately the same frequency separations from their respective parent lines, because of the great similarity of both the initial and the final doubly ionized states; for $M\alpha_1$ satellites, the transition is $M_V N_{IV,\ V} \rightarrow N_{VII} N_{IV,\ V}$, while for the $M\beta$ satellites the transition is $M_{IV} N_{IV,\ V} \rightarrow N_{VI} N_{IV,\ V}$. To confirm this, one can inspect the superimposed semi-Moseley graphs, as shown in Fig. 5, p. 922, ref. 11. The curves for $M\alpha^{ii}$ and $M\beta^{ii}$, the strongest satellites in their respective groups, are practically coincident, while $M\alpha^{i}$ and $M\beta^{i}$ and likewise $M\alpha^{iv}$ and $M\beta^{iii}$ have roughly the same frequency separations.

While making the wave-length measurements previously mentioned[11] a plate was made of the Bi(83) x-ray spectrum which shows both the $M\alpha_1$ and $M\beta$ lines. The $M\alpha_1$ line ($\lambda = 5.11$A) has a density of 0.59 on this particular plate, while the $M\beta$ line ($\lambda = 4.89$A) has a density of 0.81 (the spectrograph was set to photograph $M\beta$). Hence, density is proportional to intensity on this plate[9] and microphotometric curves made from this plate will be undistorted.

Fig. 7 gives the microphotometric curves for the Bi(83) $M\alpha_1$ and $M\beta$ lines just mentioned. The curve for $M\alpha_1$ is at the top; the middle curve is that of $M\beta$, while the lower curves are $M\alpha_1$ and $M\beta$ superimposed by tracing the two upper curves, rotating the $M\alpha_1$ curve slightly to eliminate its uneven background. It may be readily seen that for Bi(83) the satellites of $M\alpha_1$ and $M\beta$ have roughly the same intensity, with the $M\beta$ satellites possibly a little more intense. This last fact is to be expected because of the higher probability of double ionization due to the Auger effect, since the intersection of the curve for the energy difference M_{III}-M_{IV} and the $N_{IV,\ V}$ ionization energy curve, lies nearer atomic number 83 than does the intersection of the curve for the energy difference M_{III}-M_V and the $N_{IV,\ V}$ ionization energy curve (see Figs. 5 and 6).

It is unfortunate that the $M\alpha_1$ satellite intensity maximum should lie in a region which is difficult for the x-ray spectroscopist to study completely because of the presence of several radioactive elements. However, Dr. L. G. Parratt has recorded ionization curves of several M-lines in the (1, +1) position with the two-crystal vacuum spectrometer. For Au(79) he finds a line decidedly asymmetrical near the base with suggestive irregularities indicating satellite lines. The relative intensity of the $M\alpha_1$ satellites is apparently much less than the relative intensity indicated by the author's photometer record (Fig. 7) for Bi(83), $M\alpha_1$. This intensity difference is in agreement with predictions to be made from Fig. 5, since Au(79) is farther removed from the intersection of the curve for the energy difference M_{III}-M_V and the $N_{IV,\,V}$ ionization energy curve, than is Bi(83). Although quantitative comparison of the relative satellite intensities for these elements cannot be made from these data, because of the different types of instruments used, the qualitative conclusion stands. Furthermore, U(92), $M\alpha_1$ should have very faint satellites, since the Auger effect is very improbable (see Fig. 5). Preliminary measurements by Dr. Parratt on the U(92), $M\alpha_1$ line indicate less asymmetry at the base than in the case of the Au(79), $M\alpha_1$ line. This experimental agreement with the predicted intensity anomaly is suggestive, but requires further investigation for its final confirmation.

Conclusions

1. The experimental existence of an intensity anomaly for the satellites of $L\beta_1$ is demonstrated.

2. Satellite enhancement is studied, in line with the suggestion of Coster and Kronig, for the *M*-series, and is shown to agree qualitatively with existing data.

Acknowledgments

It is a pleasure to acknowledge Dean Richtmyer's continued interest in these studies, and to thank him for permission to use certain equipment granted him by the Heckscher Research Council of Cornell University.

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Fine Structure in the *K* X-Ray Absorption Edge of Gallium*

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The absorption of x-rays by a Ga foil in the region extending from the main *K* absorption edge of Ga toward shorter wave-lengths for a distance of about 250 volts has been investigated by the ionization method. The absence of any extended fine structure at room temperature is confirmed. The temperature of the Ga has been reduced to −67°C and −140°C, and a progressive appearance of extended fine structure has been noted as the temperature decreased. Checks have been made to prove the validity of the conclusions. The results of the investigation are presented in graphical and tabular form. A value of 1192.5 x.u. for the wave-length of the main *K* absorption edge of Ga is determined. This value is believed to be more accurate than the value of 1190.2 x.u. found in most tables.

Introduction

Two distinct types of fluctuation have been noted in the values of x-ray absorption coefficients in the neighborhood of the main absorption discontinuities for various substances. These two types are distinguished by their energy separations from the main absorption edge, both occurring on the short wave-length side of the main edge. The fluctuations within energy separations of a few tens of volts of the main absorption edge have been called the Kossel type of fine structure. Those fluctuations occurring at energies between fifty and several hundred volts greater than the energy of the main edge have been called the Kronig type of fine structure. The existence of this extended fine

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