# The Absence of the M<sup>3</sup> X-Ray Satellite Intensity Anomaly\*

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The absence of the  $M\beta$  x-ray satellite intensity maximum is shown, and explained in terms of the relative probability of Auger transitions, the relative probabilities being determined by means of diagram line widths.

### INTRODUCTION

 $\mathbf{I}_{\text{the writer especially noted the similarity of}}^{\text{N a former study of the } M\alpha_1 \text{ and } M\beta \text{ satellites},^1}$ the "semi-Moseley" graphs for the maxima of these two groups: they are practically identical. Moreover, in a subsequent paper<sup>2</sup> the writer pointed out how similarly shaped the  $M\alpha_1$  and  $M\beta$  lines of Bi(83) were (Fig. 7, reference 2). In that same paper,<sup>2</sup> the present writer proposed that the  $M\alpha_1$  satellites were due to the transition  $M_{\rm V}N_{\rm IV,V} \rightarrow N_{\rm VII}N_{\rm IV,V}$  effected by the radiationless transition  $M_{\rm III} \rightarrow M_{\rm V}$  with ejection of an  $N_{\rm IV,V}$ electron; that the  $M\beta$  satellites were due to the transition  $M_{IV}N_{IV,V} \rightarrow N_{VI}N_{IV,V}$  effected by the radiationless transition  $M_{\rm III} \rightarrow M_{\rm IV}$  with ejection of an  $N_{IV,V}$  electron. Thus the satellites of both the  $M\alpha_1$  and  $M\beta$  groups could be accounted for by the Auger effect. Moreover, the very similar nature of the two, single-electron transitions between doubly-ionized states, just mentioned, practically ensures the similarity of the semi-Moseley graph groups for  $M\alpha_1$  and  $M\beta$  as well as that of the over-all line shapes. In Munier, Bearden, and Shaw's article,<sup>3</sup> the  $M\alpha$  and  $M\beta$ groups for W(74), (p. 541), are very similar, except for fine detail.

With this situation in mind, the present writer investigated the plates from which the measurements of reference 1 were made. It was simple to show photographically that the  $M\alpha_1$ lines revealed a maximum of intensity<sup>4</sup> for their satellites near the proper atomic number. In the case of the  $M\beta$  satellites, the energy curve for

the radiationless transition  $M_{\rm III} \rightarrow M_{\rm IV}$  intersects and passes above the ionization-energy curve for the  $N_{IV,V}$  shell (necessarily for Z+1 as an inner M electron is missing), at Z=84 (see Fig. 1). Thus we might expect the Auger effect to occur and doubly ionize atoms below Z = 84, producing an Auger intensity maximum (anomaly), as in the case of the  $M\alpha_1$  satellites.

### EXPERIMENTAL

The plates for the  $M\beta$  lines<sup>1</sup> (all lines except those for Pt and Ir were taken with a calcite crystal; the two named were taken with a quartz crystal) were photometered by using a Koch microphotometer; the constants were secured and density plotted as a function of wave-length for each x-ray line. The range of the present wave-lengths, from 3.7 to 6.0A, has been studied by the writer<sup>5</sup> who has shown density to be proportional to exposure (intensity constant), over a considerable range of densities. The present writer is not alone in this result.<sup>5</sup> Having



FIG. 1. Coster-Kronig diagram for the satellites of the  $M\beta$  line: energy released by the radiationless transitions  $M_{II} \rightarrow M_{IV}$  and  $M_{III} \rightarrow M_{IV}$  plotted as a function of atomic number (full line); ionization energies for the various N shells, plotted for Z+1 as an M electron is missing (dashed lines)

<sup>5</sup> F. R. Hirsh, Jr., J. Opt. Soc. Am. 25, 229 (1935); 28, 463 (1938).

<sup>\*</sup> The absence of the  $M\beta$  satellite intensity anomaly was briefly commented on in a Letter to the Editor of *The Physical Review* [Phys. Rev. **59**, 766 (1941)]. <sup>1</sup> F. R. Hirsh, Jr., Phys. Rev. **38**, 914 (1931). <sup>2</sup> F. P. Hirsh, Jr., Phys. Rev. **36**, 101 (1936).

<sup>&</sup>lt;sup>2</sup> F. R. Hirsh, Jr., Phys. Rev. 50, 191 (1936). <sup>3</sup> J. H. Munier, J. A. Bearden, and C. H. Shaw, Phys. Rev. 58, 537 (1940).

<sup>&</sup>lt;sup>4</sup> F. R. Hirsh, Jr., Phys. Rev. 57, 662 (1940).



FIG. 2. Density (intensity) plots for  $M\beta$  x-ray lines of the elements from U(92) to Ir(77). Vertical lines indicate visual measurements of maxima on the original plates (reference 1).

secured the true over-all intensity shapes for each line (see Fig. 2), a suitable and "reasonable" background for each satellite group was drawn in with a spline and the satellites were delineated. Next, the microphotometer magnification was secured, the  $\Delta$ 's (satellite separations) were computed easily from the  $\Delta\lambda$  values of reference 1, and the spectrograph radius was known to be 36.728 cm. These  $\Delta$  values are seen to be quite accurately related to the satellites of Fig. 2, with one exception: the satellite  $M\beta^{ii}$  is seen from the density (intensity) plots to be double (two components) for Pb(82), Tl(81), and Au(79), showing without a doubt that the semi-Moseley graph group for the  $M\beta$  satellites is the exact counterpart of the semi-Moseley graph group for the  $M\alpha_1$  satellites.

In each case the  $M\beta^{ii}$  satellite is seen to be the most intense component, and easily the best defined. For this reason the intensity of the  $M\beta^{ii}$ group, with respect to the parent line, was taken as a measure of x-ray line energy produced by double ionization as compared with the x-ray line energy produced by single ionization. These data are presented in Table I. While there should be an increase in the relative energy (ratio S/P) starting just below Z = 84, coming to a maximum and falling off with decreasing atomic number, it is quite evident that the intensity maximum is not present for the M $\beta$  satellites.

The absence of the intensity maximum for the  $M\beta$  satellites is made very obvious in an illustration (made from these same plates taken by the TABLE I. Relative energy (by areas) for the  $M\beta^{ii}$  satellite.

| Element | $M\beta^{n}$ satellite area (S) | Parent line area<br>(P) | Ratio S/P |  |
|---------|---------------------------------|-------------------------|-----------|--|
| U(92)   | 0.01×10 sq. in.                 | 0.50×10 sq. in.         | 0.020     |  |
| Th(90)  | 0.01                            | 0.44                    | 0.023     |  |
| Bi(83)  | 0.01                            | 0.49                    | 0.020     |  |
| Pb(82)  | 0.03                            | 1.22                    | 0.025     |  |
| TI(81)  | 0.045                           | 1.97                    | 0.023     |  |
| Au(79)  | 0.07                            | 2.76                    | 0.025     |  |
| Pt(78)  | 0.02                            | 0.78                    | 0.026     |  |
| Ir(77)  | 0.028                           | 0.86                    | 0.032     |  |
|         |                                 |                         |           |  |

present author<sup>1</sup>) on page 305 of H. E. White's book, Introduction to Atomic Spectra. Here the satellites of  $M\alpha_1$  show an unmistakable maximum of intensity at Pb(82), while it is absent for the  $M\beta$  satellites.

## DISCUSSION OF EXPERIMENTAL RESULTS

One fact that is evident in Fig. 1, is that the radiationless transition  $M_{II} \rightarrow M_{IV}$  can eject an  $N_{I}$ electron at Z=84, and below that atomic number. Thus there are two Auger transitions possible at and below Z=84: one which will produce the  $M\beta$  satellite group,  $(M_{\rm III} \rightarrow M_{\rm IV})$  and one which will not,  $(M_{II} \rightarrow M_{IV})$ . If it could be shown that the radiationless transition  $M_{II} \rightarrow M_{IV}$  was more probable than the radiationless transition  $M_{\rm III} \rightarrow M_{\rm IV}$ , the first transition would rob the second to its effective exclusion. This seems to be actually the fact, and will now be discussed.

A very interesting fact, which is not necessarily essential to this argument, but which tells us what intra-level transfers are effective as radiationless transitions, is that all the known radiationless transitions, which cause the known x-ray satellite intensity anomalies, are permitted by the x-ray quantum number selection rules:  $\Delta j = \pm 1, 0;$  $\Delta k = \pm 1$ ;  $\Delta n$  is arbitrary. For  $L_{I} \rightarrow L_{III}$  ( $L\alpha_{1}$  and  $L\beta_2$  satellites),  $\Delta j = -1$ , and  $\Delta k = -1$ ; for  $L_{I} \rightarrow L_{II}$  $(L\beta_1 \text{ satellites}), \Delta j = 0 \text{ and } \Delta k = -1; \text{ for } M_{III} \rightarrow M_V$ ( $M\alpha_1$  satellites),  $\Delta j = -1$  and  $\Delta k = -1$ . Similarly for the two radiationless transitions under discussion: for  $M_{\rm III} \rightarrow M_{\rm IV}$ ,  $\Delta j = 0$  and  $\Delta k = -1$ ; for  $M_{\rm II} \rightarrow M_{\rm IV}, \ \Delta j = -1 \text{ and } \Delta k = -1.$ 

Theoreticians might immediately raise a protest as to the significance of these last observations. However, it will be remembered that in 1922 D. Coster<sup>6</sup> was searching for radiations corresponding to the transition  $L_{I} \rightarrow L_{III}$  (permitted by selection rules). He failed in this first search; he later reported<sup>7</sup> that radiation had been observed very faintly for a few atomic numbers. We now know why this search failed at first:  $L_{I} \rightarrow L_{III}$  is much more probable as a radiationless transition (see reference 7). Such electron jumps are intra-level transfers as compared with the usual inter-level transfers which give rise to the ordinary x-ray diagram lines. Thus it would seem evident that these intra-level transfers, while prob-



FIG. 3. Energy level diagram showing relation of radiationless transitions to radiation transitions in interpreting Auger probabilities in terms of line widths.

able to some extent as ordinary permitted transitions yielding radiation, are much more probable as radiationless transitions. The significance of the radiationless transitions being permitted by selection rules is that the selection rules point out where the radiationless transitions are sure to occur.

With this last fact well in mind, let us proceed to the solution of the problem caused by the absence of the  $M\beta$  x-ray satellite intensity anomaly. Figure 3 shows the situation as regards the radiationless transitions: all are permitted by selection rules; two result in ionization of the  $M_{\rm IV}$  shell  $(M_{\rm III} \rightarrow M_{\rm V} \text{ ionizes the } M_{\rm V} \text{ shell})$ , but the  $M_{\rm III} \rightarrow M_{\rm IV}$  transition alone could cause enhancement of the  $M\beta$  satellite group, as has been previously discussed in this paper. The facts are as follows:  $M_{\rm III} \rightarrow M_{\rm IV}$  and  $M_{\rm III} \rightarrow M_{\rm V}$  both broaden the  $M_{\rm III}$  level by decreasing its mean ionized life;  $M_{II} \rightarrow M_{IV}$  broadens the  $M_{II}$  level similarly by decreasing its mean ionized life. If the  $M_{\rm II}$  level is broader than the  $M_{\rm III}$  level, we would immediately see that  $M_{II} \rightarrow M_{IV}$  has an extremely high probability of occurrence. Ramberg and Richtmyer<sup>8</sup> ascribe practically the entire breadth of such levels to Auger transitions. How may we measure the breadth of the  $M_{\rm II}$  and  $M_{\rm III}$  levels? Fortunately, there are two radiation transitions starting from these levels and ending in a common level:  $L\beta_4$  and  $L\beta_3$  (see Fig. 3). Any difference in the width of the  $L\beta_4$  line as <sup>8</sup> E. Ramberg and F. K. Richtmyer, Phys. Rev. 51, 913 (1937).

<sup>&</sup>lt;sup>6</sup> D. Coster, Phil. Mag. **43**, 1089 (1922). <sup>7</sup> D. Coster and R. DeL. Kronig, Physica **2**, 13 (1935).

|       | Yb(70) | Lu(71) | Ta(73) | W(74) | Re(75) | Os(76) | Ir(77) | Pt(78) | Au(79) | Tl(81) |
|-------|--------|--------|--------|-------|--------|--------|--------|--------|--------|--------|
| Lβ4   | 13.9   | 12.8   | 14.1   | 15.1  | 16.4   | 17.1   | 17.7   | 18.4   | 19.6   | 20.4   |
| Lβ3   | 12.9   |        | 11.7   | 12.3  | 13.6   | 14.7   | 14.9   | 16.1   | 17.2   | 18.4   |
| Diff. | 1.0    |        | 2.4    | 2.8   | 2.8    | 2.4    | 2.8    | 2.3    | 2.4    | 2.0    |

TABLE II. Corrected line breadths (ev).

compared with the  $L\beta_3$  line, must be due to the greater width of the  $M_{\rm II}$  level compared with the  $M_{\rm III}$  level. The breadth of a diagram line has been shown to be equal to the sum of the breadths of the two energy levels between which the electron transition takes place.<sup>9</sup>

One way of expressing the Bohr-Heisenberg indeterminacy principle is:

$$\Delta E_l \cdot \Delta T_l \approx \hbar, \tag{1}$$

where  $\Delta E_l$  is the uncertainty in measuring the energy of a certain atomic phenomenon, and  $\Delta T_l$  is the uncertainty in measuring the time of its occurrence. Equation (1) is dimensionally equivalent to the more commonly quoted form. Let  $\Delta E_l$  be considered to be the energy breadth of a given electron energy level, and  $\Delta T_l$  the mean ionized life: we then see that the indeterminacy principle applies to our problem. Let  $\Gamma_l = 1/\Delta T_l$ , where  $\Gamma_l$  is the reciprocal of the mean ionized life. Then

But

$$\Delta E_l \approx \hbar \cdot \Gamma_l. \tag{2}$$
$$\Gamma_l = \sum_{(A)} \gamma_l{}^{(A)} + \sum_{(R)} \gamma_l{}^{(R)}, \tag{3}$$

which says that for a particular level  $\Gamma_l$  is the sum of all the  $\gamma$ 's contributed by the Auger transitions, plus the sum of all the  $\gamma$ 's contributed by ordinary radiation transitions.<sup>8</sup>

Now Ramberg and Richtmyer<sup>8</sup> have shown that in the M and N levels where the Auger transitions are the chief contributors to the breadth of levels:

$$\Gamma_l = \sum_{(A)} \gamma_l^{(A)}, \qquad (4)$$

i.e.,

$$\sum_{(A)} \gamma_{l}{}^{(A)} \gg \sum_{(R)} \gamma_{l}{}^{(R)}.$$

Then from (2) and (4) we have

$$\Delta E_l \approx \hbar \sum_{(A)} \gamma_l^{(A)}.$$
 (5)

<sup>9</sup> V. Weiskopf and E. Wigner, Zeits. f. Physik **63**, 54 (1930); **65**, 18 (1930).

From (5), for the  $M_{\rm II}$  level:

$$\Delta E M_{\rm II} \approx \hbar \gamma (M_{\rm II} \to M_{\rm IV}). \tag{6}$$

For the  $M_{\rm III}$  level:

$$\Delta E M_{\rm III} \approx \hbar \{ \gamma (M_{\rm III} \rightarrow M_{\rm IV}) + \gamma (M_{\rm III} \rightarrow M_{\rm V}) \}.$$
(7)

For the  $L\beta_4$  line Weiskopf and Wigner have shown:<sup>9</sup>

$$\Delta E L \beta_4 = \Delta E M_{\rm II} + \Delta E L_{\rm I}. \tag{8}$$

For the  $L\beta_3$  line:

$$\Delta E L \beta_3 = \Delta E M_{\rm III} + \Delta E L_{\rm I}. \tag{9}$$

Subtracting (9) from (8) we have:

$$\Delta E L \beta_4 - \Delta E L \beta_3 = \Delta E M_{\rm II} - \Delta E M_{\rm III}.$$
(10)

Substituting in (10) from (6) and (7) we then have:

$$\Delta E L \beta_4 - \Delta E L \beta_3 \approx \hbar \{ \gamma (M_{\rm II} \rightarrow M_{\rm IV}) - [\gamma (M_{\rm III} \rightarrow M_{\rm IV}) + \gamma (M_{\rm III} \rightarrow M_{\rm V})] \}.$$
(11)

But  $\Delta E_{L\beta_4} - \Delta E_{L\beta_3}$  is always + (positive) between Z = 70 and Z = 81 as is shown in Table II, data from the thesis of Dr. John N. Cooper,<sup>10</sup> written at Cornell University in 1940. I am indebted to Dr. Cooper for an admirable presentation of the subject of line breadths.

This, then, affirms the idea that  $M_{\rm II} \rightarrow M_{\rm IV}$  is more probable, according to line widths, than  $M_{\rm III} \rightarrow M_{\rm IV}$  and  $M_{\rm III} \rightarrow M_{\rm V}$  combined; this fact prevents the occurrence of the  $M\beta$  satellite intensity anomaly.

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<sup>10</sup> J. N. Cooper, Phys. Rev. 61, 224 (1942).