The M_1 and M_2 X-Ray Absorption Edges of Lead

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(Received August 7, 1939)

The M_1 and M_2 edges of lead, not having been previously measured, were investigated. They were found to occur at wave-lengths: M_1, 3.219A; M_2, 3.469A. A brief discussion of M edges is given and the fact that many M edges show discrepancies between observed and calculated values is noted. Methods of computing edge energies are discussed. The proposed explanation and meaning of these discrepancies are discussed with particular reference to lead.

INTRODUCTION

A KNOWLEDGE of the wave-lengths of the x-ray absorption edges of the elements is of importance in many connections. Many of the five M edges of 20 of the heavier elements have been measured.[1–13] The M_1 and M_2 edges have so far been measured in only eight of these elements, mainly because the experimental difficulties in observing them are greater than for the other M edges. It seemed worth while to attempt to photograph M_1 and M_2 edges. These edges of lead[6] had not been studied and it was chosen[14] for investigation because it lends itself to easy preparation in thin absorbing films.

THE METHOD

For edge contrast there is an optimum absorber thickness given by a formula derived by Sandström.[15] The values needed for the linear absorption coefficient on the short and long wave-length sides of the edge were obtained from Jönsson's[16] formula and tables[17] of Jönsson's values of the electron absorption coefficient. Computed optimum thicknesses for lead M_1 and M_2 edges were 7.3×10^{-5} cm and 6.9×10^{-5} cm, respectively. The screens used were from 5 to 13×10^{-5} cm thick.

The lead absorbing films were made by evaporation in a vacuum, and their thickness was governed, in a manner previously described.[9]

The self-rectifying x-ray tube and vacuum spectrograph have been described elsewhere.[5, 7] Only minor modifications were made. A.c. voltages on the tube were about 5100, currents of 50 to 200 milliamperes were used, and exposure times were from 2 to 12 hours depending on whether the photograph was one of emission or absorption.

The wave-lengths of the edges were obtained by measuring visually[18] with a traveling "one-power microscope" the distances between known emission lines and edges[19] and the lead edges on the photographs, and then interpolating with a formula given by Whitmer.[4]

RESULTS

In Table I are given the values of the edges in terms of wave-length and energy.

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[1] H. W. B. Skinner and J. E. Johnston, Proc. Roy. Soc. **161**, 420 (1937).

[2] V. H. Sanner, Zeits. f. Physik **94**, 523 (1935).

[3] J. A. Prins and A. J. Takens, Zeits. f. Physik **84**, 65 (1933).

[4] C. A. Whitmer, Phys. Rev. **38**, 1164 (1931).

[5] R. V. Zumstein, Phys. Rev. **25**, 747 (1925).

[6] E. Lindberg, Zeits. f. Physik **54**, 632 (1929); **56**, 402 (1929); **57**, 797 (1929).

[7] R. A. Rogers, Phys. Rev. **30**, 747 (1927).

[8] A. J. M. Johnson, Phys. Rev. **34**, 1106 (1929).

[9] J. W. McGrath, Phys. Rev. **56**, 137 (1939).

[10] W. D. Phelps, Phys. Rev. **46**, 357 (1934).

[11] D. Coster, Phys. Rev. **19**, 20 (1922).

[12] W. Stenström, Dissert., Lund., (1919).

[13] A table of wave-lengths of the M edges investigated before 1931 is given in M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Julius Springer, 1931), p. 277.

[14] An attempt was made to photograph Au M_2 (which had not been done (references 6, 8, 9)). However, the Ag $L\beta_1$ line (3.927A) was always present on the plate. Location and removal of the Ag source was not accomplished in the time available. But several gold absorption photographs were taken and it can be said that Au M_2 is very near the Ag $L\beta_1$ line.

[15] A. Sandström, Zeits. f. Physik **65**, 632 (1930).

[16] A. Jönsson, Dissert., Upsala, (1928).

[17] Reference 13, p. 470.

[18] Measurements were made visually rather than with a microphotometer for reasons given in reference 9.

[19] Reference lines were: Sb $L\beta_1$ (3.218A), Ag $L\gamma_2$ (3.300A), Sb $L\alpha_1$ (3.432A), Ag $L\gamma_1$ (3.515A), Ag $L\beta_2$ (3.694A); wave-length values from reference 13, p. 476. Sb lines were not used in M_1 photographs. The Ca K edge, from the gypsum spectrometer crystal, was very sharp and convenient so it was also used. Its gypsum crystal value of 3.059A as given by G. A. Lindsay and G. D. Van Dyke, Phys. Rev. **28**, 613 (1926) was used.

Discussion

After a consideration of possible apparatus and measurement errors it was estimated that these values are accurate to within: ±5.8 electron volts (±0.005A) for M_1, and ±5.3 electron volts (±0.005A) for M_2. These estimates are comparable with those of others who have operated this apparatus in this wave-length region.

It was found that absorbing screens slightly thicker than the calculated optimums gave better contrast. In agreement with these computed optimum thicknesses was the fact that greater thickness was required for M_1 than for M_2.

Siegbahn[20] has computed values of the M energy levels of the elements on the basis of known L edges and appropriate known emission lines. His values for lead are: M_1, 3840.5 electron volts; M_2, 3548.1 ev; M_3, 3058.0 ev; M_4, 2576.1 ev; M_5, 2474.6 ev. If one takes these as computed edge energies, there are apparent discrepancies between computed and measured values. For the lead edges here studied they are −8.5 ev for M_1 and 7.9 ev for M_2; these differences are probably not significant.

In other observed M edges significant discrepancies appear: usually for the M_4 and M_5 edges, fairly often for the M_1 edge, and occasionally for the M_2 and M_3 edges. Siegbahn[21] proposed that the M discrepancies arise because atomic electrons may not all go to the same final level in an absorption edge transition. Phelps[10] further suggested that the final levels are lattice levels.

Table I. *Lead M_1 and M_2 edges.*

Plate	M_1	M_2
16		3.471A
17		3.471
20	3.216A	
22	3.214	3.472
24	3.223	
25	3.217	3.470
26	3.223	3.471
27	3.221	3.468
29		3.465
31		3.464
Average Wave-length	3.219A	3.469A
Average Energy (Electron Volts)	3832.0	3556.0

[20] Reference 13, p. 346.
[21] M. Siegbahn, Zeits. f. Physik **67**, 567 (1931).

McGrath[9] found that when gold was alloyed with copper its M_4 and M_5 edges occurred at energies greater by several electron volts. Since the alloying changed the atomic spacing, which should in this case increase the energies of the lattice levels, he concluded that the final levels must be lattice levels. He gave a brief review of experimental results of others which indicated that, upon assigning to the low lattice levels the values of the quantum number l which the optical levels from which they originate have in free atoms, there are preferred atomic to low lattice level edge-giving transitions which are often given by $\Delta l = \pm 1$.

One should not expect, therefore, that the energies of the atomic levels, as calculated by Siegbahn,[20] would be the edge energies. Further, to obtain absolute term values one should not average calculations based on several different edges of the element since, in many cases, the final levels for these edge transitions are not the same. Ruark[22] computed absolute term values of several elements by a method seemingly better. To values of small x-ray terms obtained from optical spectra he added term differences obtained from x-ray emission lines. He estimated that the values obtained in this way are in error by not more than about 11 electron volts. So far as the author knows, there is not sufficient data to carry out this method of calculation for lead.

Since the atomic electrons do not all go to the same final level in the edge-giving transitions it is of interest to calculate the energies of the edges of an element using only one given edge and known emission lines. If these values are then compared to observed values any discrepancies arising are the energies of the final levels (which are lattice levels) with respect to the final level of the given edge transition.[23] The author has done this[24] for most of the edges

[22] A. E. Ruark, Phys. Rev. **45**, 827 (1934).
[23] While in recent years investigators of M edges have been concerned with these discrepancies and their meaning, so far as the author knows, no investigator of K or L edges has mentioned any such differences in them. Yet he has compared their observed values with his calculated values and finds, in several instances, discrepancies which appear to be significant. Probably, any such K and L edge discrepancies could also be explained on the proposal of Siegbahn[20] and Phelps.[19]
[24] The relations (in energy units) used for calculating the M edges, for example, were: $M_1 = L_3 - L_l$; $M_2 = L_3 - L\beta_{15} + (N_4 \rightarrow M_2)$; $M_3 = L_3 - L\beta_{15} + (N_4 \rightarrow M_3)$, and $M_3 = L_3 - L\beta_2 + (N_5 \rightarrow M_3)$ averaged; $M_4 = L_3 - L\alpha_2$; $M_5 = L_3 - L\alpha_1$.

of the heavier elements, using the L_3 edge as the given edge. Since values thus obtained are usually within 3 ev of those given by Siegbahn, with a few being as much as 10 ev different, the discrepancies noted on this basis are not much different in magnitude than those quoted on the basis of Siegbahn's[20] values by some M edge investigators.[4–10] The author's computed values for lead are: M_1, 3840.7 ev; M_3, 3052.6 ev; M_4, 2577.4 ev; M_5, 2475.9 ev; (there is not enough data for this calculation of M_2). Lindberg[6] found these energy values for the lead edges: M_3, 3058.0 ev; M_4, 2599.1 ev; M_5, 2494.9 ev. There appear, then, these discrepancies: M_1, -8.7 ev; M_2, 7.9 ev (on Siegbahn's value); M_3, 5.4 ev; M_4, 21.7 ev; M_5, 19.0 ev. The normal state of the lead atom is $^3P_0$, the outer electron configuration being $6s^26p^2$, according to Bacher and Goudsmit.[25] Upon assuming the previously mentioned edge-giving transition l selection rule, and assuming that the order of the low lattice and valence levels is the same as that of the free-atom optical levels[25] from which they originated, one would expect: negative and equal M_1, M_4, and M_5 discrepancies, but none for the M_2 and M_3 edges. However, if for some reason the $M_{4,5}$ electrons preferred the $O_{2,3}$ virtual level to the partially occupied $P_{2,3}$ level, on the same assumptions as before, one would expect the M_4 and M_5 discrepancies to be positive and equal. The discrepancy magnitudes cannot be estimated by this scheme. These expectations, with positive M_4 and M_5 discrepancies, are fulfilled.

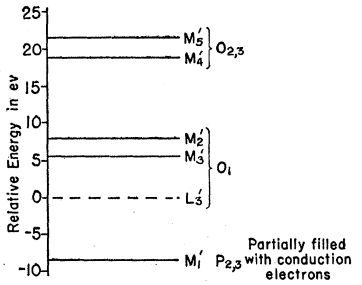

FIG. 1. Low lattice levels in lead as indicated by M edges.

In Fig. 1 a lattice energy level diagram is shown for lead as determined experimentally on the basis of M discrepancies. The primed letters indicate the final levels for the respective atomic electrons in edge transitions. The separations of the levels are drawn to scale but their widths are not indicated. There is probably some overlapping, especially for the M_2', M_3', L_3', and M_1' levels. While the last mentioned levels are shown as distinct the magnitudes of their separations from the L_3' level, with the possible exception of the M_1' level, are not significant. To the right are given virtual optical levels from which these lattice levels possibly originated.

It appears that continued study of the M edges and their discrepancies will contribute considerably in a roughly quantitative way to our understanding of lattice energy levels.

The author appreciates the kindness of the Department of Physics of the State University of Iowa, in extending the opportunity and facilities for this investigation.

[25] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932), p. 356.