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Absorption by Aluminum in the Soft X-Ray Region*

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Measurements on the absorption by aluminum in the spectral range extending from 80A to 600A have been carried out by the use of a grazing incidence spectrograph. The investigation has revealed that the strong absorption band centered at 129A is a "surface" phenomenon which takes place in the metal-substrate interface of absorbers prepared by evaporation. Thin metallic foils without a substrate do not show this absorption band. The present data have yielded consistent results for the mass-absorption coefficient, whose value ranges from 1.0×10^4 cm^2/g to 2.8×10^4 cm^2/g in the above spectral region. As observed previously in connection with the K edge, a secondary structure is also present on the short wavelength side of the $L_{2,3}$ edge. The L_1 absorption limit has not been detected.

INTRODUCTION

THE soft x-ray emission spectra of many crystalline metallic and nonmetallic elements of low atomic number have been investigated rather thoroughly.[1,2] The emission spectra referred to are due to electron transitions from the valence band to vacant K or L levels. Since the width of these inner levels is relatively small, the observed intensity distribution in the emission spectrum furnishes information concerning the level density of the populated states of the crystal lattice.

Measurements on the absorption by the light elements are less extensive. Since the absorption process involves the transition of electrons into unoccupied levels such measurements yield additional information concerning the level structure. If the absorber be irradiated by photons of energy greater than $h\nu_q$, where ν_q is the frequency corresponding to the q absorption edge, the incident photon may be absorbed by an electron in the q level. If the photon energy is less than $h\nu_q$ the absorption does not involve the q level. For example, in the case of aluminum, the absorption of photons of energy somewhat greater than $h\nu_L$ involves primarily an L electron; while photons whose energy is less than $h\nu_L$ may only be absorbed by electrons in the conduction band. Thus, the absorption on the short wavelength side of the edge reflects the characteristics of the unoccupied levels, while that on the long wavelength side portrays the combined features of filled as well as unfilled levels.

Measurements on various metallic elements whose absorption edges lie in the soft x-ray region have been reported by several investigators.[3-7] These observations deal with the K-edge of Li; the $L_{2,3}$ edges of Na, Mg, and Al; and the $M_{2,3}$ edges of Ni, Cu, and Zn. A summary of the numerical absorption data for the foregoing elements (except Na) are given in reference 6. Although the K-edge of Be and B; and the L-edges of Si, P, and S also fall in this region, no measurements seem to have been carried out on these elements as yet.†

A survey of the results obtained previously leads to the following summary with regard to the characteristic features of the absorption curve in the neighborhood of the K or L limit.

(1). The metals Li, Na, Mg, and Al show a well-defined K or $L_{2,3}$ absorption edge. A somewhat diffuse L_1 edge should also appear in the spectra of the last three metals. The observations yield no conclusive evidence of the presence of this edge, though it should lie in the wavelength range investigated.

(2). In the M-absorption spectra of Ni, Cu, and Zn, a somewhat diffuse $M_{2,3}$ edge is established, though the M_1 limit is not observed definitely.

(3). The absorption curves in general show secondary structure. On the short wavelength side of the K edge in Li and of the $L_{2,3}$ edge in the case of Mg and Al, there appears a surprisingly intense absorption band. A correspondingly strong absorption is not observed near the K edge of the latter elements.

(4). The reported measurements indicate the presence of large discrepancies in the values of the absorption coefficient as arrived at from absorbers which differ in thickness.

The experimental procedures in the 50 to 500A region, are subject to difficulties. Of prime importance in making reliable absorption measurements is a source of strong more or less continuous radiation. Such a source does not exist. The continuum emitted by x-ray targets is extremely weak in this region. One is therefore limited to the use of line spectra emitted by highly excited atoms in a condensed spark discharge. Aside from the discontinuous nature of such a source, measurements become less reliable due to the variation in the relative intensities of lines and due to the presence and overlapping of higher order spectra.

A second difficulty lies in the preparation of suitable

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* Work supported by the ONR.

[1] H. W. B. Skinner and H. M. O'Bryan, Trans. Roy. Soc. (London) **239**, 95 (1940).

[2] W. M. Cady and D. H. Tomboulian, Phys. Rev. **59**, 381 (1941).

[3] V. H. Sanner, Z. Physik. **94**, 523 (1935).

[4] H. M. O'Bryan, Phys. Rev. **49**, 944 (1936).

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

[6] J. E. Johnston, Proc. Cambridge Phil. Soc. **35**, 108 (1939).

[7] H. M. O'Bryan, Phys. Rev. **57**, 995 (1940).

† *Note added in proof:* Preliminary measurements on Be were reported by D. H. Tomboulian and R. W. Johnson at the Washington meetings of the Am. Phys. Soc., Phys. Rev. **83**, 220 (1951).

absorbers. For this purpose one needs uncontaminated metallic films preferably of known thickness not exceeding 5000A. Usually such absorbers are made by evaporating the substance on a transparent supporting film or on a backing layer which can be removed. Samples prepared in this manner may contain traces of impurities or may not be crystalline in character. Furthermore, if absorption coefficients are to be evaluated, one has to contend with the problem of ascertaining the thickness of the absorber with some degree of precision.

Finally, there are the limitations in intensity measurements imposed by the photographic method. This method is at present the one generally used for the comparison of intensities although recent techniques involving photomultipliers show promise.

The foregoing troublesome experimental features are to a large extent responsible for the scarcity and lack of refinement in absorption measurements in the far ultraviolet region.

It was considered worthwhile to select an absorber, such as aluminum, which is convenient to work with and to re-examine the various features of the absorption curve in the neighborhood of the L limit. In particular the investigation was undertaken (1) to institute a search for the L_1 edge, whose location had more recently been predicted[8] on the basis of radiative transitions within the L shell; (2) to investigate the intense selective absorption on the short wavelength side of the edge as indicated by previous measurements; (3) to extend the range of measurements and if possible to arrive at more definitive values for the absorption coefficient.

EXPERIMENTAL

The source of radiation was a condensed spark discharge in a glass capillary. Such a source produces an intense line spectrum superimposed on a relatively weak continuum. The lines emitted by this source are due primarily to ionized atoms of oxygen, nitrogen, silicon, and sodium, and except for the very short wavelengths are sufficiently densely distributed over the range of interest. The intense lines of this spectrum are classified and their wavelengths have been determined accurately by Edlen.[9] A large number of tests have established the fact that if operated under carefully controlled conditions, the relative intensities of the lines from the capillary discharge do not differ by more than a few percent from one exposure to another though the absolute intensities for a dozen or more sparks are subject to somewhat greater variation (about 5 percent).

The dispersing instrument was a grazing incidence spectrograph which in the neighborhood of 200A had a dispersion of 1A per mm. For photometric purposes a slit width of 0.10 mm was used, and for this slit width a practical instrumental resolving power of 400 was readily attainable for the wavelength region specified above.

Several types of absorbers were utilized. The thickest sample consisted of rolled aluminum foil while the thinner ones were prepared by condensing the metal on thin backing films of zapon. Two samples of intermediate thickness were prepared by careful etching of the rolled foil. Foils whose thickness was in excess of 6000A practically absorbed all the wavelengths shorter than that of the edge, while those of only several hundred angstroms in thickness were almost equally transparent on either side of the edge. Calculation[10] indicates that the optimum thickness of the absorber should be about 1500A. The present measurements were conducted with absorbers whose thickness ranged from 200 to 6500A. The backing films used had a transmission of 50 percent in the vicinity of 300A and were considerably more transparent at shorter wavelengths. The absorption by the backing film varied only slowly with wavelength and was free from selective effects.

For the rolled foils, the absorber thickness was arrived at by weighing samples on a microbalance, successive weighings being in agreement within $\frac{1}{2}$ percent. The samples selected were tested for uniformity in thickness by placing a large sample in the path of the incident beam and by comparing the absorption produced by different regions of the foil. The thickness of the etched foils was determined indirectly by a scheme to be mentioned later. In the case of evaporated films the sample thickness was estimated[11] by distilling a known weight of the metal from a battery of tungsten evaporators so arranged as to insure a uniformly deposited layer. The thickness so calculated was checked by weighing a deposit of known area. The two results differed by about 1 percent. It is known[12] that in this procedure the evaporated Al film is not contaminated by tungsten. Extreme precautions were taken to maintain cleanliness of the apparatus and good vacuum conditions within the distilling chamber. The absorbers of different thicknesses were prepared under as reproducible conditions as possible.

Electron diffraction experiments by Stahl[13] seem to indicate that if the evaporation is carried out in an interrupted fashion, the deposits obtained consist of sandwiched layers of the pure metal and its oxide. Such studies indicate further that an amorphous deposit may be present on the outer surface and that on exposure to air the fresh surface layers become oxidized only to a depth of 50A. The present measurements gave no evidence that samples prepared by continuous or by interrupted evaporation were sufficiently different in structure as to affect the character of the observed absorption curves. In all but the thinnest absorbers

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[8] D. H. Tomboulian, Phys. Rev. **74**, 1887 (1948).

[9] B. Edlen, Nova Acta Regiae Societatis Scientiarum Upsaliensis **9**, No. 6, (1934).

[10] A. Sandstrom, Nova Acta Regiae Societatis Scientiarum Upsaliensis Ser. IV **9**, No. 11 (1935).

[11] R. C. Williams, J. Appl. Phys. **20**, 98 (1949).

[12] J. Strong, *Procedures in Experimental Physics* (Prentice-Hall, Inc., New York, 1946), p. 173.

[13] H. A. Stahl, J. Appl. Phys. **20**, 1 (1949).

FIG. 1. Absorption curve in the neighborhood of the $L_{2,3}$ edge of aluminum. The absorber was prepared by depositing a 1000A layer of the metal onto a zapon substrate.

used, the influence of the oxide layer was considered to be negligible.

PROCEDURE

For the actual runs, two mountings were prepared from the same zapon film. These two supporting layers received identical treatment with regard to aging and exposure to vacuum conditions except that one of them was coated with the desired thickness of aluminum. The two specimens were then mounted on a rotary shaft behind the spectrograph slit, and as close to the slit as possible. This should minimize fogging and deterioration of the image due to radiation which is scattered by the foil and falls on the grating at angles other than those necessary for focusing. By means of external controls, it was possible to rotate the specimens in the interval between sparks so that either the bare zapon film or the one coated with aluminum was introduced in the path of incident beam. The arrangement of the plate holder was such that it could also be raised or lowered quickly behind an occulator without disturbing the vacuum. Two juxtaposed spectra could thus be obtained on the same plate, one representing the absorption by the bare zapon film and the other that due to the metal and zapon films in combination. In order to smooth out the effect of fluctuations in the intensity of individual sparks, intermingled exposures were made on the same plate by inserting the coated and uncoated films alternately in the path of the beam.

The ratio of the total number of sparks used for the individual exposures was adjusted so as to obtain comparable photographic densities in the adjacent spectra. This ratio was varied from 2 to 20 depending on the thickness of the absorber and no exposures were made in which the total number of sparks was less than 10. The photographic plates (Ilford QI) were calibrated by utilizing the L-emission band of aluminum[2] and also by a procedure described by Skinner and Johnston.[5] Calibration curves were obtained over the required wavelength range by the latter scheme, which assumes the constancy of the intensity ratios of lines in two spectra taken with different number of sparks. Over the region of overlap, the two methods gave results which were in good agreement.

RESULTS

A typical absorption curve obtained by the use of evaporated samples of aluminum is reproduced in Fig. 1. (For the given curve the thickness of the deposit was 1000A.) In the quantity plotted as the ordinate, I_0 represents the intensity of the radiation emergent from the uncoated zapon absorber, while I stands for the intensity of the beam after passage through the absorbing layers of aluminum and zapon. In accordance with the relation $-\mu x = 2.30 \log_{10}(I/I_0)$ the ordinate corresponding to a given wavelength λ is proportional to the linear absorption coefficient μ since x, the absorber thickness, is fixed. The experimental points represent averages determined from six to ten plates taken with varying exposure ratios. The general features of the absorption curve, such as the $L_{2,3}$ limit at 170A, the intense absorption band centered at 129A, and the secondary structure were also observed on similar curves obtained with five different samples of deposited layers whose thicknesses ranged from 500A to 2500A.

It follows from the aforementioned relation that for a given wavelength, the quantity $\log_{10}(I_0/I)$ should be directly proportional to the absorber thickness x. When the measurements on evaporated samples were tested for this consistency, it was found that, for wavelengths in the neighborhood of the edge, the expected regularity was valid within the limits of experimental uncertainty. It must be mentioned that reproducible values of $\log_{10}(I_0/I)$ were achieved only through the maintenance of scrupulous cleanliness in the evaporation process. However, over the general region of the selective absorption band (110 to 150A) the data failed to follow the expected linear relation. Examples of this behavior are shown in the plot of Fig. 2 for the three wavelengths indicated thereon. The data represented by circles are based on absorbers prepared by distillation. The estimated error in $\log_{10}(I_0/I)$ and that in x is indicated by the sides of the rectangles. The two points designated by triangles (△) were obtained from measurements on rolled metal foil, whose thickness was

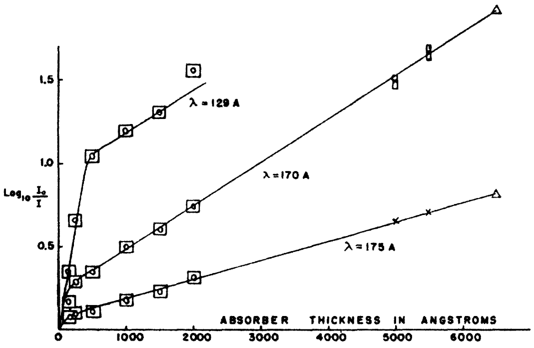

FIG. 2. A plot of $\log_{10}(I_0/I)$ *versus* x, the absorber (Al) thickness. The data for absorbers with zapon substrate are designated by circles. The data for the absorbers thicker than 3000A were obtained by the use of foils without substrate.

determined by weighing. The determinations represented by crosses (X) will be commented upon in the discussion which follows.

The discrepancy observed in connection with the plot of Fig. 2 suggested the desirability of testing absorbers free from zapon backing and led to the use of self-supported metallic foils. When rolled foils were used the intensity transmitted on the high energy side of the edge was too feeble for reliable measurements. It was therefore necessary to reduce the thickness of such absorbers. This was accomplished by etching the foils gradually until samples of sufficient transparency were obtained. The absorption curve of the thinnest sample of this type is reproduced in Fig. 3. Here I_0 represents the intensity of the radiation incident upon the foil and I is the intensity emergent from it. A comparison of the shape of this curve with that of the one shown in Fig. 1 reveals the striking fact that the intense absorption band, which is invariably present in the observations made on evaporated layers, no longer exists when etched foils free from a substrate are used for absorbers. Since the absorption on the long wavelength side of the edge seemed to be linear with x in each case, the thickness of the particular etched sample was determined with the aid of the linear relationship between $\log_{10}(I_0/I)$ and the absorber thickness given in Fig. 2. Thus, from the value of the ordinate of the curve in Fig. 3 at a wavelength (175A) selected previously for one of the linear plots in Fig. 2, the thickness of the etched absorber was found to be 5000A. As a check the value of $\log_{10}(I_0/I)$ at a second wavelength (170A) was plotted in Fig. 2 against the absorber thickness arrived at in the manner just described. Such points, corresponding to the two etched samples, are indicated by crosses in Fig. 2. Unfortunately, due to the extreme fragility of the etched absorbers, it was not practical to prepare thinner specimens.

As a possible cause for the large dip observed in the absorption curves of samples prepared by evaporation one may consider the introduction of impurities, the formation of oxide layers, or the properties of the supporting film. Or, the effect may arise from peculiarities inherent in the crystalline structure of the evaporated film. A similar dip in the absorption is also present in the curve obtained by Johnston[6] who used foils prepared by vaporizing aluminum from a molybdenum crucible under electron bombardment and condensing the metal onto thin backing films of celluloid. Since the absorbers used in the present measurements were prepared by a different procedure, it is unlikely that the effect is due to peculiarities of the distillation process, such as the presence of impurity atoms of tungsten or molybdenum. Absorbers prepared by interrupted evaporation and presumed to contain sandwiched layers of the oxide[13] did not behave differently from other absorbers. The effect cannot arise from the unavoidable surface layer of oxide since the latter must also be present in the case of etched foils which show no selective absorption. In addition, the absorption curve of pure Al_2O_3 was determined for comparison purposes. No similarities were found between the absorption curve of the oxide and that of the evaporated metal.

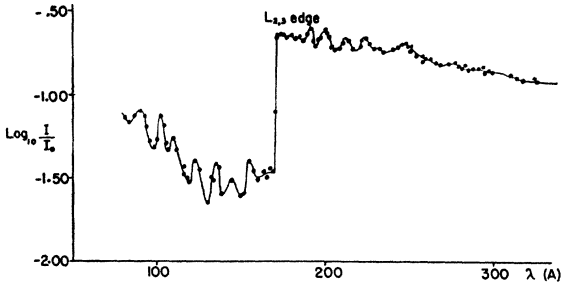

FIG. 3. Absorption curve for aluminum in the region of the $L_{2,3}$ edge. The absorber consisted of a metallic foil (no substrate) 5000A in thickness.

It is possible to determine the thickness of evaporated films very precisely by the methods of multiple-beam interferometry.[14] Such thickness determinations in conjunction with microchemical techniques indicate that thin films (100 to 500A) of Al, Cu, and Ag have densities which are very nearly the same as those of the bulk metal. Furthermore, an electron diffraction pattern of one of our samples has confirmed the crystalline nature of the deposit. Thus, one is led to believe that thin Al films possess the characteristic structure of the metal lattice.

In the present tests both zapon and polystyrene substrates were used and Johnston used a celluloid backing film in his experiments. The absorption by these materials has been studied over the spectral range concerned and is found to be quite free from large fluctuations. When metals are deposited on thin films of these plastics the extra absorption is present in all cases and does not seem to be influenced by the chemical nature of the supporting film.

From the plot shown in Fig. 2, it is seen that, in particular, the 129A radiation is more strongly absorbed in the first 500A of Al than it is in the rest of the sample. By reference to the slope of this curve it is seen that the absorption beyond this thickness is about the same as at 170A, as it should be if the peculiar absorption structure were absent. This suggests that the strong dip in the absorption curve centered at 129A arises from some sort of "surface" effect limited to a depth of about 500A taking place in the region of the aluminum-substrate interface.

Although the unexplained absorption seems to be associated with the metal-backing interface, the mechanism that accounts for it is not known. The absorption may arise from transitions between energy levels in the metal and levels in some element common to the different substrates used. Or it may be due entirely to the

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[14] S. Tolanski, *Multiple-Beam Interferometry* (Clarendon Press, Oxford, England, 1948), p. 148.

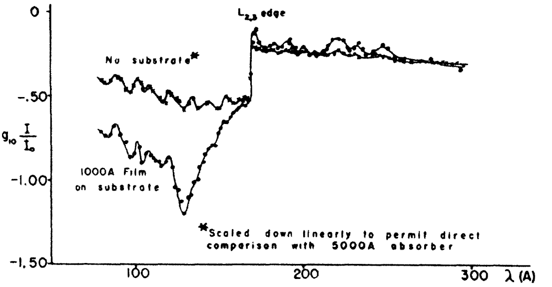

FIG. 4. The effect of substrate on absorption. A comparison of the results shown in Figs. 1 and 3.

metal, the substrate serving only to change the metal lattice near the surface or perhaps serving as a medium into which metallic atoms or ions can diffuse.

That the absorption is characteristic of the metal and not of the substrate appears to be confirmed by the results obtained by Skinner and Johnston[5] who used lithium and magnesium deposits on celluloid. Unexplained dips are present in their results. But in the case of lithium there are two dips instead of one and the distance of either to the absorption edge is appreciably smaller than in the case of Al or Mg. If the absorption is due to an energy level provided by a common element in the substrate, one would not expect an additional absorption band to show up merely through the use of Li instead of the other metals.

It is likely that in the condensation process the metal atoms penetrate the body of the substrate thus forming an interface region several hundred angstroms thick. Only at the pure aluminum boundary is the lattice characteristic of the metal. In the transition region, each metal atom is surrounded by substrate atoms in neighborhood configurations that vary greatly for different metal atoms. Upon the absorption of a photon, the $L_{2,3}$ electron is ejected from the metal atom and goes to an outer level which is essentially atomic in origin and character. Such a selective transition would give rise to a rather sharp absorption line or lines. But because of the difference in the immediate surroundings, the sharp lines may overlap in energy positions and thus give rise to the observed band or dip in absorption.

The wavelengths of the positions of the absorption dips are all within a few electron-volts of the wavelengths corresponding to certain atomic transitions in the metallic ions stripped to their rare gas cores. It may be proposed that the metal might diffuse into the substrate, there forming an ionic structure with the cation stripped of all its valence electrons. This seems possible energetically. Estimates indicate that even if the initial state is strongly localized in the neighborhood of the positive ion, the final state in the absorption process would probably overlap with neighboring negative ions. The energy of the final state would therefore be affected by coulomb and exchange interaction, as well as by the change in the Madelung potential. It is conceivable that these factors might compete with each other, in such a way that the energy would be changed only slightly relative to what it would be in the gaseous ion. No calculations have been made to prove or disprove these hypotheses and such explanations must be regarded as pure speculation.

The lower curve in Fig. 5 is a plot of the present measurements showing the secondary structure on the high energy side of the $L_{2,3}$ edge. The data for this curve were derived from a study of etched-foil absorbers, though many of the characteristic peaks and valleys were also present in the measurements made on absorbers prepared by evaporation (see Fig. 4). It is interesting to note that appreciable structure is observable to within a few electron-volts of the L-edge. The upper curve in Fig. 5 is reproduced from a study[15] of the structure in the neighborhood of the K-limit (7.95A). The vertical scales in Fig. 5 are arbitrary. The curves are drawn so as to match the positions of the K and L limits approximately. The secondary structure observed in these experiments falls within 75 ev of the edge and theerfore cannot be accounted for on the basis of Kronig's theory.[16] The structure in this energy region is usually regarded[17] as atomic in character. The positions of the observed maxima and minima, the shapes of the peaks and valleys should be dependent on the initial state of the photoelectrically ejected electron (s electron from the K shell and p electron from the L shell).

COMMENTS ON THE L_1 EDGE

Studies in the soft x-ray spectra of the light metallic elements have been unsuccessful in detecting the emission band which should be observed when conduction electrons make transition into a vacated L_1 level. The absence of such an emission band is ascribed to the operation of other processes whereby an excited atom may leave the L_1 state by a radiationless transition (Auger effect) or by a radiative transition within the L-shell. Because of such competing transitions the intensity of the L_1 emission band is so weakened and/or broadened as to escape detection. However, in ab-

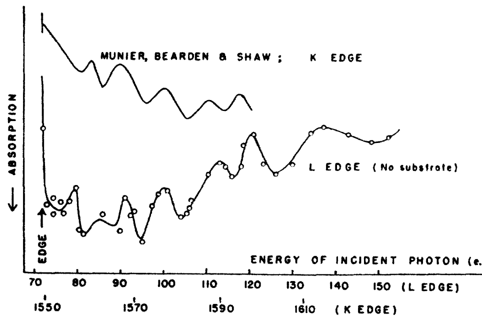

FIG. 5. Secondary structure on the short wavelength side of the $L_{2,3}$ absorption edge of aluminum.

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[15] Munier, Bearden, and Shaw, Phys. Rev. 58, 537 (1940).
[16] R. DeL. Kronig, Z. Physik 75, 191 (1932).
[17] D. Coster and S. Kiestra, Phil Mag. 41, 144 (1950).

sorption the L_1 edge should have a better chance of being observed, since it is expected that in the absorption process the transition probability from an L_1 to empty conduction levels ($s \rightarrow p$) should compare favorably (in the ratio 4 to 11 by calculation[18]) with those from $L_{2,3}$ into empty valence levels ($p \rightarrow s$). Previous investigations[5,6] in the absorption spectra of Mg and Al have clearly revealed the position of the $L_{2,3}$ edge. The L_1 edge should be greatly broadened relative to the $L_{2,3}$ edge, because of the above factors reducing its life time. And in fact, the location of the L_1 edge cannot be regarded as experimentally established.

In two previous reports[19,20] experimental evidence has been presented for the existence of radiative transitions within the L-shell of the four light elements Na, Mg, Al, and S. On the basis of such identifications, the L_1 edge in Al should appear at about 105A. Unfortunately, the present measurements do not show evidence of an absorption edge at the predicted position. Presumably, the secondary structure associated with the $L_{2,3}$ edge masks the L_1 absorption edge which is expected to be somewhat weak and very diffuse.

ABSORPTION COEFFICIENT AS A FUNCTION OF WAVELENGTH

The available experimental data on (τ/ρ) the mass absorption coefficient for aluminum over the region 1A to 600A are summarized graphically in Fig. 6. The data in the region of the K limit are taken from the papers by Allen[21] and Hill,[18] while those in the region of the L-edge are based on the present measurements. The experimental determination of the mass absorption coefficient includes the effects of scattering and reflection in addition to the photoelectric absorption which predominates. No direct determination of the scattering is available above 1.6A; and the effect of scattering is assumed to be negligible.

Sabine's[22] measurements on evaporated films of Al indicate that the reflectivity of the metal is less than 3 percent below 600A. Hence the effect of reflection may also be ignored, and the measurements in the region concerned essentially represent the photoelectric absorption only.

A discussion of the photoelectric absorption for x-rays is given by Hall.[23] By the use of the expression for the dependence of (τ/ρ) on frequency, as given by Eq. (6) in Hall's paper, the theoretical values of the mass-absorption coefficient on the short wavelength side of the K edge were calculated for the ideal absorption limit $\lambda' = 5.40$A. Similar calculations were carried out for the long wavelength side of the K edge utilizing the general functions listed in Table II of Hall's article. In the latter computation, λ'', the hypothetical wavelength of the L edge was determined using the screening constant for the L-shell as given by Slater.[24] The numerical value of λ'' turns out to be 46.6A.

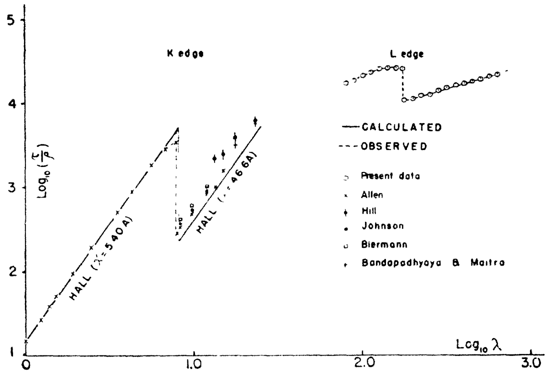

FIG. 6. A plot of the mass absorption coefficient as a function of wavelength. The spectral region extends from 1A to 600A. The present measurements cover the region on either side of the $L_{2,3}$ edge.

A more refined value of the wavelength corresponding to the K edge may be predicted on the basis of a formula derived by Kennard and Roess.[25] This relation yields the value of 8.20A for the position of the K edge.

The results of the theoretical calculations mentioned above are indicated on Fig. 6 by the solid limes. The agreement with the experimental measurements is satisfactory as far as the short wavelength side of the K edge is concerned. The departure on the long wavelength side of the K edge is not surprising since the theory ignores the effect of the crystal lattice of the absorber. So far as the authors are aware, the present measurements constitute the only attempt to extend the determination of absorption coefficients into the very soft x-ray region. It is gratifying that the L-region coefficients are not seriously out of line with an extrapolation from the K-region measurements and calculations.

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