

Structure in the $L_{II,III}$ Absorption of Aluminum and its Oxides

K. CODLING* AND R. P. MADDEN

National Bureau of Standards, Washington, D. C.

(Received 30 August 1967)

The $L_{II,III}$ region of absorption has been observed for thin films of evaporated aluminum, for amorphous (anodized) Al_2O_3 , and for crystalline (γ -alumina) Al_2O_3 . The spectra were obtained in high resolution (0.06 Å), using the NBS 180-MeV electron synchrotron as a background source. The $L_{II,III}$ absorption edges of Al are located with improved accuracy at 169.49 ± 0.05 Å and 170.49 ± 0.05 Å. This new value for the L_{III} edge can be combined with recent accurate determinations of the $K\alpha_1$ emission line to locate also the K absorption edge of aluminum with a significant improvement in accuracy. Structure on the high-energy side of the $L_{II,III}$ edges is compatible with other recent observations. The L absorption edge of Al in Al_2O_3 is not split in high resolution, and is located at 162.11 ± 0.15 Å for the amorphous form and 160.15 ± 0.15 Å for the γ -alumina. Both forms show considerable structure on the high-energy side of the edge. That observed for the amorphous form is in agreement with other recent observations, while the absorption structure in γ -alumina (with maxima at 78.0, 78.6, 79.5, 84, and 99 eV) is reported here for the first time.

I. INTRODUCTION

THE $L_{II,III}$ absorption x-ray edge of aluminum was first measured by Holweck,¹ with a claimed accuracy of about 5 Å. Sanner,² and later Johnston,³ remeasured the L absorption edge using multiline sources which did not resolve the $L_{II,III}$ structure. Sanner did not state his accuracy, but his measurement was earlier than Johnston's, who quoted ± 0.2 Å. Tomboulian and Pell,⁴ and Hunter⁵ also studied the L absorption of aluminum with multiline sources but did not extend the accuracy of the edge location. The Tokyo synchrotron group,⁶ and Fomichev,⁷ using continuum sources have resolved the edge structure; however, the Tokyo group attempted no improvement in the position, while Fomichev does not state his accuracy. Hence the best stated accuracy for the $L_{II,III}$ absorption edge is ± 0.2 Å, while the $L_{II,III}$ emission edge has been measured to 0.1–0.05 Å by Skinner.⁸

Structure in the absorption spectrum of aluminum at energies above the $L_{II,III}$ edge was first observed by Johnston.³ His aluminum films were backed by thin films of celluloid. Tomboulian and Pell⁴ observed

similar gross structure for aluminum backed with Zapon; however, they found quite a different structure when studying unbacked aluminum films. More recent observations,^{6,9} using unbacked aluminum films, are in good agreement with each other, and show absorption features grossly similar to Johnston's; they are not in agreement with the measurements of Tomboulian and Pell on unbacked aluminum films.

The $L_{II,III}$ absorption edge of Al in amorphous Al_2O_3 was first observed by Sanner² and again, recently, by Fomichev.⁷ Watanabe¹⁰ and, recently, Swanson and Powell¹¹ have investigated the energy lost by kilovolt electrons in transit through both Al and Al_2O_3 in this region.

This paper reports measurements of structure in the absorption of aluminum, amorphous Al_2O_3 (anodized), and crystalline Al_2O_3 (γ -alumina). The measurements were taken in the L absorption region utilizing a precise high-resolution grating spectrograph and the NBS 180-MeV electron synchrotron as a background source¹²—which has no structure of its own.

The $L_{II,III}$ edges in Al are resolved, and located to a higher accuracy than heretofore. The new value for the L_{III} edge is combined with the known $K\alpha_1$ emission energy to derive the K absorption edge energy. The accuracy of this location is an order of magnitude better than the scatter of the various direct K edge determinations.

The structural details on the high-energy side of the $L_{II,III}$ edges have been found to confirm the most recent experimental results for Al and amorphous Al_2O_3 , while the structure in the absorption of γ -alumina different from that in amorphous Al_2O_3 , has not previously been reported.

* Present address: University of Reading, Reading, Berkshire, England.

¹ F. Holweck, *De la Lumiere aux Rayons X, Recueil des Conferencess Rapports de Documentation sur la Physique* (University of France Press, Paris, 1927), Vol. 13, 2nd series; see also *Compt. Rend.* **173**, 709 (1921).

² V. Sanner, *Z. Physik* **94**, 523 (1935).

³ J. E. Johnston, *Proc. Cambridge Phil. Soc.* **35**, 108 (1939).

⁴ D. H. Tomboulian and E. M. Pell, *Phys. Rev.* **83**, 1196 (1951).

⁵ W. R. Hunter, in *Proceedings of the 1965 International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Co. Amsterdam, 1966), p. 136.

⁶ T. Sagawa, Y. Iguchi, M. Sasanuma, A. Ejiri, S. Fujiwara, M. Yokota, S. Yamaguchi, M. Nakamura, T. Sasaki, and T. Oshio, *J. Phys. Soc. Japan* **21**, 2602 (1966).

⁷ V. A. Fomichev, *Fiz. Tverd. Tela* **8**, 2892 (1967) [English transl.: *Soviet Phys.—Solid State* **8**, 2312 (1967)].

⁸ H. W. B. Skinner, *Phil. Trans. Roy. Soc. London* **A239**, 95 (1940).

⁹ V. A. Fomichev and A. P. Lukirskii, *Fiz. Tverd. Tela* **8**, 2104 (1967) [English transl.: *Soviet Phys.—Solid State* **8**, 1674 (1967)].

¹⁰ H. Watanabe, *J. Appl. Phys.* **3**, 804 (1964).

¹¹ N. Swanson and C. J. Powell, following paper, *Phys. Rev.* **167**, 000 (1968).

¹² K. Codling and R. P. Madden, *J. Appl. Phys.* **36**, 380 (1965).

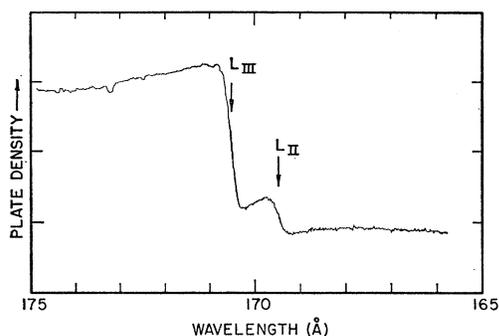


Fig. 1. Microdensitometer trace of the absorption spectrum of solid aluminum in the region of the $L_{II,III}$ edge.

II. EXPERIMENTAL PROCEDURE

Films of 99.99% pure aluminum were prepared by thermal evaporation in a vacuum system of 2×10^{-7} -Torr base pressure. The films were evaporated onto fuchsin-coated glass substrates with deposition rates on the order of $1000 \text{ \AA}/\text{sec}$. The films were then floated off the substrates in water and picked up on Pt or Ni fine-mesh screens, having approximately 80% transmission. The aluminum films, thus mounted, were placed in the synchrotron light beam in front of a 3-m grazing-incidence spectrograph¹³ operating with a spectral slit width of 0.06 \AA . The wavelength calibration of this instrument is known to about 0.02 \AA in this region, and is based primarily on He II wavelengths.

Two forms of Al_2O_3 were prepared for study. The amorphous Al_2O_3 was formed by anodizing evaporated aluminum films in a tartaric acid bath.¹⁴ The oxide thus formed and the remaining underlayer of aluminum were floated off in dilute HCl. When the aluminum was completely dissolved, the Al_2O_3 films were transferred to distilled water and picked up on a Ni fine-mesh screen. The samples were placed in the synchrotron light beam and their absorption spectra photographed.

The crystalline Al_2O_3 (γ -alumina) was formed by placing aluminum film samples, mounted on Ni and Pt mesh, in an oven and heating in air to 630°C for 22 h.¹⁵ After oxidation, the absorption spectrum was photographed as above.

III. RESULTS

A. Aluminum

The $L_{II,III}$ absorption edge of aluminum is shown with high resolution in Fig. 1. The curve is a densitometer trace of a plate exposed with an aluminum film approximately 1000 \AA thick in the optical path. The L_{II} and L_{III} edges are seen to be very steep and clearly resolved at $1.00 \pm 0.05 \text{ \AA}$ separation. To locate the edge positions, a smooth curve was first drawn through the densitometer noise. We find experimentally that the

¹³ R. P. Madden, D. L. Ederer, and K. Codling, *Appl. Opt.* **6**, 31 (1967).

¹⁴ G. Hass, *J. Opt. Soc. Am.* **39**, 532 (1949).

¹⁵ G. Hass, *Z. Anorg. Allgen. Chem.* **254**, 96 (1947).

curve which best fits the trace is one having a continuously changing slope—which is also expected theoretically for a temperature and lifetime broadened absorption edge. The energy of the maximum slope point of this smoothed curve was determined from the densitometer trace of each photographic plate. Several plates were taken for each of two aluminum films of thickness $700\text{--}1000 \text{ \AA}$. In all, six photographic plates of varying density were used for the determinations. The standard deviation of the independent measurements was 0.03 \AA . Combining, by rms, this random error with the possible systematic calibration and densitometer errors, we estimate the location has a probable error of $\pm 0.05 \text{ \AA}$. Thus the maximum slope points of the density curves for the L_{II} and L_{III} edges are found to be at 169.49 \AA (73.15 eV) and 170.49 \AA (72.72 eV), and, because of the symmetry of the smearing effects, these energies should be the best location of the L_{II} and L_{III} absorption edges.

It is of interest to compare our determinations of the absorption edges with the emission $L_{II,III}$ edges as recorded by Skinner.⁸ This comparison is shown in Table I, along with Johnston's determination of the unresolved $L_{II,III}$ absorption edges.

Fomichev⁷ lists the $L_{II,III}$ edges at 169.8 and 170.8 \AA with no statement of accuracy. However, he does state that the $L_{II,III}$ splitting is $1.0 \pm 0.1 \text{ \AA}$, with which we are in excellent agreement. Sagawa *et al.*⁶ quote a splitting of 0.4 eV .

Using longer exposures than shown in Fig. 1, features in the stronger absorption region on the high-energy side of the $L_{II,III}$ edge have been obtained. In particular, absorption maxima have been seen at 84 , 96 , and 117 eV , the 84-eV feature being quite weak in comparison with the other two. These absorption peaks have been reported by Sagawa *et al.*,⁶ and by Fomichev and Lukirskii⁹ at the same spectral positions. Tomboulia and Pell report⁴ a peak at 129 \AA (96 eV) for their unsupported aluminum film and additional structure we do not confirm. This additional structure was not the same when they studied the absorption of aluminum on Zapon, in which case the spectrum was similar to the newer measurements. In view of the unanimity of the three most recent studies, it would appear that the anomalous spectra of Tomboulia and Pell are not representative of pure aluminum.

Watanabe, using 50-KeV incident electrons, found electron energy-loss peaks in transmission through Al foils which we estimate at approximately 72 , 82 , and

TABLE I. Location of aluminum $L_{II,III}$ edges (in units of \AA).

	Emission (Skinner ^a)	Absorption (Johnston ^b)	Absorption (present work)
L_{II}	169.62 ± 0.1	170.0 ± 0.2	169.49 ± 0.05
L_{III}	170.56 ± 0.05	170.0 ± 0.2	170.49 ± 0.05

^a See Ref. 8.

^b See Ref. 3.

94 eV.¹⁰ The first of these corresponds to the $L_{II,III}$ edge, the others to our observed absorption peaks—all three somewhat shifted to lower energy. In closer agreement with the absorption data are the recent energy-loss determinations of Swanson and Powell¹¹ who discuss the comparison in more detail.

We have also seen a small feature near 77 eV, presumably caused by the $L_{II,III}$ edge of Al_2O_3 , since we anticipate approximately 35–40 Å of Al_2O_3 on each surface of the aluminum film.¹⁶

B. Al_2O_3

1. Amorphous Form

In Fig. 2, the upper curve is a densitometer trace of a plate taken with no absorber in the beam, showing an anomaly in the grating efficiency near 170 Å which will be discussed further in the Appendix. The middle curve, with an arbitrary vertical displacement, is a densitometer trace of a plate that was exposed with a film of anodized Al_2O_3 , 850 Å thick, in the light beam. An examination of this curve shows that the L edge of Al has shifted in the amorphous oxide to 162.11 ± 0.15 Å or 76.48 eV, and that absorption peaks at 77.1 ± 0.2 , 79.8 ± 0.2 , 86 ± 1 , and 99 ± 2 eV exist. Fomichev⁷ also studied amorphous Al_2O_3 , locating the L edge at 76.3 eV and maxima at 76.8, 79.5, 84.5, and 98 eV.

Although our resolution was considerably higher than Fomichev's, no further structural detail has been observed. In particular there is no evidence of a double step at the L edge. The large errors quoted above for the location of the absorption maxima are due mainly to the breadth and/or weakness of the features. Errors introduced by improperly accounting for the non-linearity of the emulsion characteristic curve and the sloping background are estimated to amount to less than half of the quoted error.

The absorption features can be compared with Watanabe's electron energy-loss peaks¹⁰ also obtained for anodized Al_2O_3 . He obtained losses of 77, 79, and 94 eV. The first two of these are in agreement with the photon-absorption results; however, Watanabe found the higher loss to be the same as that observed in aluminum. Our peak at 99 eV appears shifted by about 3 eV to a higher energy from the similar peak seen in aluminum. Swanson and Powell¹¹ find this energy loss at 97.8 eV in amorphous Al_2O_3 .

We find the L edge in amorphous Al_2O_3 shifted from the L_{III} edge in Al by 3.76 ± 0.10 eV, in agreement with Fomichev who found the chemical shift to be 3.7 eV.

2. Crystalline Form

The γ -alumina, formed by heating aluminum foil in air, yielded an absorption spectrum represented by the lower densitometer trace of Fig. 2, with features quite

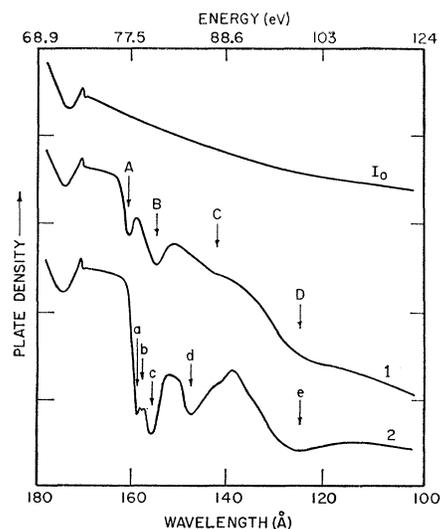


FIG. 2. Microdensitometer trace of the absorption spectrum of Al in Al_2O_3 . (1) Amorphous Al_2O_3 : L_{III} edge at 76.48 ± 0.08 eV; (A) 77.1 ± 0.2 eV; (B) 79.8 ± 0.2 eV; (C) 86 ± 1 eV; (D) 99 ± 2 eV. (2) Crystalline Al_2O_3 (γ alumina): L_{III} edge at 77.41 ± 0.08 eV; (a) 78.0 ± 0.2 eV; (b) 78.6 ± 0.2 eV; (c) 79.5 ± 0.2 eV; (d) 84.0 ± 0.5 eV; (e) 99 ± 2 eV. The structure at the far left of all three traces is due to a reflection anomaly in the aluminum-coated grating (see Appendix).

different from the amorphous oxide. The aluminum L edge shifts slightly to higher energy, 160.15 ± 0.15 Å, or 77.41 eV, and additional absorption features appear. Note particularly the small absorption peak at 78.6 eV, and the strong feature which has been introduced at 84 eV.

There are no other absorption data on this form of the oxide with which to compare these results. However the absorption details can be compared with the recent electron-loss measurements of Swanson and Powell,¹¹ who further discuss the essential consistency of the results of these two experimental approaches.

IV. FURTHER DISCUSSION

A. Aluminum $L_{II,III}$ Edges

The excellent agreement between the independently measured $L_{II,III}$ emission and absorption edges in aluminum locates the position of the L_2 and L_3 subshells relative to the Fermi level in aluminum to within 0.04 eV. According to Parratt,¹⁷ the experimentally observed emission and absorption edges are expected to coincide for "good" metals in the absence of an adverse effect of excitation structure on the measurements. He cautions, however, that if the lifetime of the initial state in emission is sufficiently long, significant phonon interaction may take place to shift the energy of the state, or some crystal lattice relaxation may take place, before the emission occurs. The agreement between the emission and absorption edges shown here puts a rather small upper limit on such effects for the L edge of aluminum.

¹⁷ L. G. Parratt, Rev. Mod. Phys. 31, 616 (1959).

¹⁶ R. P. Madden, L. R. Canfield, and G. Hass, J. Opt. Soc. Am. 53, 620 (1963).

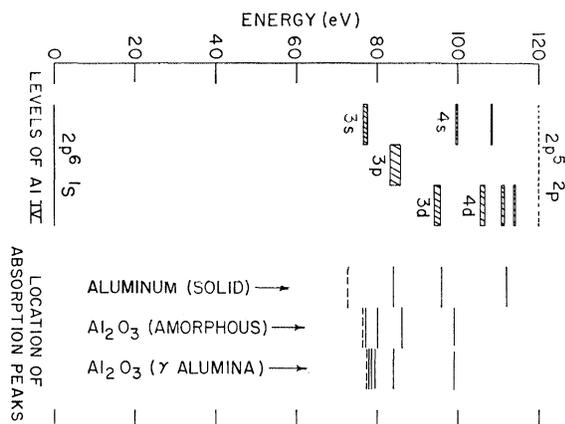


FIG. 3. A comparison of the known energy levels of atomic Al IV with the experimentally observed peaks in the absorption spectra of solid aluminum and the two types of aluminum oxide (shown in Fig. 2). The dashed lines give the location of the L_{II} and L_{III} edges.

The spin-orbit splitting, measured to be 1.00 ± 0.05 Å or 0.43 eV, can be compared to the splitting of the $K\alpha_1$ - $K\alpha_2$ lines determined by Nordfors¹⁸ to be 0.42 eV.

Nordfors's value for the $K\alpha_1$ emission line is 8321.96 ± 0.20 xu. Using the conversion 12372.42 xu-keV for the Uppsala xu scale in consistency with Bearden's evaluation¹⁹ of the conversion constants, the energy of this line is 1486.69 ± 0.04 eV. Adding this to the L_{III} absorption edge energy determined in this experiment yields the value 1559.41 ± 0.06 eV, which should be the K -absorption-edge energy in a "good" metal such as aluminum appears to be. In comparison, the photoelectron technique²⁰ has yielded the value 1559.6 eV (with an error estimated by Bearden and Burr²¹ to be ± 0.4 eV). Rudstrom,²² in an absorption experiment, determined the K edge to be 7931.66 ± 0.40 xu which converts to 1559.88 ± 0.08 eV,²³ while Nordfors¹⁸ finds the K emission edge at 7932.6 xu or 1559.69 eV. More recently, Nagakura²⁴ determined the K absorption edge to be 1559.3 eV. Thus the best values vary over a 0.6-eV range. Since the $K\alpha_1$ line was very carefully measured and the L_{III} edge uncertainty is small, the value 1559.41 ± 0.06 eV should be the most reliable at present. The energy determined from Rudstrom's absorption experiment is higher by three times the combined error estimated, and is not confirmed by Nagakura.

B. Aluminum Absorption Structure

There is now general experimental agreement (see Sec. III A) regarding the most prominent absorption

¹⁸ B. Nordfors, Arkiv. Fysik **10**, 20 (1955).

¹⁹ J. A. Bearden, Rev. Mod. Phys. **39**, 78 (1967).

²⁰ S. Hagstrom and S.-E. Karlsson, Arkiv. Fysik **26**, 451 (1964).

²¹ J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

²² L. Rudstrom, Arkiv. Fysik **12**, 287 (1957).

²³ Bearden (Ref. 19) uses Rudstrom's K edge value in his table, indicating a probable error of 0.01 eV. This appears to be a mistake.

²⁴ I. Nagakura, Sci. Rept. Tohoku Univ. First Ser., **48**, 166 (1965).

features on the high-energy side of the $L_{II,III}$ edges; however a theoretical interpretation is not yet available. The density of states below the Fermi level has been calculated for aluminum, but the structure above remains uncertain. Lattice effects may be dominant, and certainly must be considered; however, the absorption structure on the high-energy side of the $L_{II,III}$ edge may also be due to an atomic influence on the excited states and/or transition probabilities. In particular, Sagawa *et al.*⁶ suggest that the 96-eV peak might be a delayed onset of oscillator strength due to transitions of the type $2p \rightarrow nd$ in atomic aluminum.

C. Amorphous Al_2O_3

The $L_{II,III}$ edges of amorphous Al_2O_3 remain unresolved at room temperature even with a spectral slit width which is one-twentieth the size of the expected $L_{II,III}$ splitting. The implication seems to be that the onset of oscillator strength or state density in the upper state is sufficiently gradual to cause a merger of the L_{II} and L_{III} edges. We note also that the $L_{II,III}$ edge in the amorphous Al_2O_3 is shifted to higher energy from the aluminum L_{III} edge by 3.77 eV. The shift of the K edge from aluminum to the amorphous oxide has been measured as 5.3 eV by Rudstrom,²² 5.7 eV by Nagakura,²⁴ and, recently 5.7 ± 0.2 eV by Deslattes.²⁵ Thus the chemical shift of the K edge is greater than that of the L edge by about 1.8 eV.

It should be noted that in the oxide, the sum of the L absorption energy and the $K\alpha_1$ transition energy of aluminum in amorphous Al_2O_3 measured by Nordfors¹⁸ is lower than the K absorption energy determined by Nagakura²⁴ for aluminum in Al_2O_3 by 1.6 eV. A difference is to be expected, since the screening of the excited electron on the K and L shells need not be identical and/or the upper states of the K and L absorption transitions need not be identical in energy.

It is of further interest to note that the energy required to raise an electron from the L shell to the lowest unfilled level in Al_2O_3 (76.48 eV) is nearly identical to that required by an isolated Al^{+++} ion to make its lowest optical absorption transition (76.45 eV).²⁶ This

²⁵ R. Deslattes (private communication).

²⁶ Lukirskii and Brytov {Fiz. Tverd. Tela **6**, 43 (1964) [English transl.: Soviet Phys.—Solid State **6**, 33 (1964)]} have investigated the K edge of Be and BeO and find a chemical shift of 6.7 eV. There, the K edge of Be in BeO is found at 118.1 eV. The lowest possible absorption for the isolated Be^{++} ion is 118.6 eV. Tomboulian and Bedo [D. H. Tomboulian and D. E. Bedo, Phys. Rev. **104**, 590 (1956)] studied the $L_{II,III}$ absorption of Si and Si in SiO_2 which showed a chemical shift of 5.1 eV. However, the L edge in SiO_2 occurred at 105.1 eV, and the lowest possible absorption for the isolated Si^{++++} ion is 104.2 eV. These lowest possible transitions in general do not obey ordinary optical selection rules, but this may be permissible in the solid. In any case, optically allowed transitions are available very close to these lowest transitions. [In Si^{++++} the lowest L - S coupling allowed transition is at 105.2 eV (C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.), Circ. No. 467, (1949)).] One might thus consider that the absorption edge is chemically shifted primarily in the pure metal rather than in the oxide, where the lowest absorption transition for the outer electron of the metallic ion is characteristic of a free ion.

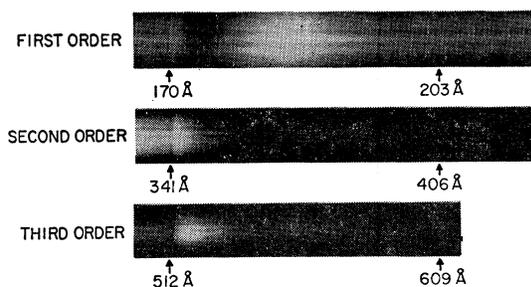


FIG. 4. Photographs of the reflection anomaly in the aluminum-coated grating shown in first, second, and third order. (Black denotes absorption.)

point is demonstrated by Fig. 3, where the experimentally observed absorption peaks for solid Al and for Al_2O_3 in the amorphous and crystalline forms are compared with the atomic energy levels for Al^{+++} .

One notes also that the locations of the absorption maxima of aluminum in the three solids also show some remarkable similarities to those of the free ion.²⁷ While a number of theories have been proposed²⁸ to account for fine structure in x-ray absorption edges from the solid state point of view, none has been completely successful. It may be that atomic states have a substantial influence on optical spectra of solids in this energy region. In atomic spectra, high-lying states cause the appearance of prominent resonances in the photo-ionization continuum—well above the ionization threshold.²⁹ These resonances are the result of the interference of the discrete levels with the adjacent continuum of states.³⁰ Analogous resonances could conceivably occur in the conduction-band continuum due to high-lying states of the ions in the crystal lying near the absorption threshold. Additional measurements on other materials will be required to establish whether or not this point of view has any validity.

D. γ -Alumina

The chemical shift of the L_{III} edge from pure aluminum to aluminum in the crystalline γ -alumina is 4.69 eV in comparison to 3.76 eV for the amorphous oxide. The γ -alumina also shows a more complex absorption

²⁷ In BeO, Lukirskii and Brytov (Ref. 26) found prominent absorption peaks at 118.75, 123.75, and 139.1 eV. For the free ion Be^{++} , the lowest-lying transition $1s^2\ ^1S-1s2s\ ^3S$ lies at 118.6 eV, the $1s^2\ ^1S-1s2p\ ^1P$ lies at 123.7 eV, and the $1s^2\ ^1S-1s3p\ ^1P$ lies at 140.4 eV (Ref. 28).

²⁸ For a review see L. V. Azaroff, Rev. Mod. Phys. **35**, 1012 (1963).

²⁹ K. Codling, R. P. Madden, and D. L. Ederer, Phys. Rev. **155**, A26 (1967).

spectrum above the L edge. While there are no calculations available for comparison with this experimental spectrum or that of the amorphous oxide, it would appear from the differences between the spectra of the oxides (Fig. 2) and the similarities with the ionic energy levels (Fig. 3) that both lattice and atomic effects are in evidence.

ACKNOWLEDGMENT

The authors wish to thank R. Deslattes for several helpful discussions and the use of unpublished K absorption data.

APPENDIX

We would add a word of caution regarding the possible effect of sharp absorption edges, such as the Al $L_{\text{II,III}}$ on the performance of diffraction gratings. The optical constants of the material coating the grating obviously determine its blaze or efficiency characteristics. In the soft x-ray region, as has been recognized by workers close to this field,²⁷ the sharp changes in absorption coefficient cause rapid variations in the reflective efficiency of the grating, as seen by the structure near 170 Å in the densitometer traces of Fig. 2 for our aluminized grating.

Similar, but not identical, effects exist in the spectrum of the higher orders of the grating. Figure 4 shows photographs of the first, second, and third order of the 170 Å region for our grating³¹ with no absorber in the beam. By photographic enlargement the dispersions have been adjusted to the same value in these three spectra. The variation in intensity with wavelength between 170–180 Å is due to the changing absorption coefficient of the aluminum. In Fig. 4, the corresponding effect observed in the higher orders can be evaluated by a vertical displacement between the aligned spectra. Note, in particular, that the variation of intensity with wavelength in the third order is intensity inverted relative to the corresponding variation in the first order.

In Fig. 1, the first order of this feature is broad and weak in comparison with the $L_{\text{II,III}}$ structure of the absorbing film. A careful check shows that the sharp drop in this feature (seen in Fig. 2) occurs almost exactly at the L_{III} absorption edge. This fact, plus the weakness of the feature, makes us believe that it causes little error in the edge location. The error quoted includes an allowance for this effect.

³⁰ U. Fano and J. Cooper, Phys. Rev. **137**, A1364 (1965).

³¹ 600 lines/mm replica, 2°35' blaze angle, used at 84.5° angle of incidence.

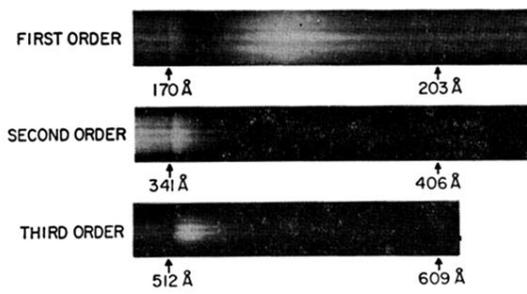


FIG. 4. Photographs of the reflection anomaly in the aluminum-coated grating shown in first, second, and third order. (Black denotes absorption.)