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# Role of the density of conduction states on the $L_{2,3}$ absorption spectrum of aluminum*

A. Balzarotti, A. Bianconi, and E. Burattini
*Istituto di Fisica dell'Università di Roma, Italy*
*Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Sezione di Roma, Rome, Italy*

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The fine structure just above the $L_{2,3}$ edge of aluminum at 72.72 eV has been examined with high resolution using the radiation of the Frascati electron synchrotron. A sensitive system providing normalization between the incident and transmitted light has allowed detection of absorption peaks not previously recorded in other measurements. It has been found that the optical response of the Al at these energies is strongly influenced by the oxide grown on its surface, so that corrections for the absorption of the oxide are necessary to yield only spectral features intrinsic to the metal. The results indicate that most of the fine structure of the $L$ absorption spectrum is directly related to structure in the density of conduction-band states above the Fermi level.

## I. INTRODUCTION

Among the light metals, aluminum is one whose electronic properties have been extensively investigated. At present, satisfactory agreement exists between the calculated and the experimental density of states of the filled states.[1–4] The existence of three peaks within 5 eV below the Fermi level has been recognized by x-ray emission[1] and, more recently, reconfirmed by an accurate x-ray photoemission experiment.[5] These peaks have been assigned to structure in the density of valence states near $L_2'$, $X_4$, and $K_1$ points of the Brillouin zone (BZ).

In contrast, the empty states of the conduction band above the Fermi level are not known with comparable accuracy. This is, to some extent, due to the scarcity of information supplied by the reflectivity spectra, since the reflectivity of this material does not show any sharp features up to 15 eV except for two peaks at 0.5 and 4.6 eV.[6] On the other hand, the soft-x-ray absorption (SXA) spectra are rich in structure, but their interpretation in terms of density of states is complicated by additional effects which go beyond the one-electron approximation.

At the $L_{2,3}$ threshold, the influence of the deep hole potential on the electron states near the Fermi surface results[7] in a sharpening of the edge.[8–10] At energies far above the edge, collective oscillations of the electron gas, associated with band-to-band transitions[8] and atomic effects, like the delayed $2p$-$nd$ transitions[8,11] seem to account for some peaks and for the large absorption cross section, respectively. The region just above the edge seems, therefore, the one where the absorption shape should reproduce the main features of the conduction-band-state density.

Although the weak structure near the edge has been recorded in several experiments,[8–10] considerable differences exist in the spectra, both in the number and in the energy position of the absorption maxima. Perhaps the most detailed list of the energies of the peaks in this region is that reported by Haensel *et al.*[10] who also quote the energies of similar peaks observed in Na and Mg.

The possibility that part of this structure could be due to the oxide has been suggested,[8] but no special effort has been devoted so far to test this hypothesis.

In this paper we report the results of a close experimental examination of the SXA spectrum of Al, in the region extending 7 eV above the $L_{2,3}$ edge. Our measurements show that aluminum oxide has strong absorption peaks here, so that even a very thin layer of oxide on the Al alters the true SXA spectrum of the metal. The effect of the oxide was clearly identified and the corrected absorption spectrum was obtained. New components of the fine structure have been resolved and, therefore, a significant comparison with density-of-states calculations becomes possible for the first time.

## II. EXPERIMENTAL

The continuum of the synchrotron radiation emitted by the Frascati electron synchrotron is used as the source of soft x rays. The radiation is dispersed by a 2.2-m grazing-incidence monochromator (McPherson model 247) and the transmission is measured with an open magnetic-type multiplier (Bendix M306). The resolution achieved is better than 0.1 Å at 170 Å. The sample chamber, mounted behind the exit slit, is equipped with a system providing instantaneous normalization between the incident light and that transmitted through the sample. The films are placed on one of the two holes made in a turning wheel. The other hole is either free or covered by the same substrate as the sample if the sample is supported. The wheel rotates synchronously with the light pulse so that one pulse goes through the sample while the next pulse goes directly into the detector.

After amplification, the two successive trains of pulses are separated and averaged by two boxcar integrators. The output of the boxcar integrators is fed into a digital ratiometer giving the transmittance of the sample, which is converted to analog form and displayed on an *X-Y* chart recorder. The digital data are also recorded on magnetic tape and then processed by an IBM 360/44 computer. The system, which makes use of a single detector, strongly improves the signal-to-noise ratio, so that structure-producing changes greater than 0.2% of the absorption coefficient can be safely detected.[12] Figure 1 shows a block diagram of the experimental apparatus.

Aluminum films of different thicknesses ranging from 800 to 1500 Å were evaporated from a 99.999% pure metal at $10^{-6}$ torr at a rate of about 100 Å/sec. The film thickness was monitored during the evaporation with a quartz monitor calibrated by the Tolansky method. Unbacked Al films were obtained by evaporating the aluminum on NaCl substrates prepared on microscope glasses. The samples were floated off the substrate in water and picked up on thin copper or nickel fine-mesh screens of high transparency (~80%). The measurements were performed at room temperature, both on samples deposited on Formvar substrates and on unbacked films. We have considered our samples as a system formed by an aluminum film of thickness $d$ covered by a uniform film of amorphous oxide of thickness $d_{ox}$. It is known[13] that an oxide layer grows in a few minutes on the surface of the Al exposed to air at room temperature, and that the growth rate saturates quickly at an oxide thickness of about 25 Å, indicating that the first layers of the oxide prevent further oxidation of the metal. We have measured both the absorption coefficients $\alpha_M$ of the system and the $\alpha_{ox}$ of amorphous-oxide films prepared by the anodization technique.[14] The absorption coefficient of the aluminum $\alpha_c$, corrected for the oxide, is given by the equation

$$\alpha_c = (\alpha_M d_M - \alpha_{ox} d_{ox})/(d_M - d_{ox}) , \tag{1}$$

where $d_M = d_{ox} + d$ is the measured thickness of the films. The only quantity we have not directly measured is $d_{ox}$ which was taken as a parameter. Through data analysis we found different values of $\alpha_M$ using samples of different thicknesses. Since $d_{ox}$ does not change appreciably from sample to sample, the ratio $d_{ox}/d$ changes with $d$ and therefore $\alpha_M$. By introducing as the average value of $d_{ox} = 25 \pm 5$ Å in Eq. (1) we obtained the same $\alpha_c$ for different sets of data. In the case of unbacked films the value of $d_{ox}$ had to be almost doubled.

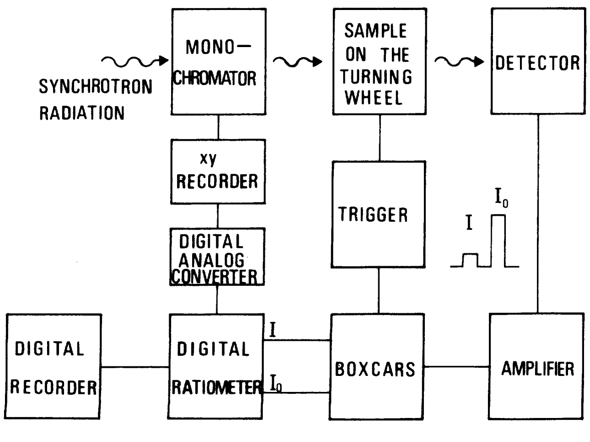

FIG. 1. Schematic block diagram of the experimental set-up.

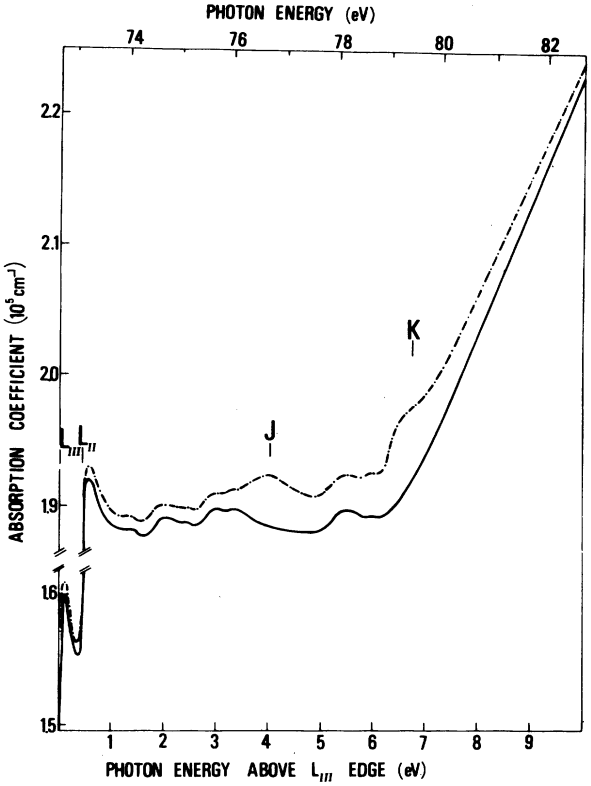

FIG. 2. High-resolution soft-x-ray absorption coefficient of aluminum just above the $L_{2,3}$ edge. The upper curve is the measured spectrum, the lower curve is the spectrum corrected for the absorption in the oxide.

An alternative procedure to eliminate oxide effects without requiring $\alpha_{ox}$ utilizes the absorption of two films of different thicknesses. In this case, $\alpha_c$ is obtained from Eq. (1) by replacing $\alpha_{ox}$ and $d_{ox}$ with the corresponding quantities appropriate to the second film. This method assumes that the films have oxide layers of the same thickness, which is a reasonable assumption if each film has been subjected to the same treatment.

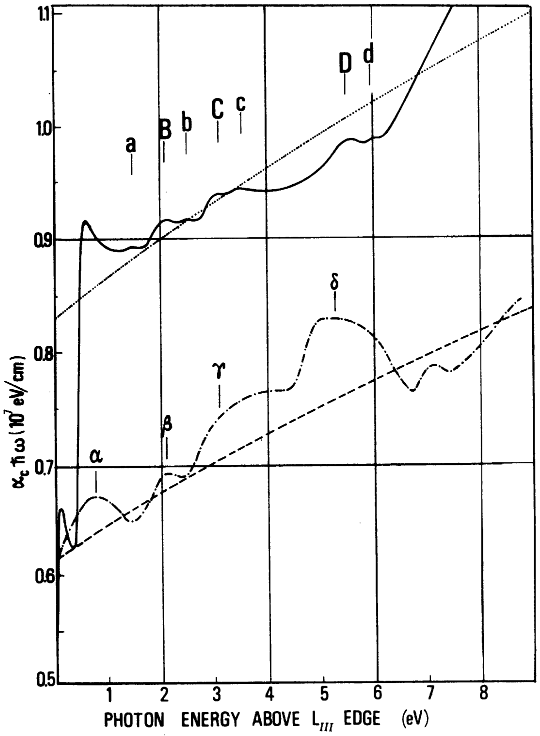

FIG. 3. Experimental (solid curve) and theoretical conduction-band-state density (dash-dotted curve), according to Connolly, Ref. 3. The scale on the ordinate refers to the experimental curve. The dotted and dashed lines represent the free-electron density of states.

## III. RESULTS AND DISCUSSION

In Fig. 2 we show the $\alpha_M$ of an unbacked film as well as $\alpha_c$ obtained after correcting with Eq. (1) for an amorphous oxide layer of thickness $d_{ox} \simeq 50$ Å. Comparison between the two spectra shows that the peaks $J$ and $K$ are not intrinsic to the aluminum, but are due to absorption in the oxide. Their positions correspond to those of the two strong peaks of the oxide[14] at 76.67 and 79.6 eV and, in addition, they disappear after the correction. The broad band between 3 and 6 eV, reported in other spectra,[8,9] actually consists of two quite distinct peaks centerd at about 3 and 5.5 eV from the $L_{2,3}$ edge. Note also the spin-orbit components on the high-energy side of the main peaks ($\Delta_{so} \simeq 0.46$ eV). The quantity $\alpha_c \hbar\omega$ is shown in the upper part of Fig. 3 (solid line). A background absorption of $0.66 \times 10^5$ cm$^{-1}$, associated with transitions of the valence electrons, has been subtracted from the curve of Fig. 3. From the well-known theory of interband transitions,[15] the absorption coefficient $\alpha$ is given by

$$\alpha = \frac{2}{3}\left(\frac{eh}{m}\right)^2 \frac{1}{nc\omega} \sum_{if} \int_{BZ} \frac{1}{(2\pi)^3} d\vec{k}$$

$$\times \left|M_{if}(\vec{k})\right|^2 \delta(E_f - E_i - \hbar\omega) , \qquad (2)$$

where $n$ is the refractive index of the medium, $m$ the electron mass, and the summation is over all the initial (occupied) and final (empty) states. If the initial state of the transition is independent of $\vec{k}$ (flat core state) and the matrix elements $|M_{if}(\vec{k})|^2 = |\langle \mu_{\vec{k},f} | \nabla | \mu_{\vec{k},i} \rangle|^2$ are constant, $\alpha_c \hbar\omega$ is proportional to the density of the final states. These assumptions lead, in the free-electron approximation, to the well-known parabolic dependence for the density of states. Deviations arise both from corrections due to the matrix elements and from changes in the density of states. The latter occur mainly at critical points (van Hove singularities) of the BZ.

The dotted line in Fig. 3 shows the free-electron curve calculated with the formula

$$\mathfrak{D}(E) = A(E_{\text{phot}} - E_{L_{111}} + E_F)^{1/2} , \qquad (3)$$

where $E_F$ is the Fermi energy taken as 11.4 eV[6] and $A$ is an appropriate scale factor. Let us note that, except for intensity modulations, the experimental curve increases with energy less rapidly than $E^{1/2}$. This behavior may be understood as being caused by the matrix element in Eq. (2). In the framework of the orthogonalized-plane-wave (OPW) method, Harrison[16] has explained this deviation, in the case of transitions from the core $2p$ states in the aluminum, as being caused by the balancing between the overlap integral and the orthogonalization term in the expression of the

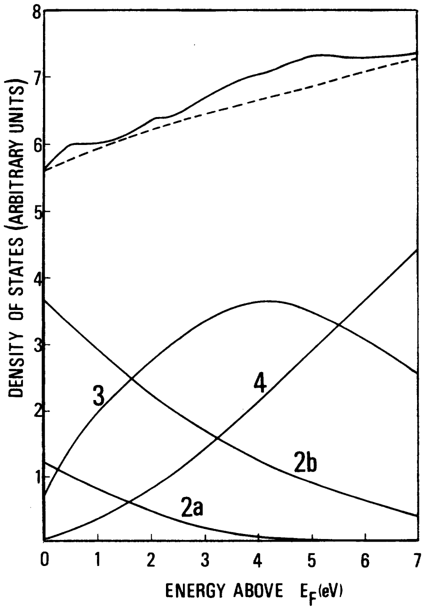

FIG. 4. Decomposition of the contributions from each Brillouin zone to the perturbed density-of-states distribution. The curves $2a$ and $2b$ refer to the second zone in the [100] and [111] direction, respectively.

matrix element, to zero order in the pseudopotential. First-order corrections to the oscillator strength are pronounced only at the boundaries of the BZ, so we do not expect that intensity changes other than those associated with the density of states occur (up to 6 eV from the Fermi energy). The reason for this is twofold. First of all, we have computed, following Rooke,[1] the transition probabilities for the [100] and [111] directions in the second BZ, using a reasonable extrapolation for normalized wave functions calculated by Segall.[17] Within the approximations discussed in Rooke's paper, the relative transition probabilities increase slightly with energy up to 5 eV from the Fermi level for both directions. In the calculation, the transition probability of the third zone is assumed[1] independent of $\vec{k}$, which is reasonable at least far from the zone boundary at $X$. The second reason is based on the correspondence existing between some experimental ($B, C$) and theoretical ($\beta, \gamma$) peaks of the density-of-states function. To stress this point, we have shown in the lower part of Fig. 3 the curve (dash-dotted) of the theoretical conduction-band-state density calculated by Connolly.[3] In order to obtain a better insight into the individual contributions to the total density of states, we have adopted the procedure of modifying the free-electron density of states of each BZ, calculated by Ashcroft, in a manner similar to that described by Rooke.[1,18] In Fig. 4 we have sketched the distorted densities of states of the zones contributing to the absorption in the energy range of interest. The curves of the second and third zone are matched to the *same* curves used by Rooke below $E_F$ to reproduce the singularities of the emission spectrum, while the curve 4 is left unchanged. In calculating these bands, the whole area under each curve was maintained the same as that of the corresponding free-electron curve. This amounts to assuming that the whole perturbed density of states should not differ too much from a parabola, which is a good approximation in the case of aluminum.[17] The maximum of curve 3 was put near the energy of the $X_5'$-$X_3$ gap found in the band schemes.[3,6,20]

The decomposition in Fig. 4 shows that the structure $B$ of Fig. 3, previously seen in other SXA spectra,[8,10] and the new peak $C$ do not arise from critical regions of a given zone, but instead are due to the overlap of several bands at a general $\vec{k}$ point of the BZ where the crystal states presumably do not have a definite atomic symmetry. This might explain why optical transitions starting from a core state of $s$-like symmetry take place at the same energies above the $K$ edge, as observed in the $K$ spectrum of Al.[19] The region around 5 eV is instead dominated by contributions of points of the BZ near $X$,[6] where the crystal eigenfunctions have mostly $p$-like character. Since the $L_2$ and $L_3$ core levels have $p$-like symmetry, and because the selection rules prevent $p$-state to $p$-state dipole transitions, we expect a very weak contribution to the absorption in the $L$ spectrum at this energy. The situation is reversed in the $K$ spectrum, since both the transition probability and the density of final states are large for transitions starting from $s$-like core levels. As a matter of fact, a strong peak at about 5.5 eV above the $K$ edge is seen in the $K$ spectrum.[19,20] On the basis of the above arguments, we assign the weak structure $D$ of the $L$ spectrum to transitions near the $X_3$ $d$-like states.[3,6,21]

A final comment concerns the first maximum of the density of states near the $L_2$ edge. States of the fourth zone around $W_1$ ($s$-like) should be involved in the absorption from the $2p$ levels, but we are presently not able to determine the weight of this contribution to the enhancement of the absorption at the edge. In any case, contributions due to electronic transitions between parallel bands, of the type occurring at low energy,[2,22] can be excluded in the case of transitions from $\vec{k}$-independent core states.

## IV. CONCLUSIONS

We have found that the structure in the density of states of the conduction band is the most probable source of the fine structure observed in the $L$ spectrum of aluminum. The effects due to matrix elements seem effective in determining the spectral shape near 6 eV from the Fermi level. It will be very interesting to reexamine the $L$ edges of other light metals, such as sodium and magnesium, which also present fine structure near their edges,[10] thus providing a direct experimental check of the unoccupied electron states of these materials.

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