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On the $L_{2,3}$ Soft X-Ray Emission of Al in Al–Mg Alloys

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A special self-absorption effect of the Mg-enriched surface of AlMg alloys is described for Al $L_{2,3}$ emission spectra. In the light of these new considerations, the evaluation of the experimental data have to be modified and the earlier results in this field should be reevaluated. The problem is more general than this actual one, focusing attention on the complexity of the evaluation of emission spectra of alloys and compounds which have emission spectra, of the components nearby or overlapping each other.

Ein spezieller Eigenabsorptionseffekt an der Mg-angereicherten Oberfläche von AlMg-Legierungen wird für das Al- $L_{2,3}$ -Emissionsspektrum beschrieben. Angesichts dieser Überlegungen erscheint eine Modifizierung der Auswertung experimenteller Ergebnisse notwendig. Das Problem ist allgemeiner als im vorliegenden Fall, in dem das Hauptaugenmerk auf der Komplexität der Auswertung der Emissionsspektren von solchen Legierungen und Verbindungen liegt, deren Komponentenspektren nahe beieinander liegen oder sich überlappen.

1. Introduction

Aluminium alloys are interesting and widely investigated regarding both some modern topics (for example the quasi-crystalline alloys [1]), and some classical fields (for example, the age-hardening alloys [2]), too. Furthermore the Al $L_{2,3}$ soft X-ray spectrum is one of the popular model spectra of the soft X-ray emission (SXES) investigations [3], because of its relatively high intensity [4] and clear theoretical interpretation [3] in the very soft (about 72 eV) X-ray regime.

Especially the soft X-ray emission of the Al–Mg alloys has been widely measured by the Al $L_{2,3}$ [5] and also by the Mg $L_{2,3}$ spectra [6]. The spectra refer to the partial density of $s + d$ electronic states ($s + d$ PDOS) [3] and are sensitive enough to the chemical bonds of aluminium [7]. Moreover the Fermi energy (E_F) of the Al $L_{2,3}$ spectra is very accurately determinable, also its definite sharp edge in the spectra caused by the so-called Mahan singularity [8]. The Fermi edge itself is sensitive to band effects [7, 8] and to the stability of alloys [9 to 11]. The spectra give good information on surface effects [6], because the penetration of the exciting electrons and the attenuation length of the outgoing photons are small, giving proper information from the near vicinity of the surface [12, 13]. On the other hand, the obtained soft X-ray signal characterizes a layer which is deep enough to neglect the direct, hardly controllable surface effects, as for example the roughness, pollutions, adsorbates, etc.

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The Mg concentration dependence of the Al $L_{2,3}$ spectra of AlMg alloys has been studied [5] showing an enhancement in the low-energy part of the spectra, caused by the s-electron charge transfer from Mg into the vicinity of Al. Other investigations [14, 15] have shown the increase of the same low-energy part due to the enrichment of oxides in the surface layers. The effect of surface oxide (Al_2O_3) on the low-energy part of the Al $L_{2,3}$ spectra is well established [16] and used for identification of the surface depth profiling [12].

In general, the effect of self-absorption of an Mg layer on Al has been realized in Al $L_{2,3}$ emission [17, 18] but was not taken into serious consideration in the evaluation of the spectra. This effect was regarded as only slightly modificative on the general form of the spectra. Unfortunately — as we shall show below — in the course of the evaluation of such ultra-soft spectra as the Al $L_{2,3}$, the self-absorption should be seriously considered. Consequently a reevaluation of the measured spectra modified by the absorption of the top layers has to be theoretically approximated and/or measured. This problem is especially interesting in the case of AlMg alloys, where the effects are most predominant in the low-energy part of the spectra. Of course this low-energetic part is the most sensitive region of the self-absorption as well.

It is a well-known fact [19] that the Mg concentration changes on the surface of Mg-containing aluminum alloys during heat treatment. Enrichment of Mg has been observed in most of the cases [20 to 22], accompanied by an extra evaporation of Mg from the free surface [22]. The inhomogeneous distribution of Mg is measured directly by a microprobe [23], finding four times more Mg in the $\approx 0.5 \mu m$ thick surface layer, than in the bulk homogeneous material. These facts are prompting the study of the self-absorption problem, which is important for obtaining a more exact picture.

The aim of our present paper is to study the special self-absorption problems and to measure directly their modifications in spectra of AlMg alloys.

2. Experimental

The soft X-ray emission measurements were made on a home-made device operating in the 5 to 50 nm wavelength range with a grating mirror (600 grids/inch) fitted to a 2 m Rowland circle. The measurements were done at room temperature, maintained by intensive water cooling during the electron bombardment. The penetration depth is controlled by changing the exciting electron energy [12]. The $L_{2,3}$ lines of Al and Mg emission spectra

Table 1
Composition of the investigated samples

No.	alloy	composition (wt%)		
		Mg	Si	Fe
1	AlMgSi	0.58	0.35	0.14
2	AlMg (0.25)	0.25	<0.01	<0.01
3	AlMg (0.5)	0.5	<0.01	<0.01
4	AlMg (0.7)	0.7	<0.01	<0.01
5	AlMg (1.4)	1.4	<0.01	<0.01
6	AlMg (4.0)	4.0	<0.01	<0.01
7	AlMg (9.0)	9.0	<0.01	<0.01

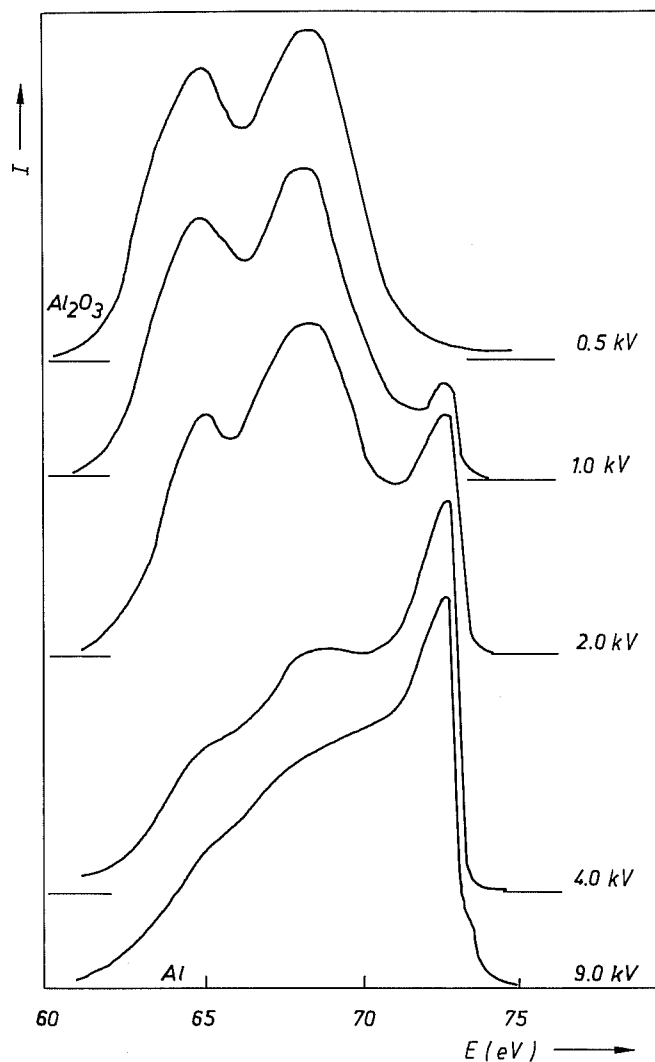


Fig. 1. Spectra of oxidized pure aluminium metal for various excitation voltages. The additional doublet of the oxide in the standard pure Al spectra appears

were measured with a relatively high wavelength resolution ($\Delta\lambda = 0.1$ nm), while the overall resolution (the reproducibility and other factors are also counted) is $\Delta E \approx 0.15$ eV.

The compositions of the samples are collected in Table 1. The heat treatments were done in air and in the equipment under a vacuum of 3×10^{-4} Pa. The Mg evaporation was done from pure 99.9% Mg, the MgO layer was made by its oxidation.

3. Results

The spectrum of the oxidized pure aluminium metal is such as expected [5, 6] (Fig. 1). The variation of the excitation voltage smoothly sweeps the surface region in depth, giving the pure aluminium signal by the deeper penetration. The spectra are convoluted by the emission

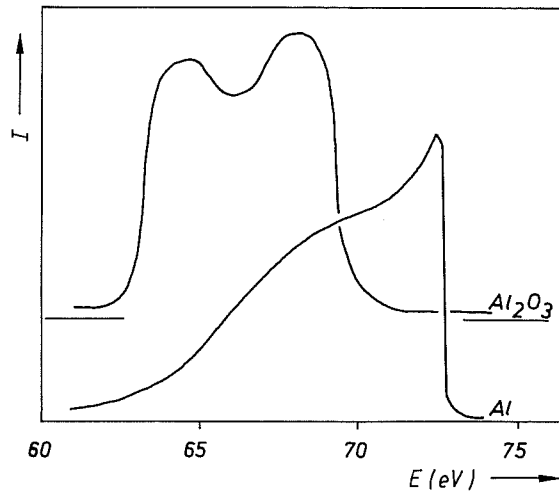


Fig. 2. Spectra of aluminium metal and aluminium oxide

coming from the pure metal and from the stoichiometric oxide (Al_2O_3 , Fig. 2). The spectra of the magnesium is similar to Al $L_{2,3}$ and constructed in the same way [24, 25] as the corresponding emission spectrum of aluminum [3].

Some of the measurements of Al $L_{2,3}$ are collected in Fig. 3 to 5. The essential modification of the Al $L_{2,3}$ and Mg $L_{2,3}$ spectra is trivial; basically a massive double-peak has appeared. The basic characteristic of the new pattern is the oxidation [24, 25], but a slight shift in the energy is observable from the standard oxide doublet.

4. Discussion

The main problem of the evaluation of the measurements is the overlapping of the Al and Mg $L_{2,3}$ emission spectra. The Al $L_{2,3}$ line has a couple of low-energetic satellites [26],

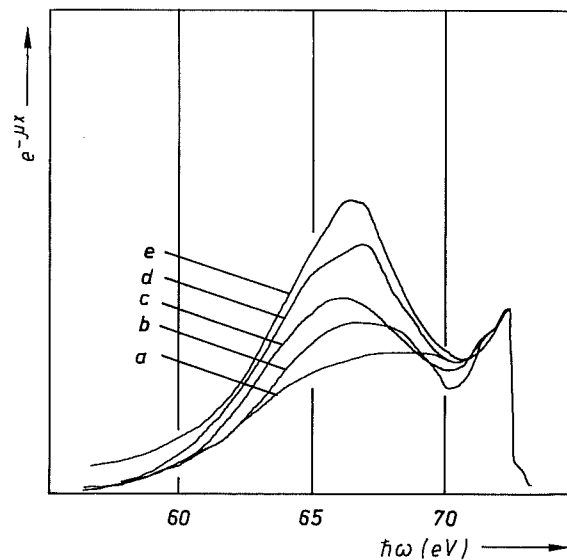


Fig. 3. The experimental Al $L_{2,3}$ emission spectra of the heat-treated AlMg and AlMgSi alloys. (The spectra are normalized to the peak at the Fermi edge.) (a) pure Al (as reference) [5], (b) $\text{AlMg}_{0.5}$, (c) $\text{AlMg}_{0.7}$, (d) $\text{AlMg}_{1.4}$, (e) $\text{AlMg}_{9.0}$

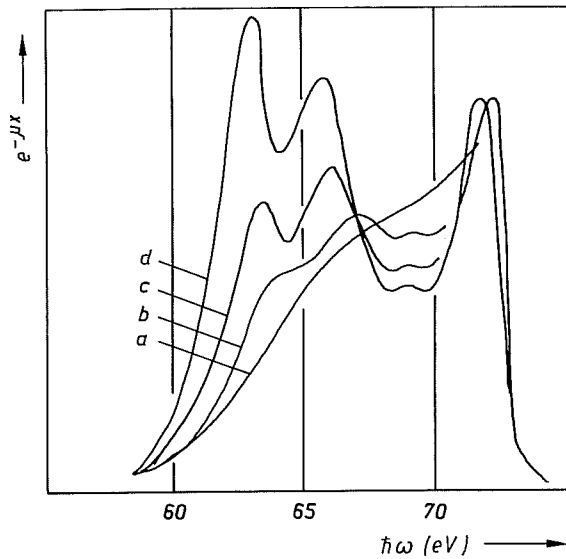


Fig. 4. The experimental Al $L_{2,3}$ emission spectra of the heat-treated AlMg and AlMgSi alloys. (The spectra are normalized to the peak at the Fermi edge.) (a) Pure Al (as reference) [5]; (b) AlMg_{0.58} · Si_{0.35}Fe_{0.14}, 530 °C in air for 30 min; (c) AlMg_{0.5}, 530 °C in air for 30 min; (d) AlMg_{0.7} 470 °C in air for 60 min

(plasma-excitation satellite and a special satellite corresponding to the $L_1 \rightarrow L_{2,3}$ transition), which are situated in the region of the Mg $L_{2,3}$ emission curve (Fig. 6). Furthermore, the plasmon satellite shifts monotonously with the concentration of the alloy [18], but the largest modification is caused by the Mg absorption, overlapping the Al $L_{2,3}$ emission line. In the following we concentrate on the spectrum of the majority component of the alloy, i.e., on the aluminium spectra.

The absorption spectrum of magnesium has been investigated at the $L_{2,3}$ threshold by Fomichev and Zhukova [27]. The thickness of the Mg layer was not measured by them, the results were interpreted in the only numerical term of μx (where μ is the linear absorption coefficient, x the thickness of the absorption layer involved in the absorption), so the data should be reevaluated considering the surface layers. In the light of these measurements the Al $L_{2,3}$ emission spectrum indeed overlaps with the Mg $L_{2,3}$ spectrum, and consequently the fine structure of the Mg absorption can essentially modify the Al emission in its low-energy part (Fig. 7).

The effect of the Mg absorption on the Al $L_{2,3}$ emission spectra is well seen on Fig. 8. The convolution of the Mg absorption and Al emission can be described by the formula

$$I_{Al}(\hbar\omega) = I_{Al}^{(0)}(\hbar\omega) \exp(-\mu x n),$$

where $I_{Al}(\hbar\omega)$ is the measured intensity, $I_{Al}^{(0)}(\hbar\omega)$ is the original intensity without the absorption and n is an integer which characterizes the thickness of the absorbed layer. In the same way the effect of the absorption of MgO on the emission of Al $L_{2,3}$ is shown on Fig. 9.

In this energy region the transmission of Mg decreases by a factor of about seven in the energy interval of 55 to 72 eV. The variation of the Mg absorption function in the region of Al $L_{2,3}$ is large enough to modify considerably the low-energy part of the measured emission spectra. The modification will be larger for deeper generation (thicker effective layer) of the soft X-ray emission, and thus depends on the excitation voltage.

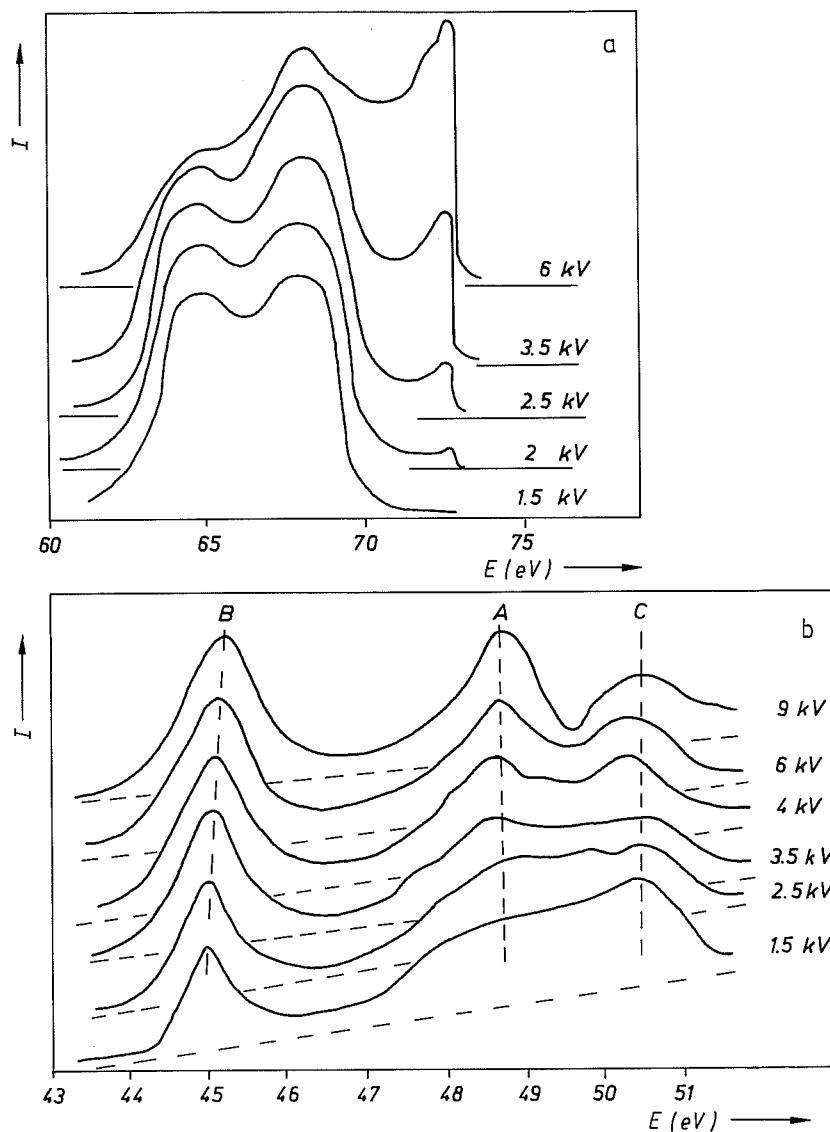


Fig. 5. Spectra of AlMg (0.25) sample measured after annealing at 300 °C for 5 h in air from different depths. a) Al $L_{2,3}$, b) Mg $L_{2,3}$

The Al $L_{2,3}$ spectra modified by the Mg absorption shows a surprising fact: the changes are similar to the experimental curves (see Fig. 3 and 4) which were interpreted [5, 6] by assuming special surface reactions on the Al–Mg alloy. The effective absorption of Mg increases by the Mg concentration, which is one of the factors of the changes in the low-energy part of Al $L_{2,3}$ emission spectra (Fig. 3). Consequently the explanations given for the emission spectra have to be revised taking into consideration the self-absorption of the top layers as well.

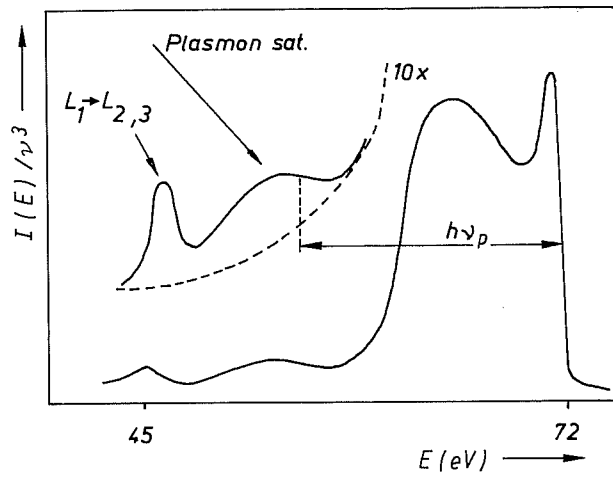


Fig. 6. Low-energy satellites of the aluminium $L_{2,3}$ emission spectrum

The careful study of the measured curves shows a double-peak in the low-energy region which was identified as the superimposed double-peak of the oxides on the standard Al $L_{2,3}$ spectra [16]. However, the changes by the variation of the penetration depth (varying the excitation voltage) are not fully supporting the oxide idea. This is due to the above-described self-absorption effect; that is, the peak at about 65 and 68 eV is a real oxidation effect [16], while the peak at about 67 eV is only apparent, caused by the overlapping of the absorption spectrum of Mg with the emission of Al.

The absorption effect of surface MgO is complicated, because the non-monotonic, complicated absorption spectra of MgO (Fig. 8, curve a) in the energy interval of Al $L_{2,3}$.

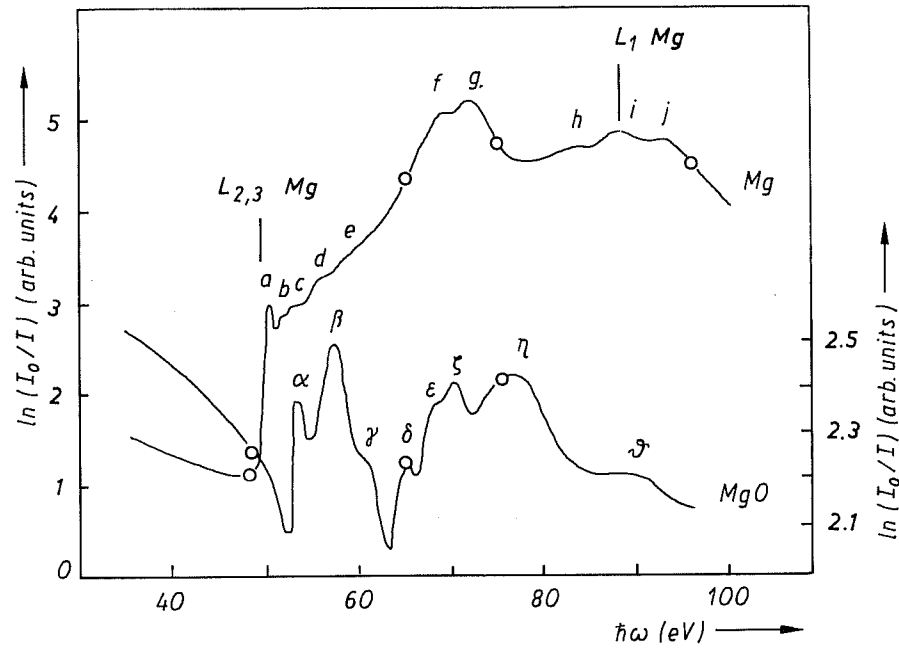


Fig. 7. The absorption spectra [15] of pure Mg and MgO

The maxima of the Al emission spectra of the heat-treated (heavily oxidized) alloys agree well with the maxima of the MgO absorption for Al–Mg alloys, pointing out the essential effect of the self-absorption in these cases. The peaks caused by the absorption (at about 63.5 and 66 eV) (Fig. 9), and the measured one for AlMg alloys (about 64 eV) (Fig. 5) show the overcoated oxidation enrichment effect which is described elsewhere [6]. The control measurements on the Mg $L_{2,3}$ emission spectra clearly show the oxidation, but from the Al $L_{2,3}$ emission alone the deconvolution of the real Mg enrichment and oxidation effects is not possible because the heavy overlapping of these peaks. However, in some cases the peaks appear independently (Fig. 10).

For the Al–Mg–Si alloy the effect of MgO is not so characteristic, the low-energy peaks do not correspond to the absorption peaks. This difference may be due to the relatively small Mg concentration in the alloy, and the presence of Si which is fixing the Mg in the strongly bound Mg_2Si compound, acting against the surface enrichment of Mg. For such systems the Al $L_{2,3}$ emission spectra alone yield information on the surface oxidation processes, without taking seriously into account the modifications due to Mg.

In general, for studying the Mg-enriched surface layers it is more practical to use small excitation energies, because the thinner modificative absorption layer on the top. This effect is well illustrated on Fig. 10, where the peak characterizing the oxides appears at lower excitation. According to our study we can be sure that the explanations of the effects measured before [6] are essentially correct, only a refinement is needed taking into account the absorption effects as well. The magnesium side has also been examined, and all the previous conclusions have been found correct in the light of these new facts, too. The not fully understood structure of Al $L_{2,3}$ in AlMg alloys [5] is explained now: The self-absorption causes a massive modifying effect and has to be considered at the evaluation of the spectra.

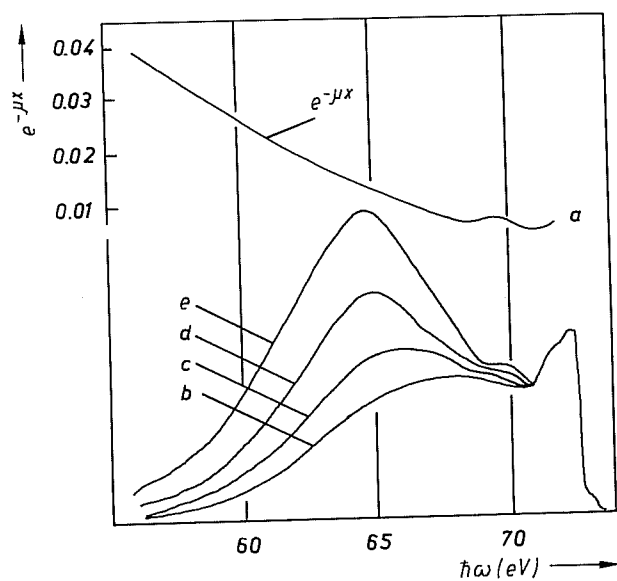


Fig. 8. The effect of the Mg absorption on the Al $L_{2,3}$ emission spectra (the spectra are normalized to the peak at the Fermi edge). (a) Function of the transmission of a Mg layer in the given energy range [15]; (b) Al $L_{2,3}$ emission spectra, $I_{Al}^{(0)}(\hbar\omega)$ [5]; (c) the modified Al $L_{2,3}$ emission spectra, $n = 3.0$; (d) the modified Al $L_{2,3}$ emission spectra, $n = 1.5$; (e) the modified Al $L_{2,3}$ emission spectra, $n = 1.0$

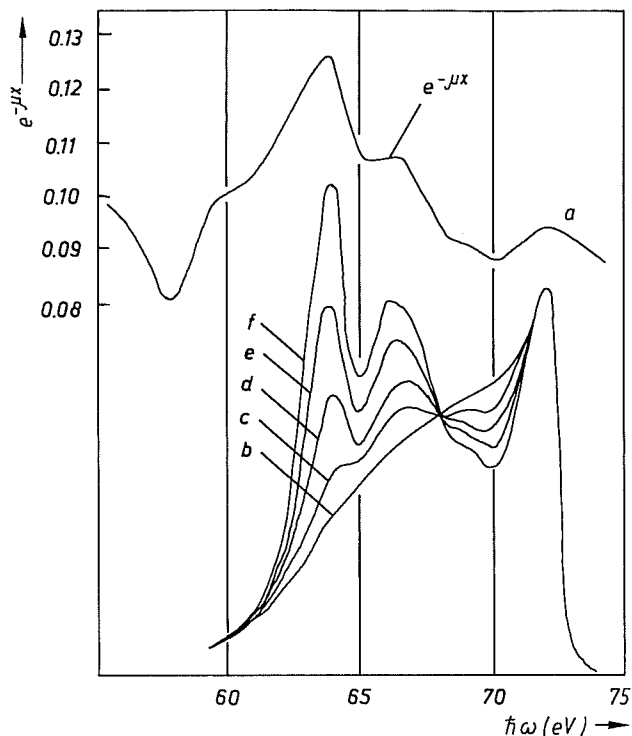


Fig. 9. The effect of the absorption spectrum of the MgO compound on the Al $L_{2,3}$ spectra (the spectra are normalized to the peak at the Fermi edge). (a) Function of the transmission of MgO layer in the given energy range [15]; (b) the Al $L_{2,3}$ emission spectra, $I_{Al}^{(0)}(\hbar\omega)$ [5]; (c) the modified Al $L_{2,3}$ emission spectra, $n = 1.0$; (d) the modified Al $L_{2,3}$ emission spectra, $n = 2.0$; (e) the modified Al $L_{2,3}$ emission spectra, $n = 3.0$; (f) the modified Al $L_{2,3}$ emission spectra, $n = 4.0$

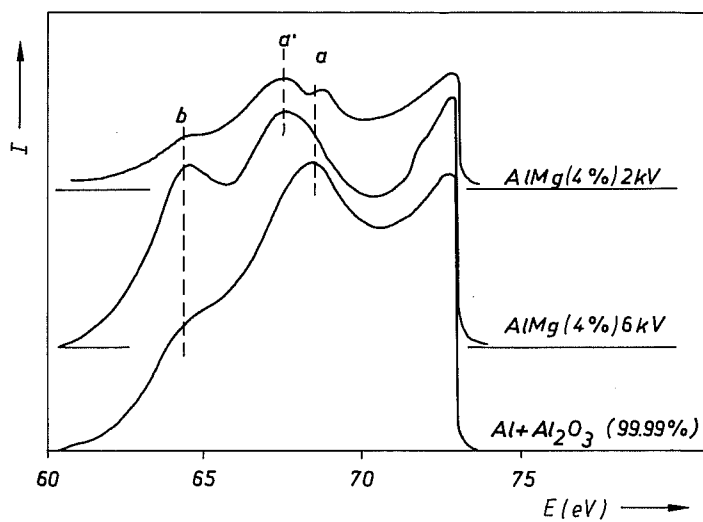


Fig. 10. Comparison of the spectra of oxidized pure Al, AlMg (4.0) excited by 6 kV and 2 kV

Note, this absorption effect of surface layers (first of all oxides) is very relevant in all of the cases when the involved components have emission spectra very near to each other in the soft and/or ultrasoft energy region: For example, alloys containing neighboring d-elements (different kinds of steels, catalysts, etc.), compounds with an accidental correspondence in the emission spectra of the constituents (for example TiN), or other compounds and alloys, having an overlap of the primary spectrum of one component with the second- or higher-order of the other one (for example, FeB). Investigations of these effects are in progress.

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