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SOFT X-RAY EMISSION SPECTRA FROM ALUMINIUM-NIOBIUM AND ALUMINIUM-PALLADIUM ALLOYS

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Résumé. — Les spectres X d'émission L d'aluminium dans les alliages des Al-Nb et Al-Pd ont été mesurés et comparés avec les spectres X d'émission K d'aluminium dans les mêmes alliages ; des informations concernant les distributions d'états dans la proxiimité des ions d'aluminium ont été déduites.

Abstract. — Al L2,3 emission spectra from Al-Nb and Al-Pd alloys have been measured and compared with the Al K emission spectra from the same alloys. Information regarding the density of states in the vicinity of aluminium ions has been deduced.

1.0 Introduction. — Soft X-ray spectrometry is a well established technique for investigating the density of electron states throughout the valence band of metals or alloys. Nevertheless, the results are difficult to interpret because the effects of transition-probabilities can not be estimated without an a priori knowledge of both the initial and final state wave functions of the electrons involved in the emission process and because the broadening of spectra due to many body effects can not easily be estimated. Aluminium is one of few metals for which the soft X-ray emission spectrum is fairly well understood [1] and as such, it provides a good basis for the investigation of binary alloys.

However, although the shape of the pure aluminium emission spectrum may be explained, the explanation of the aluminium spectrum from alloys again becomes difficult since it is hard to predict to what extent changes in the spectrum shape are due to changes in the density of states and to changes in transition probabilities. The latter has received little theoretical attention although it has been pointed out by Stott [2] that, in dilute alloys, the transition probability for a solvent atom depends on its position relative to the solute atom. A further aspect which must be borne in mind when attempting to draw conclusions from the emission spectra of alloys is that the emission from, in our case, the aluminium atom is a function of the density of states and the symmetry of the valence band wave functions in the vicinity of the aluminium ion core. Recently Soven [3] has predicted that the density of states in the vicinity of the solvent and solute atoms will differ. The results presented here support this prediction.

In effect, then, the soft X-ray emission spectra give information about the density of states in a localised region about the emitting atom; and this must be a function of the configuration of the different types of atom surrounding the emitting atom. In the case of random substitutional solid solutions, the emission spectrum will reflect an average of the above effects and changes in the emission spectrum would be expected to vary smoothly with changes in the concentration of the alloy. This was found to be the case in the aluminium-silver system [4]. For ordered intermetallic compounds, however, each emitting atom for a particular compound will be in more or less the same environment and one might expect that for different intermetallic compounds of the same alloy system, the changes in the emission spectrum from each component might be quite considerable due to changes in the environment of the emitting atom. We shall see in the results presented here, that this is the case in at least one alloy system.

2.0 Experimental. — The work presented here is complementary to the work reported in [5] and [6]. The alloys (prepared in Kiev ; Ukr. Ac. Sci., Institute of Metal Physics) were made in an argon atmosphere in an electric arc furnace having a tungsten electrode. They were then annealed at a suitable temperature to homogenise them.

The apparatus has been described in detail elsewhere [7]. Briefly, the spectrometer uses a ruled concave diffraction grating at grazing incidence with a scanning photomultiplier detector. The grating has a radius of curvature of 99.88 cm, a blaze angle of 2° 4', 600 lines/mm. and is coated with platinum to enhance reflection. The detector is a Bendix M 306...
photomultiplier with a copper-beryllium photocathode. The spectrometer chamber is maintained at a pressure of \(2 \times 10^{-6}\) torr during operation, by a mercury diffusion pump and two liquid nitrogen vapour traps.

The X-ray tube consists of a rotatable, water-cooled, stainless steel anode on to which four specimens are attached using a conducting cement. X-rays are produced by electron bombardment from an electron gun consisting of a barium oxide coated nickel filament and a slit which focuses the beam on to an area of the target of approximately 0.05 cm by 1 cm. A mechanical scraper is incorporated into the tube so that, by rotating the target to face the scraper, the surface of the target may be scraped to expose clean metal. The X-ray tube is maintained at a pressure of \(2 \times 10^{-6}\) torr during operation by a separate mercury diffusion pump and liquid nitrogen vapour trap system. A potential of 2 kV is applied to the target and a bombarding current of 5 to 9 mA is normally used. The power supplies are stabilised to better than 0.1%.

The results were obtained by repeated scanning of the same spectrum until enough counts had been accumulated to reduce the statistical counting error to an acceptable level. Before each scan, the target was scraped to prevent the build up of contaminants on the surface. This was not completely successful as we discuss later. The data was collected on punched tape for subsequent processing by computer.

2.1 PROCESSING. — The results are presented as processed and unprocessed. The processed results have undergone the following treatment.

a) The background intensity, which is assumed to vary linearly between suitable points beyond the high and low energy limits of the band, has been subtracted.

b) Each point in the spectrum has been divided by the fifth power of the frequency \(\gamma^5\), \(\gamma^2\) because the spectrometer measures \(I(\lambda) \, d\lambda\), where \(I(\lambda)\) is the intensity at wavelength \(\lambda\) and \(d\lambda\) is the wavelength interval embraced by the detector slit width, and converting this to \(I(E) \, dE\), where \(E\) is the energy of the radiation, introduces the factor of \(\gamma^{-2}\). The remaining \(\gamma^3\) term is to account for the frequency dependent factor of the transition probabilities.

c) Intensity loss, due to the build up of contaminants on the surface of the target during each scan, is measured by measuring the intensity at some fixed point in the spectrum before and after each scan. Using these data, each point in the spectrum is corrected for intensity fall off by assuming the fall off to be linear in time. (This has been measured and was found to be a good approximation.) Because the above corrections, in particular (a), may be open to question, the results are also presented in the unprocessed form. In this case only the conversion from \(I(\lambda) \, d\lambda\) to \(I(E) \, dE\) has been made. In both cases the error bars, representing the 67% confidence levels, have been drawn.

3.0 Results and discussion. — Figures 1a and 4a show the processed Al \(L_{2,3}\) emission spectra from the alloys drawn one vertically above the other. The straight vertical lines are at 1 eV separation. Figures 1b and 4b show the unprocessed spectra and, since the background radiation has not been subtracted, the horizontal lines have been drawn to show the zero intensity levels of the spectra.

No attempt has been made to estimate the band width of the alloy spectra for two reasons, firstly alloying with niobium or palladium is seen to have profound effects on the low energy end of the spectra which renders an \(E^{1/2}\)-extrapolation invalid; secondly
as the aluminium content of the alloys decreases, the intensity for each scan decreases and the effects of contaminants become more obvious. One such effect is the presence of two second order lines at 59.7 eV and 62.2 eV. These become significant in the spectra from AlNb, AlNb, and AlPd and again make it difficult to determine the position of the bottom of the band. The origin of these contamination lines is as yet undetermined.

3.1 ALUMINIUM-NIOBIUM ALLOYS. — The most striking feature of the Al L₂,₃ emission spectra from these alloys is the very considerable change in their shape as the niobium content of the alloy is increased; further, the changes in shape are not progressive with concentration since the Al₃Nb spectrum bears little similarity to the pure aluminium spectrum or the spectra from AlNb₂ or AlNb₃.

Al₃Nb. — The Fermi edge of this spectrum has shifted by 0.08 eV to lower energies with respect to the pure aluminium spectrum, also, unlike the aluminium spectrum, the intensity falls off rapidly in the region of the Fermi edge. This could be due to two factors; either the density of states is decreasing rapidly at the Fermi energy or the states in this region are predominantly p-like. If the latter were the case, the aluminium K-emission spectrum from this alloy would show an increase in intensity close to the Fermi energy. This is found not to be the case [see Fig. 2]. In fact the density of p-states in the band moves to lower energies. We can therefore conclude that, at least around the aluminium atom sites, the density of states has been considerably modified.

The peak in the spectrum at 67.25 eV suggests the existence of localised states about the aluminium atoms and may be correlated with the more intense peaks which occur in AlNb₂ and AlNb₃.

AlNb₂. — The Fermi edge in this case has shifted 0.56 eV to lower energies with respect to the pure aluminium spectrum, and the high energy region of Fig. 2. — Kβ₂ band of aluminium in the spectra of the pure metal and alloys: (1) Al; (2) Al + 25 % Nb; (3) Al + 64 % Nb; (4) Al + 75 % Nb; the broken line shows the extrapolation of the long-wave branch in accordance with the law

\[ I \propto (E - E₀)^{3/2} \]

(After Nemoshkalenko and Krivitskii.)
the band has reverted to a form more like that of the pure metal spectrum. The dominating feature of the spectrum is the intense peak with a maximum at 66.5 eV. This again must be due to the localisation of states in the region of the aluminium atoms.

AlNb₃ — The spectrum in this case is similar in overall shape to that of AlNb₂. The Fermi edge has shifted 0.71 eV to lower energies with respect to the pure metal spectrum and the maximum of the low energy peak now comes at 65.95 eV. The peak itself is narrower and more symmetrical which suggests even stronger binding of the states in this energy region to the aluminium atoms.

In the unprocessed spectra of figure 1b the third order niobium Mᵥ NᵥI line appears at 57.3 eV. That the line does not shift in energy lends confidence to the fact that edge and peak shifts in the alloys are genuine and a function of alloy composition or structure. Table I summarises the energies of the Fermi edge and peak maxima for the above alloys.

Table I

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystal structure</th>
<th>Fermi energy</th>
<th>Peak maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>f. c. c.</td>
<td>72.76 eV</td>
<td>66.50 eV</td>
</tr>
<tr>
<td>Al₃Nb</td>
<td>Tetragonal of the type TiAl₃</td>
<td>72.68 eV</td>
<td>67.25 eV</td>
</tr>
<tr>
<td>AlNb₂</td>
<td>σ-phase</td>
<td>72.20 eV</td>
<td>65.95 eV</td>
</tr>
<tr>
<td>AlNb₃</td>
<td>β-W structure</td>
<td>72.05 eV</td>
<td>65.95 eV</td>
</tr>
</tbody>
</table>

3.2 CONCLUSIONS. — We may draw the following conclusions on the aluminium-niobium system by considering the above results in conjunction with the aluminium Kᵦ₂ spectra from the alloys (Fig. 2) and the niobium Lβ₂ and Lγ₁ spectra from the alloys (Fig. 3).

a) The density of states in the vicinity of the emitting aluminium atoms changes considerably from that of pure aluminium. This is discussed under Al₃Nb above. The density of states also changes on changing alloy composition in a way which bears no relation to either a rigid band model or a common valence band model. In the former, the alloy spectra would be similar to those from the pure metals and in the latter the L-emission spectra from both aluminium and niobium in a particular alloy should be similar.

b) A corresponding change in the density of states in the vicinity of the niobium atoms is not seen. The Lγ₁ spectra show a slight bulge at the low energy end of the band as the aluminium content is increased which suggests some localisation of states in the region of the niobium atoms in these alloys. This is estimated to account for about 6% of the total integrated intensity of the band. Otherwise, the bands are much the same as for pure niobium. Comparing this with the gross changes that occur in the aluminium L spectra from the same alloys, we can conclude that the density of states in the vicinity of the aluminium atoms is different from the density of states in the vicinity of the niobium atoms.

c) Nemoshkalenko concludes, from the shift to

Fig. 3. — (a) Lβ₂ bands of niobium in the spectra of the pure metal and alloys; (b) Lγ₁ bands of niobium in the spectra of the pure metal and the alloys: 1) Nb; 2) Nb + 8% Al; 3) Nb + 25% Al; 4) Nb + 36% Al; 5) Nb + 75% Al. The full lines show the experimental results; the broken lines show the results after correcting for the width of the inner level and the apparatus distortions. (After Nemoshkalenko and Krivitskii.)
lower energies accompanied by the decrease in width of the aluminium $K\beta_4$ bands in the alloys, that the p-states are becoming more localised in the vicinity of the aluminium atoms and are possibly forming additional covalent bands. We can likewise conclude that the strong peak in the aluminium $L$-bands from the alloys is due to the localisation of states of s or d symmetry about the aluminium atoms. These states may be due to the hybridisation of the niobium d-states with the s- or p-states of aluminium. The d-states of niobium in the pure metal are closer to the Fermi level than is the peak in the aluminium $L$-spectra so the hybridisation would have to account for a considerable shift of these states to lower energies. That the peak shifts to lower energies and becomes more symmetrical also suggests that the binding of the states becomes stronger as the niobium content of the alloy is increased.

3.3 ALUMINIUM-PALLADIUM ALLOYS. — The processed and unprocessed aluminium $L_{2,3}$ bands from pure Al, Al$_3$Pd, Al$_3$Pd$_2$ and AlPd are shown in figures 4a and 4b respectively. In the processed spectra the broad band between 53 and 46 eV is due to the Pd $N_{2,3}$ emission and there will also be a contribution from the plasmon satellite. However, the band is too low in intensity to be of much interest in the results shown here. The line at 45 eV is due to the Al $L_1 L_3$ transitions, and the fourth order Pd $M_y N_{II}$ line is expected to overlap the aluminium band at about 70.9 eV [8]. This could account for the slight hump seen in the alloy spectra in this region.

The alloy spectra in this case are rather similar with the dominant feature again being the high electron density peak to the low energy end of the band. As the palladium content of the alloys is increased, the Fermi edge moves to higher energies — unlike the aluminium — niobium results — while the peak moves to lower energies and becomes narrower. These results are summarised in table II.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Crystal structure</th>
<th>Fermi energy $+0.10\text{ eV}$</th>
<th>Peak maxima $+0.05\text{ eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>f. c. c.</td>
<td>72.76</td>
<td></td>
</tr>
<tr>
<td>Al$_3$Pd</td>
<td>Orthorhombic of</td>
<td>72.78</td>
<td>66.40</td>
</tr>
<tr>
<td>Al$_3$Pd$_2$</td>
<td>Hexagonal of the type Ni$_3$Al$_3$</td>
<td>72.88</td>
<td>65.90</td>
</tr>
<tr>
<td>AlPd</td>
<td>Uncertain</td>
<td>72.90</td>
<td>65.80</td>
</tr>
</tbody>
</table>

Figures 5 and 6 show the aluminium $K\beta_4$ and the palladium $L_\gamma_1$ bands from the alloys respectively. In many respects this alloy system is similar to the aluminium-niobium system and many of the comments made above would apply here also. The narrow intense peak in the $L_{2,3}$-bands again suggests the existence of s- or d-states fairly strongly bound to the aluminium atoms also, in this case, the $K\beta_4$ bands show the existence of a peak in the density of p-states at the low energy region of the band. It would appear, then, that the density of states is concentrated at the low energy region of the valence band around aluminium atoms in these alloys and this concentration increases as the palladium content of the alloy is increased.
The palladium $L\beta_2$ bands, on the other hand, show very little change on alloying. Probably the most remarkable point about the aluminium $L_{2,3}$ emission spectra from these alloys is the narrow width of the low energy peak — especially in the aluminium-palladium system. If broadening due to auger transitions within the band and instrumental broadening were taken into account, the peak would be much narrower and sharper, giving the appearance of a line state superimposed on the valence band.

Much more work is required on aluminium — second transition series alloys to show more clearly the effects of the population of the outer d-states on the alloys. Also measurements using other techniques such as E. S. C. A would show the average effects of alloying on the valence bands and would perhaps reduce the uncertainties in interpretation which arise from a lack of knowledge of the precise effects of transition probabilities.

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References

[5] NEMOSHKALENKO (V. V.) and KRIVITSKII (V. P.), Ukrainian Physics Journal, 1969, 13, 911.

DISCUSSION

Mr. URCH. — The shape of spectra presented by Dr. Watson et al, is so similar to those of chemical compounds (i. e. sharp symmetric peaks rather than broad bands) that it would seem that band localisation about the aluminium atoms must be taking place. This suggests that it might be possible to extend simple molecular orbital calculations, based on local interactions about a particular atom, to alloy systems. This is both surprising and promising!