

## Electronic Densities of States and Pseudo-gaps in Al-based Complex Intermetallics\*

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*Abstract.* The results of an investigation of the electronic structure of the valence band of various Al-based complex intermetallic alloys, carried out using the X-ray emission spectroscopy technique, are presented and discussed. It is shown that the electronic structure results from an interplay between covalency and repulsive interactions that contributes to the formation of a pseudo-gap at the Fermi level in the Al electronic distributions.

*Keywords:* electronic structure, pseudo-gap

### INTRODUCTION

Investigation of the atomic structure of complex stable crystalline intermetallic alloys has pointed out that atoms are arranged in large unit cells containing up to more than thousand atoms in a complex packing involving clusters with often partial occupancy of several of the atomic sites. What is the electronic structure of such complex intermetallic compounds? To achieve some insight into this issue, we have undertaken a study of the electronic structure of the valence band of several intermetallic compounds using the X-ray emission spectroscopy technique. The major point of interest here is to provide separately partial occupied densities of states (DOS) around each chemical species in the compound. Note that the data is averaged over all atomic sites of each species. Note also that the technique probes p DOS alone but s and d DOS together. However, transition probabilities favour d states with respect to s ones. The electronic distributions of the various constituents of a compound are obtained separately, each one in its own X-ray transition energy scale. Therefore, for meaningful comparison, it is necessary to adjust them in an identical energy scale. It is convenient to use the binding energy scale so that a picture of the valence band is obtained and allows discussion of the electronic interactions between its various components of the compound.

We present here our X-ray emission spectroscopy results for four binary samples, namely Al<sub>3</sub>Fe, Al<sub>3</sub>Ni, Al<sub>11</sub>Mn with almost filled transition metal d states, and Al<sub>8</sub>V<sub>5</sub> where the d states are almost empty. We also revisit briefly our data obtained for ternary Al-Co-Ni and Al-Fe-Cr alloys. As mentioned above, X-ray transition probabilities favour d states with respect to s ones. In the case of transition metals, for the 3d-4s distributions, the contribution of the s states is hidden by the d ones. So, in the following, we will refer to these distributions as 3d. The X-ray emission spectroscopy technique does not deliver absolute values for the DOS, hence we display the various partial distribution curves normalised to their own maximum intensity. Information about the experimental procedure and energy resolution may be found in Ref.1.

### RESULTS AND DISCUSSION

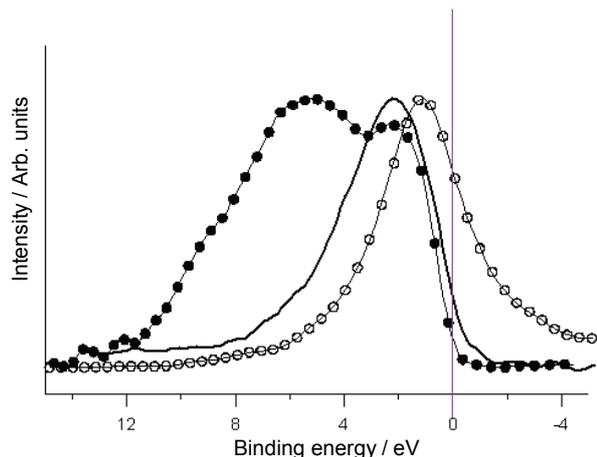
#### Binary Alloys

The picture of the valence band we have obtained for Al<sub>3</sub>Fe from the investigation of the Al 3s,d, Al 3p and Fe 3d distributions is displayed in Figure 1. From the Fermi level towards the centre of the valence band, one finds first Fe 3d states, at  $1.0 \pm 0.1$  eV and then the Al sub-bands. The maximum of the Al 3p sub-band, at

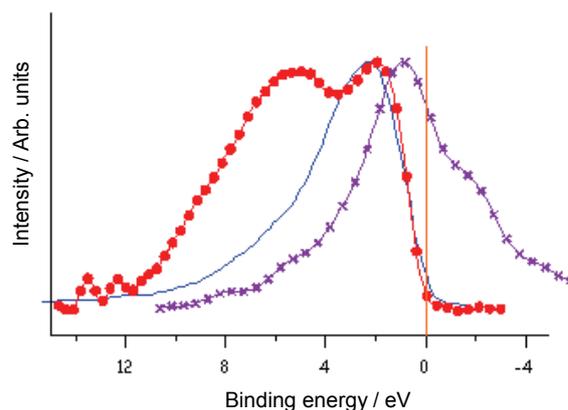
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Dedicated to Professor Boran Leontić on the occasion of his 80<sup>th</sup> birthday.

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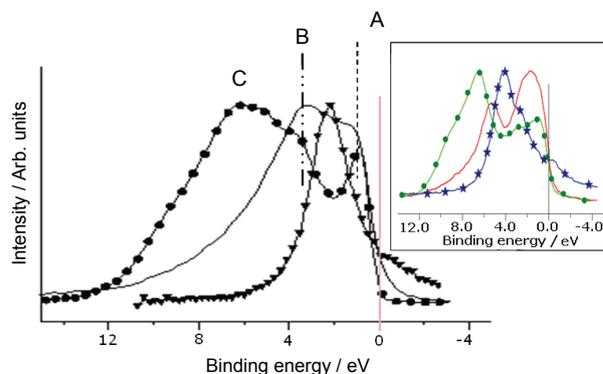
**Figure 1.** Valence band of  $\text{Al}_3\text{Fe}$ . Al 3p DOS: solid line, Al 3s,d DOS: dots, Fe 3d DOS: open dots.



**Figure 2.** Valence band of  $\text{Al}_{11}\text{Mn}_4$ . Al 3p DOS: solid line, Al 3s,d DOS: dots, Mn 3d DOS: stars.

$2.2 \pm 0.1$  eV, coincides with a secondary maximum of the Al 3s,d distribution whose main maximum is at  $5.2 \pm 0.1$  eV. The main maximum reflects states with s character whereas the states close to  $E_F$  are d-like<sup>1</sup>. The Al 3p and Al 3s,d states fully overlap from about 1 to 3 eV below  $E_F$ . This points out covalency effects between Al states over this energy range. The maxima of the Fe and Al curves are distant by  $1.2 \pm 0.1$  eV. This suggests that a repulsive interaction occurs in this part of the band between localised Fe states and hybridised Al states. As a consequence, the Al sub-band edges are repelled towards the centre of the valence band and therefore the intensity of the Al distributions at  $E_F$  is low. Namely, formation of a pseudo-gap occurs in the Al DOS. We have already discussed elsewhere that the formation of this pseudo-gap mainly results from the repulsion between the transition metal localised d states and states of Al with a d-like character.<sup>1</sup> This result is in line with calculations that have demonstrated the role played by the so called sp-d hybridisation close to the Fermi level in the formation of the Al pseudo-gap, especially in Al-transition metal compounds, and the behaviour of the corresponding compounds with respect of electronic properties such as electric and thermal conductivities.<sup>2</sup>

The same kind of interactions is found in other alloys such as, for instance,  $\text{Al}_{11}\text{Mn}_4$  as shown in Figure 2. Note that the bump present above  $E_F$  in the Mn 3d distribution is due to a satellite emission that forms during the X-ray emission process. The peak of the Al 3s,d curve nearby  $E_F$  is here the most intense and overlaps totally the maximum of the Al 3p contribution. This indicates that the covalent interaction between s,d and p states of Al is more marked than in the previous example and the corresponding states are therefore less extended in character than in  $\text{Al}_3\text{Fe}$ . The separation between the maxima of the Mn 3d and Al p-s,d distributions is of  $1.6 \pm 0.1$  eV. This shows a stronger repulsive interaction between the localised 3d states of Mn and



**Figure 3.** Valence band of  $\text{Al}_3\text{Ni}$ . Al 3p DOS: solid line, Al 3s,d DOS: dots, Ni 3d DOS: triangles. The insert shows the valence band of AlCu; full line: Al 3p DOS, dotted line: Al 3s,d DOS and stared line: Cu 3d DOS.

localised-like states of Al. As a consequence, the intensity of the Al 3p sub-band at  $E_F$  is significantly lower than in  $\text{Al}_3\text{Fe}$ , namely  $15 \pm 2$  in  $\text{Al}_{11}\text{Mn}_4$  against  $25 \pm 2$  in  $\text{Al}_3\text{Fe}$ . One may expect a less metallic character for  $\text{Al}_{11}\text{Mn}_4$  than for  $\text{Al}_3\text{Fe}$ .

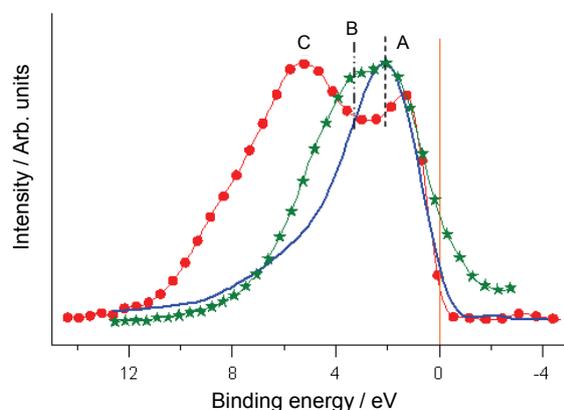
Figure 3 shows the valence band of  $\text{Al}_3\text{Ni}$  that noticeably departs from the two previous examples. In this compound, Ni 3d states are found at about 2 eV from  $E_F$ . They lie in an energy range where both Al 3p and Al 3s,d distributions present a marked depletion. This interaction is analogous to the one found in Cu-Al alloys<sup>4</sup> that was interpreted in terms of a Fano-like interaction between localised and extended states (see insert in Figure 3). As a result, the extended states are split into two parts located on each side of the maximum of the localised states distribution. Here, the overlap between the Al distributions in ranges labelled A and B points out covalency in these energy ranges whereas Al s states pure in character are found alone beyond feature noted C, towards increasing binding energies. Again in this compound, an interplay between covalency and repulsive interactions is noticeable. These effects push

Al states towards  $E_F$  and the Al 3p intensity at  $E_F$  is about  $22 \pm 2$ . Hence, properties such as thermal or electric conductivities should be similar in this compound and in  $\text{Al}_3\text{Fe}$ , despite the existence of a different balance between sp and d electronic interactions.

Let us now consider the case of  $\text{Al}_8\text{V}_5$ . The valence band of this complex intermetallic alloy is plotted in Figure 4.

From  $E_F$  towards increasing binding energies, the peak in the Al 3s,d distribution at  $1.4 \pm 0.1$  eV is followed by a feature labelled A at  $E_F + 2 \pm 0.1$  eV that shows an overlap between the maximum of the Al 3p DOS and a maximum in the V 3d DOS. A large minimum in the Al 3s,d distribution curve extends over feature A and a shoulder coined B on the V 3d DOS curve. Then Al 3s,d states extend beyond feature C till about 10 eV from  $E_F$ . Again covalent and repulsive interactions are encountered in this alloy. Covalency exists between Al 3p and V 3d states whereas repulsive interactions take place between V 3d and Al 3s,d states on the one hand and Al 3s,d and Al 3p states mixed to V 3d ones on the other hand. The Al 3p intensity at  $E_F$  is  $21 \pm 0.2$ , indicating again rather poor metallic properties for this alloy in which the interplay between covalency and repulsive interaction is quite complex.

It is to note that in Al based alloys for which DOS calculations are possible, computations have shown that the Al 3s,d states are actually almost pure in d character close to  $E_F$  and over a few eV.<sup>7-11</sup> Hence in all samples presented here, the Al states at the edge of the valence band are actually mixed p and d states, thus pointing out a somewhat localised-like character. They may contribute to repulsive interactions between d states of the transition metal that are located in the vicinity of the Fermi level like in  $\text{Al}_3\text{Fe}$  or  $\text{Al}_{11}\text{Mn}_4$  whereas a repulsive interaction is less likely if these d states are beyond about 2 eV from  $E_F$ .

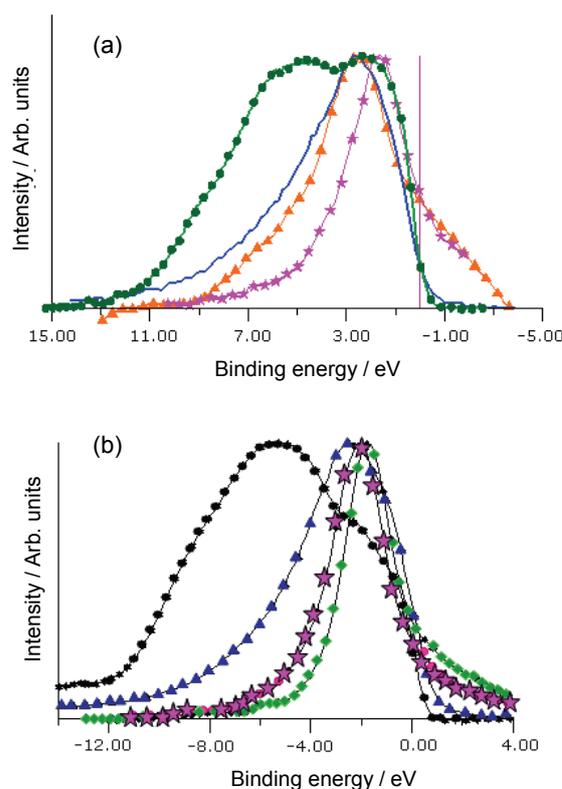


**Figure 4.** Valence band of  $\text{Al}_8\text{V}_5$ . Al 3p DOS: solid line, Al 3s,d DOS: dots, V 3d DOS: stars.

## Ternary Alloys

We will not discuss in details the case of ternary alloys, more information can be found in Refs. 5 and 6. Let us simply depict two examples, namely the  $\text{Al}_{77.5}\text{Cr}_{16.5}\text{Fe}_6$  and  $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$  approximants of decagonal quasicrystals. Their valence bands are displayed in Figure 5 (a) and (b).

The electronic interactions are more complex than in the previous examples but nevertheless they are of the same kind. Overlap between Al 3p states and Al 3s,d nearby  $E_F$  still exists, but is more manifest in Al-Cr-Fe than in Al-Ni-Co. In Al-Cr-Fe, the mixed Al s,d-p states and Cr 3d overlap whereas the Fe 3d states overlap only Al 3s,d ones close to  $E_F$ . Hence, we can conclude that there is covalency between Al s,d-p states and Cr d states and also covalency between Al 3s,d states and Fe 3d ones. The Cr and Fe d states repel each other and are separated by an energy distance of  $0.9 \pm 0.1$  eV. In  $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$ , the Al 3p states show little mixing with the Al 3s,d and partly overlap the transition metals 3d DOS. Here, the Co-Ni repulsion is less effective than in the previous example and the maxima of the corresponding 3d DOS curves are separated only by  $0.5 \pm 0.1$  eV. In both ternary alloys, the Al 3p intensity at  $E_F$  is very low, namely  $16 \pm 2$  in  $\text{Al}_{77.5}\text{Cr}_{16.5}\text{Fe}_6$  and  $12 \pm 2$  in



**Figure 5.** Valence band of (a)  $\text{Al}_{77.5}\text{Cr}_{16.5}\text{Fe}_6$ ; Al 3s,d: dots, Al 3p: full line, Cr 3d: triangles, Fe 3d: stars, and of (b)  $\text{Al}_{70}\text{Ni}_{15}\text{Co}_{15}$ ; Al 3s,d: dots, Al 3p: triangles, Ni 3d: stars, Co 3d: diamonds.

Al<sub>70</sub>Ni<sub>15</sub>Co<sub>15</sub>. Accordingly, both alloys are poor metals as far as thermal and electric transport properties are concerned.

## CONCLUSION

We have reported and discussed data about the electronic structure of the valence band of various complex intermetallic alloys obtained by X-ray emission spectroscopy. We have pointed out that the electronic structure results from an interplay between covalency on the one hand and repulsive interactions between localised state, on the other hand. The balance between these two kinds of interactions varies from alloy to alloy. However, in all cases, states with a localised character are present at and nearby the Fermi level. They are involved in the formation of a pseudo-gap in the Al DOS at  $E_F$  that governs the metallic character of the the compound.

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## SAŽETAK

### Raspodjela elektronske gustoće i pseudošupljine u kompleksnim intermetalnim legurama na bazi aluminija

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U radu su prikazani i diskutirani rezultati istraživanja elektronske strukture valentne vrpce različitih kompleksnih intermetalnih legura na bazi aluminija, dobiveni korištenjem tehnike emisivne spektroskopije X zraka. Pokazano je, da je elektronska struktura rezultat međugre kovalentnog i repulzivnog djelovanja koje doprinosi stvaranju pseudošupljina u blizini Fermijevog nivoa u raspodjeli elektronske gustoće aluminija.