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Experimental evidence of the formation of *d*-like states near the Fermi energy in Complex Metallic Alloys

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Abstract. The structure of the valence bands of several complex alloys was investigated using the X-ray emission spectroscopy technique. In this paper, we focus on the *d*-like states distributions in a series of Al-based and Mg-based alloys. It is pointed out that a substantial density of *d*-like states is found at or just under the Fermi level in the Al *s,d* and Mg *s,d* distributions of these complex systems. It is suggested that *d*-like states play a significant role in the local symmetry of the crystals and contribute to select and stabilize their structures.

Keywords: complex alloys, electronic structure, *d*-states, Fermi level.

Introduction

The variety of solid structures that go from simple, close packed and periodic to non-periodic arrangements questions about why Nature builds complex systems. Knowledge of their electronic structure is one of the means that may help to approach an answer. The electronic structure can be investigated by various means among which Soft X-ray Spectroscopy techniques. For the valence band (VB), Soft X-ray Emission Spectroscopy (SXES) probes separately the distribution of partial and local occupied states around each chemical species in the solid, averaging data over the various atomic sites. At a given energy, the intensity of the emitted x-rays is proportional to the probed partial density of states (DOS). Therefore, comparison of the shapes of the distribution curves for a given spectral character around a specific component in various materials informs about changes of the electronic interactions from one compound to another.

The SXES technique was extensively applied to the investigation of the VB structure in series of Al and (or) Mg-based compounds, ranging from conventional to complex systems, including quasicrystals and approximants, with special attention paid to Al *s,d* and Mg *s,d* distributions in the pure fcc Al and hcp Mg metals, respectively. In this article, we analyse new binary compounds and revisit ternary systems (Al-Mg-Zn) with better experimental accuracy than previously done [1]. *s* and *d* states are obtained together. Because transition probabilities favour *d* states with respect to *s* ones, we focus at those states and come to the conclusion that complexity of the crystal structure is linked to the occurrence of *d*-like states close to the Fermi energy.

To the best of our knowledge, our present data bring, for the first time, direct experimental confirmation of the formation of localised states at the edge of the VB of compounds based on *sp* elements. To achieve this conclusion, we first locate *d*-like states on the binding energy scale in Al-TM and Mg-TM samples (TM stands for transition metals). These states form due to *sp-d* hybridization and are readily observed on the partial DOS of the *sp*-element. Then we focus at Al-Mg alloys, and show that they exhibit a pronounced *d*-like peak just below the Fermi energy, although they are formed of pure *sp* elements.

Experimental

Except for two meta-stable compounds, we have revisited previous data [1] by producing new stable samples synthesized according to new techniques set up by Brunet et al. on the one hand and Feuerbacher et al. on the other (see Ref. 2 for details). All stable samples were cut in the shape of bulk slabs of about 1cm² cross section. They were carefully polished down to mirror polish and placed perpendicular to the electron beam axis in the SXES spectrometer. Details about SXES measurements,

especially positioning of the Fermi energy E_F on the X-ray transition energy scale, may be found in Ref. 3.

In strong contrast to photoemission spectroscopy, which investigates the total DOS (but requires knowledge of cross sections for a better understanding of the total DOS), SXES delivers only a partial DOS corresponding to a single species. Therefore, each spectral curve refers to the atom that produces the signal. We insist on this: the spectral character pointed out in a series of SXES experiments belongs to the source atom, in this study either Al or Mg, and not to the other alloy constituents. SXES intensities need to be expressed in arbitrary units. To this end, the most frequently applied scheme in the SXES community is a normalization to maximum intensity, instead of a normalisation to the total integrated intensity, which as a matter of facts makes little difference. After normalisation, intensities obtained from various samples, but in the same experimental conditions, may be compared.

Results

1. Locating *d*-like states in Al-TM based alloys

Figure 1 shows three sets of distribution curves in the binding energy scale representing the VB of stable Al_2Cu , Al_3Fe and Al_3Ni compounds. The data for Al_2Cu , in line with our previous results, may be summarised as follows: the Cu $3d$ states lie in the middle of the VB (they do not contribute to the intensity at E_F) whereas the Al $3p$ and $3s,d$ sub-bands overlap and are separated in two parts located on each side of the maximum of the Cu $3d$ states curve. DOS calculations have shown that Al s states extend between 4 and 11 eV below E_F whereas Al d states are hybridized to Al p states in the upper part of the VB below E_F [4]. This is also true for many other systems including approximants of quasicrystals, for which VB DOS calculations [4,5] have pointed out that Al $3s,d$ states close to E_F are essentially of d character.

In the structurally complex Al_3Fe binary alloy, from E_F towards the centre of the VB, one finds first Fe $3d$ states, then Al $3p$ states that overlap over about 3eV the Al $3s,d$ states, and then Al $3s,d$ states alone. This picture of the VB in Al_3Fe has been found to hold true in Al-TM-based quasicrystals and their approximants [3,5]. It has been argued that the stability of these complex structures is to a large extent due to the interaction near E_F between the TM d states and Al spd states through $sp-d$ hybridisation effects [6].

In Al_3Ni , another structurally complex alloy, Ni plays the same role as Cu in Al_2Cu . As a result, a significant proportion of Al states lies in a narrow energy range of about 1 eV below E_F . According to DOS calculations available for Al-MT systems, these states have a localised, or for short a d -like, character.

Conclusively at this stage, we have shown experimentally that in stable complex structures d -like states arising from hybridization effects of Al states with TM states are present close to E_F , at the top of the VB.

2. Alloys based solely on *sp* elements

Fcc Al and hcp Mg are free-electron metals with not only sp electronic states, but also a faint proportion of d -like states located close to their VB edge. Actually, according to Papaconstantopoulos [7], the VB of Al contains 1.55 s and 0.07 d electronic states whereas in hcp Mg, there are 0.77 s and 0.11 d electronic states. The other electronic states of the VB are of character p . The two Al and Mg $3s,d$ distributions curves are displayed in Figure 2. In both cases, below the Fermi energy, in the energy range of the d -like states, exists an intense and narrow peak that arises from a many-body effect following the x-ray emission process [8]. This peak is much more narrow in Mg than in Al. Qualitative comparison of Al- or Mg-based alloys with the respective pure element is possible. The presence of a sharp narrow peak just below E_F in such an alloy would reveal a free-electron-like behaviour. However, in the pure metals, the occurrence of the many-body peak obscures the contribution of the d -like states, therefore, we shall not make any comparison to the pure metals in the following and restrict ourselves to studying the compounds only.

The compounds for which we have investigated the Al and/or Mg $3s,d$ distributions are listed in Table 1, namely the stable β -Al₃Mg₂ so-called Samson phase [9], one metastable quasiperiodic counterpart of composition Al₆₁Mg₃₉ (also noted Mg-61at% Al in the original article [10] which the Reader may consult for details about the crystal aperiodic structure and that is quoted QP-Al-Mg hereafter), the Laves phase Zn₂Mg [11], the stable crystalline phases Mg_{39.5}Al₃₀Zn_{30.5}, Mg_{39.5}Al₄₀Zn_{20.5}, Mg_{39.5}Al₅₀Zn_{10.5} and a metastable quasicrystalline phase of nominal composition Mg₄₃Al₁₅Zn₄₂ [12].

For all the compounds, the Al $3s,d$ as well as the Mg $3s,d$ curves consist in a broad peak near E_F (denoted P) followed by a large marked bump whose maximum intensity is set around 4 eV below P (Figures 3 and 4). This emphasises a complete redistribution of the $3s,d$ states in the compounds.

In an attempt to put this observation on a more quantitative basis, we have measured the energy extent W of the base of peak P in each of the compounds. This was done by extrapolating first the part of the curve corresponding to the bump on the low energy side of peak P, and second by measuring the energy distance between this point and the point on the other side of peak P at the same intensity. The values are given in Table 1 together with the height H (intensity difference between maximum intensity of the peak and its base line) and the approximate area $A=W \times H/2$ of the peak P. It is worth insisting at this point that this approximation of the true area is by far sufficient for the present purpose, although it does obviously not offer a rigorous measure of the actual area. The extent of the spectral distribution of the peak, of the order of $0.9 \leq W/2 \leq 1.2$ eV, signals a well defined peak and therefore the occurrence of localized, or equivalently d -like, states. In this table, we have reported the Al $3s,d$ data obtained from a sample of icosahedral Mg₄₃Al₁₅Zn₄₂ phase because, although of rather bad quality due to experimental constrains, it follows the same trend as found for the Mg $3s,d$ states.

Table 1

Sample	Atomic Structure	Stability	Al $3s,d$			Mg $3s,d$		
			W (± 0.1 eV)	H \pm 2%	A = WxH/2 Arb. Units	W (± 0.1 eV)	H \pm 2%	A = WxH/2 Arb. Units
β -Al ₃ Mg ₂	Cubic	Stable	2.0	52	52	1.8	56	50
Mg-61at%Al (QP-AlMg)	Quasi periodic	Metastable	1.7	33	28	1.7	49	41
Zn ₂ Mg	Hexagonal	Stable				0.9	28	13
Mg _{39.5} Al ₃₀ Zn _{30.5}	Cubic	Stable	1.8	34	31			
Mg _{39.5} Al ₄₀ Zn _{20.5}	Cubic	Stable				1.2	48	29
Mg _{39.5} Al ₅₀ Zn _{10.5}	Cubic	Stable				1.2	51	31
Mg ₄₃ Al ₁₅ Zn ₄₂	Icosahedral	Metastable	1.7	28	24	1.0	26	13

From the values obtained for area A in Table 1, it is clear that the number of d -like states originating from Al or Mg atoms in stable crystalline compounds is significantly larger than in metastable quasiperiodic or quasicrystalline counterparts. This difference, in our opinion, is related to the occurrence of a significant degree of disorder in the metastable compounds, as can be assessed from the width of x-ray diffraction lines (not shown here), whereas stable compounds show less, but not absent, disorder like in all stable complex metallic alloys studied so far. For Mg d states, the values corresponding to the two Mg-Al-Zn cubic approximant alloys only slightly differ from each other, which gives confidence in our approximation. However, a more meaningful quantitative comparison between systems whose atomic structures are strongly different still remains a very difficult task and certainly cannot be achieved without theoretical modelling.

Conclusion

Our new SXES investigation of the Al $3s,d$ and Mg $3s,d$ partial DOS in a series of binary Al- and Mg-based compounds of varying complexity has focused at the s,d spectral distribution in a narrow range below the Fermi energy. It has featured that a significant amount of states with a d -like character exists

near, and just below, the Fermi energy in these complex compounds, and especially in the very complex β - Al_3Mg_2 phase. They are far more abundant in stable than in metastable counterparts, although similarities are exhibited in the local atomic environments. This issue suggests that localised states should form at E_F for a complex compound to be stable. At this point, it is clear that more work is needed, especially on Mg-based compounds, to ascertain our findings and possibly put our conclusions on a more quantitative basis.

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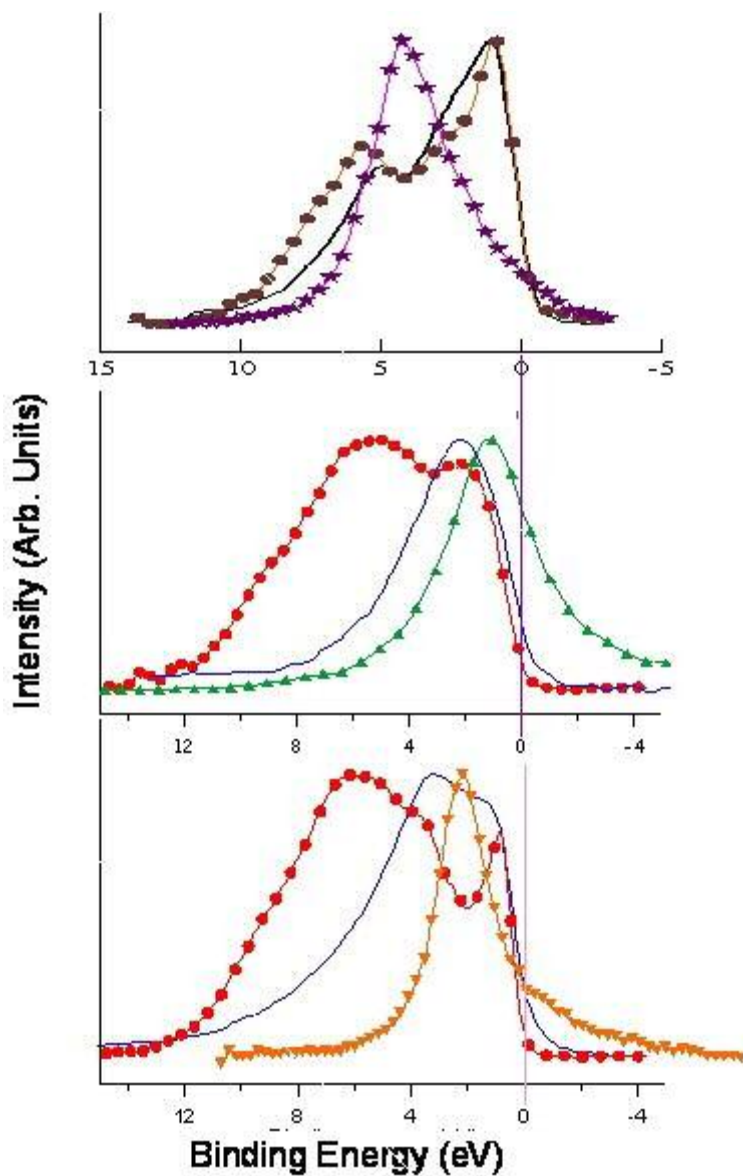
Figure Captions

Figure 1: From bottom to top, valence band of stable Al_3Ni , Al_3Fe and Al_2Cu . (Al $3p$ states: full line, Al $3s,d$ states: dotted line. Stars and triangles are for $3d$ distribution curves of Cu, Fe and Ni, respectively.

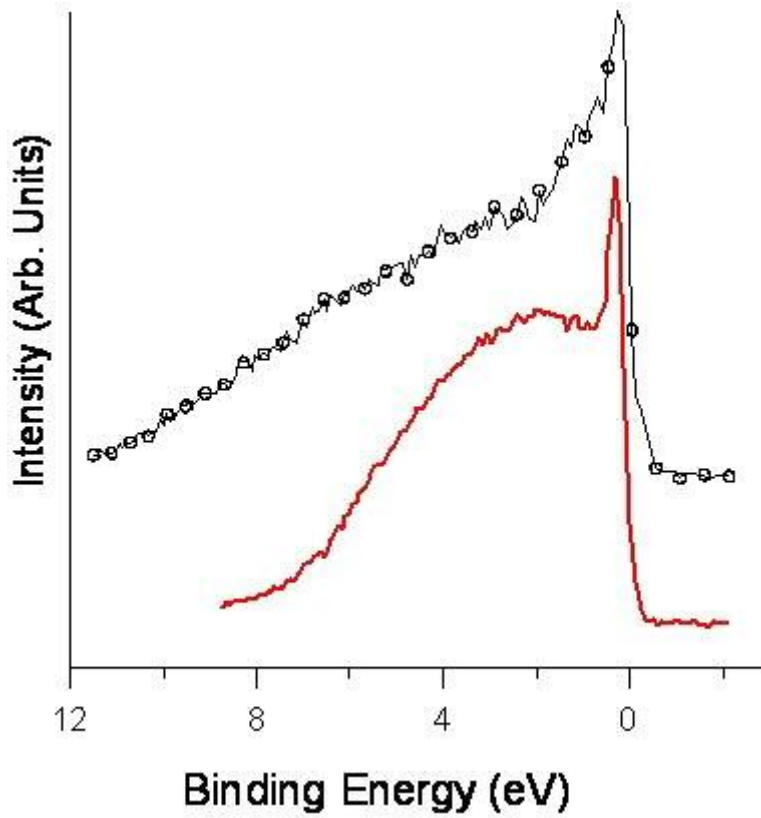
Figure 2: From bottom to top, $3s,d$ electronic distribution curves in hcp Mg and fcc Al.

Figure 3: From bottom to top, Al $3s,d$ electronic distribution curves in $\beta-Al_3Mg_2$, QP-Al-Mg, $Mg_{39.5}Al_{30}Zn_{30.5}$ and icosahedral $Mg_{43}Al_{15}Zn_{42}$.

Figure 4: From bottom to top: Mg $3s,d$ electronic distribution curves in $\beta-Al_3Mg_2$, QP-Al-Mg, the two crystalline alloys $Mg_{39.5}Al_{40}Zn_{20.5}$ and $Mg_{39.5}Al_{50}Zn_{10.5}$, as-quenched icosahedral $Mg_{43}Al_{15}Zn_{42}$ and in the Zn_2Mg Laves phase.

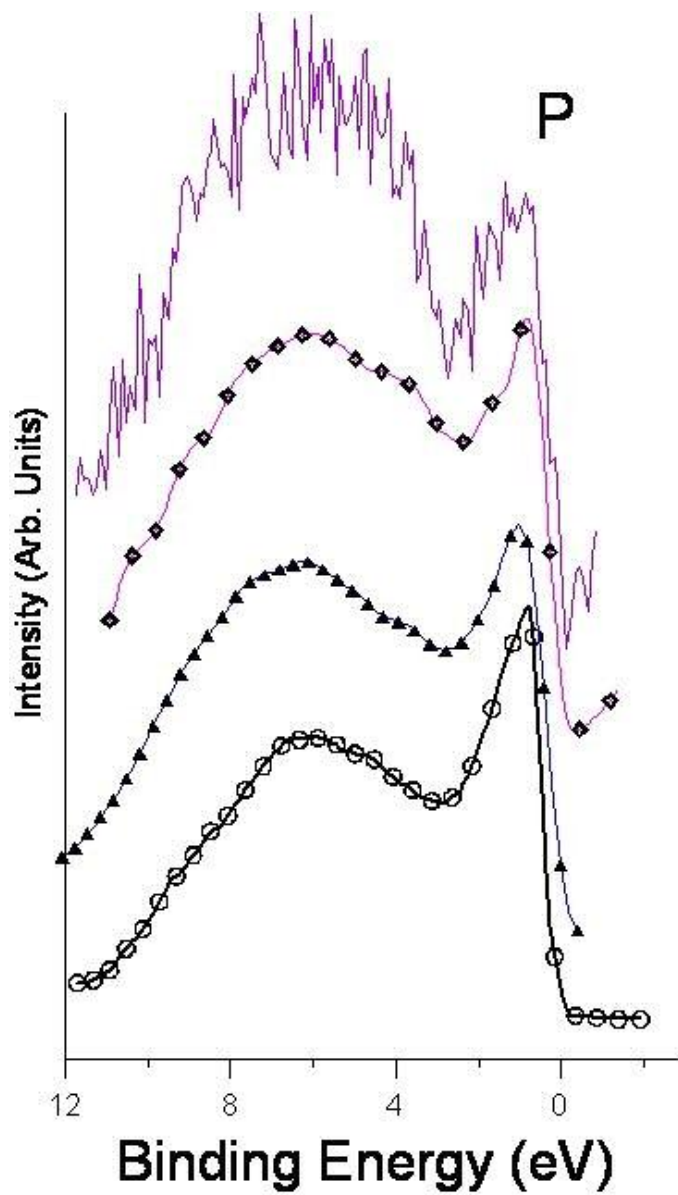


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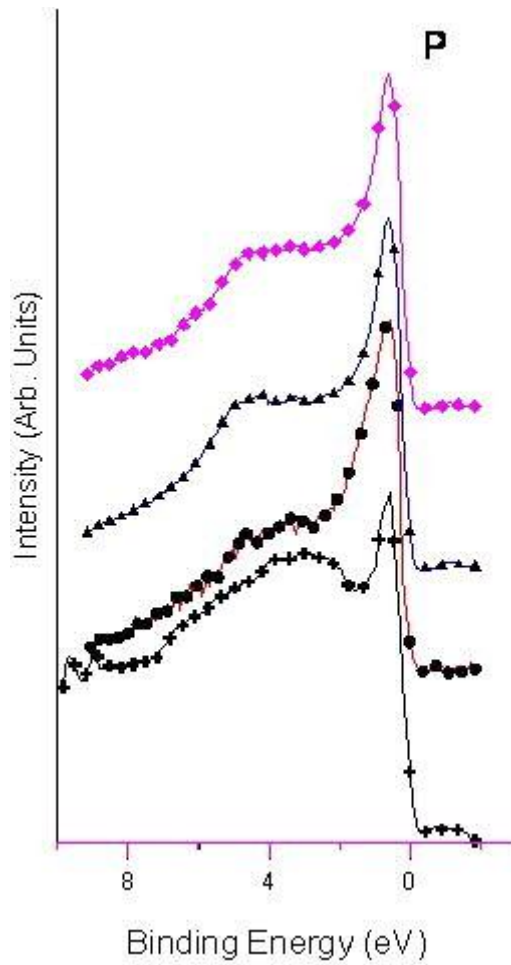
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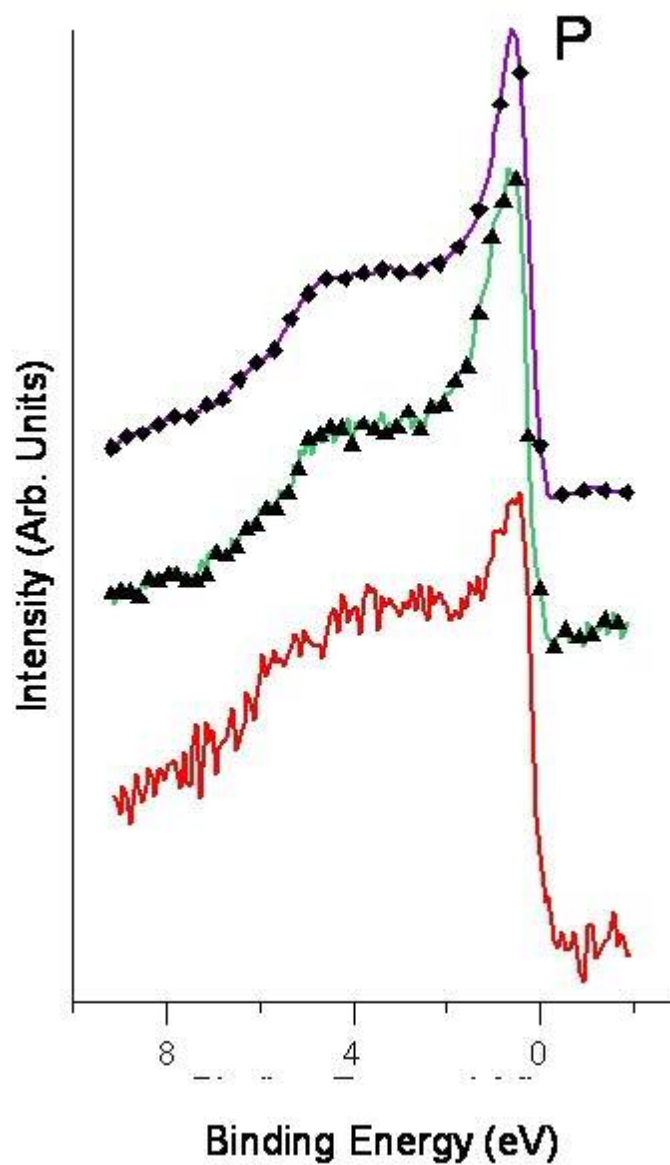
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