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On the formation of the d bands in alloys of simple metals with d metals

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Received 2 November 1992

Abstract. The problem of the formation of the d resonances in alloys of Mg and Al with a number of d metals (Ni, Cu and Zn) has been investigated both experimentally and theoretically. High-resolution ultraviolet photoelectron spectroscopy (UPS) spectra have been taken for these alloys and the electronic structure has been calculated by the linear muffin-tin orbital (LMTO) method, within the atomic sphere approximation. The theoretical results allow for the interpretation of the shapes of experimental spectra, while it turns out that the widths of the d bands can be described by the Friedel-Anderson model only qualitatively.

1. Introduction

The electronic structure of the alloys of d metals with simple metals is interesting not only because of the metallurgical importance of these materials (for instance Al-Ni or Al-Cu systems) but also because they can be regarded as models for the study of localized electron d states in a sea of nearly free electrons. It is of some interest to discover how far simple theories for the formation of these states can be relied upon for estimating the energy and widths of the d bands. High-resolution ultraviolet photoemission spectroscopy (UPS) measurements show that the d-band widths in Mg-M alloys (M=Ni, Cu, Zn) are consistently narrower than those in Al-M systems. This has been observed to be the case for dilute solid solutions of the d metals in simple metals as well as for pairs of intermetallic compounds containing similar high concentrations of Mg and Al.

We consider here whether the Friedel-Anderson model gives an adequate description of the differences between band structures of the compounds under investigation. The Friedel-Anderson model for virtual bound states is widely used to explain the observed widths of transition metals in different host crystals [1,2]. In this model the width of the d resonance is explained in terms of s-d scattering but in addition to this other effects (spin-orbit interaction, exchange splitting, final state lifetimes) may contribute to the width. We can study the effects of these different contributions on the d bands by making calculations of the local electronic structure

of the d-metal atoms in the simple metal atomic environment. In the present work we report the results of both experimental (UPS) and theoretical studies of the electronic structure of Mg-M and Al-M compounds. We have analysed the energy distribution of the valence electrons and tested the conformity of the calculated parameters to those obtained from the Friedel-Anderson model.

2. Experimental procedure

Sample of alloys were prepared by melting the pure constituents together in an argon arc furnace on a copper hearth. The compositions were determined by weighing the constituents before melting and the alloys after melting to establish the size of any weight loss due to evaporation. Magnesium evaporated to a small extent but the weight loss was never sufficient to change the composition by as much as 1 at.%. The alloys were homogenized by repeatedly inverting and remelting the ingots while in the furnace. Flat slabs were cut from the polycrystalline ingots.

Angle integrated photoelectron spectra were recorded in an ultraviolet-photoemission spectrometer with a hollow cathode helium discharge lamp and a 180° hemispherical analyser having a mean radius of 47.5 mm and an energy resolution of 0.1 eV FWHM. The specimens were cleaned by scraping the surfaces with a tungsten carbide blade under a vacuum of $< 5 \times 10^{-8}$ Pa in the spectrometer just before the photoemission spectra were recorded.

The spectra shown in this paper were excited by HeII radiation ($h\nu = 40.8$ eV) because the secondary electron background is much less than when using HeI light ($h\nu = 21.2$ eV) and the variations of cross section across the d-band spectrum is likely to be smaller. However, the binding energies and total widths of the narrow alloy d bands measured with HeI were not significantly different from the values found using HeII.

3. Calculations

Both Mg₂Cu and Al₂Cu have complicated crystalline lattices [3]. Al₂Cu has the tetragonal C16 structure with 12 atoms per unit cell whereas Mg₂Cu has an orthorhombic lattice with 48 atoms per unit cell. Band structure calculations for these compounds with the correct lattices would be excessively time consuming and instead we have calculated the electronic states in model crystals having simpler lattices: B2 (or CsCl type) and A1 (face centred cubic type) structures with two and four atoms per unit cell, respectively. The comparison of the results of our calculations with the band structure of Al₂Cu calculated in [4] suggests that the study of model crystals instead of real crystal structures is satisfactory for our purpose. Moreover, using the same crystal lattices for both the Mg and Al compounds has the advantage that we can study the electron-electron interactions without having to estimate the size of any changes due to differences in crystal structure.

We have calculated the density of states (DOS) of valence electrons in the MgCu and AlCu compounds (B2 structure) and in the Mg₃Cu and Al₃Cu compounds (A1 structure). The electron states in Mg₃Cu□ and Al₂Cu□ model compounds have also been calculated to compare with the experimental data for these compositions. The lattice structure of these model compounds is A1 with an empty lattice site (denoted

here by the symbol \square) in the cell as shown in figure 1. We will denote this structure by $A1'$. In $AlCu$ and $Al_2Cu\square$ model crystals each Cu atom is surrounded by eight atoms of Al as it is in real Al_2Cu . The lattice parameters for the model structures (table 1) have been chosen so that the average volumes per atom are equal to those in the real Mg_2Cu and Al_2Cu (0.0182 nm^3 for Mg_2Cu and 0.0149 nm^3 for Al_2Cu). This results in the distances from the Cu atoms to the nearest-neighbour Mg or Al atoms for the real lattice being between the corresponding values in model lattices. For example, in Al_2Cu the Al-Cu distance is equal to 0.2585 nm while in our model structures it is 0.2512 nm for $Al_2Cu\square$ ($A1'$) and 0.2688 nm for $AlCu$ ($B2$).

Table 1. Parameters of the lattice structure for the model compounds.

Compound	Lattice structure	Lattice parameter (nm)	Distance from the d atom to next neighbours (nm)	Volume of the unit cell Ω (nm^3)
$MgCu$	B2	0.3316	0.2871	0.0364
$Mg_2Cu\square$	$A1'$	0.3796	0.2684	0.0547
Mg_3Cu	A1	0.4178	0.2988	0.0729
$AlCu$	B2	0.3104	0.2688	0.0299
$Al_2Cu\square$	$A1'$	0.3553	0.2512	0.0448
Al_3Cu	A1	0.3910	0.2765	0.0598
$Mg_2Ni\square$	$A1'$	0.3719	0.2630	0.0514
Al_3Ni	A1	0.3884	0.2746	0.0586
Mg_3Zn	A1	0.4530	0.3203	0.0930
Al_3Zn	A1	0.4049	0.2863	0.0664

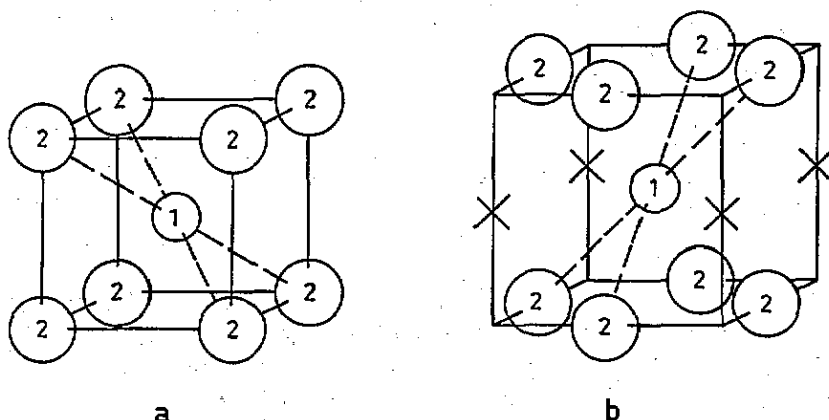


Figure 1. The unit cells of the B2 (a) and $A1'$ (b) lattice structures: 1, Cu atom; 2, simple metal atom. The symbol \times denotes the empty lattice site; in the A1 structure these sites are occupied by simple metal atoms.

Mg_2Ni has the hexagonal structure with 18 atoms per unit cell whereas Al_3Ni has an orthorhombic lattice with 16 atoms per unit cell. We have performed the calculations of the electron states for model crystals with cubic A1 structure. In the

case of the Al_3Ni model compound there are three Al atoms and one Ni atom in the unit cell. For Mg_2Ni one lattice site in the unit cell is empty (Al' structure). The lattice parameters for model structures (table 1) have been chosen so that the average volumes per atom were equal to those in real crystal structures (0.0171 nm^3 for Mg_2Ni and 0.0146 nm^3 for Al_3Ni). The electronic structure of the Al_3Ni compound has been calculated in [5] in order to investigate the electronic, magnetic and cohesive properties of some Ni–Al compounds. Because of the complexity of the crystal structure of the Al_3Ni compound, in that paper the calculations were performed by using the same cubic model structure as in our work. The results obtained in [5] suggest that in the case under consideration the study of model crystals instead of real ones is fairly reasonable.

In the case of Mg–Zn and Al–Zn systems the experimental photoelectron spectra have been obtained for dilute solid solutions with very small Zn content. For the calculations we have chosen the Mg_3Zn and Al_3Zn model compounds with Al crystal structure, in which each Zn atom is surrounded by 12 simple metal atoms, as in the case of dilute solutions. The lattice parameters for these model structures (table 1) have been chosen so that the average volumes per atom were equal to those of pure Mg and Al metals (0.0232 nm^3 for Mg and 0.0166 nm^3 for Al).

The electronic structure of the crystals has been calculated by the linear muffin-tin orbital (LMTO) method using the atomic sphere approximation (ASA) [6] and the exchange–correlation potential proposed in [7], which is suitable for strong localized electron states. The electron states were computed on a uniform mesh of 84 points in the irreducible part of the Brillouin zone. The calculations were fully relativistic. We have investigated the influence of the spin–orbit splitting on the energy distribution of the Cu d states in the Mg_2Cu compound. It can be seen from figure 2 that the effect of the spin–orbit interaction on the width of the band is small and can be neglected. In the other model crystals containing Cu and Ni the valence d band is broader, therefore the spin–orbit splitting was excluded from the calculations. In contrast, for the Mg–Zn and Al–Zn alloys the spin–orbit interaction is the most essential of the interactions which determine the width of the d bands, and in this case it is not possible to neglect it.

4. Discussion

4.1. Mg–Cu and Al–Cu alloys

The results of the calculations of the electronic structure of the Mg–Cu and Al–Cu model alloy systems are presented in figures 3–5 and in table 2. The calculations have also been performed for the Al–Cu compounds with the lattice parameters changed to be equal to those in the corresponding Mg–Cu compounds. These compounds are denoted in what follows by the symbol *.

We have defined the d-band width Δ_d as the full width at half intensity of the local partial DOS, broadened by convolution with a Gaussian with a σ of 0.3 eV. This allowed the results to be compared with the experimental spectra and Δ_d to be estimated without complications from the band fine structure. It can be seen that for all the lattice structures under consideration the Cu d bands in the Al–Cu alloys are wider and have lower energies (higher binding energies) than those in the Mg–Cu alloys. Increasing the lattice parameters in the Al–Cu compounds (the Al–Cu* case)

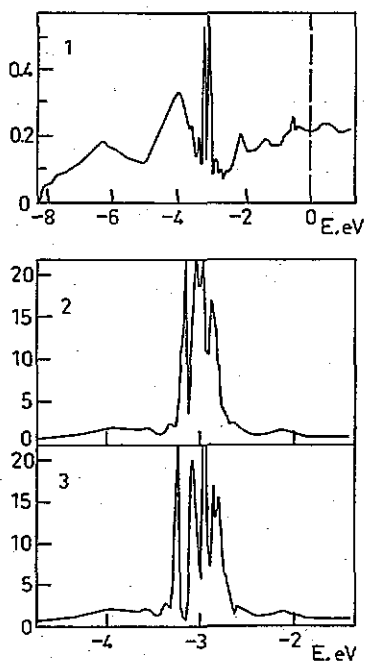


Figure 2. Local DOS in the Mg_2Cu model compound: Mg valence states (1) and Cu d states, calculated without (2) and with (3) spin-orbit interaction.

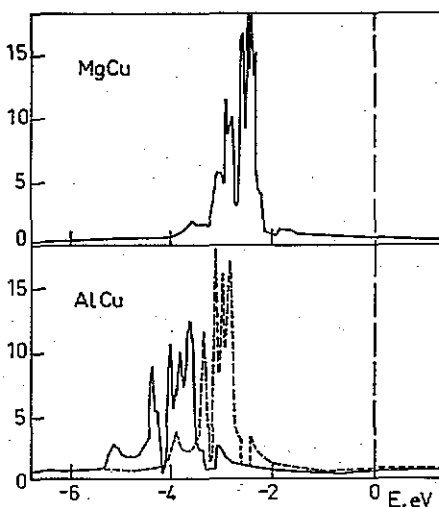


Figure 3. Valence DOS for the compounds with the B2 lattice structure. The broken curve represents the $AlCu^*$ DOS.

leads to a shift of the Cu d bands to higher energies. The d bands become narrower but all the features of the d-DOS fine structures are retained.

We now consider how well the Friedel-Anderson model explains the differences between the bands in the alloy systems under consideration. In this model the width of the resonant d state is given by

$$\Delta_d \sim |V_{kd}|^2 \bar{\rho}(\epsilon_d) \tag{1}$$

where $\bar{\rho}(\epsilon_d)$ represents the density of the nearly free electron (NFE) states at the energy of the d resonance and V_{kd} is the matrix element of the NFE-d-electron interaction. If we assume a constant average value of V_{kd} , the width of the d bands Δ_d is proportional to the NFE DOS. The direct estimation of $\bar{\rho}(\epsilon_d)$ from the calculated local DOS is difficult because the valence states of a simple metal at the energy of the d states are already redistributed owing to the NFE-d-electron interaction (see figure 2). For this reason $\bar{\rho}(\epsilon_d)$ has been estimated using the calculated parameters of the valence band, which are given in table 2, and assuming the $E^{1/2}$ dependence of the NFE energy distribution. Further we have assumed that all the electrons in the unit cell are nearly free except for the d electrons inside the d-metal atomic sphere. This NFE charge will be denoted by Q_{NFE} . Thus, the NFE DOS per unit cell is given by

$$n(\epsilon_d) = \frac{3}{2} Q_{NFE} (\epsilon_d - E_0)^{1/2} / (E_F - E_0)^{3/2}. \tag{2}$$

Note that the NFE DOSS per atom are very similar for all the compounds considered here although the parameters E_0 , ϵ and Q_{NFE} , used for their computation, are quite

Table 2. Calculated parameters of the electronic structure for the model compounds. E_0 , the bottom of the NFE band, and ϵ_d are referred to the Fermi energy E_F . Q_d is the d charge, Q_{NFE} is the NFE charge.

	Δ_d (eV)	E_0 (eV)	ϵ_d (eV)	Q_d	Q_{NFE}	Density of states		
						$n(\epsilon_d)$ (states eV ⁻¹ /unit cell)	$\bar{\rho}(\epsilon_d)$ (states eV ⁻¹ /atom)	$\bar{\rho}(\epsilon_d)$ (states eV ⁻¹ nm ⁻³)
Mg Cu	0.77	-7.83	-2.49 ^a	9.75	3.25	0.51	0.26	14.12
AlCu*	0.75	-9.77	-2.94 ^a	9.84	4.16	0.53	0.27	14.67
AlCu	0.96	-11.68	-3.72 ^a	9.79	4.21	0.45	0.22	14.93
Mg ₂ Cu□	0.59	-8.30	-3.03 ^a	9.63	5.37	0.77	0.26	14.14
Al ₂ Cu□*	0.80	-10.44	-3.35 ^a	9.64	7.36	0.87	0.29	15.93
Al ₂ Cu□	1.07	-12.06	-4.15 ^a	9.58	7.42	0.75	0.25	16.68
Mg ₃ Cu	0.64	-8.67	-3.05 ^a	9.76	7.24	1.01	0.25	13.83
Al ₃ Cu*	1.20	-11.25	-3.21 ^a	9.93	10.07	1.14	0.28	15.57
Al ₃ Cu	1.39	-13.36	-3.96 ^a	9.91	10.09	0.95	0.23	15.89
Mg ₂ Ni	0.86	-7.46	-1.39 ^a	8.81	5.19	0.94	0.31	18.33
Al ₃ Ni	1.61	-11.17	-2.30 ^a	8.87	10.13	1.21	0.30	20.69
Mg ₃ Zn	0.52 (0.24 ^b)	-7.12	-8.09 ^c -7.73 ^d	10.03	7.97	0.0	0.0	0.0
Al ₃ Zn	0.60 (0.32 ^b)	-10.86	-7.98 ^c -7.62 ^d	10.09	10.91	0.78 ^c 0.82 ^d	0.19 ^c 0.21 ^d	11.68 ^c 12.41 ^d

^a ϵ_d is the centroid energy for Cu and Ni d bands.

^b for each component of spin-orbit doublet.

^c for $d_{3/2}$ component.

^d for $d_{5/2}$ component.

different. For each lattice structure the Al-Cu* alloys have the biggest value of $n(\epsilon_d)$. This is because increasing the lattice parameter in the Al-Cu alloys leads to a decrease of the width of the NFE band ($E_F - E_0$) but Q_{NFE} is practically unchanged.

The DOS per unit volume has been calculated from

$$\bar{\rho}(\epsilon_d) = n(\epsilon_d)/\Omega \quad (3)$$

where Ω is the volume of the unit cell. From table 2 it can be seen that for all lattice structures the value of $\bar{\rho}(\epsilon_d)$ for Al-Cu alloys exceeds that for Mg-Cu alloys and the value of Δ_d for the Al-Cu alloys is also larger than for Mg-Cu alloys, as predicted by the Friedel-Anderson model.

Let us now consider the dependence of Δ on $\bar{\rho}(\epsilon_d)$ in more detail. In figure 6 the calculated results for the compounds with the A1' structure are compared with the experimental data ($\Delta_d = 0.84$ eV for Mg₂Cu and 1.24 eV for Al₂Cu). The slope of the lines relating Δ_d to $\bar{\rho}(\epsilon_d)$ for the calculated and measured values are similar. The corresponding lines for the calculations on the lattice structures B2 (MgCu→AlCu) and A1 (Mg₃Cu→Al₃Cu) have higher slopes than that for the A1' structure, i.e. the slope of the line is higher for the lattice structures with larger distances between Cu and its next-nearest neighbour Cu.

We can use the calculated values to consider the transition from the Mg-Cu compounds to the Al-Cu compounds in two steps: (1) all Mg atoms in the Mg-Cu

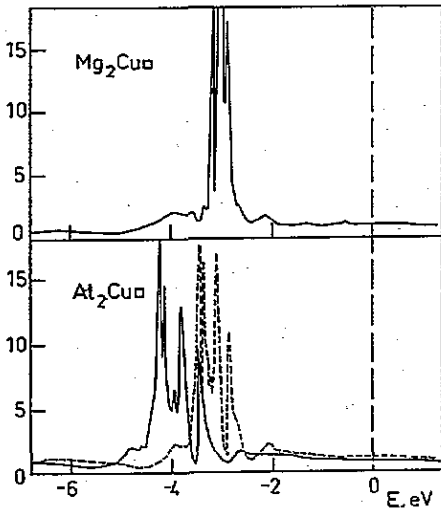


Figure 4. Valence DOS for the compounds with the Al' lattice structure. The broken curve represents the $\text{Al}_2\text{Cu}\square^*$ DOS.

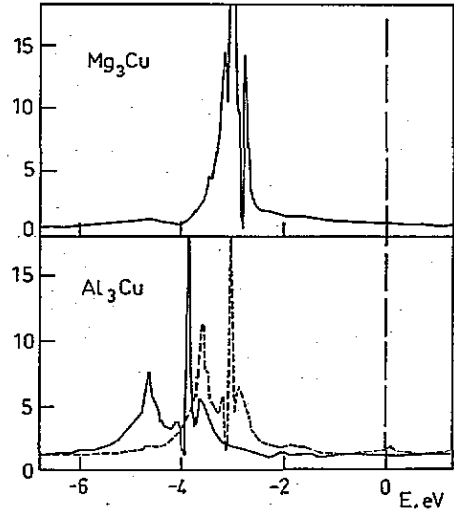


Figure 5. Valence DOS for the compounds with the Al lattice structure. The broken curve represents the Al_3Cu^* DOS.

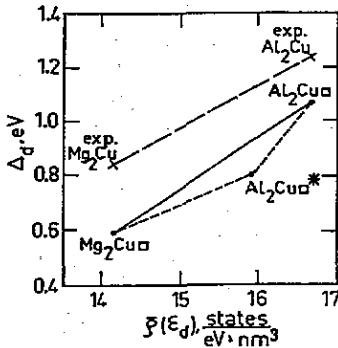


Figure 6. Cu d band width Δ_d versus electron density $\bar{\rho}(\epsilon_d)$.

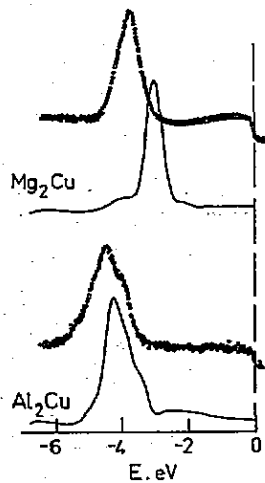


Figure 7. Comparison of the calculated DOS (full curve) with the experimental UPS spectra (dots).

compound are replaced by Al atoms ($\text{Mg-Cu} \rightarrow \text{Al-Cu}^*$) and (2) the crystal lattice is compressed ($\text{Al-Cu}^* \rightarrow \text{Al-Cu}$). In figure 6 the point for $\text{Al}_2\text{Cu}\square^*$ lies under the line connecting the points for $\text{Mg}_2\text{Cu}\square$ and $\text{Al}_2\text{Cu}\square$. A similar result is obtained for other lattice structures. This shows that the compression of the lattice has a stronger influence on the width of the Cu d band than the substitution of Mg by Al.

The calculated results deviate from the proportionality predicted by the Friedel-Anderson model. This deviation can be explained by the inhomogeneity of the distribution of the local electron density in the crystal. The first step, substitution of Mg by Al, causes an increase in the electron density near the simple metal sites

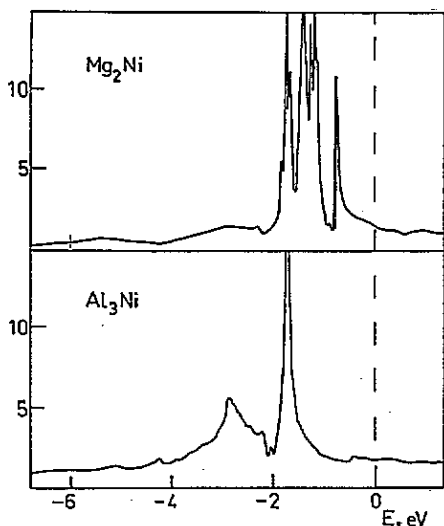


Figure 8. Valence DOS for the model compounds Mg_2Ni and Al_3Ni .

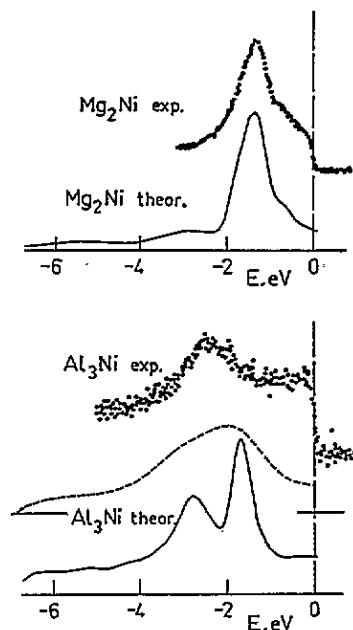


Figure 9. Comparison of the calculated DOS (full curve) with the experimental UPS spectra (dots) for the simple-metal-Ni alloys. The broken curve represents the calculated DOS broadened by convolution with a Gaussian with a σ of 0.9 eV.

(screening of the additional positive charge) whereas the second step, compression of the lattice, raises the local NFE density near the Cu sites (superposition of the tails of the distributions of the simple metal electrons). It should be noted (see table 2) that the contribution of the first step to the broadening of the Cu d band increases with increasing simple metal content (i.e. from $MgCu$ to Mg_3Cu).

The calculated DOS for the Mg_2Cu and Al_2Cu model compounds are compared with experimental UPS spectra obtained for the Mg_2Cu and Al_2Cu compounds in figure 7. In order to compare the valence DOS with the UPS spectra we have assumed that the shape of the Cu d peak is not significantly modified by the photoemission cross-section effects. It can be seen that the calculated results reflect the shape of the energy distribution of the valence electrons in Mg_2Cu and Al_2Cu compounds quite well. There are only small differences of the calculated binding energies of the Cu d peaks from those obtained experimentally (for Al_2Cu the experiment gives 4.55 eV while the calculated value is 4.15 eV). Previously published results of calculations underestimate the binding energies: 3.7 eV for the Al_2Cu compound in [4] and about 3.1 eV for Cu impurity in Al in [8, 9].

4.2. Mg-Ni and Al-Ni alloys

The calculated valence DOS for the Mg_2Ni and Al_3Ni model compounds are presented in figure 8. One can see high and sharp peaks of Ni d states on the background of the smooth density of the NFE states. The Ni band in the Mg-Ni alloy is located at energies between -1 and -2 eV and has a fine structure (many narrow peaks on the d DOS). In the Al-Ni alloy the Ni d states are shifted towards energies lower

than those in Mg-Ni alloys and there is not a fine structure similar to that of the latter systems. The energy distribution of the d states forms a two-peak DOS: a wide low-energy peak and an intense narrow high-energy peak. This result is in excellent agreement with the DOS obtained in [5], where the augmented-spherical-wave method has been used.

In order to compare the experimental spectra with the calculated DOSS, the latter have been broadened by the Gauss curve with a 0.3 eV parameter. As it can be seen from figure 9, for Mg₂Ni the calculated width and energy position of the d resonance are in accordance with the experimental data. The broadened theoretical DOS presents the main peak at an energy of -1.4 eV with a shoulder on the high-energy side, caused by the narrow peak which is separated from the rest of the Ni d states. All these features are present in the UPS spectrum. In contrast, for the Al-Ni compound the broadened DOS keeps its double-peak shape which is not observed in the UPS spectrum. We could attempt to explain this discrepancy by the decreased energy resolution because of a poor signal-to-noise ratio for the Ni d band. However, we can remove the double-peak structure of the calculated DOS only by increasing the broadening parameter by a factor of three (figure 9), and we do not believe that such a drastic reduction of the energy resolution takes place. Another possible explanation for the discrepancy could be a transition probability effect which could modify the DOS curve, in particular by reducing the high-energy peak intensity. In that case we should have to explain why that effect does not influence the shape of the Ni d DOS in the Mg-Ni alloy. Thus an additional study would be needed to explain that discrepancy.

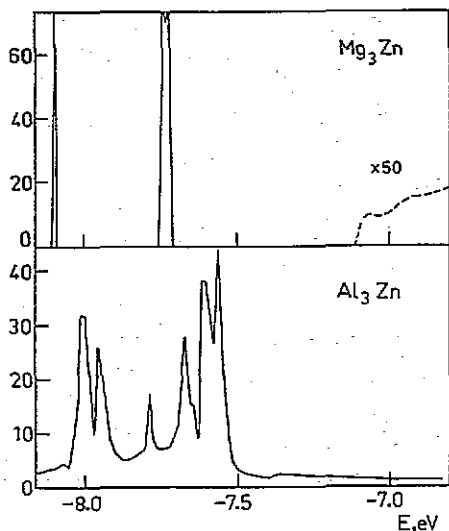


Figure 10. Valence DOS for the model compounds Mg₃Zn and Al₃Zn. The broken curve represents the bottom of the Mg s-p band.

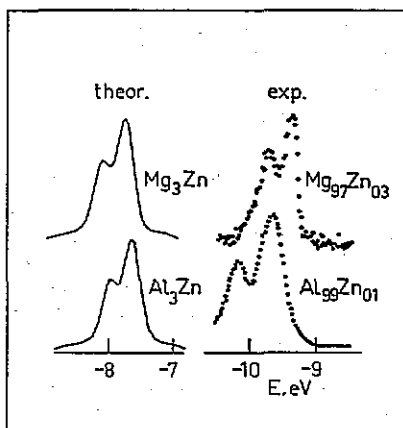


Figure 11. Comparison of the calculated DOS (full curve) with the experimental UPS spectra (dots) for the simple-metal-Zn alloys.

Let us consider the width of the Ni d band in connection with the density of the NFE states in which those localized d states are embedded (see table 2). It can be noted that the values of the NFE DOS per atom, $n(\epsilon_d)$, are very close for both

the compounds under study. Moreover, they exceed the corresponding values for the alloys containing Cu atoms, because of the higher energies of Ni d states.

From table 2 it can be seen that for Al-Ni the values of both Δ_d and $\bar{\rho}(\epsilon_d)$ are larger than those for Mg-Ni. However, Δ_d for the Al-Ni alloy exceeds the corresponding value for the Mg-Ni alloy by a factor of two, whereas the difference in values of $\bar{\rho}(\epsilon_d)$ is only of the order of 10%. The experimental d-band widths are 0.73 and 1.12 eV for Mg-Ni and Al-Ni alloys, respectively, so that the difference between these values is also quite large. Thus, consideration of the Δ_d and $\bar{\rho}(\epsilon_d)$ values shows that we cannot speak about a proportionality between these two quantities. We suppose that this deviation from the Friedel-Anderson model is connected with the interaction between d states localized on different Ni atoms in the compound, which has to be taken into account in addition to the s-d interaction already included in that model. In this case, speaking about virtually bound d states is quite rough, because there are in the crystal d bands with their energy structure. The Cu atoms have d states which are more localized than those of Ni atoms, and this explains the better agreement with the Friedel-Anderson model presented by the results for Cu alloys.

4.3. Mg-Zn and Al-Zn alloys

From figure 10 one can see that in the Mg-Zn alloy the d states lie under the bottom of the NFE band and thus they must not be broadened because of the s-d interaction. The calculated electronic structure of the Mg_3Zn compound shows the narrow atomic-like Zn d levels, and there is no broadening due to the interaction of d states from different Zn atoms. It is evident that the d states in Zn are strongly localized and the model compounds Mg_3Zn and Al_3Zn may be used for the description of the electronic structure in dilute solid solutions with a slight Zn content. In the Al-Zn alloy the Zn d states are embedded into the NFE band and the s-d interaction leads to the broadening of the d levels (it cannot be excluded that the indirect interaction between d states from different Zn atoms could also contribute to the broadening). It can be seen from the results of the calculations that the spin-orbit splitting of Zn d states is equal to 0.36 eV. This value is influenced very little by the local atomic environment and it is very close to the free ion value, which for Zn amounts to 0.34 eV.

It must be taken into account that the total (unresolved) d width is determined by the value of the spin-orbit splitting. If we consider separately the components of the doublet, the value of Δ_d , as defined before, is mostly determined by the spectrometer energy resolution (see table 2). Under this condition it remains to study the widths of the calculated doublet components shown in figure 10. For Al-Zn alloy the estimated values are 0.10 eV for the $d_{3/2}$ component and 0.13 eV for the $d_{5/2}$ one and the approximate proportionality of these values to the values of $\bar{\rho}(\epsilon_d)$ given in table 2 may be supposed.

The theoretical and experimental results obtained for Mg-Zn and Al-Zn alloys are compared in figure 11. It can be seen that the shape of the calculated d peaks in the Mg-Zn alloy agree very well with the experimental UPS spectrum. This cannot be said about the results for Al-Zn alloy: the experimental spectrum has a larger width (0.88 eV) than the calculated one, although the width of each component of the spin-orbit doublet (0.36 eV) is in agreement with the calculated results. The discrepancy is caused by the difference between the experimental value of the spin-orbit splitting, which is 0.51 eV, and the calculated one, which is 0.34 eV. Another

significant discrepancy between experimental and theoretical results is due to the energy location of the d states. Here the differences in the binding energy are of the order of 2 eV. The underestimation of the binding energy of the localized electron states has been mentioned above for the calculated Cu d states. For the Zn d electrons this effect is more essential, because of the stronger localization of the Zn d states with respect to those of Cu. It has to be noted that other published calculations for the Al-Zn system underestimate the binding energy of the Zn d states (7.6 eV in [8] and 6.9 eV in [9] for Zn impurity in pure Al metal). These systematic errors are caused by the local-spin-density approximations for exchange and correlation which are used in most of the electron structure calculations. The values of the calculated binding energies can be improved if one includes the self-interaction corrections in the self-consistent one-electron potential [7], but this would lead to the difficulty of having an orbital-dependent potential.

5. Conclusions

We have calculated the electronic structure of the Mg-M and Al-M (M=Ni, Cu and Zn) model alloys using the LMTO-ASA method. On the basis of the theoretical results it is possible to interpret the shape of the experimental UPS spectra and to explain the processes of formation of the narrow d band in alloys with a high concentration of simple metals. The width of the Cu d states can be described by the Friedel-Anderson model only qualitatively. For each lattice structure considered the increase of the average DOS $\bar{\rho}(\epsilon_d)$ is accompanied by the increase in the width of the d band Δ_d , but the proportionality predicted by the Friedel-Anderson model is not confirmed by the results of our calculations. The electron density in the crystal could be changed by different effects: the variation of the lattice parameter, the change of the type of the host simple metal or its concentration. All these effects have a different influence on the d-band width, because they lead to different modifications of the local electron density, either near the simple metal site and/or near the d-metal site. Thus, the inhomogeneity of the valence electron distribution must be taken into account for a correct quantitative description of the real metal alloys.

The calculated results for the model compounds with A1' structure ($\text{Mg}_2\text{Ni}\square$, $\text{Mg}_2\text{Cu}\square$ and $\text{Al}_2\text{Cu}\square$) show the best agreement with the experimental spectra. They give us the energy location of the d band and even the valence DOS fine structure correctly.

The Friedel-Anderson model, which describes the dependence of the width of the d states on the density of the NFE states at the energy of the localization of the d resonance, could be confirmed for the Zn containing alloys. For the Mg_2Ni and Al_3Ni compounds the proportionality between Δ_d and $\bar{\rho}(\epsilon_d)$, predicted by this model, cannot be supposed because of a large degree of interatomic d-d interaction, leading to the formation of the energy structure of the d band.

The methods mostly used for calculation of the energy structure in crystals give underestimated binding energies for the localized electron states. This is caused by the local approximations for the exchange-correlation potential used in the calculations. It is the reason for the discrepancies in the energy location of the d states in the Mg-Zn and Al-Zn alloys. The theoretical results could be improved by using the orbital-dependent potential which takes into account the self-interaction corrections.

Acknowledgments

This research was supported by a twinning contract between the Universities of Liverpool, Groningen and Messina, awarded under the EC Stimulation Action Programme.

We are deeply indebted to Professor P Weightman for many helpful discussions and suggestions.

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