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High d-band occupancy in alloys of Mg with some 4d and 5d transition metals: a photoemission study

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Abstract. Photoemission data from co-sputtered films of binary alloys of Ru, Rh, Pd, Ir, Pt and Au with Mg show that the transition metal (TM) d band narrows as the TM concentration is reduced, reaching a minimum after which the intensity decreases but the width remains constant. The continuity of binding energy, spin–orbit splitting and width of the resulting d states suggests a high level of d-band occupancy in all cases. LMTO bandstructure calculations for pure TM and ordered intermetallic compounds of the form MgTM and Mg_3TM also show narrowing of the d bands, with binding energies and widths which indicate that they are fully, or nearly fully occupied in all cases where the TM is dilute. We suggest that the additional d intensity results from a spread of the TM d wavefunctions on to the surrounding Mg sites, allowing high d-band occupancy whilst preserving charge neutrality.

1. Introduction

Magnesium forms a wide range of ordered intermetallic compounds with the 4d and 5d transition metals (TM). Where the TM is dilute the resulting crystal structures are often complex, for example the Mg_{44}TM structure [1, 2] found in the Mg–Rh, Mg–Ir and Mg–Ru systems, and have extremely short Mg–TM separations, of the order of 2.7 Å. In addition the Mg–Mg separation is usually less than the value of 3.2 Å found in HCP Mg, typically around 3.0 Å on average. For all phases where the TM concentration is less than or equal to 50 at.% the TM sites are completely surrounded by Mg sites, with the TM atoms well separated.

The electronic structure of intermetallic compounds of Mg with 4d and 5d TM has been little studied, either experimentally or theoretically. Alloys of Pd [3] and Ag [4] in Mg were studied by Weightman and Andrews using x-ray excited photoemission (XPS) and Auger spectroscopies. Their primary interest was in evolution of the Pd and Ag $M_{4,5}N_{4,5}N_{4,5}$ Auger lineshapes as the TM concentration was reduced, but their XPS valence band spectra are of interest since they showed very narrow d states in cases where the TM was dilute. Similar behaviour was observed by Fuggle *et al* [5] in an XPS study of a series of Mg–Au alloys. The Fermi surfaces of MgAg [6]

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and MgAu [7] were studied by Dunsworth *et al* using de Haas–van Alphen (dHvA) measurements and linear muffin tin orbital (LMTO) bandstructure calculations. Their calculations showed some degree of narrowing of the Ag and Au d bands, and Fermi surfaces in good agreement with experiment. A symettrized augmented plane wave (SAPW) bandstructure calculation for MgY, of interest as the electronic structure will be similar in other Mg–rare-earth compounds, has been reported by Schmitt *et al* [8].

In this paper we report a combined experimental and theoretical study of the electronic structure of intermetallic compounds of Mg with the 4d TM Ru, Rh, Pd and Ag, and the 5d TM Ir, Pt and Au. Experimentally we have used UV photoemission to study the d-band widths and binding energies as the TM concentration is reduced, with particular interest in the limiting cases where the TM is dilute. In addition we have performed self-consistent LMTO bandstructure calculations for pure TM, and two intermetallic Mg–TM compounds: MgTM and Mg_3TM. The complexity of the crystal structures for TM concentrations less than 24 at.% prevents calculations being performed for the more dilute TM compounds, but we were at least able to follow the trends in bandwidth and binding energy down to reasonably low concentrations.

2. Photoemission experiments

The UV photoemission experiments were performed in a diffusion and titanium sublimation pumped vacuum system, consisting of an experimental chamber and a preparation chamber connected via a gate valve, with a base pressure $< 5 \times 10^{-11}$ mbar. HeI radiation ($h\nu = 21.2$ eV) was produced by a hollow cathode gas discharge lamp and the spectra were recorded using a hemispherical electron energy analyser (of radius 45 mm)incorporating an input lens, both of our own construction. The energy resolution was of the order 0.1 eV.

The normal preparation of magnesium intermetallic compounds involves heating the constituents together in a silica ampoule. The resulting solid, being very brittle, is very difficult to clean by mechanical scraping under UHV conditions to provide a suitable surface for photoemission spectroscopy. The alternative method, argon ion bombardment followed by annealing (to remove embedded argon), is also unsuitable since this is likely to lead to problems with preferential surface segregation of one or the other of the components. For this reason the samples were prepared *in situ*, as co-sputtered films [9], in the preparation chamber of the spectrometer. Samples of the constituents ($\sim$ 7 mm in diameter) were mounted 15 mm apart, 25 mm above a polished metal substrate. Alloy films were formed by running a discharge to the two cathodes simultaneously, in an argon atmosphere of $\sim 5 \times 10^2$ Pa for $\sim$ 30 min. The titanium sublimation pump in the preparation chamber was fired immediately before the introduction of the argon, in order to clean the Ar of any reactive contaminants. Since Mg forms a wide range of ordered intermetallic compounds with all the TM studied it is likely that polycrystalline films were formed rather than glasses, although it was not possible to confirm this. Film composition was controlled by varying the ratio of sputter currents (of order 50 μA) to the two cathodes, which enabled the production of steadily more dilute alloys of TM in Mg, although the exact composition of any particular film remained unknown. The films with the lowest TM concentrations presumably consisted of a Mg matrix containing precipitates of the intermetallic with the lowest TM:Mg ratio as, with the exception of Ag, solid solutions of these metals in Mg have not been found [10]. For the TM studied these intermetallics are Mg_3TM

(TM ≡ Au,Ag), Mg_6TM (TM ≡ Pt,Pd) and $Mg_{44}TM_7$ (TM ≡ Ir,Rh, Ru), and we assume that in the dilute limit we are performing measurements on these compounds, with the possible exception of MgAg.

After preparation the films were transferred to the experimental chamber without breaking vacuum. Photoemission spectra of the valence band were recorded for up to one hour after transfer to minimize the effects of contamination, as Mg alloys react readily with the common UHV residual gases [4]. Wider scans were recorded afterwards to enable an estimate of contamination levels to be made by monitoring the intensity of the oxygen 2p-derived feature at ~ 6 eV binding energy. In all cases we estimate contamination levels after one hour to be < 0.15 monolayers.

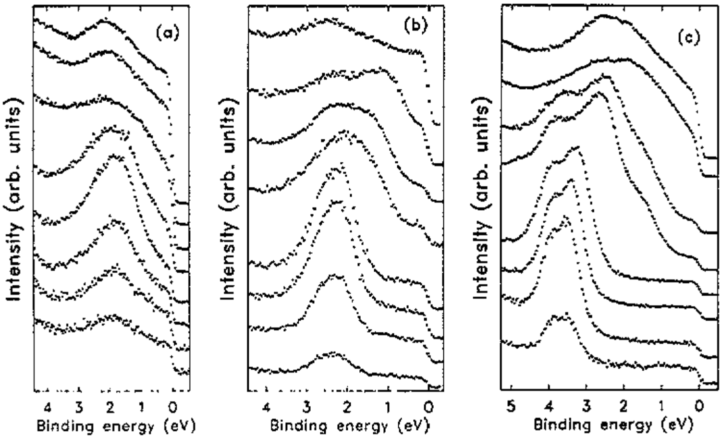

Figure 1. UV photoemission spectra ($h\nu = 21.2$ eV) of TM (top) and successively more dilute Mg–TM alloys, where TM ≡ (*a*) Ru, (*b*) Rh and (*c*) Pd.

UV photoemission spectra of the valence bands of Ru, Rh, Pd and successively more dilute alloys with Mg are shown in figure 1. In all three cases the TM d bands narrow, reaching a minimum width after which their intensity reduces relative to the background (which comprises emission from sp bands, and inelastically scattered and secondary electrons). The spin–orbit splitting of the resulting state is visible in MgPd but is too small to resolve in either MgRu or MgRh. The same behaviour is seen in the spectra of Ir, Pt and Au and successively more dilute alloys with Mg, shown in figure 2. The spin–orbit splitting in 5d TM is greater than in 4d TM and so is visible in all three of the TM d states in figure 2: note in particular that the splitting converges to atomic values (table 2), and that that of the Ir d bands remains visible even down to the dilute limit. The MgAu and MgPd data are in good agreement with XPC results of Fuggle *et al* [5] and Weightman and Andrews [3] respectively, although in the latter case the greater intrinsic linewidth of Al x-rays (compared to HeI radiation) meant that they were unable to resolve the spin–orbit splitting. The binding energies and widths of the d-state observed in all the limiting cases, i.e. where the width had reached a minimum, are plotted in figure 3. We also measured alloys of Mg and Re, but in this case the d bands remained broad, reducing in intensity as the Re concentration was reduced but not forming a narrow state.

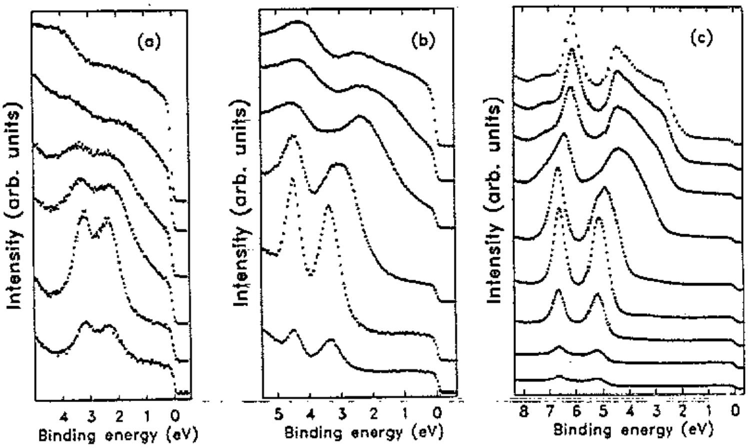

Figure 2. UV photoemission spectra ($h\nu = 21.2$ eV) of TM (top) and successively more dilute Mg–TM alloys where TM $\equiv$ (*a*) Ir, (*b*) Pt and (*c*) Au.

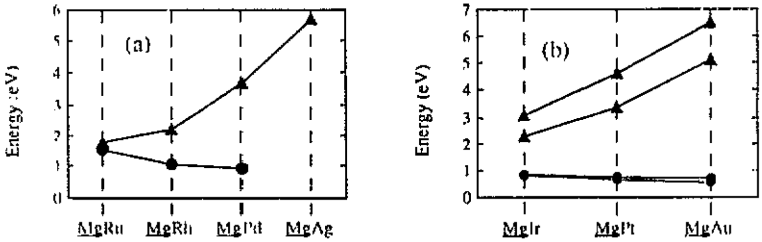

Figure 3. Binding energies (triangles) and FWHM (circles) of (*a*) the 4d and (*b*) 5d TM d states. The binding energy for Mg–Ag is taken from [4]: its FWHM is not shown as it was measured with different instrumental resolution. The spin–orbit splitting of the 4d states has been ignored in measuring the FWHM.

3. Bandstructure calculations

Self-consistent bandstructure calculations were performed using the LMTO method with the atomic sphere approximation (SCF-LMTO-ASA) [11] on the Convex C-220 at Daresbury Laboratory, UK. The atomic sphere approximation (ASA) replaces the Wigner–Seitz polyhedra of the solid with *overlapping* spheres, whose volume is equal to that of the Wigner–Seitz polyhedra. Relativistic effects were included at the level of the Pauli equation (i.e. the mass–velocity, Darwin and spin–orbit terms were included but the full Dirac equation was not solved), and the von Barth–Hedin exchange–correlation potential [12] was employed. For the transition metal calculations the observed room-temperature crystal structures and experimental lattice parameters were used. The MgTM calculations were performed using the CsCl crystal structure which occurs in the majority of these systems (see table 1), minimizing the total energy with respect to the Wigner–Seitz (WS) radius of the atomic spheres to obtain a theoretical lattice parameter. The Mg_3TM calculations used the Na_3As structure (figure 4) which occurs for some of the Mg–TM combinations (see table 1) but, as it has the TM sites surrounded by Mg atoms, was considered to reasonably model the TM coordination for all the systems studied. The complexity of the Na_3As structure

(8 atoms per unit cell) meant that these calculations took ~ 800 min CPU time to perform (cf 34 min CPU for the CsCl structure), thus it was not realistic to attempt to minimize total energy. As a result the experimental WS radii were used where available, with estimated values for the other combinations (figure 5). Because of the very long calculation times required for structures with a large number of atoms per unit cell we were unable to perform calculations for any of the more dilute compounds.

Table 1. Occurrence and lattice parameters of the CsCl and Na_3As structures found in late series 4d and 5d TM intermetallics with Mg. References are in square brackets.

	Structure		
	CsCl	Na_3As	
TM	a (Å)	a (Å)	c (Å)
Ag	3.297 [6]		†
Pd	3.160 [13]	4.613	8.410 [13]
Rh	3.099 [14]		†
Ru	†		†
Au	3.251 [7]	4.64	8.46 [15]
Pt	†	4.577	8.322 [16]
Ir	†	4.549	8.229 [17]

† Not naturally occurring.

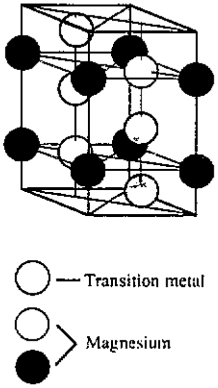

Figure 4. The Na_3As structure used for the Mg_3TM calculations.

The experimental and theoretical lattice parameters for the MgTM compounds (except MgY) are plotted as figure 6. The good agreement suggests that the bonding in these compounds is well described by the calculations. For MgY the experimental and theoretical values were 3.78 Å and 3.79 Å respectively. The energy bands and density-of-states (DOS) of MgY were very similar to the SAPW results of Schmitt *et al* [8], with separate d states formed above and below the Fermi level.

The DOS produced in the calculations are shown in figure 7 (4d TM and Mg compounds) and figure 8 (5d). The same trends as were seen in the experimental data are also visible in these results, i.e. as the TM becomes more dilute the d bands

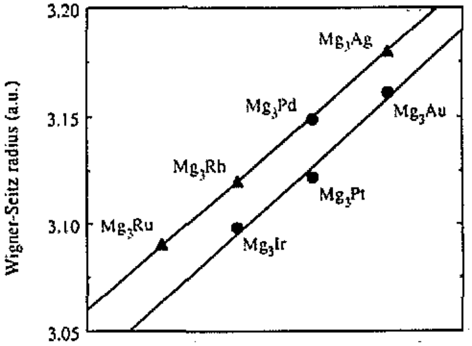

Figure 5. Wigner–Seitz radii used for Mg_3TM calculations: circles are experimental values, triangles are estimated values.

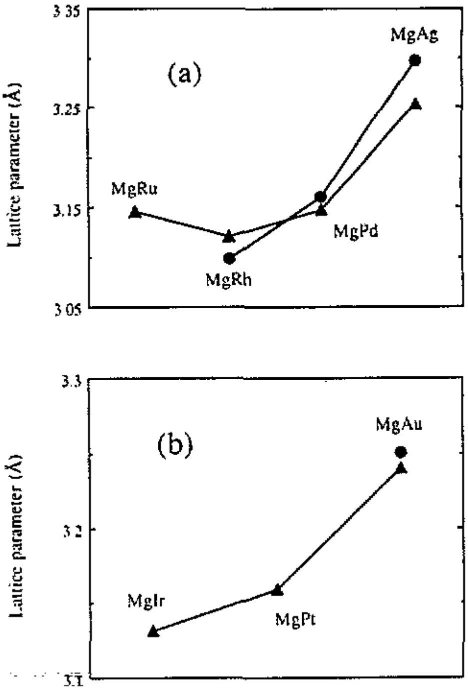

Figure 6. Expermental (circles) and theoretical (triangles) lattice parameters for (*a*) some 4d and (*b*) some 5d MgTM intermetallic compounds.

Table 2. Comparison of the spin–orbit splitting of the TM d states in MgTM with the values for atomic TM. References are in square brackets.

TM	Theory [18]	Atomic [19]	MgTM
Au	1.76	1.52	1.5
Pt	1.49	1.26	1.2
Ir	1.27	—	1.0
Ag	0.65	0.55	† [4]
Pd	0.57	0.44	0.5
Rh	0.43	0.29	†
Ru	0.35	—	†

† Not resolved.

narrow, with the binding energy and width of the d states for a given structure increasing as the atomic number of the TM increases.

4. Discussion and conclusions

Since the narrow states seen in the dilute limit evolve continuously from the TM d bands as the TM concentration is reduced, we believe we are justified in identifying them as d states. The binding energy and linewidth vary smoothly with atomic

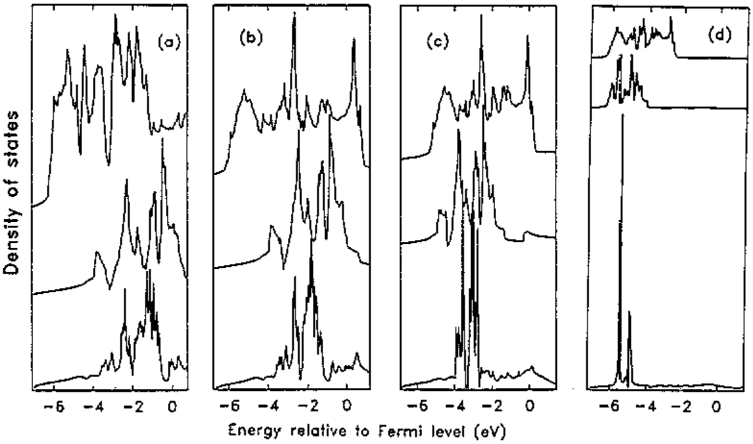

Figure 7. LMTO densities of states for TM (× 8, top), MgTM (× 4, middle) and Mg_3TM (bottom) where TM ≡ (*a*) Ru, (*b*) Rh, (*c*) Pd, (*d*) Ag.

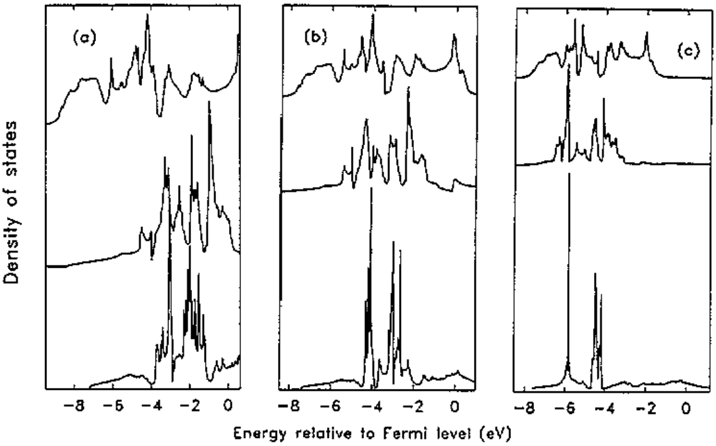

Figure 8. LMTO densities of states for TM (× 8, top), MgTM (× 4, middle) and Mg_3TM (bottom) where TM ≡ (*a*) Ir, (*b*) Pt, (*c*) Au.

number, and this variation is similar for the 4d and 5d alloy series. In the spectra of 5d alloys corresponding to the lowest TM concentrations the d states are clearly seen to be doublets, with splittings corresponding to the atomic spin–orbit splittings. The same is also true of MgPd, and it seems reasonable to suggest that the d states for the other dilute-limit 4d alloys are also doublets, with the splittings unresolved as they are too small relative to either their widths (in MgRh and MgRu) or the experimental resolution (in MgAg [4], measured by XPS). The calculated DOS show that the results are in good agreement with band theory. Even though, with the exceptions of Mg_3Au and Mg_3Ag, we cannot perform calculations for the lowest TM concentrations the calculated d-band energies approach those observed in the dilute limit, and for all the Mg_3TM compounds the main d-band weight lies below the Fermi level. In all cases the measured dilute-limit d states lie at least one linewidth below the Fermi level, and we conclude that these states are fully, or nearly fully, occupied, i.e. close to a d^{10} configuration. This would appear to imply a significant degree of charge transfer onto the TM sites, up to 3 electrons per Ru atom in the case of MgRu, which is clearly unacceptable since both calculation and experiment show these systems to be metallic. If, however, the TM d wavefunctions extend onto neighbouring Mg sites then a significant proportion of the d intensity could lie on these sites and there need not be any deviation from charge neutrality. The Mg $L_{2,3}$ x-ray emission spectrum of Mg_3Au [5] clearly shows that the Au 5d state overlaps the Mg 2p core states in this compound. In principle this overlap should be visible in the Mg local DOS produced by the calculations, and in fact this is exactly what is seen. However, this result should be treated with caution as the use of the ASA, with its overlapping spheres, means that in determining the Mg local DOS the calculations will have sampled at least part of the TM sphere. Thus the Mg DOS would be expected to imply overlap from the TM irrespective of whether the TM wavefunctions actually extend onto the Mg sites. Although the theoretical results are ambiguous it seems reasonable to suggest that the overlap shown by the Mg_3Au x-ray emission increases on going from Au to Ir (and by analogy from Ag to Ru). The d states are shown in both experiment and theory to move to higher energy, and this implies as corresponding increase in the spacial extent of the d wavefunctions.

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