Hybridization and screening effects in the Mg KL_1V Auger spectra of Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, Mg-Ag, and Mg-Al alloys

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Mg KL_1V Auger spectra from Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, Mg-Ag, and Mg-Al alloys are presented. Mg-Ni, Mg-Cu, Mg-Pd, and Mg-Ag Auger spectra show peaks to high binding energy which increase in prominence with increasing transition- or noble-metal content and which arise from hybridization of the Mg s and p bands with d bands of the other metals. The positions of these features are shown to be consistent with the positions of similar features in the $L_{2,3}V$ soft-x-ray emission spectra of corresponding Al alloys: This agrees with the prediction of the equivalent-cores model that the local density of states around a core-ionized Mg atom should correspond to that around a neutral Al atom in the same environment. In Mg-Zn and Mg-Al alloys, d-band hybridization is not important and the high-binding-energy peaks in the Mg KL_1V spectra lose intensity with decreasing Mg content, as do the corresponding features in the Al $L_{2,3}V$ x-ray spectra observed from comparable Al alloys.

I. INTRODUCTION

The line shapes of core-core-valence Auger transitions from wide-band materials such as Na, Mg, and Al are expected to be well represented by the sum of the local s and p valence-band partial densities of states (PDOS) in the vicinity of a core-ionized atom weighted by the appropriate Auger transition probabilities.[1-3] The calculations of von Barth and Grossman[2,3] indicate that whereas the shape of the local valence p PDOS is almost unchanged by the presence of a core hole the local valence s PDOS is strongly distorted by the core hole and a peak develops to high binding energy. These theoretical results are supported by the observation that due to matrix-element effects simple-metal $KL_{2,3}V$ transitions are expected to be dominated by contributions from the local valence p PDOS and the experimental profiles of these transitions are very similar to the ground-state valence p PDOS.[1-3] The experimental profiles of simple-metal KL_1V transitions are more difficult to interpret since they are expected to be influenced by both the local s and p PDOS and the former is expected to be radically distorted from the ground-state PDOS.[1-3]

In a recent paper[4] the Mg $KL_{2,3}V$ Auger spectra of Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, and Mg-Ag alloys were presented. It was shown that for Mg-Ni, Mg-Cu, Mg-Pd, and Mg-Ag alloys hybridization of the Mg valence p PDOS with the d bands of the other alloy constituents caused an extra peak to occur to high binding energy in the Mg $KL_{2,3}V$ profiles. A similar effect is known to occur in x-ray emission spectral profiles of simple metals alloyed with d-band metals and the hybridization effect is well understood.[5-9] In this work we study the Mg KL_1V Auger spectral profiles of the alloys studied previously[4] together with the Mg KL_1V and $KL_{2,3}V$ spectra of Mg-Al alloys.

II. EXPERIMENTAL

The experimental procedure employed in the present work was identical to that used previously[4] and the KL_1V experimental results were taken on the same specimens as those from which the $KL_{2,3}V$ spectra reported earlier[4] were obtained. The Mg-Al alloys were prepared by cosputtering the two elements onto a Cu substrate using the procedure described earlier.[4] The Mg-Al phase diagram is complex[10] and it is likely that the $Mg_{13}Al_{87}$ and $Mg_{23}Al_{77}$ specimens were mixtures of α and β phases and that the Mg-Al specimen was a mixture of β and γ phases. The presence of two phases in the Mg-Al specimens is not of great significance since, as found in x-ray emission spectroscopy,[11] we expect the Auger spectrum to be sensitive to the immediate Mg environment but not to the crystal structure. The three Mg-Al specimens should produce Mg sites in which the average numbers of nearest-neighbor sites occupied by Al atoms differ significantly.

III. RESULTS AND DISCUSSION

The Mg KL_1V Auger spectra of Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, Mg-Ag, and Mg-Al alloys are shown in Figs. 1–6, respectively. The Mg $KL_{2,3}V$ Auger spectra of Mg-Al alloys are also shown in Fig. 6. We expect the final-state holes to be well screened in these materials and that the interaction between them is negligibly small. If these conditions are fulfilled the binding energies of the two-hole final states, $E_B^F(L_1V)$, can be decomposed into a sum of the binding energies of the single-hole states and the shape of the Auger spectrum will be related to the local densities of states around a core-ionized Mg atom modified by matrix-element effects. We may determine the binding-energy scale of these densities of states from

$$E_B^F(V) = E_B^F(K) - E_B^F(L_1) - E_{\text{kin}}^F(KL_1V) , \qquad (1)$$
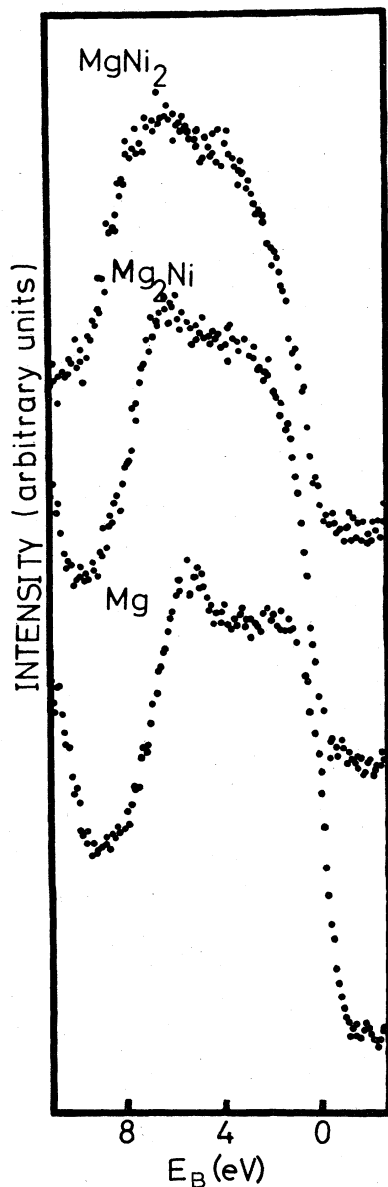
FIG. 1. Mg KL_1V Auger spectra of Mg-Ni alloys.
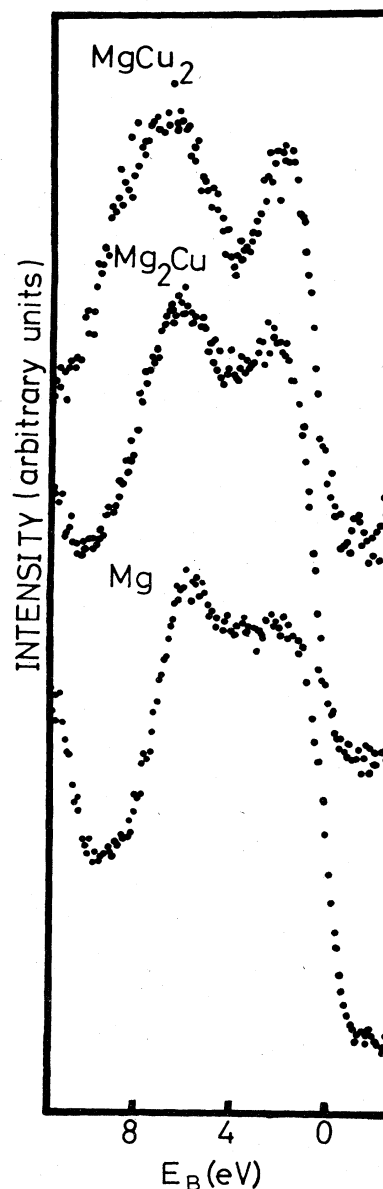
FIG. 2. Mg KL_1V Auger spectra of Mg-Cu alloys.

where the quantities are all referenced to the Fermi energy and those on the right-hand side are, respectively, the binding energies of the K and L_1 core levels found from x-ray photoelectron spectroscopy (XPS) and the observed kinetic energies of the KL_1V Auger spectra. The profile of the KL_1V spectrum of pure Mg, shown for comparison purposes in all the figures, is now well understood.[1-3] The peak just below the Fermi energy is due to the p PDOS in the vicinity of a core-ionized Mg atom: the shape of the p PDOS is not significantly changed by the presence of the core hole. The shape of the s PDOS is changed by the core hole and the peak to high binding energy in the Mg KL_1V spectrum is due to the sharp peak created at the bottom of the s PDOS by the core hole.[1-3] The figures show that on alloying with Ag, Pd, Cu, and to

TABLE I. Binding energies (in eV) of peaks in the s PDOS in the Mg KL_1V Auger spectra of Mg alloys and Al $L_{2,3}V$ x-ray spectra of Al alloys.

Mg KL_1V spectra		Al $L_{2,3}V$ spectra	
Alloy	Peak position[a]	Alloy	Peak position[a]
Mg_2Cu	5.4	$Al_{70}Cu_{30}$	5.9 (Ref. 14)
$MgCu_2$	5.9	$Al_{32}Cu_{68}$	6.8 (Ref. 14)
Mg_2Ni	5.5	$Al_{74}Cu_{26}$	5.9 (Ref. 14)
$MgNi_2$	5.5	$Al_{25}Cu_{75}$	8.1 (Ref. 14)
Mg_3Pd	5.8	Al_3Cu	6.4 (Ref. 11)
$MgPd$	6.4	$AlPd$	6.9 (Ref. 11)
$MgAg$	7.2	$Al_{35}Cu_{65}$	7.8 (Ref. 5)

[a]Peak positions are given relative to the Fermi edge in the spectra.
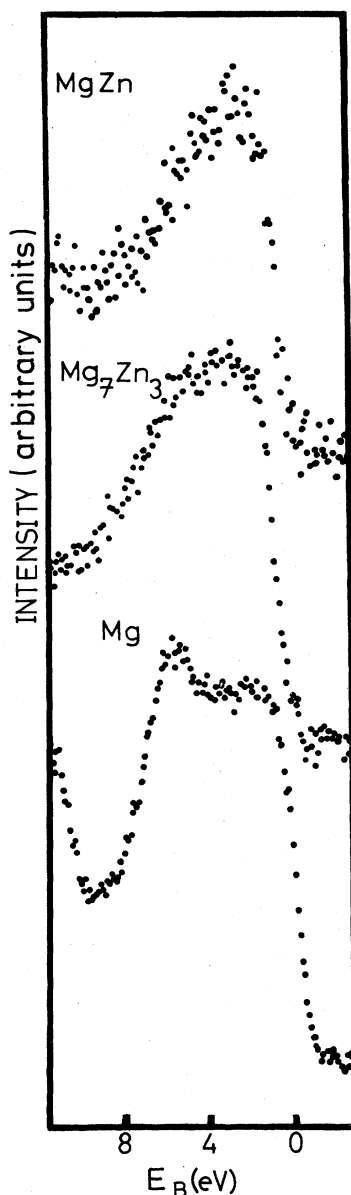
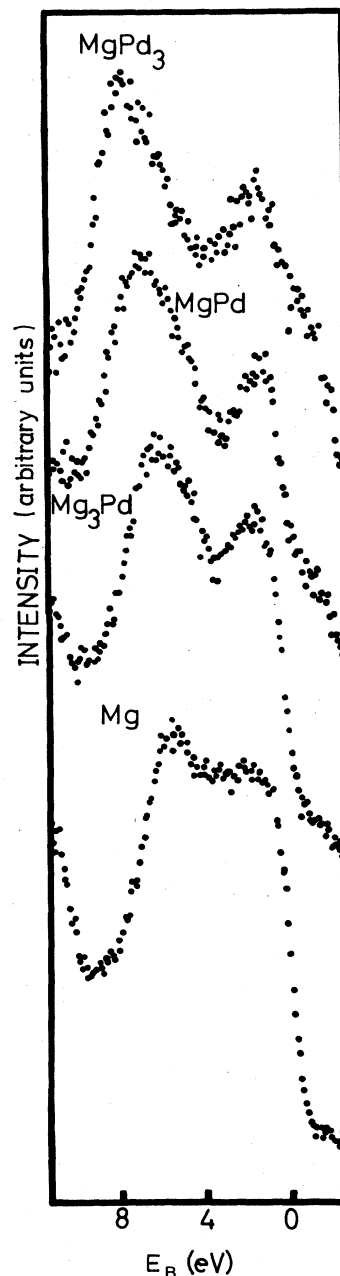FIG. 3. Mg KL_1V Auger spectra of Mg-Zn alloys.

FIG. 4. Mg KL_1V Auger spectra of Mg-Pd alloys. The spectral profile is distorted in the region of the Fermi level by the Pd $3d$ XPS line excited by Al $K\beta$ x rays. This line produces a shoulder on the extreme right of the MgPd$_3$ and MgPd spectra.

a lesser extent with Ni, this peak in the s PDOS moves to higher binding energy and becomes more pronounced while the peak associated with the p PDOS remains near E_F: thus the separation between the two peaks increases. The positions of the peaks in the s PDOS in the Mg KL_1V spectra of these alloys are shown in Table I. The peak associated with the s PDOS is not enhanced by alloying with Zn or Al (Figs. 3 and 6). In both these cases alloying tends to reduce the intensity of the peak in the s PDOS and eventually the Mg KL_1V profile resembles the $KL_{2,3}V$ profile (Fig. 6 for Mg-Al, the earlier work[4] for the Mg-Zn $KL_{2,3}V$ profiles). We postpone discussion of the Mg-Zn and Mg-Al spectra until Sec. III C and consider first the other alloy systems.

In the earlier work[4] we established the identity of peaks

induced in the Mg $KL_{2,3}V$ Auger spectrum by alloying by comparing the Auger profiles with corresponding Mg KV x-ray spectra. The extra peaks, which occurred at high binding energies in the $KL_{2,3}V$ Auger spectra, were shown to arise from hybridization of the Mg p PDOS with the d band of the other alloy constituent. The identification was straightforward because the Mg $KL_{2,3}V$ spectra are dominated by the p PDOS around a core-ionized Mg atom and this is expected[1-3] to be almost unchanged from that around a neutral Mg atom. Furthermore, the
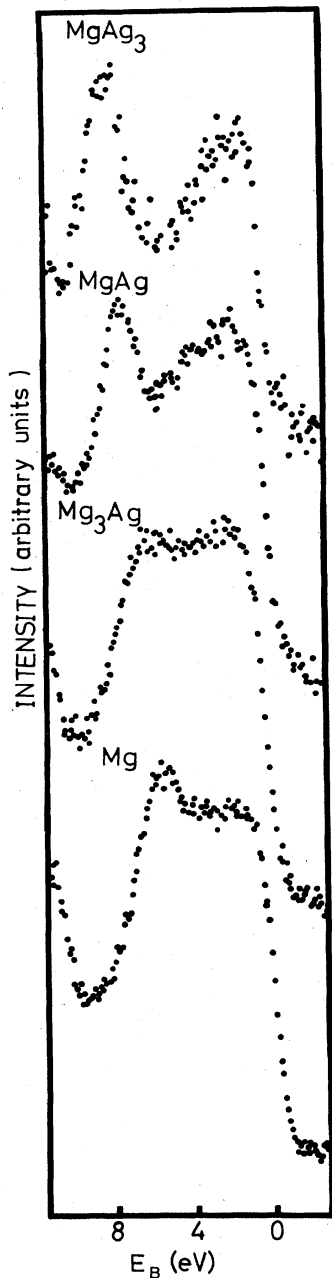
FIG. 5. Mg KL_1V Auger spectra of Mg-Ag alloys.

FIG. 6. (a) Mg $KL_{2,3}V$ and (b) Mg KL_1V Auger spectra of Mg-Al alloys.

shape of the Mg p PDOS is revealed by Mg KV spectra. Due to the distortions induced by the presence of the core hole we do not expect the s PDOS revealed by the Mg $L_{2,3}V$ x-ray spectra of these alloys to correspond to the s PDOS contributing to the Mg KL_1V Auger spectra. However, making the equivalent-cores approximation, we expect the s PDOS around a core-ionized Mg site in a Mg—noble-metal or Mg—transition-metal alloy to be similar to the s PDOS around a neutral Al site in the corresponding Al—noble-metal or Al—transition-metal alloy. We expect the shape of the s PDOS around a neutral Al
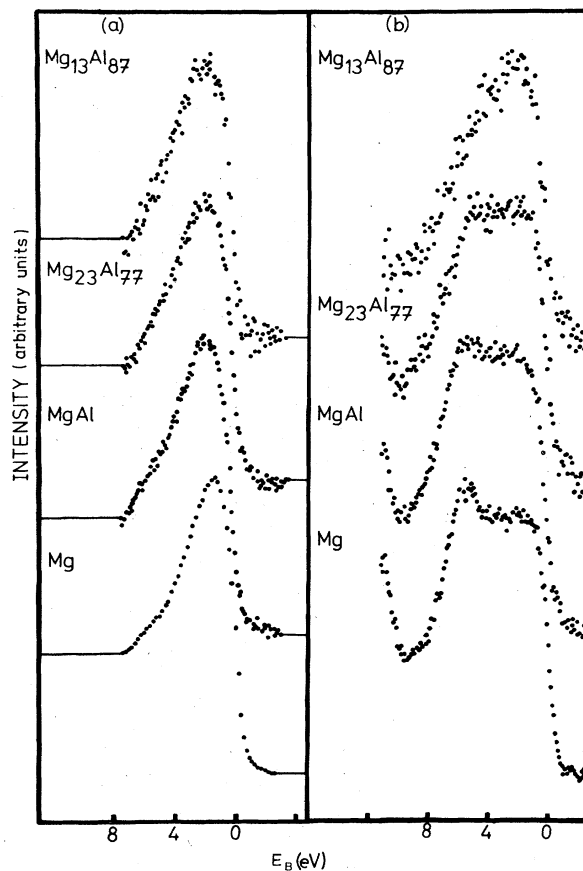
site to be revealed by Al $L_{2,3}V$ x-ray spectra and the profiles of these transitions observed from Al-Ni, Al-Cu, Al-Pd, and Al-Ag alloys do show additional peaks induced by alloying.[5,11–14] The positions of these peaks in the Al $L_{2,3}V$ x-ray spectra of Al alloys are shown in Table I. If the peaks to high binding energy in the Mg KL_1V Auger spectra result from the hybridization of the Mg s PDOS with the d band of the alloying constituent we expect them to have the same binding energies as the peaks in the Al $L_{2,3}V$ x-ray spectra of corresponding Al alloys. Table I shows that this expection is borne out quite well by the data.

A. Mg-Cu and Mg-Ag alloys

Figures 2 and 5 show that the peaks to high binding energy in the Mg s PDOS in Mg-Cu and Mg-Ag alloys become more pronounced with increasing noble-metal content. This is similar to the behavior of the peaks to high binding energy in the Mg p PDOS observed in the $KL_{2,3}V$ Auger spectra of the same alloys.[4] We interpret the effect as being due to the increased hybridization with the d band as the number of noble-metal nearest neighbors increases. Table I shows that the positions of these features

in the Mg KL_1V Auger spectra are in reasonable agreement with the positions of corresponding peaks in the Al $L_{2,3}V$ x-ray spectra of Al-Cu and Al-Ag alloys of similar composition. In particular, in both the Mg-Cu $KL_{2,3}V$ spectra and the Al-Cu $L_{2,3}V$ spectra the peaks to high binding energy in the s PDOS move to higher binding energy with increasing Cu content.

B. Mg-Ni and Mg-Pd alloys

The Mg KL_1V Auger spectra of Mg-Pd alloys overlap with Pd $3d$ photoelectron lines excited by the weak Al $K\beta$ x rays which accompany the Al $K\alpha$ x rays generated by the x-ray gun of the instrument. However, the distortions produced by this overlap are small, they are confined to the region of the Mg KL_1V profile which corresponds to the Fermi edge, and they are only significant for alloys with high Pd content (Fig. 4).

The KL_1V Auger spectra of Mg-Pd alloys show the trends noted in the KL_1V and $KL_{2,3}V$ Auger spectra of Mg-Ag and Mg-Cu alloys: the high-binding-energy peaks become more bound with increasing transition-metal content. This behavior is reflected in the Al $L_{2,3}V$ x-ray spectra of Al-Pd alloys. The trend is less obvious in the Mg-Ni system since the peak in the s PDOS is less bound than in the Mg-Cu, Mg-Pd, and Mg-Ag systems. A comparison of the KL_1V spectra of alloys of the same composition in the Mg-Ag and Mg-Pd systems shows that in Mg-Ag alloys there is more *intensity* in the unhybridized peak in the p PDOS near the Fermi energy than in the hybridization feature to high binding energy in the s PDOS whereas in Mg-Pd alloys this situation is reversed. The peak in the p PDOS is also less prominent relative to the s PDOS peak in the KL_1V spectra of Mg-Ni alloys than in corresponding Mg-Cu alloys. Similar differences were noted between Mg—transition-metal and Mg—noble-metal $KL_{2,3}V$ spectra[4] and we suggested earlier[4] that the explanation for these differences is that the hybridization of the d levels with the Mg s and p levels is stronger in the Mg—transition-metal alloys than in the Mg—noble-metal alloys.

C. Mg-Al and Mg-Zn alloys

The Mg KL_1V spectra of Mg-Al and Mg-Zn alloys are strikingly different to those of the Mg—transition-metal and Mg—noble-metal alloys. With increasing Al or Zn content the peak in the s PDOS in the Mg KL_1V spectrum falls in intensity and eventually with low Mg concentration the Mg KL_1V profile has a similar shape to the Mg $KL_{2,3}V$ profile. The fact that this behavior is observed in Mg-Zn and Mg-Al suggests that the Zn d band is too bound to hybridize with the Mg bands and that both the Mg-Zn and Mg-Al alloys can be considered as alloys between two simple metals.

The expectation, based on the equivalent-cores model, that the PDOS of states around a core-ionized Mg site should correspond to the PDOS around a neutral Al site in the same atomic environment is borne out for the Mg-Al system by the experiments of Neddermayer[15] which show that as the Al content of Mg-Al alloys is increased

the broad peak at the bottom of the Al $L_{2,3}V$ x-ray emission spectrum falls in intensity relative to the intensity of the peak near the Fermi edge: this corresponds to the loss of intensity of the s PDOS peak in the Mg KL_1V spectrum with increasing Al content. A similar consistency between the Mg KL_1V spectrum and Al $L_{2,3}V$ x-ray spectrum is shown for the Mg-Zn and Al-Zn alloys.[13] Kapoor et al.[13] have shown that the Al $L_{2,3}V$ x-ray spectra of Al-Zn alloys show little change in shape as the Zn content is increased for 0% to 55% and do not show a peak to high binding energy. This is consistent with the absence of the s PDOS peak in the Mg KL_1V spectrum of MgZn. We may conclude that the Al $L_{2,3}V$ x-ray and Mg KL_1V Auger profiles establish that in Mg-Al and Mg-Zn alloys the presence of a core hole on the Mg site does not produce the sharp feature in s PDOS at the bottom of the band that occurs in pure simple metals[1-3] and in Mg—transition-metal and Mg—noble-metal alloys.[4] In alloys between simple metals there is clearly some change in the mechanism of core-hole screening.

IV. CONCLUSIONS

It has been shown that for Mg-Ni, Mg-Cu, Mg-Ag, Mg-Pd, Mg-Zn, and Mg-Al alloys the Mg KL_1V Auger spectral profiles may be understood by comparison with the Al $L_{2,3}V$ x-ray spectral profiles of Al alloys of similar composition. The shape of the Mg KL_1V spectra reflect the s and p PDOS around core-ionized Mg sites. The shape of the s PDOS around a core-ionized Mg atom is sensitive to the environment of the Mg site and by the equivalent-cores model should correspond to the s PDOS around a neutral Al atom in the same environment. The close agreement between trends in the contribution from the s PDOS to the Mg KL_1V Auger and Al KV x-ray spectra on alloying confirms the equivalent-cores model. In the Mg—transition-metal and Mg—noble-metal alloys hybridization of the Mg s band with the other alloy component's d band causes the peak derived from the s PDOS to grow in intensity in the Mg KL_1V spectra with increasing transition- or noble-metal content, the effect being more pronounced in the Mg—transition-metal alloys than in the Mg—noble-metal alloys. It is also likely that there is some contribution to the peaks to high binding energies from d hybridization with the Mg p PDOS since the p PDOS also contributes to the pure Mg KL_1V profile and the Mg $KL_{2,3}V$ spectra of these alloys, which are dominated by the p PDOS, show similar features.[4] In Mg-Zn alloys the peak in the Mg s PDOS is reduced in intensity with increasing Zn content indicating that the Zn d band does not hybridize with the Mg s band and that Mg-Zn alloys should be considered as alloys between simple metals. For both Mg-Zn and Mg-Al alloys the presence of a core hole on a Mg site does not induce a peak in the s PDOS at the bottom of the band. This is contrary to the behavior of the s PDOS around core-ionized sites in pure simple metals or in Mg—transition-metal or Mg—noble-metal alloys.

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