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Hybridization effects on the Mg $KL_{2,3}V$ Auger spectra of Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, and Mg-Ag alloys

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X-ray-excited Mg $KL_{2,3}V$ Auger spectra for various alloy compositions in the Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, and Mg-Ag systems have been measured. The spectra are dominated by transitions which create p-like valence holes in the final state and exhibit resonant peaks below the Fermi level similar to those observed by earlier workers in the KV x-ray emission spectra of similar alloys. These peaks are interpreted in terms of hybridization of the Mg p bands with the d bands of the transition- or noble-metal components. Particularly strong hybridization effects are observed in the Mg-Ni and Mg-Pd systems.

INTRODUCTION

It is well established that valence-band soft-x-ray emission spectra of simple metals such as Mg and Al, when alloyed with transition or noble metals, exhibit secondary peaks below the Fermi energy.[1-4] These peaks have been shown to increase smoothly in intensity with increasing transition-metal content.[5] The peak intensities show almost no dependence on crystal structure, suggesting that only the atoms within the first coordination sphere are important to the phenomenon.[3] The single-particle wave function of the orbital containing the core hole in the initial state of the x-ray emission process has a significant overlap only with the valence-band conduction states in the immediate vicinity of the core. Consequently, x-ray emission profiles are only expected to give information on the density of states local to the emitting atomic site. The observed peaks in the x-ray emission spectra of transition-metal—simple-metal alloys are generally accepted as being due to the effect of hybridization of the transition-metal d bands with the simple-metal sp bands.[3,5-7] This interpretation is supported by the augmented plane wave (APW) calculations of Switendick[8] and the coherent-potential approximation (CPA) calculations of Kudrnovský *et al.*[9] The influence of hybridization can be seen in the local densities of states of impurities in Cu alloys, given by the density-functional calculations of Braspenning *et al.*[10]

Valence-band Auger electron spectroscopy like soft-x-ray emission spectroscopy can be used to probe the local density of states of the atomic species containing the initial state core hole. The most direct density-of-states information can be gained from core-core-valence (CCV) spectra. Such spectra, however, reflect the local densities of states around a core-ionized atom. The core hole attracts screening charge which can change the shapes of the local partial densities of states. In pure Mg metal, for example, the presence of a core hole causes the local s density of states to be reduced in amplitude at the Fermi energy and a peak to develop at ~6 eV below the Fermi level, while the local p density of states is almost unchanged.[11,12] This paper is concerned with the spectral profiles of Mg $KL_{2,3}V$ Auger transitions observed from the Mg-Ni, Mg-Cu, Mg-Zn, Mg-Pd, and the Mg-Ag alloy systems. As in the case of pure Mg we expect the spectral profile of these transitions to be dominated by contributions from the local p density of states in the valence band since we expect the radial parts of the s and p wave functions to be similar and the integration over angular parts to weight the s and p contributions to the transition rate in the ratio 1:3.[12,13] If, as in pure Mg, the local p density of states in the alloys is changed little by the presence of a core hole, then we expect the $KL_{2,3}V$ profile to reflect the ground-state Mg p density of states in the alloys. This is shown to be true for the Mg-Cu and Mg-Ag alloy systems by comparing their $KL_{2,3}V$ Auger and KV x-ray emission spectral profiles.[2,14,15] It is argued that the peaks which occur to high binding energy in the $KL_{2,3}V$ Auger spectra of some Mg alloys are caused by hybridization of the simple-metal p density of states with the d bands of transition or noble metals.

EXPERIMENTAL

Auger and photoelectron spectra were measured with a modified Kratos ES200 photoelectron spectrometer equipped with a nine-channeltron multidetector.[16] The Auger spectra were excited by Al $K\alpha$ rays and the x-ray photoelectron spectroscopy (XPS) conduction-band spectra were excited with a monochromated Al $K\alpha$ source. The spectra are shown in Figs. 1—5. The binding-energy scales are referred to the Fermi level. The spectrometer is pumped by ion pumps and titanium sublimation pumps and these experiments were conducted in pressures of 7×10^{-10} Torr.

Alloy specimens were made by co-sputtering the two elements onto an Al substrate at room temperature in an Ar atmosphere of 3×10^{-2} Torr, using an arrangement

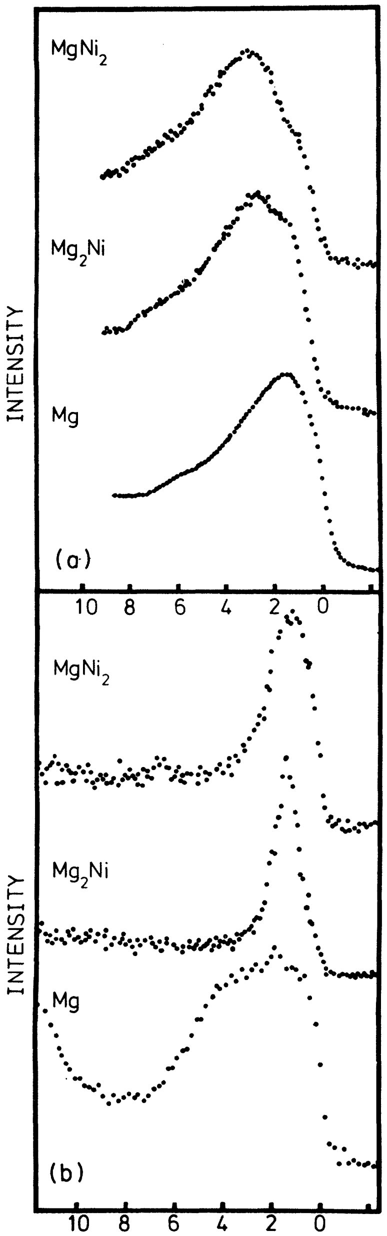

FIG. 1. (a) Mg $KL_{2,3}V$ Auger spectra of Mg-Ni alloys. (b) Monochromated XPS valence-band spectra of the same alloys. The pure Mg spectra have also been given for comparison.

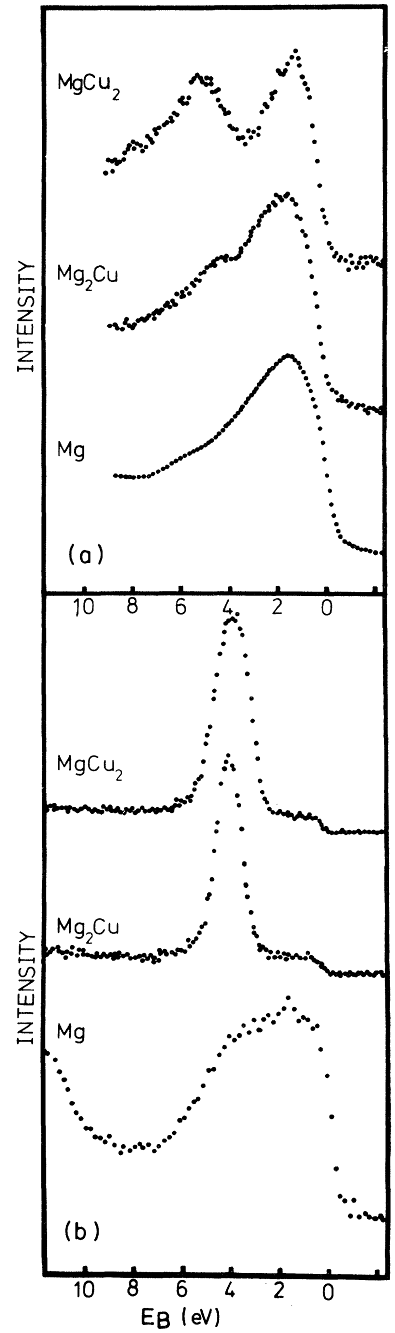

FIG. 2. (a) Mg $KL_{2,3}V$ Auger spectra of Mg-Cu alloys. (b) Monochromated XPS valence-band spectra of Mg-Cu alloys.

similar to that described by Shevchik and Goldman.[17] The argon was purified by pumping on it with a film of titanium which was deposited, prior to Ar introduction, onto the walls of a pump chamber closely connected to the specimen preparation chamber. The composition of the cosputtered films was determined by measuring the relative intensities of the core-level XPS signals observed from the two metals, the procedure having been calibrated beforehand by determining these relative intensities in alloys of accurately known composition. In all cases the compositions thus deduced agreed to within an accuracy of 10% with those calculated from the observed relative intensities of the core-level XPS lines weighted by using the cross sections of Scofield[18] and the electron mean free paths of Penn.[19] The oxygen and carbon 1*s* photoemission peaks were monitored during the experimental periods on all specimens. The surfaces were renewed in all cases before 0.2 monolayers of oxygen was detected on the surfaces of the samples. In most cases this involved the creation of a fresh specimen every half hour.

The phase diagram of Mg-Zn alloys[20,21] shows that Mg_7Zn_3 does not exist below ~330 °C and if the specimen did not "freeze" into this phase during manufacture we

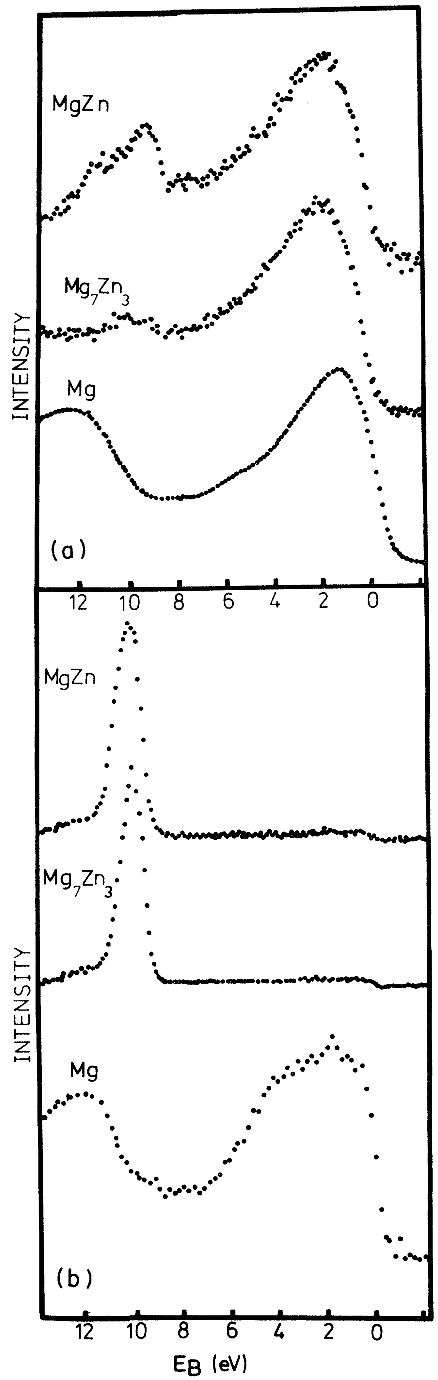

FIG. 3. (a) Mg $KL_{2,3}V$ Auger spectra of Mg-Zn alloys. The features in the Mg-Zn alloy spectra at binding energies of 9 eV are Ar $2p$ photoelectron lines as described in the text. The feature at 12 eV in the Mg spectrum is a plasmon. (b) Monochromated XPS valence-band spectra of Mg-Zn alloys.

expect it to consist of a mixture of phases. The same may also be true of the MgZn specimen since there is uncertainty as to the existence of this phase.[20,21] However, the XPS and Auger spectra observed from the Mg-Zn specimens did not show the characteristic plasmons observed from pure Mg, indicating that if the specimens were of mixed phase the phases were all Mg-Zn alloys of some

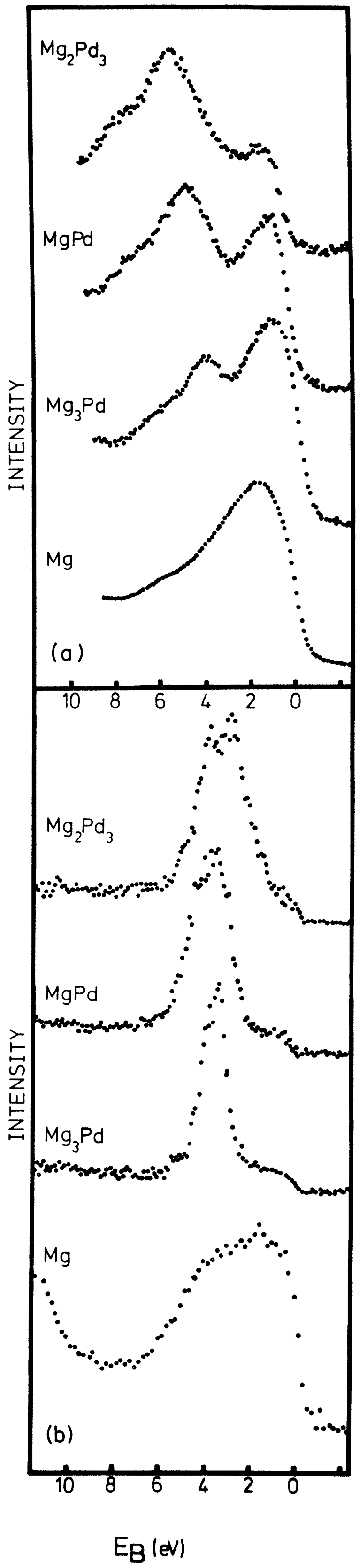

FIG. 4. (a) Mg $KL_{2,3}V$ Auger spectra of Mg-Pd alloys. (b) Monochromated XPS valence-band spectra of Mg-Pd alloys.

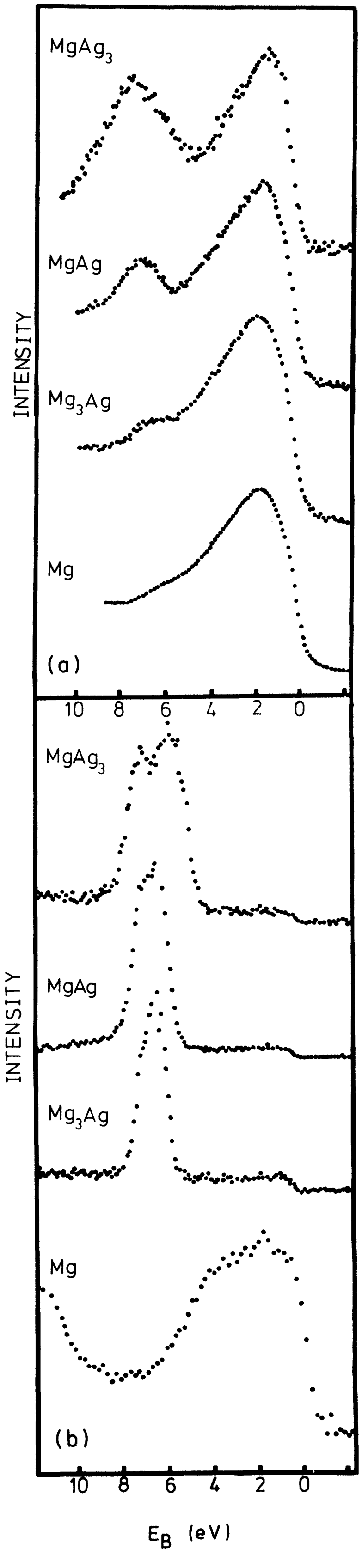

FIG. 5. (a) Mg $KL_{2,3}V$ Auger spectra of Mg in Mg-Ag alloys. (b) Monochromated XPS valence-band spectra of Mg-Ag alloys.

composition. Studies of the variation of energy loss and band spectra with composition lead us to believe that specimens of the other alloy systems adopted the phases given on the phase diagrams[20,21] and photoelectron and Auger spectra observed from bulk specimens of known composition agreed with those obtained from the co-sputtered specimens. The XPS spectra of the d bands of Mg_2Ni and $MgNi_2$ are in good agreement with those of Fuggle *et al.*[22]

Some of the specimens were contaminated by Ar absorbed during manufacturing. The photoelectron spectrum of the Ar $2p$ lines occurs to low energy of the Mg $KL_{2,3}V$ spectrum and was closely monitored in the experiments. This was a particular problem for $MgNi_2$ and MgZn and the Ar $2p$ spectrum of the latter can be seen to low energy of the Mg $KL_{2,3}V$ peak in Fig. 3. In assessing the importance of the Ar contamination, it should be remembered that the Mg $KL_{2,3}V$ transition, also shown in Fig. 3, is quite a weak feature in the Mg electron spectrum. When the intensity of the Ar $2p$ XPS line is compared to that of the Mg $2p$ XPS line and allowance is made for the different photoelectron cross sections,[18] we find the Ar $2p$ lines occurring in the MgZn spectrum in Fig. 3 to correspond to an Ar concentration of $\sim 1\%$ of the Mg concentration. A similar Ar concentration was observed for $MgNi_2$ and lower values for the other alloys ($<$ 0.5 at. % for $MgCu_2$, Mg_2Ni, MgPd, Mg_3Pd, <0.2 at. % for Mg_7Zn_3 (Fig. 3), MgAg, Mg_3Ag $\sim 0.0\%$ for Mg_2Cu, Mg_2Pd_3). In view of the low level of Ar contamination, we do not expect it to have any influence on the Mg $KL_{2,3}V$ Auger spectral profiles.

RESULTS AND DISCUSSION

The $KL_{2,3}V$ Auger spectra of Mg_2Cu has been studied by Fuggle *et al.*[23] Current ideas on the interpretation of Auger spectral profiles have been reviewed recently by Fuggle[24] and Weightman.[25]

The Mg $KL_{2,3}V$ Auger and monochromated XPS conduction-band spectra obtained in this work are shown in Fig. 1 for the Mg-Ni system, Fig. 2 for the Mg-Cu system, Fig. 3 for the Mg-Zn system, Fig. 4 for the Mg-Pd system, and Fig. 5 for the Mg-Ag system. The energy scales of the Auger spectra shown in the figures have been chosen to correspond to the binding energy of single-particle valence-band densities of states, i.e.,

$$E_B^F(V)=E_B^F(K)-E_B^F(L_{2,3})-E_{\text{kin}}^F(KL_{2,3}V) , \qquad (1)$$

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 $L_{2,3}$ core levels found from XPS and the observed kinetic energies of the $KL_{2,3}V$ spectra.

Equation (1) is based on a decomposition of the binding energy of the two-hole final states, $E_B^F(L_{2,3}V)$, created in the Auger process into a sum of the binding energies of the single-hole states. This decomposition is expected to be valid for these transitions since the final states are expected to be well screened and the Coulomb repulsion between the two final-state holes should be negligibly small. In these circumstances the shape of the Auger spectrum is related to the local densities of states around a core-ionized Mg atom modified by matrix element effects. In pure Mg the $KL_{2,3}V$ spectral shape is dominated by the valence-band p density of states and the shape of the p density of states around a site with a core hole and even with two core holes[26] cannot be readily distinguished from that around a neutral Mg site.[12]

Except for Mg-Zn alloys, we find that the Mg $KL_{2,3}V$ spectral profiles of these alloys develop a peak to high binding energy which increases in intensity and becomes more bound with increasing transition- or noble-metal content (Figs. 1—5). This information is summarized in Table I. It should be noted that both the "main peak" which we associate with the most intense part of the $KL_{2,3}V$ spectral profile of pure Mg, and the "second peak" that develops on alloying are often rather broad and in some cases are not well resolved, so the results in Table I should be taken as a rough guide to trends in the profiles. The distinguishing feature of the Mg alloys studied here is that the other alloy component is a *d*-band metal, and this suggests that the second peak in the Mg $KL_{2,3}V$ profiles of the alloys is associated with the *d* band of the alloy. A comparison of the $KL_{2,3}V$ profiles with the conduction-band photoelectron spectra shows that the second peak is usually ~ 1 eV more bound than is the *d* band (Figs. 1—5 and Table I). One possible explanation for the shift of the position of the second peak from the position of the *d* band is that the Mg *p*-*d* resonance is shifted to higher binding energy in the $KL_{2,3}V$ profile by the relaxation of the local density of states around a core-ionized Mg atom. Since the Mg $KL_{2,3}V$ profile will be dominated by the local *p* density of states this would imply that, unlike the behavior in pure Mg, the local *p* density of states around a core-ionized Mg atom in the alloy is different from that around a neutral Mg atom. However, we are able to rule out this hypothesis by consideration of the KV x-ray emission profiles of some of these alloys. The KV profile should reflect the local *p* density of states around a neutral Mg atom. The Mg KV spectra of Mg, Mg_2Cu, and $MgCu_2$ (Ref. 2) are compared with the corresponding Mg $KL_{2,3}V$ Auger spectral profiles in Fig. 6. We do not expect the KV x ray and $KL_{2,3}V$ Auger spectra to have identical profiles due to the different matrix elements involved in the transitions but the close correspondence of the position of the main and second peaks in the two sets of alloy spectra shows that, as in pure Mg, the local *p* density of states around a core-ionized Mg atom in the alloys is very similar to that around a neutral Mg atom. This view is supported by the comparison of the Mg $KL_{2,3}V$ Auger and Mg KV x-ray spectrum of Mg_2Cu with the Al KV x-ray emission spectrum of $Al_{50}Cu_{50}$ (Ref. 14) shown in Fig. 7. All three spectral profiles are very similar. The x-ray spectra reflect the local *p* densities of states around neutral Mg and neutral Al sites in the alloys. Using an equivalent cores argument, we expect the local *p* density of states around a core-ionized Mg atom to be intermediate between those around neutral Mg and neutral Al atoms and consequently if the latter two resemble each other we expect all three to be similar. Unpublished x-ray spectra of Watson[15] confirm that the arguments we have advanced for the Mg-Cu alloy system also apply to Mg-Ag alloys.

We have established that Mg-Cu and Mg-Ag alloys are similar to pure Mg in that the local *p* density of states around core-ionized Mg sites are little changed from those around neutral Mg sites. Given the systematic shift in the position of the second $KL_{2,3}V$ peak from the binding energy of the *d* bands (Table I) this conclusion is probably also true for the Mg-Ni and Mg-Pd alloys. We now need to account for the positions of the second peaks in the Mg $KL_{2,3}V$ spectra. These are adequately explained by the work of Kudrnovský *et al.*,[9] who carried out CPA calculations of the local densities of states in random binary alloys of simple metals with noble or transition metals. They showed that hybridization of the simple-metal *sp* electrons with the transition- or noble-metal *d* electrons produced peaks in the simple-metal *s* and *p* partial densities of states. The peak in the *p* partial density of states is predicted to occur at a higher binding energy than the *d* resonance position in the conduction band. This prediction is in accord with the observed peak positions in the $KL_{2,3}V$ Auger spectra presented here.

It remains to consider the Mg $KL_{2,3}V$ profiles in the Mg-Zn alloys (Fig. 3). As explained earlier, there is some doubt as to exact phases of these specimens. However, the absence of Mg plasmons from the energy loss accompany-

TABLE I. Binding energy of features in valence-band spectroscopies of Mg alloys (eV).

	XPS	$KL_{2,3}V$ Auger		KV x-ray emission	
	d band	Second peak	Main peak	Second peak	Main peak
Mg			1.8		
MgZn	9.7		1.6		
$MgCu_2$	3.7	4.8	1.0	4.9	1.2
Mg_2Cu	3.7	4.0	1.4	4.3	1.2
$MgNi_2$	1.2	2.4			
Mg_2Ni	1.3	2.2			
$MgAg_3$	6.0	7.1	1.3		
MgAg	6.0	7.0	1.6		
Mg_3Ag	6.2	6.3	1.8		
Mg_2Pd_3	3.1	5.0	1.1		
MgPd	3.5	4.6	1.1		
Mg_3Pd	3.5	4.2	1.4		

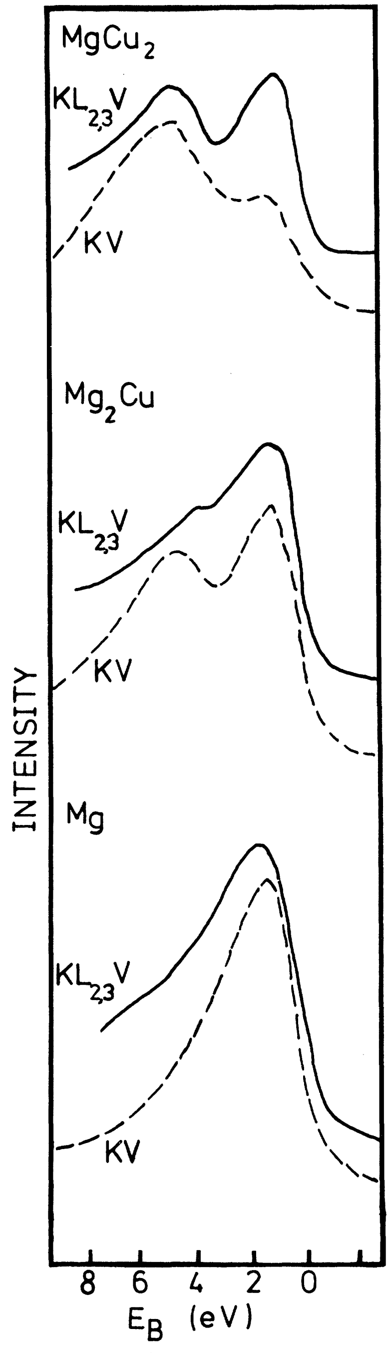

FIG. 6. A comparison of Mg KV x-ray emission (Ref. 2) and Mg $KL_{2,3}V$ Auger emission spectral profiles in Mg, Mg_2Cu, and $MgCu_2$.

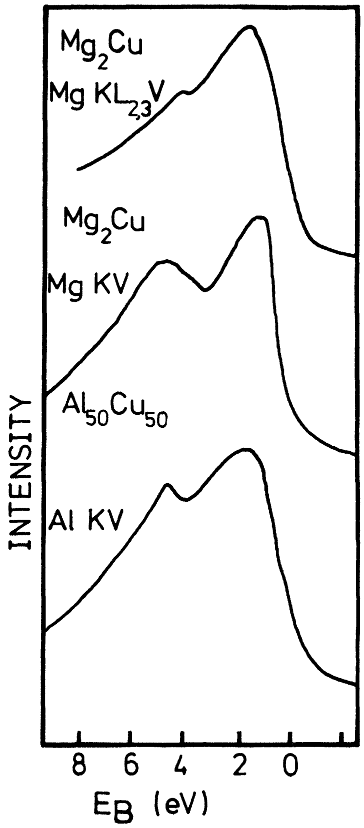

FIG. 7. A comparison of the spectral profiles of Al KV x rays from $Al_{50}Cu_{50}$ (Ref. 14), Mg KV x rays from Mg_2Cu (Ref. 2), and Mg $KL_{2,3}V$ Auger electrons from Mg_2Cu.

ing XPS and Auger lines establishes that the specimens did not include a pure Mg phase and that if the specimens were of mixed phase the phases were Mg-Zn alloys of some composition. Consequently we might expect the $KL_{2,3}V$ profiles of these alloys to show a second peak associated with the hybridization of the Mg p and Zn $3d$ bands. We would expect to see this second peak at ~ 1 eV higher in binding energy than the Zn d band. Unfortunately, this is the region of the spectrum where the Ar $2p$ peaks are observed and we cannot establish conclusively whether or not the peak is present. Experiments on specimens which had lower levels of Ar contamination, such as Mg_7Zn_3 (Fig. 3) show that if the second peak is present in the Mg $KL_{2,3}V$ spectra of Mg-Zn alloys it is much weaker than in the other alloy systems. The absence of the second peak from the Mg-Zn system is quite consistent with its identification with p-d hybridization since in these alloys the Zn d band is probably outside the range of the Mg sp band, and the two bands would not be expected to mix strongly even in the presence of a Mg core hole. The Mg $KL_{2,3}V$ spectra of Mg-Zn alloys (Fig. 3) and the almost invariant position of the main peak in all the alloys studied (Table I) suggests that the shape of the local density of states of the least-bound p states around a Mg site in the alloys is very similar to that around a Mg site in pure Mg.

A comparison of the Mg $KL_{2,3}V$ spectra of Mg-Ag (Fig. 4) with Mg-Pd (Fig. 5) shows that the p-d hybridization is significantly stronger in Mg-Pd. A careful comparison of the spectra of $MgNi_2$ (Fig. 1) and $MgCu_2$ (Fig. 2) shows a similar effect, though this is harder to establish due to the low binding energy of the peak arising from d-band hybridization in $MgNi_2$. It is likely that this increase in the intensity of the peak induced by the d band in $MgNi_2$ and Mg-Pd alloys is due to the small energy difference between the Mg p and transition-metal d resonance in these alloys.

CONCLUSIONS

The Mg $KL_{2,3}V$ Auger spectra of Mg-Ni, Mg-Cu, Mg-Pd, and Mg-Ag alloy systems have been shown to exhibit peaks at higher binding energies than the *d*-band positions in the monochromated XPS conduction-band spectra. These peaks are explained by hybridization of the Mg *p* bands with the transition- or noble-metal *d* bands and their peak positions are in qualitative accord with the CPA predictions of Kudrnovský *et al.*[9] In the alloys the local *p* densities of states around core-ionized Mg atoms are similar to those around neutral Mg atoms.

It is not clear whether or not a second peak occurs in the Mg $KL_{2,3}V$ spectra of Mg-Zn alloys. If the peak is present it is weaker than in the other alloy systems. The absence of this feature in Mg-Zn spectra would be quite consistent with the view that its presence in the spectra from the other alloy systems is due to Mg *p*—metal *d* hybridization since there is little or possibly no overlap of the two bands in Mg-Zn alloys.

The *p*-*d* hybridization effects are stronger in $MgNi_2$ and Mg-Pd than in the corresponding Mg—noble-metal alloys. This is attributed to greater hybridization between the Mg *p* and transition-metal *d* levels due to the proximity in energy of the Mg *p* resonance and the *d* resonance in the group-VIII metals compared with the noble metals.

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[1] C. Curry and R. Harrison, Philos. Mag. 21, 659 (1970).

[2] W. L. Baun and D. W. Fisher, U.S. Air Force Materials Laboratory International Research Publication No. AFML-66-191 (unpublished).

[3] Q. S. Kapoor, Solid State Commun. 11, 1755 (1972).

[4] L. M. Watson, in *Band Structure Spectroscopy of Metals and Alloys,* edited by D. J. Fabian and L. M. Watson (Academic, London, 1973), p. 125.

[5] K. Ichikawa, J. Phys. Soc. Jpn. 37, 377 (1974).

[6] C. A. W. Marshall, L. M. Watson, G. M. Lindsay, and G. A. Rooke, Phys. Lett. 28A, 579 (1969).

[7] Q. S. Kapoor, L. M. Watson, D. Hart, and D. J. Fabian, Solid State Commun. 11, 503 (1972).

[8] A. C. Switendick, in *Electronic Density of States,* Natl. Bur. Standards (U.S.) Spec. Publ. No. 323 (NBS, Washington, D.C., 1971), p. 297.

[9] J. Kudrnovský, L. Smrčka, and B. Velický, in Proceedings of the International Symposium on X-Ray Spectra and Electronic Structure of Matter, München, 1972 (unpublished).

[10] P. J. Braspenning. R. Zeller, P. H. Dederichs, and A. Lodder, J. Phys. F 12, 105 (1982).

[11] U. Von Barth and G. Grossman, Solid State Commun. 32, 645 (1979).

[12] R. Lässer and J. C. Fuggle, Phys. Rev. B 22, 2637 (1980).

[13] J. C. Fuggle and R. Lässer, J. Vac. Sci. Technol. 17, 251 (1980).

[14] W. L. Baun and D. W. Fischer, J. Appl. Phys. 38, 2092 (1967).

[15] L. M. Watson (private communication).

[16] P. Weightman and P. T. Andrews, J. Phys. C 13, 3529 (1980).

[17] N. J. Shevchik and A. Goldman, J. Electron Spectrosc. 5, 631 (1974).

[18] J. H. Scofield, J. Electron Spectrosc. 8, 129 (1976).

[19] D. R. Penn, J. Electron Spectrosc. 9, 29 (1976).

[20] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).

[21] P. R. Elliott, *Constitution of Binary Alloys, First Supplement* (McGraw-Hill, New York, 1965).

[22] P. A. Bennett, J. C. Fuggle, F. U. Hillebrecht, R. Zeller, Z. Zolnierek, and C. Freiburg, Phys. Rev. B 27, 2194 (1983).

[23] J. C. Fuggle, L. M. Watson, P. R. Norris, and D. J. Fabian, J. Phys. F 5, 5905 (1975).

[24] J. C. Fuggle, in *Electron Spectroscopy Theory, Techniques and Applications,* edited by C. R. Brundle and A. D. Baker (Academic, New York, 1981), p. 85.

[25] P. Weightman, Rep. Prog. Phys. 45, 753 (1982).

[26] M. Davies, D. R. Jennison, and P. Weightman, J. Phys. C 17, L107 (1984).