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## A theoretical study of the KLV Auger transitions of Mg in LiMg, Mg and AlMg alloys

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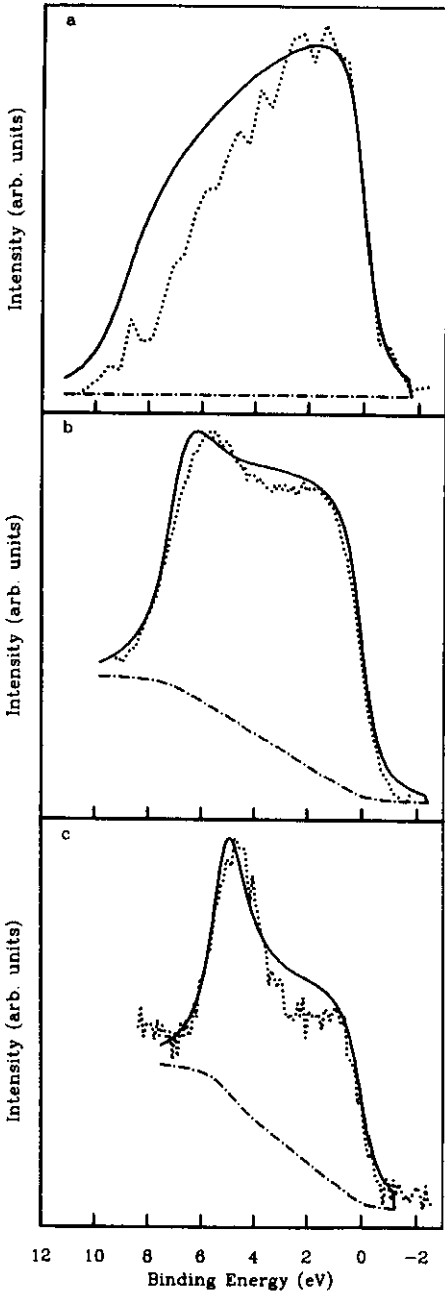
**Abstract.** It is shown that the influence of the local environment on the KLV Auger spectra of Mg can be understood via a theoretical approach which uses the embedding technique to calculate the local density of states around a core-ionized Mg site. This approach is applied to  $\text{Al}_{85}\text{Mg}_{15}$ ,  $\text{Mg}_{100}$  and  $\text{Li}_{85}\text{Mg}_{15}$  and, providing matrix element effects are included, the results obtained are in good agreement with measurements of the  $\text{KL}_1\text{V}$  Auger profiles for these materials. The approach is less successful for the Mg  $\text{KL}_{2,3}\text{V}$  transitions. The theoretical study predicts the formation of a bound state of s character on the Mg site in  $\text{Li}_{85}\text{Mg}_{15}$  and this is supported by the good agreement obtained between theoretical and experimental  $\text{KL}_1\text{V}$  Auger lineshapes.

### 1. Introduction

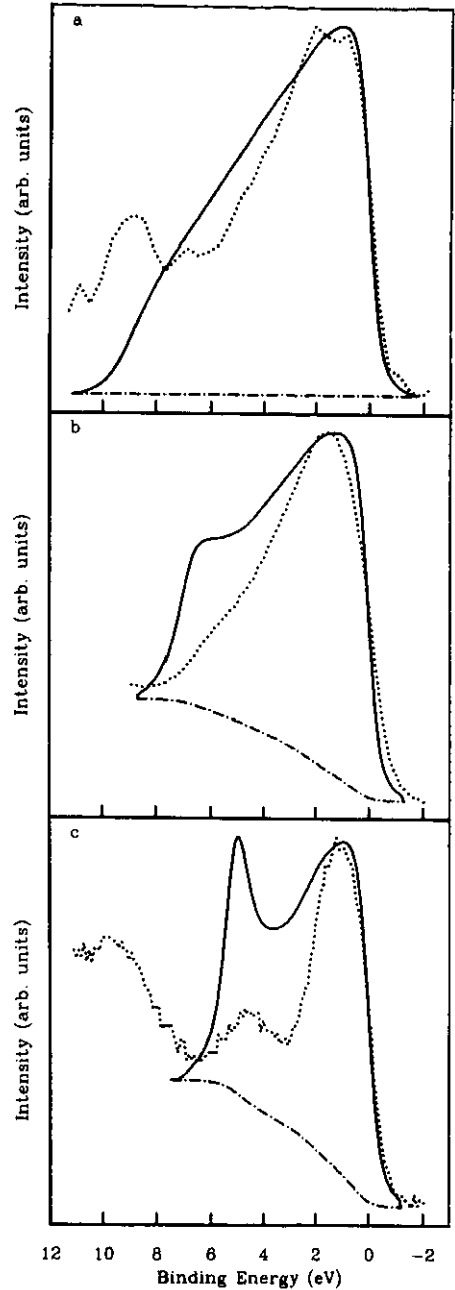
The nature of the core hole screening in simple metals has been the subject of much detailed investigation, both theoretical and experimental [1–13]. A primary tool for the study of such effects has been the core–core valence (CCV) Auger transitions of the free-electron-like metals and their alloys. This is because the spectral profiles of these transitions are known to be related to the distribution of the local density of states (LDOS) on a site in the presence of a core hole [3, 5, 8, 10–13]. However it is not possible to deduce the energy distribution of the LDOS directly from these spectra due to the influence of both radial and angular Auger matrix elements. In this work we evaluate the importance of such matrix element effects for the case of pure Mg and dilute Mg alloys with other simple metals by comparing the experimental Mg KLV Auger profiles with calculations of the LDOS and Auger profiles.

Previous experiments [10–13] have shown that alloying Mg with other metals gives rise to differences in the Mg  $\text{KL}_1\text{V}$  and  $\text{KL}_{2,3}\text{V}$  Auger lineshapes. The Mg  $\text{KL}_1\text{V}$  profile is made up of approximately equal contributions from the valence s and p LDOS around the core-ionized site. This gives rise to the double-peaked structure of the profile in pure Mg metal. The Mg  $\text{KL}_{2,3}\text{V}$  profile is dominated by the contributions from the p LDOS and shows only one peak. In this work we consider theoretically the LDOS and KLV profiles of Mg, where the Mg atom is present as an impurity in Al and Li respectively.

The experimental Mg KLV profiles of  $\text{Al}_{85}\text{Mg}_{15}$ ,  $\text{Mg}_{100}$  and  $\text{Li}_{85}\text{Mg}_{15}$  have been measured previously [5, 10, 13] and we relate our calculations to these results which



**Figure 1.** The dotted line shows the experimentally determined  $\text{KL}_{1V}$  spectra of Mg in (a)  $\text{Al}_{85}\text{Mg}_{15}$  [10], (b) pure Mg [5] and (c)  $\text{Li}_{85}\text{Mg}_{15}$  [13] respectively. The solid line is the theoretical lineshape broadened to allow for experimental and lifetime effects and with a background (dot-dashed line) added.



**Figure 2.** The dotted line shows the experimentally determined  $\text{KL}_{2,3V}$  spectra of Mg in (a)  $\text{Al}_{85}\text{Mg}_{15}$  [10], (b) pure Mg [5] and (c)  $\text{Li}_{85}\text{Mg}_{15}$  [13] respectively. The solid line is the theoretical lineshape broadened to allow for experimental and lifetime effects and with a background (dot-dashed line) added. The feature at 9 eV in the experimental  $\text{KL}_{2,3V}$  spectrum of  $\text{AlMg}$  is an Ar photoemission line due to the method of sample preparation [9].

are shown by the dots in figure 1 ( $KL_1V$ ) and figure 2 ( $KL_{2,3}V$ ). As can be seen by comparison with the Mg  $KL_1V$  spectrum of pure Mg (figure 1(b)), in the AlMg alloy the peak to high binding energy has all but disappeared (figure 1(a)) while in the LiMg alloy this feature is greatly enhanced (figure 1(c)). A similar if less pronounced trend may also be seen in figure 2 for the  $KL_{2,3}V$  Auger profiles of Mg in such alloys.

The general dependence of the Mg  $KL_1V$  and  $KL_{2,3}V$  on alloy composition has previously been qualitatively understood in terms of a weighting of the s and p components of the LDOS, the shape of which may be understood in terms of the final state rule [9, 14–16], and the equivalent cores approximation. Considering such alloys in terms of the equivalent cores approximation, the difference in local charge between host and ionized Mg site,  $\Delta Z$ , changes from 0 to +1 and to +2 respectively in the series AlMg, Mg and LiMg. In this work we carry out first-principles calculations of the Auger profile treating the local environment using the embedded technique [17] which is well suited to the modelling of such an impurity system.

## 2. Theory

The alloy systems which we consider are nearly-free-electron-like and are treated using the theoretical framework developed in Fowles *et al* [5]. The Mg atom involved in the Auger process is embedded in a free-electron gas having the electronic properties of the host metal or alloy. In this case the compositions of the systems studied are  $Li_{85}Mg_{15}$ ,  $Mg_{100}$  and  $Al_{85}Mg_{15}$  which correspond to 1.15, 2.0 and 2.85 valence electrons per lattice position. The free-electron-like properties of the host were calculated by assuming the lattice spacing to be that of pure Li, Mg and Al respectively which is equivalent to considering the ionized Mg site as an isolated impurity. The free-electron bandwidths were calculated to be 5.09 eV, 7.08 eV and 9.34 eV for  $Li_{85}Mg_{15}$ ,  $Mg_{100}$  and  $Al_{85}Mg_{15}$  respectively (see for example [18]). The ionized Mg site was allowed to relax and a screened self-consistent potential constructed for the impurity Mg atom embedded in the host. Using this potential the LDOS was calculated by the Green function formalism and KLV Auger profiles calculated from first principles, integrating the radial and angular Auger matrix elements up to the Wigner-Seitz radius.

## 3. Results

### 3.1. Theoretical calculations

Figure 3 shows the results of calculations of the LDOS of the Mg impurity core-ionized site in the three materials studied. In  $Al_{85}Mg_{15}$  (figure 3(a)), the greater valence bandwidth and number of valence electrons available to screen the core-ionized site means that the shape of the LDOS is similar to that of the Fermi-like distribution of a simple metal ground state LDOS. For a core-ionized site in pure Mg (figure 3(b)), the LDOS is distorted from the Fermi-like distribution associated with simple metals as the valence electrons attempt to screen the extra positive charge. The s LDOS shows a considerable change in shape associated with this screening, whilst the shape of the p LDOS is little changed. In  $Li_{85}Mg_{15}$  (figure 3(c)), the creation of a core hole causes the LDOS to become distorted to such an extent that an s-like bound state is created below the bottom of the band. Previous x-ray emission [19] and

theoretical work [20,21], has revealed distortion of the ground state LDOS of Mg in an Li environment; our results indicate that the presence of a core hole causes a bound state to be formed to provide the screening required.

Figure 4 shows the theoretical  $KL_1V$  profiles generated by evaluating the expressions given in [4]. Calculated profiles for the  $KL_{2,3}V$  transitions are similar to those of the  $KL_1V$  in figure 4 but with the intensity of the s component reduced relative to the p component by approximately a third due to the effect of angular Auger matrix elements.

### 3.2. Comparison with experiment

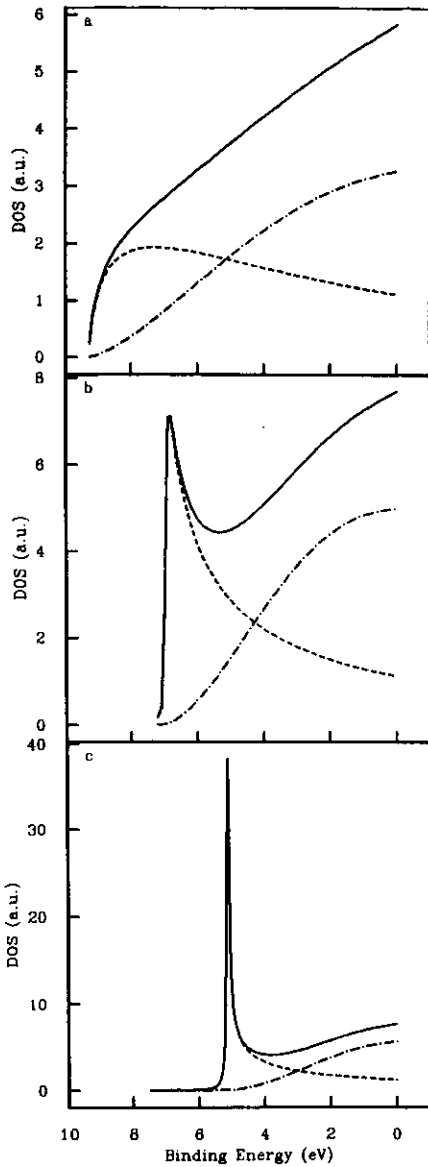
In order to compare our calculated results with the experimentally measured spectra, it is necessary to include contributions from instrumental and lifetime broadening and add an integrated background to represent the contribution of scattered electrons to the experimental spectra. The instrumental broadening is represented by Gaussians of 0.5 eV (FWHM) and the lifetime broadening by Lorentzians of 0.81 eV and 0.38 eV (FWHM) for the  $KL_1V$  and  $KL_{2,3}V$  respectively [22, 23]. In addition we have also applied an energy dependent broadening to allow for self-energy effects following the procedure of Jackson and Allen [24] for semiconductors. This relates the full width broadening at half maximum,  $\Gamma(E)$ , due to the imaginary part of the self-energy,  $\Sigma(E)$ , to the escape depth using the following equation:

$$\Gamma(E) = 2 \text{Im} \Sigma(E) = h(2E/m)^{1/2}/\lambda(E) \quad (1)$$

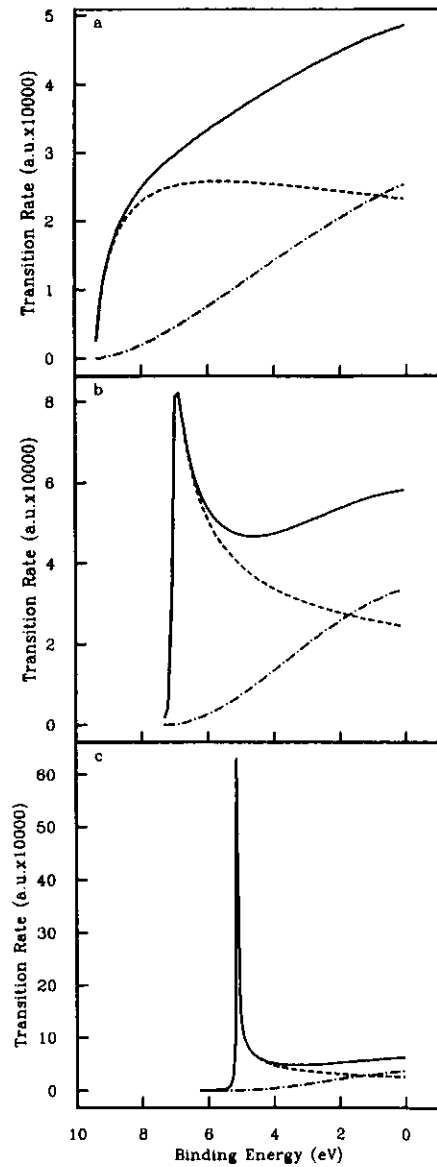
where  $\lambda(E)$  is the escape depth of an electron of energy  $E$  and mass  $m$ . In this case we have simple metal alloys of Mg and the escape depths for Mg have been estimated from the data of Penn [25]. The values of the self-energy broadening obtained vary smoothly from 0 eV at the Fermi energy to approximately 1 eV at an electron energy of  $|E - E_f| = 10$  eV. The self-energy broadening we are using is strictly that for a ground state atom; however the good agreement between theory and experiment for the  $KL_1V$  profile indicates that the values for a core-ionized site are similar.

The full lines in figures 1 and 2 show the theoretical profiles after allowing for these contributions. Comparing the theoretical and experimental profiles, it is apparent that the quantitative agreement is very good for the  $KL_1V$  profile (figure 1). However the low kinetic energy peak of the  $KL_{2,3}V$  in each material has more intensity in the calculated profile than in the experimental results. This effect has been noted previously for pure Mg [5] using the first-principles approach we adopt here and the reasons for this difference are not known. It should however be noted that the problem is not only one of excess intensity in the s component but also of too great a width of the p component in the calculation of the  $KL_{2,3}V$  Auger profile, since if the intensity of the s component is scaled to that of the experimental result it is still not possible to obtain a good fit to the data. It is not clear why such a discrepancy should arise for the  $KL_{2,3}V$  profile when that of the  $KL_1V$  agrees well with the experiment. One possible reason for the discrepancy may be the neglect of scattering of the valence and Auger electrons by the surrounding lattice, which will affect the matrix elements for the s and p contributions differently in the two cases.

The KLV Auger profiles of  $Li_{85}Mg_{15}$  alloy provide a sensitive test of our model since the s and p components are clearly defined in these spectra. The bound state just below the free-electron band in the calculated LDOS (figure 3) extends the Auger profile by an amount dependent on the binding energy of the state. The



**Figure 3.** Comparison of the local density of states of core-ionized Mg present as an impurity in (a) Al<sub>85</sub>Mg, (b) Mg<sub>100</sub> and (c) Li<sub>85</sub>Mg<sub>15</sub> respectively. In each case the s component is shown by the dashed line, the p component by the dot-dashed line and the total by the solid line.



**Figure 4.** Comparison of the calculated KL<sub>1</sub>V Auger lineshape of core-ionized Mg present as an impurity in (a) Al<sub>85</sub>Mg<sub>15</sub>, (b) Mg<sub>100</sub> and (c) Li<sub>85</sub>Mg<sub>15</sub> respectively. In each case the s component is shown by the dashed line, the p component by the dot-dashed line and the total by the solid line. We present here revised results for the KL<sub>1</sub>V profile of Mg; the shapes of the s and p components of this profile were slightly in error in the previous work of Fowles *et al* [5] though the changes from earlier results are small and do not affect the overall Auger lineshape or the conclusions of [5].

good agreement between the widths of the spectrum given by theory and experiment provides strong evidence that a bound state is indeed created below the valence band of core-ionized Mg in an Li-rich system.

### 3.3. Comparison with a weighted LDOS approach

A common approximation in the analysis of CCV Auger transitions is to separate the matrix element and LDOS contributions to the Auger profile. The lineshape is then related to the angular components of the LDOS weighted by numerical factors due to energy independent Auger matrix elements. For simple metals this leads to an expression of the form

$$A(E) = M_s D_s(E) + M_p D_p(E) \quad (2)$$

where  $A(E)$  is the Auger lineshape,  $D_s(E)$  and  $D_p(E)$  are the s and p components of the LDOS and  $M_s$  and  $M_p$  are matrix elements. We have shown previously for pure Mg [5] that the approximation represented by (2) does lead to significant errors in calculating the theoretical Auger profile due to the energy dependence of the Auger matrix elements. We now assess the value of (2) in understanding the Auger profiles of alloys and in particular we evaluate the common assumption that the matrix elements are independent of environment. Due to the unresolved problem in understanding the  $KL_{2,3}V$  profiles we concentrate on the results for the  $KL_1V$  transitions. Using the broadening and background contributions previously described for the first-principles calculation we find no difficulty in fitting the LDOS (figure 3) to both the experimental and theoretical results using (2) with the ratio  $M_s/M_p$  as a free parameter. These fits are not shown but are as good as the agreement obtained between theory and experiment in figure 1. The value of such a procedure is however dependent on whether the values of the matrix elements necessary to reproduce the experimental profile correspond to the calculated rates for such KLV transitions. Since the weighted LDOS does not provide an absolute measure of the transition rate, the useful quantity is in this case the ratio of the matrix elements  $M_s/M_p$ . The value of  $M_s/M_p$  will be comparable with the transition rate ratio, given by the ratio of the integrals under the s and p components of the first-principles calculation, and these values must be in good agreement in order to validate the approximation represented by (2). We show our results for the ratios of the matrix elements in table 1. We find that the results for the LDOS in (2) with  $M_s/M_p$  as a free parameter diverge considerably from the rigorous calculation. This is a result of differences in the contributions of the valence s and p components across the band and is a greater effect than might have been anticipated given the apparently similar shapes. We conclude that care must be exercised when applying the approximation (2) to the analysis of KLV lineshapes and that the common assumption that the ratio of matrix elements is independent of environment does not hold for Mg. The results in table 1 clearly show that not only the shape of the LDOS but also the transition rate ratio is strongly dependent on the local electronic structure of the host.

## 4. Conclusions

This theoretical study of the Mg  $KL_1V$  Auger transitions in  $Al_{85}Mg_{15}$ ,  $Mg_{100}$  and  $Li_{85}Mg_{15}$  shows that a calculation within an embedding framework can account for

Table 1.

	LiMg	Mg	AlMg
Calculated Auger rate s/p ratio	3.1	2.4	2.0
Weighted DOS s/p (fit to calculation)	2.5	1.5	0.8
Weighted DOS s/p (fit to experiment)	2.7	1.5	0.2

the distortions undergone by the LDOS around a core-ionized Mg site, where, in an equivalent cores approximation, there is an effective  $\Delta Z$  of +2, +1 and 0 relative to the host. The  $KL_1V$  profiles illustrate the sensitivity of both the shape and intensity of the Auger profile components to the local electronic environment. By calculating from first principles the KLV Auger transitions of Mg as an impurity in simple metal alloys we have found good agreement between theory and experiment for the  $KL_1V$  lineshape while for the  $KL_{2,3}V$  transition we find differences between theory and experiment, the reason for which is not understood. It may be that the discrepancy is due to the failure of the single-particle approximation we have used to calculate the Auger lineshapes.

Although clear similarities may be seen between the Auger lineshapes and the LDOS around core-ionized site, the energy dependence of the matrix elements across the valence band has a significant effect on the calculated Auger profile.

From the results of electronic structure calculations of a core-ionized Mg site in Li we find that a bound state is created below the valence band. This result is supported by the agreement of the experimental spectra of such an alloy with the result of calculations of the  $KL_1V$  Auger profile.

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