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L-EDGE XANES STUDIES OF CHARGE REDISTRIBUTION UPON COMPOUND FORMATION IN GOLD AND NICKEL METALLIC COMPOUNDS

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Abstract: L-edge XANES of a series of gold (AuAl_2 , AuGa , and Au_2Ag) and nickel (NiSb , $\text{Ni}_{0.64}\text{Fe}_{0.36}$, NiAl , and NiAl_3) intermetallic compounds have been measured. It is found that the $L_{\text{III,II}}$ edges of AuAl_2 and AuGa exhibit very intense whiteline indicating a significant depletion of d character at the Au site of these compounds. This observation is interpreted in terms of a mechanism in which s-d interplay determines the overall charge redistribution. In the case of Ni compounds, the effect of s-d interplay is found to be less dramatic.

Introduction

Charge redistribution upon alloying and formation of intermetallic compounds is of particular interest in the studies of the electronic structure of intermetallic systems containing noble metals [1]. Two questions often arise: one concerns the behavior of the d band, the other concerns the nature of the actual electron redistribution (charge transfer or rehybridization) and its correlation with the difference in the electronegativity of the constituents.

Here we report a L edge XANES study of a series of gold (AuAl_2 , AuGa , and Au_2Ag) and nickel (NiSb , $\text{Ni}_{0.64}\text{Fe}_{0.36}$, NiAl and NiAl_3) intermetallics. This study is an extension of our recent study of Pd L edges in Pd intermetallics [2]. Since $L_{\text{III,II}}$ XANES arise primarily from p to d transitions, the $L_{\text{III,II}}$ edge XANES (particularly the whiteline features) of the noble metal components in these compounds is a direct measure of the density of the unoccupied d states above the Fermi level.

Experimental

The intermetallics investigated in this study were prepared with standard procedures. Au_2Ag was rolled to thin foils and AuAl_2 and AuGa were in the form of fine powders. All the nickel compounds were in the form of ingots except $\text{Ni}_{0.64}\text{Fe}_{0.36}$ (fcc structure, γ phase) which was a foil. L edge absorption measurements of the Au compounds were made in a transmission mode at the C2 station of the Cornell High Energy Synchrotron Source (CHESS) using a channel-cut Si(220) monochromator. The measurements of the Ni series were carried out in a total-electron-yield mode at the U15 beamline of the National Synchrotron Light Source (NSLS). U15 is equipped with a Toroidal Grating Monochromator (TGM) that covers an extended range of soft x-ray energies (200 to >1000 eV). The energy resolution was a moderate ~ 2 eV at the Au L-edge and was ~ 6 eV at the Ni L edge. The Ni samples were Ar ion etched in a vacuum chamber prior to measurement. The specimen current was measured as the total electron yield [3].

Results and Discussion

The Au L edge XANES of AuAl_2 , AuGa_2 and Au_2Ag are shown in Fig. 1 where the spectra of Au_2Ag are very similar to those of pure Au except for a small increase in the absorption coefficient just above the threshold (within $\sim 20\text{eV}$). The spectra of AuAl_2 and AuGa_2 clearly exhibit whiteness features.

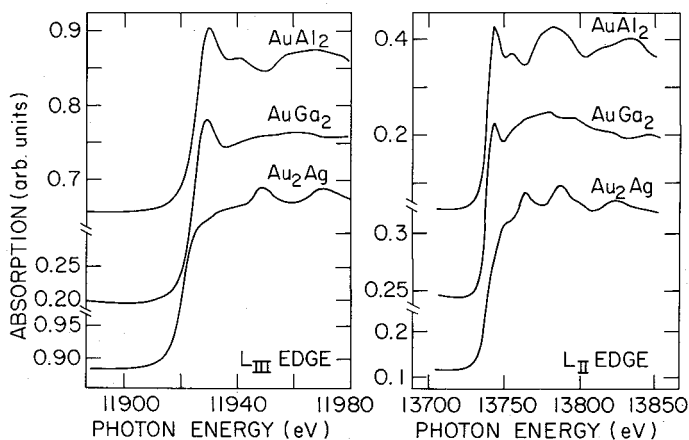


Fig. 1. Au L_{III} , L_{II} edge XANES of AuAl_2 , AuGa_2 and Au_2Ag .

The Ni $L_{\text{III,II}}$ edge XANES of the Ni compounds are shown in fig. 2 together with a theoretical spectrum of Müller et al [4]. The L_{III} , L_{II} whiteness are separable despite the poor resolution. The theoretical spectrum has been broadened with the core hole width [4].

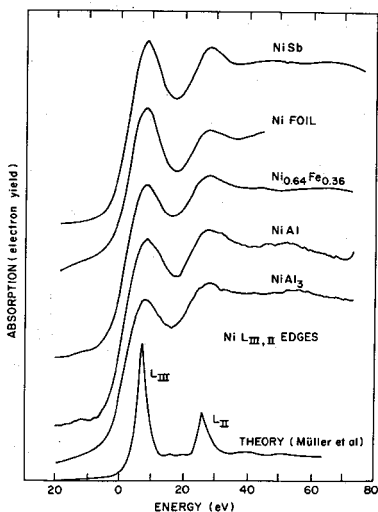


Fig. 2. L-edge XANES spectra (raw data) of NiSb, Ni, $\text{Ni}_{0.64}\text{Fe}_{0.36}$, NiAl and NiAl_3 in the order of increasing electronegativity difference (from top to bottom) and the theoretical spectrum of Ni by Müller et al.

Let us first discuss the Au results. From fig. 1 the whitelines in the AuAl_2 and AuGa_2 spectra are clearly observed while only a small increase in the absorption coefficient is seen in the Au_2Ag XANES relative to pure Au. This observation immediately indicates the presence of high density of unoccupied d states above the Fermi level in AuAl_2 and AuGa_2 . The implication is that the d states at the Au site which are full in elemental Au are depleted upon alloying with electropositive elements. This is in contrast to Paulings electronegativity considerations since Au is the most electronegative metallic element and charge is expected to flow onto the Au site upon compound formation. The electronegativity (E.N.) values of elements of interest are listed in table 1.

Table 1. Paulings Electronegativity Values of Elements of Interest

Element	Al	Ga	Fe	Ni	Ag	Sb	Pd	Au
E.N. values	1.61	1.81	1.83	1.91	1.93	2.05	2.20	2.54

The same situation was encountered in the Pd L edge study [2] and the photoemission and Mössbauer studies of Au alloys [5]. These observations can be interpreted in terms of a charge compensation (rehybridization) model described earlier [5] in which d charge depletion at the Au site is overcompensated by s-p (conduction) charge gain so that the direction of the net charge flow (of the order of 0.1 electron) is in agreement with Paulings electronegativity. The order of the change of d counts at the Au site, Δn_d (a negative number in all Au metallic compounds), was previously estimated [5] to be $|\Delta n_d|(\text{AuAl}_2) > |\Delta n_d|(\text{AuGa}_2) > |\Delta n_d|(\text{Au}_2\text{Ag})$. This trend is confirmed by the relative intensity of the whitelines shown in fig. 1. The area under the whiteline is known to be a good measure of unoccupied d states [6,7,8].

We now turn to the Ni results. It is apparent from fig. 2 that alloying has a reverse but less significant effect on the $L_{\text{III,II}}$ edge of Ni compared to that of Pd and Au (partly because of the poor resolution). Some crude parameters are listed in table 2. A qualitative trend is nevertheless obtained from these results.

Table 2. Parameters for the L_{III} whiteline of fig. 2.

Sample	Ni	NiSb	$\text{Ni}_{0.64}\text{Fe}_{0.36}$	NiAl	NiAl_3
$\frac{1}{2}$ WIDTH ^a ($\pm 0.2\text{eV}$)	4.5	4.4	4.9	6.1	5.9
Height ^b (± 0.05)	1.0	0.89	0.84	0.88	0.87

a. halfwidth of the rising L_{III} edge whiteline profile

b. relative to Ni (the height is normalized to absorption at 40eV)

What emerges from table 2 is that the L edge changes slightly with an apparent decrease in the white line intensity in the compounds, the height of the whiteline drops in all compounds but substantial broadening is observed in the case of NiAl and NiAl_3 , indicating a spreading out of the d character in these compounds. Further analysis using the smooth Cu $L_{\text{III,II}}$ edge as a step function shows that the area under the Ni L_{III} white line in all the compounds is indeed decreased indicating a gain of d character at the Ni site upon compound formation. This behavior is in contrast to that of Pd and Au compounds.

Summary

It is found that the $L_{\text{III,II}}$ edges of AuAl_2 and AuGa_2 exhibit intense whitelines and that a small increase in intensity is observed at the $L_{\text{III,II}}$ edges of the Au, Ag, indicating a depletion of d character at the Au site upon compound formation. This observation is interpreted in terms of a mechanism in which s-d interplay (rehybridization) determines the overall charge redistribution (a gain of s charge is accompanied by a loss of d charge). In the case of Ni compounds, the effect of s-d interplay is found to be less dramatic.

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