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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 (AuAl₂, AuGa, and Au₂Ag) and nickel (NiSb, NiFe₀.₆₄Fe₀.₃₆, NiAl, and NiAl₂) intermetallic compounds have been measured. It is found that the L₃ edges of AuAl 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 (AuAl₂, AuGa, and Au₂Ag) and nickel (NiSb, NiFe₀.₆₄Fe₀.₃₆, NiAl, and NiAl₂) intermetallic compounds. This study is an extension of our recent study of Pd L edges in Pd intermetallcics [2]. Since L₃, L₄, XANES arise primarily from p to d transitions, the L₃ 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 intermetallcs investigated in this study were prepared with standard procedures. Au₂Ag was rolled to thin foils and AuAl₂ and AuGa₂ were in the form of fine powders. All the nickel compounds were in the form of ingots except NiFe₀.₆₄Fe₀.₃₆ (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 >1000eV). The energy resolution was a moderate ~2eV at the Au L-edge and was ~6eV 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].

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Results and Discussion

The Au L edge XANES of AuAl₂, AuGa₂, and Au₂Ag are shown in Fig. 1 where the spectra of Au₂Ag are very similar to those of pure Au except for a small increase in the absorption coefficient just above the threshold (within ~20eV). The spectra of AuAl₂ and AuGa₂ clearly exhibit whiteline features.

![Fig. 1. Au L edge XANES of AuAl₂, AuGa₂ and Au₂Ag.](image)

The Ni L edge XANES of the Ni compounds are shown in Fig. 2 together with a theoretical spectrum of Müller et al [4]. The LIII, LII whitelines 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, Ni₀.₆₄Fe₀.₃₆, NiAl and NiAl₃ in the order of increasing electron-negativity difference (from top to bottom) and the theoretical spectrum of Ni by Müller et al.](image)
Let us first discuss the Au results. From fig. 1 the whitelines in the AuAl₂ and AuGa₂ spectra are clearly observed while only a small increase in the absorption coefficient is seen in the Au₃Ag XANES relative to pure Au. This observation immediately indicates the presence of high density of unoccupied d states above the Fermi level in AuAl₂ and AuGa₂. 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

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Ga</th>
<th>Fe</th>
<th>Ni</th>
<th>Ag</th>
<th>Sb</th>
<th>Pd</th>
<th>Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.N. values</td>
<td>1.61</td>
<td>1.81</td>
<td>1.83</td>
<td>1.91</td>
<td>1.93</td>
<td>2.05</td>
<td>2.20</td>
<td>2.54</td>
</tr>
</tbody>
</table>

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, ∆nₚ (a negative number in all Au metallic compounds), was previously estimated [5] to be |∆nₚ| (AuAl₂) > |∆nₚ| (AuGa₂) > |∆nₚ| (Au₃Ag). 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 L₃₄ 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 L₃₄ whiteline of fig. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni</th>
<th>NiSb</th>
<th>Ni₈₄Fe₀.₃₆</th>
<th>Ni₈Al</th>
<th>Ni₈Al₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>½ WIDTH² (±0.2eV)</td>
<td>4.5</td>
<td>4.4</td>
<td>4.9</td>
<td>6.1</td>
<td>5.9</td>
</tr>
<tr>
<td>Height ² (±0.05)</td>
<td>1.0</td>
<td>0.89</td>
<td>0.84</td>
<td>0.88</td>
<td>0.87</td>
</tr>
</tbody>
</table>

a. halfwidth of the rising L₃₄ 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 NiAl3, indicating a spreading out of the d character in these compounds. Further analysis using the smooth Cu L$_{III,II}$ 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$_{III,II}$ edges of AuAl$_2$ and AuGa$_2$ exhibit intense whitelines and that a small increase in intensity is observed at the L$_{III,II}$ 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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