

# X-ray absorption near-edge studies of 5d transition metal compounds

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Theoretical discussions of noble metal bonding to less electronegative atoms have emphasized the important role of the  $d$ -orbitals of the noble metal. The striking violet-metallic compound  $\text{AuAl}_2$  provides an excellent example of this type of bonding. As the most electronegative metal, Au in compounds tends to demand a charge transfer to the Au sites. In  $\text{AuAl}_2$  Watson *et al.* have calculated that this charge transfer to the Au is of *non-d character* and is roughly one electron per Au atom. They emphasized, however, that roughly one electron of *5d character* is backtransferred *away* from the Au sites in order to maintain charge neutrality. This compensating flow of  $d$  and *non-d* charge density is effected through Au–Al hybridization (or covalent mixing). Here the creation of mixed (Au  $5d$ )–(Al  $sp$ ) antibonding states above the Fermi level leads to the effective decrease in net Au- $5d$  orbital occupancy.

Transition metal ( $T$ )  $L_2$ - and  $L_3$ -edge x-ray absorption near-edge spectroscopy (XANES) measurements can provide valuable insight into the effective  $5d$ -orbital electron (or hole) count. The  $L_{2,3}$  near-edge spectrum of a  $5d$  transition metal is dominated by a strong white line (WL) feature caused by atomic-like  $2p \rightarrow 5d$  transitions. We correlate the strength of the white line feature at these edges to

the degree of chemical-bonding-induced  $5d$ -orbital charge transfer in transition metal based materials.

The elemental Au  $L_{2,3}$  spectra have almost no WL feature, indicating almost no  $5d$ -band holes. The substantial WL feature in AuAl<sub>2</sub> arises from an increase in the effective Au  $d$ -hole count due to the chemical bonding in the compound. We have studied many other Au, Pt, Ir, and Re compounds with Al, Si, and Ge and have found similar results. We find this same type of increase in the  $L_{2,3}$  near-edge WL feature and associate it with compound formation. We therefore believe that such an WL feature increase can be used as a measure of the strength of chemical bonding upon compound formation.

Furthermore, we study multi-layered Au-Si thin films which have been deposited with the net compositions “Au<sub>1-x</sub>Si<sub>x</sub>,”  $x=0.29, 0.5,$  and  $0.8$ . After ion-beam mixing with Xe<sup>2+</sup> these films exhibited superconductivity in the 0.3–1.2 K range despite the non-superconducting character of both Au and Si. XANES measurements on the Au  $L_3$  edge in these films indicate that metastable Au-Si compound formation occurs in these ion-beam-mixed materials. Specifically the XANES indicate changes in Au  $5d$ -orbital occupancy and changes in the local Au structural environment which are both consistent with local compound formation.