Electronic Structure of Au-Pd and Au-Pt Alloys: An XAFS Study

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Introduction

Charge redistribution upon alloy formation continues to be an interesting topic for investigation. This is partly because of the fact that alloying permits the fine-tuning of the properties of materials, (this technique may have profound implications to application in low-dimensional and nanostructure materials), and partly because of advancement in the tools, both experimental and theoretical. We recently conducted x-ray absorption fine structure (XAFS) measurements of a series of Au-Pd and Au-Pt alloys at the PNC-CAT bending magnet beamline and observed an anomalous behavior: that both Au and Pt appear to be gaining d charge upon alloy formation. The experiments were conducted using total electron yield.

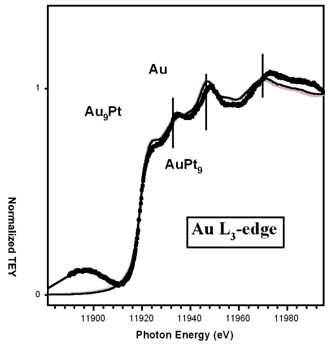

FIG. 1. Au L_3-edge XANES of Au, Au_9Pt, and $AuPt_9$.

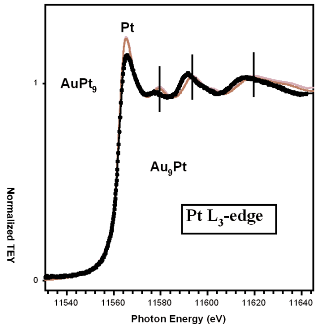

FIG. 2. Pt L_3-edge of the same samples shown in Fig. 1.

Results and Discussion

Representative results in the L_3-edge measurements are shown in Figs. 1 and 2. Both sets of near-edge spectra shown have been normalized to unity edge jump. The broad feature in the pre-edge region of $AuPt_9$ in Fig.1 is due to the extended x-ray absorption fine structure (EXAFS) of the Pt L_3-edge. The vertical bars mark the positions of the first three resonances of the pure metals beyond the whiteline.

Both Au and Pt are fcc metals with similar lattice spacing (Au: 4.08 Å; Pt: 3.92 Å). They are miscible, forming a continuous composition of alloys. The Au d bands are full and the Pt unfilled 5d holes are of primarily $d_{5/2}$ character.[1,2] Thus, Au $L_{3,2}$-edges do not exhibit intense whiteline, and only the Pt L_3-edge exhibits an intense whiteline.[1,2] Pd, on the other hand, exhibits a closer- to-statistical distribution of 4d holes[3] relative to Pt 5d.[1,2]

At least a couple of interesting features are clearly noticeable in Figs. 1 and 2. First, they both exhibit similar resonance patterns characteristic of a fcc lattice, although a progressive mismatch of the position of the resonance and broadening are observed in the alloys. Note that the mismatch is in opposing directions: Au diluted in Pt becomes Pt-like and Pt in Au becomes Au-like. Second, the dilute alloy (10% Au in Pt and 10% Pt in Au) exhibits a noticeable reduction in the first resonance of the L_3-edge. The latter observation immediately indicates that both Au and Pt sites in the dilute alloy gain d-charge locally upon alloying, since $2p_{3/2}$ to $5d_{5/2,3/2}$, transition probes the unoccupied densities of states (d holes) of primarily d character at the Fermi level.[1,2,4,5] This is an unusual behavior for Au in that, so far the in the majority of Au bimetallic alloys, Au always loses d charge locally and exhibits a more intense whiteline than that of the Au metal.[6] In addition, the ratio of the Pt L_3, to L_2 whiteline intensity also exhibits a significant change in the dilute alloy in that the Pt L_2-edge whiteline in the dilute alloy is reduced considerably. This observation necessitates the modification of Mott's original model of band filling in relativistic 5d metal d-bands.[1,2] This behavior is now being further investigated with photoemission spectroscopy.

These results can be considered together with previous results for Au-Pd alloys[7] at the Pd L-edges. A similar observation has also been made in the study of Au-Pd alloying, namely that both Au and Pd gain d charge upon alloying. It appears that the relativistic effect is less significant in Pd 4d bands than in the Pt 5d bands. The observation reported here leads to interesting questions concerning the chemical sensitivity of relativistic d bands (where the effect of spin-orbit interaction is comparable to banding) and the universality of charge transfer behavior in bimetallic Au alloy where Au is the most electronegative element of all metallic elements.

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References

[1] N.F. Mott, Proc. Phys. Soc. **62**, 416 (1949).

[2] M. Brown, R.E. Peierls and E.A. Stern, Phys. Rev. B **15**, 738 (1977).

[3] T.K.Sham, Phys. Rev. B **31**, 1903 (1985).

[4] A.N. Mansour, J.W. Cook, Jr. and D.E. Sayers, J. Phys. Chem. **88**, 2330 (1984).

[5] L.F. Mattheiss and R.E. Deitz, Phys. Rev. B **22**, 1663 (1980).

[6] A. Bzowski, Y.M. Yiu and T.K. Sham, Phys. Rev. B **49**, 13776 (1994).

[7] P.S. Kim and T.K. Sham, to be published.