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X-ray Photoelectron Spectroscopic Investigations of Cu−Ni, Au−Ag, Ni−Pd, and Cu−Pd Bimetallic Clusters[†]

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Core-level binding energies of the component metals in bimetallic clusters of various compositions in the Ni−Cu, Au−Ag, Ni−Pd, and Cu−Pd systems have been measured as functions of coverage or cluster size, after having characterized the clusters with respect to sizes and compositions. The core-level binding energy shifts, relative to the bulk metals, at large coverages or cluster size, ΔE_a, are found to be identical to those of bulk alloys. By substracting the ΔE_a values from the observed binding energy shifts, ΔE, we obtain the shifts, ΔE_c, due to cluster size. The ΔE_c values in all the alloy systems increase with the decrease in cluster size. These results establish the additivity of the binding energy shifts due to alloying and cluster size effects in bimetallic clusters.

Introduction

Clusters of metals such as Au, Ni, Cu, and Ag deposited on solid substrates have been studied extensively by employing X-ray photoelectron spectroscopy and cognate techniques.[1−6] These studies have shown that the increase in the metal core-level binding energy with the decrease in cluster size is not merely due to final-state effects but arises from the decrease in the core hole screening and the occurrence of a metal-to-nonmetal transition with decrease in cluster size.[7−9] We have been interested in investigating bimetallic clusters for some time. A preliminary study of certain specific compositions of three alloy systems, namely, Cu_7Ni_3, Ni_3Pd_2, and Cu_3Au, showed that the core-level binding energies of the component metals increase with the cluster size after accounting for the effect of alloying.[10] We considered it important to establish not only that alloying occurs in bimetallic clusters over a wide range of compositions but, more importantly, that the shifts in the core-level binding energies in the clusters due to alloying and cluster size are additive. For this purpose, we have carried out a detailed investigation of several compositions each of four alloy systems, including those compositions which are rich in either component. The alloy systems that we have investigated are Au−Ag, Cu−Ni, Ni−Pd, and Cu−Pd.

Bimetallic clusters of varying sizes were generated by resistive evaporation of the alloys under ultrahigh-vacuum conditions. The clusters were deposited on amorphized graphite surfaces and characterized by high-resolution electron microscopy and EDAX analysis, before recording the core-level spectra. It may be noted that while the Au−Ag, Cu−Ni, and Ni−Pd systems form alloys over the entire range of compositions, the phase diagram of the Cu−Pd system is somewhat more complex, involving the formation of certain line phases.[11] In the present study, we find that the shifts in the core-level binding energies of the large bimetallic clusters of the various compositions of Cu−Ni (Ni_9Cu, Ni_3Cu_2, Ni_3Cu_7, $NiCu_9$), Au−Ag (Ag_9Au, Ag_4Au, AgAu, Ag_2Au_3), Ni−Pd (Ni_4Pd, NiPd, $NiPd_4$, Ni_3Pd_2), and Cu−Pd (Cu_4Pd, Cu_7Pd_3,Cu_3Pd_2, Cu_2Pd_3) systems truly correspond to those of the alloys. By substracting out the binding energy shifts due to alloying from the observed binding energy shifts, we obtain the shifts arising from the cluster size. Such additive effects of alloying and cluster size on the core-level binding energy shifts also support the view that the increase in core-level binding energy found at small cluster size is not due to final-state effects alone.[8]

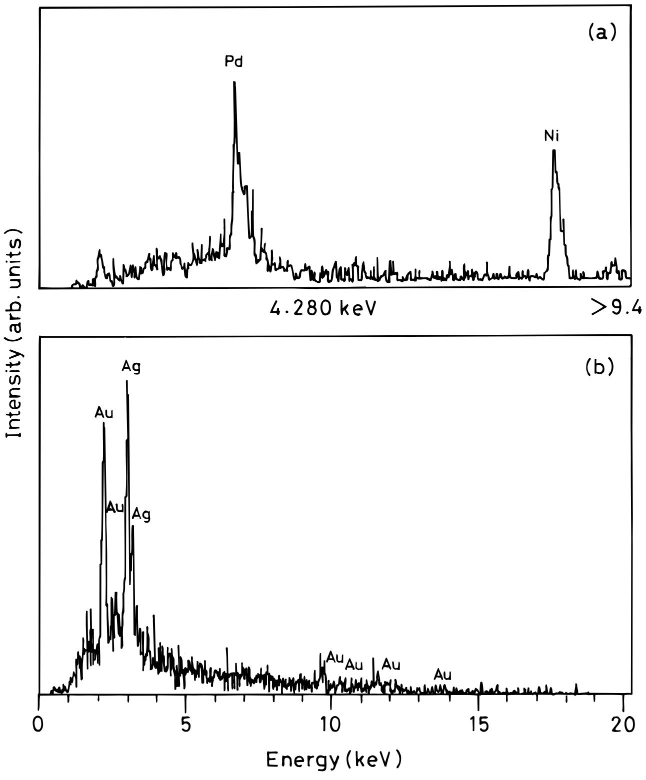

Figure 1. EDAX patterns of (a) Ni_3Pd_2 clusters corresponding to $I_{Ni} + I_{Pd}/I_C$ of 2.4 and (b) Ag_4Au clusters corresponding to $I_{Au} + I_{Ag}/I_C$ of 3.6.

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[†] Dedicated to Professor Saburo Nagakura.

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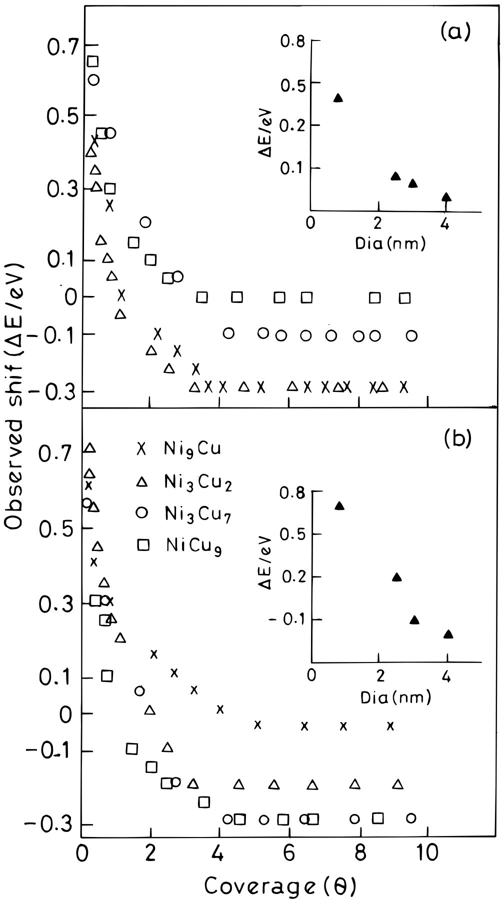

Figure 2. (a) Variation of the shift in the Cu($2p_{3/2}$) binding energy (relative to the bulk metal), ΔE, of Cu−Ni bimetallic clusters of different compositions with the coverage as determined by the ($I_{\mathrm{Cu}} + I_{\mathrm{Ni}}$)/$I_{\mathrm{C}}$ ratio. (b) Variation of the shift in the Ni($2p_{3/2}$) binding energy, ΔE, with the coverage. Insets show variation of ΔE with actual cluster size in the case of Ni_3Cu_2.

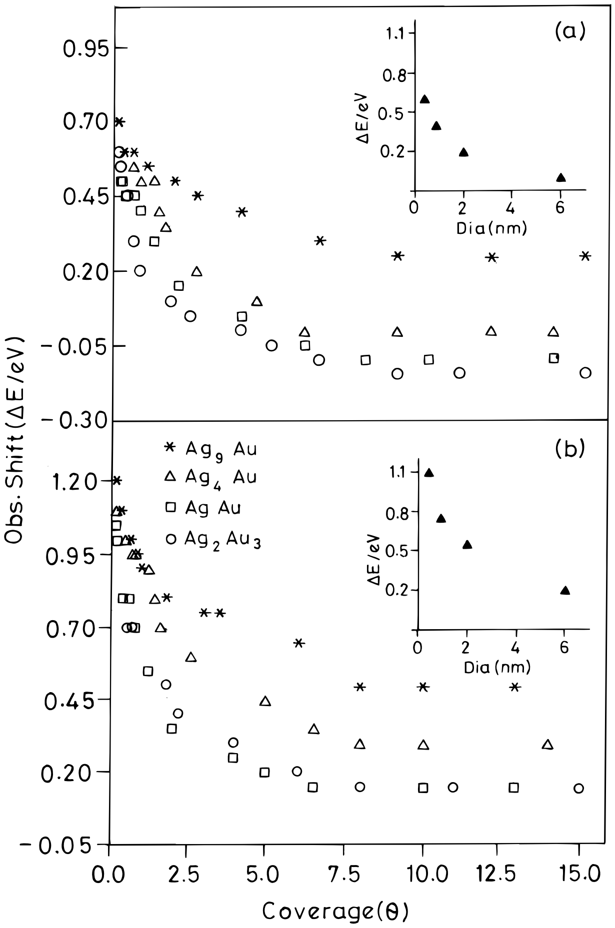

Figure 3. (a) Variation of the shift in the Ag($3d_{5/2}$) binding enery (relative to the bulk metal), ΔE, of Au−Ag alloy clusters of different compositions with the metal coverage as determined by the ($I_{\mathrm{Au}} + I_{\mathrm{Ag}}$)/$I_{\mathrm{C}}$ ratio. (b) Variation of the shift in the Au($4f_{7/2}$) binding energy, ΔE, with the coverage. Insets show variation of ΔE with actual cluster size in the case of Ag_4Au.

Experimental Section

Electron spectroscopic measurements were carried out with a VG ESCALAB V spectrometer fitted with a sample preparation chamber at a base pressure of $\sim 2 \times 10^{-10}$ Torr. Al Kα (1486.6-eV) radiation was employed for the XPS measurements. Bimetallic clusters were deposited at room temperature under ultrahigh-vacuum conditions on amorphous graphite surfaces (obtained by Ar^+ ion bombardment of graphite surfaces) by means of resistive evaporation by taking an appropriate mixture of the two high-purity metals wound around a thoroughly degassed tungsten filament.[10] When the filament was heated in the preparation chamber of the spectrometer, the metals melted and formed an alloy. We take the metal coverage θ to be proportional to the intensity ratio ($I_A + I_B$)/I_C where I_A and I_B are the core-level intensities of the metals and I_C is the C(1s) intensity of the support. We have used these intensity ratios throughout the paper to describe the coverage, θ.

Analysis of the bimetallic clusters was carried out using quantitative energy dispersive X-ray (EDAX) analysis. A Leica S-440i microscope operating at 20 kV fitted with a link ISIS, Oxford, and the ZAF-4/FLS program was used for analysis. Typical EDAX patterns of two bimetallic clusters corresponding to the compositions Ni_3Pd_2 and Ag_4Au are shown in Figure 1. We have similarly obtained the compositions of the other alloys studied here. Cluster size distributions were obtained with the help of high-resolution electron microscope (HREM) images. A JEOL JEM 200 CX electron microscope operating at 200 kV was used for the study. Samples for electron microscopy were prepared using amorphous carbon films as supports which were initially deposited on cleaned KBr crystals and subsequently transferred to a 200-mesh copper grid. The images were analyzed with respect to the size distribution by using an image analyzer (Leica Quantimet Q500MC). For example, in the case of the Au−Ag system, the cluster size distributions were fairly narrow. The cluster diameters are in the ranges 0.2−0.9, 0.5−1.8 and 5−10 nm for $\theta = 0.4$, 0.9, and 13, respectively, with mean diameters of 0.4, 0.9, and 6 nm. In the case of the Cu−Ni system, the cluster diameter ranges are 1−5 and 2−8 nm for $\theta = 1.2$ and 5, respectively, with mean diameters of 2.7 and 3.6 nm. These measurements confirmed that the θ values from surface spectroscopic methods adequately describe clusters of distinct size regimes.

Results and Discussion

We first investigated several compositions of the Cu−Ni and Au−Ag systems which readily form solid solutions over the entire composition range. In Figure 2, we show the plots of the observed shifts in the binding energies of the Cu($2p_{3/2}$) and Ni($2p_{3/2}$) levels, ΔE, relative to the bulk metals (933.1 and 852.9 eV, respectively) against the coverage for Ni_9Cu, Ni_3Cu_2, Ni_3Cu_7, and $NiCu_9$. The ΔE value should be close to zero at large coverages just as in monometallic clusters, but the behavior of the bimetallic clusters is different. In the Cu−Ni system, the ΔE of Cu($2p_{3/2}$) becomes increasingly negative at large coverages as the Cu content in the alloy decreases. Thus, Ni_9Cu

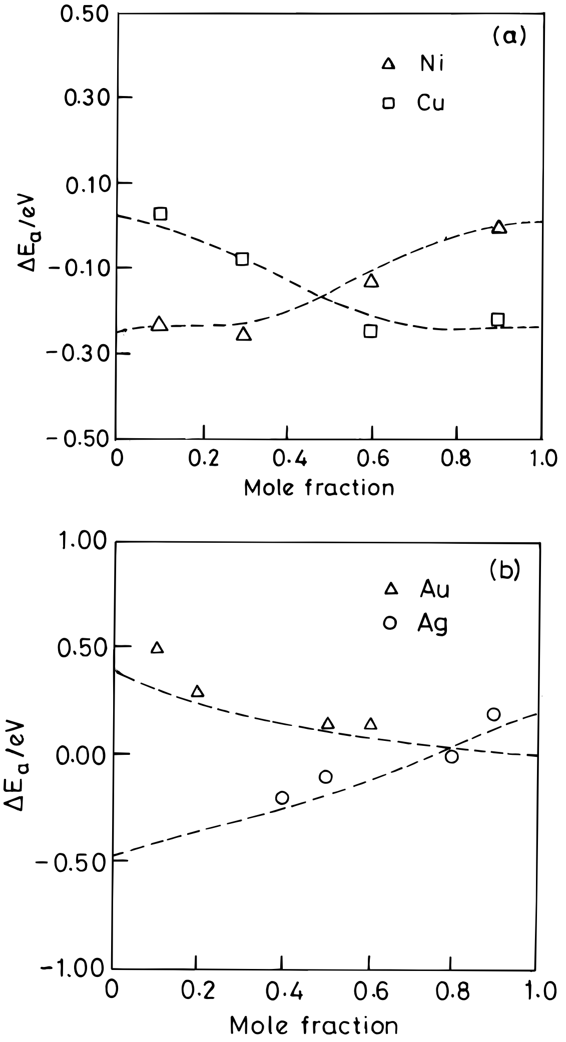

Figure 4. Plots of the core-level binding energy shifts (relative to the bulk metal value) at large coverages, ΔE_a, against the mole fraction for (a) Ni−Cu and (b) Au−Ag bimetallic clusters. Dashed lines represent the ΔE_a values for the bulk alloys, and the symbols denote the ΔE_a values for the bimetallic clusters at large coverages.

shows a ΔE value of −0.3 eV at large coverages, while it is close to 0 in $NiCu_9$. The ΔE value of $Ni(2p_{3/2})$ also becomes increasingly negative as the Ni content decreases, with the ΔE value being −0.3 eV in $NiCu_9$ and 0 in Ni_9Cu. The observed core-level binding energy shifts at large coverages are clearly due to alloying. From XPS studies of bulk alloys of Cu−Ni,[12−14] it is known that the magnitude of the shift in the core-level binding energy, of either component metal, increases as its content decreases, as is indeed observed in the bimetallic clusters in the present study.

In Figure 3, we have plotted the shifts in the binding energies, ΔE, of the $Ag(3d_{5/2})$ and $Au(4f_{7/2})$ levels of Ag_9 Au, Ag_4Au, AgAu, and Ag_2Au_3 relative to the bulk metals (368.2 and 84 eV, respectively) against the coverage. The shift in the $Ag(3d_{5/2})$ binding energy decreases as the Ag content in the alloy decreases. Thus, in Ag_9Au, the observed binding energy shift, ΔE, at large coverages is 0.3 eV, while in Ag_2Au_3 it is −0.2 eV. The ΔE of $Au(4f_{7/2})$ increases markedly with the decrease in the Au content, with a value of 0.5 eV in Ag_9Au and 0.15 eV in Ag_2Au_3 at large coverages of these compositions.

It is instructive to compare the observed core-level binding energy shifts of bimetallic clusters at large coverages with those observed for similar compositions of bulk alloys. In Figure 4a, we have plotted the observed binding energy shifts of the $Ni(2p_{3/2})$ and $Cu(2p_{3/2})$ levels in the Ni−Cu bimetallic clusters

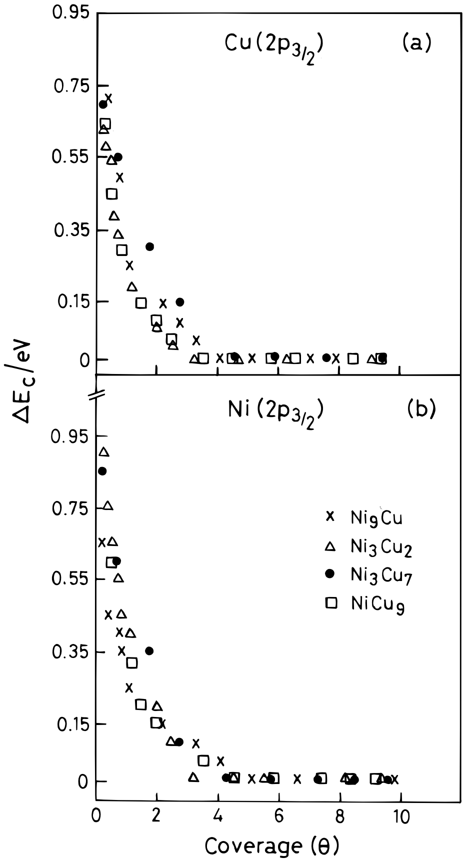

Figure 5. (a) Coverage or cluster size dependence of the shift in the $2p_{3/2}$ binding energy of Cu in Cu−Ni bimetallic clusters, ΔE_c. (b) Variation of the shift in $Ni(2p_{3/2})$ binding energy, ΔE_c, due to cluster size effect as in (a).

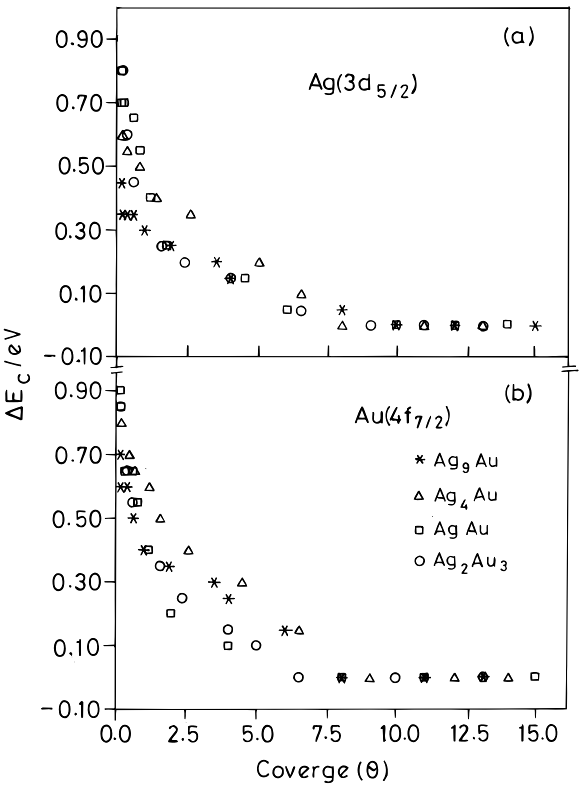

Figure 6. (a) Variation of the shift in the $3d_{5/2}$ binding energy of Ag in Au−Ag bimetallic clusters, ΔE_c, due to cluster size effect with the coverage. (b) Variation of the shift in $Au(4f_{7/2})$ binding energy, ΔE_c, due to cluster size effect as in a.

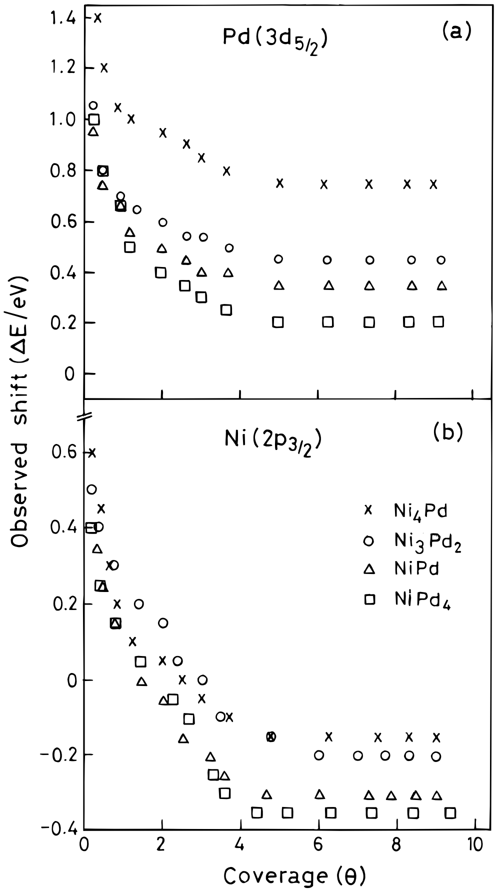

Figure 7. (a) Variation of the shift in the Pd($3d_{5/2}$) binding energy (relative to the bulk metal), ΔE, of Ni−Pd bimetallic clusters of different compositions with the metal coverage as determined by the ($I_{Ni} + I_{Pd}$)/I_C ratio. (b) Variation of the shift in the Ni($2p_{3/2}$) binding energy, ΔE, with the coverage.

at large coverages, ΔE_a, against the mole fraction. In the figure, we also show variations of ΔE_a of bulk alloys with the composition reported in the literature.[12] The observed shifts in the bimetallic clusters do indeed match closely with those of the bulk alloys. The plots in Figure 4b show the variation in the core-level binding energy shifts of Au($4f_{7/2}$) and Ag($3d_{5/2}$) in the Au−Ag bimetallic clusters at large coverages with mole fraction, along with the variation found in bulk alloys.[15] The agreement is good in this system as well. From these results, we establish that the bimetallic clusters of a wide range of compositions studied here are indeed those due to well-defined alloys without any significant surface segregation.

We obtain the binding energy shifts in the bimetallic clusters due to cluster size effect, ΔE_c, by subtracting the shifts due to alloying, ΔE_a, from the observed shifts, ΔE. The ΔE_c values so obtained are plotted against coverage (or cluster size) in Figure 5, for all the Cu−Ni compositions studied by us. We see that ΔE_c increases markedly with a decrease in coverage, reaching values of ~0.75 and 0.95 eV at very small coverages for Cu and Ni, repectively. The ΔE_c values of Au and Ag also increase with a decrease in coverage, reaching values of ~0.9 eV at very small coverages as shown in Figure 6. The ΔE_c values found at small coverages for the component metals in the Cu−Ni and Au−Ag systems are comparable to the values found in monometallic clusters of these metals.[6,8,11]

In Figure 7, we have shown the variation of ΔE values of Pd($3d_{5/2}$) and Ni($2p_{3/2}$) levels relative to the bulk metal values (335.1 and 852.9 eV, respectively) with coverage for the different compositions of the Ni−Pd system. The ΔE of Pd($3d_{5/2}$) increases markedly from 0.2 eV in $NiPd_4$ to nearly 0.8 eV in Ni_4Pd at large coverages. The ΔE of Ni($2p_{3/2}$) at

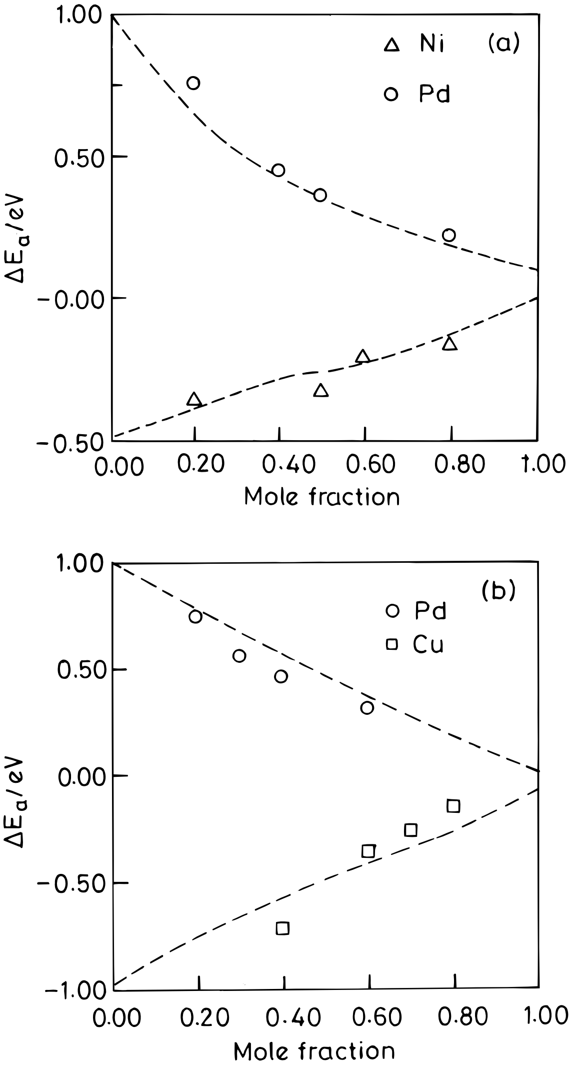

Figure 8. Plots of the core-level binding energy shifts (relative to the bulk metal values) at large coverages, ΔE_a, against the mole fraction for (a) Ni−Pd and (b) Cu−Pd bimetallic clusters. Dashed lines represent the ΔE_a values for bulk alloys, and the symbols denote the ΔE_a values for the clusters at large coverages.

large coverage is around −0.4 eV for $NiPd_4$ and only −0.2 eV in Ni_4Pd. We have plotted the Ni($2p_{3/2}$) and Pd($3d_{5/2}$) binding energy shifts at large coverages, ΔE_a, against the mole fraction in Figure 8a and compared them to the variation of binding energy shifts in bulk alloys.[12,14] The ΔE values at large coverages correspond to those found in bulk alloys in the Ni−Pd system as well. The ΔE_c values of Ni($2p_{3/2}$) and Pd($3d_{5/2}$) obtained by subtracting the shifts due to alloying, ΔE_a, from the observed ΔE values show the expected variation with coverage, increasing markedly at small coverages, reaching up to 0.7−0.8 eV at the smallest coverages examined by us.

The bimetallic clusters in the Cu−Pd system show the variation in the Cu($2p_{3/2}$) and Pd($3d_{5/2}$) binding energy shifts with coverage (see Figure 9) similar to those in the Cu−Ni, Au−Ag, and Ni−Pd systems, in spite of the complexity of the phase diagram referred to earlier.[11] The ΔE values at large coverages are plotted against mole fraction and compared with the ΔE values of the bulk alloys in Figure 8b. Clearly, the Cu−Pd bimetallic clusters also represent real alloy compositions. The ΔE_c values of the Cu−Pd bimetallic clusters increase with decrease in coverage, reaching values of ~0.6 and 0.7 eV, respectively, for Pd and Cu at the smallest coverages studied.

The above results on bimetallic clusters of varied compositions in the Cu−Ni, Ag-Au, Ni−Pd, and Cu−Pd systems

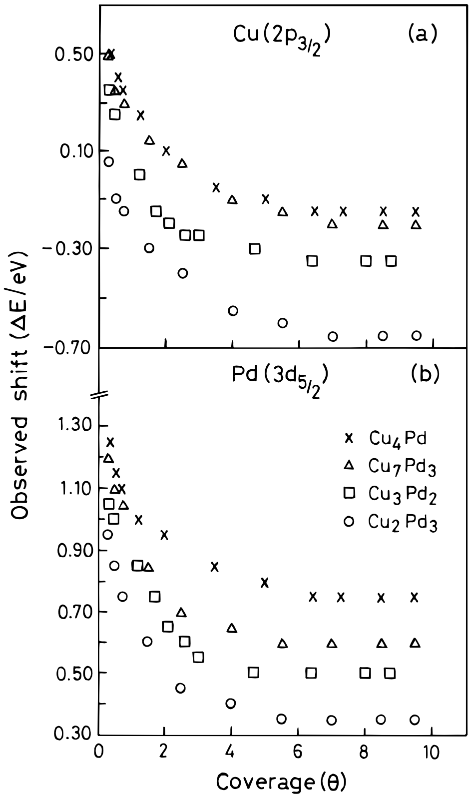

Figure 9. (a) Variation of the shift in Cu($2p_{3/2}$) binding energy, ΔE, of Cu−Pd bimetallic clusters of different compositions with the metal coverage as determined by the $(I_{Cu} + I_{Pd})/I_C$ ratio. (b) Variation of the shift in the Pd($3d_{5/2}$) binding energy, ΔE, with the coverage.

demonstrate that the observed core-level binding energy shifts of the component metals, ΔE (relative to the bulk metals), can be written as a sum of two effects, namely, those due to alloying and cluster size:

$$\Delta E = \Delta E_a + \Delta E_c$$

When the coverage is large, $\Delta E_c = 0$ and $\Delta E = \Delta E_a$. As the coverage is reduced, the contribution from ΔE_c due to cluster size increases.

References and Notes

(1) Wertheim, G. K.; DiCenzo, S. B.; Buchanan, D. N. E. *Phys. Rev. B* **1986**, *33*, 447.

(2) Mason, M. G. *Phys. Rev. B* **1983**, *27*, 748.

(3) Kohiki, S.; Ikeda, S. *Phys. Rev. B* **1986**, *34*, 3786.

(4) Eberhardt, W.; Fayet, P.; Cox, D. M.; Fu, Z.; Kaldor, A.; Sherwood, R.; Sondericker, D. *Phys. Rev. Lett.* **1990**, *64*, 780.

(5) Kuhrt, Ch.; Harsdorff, M. *Surf. Sci.* **1991**, *245*, 173.

(6) Vijayakrishnan, V.; Rao, C. N. R. *Surf. Sci.* **1991**, *255*, L516.

(7) Mason, M. G. In *Cluster Models for Surface and Bulk Phenomena*; Pacchioni, G., Eds.; Plenum: New York, 1992.

(8) Rao, C. N. R.; Vijayakrishnan, V.; Aiyer, H. N.; Kulkarni, G. U.; Subbanna, G. N. *J. Phys. Chem.* **1993**, *97*, 11157.

(9) Aiyer, H. N.; Vijayakrishnan, V.; Subbanna, G. N.; Rao, C. N. R. *Surf. Sci.* **1994**, *313*, 392.

(10) Santra, A. K.; Subbanna, G. N.; Rao, C. N. R. *Surf. Sci.* **1994**, *317*, 259.

(11) Hansen, H.; Anderko, K. *Constitution of Binary Alloys*: McGraw-Hill: New York, 1958.

(12) Steiner, P.; Hüfner, S. *Acta Metallurg.* **1981**, *29*, 1885.

(13) Steiner, P.; Hüfner, S.; Mårtensson, N.; Johansson, B. *Solid State Commun.* **1981**, *37*, 73.

(14) Hillebrecht, F. U.; Fuggle, J. C.; Bennett, P. A.; Zolnierek, Z.; Freiburg, Ch. *Phys. Rev. B* **1983**, *27*, 2179, 2194.

(15) Watson, R. E.; Hudis, J.; Periman, M. L. *Phys. Rev. B* **1971**, *4*, 4139.