

## ARTICLES

**Comparative X-ray Photoemission Spectroscopy Study of Au, Ni, and AuNi Clusters Produced by Laser Vaporization of Bulk Metals**

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Supported Au and Ni clusters as well as bimetallic AuNi clusters have been produced by laser vaporization of both pure bulk metals and alloy. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS) experiments show that they have a narrow distribution size centered around 2.5 nm and that bimetallic clusters have the same composition as the vaporized Au<sub>0.5</sub>Ni<sub>0.5</sub> alloy. X-ray photoemission spectroscopy (XPS) has been used to measure core level binding energy shifts of Au 4f<sub>7/2</sub> and Ni 2p<sub>3/2</sub>. The shifts observed in the bimetallic system show the combined effects of both alloying and surface local order in relation with strong Au surface segregation as deduced from previous low energy ion scattering (LEIS) experiments.

**Introduction**

Metallic clusters constitute an exciting field of research, and over at least the past 20 years a great deal of effort has been devoted to them. A very attractive issue in this field is certainly the transition in electronic and related properties when going from the bulk to small clusters. One can expect that all these differences should be reflected in catalytic behavior.<sup>1</sup> These particle size effects are of interest for those who investigate chemisorptive or catalytic properties since catalysts used in practice always consist of small supported particles. Moreover, in the field of heterogeneous catalysis, bimetallic particles constitute a promising class of catalysts that are found to exhibit superior properties, compared to single metals, in terms of activity, selectivity, stability, and resistance to poisoning.<sup>2,3</sup> Indeed, the alloying effects on the improvement of a catalyst may be explained by an ensemble and/or a ligand effect.<sup>2,3</sup>

Numerous studies have been devoted to the characterization of supported pure or bimetallic particles by using photoelectron spectroscopy.<sup>4–8</sup> They have shown that the shifts of the core level binding energy can be related to cluster size and/or alloying effects.

In bimetallic particles, the core level binding energy of each component is shifted with respect to the corresponding bulk phases. These shifts will be strongly influenced by the dispersion

of size or composition as well as by surface segregation processes. Photoemission spectroscopy is a powerful tool to investigate bimetallic clusters, but drawing definitive conclusions on the contribution of each effect requires rather well-defined clusters and additional analyses. Unfortunately, these precautions are rarely undertaken. We therefore consider it important to support our XPS investigations with a thorough analysis of supported clusters by using transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), low energy ion scattering (LEIS), and Monte Carlo simulations of the equilibrium structure.

Generally, supported bimetallic particles are produced either by chemical methods<sup>9–12</sup> or by atomic vapor deposition.<sup>13–15</sup> In the present study the Au, Ni, and AuNi particles are obtained by low energy cluster beam deposition onto HOPG or amorphous carbon with a laser vaporization generator. Laser vaporization permits the generation of ligand free metal clusters. In the case of bimetallic systems the advantage of this technique is essential since the composition of each produced particles is identical to that of the vaporized rod.<sup>16,17</sup>

In this work we report the shifts in binding energy of the Ni 2p<sub>3/2</sub> and Au 4f<sub>7/2</sub> levels in Ni, Au, and AuNi clusters deposited on HOPG. The results show that the shift of the bimetallic system is governed by alloying effects and local order at the atomic scale.

**Experimental Section**

The laser vaporization cluster source has been extensively described elsewhere.<sup>16,18</sup> The second harmonic of a Nd :YAG pulsed laser is used to vaporize the metal from a rod in order

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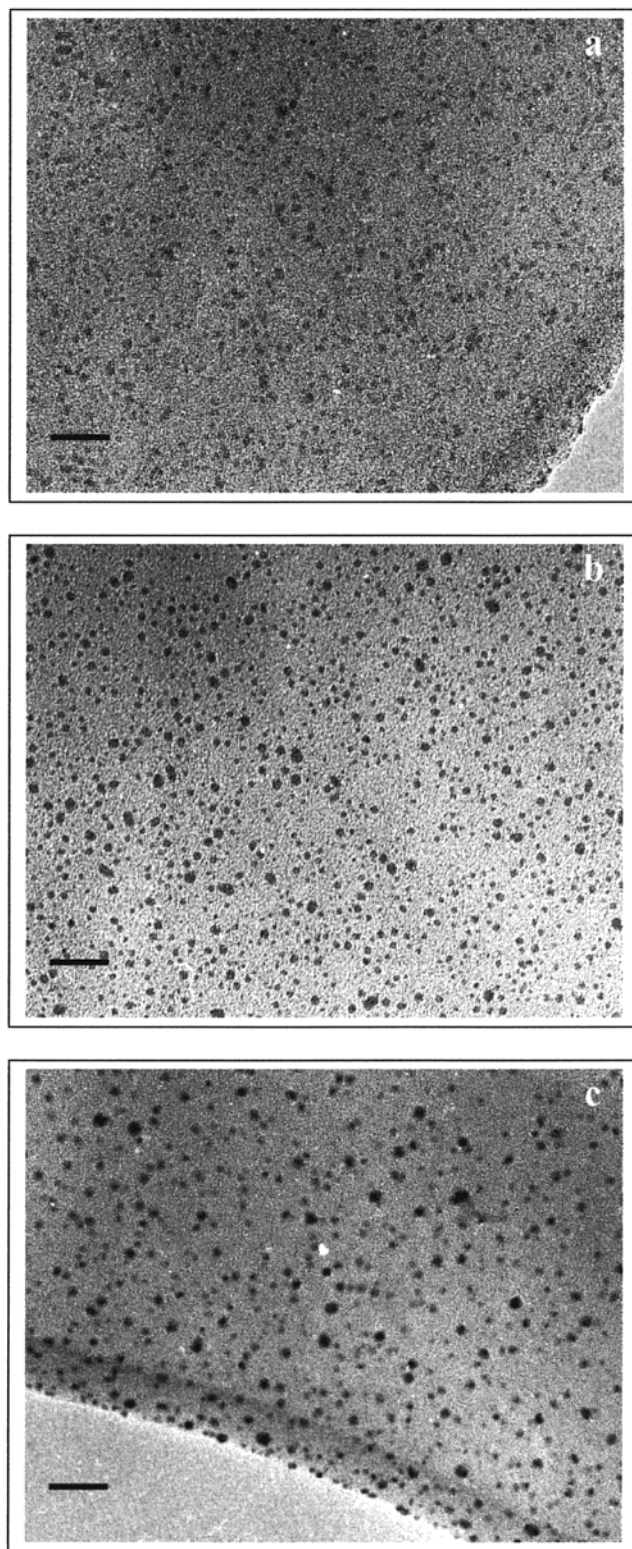
to create a plasma. Cluster nucleation and growth occur when an inert gas is introduced in synchronization with the laser. Differential pumping extraction of the clusters through a skimmer yields a cluster beam that carries neutral and ionized species. The ionized clusters can be analyzed by time-of-flight mass spectrometry (TOFMS). After removal of the ionized clusters by electrostatic deflection, the neutral ones are deposited on the substrates. Typical deposition rates of around 1 Å/min are obtained with neutral clusters of various materials. For these experiments Ni and Au rods of 99.99% and 99.95% purity, respectively, and a Au<sub>0.5</sub>Ni<sub>0.5</sub> bimetallic rod obtained by melting gold (99.99% purity) and nickel (99.95% purity) have been used. The deposition rates were monitored using a quartz microbalance. The clusters have been deposited onto a thin amorphous carbon film evaporated onto a copper grid in order to perform electron microscopy experiments or onto HOPG for photoemission measurements. The pressure in the deposition chamber was about 10<sup>-10</sup> mbar, and the equivalent deposited thickness is 0.3 nm for each sample. Once the samples are produced, they are either transferred in a UHV suitcase under dynamic vacuum (5 × 10<sup>-9</sup> mbar) into the XPS chamber or exposed to air and characterized by energy-dispersive X-ray spectroscopy (EDX) in a transmission electron microscope (JEOL JEM 2010-F) operating at 200 kV. The EDX spectrometer is a Pentafet Link Isis (Oxford Instruments) that allows the detection of elements with atomic numbers  $Z > 4$  amu. The field emission gun allows one to obtain small electron probes that are sufficiently bright to perform EDX analysis on individual particles and attain spatial resolution better than 1 nm.

XPS was carried out with a dual XPS/Auger CAMECA Nanoscan 100 type microprobe. The XPS is performed using Al K $\alpha$  X-ray, and the photoelectron energy resolution was fixed at 1 eV.

## Results

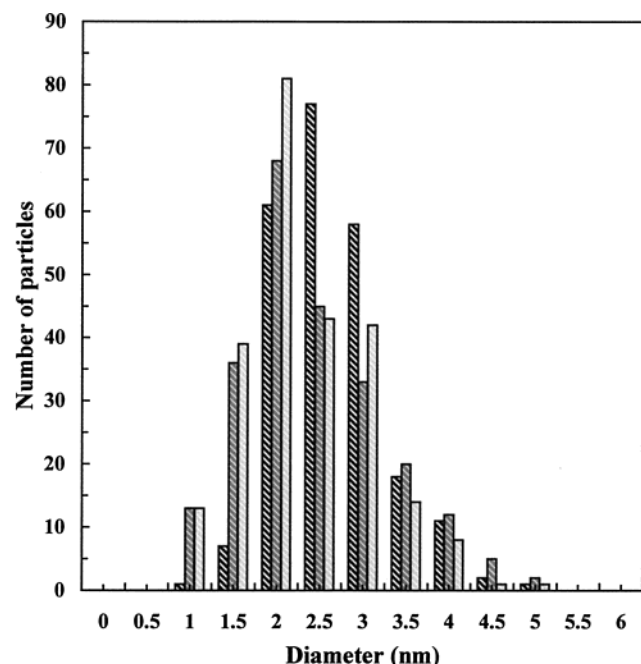
We shall first examine the size distributions of Au, Ni, and AuNi clusters determined from TEM experiments. In Figure 1, TEM images obtained with a 0.3 nm equivalent thickness deposits on a-C are presented. The size histograms corresponding to 234, 236, and 242 analyzed particles for pure gold, pure nickel, and gold–nickel alloy, respectively, are shown in Figure 2. The observed sizes and dispersions are rather similar for the three samples. The mean cluster sizes (standard deviations) are about 2.41 nm (0.72) for gold, 2.63 nm (0.39) for nickel, and 2.30 nm (0.54) for gold–nickel clusters. To check the composition homogeneity of bimetallic clusters, which is an essential condition if one deals with measurements (XPS) including numerous particles, we used the EDX technique within a field emission electron microscope that permits us to study individual particles by reducing the probe area down to about 1 nm.<sup>2</sup> The composition histogram corresponding to the analysis of a collection of isolated alloy particles is displayed in Figure 3. A quantitative analysis of the spectra gives, for each particle, a composition identical to that of the initial rod.

The binding energies of the Au 4f<sub>7/2</sub> and Ni 2p<sub>3/2</sub> levels in these clusters was then measured. The study of pure clusters of each component of the alloy is needed to clearly distinguish the effects of alloying and cluster size on core level binding energies. In Figure 4 the spectra of the Au 4f<sub>7/2</sub> both for pure gold and AuNi clusters are compared. The Ni 2p<sub>3/2</sub> spectra corresponding to pure Ni and AuNi clusters are presented in Figure 5. We observe that the Au 4f<sub>7/2</sub> level for pure gold and bimetallic system (Figure 4) has a binding energy very close to that of the bulk metal (84.0 eV), with values of 84.1 and 84.15

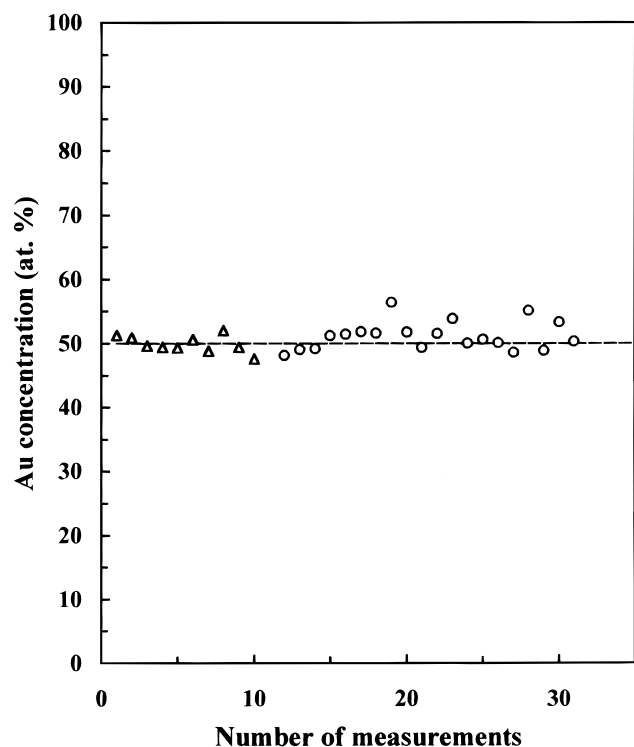


**Figure 1.** TEM micrographs of (a) Ni, (b) AuNi, and (c) Au clusters supported on amorphous carbon films. Scale bars are 25 nm.

eV corresponding to pure Au clusters and AuNi clusters, respectively. Both shifts are positive and small and are of the same order of magnitude (0.1 eV, 0.15 eV) with respect to the pure Au bulk phase. The measured binding energies of the Ni 2p<sub>3/2</sub> core level (Figure 5) are 852.75 and 852.45 eV for pure Ni and Au–Ni clusters, respectively. With comparison to the bulk nickel value (852.7 eV) a very slight positive shift (+0.05 eV) is observed for pure Ni clusters and a negative shift (−0.25



**Figure 2.** Size distribution histograms of Ni (black line), Au (gray line), and AuNi (no line) clusters.

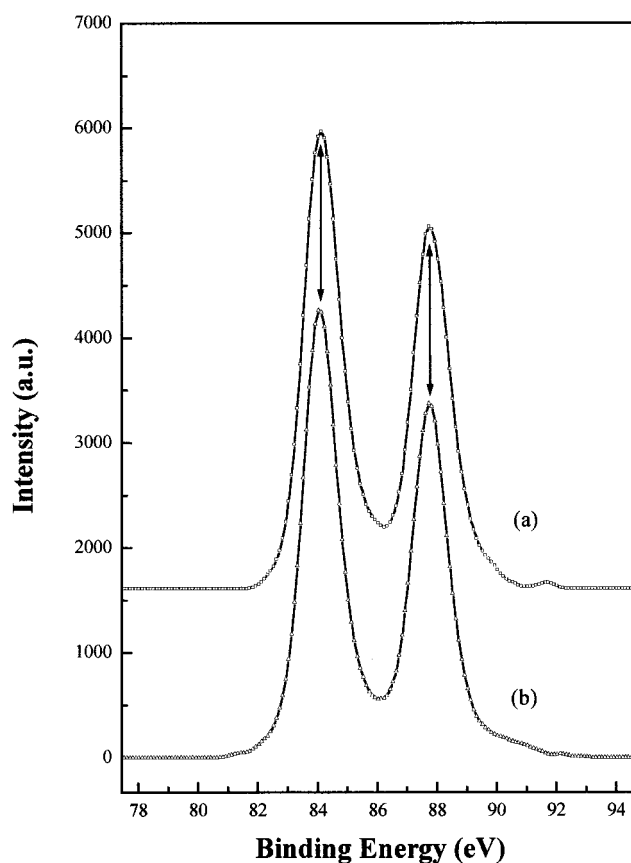


**Figure 3.** Gold concentration of a collection of Au-Ni clusters. Triangles and circles correspond respectively to large area and individual particles analysis.

eV) in bimetallic clusters. These experimental results are summarized in Table 1.

### Discussion

As pointed out by DiCenzo and Wertheim,<sup>21</sup> the binding energy is, without exception, larger in clusters than in the bulk and increases with decreasing size, even for metals that have negative surface-atom core level shifts. This is likely to be a final state effect that reflects a decrease in the core hole



**Figure 4.** Au 4f<sub>7/2</sub> photoemission spectra obtained from (a) pure gold and (b) gold-nickel cluster deposits.

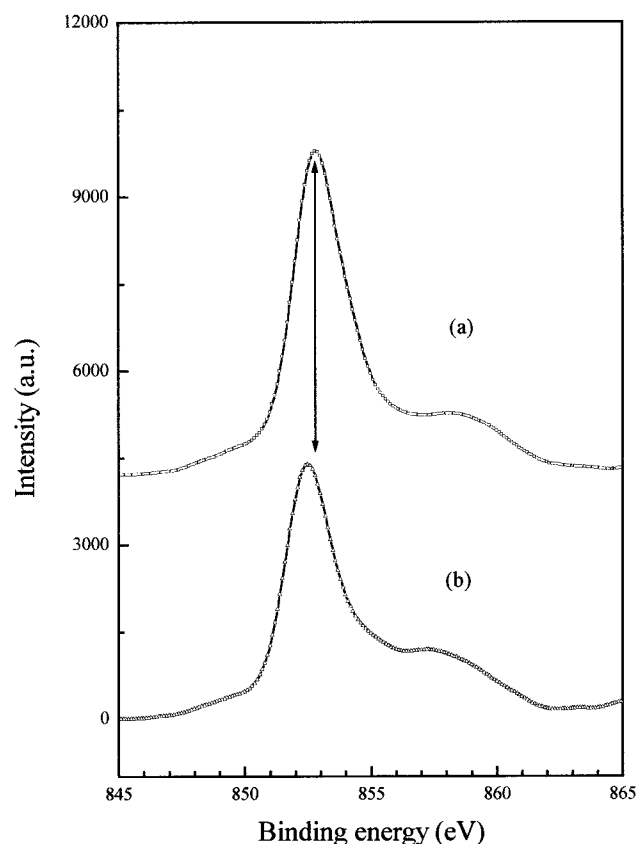
screening. This Coulombic term is not easy to calculate precisely. The XPS study of alloying in bimetallic clusters will therefore be complicated by this effect. To avoid this problem, it is useful to deposit on the *same support* pure components as well as alloyed clusters *having the same size and morphology* since in this way the size effect on the core level shifts will be of the same magnitude in pure and bimetallic clusters.

This requirement is fulfilled in this study, and a straightforward comparison of the XPS spectra corresponding to pure or alloyed metals clusters should allow the elimination of the so-called size effect and to extract the core level shifts due to alloying and/or surface segregation.

The observed core level shift for pure gold clusters agree quantitatively with the results of DiCenzo and co-workers<sup>21</sup> and those of Mason<sup>4</sup> who measured only small positive shifts on a-C supported gold clusters having a size similar to our clusters. The shift observed for pure nickel clusters confirms the one previously obtained by Egelhoff and Tibbets<sup>22</sup> on Ni clusters supported on graphite.

The Au-Ni binary phase diagram shows the absence of solid solutions over the entire range of composition at ordinary temperature.<sup>23</sup> Nevertheless, Fuggle et al.<sup>19</sup> have obtained an Au<sub>0.5</sub>Ni<sub>0.5</sub> bulk alloy by rapid quenching. They reported a negative shift of -0.45 eV for the Ni 2p<sub>3/2</sub> core level with respect to the pure bulk phase (see Table 1). In addition, the shifts of Au 4f<sub>7/2</sub> and Ni 2p<sub>3/2</sub> in dilute AuNi and NiAu alloys have been measured (see Table 1) by Steiner and Hufner.<sup>20</sup> They measured a positive shift of 0.48 eV and a negative shift of -0.70 eV, respectively, for Au diluted in bulk nickel and Ni diluted in bulk gold. On the basis of these experimental results one can try to predict the shifts that should be obtained for the clusters under investigation. Following the results of Fuggle et





**Figure 5.** Ni 2p<sub>3/2</sub> photoemission spectra obtained from (a) pure nickel and (b) gold–nickel cluster deposits.

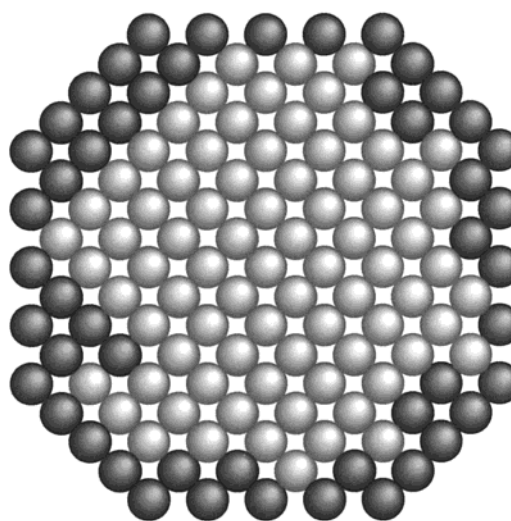
**TABLE 1: Measured Ni 2p<sub>3/2</sub> and Au 4f<sub>7/2</sub> Electron Binding Energies  $E_B$  for Ni, Au, and Au<sub>0.5</sub>Ni<sub>0.5</sub> Clusters<sup>a</sup>**

	binding energy (eV)		$\Delta E_B$ (eV)	
	Au 4f <sub>7/2</sub>	Ni 2p <sub>3/2</sub>	Au 4f <sub>7/2</sub>	Ni 2p <sub>3/2</sub>
Au bulk	84.0			
Ni bulk		852.7		
Au clusters	84.15		+0.15	
Ni clusters		852.75		+0.05
Au <sub>0.5</sub> Ni <sub>0.5</sub> clusters	84.1	852.45	+0.1	−0.25
Au <sub>0.5</sub> Ni <sub>0.5</sub> bulk (ref 19)		852.25		−0.45
Au <sub>x</sub> Ni <sub>1−x</sub> , $x \approx 0$ bulk (ref 20)	84.48		0.48	
Ni <sub>x</sub> Au <sub>1−x</sub> , $x \approx 0$ bulk (ref 20)		852.0		−0.70

<sup>a</sup> The core level shift,  $\Delta E_B$ , with respect to the pure bulk phases are also indicated with data taken from the literature.

al.<sup>19</sup> mentioned above, the binding energy of the Ni 2p<sub>3/2</sub> level in mixed Au<sub>0.5</sub>Ni<sub>0.5</sub> clusters and pure Ni clusters should differ by −0.45 eV. This expected shift is larger than the shift of −0.3 eV ( $= -0.25 - 0.05$  eV; see Table 1) observed experimentally. Concerning gold, the Au 4f<sub>7/2</sub> level binding energy shift for a Au<sub>0.5</sub>Ni<sub>0.5</sub> bulk alloy has, to our knowledge, not been reported in the literature. Nevertheless, Santra et al.<sup>14</sup> have measured this shift in very large aggregates of both Au<sub>0.75</sub>Ni<sub>0.25</sub> and Au<sub>0.25</sub>Ni<sub>0.75</sub>, which can be assimilated to bulk phases. They found shifts of 0.38 and 0.1 eV for Au<sub>0.25</sub>Ni<sub>0.75</sub> and Au<sub>0.75</sub>Ni<sub>0.25</sub>, respectively. Knowing the value of 0.48 eV for the shift of the Au 4f<sub>7/2</sub> level in a diluted AuNi alloy, and assuming a linear dependence of this shift with composition, one can find a value of 0.25 eV by extrapolation for the shift of the Au 4f<sub>7/2</sub> level in Au<sub>0.5</sub>Ni<sub>0.5</sub> alloy. Although this value is an estimate, it differs greatly from the negative shift of −0.05 eV ( $= 0.1 - 0.15$  eV; see Table 1) determined experimentally.

The significant discrepancy between the expected shift and

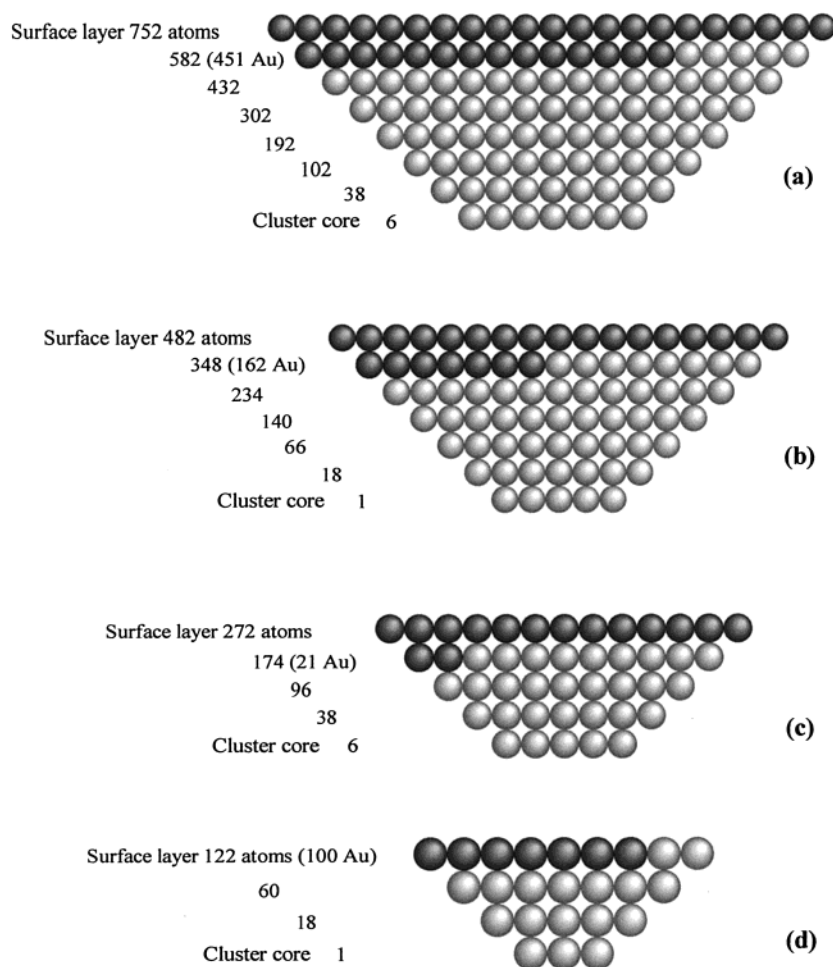


**Figure 6.** Snapshot of the centered section of a 1289 atoms cubooctahedron Au<sub>0.5</sub>Ni<sub>0.5</sub> clusters. Black and gray spheres represent respectively Au and Ni atoms.

the measured core level binding energies leads us to conclude that our experimental findings cannot only be explained by alloying effects. As already mentioned, an additional effect that can influence the core level binding energies and that is often neglected in bimetallic cluster studies is the local order at the atomic scale.

This local order is not easy to examine. However, in a recent work<sup>16</sup> we applied LEIS to determine the surface composition of supported PdPt bimetallic clusters produced by the laser vaporization source. Moreover, it has been shown that Monte Carlo (MC) simulations coupled with a recently developed energetic model<sup>24</sup> account well for the experimental findings and give information on the atomic surface distribution.

The LEIS technique has been used to study the surface composition of Au<sub>0.5</sub>Ni<sub>0.5</sub> and Ag<sub>0.5</sub>Ni<sub>0.5</sub> mixed clusters of immiscible metals, and the entire results will be reported in a forthcoming paper.<sup>25</sup> Nevertheless, preliminary results show that, for both alloys, the surface is entirely covered by gold or silver atoms. Monte Carlo simulations (based on the energetical model used in the study of PdPt clusters<sup>16,24</sup>) of the equilibrium structure of four different Au<sub>50</sub>Ni<sub>50</sub> cubooctahedron cluster diameters,  $d$ , were performed (201 atoms,  $d \sim 1.8$  nm; 586 atoms,  $d \sim 2.5$  nm; 1289 atoms,  $d \sim 3.3$  nm; 2406 atoms,  $d \sim 4.1$  nm). These results confirm the strong surface segregation of gold and indicate that the second atomic layer contains the few remaining gold atoms that tend to agglomerate. This indicates that the separation in two bulk phases, expected for bulk AuNi alloy, is replaced in small clusters by a phase separation between the surface and volume induced by a surface segregation process of gold atoms. A snapshot of the structure of the 1289 atoms clusters equilibrated at 600 K as deduced from MC simulations is displayed in Figure 6, and the overall results are schematically depicted in Figure 7. By weighting these results with the size distribution of the mixed clusters displayed in Figure 2, we deduce that almost 90% of gold atoms are located at the surface and bonded with nickel atoms in the second atomic layer. The nickel atom sites are mainly divided in two classes of nearly equal proportions. The first class corresponds to nickel atoms located in the second layer and sandwiched between gold atoms in the surface layer and nickel atoms of the third layer. The second class corresponds to Ni atoms situated in the core of the clusters. These atoms display only homonuclear bonds. From the above discussion, one can



**Figure 7.** Schematic representation of the unfolded layer structure of  $\text{Au}_{0.5}\text{Ni}_{0.5}$  bimetallic clusters as deduced from Monte Carlo simulations and LEIS experiments. (a) 2406-, (b) 1289-, (c) 586-, and (d) 201-atom cubooctahedron clusters. Black and gray spheres represent respectively Au and Ni atoms.

deduce that the Ni  $2p_{3/2}$  peak (Figure 5b) associated with Ni atoms in bimetallic clusters is the sum of two contributions. The first, corresponding to Ni atoms surrounded only by Ni atoms is not expected to be shifted with respect to pure Ni clusters, whereas the second contribution corresponding to Ni atoms alloyed with Au is expected to be shifted toward lower binding energy. Concerning gold, the very small shift of the Au  $4f_{7/2}$  core level observed in bimetallic clusters can be explained by the annihilation of two opposite effects. Indeed, the Au  $4f_{7/2}$  surface core level shift (SCLS) has been studied experimentally<sup>26</sup> and values of  $-0.35$ ,  $-0.35$ , and  $-0.38$  for the Au (111), (110)– $(2 \times 1)$ , and (100) surface orientations have been reported. This SCLS is of opposite sign and of nearly the same magnitude as the shift expected from the alloying effect. To support the fact that our clusters can schematically be described by a surface monolayer of gold on a core of pure nickel, we can compare our XPS results to those of Steiner and Hufner<sup>20</sup> who studied the Au  $4f_{7/2}$  core level binding energy shift for an overlayer of Au on a polycrystalline Ni film as a function of the Au coverage. These authors found a Au  $4f_{7/2}$  shift (compared with the bulk phase) of  $-0.13$  and  $0$  eV for 1 and 1.5 monolayer Au coverage, respectively. This agrees remarkably well with the shift ( $-0.05$  eV) we observed between Au and  $\text{Au}_{0.5}\text{Ni}_{0.5}$  clusters.

## Conclusion

Supported Au, Ni, and bimetallic  $\text{Au}_{0.5}\text{Ni}_{0.5}$  clusters have been produced by low energy cluster beam deposition. TEM-EDX

experiments indicate a narrow size distribution and a very small dispersion of the particle composition for AuNi bimetallic aggregates. Moreover, the size distributions of pure or alloyed clusters are nearly identical. This allows us to eliminate the shift due to the so-called size effect by a straight comparison between the core level binding energies of metal atoms in pure and alloyed clusters. This comparison brings us to assert that the shift observed in the bimetallic AuNi system is not only governed by alloying effects but also by a strong surface segregation of gold atoms. The segregation of gold has been confirmed by LEIS experiments and Monte Carlo simulations. Finally, we have shown in this paper that a detailed knowledge of the bimetallic cluster structure is needed to interpret precisely the results of XPS investigations.

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