

Cluster Core-Level Binding-Energy Shifts: The Role of Lattice Strain

B. Richter,¹ H. Kühlenbeck,¹ H.-J. Freund,¹ and P. S. Bagus²

¹*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195, Berlin, Germany*

²*Department of Chemistry, University of North Texas, Denton, Texas 76203-5070, USA*

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Our combined experimental and theoretical analysis of the shifts, with particle size, of core-level binding energies (BE's) of metal nanoparticles on insulating supports, shows that these shifts have an important initial state contribution arising, in large part, because of lattice strain. This contribution of BE shifts has not been recognized previously. Lattice strain changes the chemical bonding between the metal atoms and this change induces BE shifts.

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Photoelectron spectroscopy (PES) is often used to deduce information on the electronic structure of molecules, solids, and at surfaces [1]. There is increasing interest in nanostructured materials, especially in clusters grown on inert surfaces since they may have high catalytic activity [2]. Thus, the question of how the PES of deposited nanoparticles reflects their electronic and geometric structures is quite important. It is known that the core-level BE's of metal clusters on insulating supports [3–12] shift to lower BE with increasing size by $\Delta BE \sim 1$ eV from small clusters to bulk metal. However, there is substantial disagreement over the assignment of these shifts to initial or final state effects; see Ref. [13] for a rigorous definition of these two contributions. Mason [7] argued that changes in the electron configuration of the atoms in smaller clusters, not relaxation energies, were primarily responsible for the shift. On the other hand, Wertheim and collaborators [4,5] assigned the shift as due to final state screening effects and related the magnitude of ΔBE to an effective cluster radius. For Cu clusters grown on thin Al_2O_3 films, Wu *et al.* [11] concluded from an Auger parameter analysis that initial state contributions are small and may be significant only for very small clusters. This separation is quite important since the initial state ΔBE reflect changes in the electronic structure before ionization of a core level and, hence, are of direct interest for materials properties. In the present work, we show that the initial and final state contributions to the ΔBE are of comparable magnitude. Further, we relate the initial state ΔBE to a lattice strain that exists because the average bond distances in small clusters are shorter than in the bulk [14,15]. The chemical bonding is different at the shorter bond distances and this, in turn, leads to changes in the core-level BE's. The chemical changes important for the ΔBE involve an increased d to sp promotion, or hybridization, for shorter bond distances.

Our work is based on a combination of experimental and theoretical methods that allow us to decompose the ΔBE into initial and final state contributions. Our theoretical approach involves the calculation of electronic

wave functions (WF's) for clusters and the determination of the BE's where relaxation in response to ionization is excluded, a pure initial state BE, and where this relaxation is allowed [13]. Our experimental approach involves use of an Auger parameter obtained from measured Auger kinetic energies and core-level BE's. The Auger parameter concept, developed by Wagner [16], has been discussed by several authors [3,17–21]. We use the extension proposed by Hohlneicher *et al.* [21], where the two Auger final state core holes are in the same shell; this extension puts the Auger parameter analysis on a sound foundation. Previous applications of Auger parameter analysis to the ΔBE of supported clusters [11,22] have not used these refinements [21]. Both the Auger parameter analysis and the WF based separation of initial and final state contributions to the ΔBE with cluster size show that these two terms have large magnitudes.

The experiments were performed at the BESSY II synchrotron facility in Berlin. We studied Co, rather than Cu [11], clusters on Al_2O_3 films for two reasons. First, it is easier to control particle size for Co since it is less mobile than Cu [23]. Second, it is possible to study the Co $L_3M_{2,3}M_{2,3}$ Auger transition where all holes are in the core, while for Cu the best results reported [11] used the $L_3M_{4,5}M_{4,5}$ Auger lines where the Cu $3d$, $M_{4,5}$, electrons participate in the chemical bonding. However, we expect that the results for Co/ Al_2O_3 are representative for metal nanoparticles on relatively inert substrates [7]. The ultrahigh vacuum system consists of two chambers, one used for preparation purposes, the other analysis chamber carries a SCIENTA electron spectrometer as well as detectors to perform x-ray fluorescence measurements [24]. The analysis chamber is connected to an undulator beam line (U 49) equipped with a plane grating monochromator, yielding a resolution of approximately 10^4 , and a photon flux near 10^{11} photons/s. The sample, a NiAl(110) single crystal, is mounted on a manipulator which allows for translation between the chambers. The sample can be heated and cooled. The preparation of the alumina film uses established recipes [25]. Co is evaporated from an electron beam evaporator (focus

EFM4) at a rate of 0.5 \AA per minute. In separate STM experiments, the film morphology has been determined. By combining the island density as determined by STM and the deposited mass from the quartz balance, the average number of Co atoms per cluster is obtained [26].

Figure 1 shows photoelectron and Auger spectra of deposited Co aggregates for several coverages. With the data for the shifts of the Co $3p$ and $2p_{3/2}$ BE's and the $L_3M_{2,3}M_{2,3}$ Auger energies, we perform an Auger parameter analysis. The initial and final state contributions to the ΔBE obtained from this analysis are plotted in Fig. 2 as a function of particle size. The initial state shift is represented by $\Delta\epsilon$, the change in an effective orbital energy. From Koopmans' Theorem, the initial state BE = $-\epsilon$ [3,13]; thus $\Delta\epsilon < 0$ indicates a shift to higher BE. The final state, relaxation energy, contribution to the ΔBE is denoted ΔR , and $\Delta R < 0$ indicates a shift to higher BE. In Fig. 2, $\Delta\epsilon$ and ΔR , measured with respect to bulk BE's, are both negative. The mean particle radius is obtained assuming the particles are half spheres, consistent with our STM profiles [24]. For the shift between the smallest clusters, $\sim 4.7 \text{ \AA}$ radius, and thick Co films, the Auger parameter analysis gives an initial state contribution that is 31% of the total $\Delta BE = 0.98 \text{ eV}$. Clearly, initial state effects make a major contribution.

The goal of our theoretical studies of the ΔBE is to obtain an understanding of the physical mechanisms responsible for the trend of the decrease of BE with increasing particle size, observed for a variety of metals [7]. Since we do not intend to simulate the explicit dependence of the ΔBE on particle size, we are able to make approximations to simplify these studies: (i) We study isolated clusters and neglect the weak interaction of the particles with the oxide substrate [7]. (ii) We study Cu clusters in order to avoid computational difficulties related to open d shells. For a variety of noble and transition

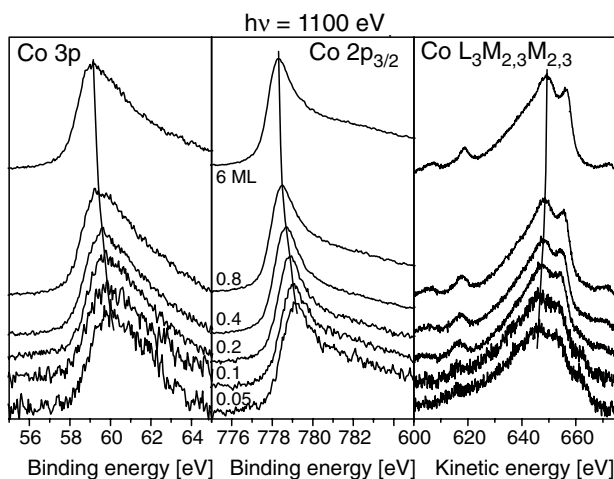


FIG. 1. The Co $3p$ and the Co $2p_{3/2}$ core-level BE's and the Co $L_3M_{2,3}M_{2,3}$ Auger transitions for Co clusters deposited onto $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ as a function of coverage; lines are drawn to show shifts with coverage

metal particles, the BE shift with particle size is $\sim 1 \text{ eV}$ [3–12]; thus, it seems appropriate to study the ΔBE for Cu. However, we also study ΔBE for small Ni clusters to confirm the generality, for open d -shell metals, of our results for Cu. (iii) The geometric structure of all Cu and Ni clusters studied was taken as that of the fcc crystal structure and the lattice strain is modeled by uniform changes in the lattice constant, a_0 . This model does not explicitly treat the specific shapes of the supported particles. (iv) Given our idealized cluster geometries, we consider only BE's for cluster atoms that have the bulk coordination. Although core-level BE's do depend on the coordination of the ionized atom [13], this dependence, especially for transition and noble metal atoms, is relatively weak; for example, the BE shifts between surface and bulk atoms of metal crystals are not large, $\sim 0.25 \text{ eV}$ [3]. Based on our results for the BE shifts with lattice strain for (100) surface atoms compared to the ΔBE for bulk atoms, we expect the contributions of differently coordinated atoms in supported particles to lead, dominantly, to broadening of the PES peaks.

Initial and final state contributions to the ΔBE were determined for a series of clusters chosen to model both particle size and lattice strain effects. The initial state BE's are obtained with Hartree-Fock self-consistent-field (SCF) molecular orbitals for the ground state of the cluster before ionization. These orbitals are used to form a frozen orbital (FO) WF for the ionic states where relaxation to screen the core hole is not allowed. The difference between the energies of the ground state and the FO ionic state WF's is BE(initial). The difference between the energies of the ground state and the SCF WF for the ionized state [BE(ΔSCF)] is the total BE. The SCF orbitals for the ionic state WF's, optimized for the presence of the core hole, fully include electronic relaxation in response to the hole [27]. The change between the initial and total BE's is the relaxation energy, E_R , associated with the final state effects;

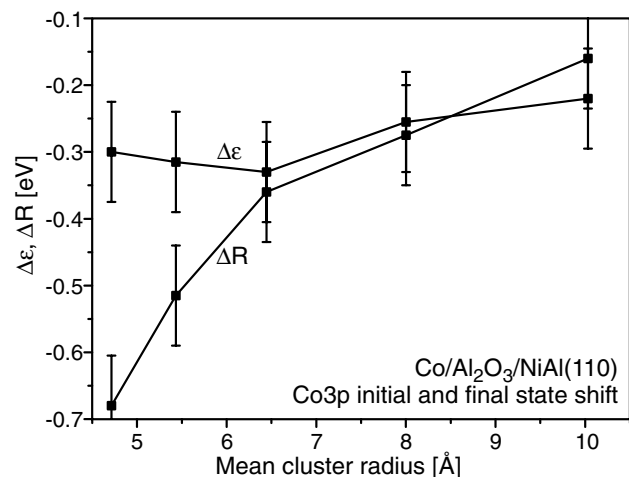


FIG. 2. Co $3p$ initial ($\Delta\epsilon$) and final state (ΔR) shifts as a function of the mean cluster radius.

$E_R = \text{BE}(\text{initial}) - \text{BE}(\Delta\text{SCF})$. The shifts are: $\Delta\text{BE}(\Delta\text{SCF})$ for the changes due to both initial and final state effects; $\Delta\text{BE}(\text{initial})$ for the initial state changes; and ΔE_R . Their relationship to the quantities obtained in the Auger parameter analysis is $\Delta\text{BE}(\text{initial}) = -\Delta\varepsilon$ and $\Delta E_R = \Delta R$. However, the quantities obtained from the SCF WF's rigorously separate initial and final state contributions [13], while the Auger parameter separation involves assumptions about the intra- and extra-atomic relaxation [16–21]. Furthermore, the SCF energies of double-hole Auger states can be used to calculate the Auger parameter β [21] and the Auger relationship that $\Delta E_R = \Delta\beta/2$ can be compared to the ΔE_R calculated directly from $\text{BE}(\text{initial})$ and $\text{BE}(\Delta\text{SCF})$.

The clusters used to study the progression of BE's toward the bulk value are shown in Fig. 3. The largest, Cu_{115} , cluster has seven layers parallel to the (100) surface; the numbers of atoms in each layer are $\text{Cu}_{115}(4,25,16,25,16,25,4)$. We use the BE's for Cu_{115} to represent the limit of a large cluster although the BE's for clusters of this size are not fully converged to the bulk [24]. The next smaller cluster, $\text{Cu}_{55}(9,12,12,12,9)$, has four layers and the smallest cluster, $\text{Cu}_{18}(5,4,5,4)$, has four layers. For Cu_{115} and Cu_{55} , we consider BE's for ionization of the central atom; for Cu_{18} , the BE's are for ionization of the central atom of the third layer. In order to study only the effect of cluster size on the BE's, we have used the bulk $a_0 = 3.59 \text{ \AA}$. However, there is evidence from transmission electron microscopy of Pd and Pt on Al_2O_3 that the effective a_0 for small clusters is reduced by $\sim 5\% - 7\%$ [14,15]; these contractions are much larger than those found for matrix isolated Cu clusters [28]. The much larger lattice strain for supported clusters may be due to their weak interaction with the support. The effect of this lattice strain on the core-level BE's is studied by determining the BE's for Cu_{18} with three reductions of a_0 to 3.52, 3.44, and 3.37 \AA . For atoms where core level BE's may be studied, all the 29 Cu electrons are explicitly included in the cluster WF's; for the other atoms, the core electrons are represented by a pseudopotential [13]. For the open shell Cu_{55} and Cu_{115} clusters, we consider BE's to the weighted averages of the

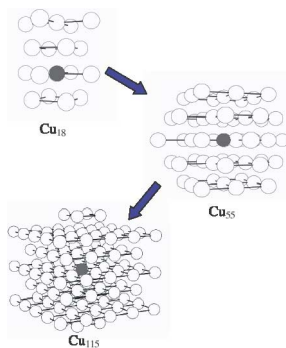


FIG. 3 (color online). Size progression of Cu_{18} to Cu_{55} to Cu_{115} clusters. The ionized atom is shaded.

ionic states. To avoid the distraction of spin-orbit splittings in the $2p$ shell, we report here shifts of the $2s$ BE's; the ΔBE 's calculated for $1s$ and $3s$ holes are very similar to the $\Delta\text{BE}(2s)$. For the theoretical determination of $\beta(2s)$ [21], we use SCF WF's for the $2s$ and $3s$ hole states and for the $3s$ double hole Auger state. We also report $\Delta\text{BE}(2s)$ for Ni_{18} clusters constructed in an analogous way to the Cu_{18} clusters; the lattice strain for Ni is examined by using contracted a_0 of 3.45, 3.37, and 3.30 \AA as well as bulk $a_0 = 3.52 \text{ \AA}$.

In Table I, we give $\Delta\text{BE}(\Delta\text{SCF})$, $\Delta\text{BE}(\text{initial})$, and ΔE_R at the bulk a_0 and, for Cu_{18} , also at a representative contracted $a_0 = 3.44 \text{ \AA}$. We also give shifts of the Auger parameter, $\Delta\beta/2$. The sequence from $\text{Cu}_{18}(a_0 = 3.44 \text{ \AA})$ to $\text{Cu}_{115}(a_0 = 3.59 \text{ \AA})$ models the progression of ΔBE from small clusters to bulk; the shift to lower BE of $\sim 1 \text{ eV}$ is consistent with the measured values for BE shifts in supported clusters and indicates that our cluster models correctly describe the physics of this shift. Note that the total shift has approximately equal contributions from initial and final state shifts.

Although the increase of the bond distance from small to large clusters is not a step function, we use the step from $\text{Cu}_{18}(a_0 = 3.44 \text{ \AA})$ to $\text{Cu}_{18}(a_0 = 3.59 \text{ \AA})$ to separate the increase of the bond distance from the change of the number of atoms. The increase of a_0 leads to a shift of 0.5 eV to lower BE, $\sim 50\%$ of the total ΔBE between small clusters and bulk; this shift is almost entirely an initial state effect (see Table I). There is a further large BE decrease of 0.67 eV when the cluster size is increased from Cu_{18} to Cu_{115} with bulk a_0 that is $\sim 2/3$ due to an increase in final state relaxation and $\sim 1/3$ to an initial state BE shift. In other words, the final state relaxation dominates the shift to lower BE with increasing cluster size for a constant a_0 ; this is consistent with a monotonic dependence of E_R on system size [3,6,13]. The $\Delta\text{BE}(\text{initial})$ do not vary monotonically with cluster size suggesting that there is a dependence of the initial state BE on the cluster morphology. However, the dependence of $\text{BE}(\text{initial})$ on the details of the cluster morphology is not particularly large and is not investigated further.

For Ni_{18} and Cu_{18} , the dependence of the $2s$ BE's on a_0 is shown in Table II. For both metals, the $\Delta\text{BE}(\Delta\text{SCF})$, and $\Delta\text{BE}(\text{initial})$ are almost the same and vary nearly linearly with Δa_0 ; these changes of ΔBE with a_0 show

TABLE I. The $2s$ BE shifts for Cu_n at bulk a_0 with respect to $\Delta\text{BE}(\text{Cu}_{115}) = 0$; for Cu_{18} , a reduced a_0 is also used. ΔE_R and $\Delta\beta/2$ are shown. All energies are in eV.

a_0 - \AA	Cu_{18} 3.44	Cu_{18} 3.59	Cu_{55} 3.59	Cu_{115} 3.59
$\Delta\text{BE}(\Delta\text{SCF})$	+1.21	+0.67	+0.34	0
$\Delta\text{BE}(\text{initial})$	+0.73	+0.22	+0.27	0
ΔE_R	-0.47	-0.45	-0.07	0
$\Delta\beta/2$	-0.67	-0.66	-0.21	0

TABLE II. $\Delta\text{BE}(\Delta\text{SCF})$ and $\Delta\text{BE}(\text{initial})$, in eV, for the Cu and Ni $2s$ BE's in 18 atom clusters. The changes in the lattice constants are given as Δa_0 in percent change from bulk a_0 . $\Delta\text{BE} = 0$ for $\Delta a_0 = 0$. For Cu, frozen core and frozen Ar core values of $\Delta\text{BE}(\text{initial})$ are given (see text).

Δa_0	-6%	-4%	-2%	0 (bulk)
Cu				
$\Delta\text{BE}(\Delta\text{SCF})$	+0.84	+0.54	+0.26	0
$\Delta\text{BE}(\text{initial})$	+0.79	+0.51	+0.25	0
Frozen core	+0.12	+0.05	+0.01	0
Frozen Ar core	+0.78	+0.51	+0.24	0
Ni				
$\Delta\text{BE}(\Delta\text{SCF})$	+0.72	+0.45	+0.21	0
$\Delta\text{BE}(\text{initial})$	+0.73	+0.47	+0.22	0

the generality of the dependence of the BE's on lattice strain. The near equality of the initial and ΔSCF values show that the increase of the BE's due to lattice contraction is a dominantly initial state effect. The origin of the large $\Delta\text{BE}(\text{initial})$ is found by separating, using constrained variations [13], the contributions due to the $4sp$ conduction band electrons from those due to the $3d$ electrons. This decomposition is given only for Cu but it is similar for Ni. For the frozen core WF, the orbitals of the electrons in the $1s$ to $3d$ shells are fixed to be the same as in the isolated atom. With this constraint, the BE(initial) depend on a_0 only because of changes in the conduction band, $4sp$ electrons. For the frozen Ar core WF, only the 18 Ar core electrons are constrained to be atomic. Now, $3d$ hybridization and bonding is allowed. It is clear that the $3d$ chemistry is the main reason for the large ΔBE as a_0 is reduced. The hybridization and promotion of a fraction of an electron from the contracted $3d$ shell into a more diffuse orbital leads to a large increase in the core-level BE's [13]. The d hybridization increases strongly for shorter a_0 since shorter bond distances favor an increased bonding participation of the compact d orbitals.

The changes of the Auger parameter, $\Delta\beta/2$, roughly follow those of the ΔE_R ; see Table I. The values of $\Delta\beta/2$ are essentially equal for Cu_{18} with $a_0 = 3.44$ and 3.59 Å; the same near equality is also found for ΔE_R . From Cu_{18} with bulk a_0 to Cu_{115} , the increases of $\Delta\beta/2$ parallel the increases of ΔE_R ; however, the increases of $\Delta\beta/2$ are larger than those of ΔE_R . While the trend of ΔE_R is correctly described by the trend of $\Delta\beta/2$, the Auger parameter analysis appears to indicate a larger contribution from final state effects than given by the *ab initio* decomposition of the BE's. This problem may be related to assumptions about the intra- and extra-atomic contributions to E_R made in the derivation of the Auger parameter relationship.

A large initial state contribution to the cluster size dependent BE shifts has been shown from both Auger

parameter analysis of the experimental data and from calculation of the ΔBE with *ab initio* cluster WF's leaving no doubt that initial state contributions are significant. Further, we have shown that the origin of the initial state effect is a lattice contraction that is part of the cluster growth morphology [14,15]. In particular, the BE shift is related to the d hybridization being larger for shorter bond distances. These are important extensions of our understanding of the origin and the physical significance of the cluster BE shifts.

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