The contribution of lattice strain to core-level binding energy shifts in metal nanoparticles: Generality and origin of the shifts

Paul S. Bagus [a,*], Andrzej Wieckowski [b], Hajo Freund [c]

[a] *Department of Chemistry, University of North Texas, Denton, TX 76203-5017, USA*
[b] *Department of Chemistry and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA*
[c] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

ARTICLE INFO

Article history:
Received 11 March 2011
Received in revised form 22 June 2011
Accepted 29 June 2011
Available online 5 July 2011

Keywords:
Nanoparticles
XPS
BE shifts
Lattice strain

ABSTRACT

Changes of the inter-atomic distances, described as lattice strain, make important, initial state, contributions to the shifts of core-level binding energies, ΔBE's, of supported nano-particles as the size of the particles changes. In the present paper, we consider how the BE shifts due to lattice strain vary for the 3d, 4d, and 5d noble metals, Cu, Ag, and Au. We identify and discuss two important but cancelling mechanisms that contribute to the total BE shifts. We predict and explain why the ΔBE will be larger for 3d series metals than for those of the 4d and 5d series.

X-ray photoemission spectroscopy, XPS, is a powerful way to obtain information about the electronic structure of a wide range of materials [1,2]. However, XPS data is most useful when there is a firm basis for relating the XPS binding energies, BE's, and BE shifts, ΔBE's, to the physical and chemical aspects of the atomistic interactions within the material. Ab initio theoretical studies of suitable model systems provide a way to definitively establish the relationship of specific features of the bonding and environment of the core ionized atom to the ΔBE [3]. These studies are especially important when there is more than one important contribution to the ΔBE and, in particular, when the contributions are cancelling. Indeed, this cancellation arises for the example of BE shifts with particle size that we consider in the present paper. For the analysis of BE shifts, there is broad agreement that the contributions to the ΔBE are divided into initial state effects that reflect the potential at the ionized atom due to the electronic charge density and final state effects that are due to the screening of the core hole by the relaxation of the ''passive'' electrons [3,4]. This distinction is quite important since the initial state effects can be directly related to the physics and chemistry of the electronic structure of the system. On the other hand, the screening that is responsible for the final state contributions to the BE and ΔBE describes the electronic structure of the core–hole state and this very excited state is not especially relevant for the ground state chemistry. Thus, it is important to be able to separate these two types of contributions; however, there is not general agreement as to the importance of these two effects in various situations; see, for example Refs. [3–6]. It is possible, in principle, to separate these two classes of contributions to the ΔBE by using an Auger parameter that combines experimental XPS and Auger data [7,8] but this may lead to conflicting results depending on the particular Auger transition used and on the definition of the Auger parameter [9]. Unfortunately, especially for metal atoms, XPS for suitable core–holes may not be available with laboratory XPS [9], which limits the applicability of Auger parameter analyses to separate initial and final state effects. On the other hand, Hartree–Fock, HF, wavefunction theory, WFT, does provide an unambiguous theoretical basis for separating initial and final contributions to BE and ΔBE [3,10].

In the present paper, we shall use WFT to study an important aspect of the origin of the BE shifts to lower BE of the core-levels of metal nanoparticles supported on ''inert'' supports as the size of the particles increases. The origin of the ~1 eV shift in the BE's as the particle size increases toward bulk [4] has been a subject of controversy for several decades. A proposal by Wertheim and collaborators, see, for example, Ref. [11], ascribed these BE shifts to final state effects and related the magnitude of the shift to the size, or radius, of the particle. However, other early proposals identified important initial state contributions to the BE shifts [12,13]. Recently, a combined experimental and theoretical study [14] showed that the contribution of initial and final state effects to the BE shifts are of comparable magnitude. The dominant origin of the initial state effect was identified as being the significant

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[*] Corresponding author.
E-mail address: bagus@unt.edu (P.S. Bagus).

reduction in the metal–metal distances in small particles from those in the bulk. This is described as a lattice strain. Furthermore, the increase in the core-level BE's was ascribed to an increased involvement of the highest d shell electrons in the chemical bonding when the bond distance is reduced; i.e., to an increased d-hybridization. In the present work, we extend and improve our analysis of the initial state effects due to lattice strain [9,14] and we show that there are two cancelling effects from environmental charge density and from d hybridization. We compare these contributions for Cu, Ag, and Au, taken as representative of atoms from the 3d, 4d, and 5d series. We find that lattice strain in Cu leads to the largest ΔBE, while the ΔBE for Ag and Au are similar and about 2/3 of the ΔBE for Cu. A major reason for the different magnitudes of the ΔBE arises from the different sizes of the 3d, 4d, and 5d orbitals.

The theoretical model that we use to study lattice strain is a cluster of 13 atoms, a central atom and its 12 nearest neighbors in the fcc geometry of the bulk materials; see Fig. 1. The lattice strain is modeled by a breathing motion of the edge atoms in steps of 0.05 Å about the bulk distances; these steps are ∼2% of the lattice constant. The central atom is an all electron atom but only the outermost 19 electrons of the 12 edge atoms are treated explicitly and the remaining core electrons are treated with a relativistic effective core potential, ECP; i.e., a pseudo potential [15]. The treatment of the central atom is non-relativistic but since our concern is for the qualitative behavior of the BE shifts, this will not be changed by relativistic effects. To test the independence of the BE shifts on whether we use a relativistic or a non-relativistic treatment, we have compared the core-level BE for different configurations of the *n*s and $(n-1)$d levels for the Ag and Au atoms. We find approximately the same shifts of the core-level BE's between the different $(n-1)$d and *n*s distributions whether we use relativistic or non-relativistic wavefunctions, WF's, for the atoms. For the X_{13} clusters with X = Cu, Ag, and Au, we obtain Hartree–Fock WF's; our extensive experience shows that HF WF's give excellent descriptions of the ΔBE [3]. The outermost d shell electrons are explicitly included in the WF's and, hence, their involvement in the chemical bonding and the ΔBE is fully taken into account. The BE's are computed taking into account only initial state effects using Koopmans' theorem [3], denoted BE(KT), and including final state effects by taking the difference of the variational HF energies for the ground and the core–hole states [3], denoted BE(ΔSCF). The difference between BE(ΔSCF) and BE(KT) provides a direct measure of the energetic importance of the final state effects. There are large final state relaxation contributions to the BE; however, our concern is for the ΔBE and, as we shall see, the differences between ΔBE(KT) and ΔBE(ΔSCF) due to lattice strain are quite small. In order to determine the relative importance of different contributions to ΔBE(KT), we use constrained variations [16] to selectively vary a subset of the full number of electrons. For the *n*sp-Only WF, the 13 electrons in the conduction band are varied but all the core electrons are fixed to be as in the isolated atom. For the $(n-1)$d-Added WF's, the 10 $(n-1)$d electrons on each atom are now varied as well as the *n*sp conduction band electrons. Even though the core electrons are frozen, the KT BE's are modified by the potential due to the charge distribution of the electrons that are varied. The *n*sp-Only BE's include the environmental potential due to the conduction band electrons but they cannot include the $(n-1)$d electron hybridization or other participation in the bonding since these electrons are frozen at their atomic character. However, the d electron's participation in the chemistry is allowed with the KT BE's for the $(n-1)$d-Added WF's. Since the remaining electrons are not involved in the chemistry, the values of the full ΔBE(KT) and the ΔBE for the $(n-1)$d-Added WF are nearly the same as we show below. The non-relativistic orbitals were expanded in terms of contracted Gaussian type basis sets developed from basis sets available in the literature. The basis set for Cu was modified from those used in prior work on Cu particles [17], the basis set for Ag was taken, with minimal modification, from Ref. [18] and the basis set for Au was taken, with extensive modification from Ref. [19]. The basis sets for the 12 edge atoms of the X_{13} clusters, where the core electrons were described with an ECP were taken from Ref. [15]. The Gaussian basis sets for the relativistic calculation on the Ag and Au atoms were not contracted; the Au basis set is the TZ basis from Ref. [20] and the Ag basis is adapted from the non-relativistic basis set of Ref. [18]. The non-relativistic and relativistic WF's were calculated with the CLIPS [21] and DIRAC [22] program systems, respectively.

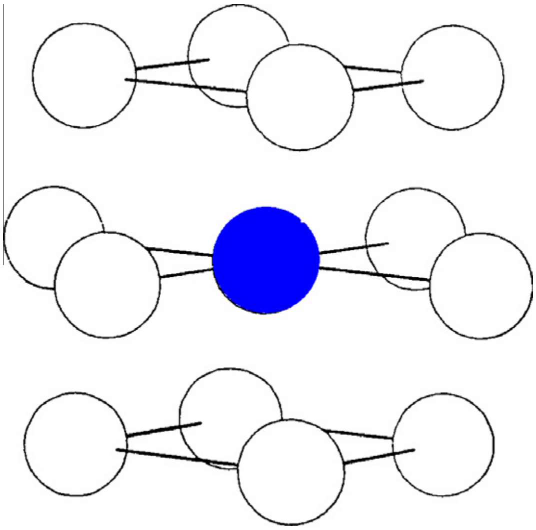

Fig. 1. The 13 atom model used to study lattice strain for Cu, Ag, and Au particles. The shaded central atom is the atom that is core ionized.

Although we have calculated the ΔBE(KT) and the constrained ΔBE(KT) for several core levels, we present results only for the representative Cu(2s), Ag(3s), and Au(4s) levels; these values are chosen to avoid the complication of spin–orbit splitting. In addition, the ΔBE's for the other core levels are quite similar to these representative values. In Table 1, detailed information is given for the Cu(2s) ΔBE for several values of the metal nearest neighbor distances, *r*(NN), about the bulk value of 2.54 Å with ΔBE = 0 at *r* = 2.54 Å. These distances range between a 2% increase and a 6% reduction of *r*(NN). The 6% maximum reduction is similar to the 5–7% reductions observed for small supported particles [23,24]. The ΔBE(ΔSCF), ΔBE(KT) and the contributions to ΔBE(KT) for the 4sp-Only and the 3d-Added constrained WF's are given. The sum of the 4sp-Only and the 3d-Added contributions to ΔBE equal the full ΔBE(KT) showing that these are the dominant contributions to the ΔBE. The small differences between the ΔBE(ΔSCF) and ΔBE(KT) indicate that, for a constant size particle, the final state relaxation energy is similar for all values of *r*(NN); thus the

Table 1

The ΔBE, in eV, due to lattice strain for the Cu 2s level for different nearest neighbor distances, *r*(NN), of the Cu_{13} cluster. Individual contributions to ΔBE(KT), 4sp-Only and 3d-Added, are also given.

	0.16	–0.11	0.05	Bulk	+0.05
r(NN)-Å	2.38	2.43	2.49	2.54	2.59
ΔBE(ΔSCF)	0.67	0.41	0.19	0	–0.16
ΔBE(KT)	0.74	0.47	0.22	0	–0.20
4sp-only	–0.67	–0.44	–0.22	0	+0.22
3d-added	+1.41	+0.91	+0.44	0	–0.42

ΔBE due to lattice strain do represent an initial state effect and we confine our attention to analysis of the ΔBE(KT). The full ΔBE and the individual contributions are nearly linear in r(NN). The environmental charge, 4sp-Only, contribution to ΔBE leads to a lower BE as r is reduced. This is to be expected since a smaller r leads to a larger charge density about the core-ionized atom and this lowers the BE. On the other hand, the greater d hybridization and participation in the chemical bonding for reduced r leads to an increase in the BE's. This follows from the fact that the 3d charge is much more compact than the conduction band charge and hybridization leads to a smaller repulsive potential for the core level ions, hence a larger BE. The electrostatic origin of these contributions is discussed in detail for condensed and molecular systems in Ref. [3]. The hybridization of the 3d orbital, which contributes to the chemical bonding between the Cu atoms, leads to changes in the ΔBE that are, for all the nearest neighbor distances we studied, about twice as large as the changes in ΔBE due to the environmental charge density. Thus, the 3d hybridization dominates and the net ΔBE arising from the reduction of the r(NN) in small particles is to a larger BE, BE > 0. In Table 2, the initial state ΔBE for a bond length shortening of 0.16 Å are compared for Cu, Ag, and Au. These ΔBE due to lattice strain are comparable for Ag and Au but about 2/3 as large as for Cu. An important reason for the smaller ΔBE for Ag and Au comes from the smaller contribution to ΔBE from the $(n-1)$d hybridization. This can easily be understood when we consider the relative sizes of the $(n-1)$d orbitals. The measure of size that we use is $\langle r\rangle$, and these are shown in Table 2 for the atomic $(n-1)$d orbitals. Since the electrostatic potential at the core is $\langle 1/r\rangle$, the ΔBE due to reducing the number of d electrons is rigorously $\propto \langle 1/r\rangle$ but we prefer to use $\langle r\rangle$ since this is a more familiar quantity. This is not a serious approximation since $\langle 1/r\rangle$ is close to $1/\langle r\rangle$ [25]. Of course, the degree of hybridization and the size of the orbital into which the d electrons are promoted also influence ΔBE; furthermore, the contribution of the conduction band charge density to the lattice strain ΔBE also changes for the different metals. However, as we see from Table 2, the changes in $\langle r\rangle$ are a useful, albeit rough, guide to the relative hybridization contributions to ΔBE. Our analysis shows that the initial state contribution to ΔBE arising from lattice strain will be largest for the 3d series transition metals because the 3d orbitals in this series are smaller than for the 4d and 5d series.

The relationship between the size of the $(n-1)$d orbitals and the magnitude of the initial state contributions to the ΔBE of supported nanoparticles has been unambiguously established through our theoretical methods of analysis of the effects of lattice strain on the core-level BE shifts. The clear indication is that initial state contributions to the BE shifts will be largest for 3d series transition metals than for the higher series. It would be very useful if our prediction could be verified. In principle, the contribution of initial and final state effects to BE shifts can be determined with an Auger parameter analysis as developed by Wagner and Joshi [8] and extended by others, in particular by Hohlneicher et al. [7]. However, in order to have a reliable separation of initial and final state effects, it is necessary to choose an appropriate Auger line for the analysis [7,9]. While this has been done for metal particles in the 3d series [14], it has not, to our knowledge, been done for particles in the 4d and 5d series. While the accurate numerical calculation of materials properties is a valuable goal of simulations, we have taken a different approach of using theory and simulation to identify and measure the importance of different chemical mechanisms on materials properties. This approach, which has allowed us to separate, analyze, and quantify the different contributions to BE shifts induced by lattice strain, is a powerful kind of contribution that theory can make for the understanding of materials chemistry.

Table 2

The ΔBE due to lattice strain for the Cu 2s, Ag 3s and Au 4s levels for an 0.16 Å, or ~6%, reduction of r(NN); the sizes of the d orbitals, $\langle r\rangle$, are given. See caption to Table I and text.

	Cu-ΔBE(2s)	Ag-ΔBE(3s)	Au-ΔBE(4s)
ΔBE (initial)	0.74	0.52	0.50
$n$sp-only	–0.67	–0.31	–0.55
$(n-1)$d-added	+1.41	+0.82	+1.00
$\langle r\rangle_{(n-1)\mathrm{d}}$-Å	0.52	0.72	0.82

Acknowledgements

This work was partially supported by the National Science Foundation under Grant NSF CHE 06-51083 and by the Geosciences Research Program, Office of Basic Energy Sciences, US DOE under Grant DE-FG02-04ER15508. HJF is grateful for financial support from the German Science Foundation (DFG) through Sonderforschungsbereich 546 and the Cluster of Excellence UNICAT coordinated by the Technical University Berlin, as well as from the Fonds der Chemischen Industrie.

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