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N.B.: When citing this work, cite the original article.

Original Publication:

Weine Olovsson, Tobias Marten, Erik Holmstrom, Borje Johansson and Igor Abrikosov, First principle calculations of core-level binding energy and Auger kinetic energy shifts in metallic solids, 2010, JOURNAL OF ELECTRON SPECTROSCOPY AND RELATED PHENOMENA, (178), Sp. Iss. SI, 88-99.

<http://dx.doi.org/10.1016/j.elspec.2009.10.007>

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Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-57401>

First Principle Calculations of Core-Level Binding Energy and Auger kinetic Energy Shifts in Metallic Solids

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Abstract

We present a brief overview of recent theoretical studies of the core-level binding energy shift (CLS) in solid metallic materials. The focus is on first principles calculations using the complete screening picture, which incorporates the initial (ground state) and final (core-ionized) state contributions of the electron photoemission process in x-ray photoelectron spectroscopy (XPS), all within density functional theory (DFT). Considering substitutionally disordered binary alloys, we demonstrate that on the one hand CLS depend on average conditions, such as volume and overall composition, while on the other hand they are sensitive to the specific local atomic environment. The possibility of employing layer resolved shifts as a tool for characterizing interface quality in fully embedded thin films is also discussed, with examples for CuNi systems. An extension of the complete screening picture to core-core-core Auger transitions is given, and new results for the influence of local environment effects on Auger kinetic energy shifts in fcc AgPd are presented.

Key words: core-level shift, disordered materials, metallic alloys, Auger kinetic energy

PACS: 71.15.-m, 71.23.-k, 79.60.Ht, 79.60.Jv, 79.20.Fv

1 Introduction

From x-ray photoelectron spectroscopy (XPS) [1,2], sometimes also referred to as electron spectroscopy for chemical analysis (ESCA) [3], it is straightforward to assess the binding energies, defined as $E_i > 0$, of the strongly bound core-electrons in a metallic system. In practice, it is often the difference in core-level binding energies of an atom in different environments, the so-called core-level shift (CLS), which is considered in a comparison between experiment and theory. From a careful investigation of the shifts it is possible to obtain information on the electronic structure and bonding in materials, as the CLSs can be highly sensitive to the specific chemical environment of an atom. One important application is structural characterization, e.g. using the binding energies as a "fingerprint" of a system, considering for instance the crystal structure, nearest neighbor or average atomic composition, and possible lattice relaxation in a bulk solid. A number of properties have previously been associated with the core-level shift; cohesive energies [4], heats of mixing [5,6], segregation energies [7] and charge transfer [8–10]. In this work we present a brief overview of theoretical CLS investigations in metallic solids within density functional theory (DFT) [11–13], with the focus on recent *first principles* calculations utilizing the complete screening picture [4] and its extension to Auger core-core-core transitions [5,14]. At this time many-body effects are not considered. In this paper we review recent theoretical results, and also demonstrate new results for the disorder broadening effect, due to the difference in atomic local environments, on the Auger $L_3M_{4,5}M_{4,5}$ spectra in fcc random phase AgPd.

In order to produce highly accurate theoretical core-level shifts there are many factors which need to be taken into account. For instance, one may consider; the screening of the final state core-hole, the Fermi-level energy reference, inter-atomic charge transfer, intra-atomic charge transfer (sp $\leftrightarrow$ d orbital character), and the redistribution of charge due to bonding and hybridization, as discussed by Weinert and Watson [15]. An advantage of using the complete screening picture is that all of the above effects are intrinsic to the *ab initio* calculations, accounting for both initial (the shift of the on-site electrostatic potential for an atom in different environments) and final state (core-hole screening by conduction electrons) effects directly in the same computation scheme. The central assumption in the complete screening picture is that for metallic systems considered in this work the symmetric part of the measured line profile for the core level corresponds to a state, in which the conduction electrons have attained a fully relaxed configuration in the presence of the core hole [4]. The CLS can then be readily calculated from the differences in the so-called generalized thermodynamic chemical potentials [16], which in

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turn are determined from *total energies* of the systems – where core electrons on the ionized atoms are promoted to the valence band, while the remaining electrons relax as they screen the core hole. First principles calculations within the complete screening picture have been successfully used in many different studies, ranging from the bulk core-level shift in disordered alloys [16–18], the disorder broadening of the spectral core-line in random phase alloys [19,20], surface core-level shifts [21–23], structural characterizations in different materials [24–27], and Auger kinetic energy shifts [28]. It was found that the transition state method, which also accounts for both initial and final state effects within a single framework without the necessity to separate them, though using one-electron eigenstates rather than total energies, gives similar results in several disordered alloys [18,29]. A recent summary on CLS calculations in metallic systems by some of the authors can be found in [30].

With the development of spectroscopy and higher resolution in experiment, it is also of interest to evaluate theoretical methods and consider their possible applications. Core-level shift calculations can be used both as a means to interpret experimental measurements, with the goal of a better understanding of physical properties, and in the direct application for structural characterization. For instance, by using computationally efficient Green’s functions methods to solve the electronic structure problem, together with the complete screening picture, it is feasible to map CLS trends as a function of only volume and composition over a wide range of systems. In order to study the effect of a difference in the local chemical environments in a material, e.g. in substitutionally disordered alloys, supercell techniques can be used instead. A very interesting prospect is to consider the interface quality in embedded thin films.

Our aim here is to give a brief introduction to recent results for core-level shifts in metallic bulk solids. For more detailed information on photoelectron spectroscopy and several applications, see [1] and the book by Hüfner [2]. Also, for further discussion about core-level shifts, see for instance [15,31–33]. The structure of this work is as follows: in the theory section we describe the complete screening picture and transition state method schemes for the *ab initio* computation of core-level shifts, using for example Green’s functions methods and supercell techniques. An extension of the complete screening picture to Auger core-core-core transitions is presented. In addition, a model for accessing interface qualities controlled by a single parameter is described. The result and discussion sections are split into three major parts; starting with i) CLSs in substitutionally disordered binary alloys. An example of the influence of global properties, volume and composition, is made for AgPd alloys, while the initial and final state effects are demonstrated for the Pd $3d_{5/2}$ shift in fcc NiPd, CuPd, AgPd and PdAu alloys. The disorder broadening of the spectral core line together with the effect of the local lattice relaxation is discussed for equiatomic CuPd, CuAu and AgPd. ii) The use of layer-resolved

CLS as a means of characterizing interface qualities for thin films embedded in solids is discussed. An example is shown for fcc (001) Ni/Cu_N/Ni for $N=1-10$ layers. iii) The Auger kinetic energy and Auger parameter shifts are computed both as functions of global properties, and the local chemical environment for Ag and Pd L₃M_{4,5}M_{4,5} in fcc AgPd.

2 Methodology

2.1 Complete screening picture

The core-level binding energy shift has been analyzed using several different theoretical approaches. Within the so-called potential model [8] the CLS is estimated by considering the change of the on-site electrostatic potential for an atom in different environments, ΔV ,

$$E_{\text{CLS}}^{\text{pot}} = \Delta V - \Delta E_{\text{R}}, \quad (1)$$

here ΔE_{R} stands for the core-hole relaxation energy, which is a contribution from the electrons screening the core-hole. While the first term, which contributes to the shift of the core-electron eigenstates, is usually referred to as the so-called initial state CLS, the second term is sometimes called the final state effect. In many works the initial and final state effects are considered separately. Also, the final state effects are often assumed to be independent of the environment, and therefore not giving rise to a shift.

The main assumption in the complete screening picture, which does not require a distinction between the initial and final state effects, is that the symmetric part of the core-line in the experimental spectra corresponds to a state in which the valence electrons are fully relaxed in the presence of a core-hole. This is valid for metallic systems [4]. In the beginning, the complete screening picture was used in a successful thermodynamical approach, by the connection of so-called Born-Haber cycles, to calculate the CLS between the free atom and the atom in a metal, see Johansson and Mårtensson [4]. From the use of Born-Haber cycles it is possible to obtain shifts as well as thermodynamic properties directly from different experimental measurements [2,4]. A recent application to metallic clusters can be found in [34].

In practical computations the CLS can be determined from the difference between effective ionization energies, which in turn are calculated by considering the total energies of their respective initial, ground state, and final, core-ionized states. One possibility, is to define an ionization energy in the

form of a generalized thermodynamic chemical potential (GTCP),

$$\mu = \left. \frac{\partial E}{\partial c} \right|_{c \rightarrow 0}, \quad (2)$$

where μ is the GTCP and E the total energy of the system with the concentration c of core-ionized atoms. The shift, ΔE_i , can now be readily obtained by taking the difference

$$E_{\text{CLS}}^{\text{cs}} = \Delta\mu_i = \mu_i - \mu_i^{\text{Ref}}, \quad (3)$$

where i is the core-level in an atom selected for the study. μ_i^{Ref} stands for the reference system, while in principle arbitrary, is usually chosen as the corresponding pure bulk metal - so also in this work. One can note that the above scheme closely follows the actual experimental situation, with the difference of chemical potentials or ionization energies corresponding to the difference between binding energies.

A common approximation in the literature is to assume that the core-hole at the ionized atom effectively acts as an extra proton, thus substituting the ionized atom of atomic number Z with the next element in the Periodic Table. This is the equivalent core or $(Z+1)$ -approximation, which typically performs very reasonably in comparison with experiment and explicit calculations for the core-ionization energy. Another common approach is to take the eigenenergy difference of a core-level i in the ground state which makes it possible to calculate a first order approximation to the core-level shift

$$E_{\text{CLS}}^{\text{is}} = -\Delta\varepsilon_i = -\varepsilon_i + \varepsilon_i^{\text{Ref}}, \quad (4)$$

where the negative sign is due the convention of positive binding energies. Note that deeply lying core states feel a change of the crystal potential as a rigid shift. Therefore, $E_{\text{CLS}}^{\text{is}}$ in Eq. (4) can be identified with ΔV term in the ESCA potential model, Eq. (1), and because of this it is also referred to as the initial state shift. While the initial-state scheme allows for very fast computations it is important to realize that it does not include the final state effects, the second term in the right-hand side of Eq. (1). Below we will often compare $-\Delta\varepsilon_i$ with the full theoretical shift obtained from the complete screening picture or within the transition state method, in order to evaluate the impact of the core-hole relaxation energy on the calculated CLS, and illustrate limitations of using Eq. (4) in practical applications.

2.2 Transition state method

Another alternative to determining core-level shifts within the complete screening picture, is the transition state method, based on the theorem by Janak for the partial occupation of electron levels within DFT [35]

$$\frac{\partial \tilde{E}}{\partial n_i} = \varepsilon_i, \quad (5)$$

where $0 \leq n_i \leq 1$ is the partial occupation number and where the total energy $\tilde{E} = E$ for a Fermi-Dirac distribution. As explained in Ref. [29], it is now possible to derive an expression for the electron binding energy by connecting the total energies of an N and $(N+1)$ electron system such that

$$E_{N+1} - E_N = \int_0^1 \varepsilon_i(n_i) dn_i. \quad (6)$$

By assuming that the eigenvalue is a linear function of the occupation number the core-level shift can then be directly determined from

$$E_{\text{CLS}}^{\text{ts}} = -\varepsilon_i(0.5) + \varepsilon_i^{\text{Ref}}(0.5), \quad (7)$$

considering the i eigenvalues with half an electron promoted to the valence band. Of course, to lineup the one-electron eigenenergies, the CLS are often related to the Fermi level, since this is convenient for metallic systems [14]. The evaluation at midpoint is often referred to as the *Slater-Janak transition state* [35,36]. Only a single calculation is sufficient to obtain the respective ionization energies, compared to the total energy approach in which two calculations are necessary. There are also other options, for instance to perform the evaluation at full and zero occupancy which has more similarity to the complete screening picture, e.g. in terms of a possibility to analyze the initial and the final state contributions [29].

Notice that while in principle Janak's theorem is only valid for the highest occupied electron, it has however also been successfully applied to core states [18,37–39]. In the practical calculations, a fractional electron is promoted to the valence band leaving a fractional core-hole, ensuring charge neutrality and a full screening in similarity with the complete screening picture. The assumption of the linearity of the eigenvalue to the occupation number made in the above equations was explicitly tested in fcc AgPd, CuPd, CuAu and CuPt disordered alloys [29]. It was shown that the linearity is valid as a first approximation in the cases of using one [Eq. (7)] or two points, while the

selection of three gives results very similar to the use of even further points. In a comparison between the transition state method and complete screening picture for the CLS in disordered alloys, it was found that the two computation schemes in most cases closely follow each other, however not with identical results [18].

2.3 Auger effect

In this section we will briefly discuss some further applications of *ab initio* calculations using the complete screening picture. Auger electron kinetic energy shifts were previously calculated in a phenomenological scheme, employing Born-Haber cycles and the $(Z+1)$ -approximation [5,14]. Recently, first principles calculations of the Auger kinetic energy and the Auger parameter shifts were performed for substitutionally disordered fcc AgPd alloys, giving good agreement with experiment [28].

The ijk core-core-core Auger transition gives a decay route for an excited atom with a hole at the core-level i , yielding a so-called Auger electron ejected from the atom with a specific kinetic energy E_{kin} . While Auger signals are detected by XPS spectrometers, E_{kin} may also be directly measured in Auger electron spectroscopy (AES), which by itself constitutes a highly developed experimental method for chemical analysis [1,40–42]. The process of the Auger transition can be described by two basic steps. First, a hole is situated at the core-level i in an atom, which is similar to the final state in the photoemission. In the second step, an electron from the lower binding energy orbital j fills the core-hole at i and the excess energy enables the simultaneous excitation of the Auger electron from k . The kinetic energy of the ejected electron is given by the difference in binding energies,

$$E_{\text{kin}} = E_i - E_{jk}, \quad (8)$$

where E_{jk} corresponds to the binding energy of the two j and k electrons at the same time (not necessarily described by the sum $E_j + E_k$). As in the previous case of the core-level binding energy, it is also possible to consider a shift in the Auger kinetic energy, ΔE_{kin} . In a similar fashion as for the single core-hole in CLSs, one can consider a double-hole shift for the doubly ionized system,

$$\Delta E_{jk} = \mu_{jk} - \mu_{jk}^{\text{Ref}} = \Delta\mu_{jk}, \quad (9)$$

in the practical calculations, the two jk electrons are promoted to the valence in the ionized state, and the full relaxation of the screening valence charge in

the presence of the two core-holes is allowed. In turn, the Auger kinetic energy shift can be written as the difference between the GTCPs

$$\Delta E_{\text{kin}} = \Delta\mu_i - \Delta\mu_{jk}. \quad (10)$$

Here one can note that a small final state effect would lead to $\Delta\mu_{jk} \approx 2\Delta\mu_i$, and further that $\Delta E_{\text{kin}} \approx -\Delta\mu_i$. That is, the Auger kinetic energy shift would be roughly equal to the negative core-level shift.

There is an interesting possibility to consider the Auger parameter analysis introduced by Wagner, which has been developed as a method for characterizing the response of materials to electron excitations [43–45]. A detailed review on its uses has been made by Moretti [46]. For instance, one type of Auger parameter shift can be defined by adding the core-level and Auger kinetic energy shifts,

$$\Delta\alpha = \Delta E_{\text{kin}} + \Delta E_i = 2\Delta\mu_i - \Delta\mu_{jk}, \quad (11)$$

which here results in a final expression with twice the i core-level shift subtracted with the jk double-hole shift. From the relation $\Delta\alpha \approx 2\Delta E_{\text{R}}$, it can be used as a way to estimate the relaxation effects. Auger parameters have been utilized in the case of metallic alloys, often in connection with potential models. See for example the work by Kleiman *et al.* and Weightman *et al.* [9,47–50].

2.4 Interface mixing

In order to model different qualities of an interface, it is possible to introduce a single parameter which controls the intermixing of atoms. Used together with Green’s functions techniques, this method provides a fast computation alternative compared with the explicit construction of interfaces, atom by atom, in supercell slabs [51]. It can be especially useful if the goal is to capture the general trends over many systems.

We start our discussion by describing the topological aspects of the interface mixing and how we model it theoretically. Let us first consider a single interface between two metals. The concentration profile around the interface due to intermixing is modeled by a general normal cumulative distribution function $\Lambda[X, \Gamma_C]$ (represented by the shaded area in Fig. 1b) where X is the distance from the interface in the growth direction and Γ_C is the standard deviation. The distribution is assumed to be symmetric around the interface. This approach is a simplification, since the inherent surface diffusion of the elements is strongly dependent on the material combination.

Fig. 1. **a)** The ideal, atomically sharp interface, **b)** interface mixing (alloying). The upper graphs show schematically the positions of the atoms of the multilayer (black and white atoms). Below each graph we show the probability density of interface defects, and the definition of the parameter, Γ_C that defines the geometrical extent of intermixing. The shaded area in b) is the concentration of white atoms at $X = -0.5$.

Fig. 2. The concentration profile as calculated by the model for an A_3B_{13} system with $\Gamma_C = 2.0$. The first terms of Eq. (12) are also displayed. The vertical lines represent the interfaces that separate the ideal layers and the black dots represent $C_A(X, \Gamma_C)$.

The concentration profile $C(X, \Gamma_C)$ of the multilayer is obtained as a sum of the layers in the sample, and the obtained expression for the multilayer concentration is,

$$C(X, \Gamma_C) = \sum_{n \neq 0} -1^{(|n|+1)} \Lambda_n(\text{sgn}(n)X, \Gamma_C), \quad (12)$$

where Λ_n is centered at interface n , see Fig. 2. Taking for example interface $n = 1$ as $X = 0$ and counting layers from this interface, we obtain the layer concentration at layer N as $C(N - 0.5, \Gamma_C)$. Once the concentration profile is obtained, the atomic core-level shifts may be calculated by means of e.g. the surface and interface Green's function method described in the next section. The n layer-resolved interface CLSs can then be written in the form of GTCPs as

$$E_{\text{ICLS}}^{\text{cs}}(n) = \mu_i(n) - \mu_i^{\text{Ref.}}, \quad (13)$$

where $\mu_i(n)$ denotes the n -layer specific chemical potential.

2.5 Computational details

All calculations have been performed within density functional theory (DFT) [11–13], employing either the local density approximation (LDA) or the generalized gradient approximation (GGA) for the exchange-correlation function, parametrized according to Perdew *et al.* [52]. In order to determine the total energies or Kohn-Sham eigenenergies needed to obtain the shifts described in the above sections, there are many methods available for solving the electronic structure problem. Typically, a code can be chosen by considering the suitability for the specific problem at hand.

For the study of shifts as system average properties, e.g. in substitutionally disordered alloys, the Green’s function technique [53–55] within the atomic sphere approximation (ASA) [56,57] was utilized, together with the coherent potential approximation (CPA) [54,55,58,59] for an efficient treatment of the disorder problem. Within ASA the radii of the spheres, S_{WS} , are chosen such that the volumes are equal to the corresponding Wigner-Seitz cell. Considering face-centered-cubic (fcc) crystals, $S_{WS} = a\sqrt[3]{3/(16\pi)}$, where a is the lattice constant. Note that CPA is very well suited for calculating partial molar properties, such as the GTCP in Eq. (2) [60]. In the demonstrations of the different shifts as average properties of volume and composition over substitutionally disordered fcc AgPd alloys in this work, the methodology is the same as in [18], however using LDA in all computational steps. The theoretical equilibrium volumes of pure metal Ag and Pd here correspond to $S_{WS}^{Ag} = 2.91$ a.u. and $S_{WS}^{Pd} = 2.79$ a.u. In order to obtain layer-resolved CLSs considering interface-systems, a surface and interfaces Green’s functions code was used, based on the principal layers technique [53].

To investigate the effect of the local chemical environment on the shifts, it is possible to use supercell techniques, in which a slab of atoms is set up to describe the system, using periodic boundary conditions. The locally self-consistent Green’s function method (LSGF) [61,62] is an order- N method in which the electronic scattering problem is solved by considering each and every atom in a local interaction zone (LIZ) embedded within an effective medium, here chosen as CPA. To calculate the Auger kinetic energy and parameter shifts in equiatomic AgPd presented in this work, a supercell of 256 atoms was used. In order to allow for local lattice relaxations in a supercell, the projector augmented wave (PAW) [63,64] method within the Vienna *ab initio* simulation package, VASP, has been used [65–68]. In this case with the GGA [69] for the exchange and correlation. While it is possible to employ core-ionized PAW-potentials for shift calculations in VASP [70], we utilize the

($Z+1$)-approximation to simulate the ionized atom. For the purpose of modeling disordered alloys in the supercell calculations, so-called special quasi random structures (SQS) first suggested by Zunger *et al.* [71] have been used. A recent discussion on the SQS-method can be found in [72]. The theoretical disorder broadening effect on the respective shifts can be calculated as the full width at half maximum (FWHM), $\Gamma_{\text{th}} = 2\sigma\sqrt{2\ln 2}$, assuming a Gaussian distribution, and with the standard deviation σ . More details on the methodology and related considerations can be found in the respective studies and references therein.

3 Core-level shift in disordered alloys

In this section we discuss theoretical results of core-level shift calculations in substitutionally disordered bulk alloys. First, we consider the CLS as a quantity only determined by the average composition and volume, i.e. global environment, with an explicit example for fcc AgPd alloys. The difference between the use of the initial state model, Eq. (4) and the complete screening picture, Eq. (3) is demonstrated for the Pd $3d_{5/2}$ shift in four binary alloys, illustrating the importance of the orbital character of the charge screening the core-hole. Next, the effect of the local chemical environment of each and every atom in the form of a broadening of the spectral core-line, is discussed, including very recent results which show a strong effect of local lattice relaxations. While we here focus on theoretical results, experimental measurements and further discussion can be found in e.g. [5,6,50,73–80] and references below.

3.1 Average global environment

Green’s function techniques within the coherent potential approximation give the possibility of fast computations of statistically averaged material properties. Applied in conjunction with the complete screening picture, CLSs can be readily calculated over a vast range of metallic materials. In the case of substitutionally disordered systems, shifts have been obtained as a function of the atomic composition in a number of binary alloys [16–18].

As discussed in [30], one of the motivations for our studies was the use of model approaches and approximations in the literature. For instance, the potential model, Eq. (1), was employed for fcc CuPd alloys [9,10] with results regarding the charge-transfer, which however were questioned on the basis of CLS calculated within the initial-state model, Eq. (4), for CuPd, AgPd and CuZn [81], followed by further discussion [82,83]. This made it interesting to perform *first principles* calculations for solid bulk alloys, including both the

Fig. 3. (Color online) The Ag $3d_{5/2}$ core-level shift (eV) in fcc AgPd disordered alloys is plotted as a function of volume, the Wigner-Seitz radius S_{WS} of the atomic spheres (atomic units), and composition, atomic % Pd. The isolines projected on the base-plane are in steps of 0.1 eV.

Fig. 4. (Color online) The Pd $3d_{5/2}$ CLS in AgPd alloys. The notation is the same as in Fig. 3.

initial and final state effects in the computation scheme, as had been done earlier in the case of surface CLS [21,22]. It was demonstrated that effects due to the core-hole screening are indeed important to describe the shift in metallic systems, e.g. CuPd and AgPd alloys, especially so in the case of Pd $3d_{5/2}$ CLS [16–18].

Eight different disordered fcc binary alloys; AgPd, CuPd, NiPd, CuNi, CuAu, CuPt, NiPt and PdAu, were investigated in [18]. Theoretical core-level shifts were found to be in a good agreement with experimental values. The complete screening picture was compared to the Slater-Janak transition state, which uses eigenenergies, but still includes core-hole screening effects, in con-

Fig. 5. (Color online) The Pd $3d_{5/2}$ CLS in fcc random phase NiPd, CuPd, AgPd and PdAu alloys, according to the initial-state approximation $-\Delta\varepsilon_i$ (empty circles) and the total CLS from the complete screening picture $\Delta\mu_i$ (filled boxes).

trast to initial-state approximations. A close agreement was obtained between the complete screening and transition state methods in the alloys, with some exception for the Cu $2p_{3/2}$ shift. Moreover, the effect of the magnetic state on the shift was shown in the case of the Ni-based alloys CuNi, NiPd and NiPt. In a separate work, the linearity of the transition state method was investigated in several disordered alloys [29].

There have been many studies on the physical properties of AgPd alloys in the literature. More specifically considering core-level shifts, there are several experiments [6,80,50], while theoretical works include results for bulk [16–18], surface [23] and thin films [25,91]. A difference between older and newer experimental values was attributed to measurements performed on surface alloys rather than bulk in the older study [50]. By using the Green’s functions calculations described in section 2.5 it is relatively easy to map overall trends in systems, as compared with more time consuming supercell techniques. In order to illustrate the effect of the overall, global, environment, we demonstrate the Ag and Pd $3d_{5/2}$ CLS as a function of only the volume and composition in fcc disordered AgPd alloys, Fig. 3, respectively Fig. 4. While it is more difficult to induce an expansion in experiment, pressure can be applied to reach the states with smaller volume.

Fig. 6. (Color online) The restricted average local density of states at Pd in fcc random phase NiPd, CuPd, AgPd and PdAu alloys. The DOS is shown in steps of 10 at. % Pd, from pure bulk metal Pd at the bottom to 10% at the top. The results for equiatomic alloys is shown with dashed lines.

3.2 Importance of complete screening picture

Fig. 5 shows the core-level shift, $-\Delta\varepsilon_i$, calculated by the means of the initial state model, Eq. (4), and the shift according to the complete screening picture $\Delta\mu_i$, Eq. (3), for Pd $3d_{5/2}$ in fcc random phase NiPd, CuPd, AgPd and PdAu alloys [18]. While the difference in electron eigenenergies can be used as a first order approximation to CLSs, the effect of the core-hole screening in the final state is seen to be important. As has been remarked many times, see for example [4,32,37,84,85], differences in the orbital character of the charge screening the core-hole can have a large impact on the final state effect contribution to the total shift. For instance, valence d electrons in transition metals are more tightly bound and therefore more efficient at screening a core-hole in comparison with the more widely distributed valence sp -type electrons. In Fig. 6 the corresponding average valence density of states at Pd is shown for the Pd-alloys, with the results from [16,18]. By comparing the trends of the calculated shifts in Fig. 5 with the average density of states at Pd shown in Fig. 6, one notes that for NiPd, with a smaller final state contribution to the shift, the DOS stays much the same at the Fermi-level. Turning to the other alloys, with a very pronounced final state effect on the shift, one also finds a large difference at E_F for the on-site, average, DOS. It can be argued that even in the case of a good agreement between the initial state shift and experiment, it is more sound to use methods including both initial and final state effects,

as the Kohn-Sham eigenenergies are not physical observables.

3.3 Disorder broadening

In a material with a random distribution of atoms over the lattice sites there are many possible local environments, considering for instance the composition of the nearest neighbors, in comparison with the ordered crystal. This difference in local chemical environments is reflected in site specific core-electron binding energies, which can give rise to an observable broadening in the XPS spectra, the so-called *disorder broadening* of the core-line. In order to measure the disorder broadening a very high resolution is needed in experiment, and only recently results were obtained by Cole *et al.* for Cu $2p_{3/2}$ in CuPd [10]. Since then, measurements have been obtained for several binary alloys [20,80,86–88]. From a theoretical point of view, it is in principle straightforward to model this kind of effect. For example, a supercell can be set up with a random distribution of atoms over the lattice sites, and the CLS calculated for each site by using the complete screening picture, as described in section 2.5. This procedure was accomplished for the equiatomic fcc AgPd and CuPd alloys [19], and for CuAu [20].

In Fig. 7 we show the theoretical disorder broadening of the $3d_{5/2}$ core-line in Ag and Pd for AgPd, presented in the form of CLSs, with data from [19]. Here one can see that the disorder broadening for Ag, 0.35 eV, is clearly larger than for Pd, 0.13 eV. The experimental value of 0.38 eV FWHM for Ag [80] agrees well with theory. In an analysis of the initial and final state contributions to the broadening, it was found that for the case of Ag the effects acts together to increase the total width, while the opposite situation holds for Pd, giving a smaller broadening. Similar results were found for CuPd [19].

Apart from the difference in composition among neighboring atoms, local lattice relaxations can also affect the chemical environments, especially in materials with a large size-mismatch between the constituent atoms. In Fig. 8 the CLSs in fcc CuPd (a), and CuAu (b), are plotted as a function of the number of opposite kind of atoms in the first coordination shell. Dotted lines and open symbols refer to the geometrically unrelaxed structure, while drawn lines and filled symbols denote relaxed structure shifts. First, considering CuPd, a somewhat larger broadening is found due to the lattice relaxation effects, however the average CLSs only changes by a small amount [19]. On the right hand side the corresponding shifts for Cu $2p_{3/2}$ and Au $4f_{7/2}$ in equiatomic CuAu is shown, with results from a very recent combined experimental and theoretical study [20]. In the case of the unrelaxed structure it is very interesting to find a reduced shift (that is, closer to zero) for the increasing number of opposite neighbor atoms. Allowing for relaxation, this trend becomes reversed. The ef-

Fig. 7. The distribution of Ag (above) and Pd (below) $3d_{5/2}$ core-level shifts in the AgPd random phase alloy. The results are from a 256 atoms SQS-supercell using LSGF [19]. Inset shows the variation of the average CLS as a function of Pd atom nearest neighbors.

Fig. 8. (Color online) Core-level shifts in Cu $2p_{3/2}$, Pd $3d_{5/2}$ and Au $4f_{7/2}$ for (a) CuPd and (b) CuAu fcc equiatomic random phase alloys as a function of the number of nearest neighbors of opposite kind in the first coordination shell. Open circles and filled squares represents the calculated CLSs at specific sites for unrelaxed and relaxed underlying lattice, respectively. Lines connect the average value at each local environment.

fect of the lattice relaxation is to provide a smaller broadening for Cu, while the average shift is almost identical. For Au the broadening is similar, but the average shift is changed.

4 Core-level shift in embedded thin films

Thin film nano-devices provide a very interesting opportunity in materials science, for instance considering the prospect of unique material properties connected to interfaces and finite size effects. In order to better understand the physics of thin film nano-materials it is important to investigate both experimental and theoretical methods which might help to characterize the actual interface qualities in a sample. Therefore, due to the high sensitivity of core-electron binding energies to the specific chemical environment of an atom, it is a natural step to evaluate the use of core-level shifts as such a tool. Further motivation comes from the good results previously obtained from using the complete screening picture, e.g. for the disordered alloys discussed in section 3, and especially considering the structural characterization of PdMn/Pd(100) [24] and AgPd structures on Ru(0001) [25]. In this section we discuss some completed studies and work in progress [26,27,89,90], and demonstrate first principles calculations of layer-resolved CLSs in embedded thin films as a function of film thickness and atom intermixing at the interface.

The relationship of the electronic structures between on the one hand disordered bulk alloys and on the other embedded thin films was studied in [26], considering spin magnetization and core-level shifts. Calculations were made for single to triple monolayers (MLs) of Cu embedded within the ferromagnetic bulk metals fcc Co and Ni, and bcc Fe. Only the sharp, ideal, interfaces were studied in this case, i.e. allowing no intermixing of the constituent atoms. In order to facilitate the comparison between the thin films and alloy systems, Cu $2p_{3/2}$ CLSs were modeled from nearest neighbor coordination in disordered alloys. The volumes in all the calculations were set to the Co, Ni and Fe pure bulk metal values. More specifically, the corresponding Cu concentrations in fcc structures are 33% for 1 ML and 66% for 2 ML, with 66 and 100% Cu in 3 MLs for the interface and center, respectively. In bcc structures the concentrations are zero (dilute limit) and 50 % for 1 and 2 ML, and 50 and 100% for 3 MLs. The result from this alloy shift model and the direct *ab initio* calculations is shown in Fig. 9. It is interesting to notice that while a good agreement is obtained for 1-2 MLs Cu in Co and Ni, there is a pronounced difference in the Cu-Fe systems. This was attributed to the possibility of induced interface states in the embedded Cu.

In a recent combined theoretical and experimental work it was suggested to use core-level shifts in a nondestructive method for characterizing the structure of deeply embedded interfaces, with results for Cu/Ni [27]. The samples used in the experiment consisted of CuNi multilayer superstructures, denoted as the ML repetitions Ni_5Cu_2 , Ni_5Cu_4 and Ni_5Cu_5 . Spectra for Cu $2p_{3/2}$ were collected over the systems as a function of annealing temperature, going from 20 to 300°C, assuming that the differences in temperature produce different

Fig. 9. The layer-resolved Cu $2p_{3/2}$ CLS from the alloy model (open circles) and directly calculated $\Delta\mu_i(n)$ (filled circles) in Me/Cu_N/Me, with Me = fcc (001) Co and Ni, bcc (001) Fe [26]. Bulk Cu metal shifts induced by the Me volumes are shown on the right side (filled boxes).

degrees of atom intermixing between the Cu and Ni layers. Moreover, the lattice mismatch is small for Cu/Ni multilayers, and the main effect on the average CLS was considered to stem from the intermixing of Cu and Ni atoms. Layer-resolved Cu shifts were calculated according to the surface and interfaces Green's function method, with the interface quality controlled by a single parameter Γ_C , as described in sections 2.4 and 2.5. Finally, the average shifts of systems with a different intermixing Γ_C was compared to the experimental shifts and peak broadening, establishing a connection between the theoretical results and a modified interface roughness in experiment. Returning to the CuNi-systems in a new experimental study, the effects of a Pt-capping layer on the evolution of spectra was investigated in more detail [89]. This time shifts were calculated for Cu and Ni $2p_{3/2}$ and Pt $4f_{7/2}$ in the ternary disordered fcc CuNiPt alloys, for comparison with the possible systems reached at higher temperatures. Results for the respective binary alloys can be found in [18].

In Fig. 10 we demonstrate the layer resolved Cu $2p_{3/2}$ CLS for Cu embedded within semi-infinite slabs of Ni, fcc (100) Ni/Cu_N/Ni, with $N=1-10$ total layers, as a function of the atomic intermixing parameter $\Gamma_C=0$ (sharp), 0.75 and 1.5 (more diffuse). The volume is set to that of pure bulk Ni metal. At

Fig. 10. (Color online) The layer-resolved Cu $2p_{3/2}$ CLS in fcc (001) Ni/Cu_N/Ni for $N=1 - 10$ layers. For sharp $\Gamma_C=0$ (black) and more diffused interfaces, $\Gamma_C=0.75$ (green) and 1.50 (red). The inner layer shifts are marked with filled diamonds and the outer shifts with hatched circles.

Fig. 11. (Color online) The Cu $2p_{3/2}$ CLSs in fcc (001) Ni/Cu₃/Ni for different interface qualities $\Gamma_C=0$ (black line), 0.75 (dashed green line) and 1.50 (dot-dashed red line), as the sum of layer-resolved shifts with a Gaussian broadening of 0.1 eV at FWHM.

the moment we do not consider possible effects such as segregation and local lattice relaxations. Here, the more positive values in Fig. 10 correspond to atoms in layers surrounded by more Cu, while the largest negative values give the shift for the dilute limit of Cu in Ni metal. A clear trend is that of

the inner Cu-layers reaching the maximum CLS, corresponding to the shift in pure Cu metal induced by the Ni volume, depending on the interface quality. For a possible direct comparison with experiment, one may for instance consider theoretical spectra. In Fig. 11 an example is made for the different interface qualities in Ni/Cu₃/Ni, by applying a Gaussian broadening on the layer-resolved shifts.

By using numerically efficient Green’s function methods together with model interfaces, it is possible to capture overall trends in shifts over a wide range of systems. A more detailed theoretical investigation considering the layer-resolved shifts in CuNi, CuCo and CuFe systems is in preparation [90]. Apart from interface qualities, there is a possibility of considering CLSs as a way to monitor special interface states. Also, one interesting option is to consider Monte Carlo methods, see for example the computation of the double segregation effect in AgPd alloy on Ru(0001) [91], in order to determine candidate structures for CLS calculations. In future work, it would be of interest to study the effect of the local environments in more detail, for instance using supercell techniques.

5 Auger kinetic energy and parameter shift

Auger electron spectroscopy (AES) is a widely used experimental method for the measurement of Auger electron kinetic energies [1,40–42]. Analogous to the case of core-level binding energies, the Auger electron kinetic energies are atom specific and sensitive to the chemical environment. Thus, they can provide valuable information on the electronic structure and bonding in materials, as well as be of use for structural characterization. Here in the last section of the results we consider core-core-core (*ijk*) Auger transitions in metallic systems, employing an extension of the complete screening picture to account for the Auger kinetic energy shifts ΔE_{kin} and parameter shifts $\Delta\alpha$ [5,14], described in more detail in section 2.3.

Previously, in a combined experimental and theoretical study, *first principles* calculations were applied to the Ag and Pd L₃M_{4,5}M_{4,5} Auger transition in fcc AgPd disordered alloys [28], finding a good agreement with experiment. After evaluating the GTCPs corresponding to the single hole core-level shift, $\Delta\mu_L$ ($2p_{3/2}$), and the double-hole shift, $\Delta\mu_{MM}$ ($2 \times 3d_{5/2}$), the Auger kinetic energy and Auger parameter shifts are quickly obtained from Eqs. (10) and (11); $\Delta E_{\text{kin}} = \Delta\mu_L - \Delta\mu_{MM}$ and $\Delta\alpha = 2\Delta\mu_L - \Delta\mu_{MM}$. As in the case of CLS, one can study the shifts as a function of the average overall environment as well as directly consider the atom specific local environment in a solid. Following the previous example in section 3, we below show the influence of these effects in random phase fcc AgPd alloys.

Theoretical Auger kinetic energy shifts for the Ag and Pd $L_3M_{4,5}M_{4,5}$ transitions are shown in the Figs. 12 and 13, respectively, as a function of only volume and the atomic composition, with isolines marking steps of 0.1 eV. The corresponding Auger parameter shifts are provided in Figs. 14 and 15. First, one notes the general trend of ΔE_{kin} with positive values for Ag (Fig. 12), and negative for Pd (Fig. 13) over a wide range of the systems. This is also true for the shifts corresponding to the theoretical equilibrium volumes, studied in [28]. A similarity between the results for Ag and Pd, is that the larger negative values are found for the higher density Ag-rich region, and the larger positive values for the opposite, low density, Pd-rich compounds. Turning to $\Delta\alpha$, a remarkable difference between Ag and Pd is found. The values for Ag are small, close to zero for a wide range of the systems in the volume and composition phase space, with some exception for very large volume and Pd-rich alloys. In comparison, the results for Pd give larger negative values as a function of the distance to pure Pd metal at theoretical equilibrium volume.

An analysis of the observed behavior of the Auger parameter shifts can be related to an influence of the final state effects (relaxation from the screening of the core-holes) on the CLS obtained by means of the initial state model, that is from the difference in core-electron energy eigenvalues. Indeed, if the contribution due to the screening of the core-holes is the same in the metal and in the alloy, that is the final state effects are small, the shifts are determined mainly by the relative positions of the one-electron eigenstates. In this case one immediately obtains a simple relation $\Delta E_{jk} \approx 2\Delta E_i$, because deeply laying core states feel a change of the crystal potential as a rigid shift. In the present case one therefore obtains $\Delta\mu_{MM} \approx 2\Delta\mu_L$, leading to vanishing Auger parameter shift, see Eq. (11). In case of Ag both Auger parameter shifts and final state effects in the CLS are relatively small as can be confirmed by inspecting Fig. 16a. As was discussed in section 3.2 the latter is so because Ag core holes are screened by mainly *sp* electrons both, in alloys and in the pure metal [16,28] - though for the lower Ag concentrations the screening charge have slightly more *d* character, giving rise to a larger final state effect.

On the contrary, the Pd metal has a partly filled *d*-band which gradually disappears under the Fermi-level with increasing Ag concentration in the AgPd alloys [16,28]. This means that the orbital character of the unoccupied valence states changes from a mostly *d* to mainly *sp*-character, switching at around 40 – 50% Pd. While the screening charge of the pure Pd metal consist of *d* and *sp* electrons, they change to purely *sp* character for the lower Pd concentrations in the alloy. It is this differential character of the screening charge that explains the complicated behavior and the larger value of the Pd Auger parameter shift, seen in Figs. 15 and 16b. This can also be a reason why $\Delta\alpha \approx 2\Delta E_R$ does not appear to hold here. Instead, in Fig. 16b we notice a similar trend between the Auger parameter shift and the contribution of the final state effects to the Pd CLS. Considering the results above for Ag and Pd, the separation of

the CLS into the initial and final state contributions used in this work seems to be justified, at least as an approximation. For related discussions including Auger parameter shifts, see e.g. Refs. [50,92].

In a similar fashion to the spectral core-lines in XPS, there can be a broadening of the Auger spectra due to differences in the specific local environment around each and every atom in a substitutionally disordered alloy. Here we present *ab initio* calculations of the E_{kin} disorder broadening for the Ag and Pd $L_3M_{4,5}M_{4,5}$ Auger transitions in fcc equiatomic AgPd, Fig. 17. For completeness, we also show the broadening of the Auger parameter in Fig. 18. A relatively large broadening of E_{kin} , 0.36 eV, is obtained for both Ag and Pd. Insets to Fig. 17 show that the same trend as the global average are found in the case of local environment variations, that is, smaller values are found at Ag-rich regions and more positive values are found at Pd-rich regions. Turning to the local environment results for $\Delta\alpha$, a substantial disorder broadening effect is found for Pd, 0.26 eV, while only a very small broadening, 0.03 eV, is seen in the case of Ag. Without going into a detailed analysis, one can immediately notice that these results are in line with the dispersions of ΔE_{kin} and $\Delta\alpha$ in Figs. 14 and 15, which is small for Ag and larger for Pd.

It is important to realize that while it is comparatively easy to estimate the local environment effects directly from calculations as demonstrated above, it is not always straightforward to extract the effect from experimental measurements. Experimental results for the disorder broadening of the Ag $M_5N_{4,5}N_{4,5}$ Auger spectra in AgPd was reported by Jiang *et al.* [93]. However, the measurability of the effect was discussed by Ohno [94] and Stoker *et al.* [95]. Finally, we note that by using the complete screening picture it is possible to estimate the magnitude of effects such as disorder broadening in a spectra. In future it would be of interest to consider calculations in more metallic materials, as well as the study of surface and interface effects using Auger transition data.

6 Summary

We have demonstrated recent first principle calculation results of core-level binding energy shifts as well as Auger kinetic energy and parameter shifts in metallic bulk solids, all within density functional theory. An advantage of using the complete screening picture for the computation is that the initial and final state effects are directly treated within the same scheme. The influence of on the one hand the average global environment, and on the other hand the atom specific local chemical environment for the different shifts was discussed, with illustrating examples for fcc random phase AgPd. Structural characterization is a very important application of theoretical CLS studies, here examples were provided for layer-resolved shifts depending on the interface quality, controlled

Fig. 12. (Color online) The Ag $L_3M_{4,5}M_{4,5}$ Auger kinetic energy shift (eV) in fcc disordered AgPd alloys is plotted as a function of volume, S_{WS} (atomic units), and composition, atomic % Pd. The isolines projected on the base-plane are in steps of 0.1 eV.

Fig. 13. (Color online) The Pd $L_3M_{4,5}M_{4,5}$ Auger kinetic energy shift in AgPd alloys. The notation is the same as in Fig. 12.

by a single parameter, for thin films embedded in solid. In addition, new theoretical results were presented for the disorder broadening of the Auger spectra in AgPd.

7 Acknowledgments

The Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF), and the Göran Gustafsson Foundation for Research in Natural Sciences and Medicine are acknowledged for financial support. E.H. would like

Fig. 14. (Color online) The Ag $L_3M_{4,5}M_{4,5}$ Auger parameter shift (eV) in fcc disordered AgPd alloys, is plotted as a function of volume, S_{WS} (atomic units), and composition, atomic % Pd. The isolines projected on the base-plane are in steps of 0.1 eV.

Fig. 15. (Color online) The Pd $L_3M_{4,5}M_{4,5}$ Auger parameter shift in AgPd alloys. The notation is the same as in Fig. 14.

to thank for support by FONDECYT grant 11070115, UACH DID grant SR-2008-0 and Anillo ACT 24/2006.

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Fig. 16. (Color online) Theoretical shifts for a) Ag and b) Pd in AgPd alloys. The Auger parameter shift is shown by diamonds. Drawn lines with empty boxes show the calculated contributions to the corresponding core-level shifts due to the relaxation from the screening of the core-holes, the so-called final state effects, obtained as differences between the CLS calculated by means of the initial state model, Eq. (4), and the complete screening picture, Eq. (3). For reference, the core-level (full boxes) and double-hole (dashed line) shifts are also displayed.

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Fig. 17. The distribution of Ag (above) and Pd (below) $L_3M_{4,5}M_{4,5}$ Auger kinetic energy shifts, ΔE_{kin} in the AgPd random phase alloy. The calculations were made using LSGF for a 256 atoms SQS-supercell. Inset shows the variation of the average ΔE_{kin} as a function of Pd atom nearest neighbors.

Fig. 18. The distribution of Ag (above) and Pd (below) $L_3M_{4,5}M_{4,5}$ Auger parameter shifts, $\Delta\alpha$, in the AgPd random phase alloy. The calculations were made using LSGF for a 256 atoms SQS-supercell. Inset shows the variation of the average $\Delta\alpha$ as a function of Pd atom nearest neighbors.

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