

Auger Energy Shifts in fcc AgPd Random Alloys from Complete Screening Picture and Experiment

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We extend the complete screening picture to *ab initio* calculations of Auger kinetic energy and Auger parameter shifts in metallic alloys. Experimental measurements of the $L_3M_{4,5}M_{4,5}$ Auger transition in fcc AgPd random alloys are compared with first-principles calculations and the results are in excellent agreement for both the Ag and Pd Auger shifts over the whole concentration range. We discuss the Auger kinetic energy shifts in terms of single-hole states for the $2p_{3/2}$ core level and double-hole states for the $3d_{5/2}$ level.

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Auger electron spectroscopy (AES) is a highly developed and widely used experimental technique for studies of surface and bulk properties of solids. The spectral lines obtained in AES by measuring the kinetic energy of the Auger electrons, E_{kin} , depend only on the electron binding energies for the particular element, and on its local chemical environment. This fact, together with the sensitivity of AES to a relatively small fraction of an element in a sample, makes it a very useful tool for chemical analysis. It is also an important tool for analyzing the electronic structure of solids. By investigating the Auger kinetic energy shift ΔE_{kin} for an element in the pure metal and in an alloy it is possible to obtain a deeper understanding of the bonding properties. Electronic relaxation and core-hole screening, associated with the Auger process, have been continuously discussed in the literature since the 1970s [1,2]. In this regard, experimental measurements of the kinetic energies of photoelectrons and Auger electrons turn out to be particularly useful since they allow unambiguous identification of a final state quantity, a key issue in interpreting spectroscopic measurements. In combined photoelectron and Auger experiments it is possible to minimize the effect of uncertainties in the energy referencing of electron spectrometers and obtain insight into how the screening of the core holes created in the photoemission process changes with concentration as well as into estimates of charge transfer effects in alloys [3].

A full interpretation of the experimental results requires a theoretical analysis. The different approaches to calculating the dependence of core-level binding energies and Auger kinetic energies on the atomic environment are basically divided between the use of potential models [4], which is the most widespread, and first-principles elec-

tronic structure calculations. A number of first-principles results have been obtained for the Auger spectral shape [5,6]. However, the previous calculations use explicitly eigenvalues and eigenstates of the one-electron Kohn-Sham equation, and, with a few exceptions [7], the effect of core-hole screening is not taken into account.

At the same time, the so-called complete screening picture, which was suggested for calculations of the core-level shifts in metals [8], includes initial state and final state effects in the same scheme with the former depending on the energy eigenvalue of the core electrons and the latter on the screening of the core hole after the electron excitation. The final state effect arises from the response of the valence electrons to the presence of core holes which lead to a redistribution of charge in order to screen the additional positive charge in the core and give rise to a relaxation in energy. This effect becomes very pronounced when there is a difference in the screening charge for a metal and an alloy, as valence electrons of *d*-orbital character screen the core hole more effectively than those with *sp* type [8–11]. The complete screening picture was first used to calculate the core-level shift between the free atom and the atom in a metal [8]. Thereafter it has been applied to calculate the core-level energy shift (CLS) in alloys [11,12] and surface core-level energy shifts [13–15]. It was also used successfully in calculations of the Auger shifts using the phenomenological approach via Born-Haber cycles and the equivalent core approximation for a number of different metals [16,17].

In this Letter we show that the complete screening picture can be extended to first-principles calculations of the Auger shifts in metallic alloys. The Auger kinetic energy shift for the $L_3M_{4,5}M_{4,5}$ core-core-core Auger

transition is calculated *ab initio* and compared with experimental measurements for fcc disordered Ag-Pd alloys. We analyze the shifts as a function of alloy compositions.

The Auger transition, which is shown schematically in Figs. 1(a) and 1(b), consists of two steps. In terms of the core-core-core Auger transition that we denote as ijk , the first step is the photoemission of the core electron from the i th orbital with a binding energy E_i [Fig. 1(a)]. This leaves a core hole, which acts on the screening charge as an extra proton. In the second step [Fig. 1(b)] an electron with lower binding energy in the core level j fills the hole, while the Auger electron situated in the k th orbital exits

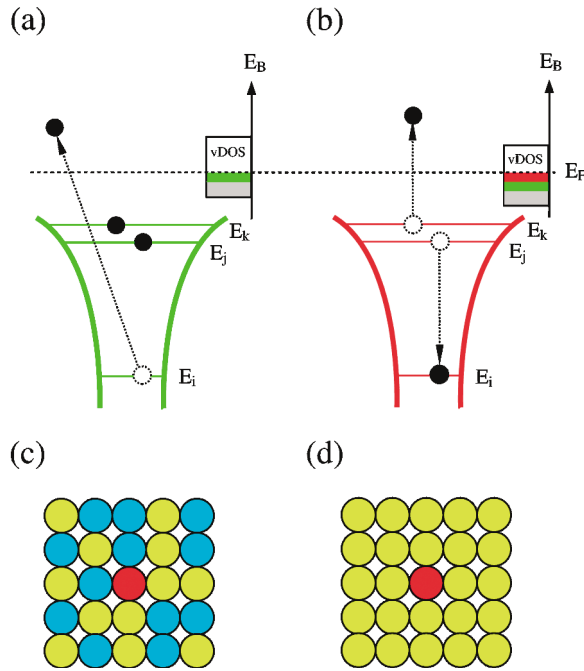


FIG. 1 (color). Schematic illustration of the complete screening picture for ijk (core-core-core) Auger transition at an atom A in the alloy $A_{1-x}B_x$. Two steps of the transition are shown, the photoemission of the core electron (black, solid circles) from the i th orbital (a) and the Auger electron emission from the k th orbital with a simultaneous annihilation of the core hole (open circles) at the i th orbital by an electron from the j th orbital (b). E_i , E_j , and E_k denote binding energies of the corresponding core states. The dashed line in (a) and (b) denotes the Fermi level E_F , and the screening of the core holes by valence electrons is indicated by increasing occupation of the valence states (gray) at the single [green in (a)] and double [green and red in (b)] core-ionized atoms, respectively. In (c) we show an $A_{1-x}B_x$ (yellow) alloy that contains an impurity atom $A_{jk}^{A_{1-x}B_x}$ (shown in red) with the double core hole at levels j and k . In (d) a double ionized impurity atom A_{jk}^A is shown in the pure A metal. Within the complete screening picture the double-hole shift ΔE_{jk}^A in the right-hand side of Eq. (1) can be evaluated as the total energy difference between these two systems. A similar figure (with single ionized impurity atom A) would illustrate the calculations of ΔE_i^A in Eq. (1).

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the atom in the same immediate process with the specific Auger kinetic energy $E_{\text{kin}} = E_i - E_{jk}$, where E_{jk} is the double core-hole binding energy required to liberate the j and k electrons from their respective core levels. In principle, similar processes would describe Auger transitions involving valence levels, but we do not consider such transitions in this work.

Following Ref. [17], the Auger kinetic energy *shift* for an atom A in a pure metal and in a disordered alloy $A_{1-x}B_x$, ΔE_{kin}^A , can be written as a combination of a single-hole metal-to-alloy shift ΔE_i^A and a corresponding double-hole shift ΔE_{jk}^A :

$$\Delta E_{\text{kin}}^A = \Delta E_i^A - \Delta E_{jk}^A. \quad (1)$$

Within the complete screening picture one assumes that the conduction electrons attain a fully relaxed configuration in the presence of a single or a double core hole. Figures 1(a) and 1(b) illustrate this increase in occupied valence band states for successive degrees of core ionization of the atom. Therefore, the double-hole shift ΔE_{jk}^A can be evaluated as a *total energy* difference between two systems, the one that contains an impurity atom $A_{jk}^{A_{1-x}B_x}$ with the double core hole at levels j and k in the $A_{1-x}B_x$ alloy [Fig. 1(c)], and the other with a double ionized impurity atom A_{jk}^A in the pure A metal [Fig. 1(d)]. For alloys an evaluation of the impurity solution energy can be done by calculating the impurity chemical potential [18]. Thus, the double-hole shift ΔE_{jk}^A can be expressed in terms of the corresponding differences between the so-called generalized thermodynamic chemical potentials (GTCP) [11] of double ionized atoms μ_{jk} in the alloy and in the pure metal,

$$\Delta E_{jk}^A = \mu_{jk}^{A_{1-x}B_x} - \mu_{jk}^A = \Delta \mu_{jk}^A. \quad (2)$$

A similar expression relates ΔE_i^A to the GTCP μ_i of single ionized atoms. The chemical potentials can be easily calculated from the density functional theory total energies as

$$\mu = \left. \frac{\partial E_{\text{tot}}}{\partial c} \right|_{c \rightarrow 0}. \quad (3)$$

E_{tot} is the total energy of an alloy $A_{1-x}B_x$ or metal A in which one (for a single-hole state) or two (for a double-hole state) core electrons are promoted from specific core levels of some A atoms to the conduction band, and a total concentration of these core-ionized atoms in the whole system is c . Finally, one may write the Auger shift in Eq. (1) as

$$\Delta E_{\text{kin}}^A = \Delta \mu_i^A - \Delta \mu_{jk}^A. \quad (4)$$

Note that the first term in Eq. (4) is exactly the CLS [11], while the second term represents the double-hole binding energy shift for the two core holes at j and k levels. One can also calculate the shift of the so-called Auger

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parameter which has become an important and convenient empirical method of characterizing the response of materials to electron excitation [1,2] and which is given by the sum of the core-level shift and Auger shift, $\Delta\xi = \Delta E_{\text{kin}} + E_{\text{CLS}}$. In terms of the GTCP, it can be expressed as

$$\Delta\xi A = 2\Delta\mu_i^A - \Delta\mu_{jk}^A. \quad (5)$$

The Auger parameter is often extracted experimentally as an estimate of the relaxation effects.

In order to check the above theory we carried out first-principles calculations and the experimental studies of Auger kinetic energy and Auger parameter shift in fcc AgPd alloys over the complete range of concentrations. The details of calculations of the GTCP adopted for this study are described in Ref. [11]. We use a scalar-relativistic approach that neglects spin-orbit coupling for valence electrons. Our test calculations were carried out for an equiatomic alloy using a fully relativistic version of our method [19] and showed that the difference between Auger shifts at Ag and Pd were well within 0.1 eV (see Fig. 2). Thus, the use of the scalar-relativistic method is justified.

Experimentally, the polycrystalline alloys were made by comelting high purity starting materials in an Ar arc furnace as described previously [21]. The measurements were made on the Scienta ESCA 300 spectrometer of the RUSTI facility of the UK Daresbury laboratory using monochromated Al $K\alpha$ and Ti $K\beta$ exciting radiation. The specimens were mechanically scrapped *in situ* to remove all traces of surface contamination.

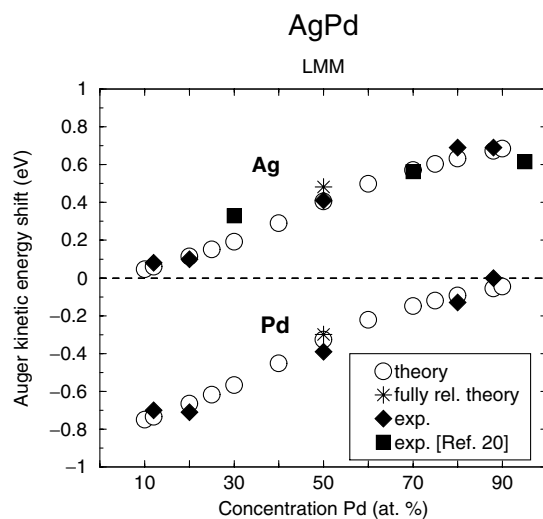


FIG. 2. Theoretical (open circles) and experimental (solid diamonds) LMM Auger shifts for Ag and Pd in random fcc $\text{Ag}_{1-x}\text{Pd}_x$ alloy. The experimental results are accurate to ± 0.1 eV. Additional experimental data for Ag (solid squares) from Ref. [20] are also shown. Our theoretical results for the equiatomic alloy where the spin-orbit interaction for valence electrons was included (stars) are also shown for comparison.

Figure 2 displays experimental and calculated Auger kinetic energy shifts for the $L_3M_{4,5}M_{4,5}$ Ag and Pd Auger transition in fcc AgPd random alloys. Additional experimental data for Ag were taken from work by Kleiman *et al.* [20]. One can see that the shifts change almost linearly as a function of alloy composition and that Ag and Pd shifts are of opposite signs. The theoretical and experimental values in Fig. 2 agree with each other within 0.07 eV over the whole range of alloy concentrations, with the only exception at 30% Pd concentration for the Auger shift of Ag, there the experimental value from [20] is about 0.15 eV larger than the theoretical result. The largest absolute values for ΔE_{kin} are found for the most dilute alloys, with the theoretical values 0.68 eV for Ag (at 90% Pd) and -0.75 eV for Pd (at 10% Pd). In general, the agreement between the theory and the experiment is very good, and this confirms the applicability of the complete screening picture for calculating Auger kinetic energy shifts in alloys.

Figure 3 shows the calculated and experimental Auger parameter shift $\Delta\xi$ as a function of concentration in random fcc AgPd alloys. Again, there is very good agreement between the theory and the experiment. Note that $\Delta\xi$ is largely determined by the relaxation effects due to the screening of the core holes and is a useful probe of the dependence of relaxation on alloy concentration. From our results one can see that the relaxation effects are rather small for Ag, but they are large for Pd.

In order to analyze separate contributions to the Auger kinetic energy and the Auger parameter shifts, we also show in Fig. 3 calculated metal-to-alloy changes of the GTCP of single ionized atoms $\Delta\mu_L$ ($2p_{3/2}$ single core hole), as well as that for double ionized atoms $\Delta\mu_{MM}$ ($3d_{5/2}$ double core hole). Remember that the difference between the two gives the theoretical LMM Auger shift in Fig. 2. The task of analyzing the Auger shift can be broken down into an investigation of the core level and double-hole shifts for Ag and Pd at different concentrations. An analysis of the different binding energy shifts can in turn be split into a comparison of initial state effects (core-electron energy eigenvalues) and final state effects (relaxation from the screening of the core holes). If the difference in final state effects is small, the shifts are determined mainly by positions of the one-electron eigenstates, and one immediately obtains a simple relation $\Delta E_{jk}^A \approx 2\Delta E_i^A$, because deeply lying core states feel a change of the crystal potential as a rigid shift. In the present case one obtains $\Delta\mu_{MM} \approx 2\Delta\mu_L$, leading to a very simple antisymmetry relation between the Auger kinetic energy shift and the core-level shift, $\Delta E_{\text{kin}} = \Delta\mu_L - \Delta\mu_{MM} \approx -\Delta\mu_L$. In the case of Ag this can be confirmed by inspecting the theoretical values in Figs. 2 and 3. This is so because Ag core holes are screened by mainly *sp* electrons both in alloys and in the pure metal [11].

A more interesting situation arises in the Pd case. The Pd metal has a partly filled *d* band located at the Fermi

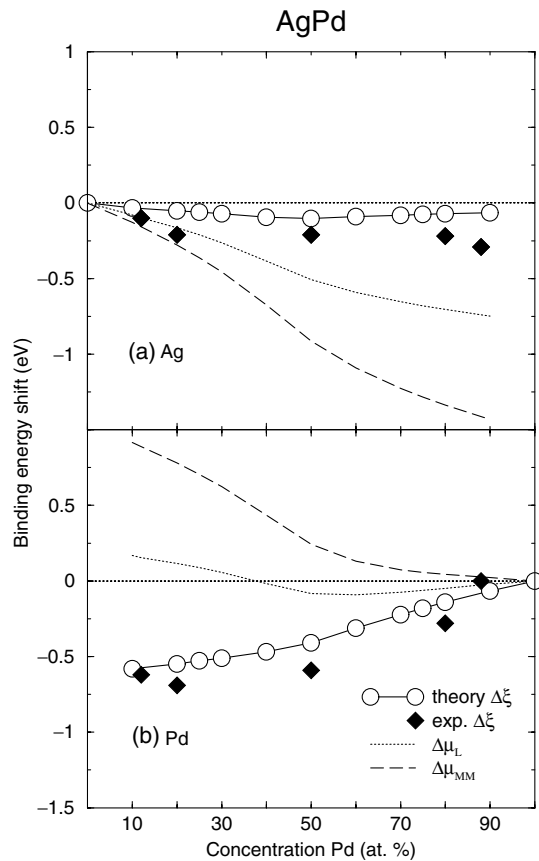


FIG. 3. Theoretical (open circles) and experimental (solid diamonds) Auger parameter shifts for (a) Ag and (b) Pd in random fcc $\text{Ag}_{1-x}\text{Pd}_x$. The experimental results are accurate to ± 0.1 eV. Also shown are calculated metal-to-alloy changes of the generalized thermodynamic chemical potentials of single ionized atoms $\Delta\mu_L$ (dotted lines) and double ionized atoms $\Delta\mu_{MM}$ (dashed lines).

level, which gradually disappears under the Fermi level in the AgPd alloy [11], changing the orbital character of unoccupied valence states from a mostly d to a mostly sp character, with the turning point around 40%–50% Pd. Thus, the screening charges of the pure Pd metal would consist of d and sp electrons. As the Pd d band becomes filled in the alloy, the screening charge would then turn to purely sp character for lower Pd concentrations. It is this differential character of the screening charge that explains the complicated behavior and the large value of the Pd Auger parameter shift seen in Fig. 3.

In conclusion, we carried out first-principles calculations and experimental measurements of the Auger kinetic energy shifts and Auger parameter shifts in random fcc AgPd alloys. We show that Auger energy shifts can be predicted across the entire composition range of an alloy system with excellent accuracy, confirming the reliability of the suggested theoretical scheme based on the complete screening picture. This opens the way for a detailed

quantitative test of models used by experimentalists for chemical shift analysis. Such models are widely employed on relevant and plausible concepts, but their validity has never been established (beyond metal-atom shifts). That can now be explored.

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