

Valence-Band Hybridization and Core Level Shifts in Random Ag-Pd Alloys

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First-principles calculations of the core-level binding energy shifts (CLS) for 3d inner-core electrons of Ag and Pd in fcc Ag-Pd alloy were carried out within the complete screening picture, which includes both initial and final state effects. These alloys show remarkable CLS that have the same sign for both alloy components, in contradiction to what would be expected from the potential model for core electron energies. We show that the main contribution to the core-level shift is due to the intra-atomic charge redistribution, which is related to the hybridization between the *valence* electron states of the alloy components. There is also a large contribution to the CLS from the core-hole relaxation energy.

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Binding energies of core electrons show energy shifts which depend on the chemical environment of the atom. This is why studies of the difference between the core-electron binding energies in the elemental metal and, for example, in a disordered alloy can help to provide a better understanding of the electronic structure and the bonding properties of a solid. The core-level energy shifts (CLS) are relatively easy to measure using x-ray photoelectron spectroscopy, and they were shown to be related to different properties of materials, such as, for example, depending on the material in question, the cohesive energy [1], the heat of mixing [2,3], the segregation energy [4], and charge transfer [5,6].

The CLS measured by electron spectroscopy for chemical analysis (ESCA) is often called the chemical shift, and different theoretical models have been suggested for its calculation and understanding. Within the so-called potential model [5] the E_{CLS} is estimated from the shift of the on-site electrostatic potential for an atom in different environments, ΔV :

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

where ΔE_R represents the core-hole relaxation energy, which is a contribution to the shift from the remaining electrons, as they screen the charge imbalance caused by the core hole. This contribution is sometimes called the final state effect, in contrast to the first term in Eq. (1), which contributes to the shift of the core-electron eigenstates, and therefore measures the so-called initial state CLS. In many works the initial and final state effects are calculated separately. Moreover, the final state effects are often assumed to be constant, independent of the environment, and therefore do not give rise to a shift.

The simplest way to estimate ΔV in Eq. (1) is to associate it with the charge transfer on an atom in different environments in the framework of the ESCA potential model [5,6],

$$\Delta V = q \left(k - 14.4 \frac{\alpha^M}{R} \right), \quad (2)$$

where q denotes the net charge on an atom, k is a constant equal to the Coulomb repulsion integral between the core and the valence electrons, and α^M and R denote the Madelung constant and the nearest-neighbor distance, respectively. In Ref. [5] such an estimate was successfully used for molecules, and recently Cole *et al.* [6] used Eq. (2) for the interpretation of the CLS in face-centered-cubic (fcc) Cu-Pd alloy. However, this interpretation was questioned by Faulkner *et al.* [7] who carried out first-principles calculations based on density functional theory [8] for Cu-Pd, Ag-Pd, and Cu-Zn alloys at selected concentrations, and did not find any correlation between the CLS and the ESCA potentials. This result seems to be in agreement with conclusions drawn by Methfessel *et al.* from their calculations of CLS for MgAu alloy [9], who also did not find any connection between the calculated CLS and the charge transfer in this system. Also in the earlier study by Weinert and Watson [10] four factors (a core-hole relaxation, changes in the Fermi energy, an intra-atomic charge transfer, and a redistribution of charge due to bonding and hybridization) were suggested to determine the CLS in solids, in addition to the interatomic charge transfer.

In a subsequent discussion about this matter [11,12] several points regarding first-principles calculations of CLS were stressed. In particular, it was emphasized that in most applications the final state effects were neglected, and the effect of local lattice relaxations was not taken into account in Ref. [7]. Therefore there is a question whether the observed failure of the ESCA potential model [Eqs. (1) and (2)] to reproduce the calculated CLS in metallic alloys [7] is an artifact of the approximations employed in that work, or if it has a fundamental physical origin.

In this Letter we present the results of our work on CLS in random Ag-Pd alloy which clarify the origin of CLS in metallic alloys. We choose this system rather than the Cu-Pd alloys studied in Refs. [6,7], because the lattice parameters of Ag and Pd are much closer to each other, compared to the case with Cu and Pd. Therefore, the effect of local lattice relaxations is eliminated from the discussion.

We calculate the core-level shifts within the complete screening picture [1], where the basic assumption is that for metals 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, and where therefore the initial and final state effects are fully included, and are treated within the same scheme, not as two separate contributions. We show that there are two factors which strongly influence the binding energy of core electrons. First, there is a large contribution to the CLS from the core-hole relaxation energy, ΔE_R , in Eq. (1). Second, we show that the first term in Eq. (1) depends strongly on the hybridization between the *valence* electron states of the alloy components that may occur in metallic alloys, and that this effect can not be accounted for by means of simple charge transfer arguments.

The complete screening picture was originally used to calculate the core-level shift between a free atom and an atom in a metal [1]. This approach was also successfully applied in studies of surface CLS [13]. Calculations that use this approach are time consuming, but because final state effects are often important this is the appropriate treatment of core-level energy shifts. An essential quantity that needs to be calculated within the complete screening approach is the generalized thermodynamic chemical potential of the core-ionized atoms

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

Here E_{tot} is the energy of a system where a core electron on the ionized atom is promoted to the valence band, the remaining electrons relax as they screen the core hole, and c is the concentration of such core-ionized atoms. The core-level shift will then be given by the difference between the chemical potentials of ionized atoms in the pure metal and in the alloy:

$$E_{\text{CLS}} = \mu_{\text{pure}} - \mu_{\text{alloy}}. \quad (4)$$

Note that for the analysis the initial and final state effects may be separated. Calculating the core level shift E_{CLS}^i according to the initial state model from the core-electron eigenvalues E_{one} , we take the difference between them in the pure metal and in the alloy, relative to the Fermi energy, E_F ,

$$E_{\text{CLS}}^i = (E_{\text{one}}^{\text{pure}} - E_F^{\text{pure}}) - (E_{\text{one}}^{\text{alloy}} - E_F^{\text{alloy}}). \quad (5)$$

Note that E_{CLS}^i corresponds to the first term in Eq. (1). Therefore, the core-hole relaxation energy ΔE_R can be estimated as the difference $E_{\text{CLS}} - E_{\text{CLS}}^i$.

The core-electron energy eigenvalues and the total energies for disordered alloys were calculated using the coherent potential approximation (CPA) [14,15] and the basis set of *s*, *p*, and *d* linear muffin-tin orbitals [16] within the atomic sphere approximation and the local density approximation [17] for the one-electron potential. We have calcu-

lated the core-level energy shift for $3d_{5/2}$ electrons of Ag and Pd in fcc Ag-Pd alloy over the complete concentration interval using theoretical equilibrium lattice parameters reported in Ref. [15]. In that paper it was also shown that our present method provides reliable electronic structure and total energies for Ag-Pd alloys. Note also that there are experimental data available for the chemical shift for the fcc Ag-Pd alloy over the whole concentration interval $0 < x < 1$ [3].

In order to investigate the accuracy of CLS obtained by the CPA method we first calculated the shift for the $\text{Ag}_{50}\text{Pd}_{50}$ alloy modeled by a supercell with up to 256 atoms using the order- N locally self-consistent Green's function (LSGF) method [18]. Comparing these supercell CLS calculated within the complete screening picture, as well as the initial state CLS, with results obtained by means of CPA calculations, we find a negligible energy difference of the order of 0.05 eV (see Table I). Our initial state CLS for Ag in $\text{Ag}_{50}\text{Pd}_{50}$ alloy also agrees well with the value calculated in Ref. [7]. The agreement is worse for the Pd CLS which could be due to the relatively large sensitivity of the initial state CLS to the details of the calculations (lattice parameter, core radius, etc.).

In Fig. 1 the calculated CLS are shown together with the experimental results [3]. The CLS calculated within the initial state model are also presented. From Fig. 1, one can see that for both Ag and Pd the core level shifts obtained within the complete screening treatment are in excellent agreement with the experimental data over the complete concentration interval. For Pd the difference between the initial state model and the complete screening picture is very large: the initial state shift even has the wrong sign compared to experiment. For Ag relaxation effects are less pronounced, but their influence increases with increasing Pd concentration. Remarkably, the initial state CLS are relatively large, and have *the same sign* for all concentrations. Note that the calculated average net charges $\langle q \rangle$ on Ag and Pd are negligibly small (Table I). If one assumes $q = \langle q \rangle$ in Eq. (2) [6], then $\Delta V \approx 0$. Thus, there must be another reason for the observed behavior of CLS in fcc Ag-Pd alloy, rather than the intersite charge transfer.

TABLE I. The $3d_{5/2}$ Ag and Pd core-level shifts, CLS (in eV), and net charges, Δq (in electrons), in fcc $\text{Ag}_{50}\text{Pd}_{50}$ alloy calculated by the LSGF and the CPA methods within the complete screening picture (CLS^{cs}) and the initial state model (CLS^{is}). Results obtained in Ref. [7] are also given for comparison.

	LSGF	CPA	Ref. [7]
CLS ^{cs} Ag	-0.469	-0.509	...
CLS ^{is} Ag	-0.518	-0.513	-0.48
CLS ^{cs} Pd	-0.065	-0.081	...
CLS ^{is} Pd	-0.404	-0.403	-0.10
Δq^{Ag}	0.036	0.036	0.05
Δq^{Pd}	-0.036	-0.036	-0.05

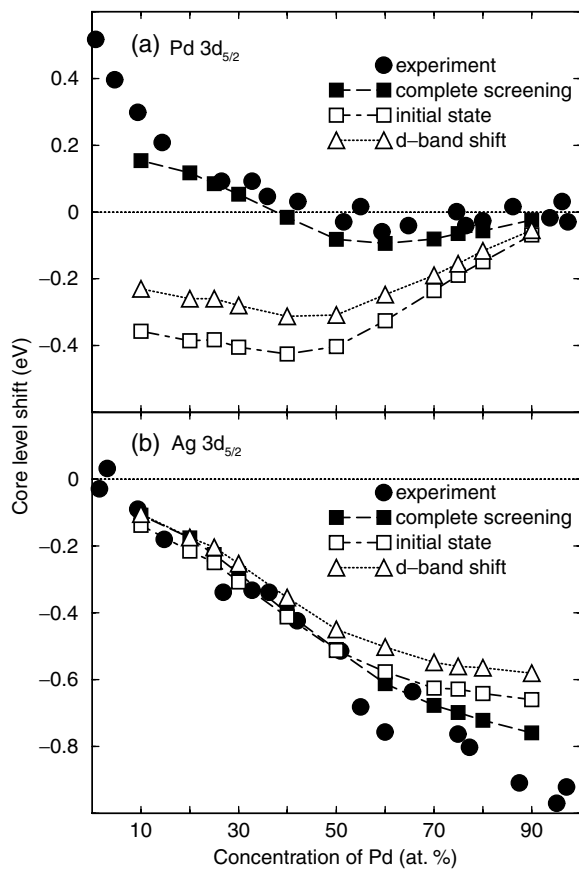


FIG. 1. The core-level binding energy shift as a function of Pd concentration in random fcc Ag-Pd alloys. The experimental chemical shifts (filled circles, Ref. [3]) are compared with the calculated core-level shift obtained within the complete screening picture (filled squares, dashed line), and from the initial state model (open squares, dot-dashed line). Also displayed are the shifts of the d -band centers (open triangles, dotted line). The $3d_{5/2}$ core-level shifts for Pd and Ag are shown in panels (a) and (b), respectively.

In Fig. 2 the average density of states (DOS) for Ag (Fig. 2a) and Pd (Fig. 2b) atoms in Ag-Pd alloy with different concentrations are displayed. One can see remarkable modifications of the DOS for these atoms in the alloy as compared to the pure elements. The system clearly shows non-rigid-band behavior, and thus one may expect substantial changes of the valence electron density and the one-electron potential on the Ag and Pd sites when they are alloyed. Thus, a shift of the on-site potential ΔV may be induced by the intrasite charge redistribution, without substantial intersite charge transfer. One can monitor this shift by looking at the shift of the centers C of the Ag and Pd d bands, shown in Fig. 2 by dotted lines. It is also well known that $\Delta C = (C^{\text{pure}} - E_F^{\text{pure}}) - (C^{\text{alloy}} - E_F^{\text{alloy}})$ gives a very good estimate of the initial state CLS E_{CLS}^i , and in Fig. 1 this is illustrated explicitly. In short, the shift of the one-electron eigenstates, the shift of the on-site potential ΔV , and the shift of the d -band center ΔC must have the same origin, and we identify this origin as the hybridization effects that take place in Ag-Pd alloys.

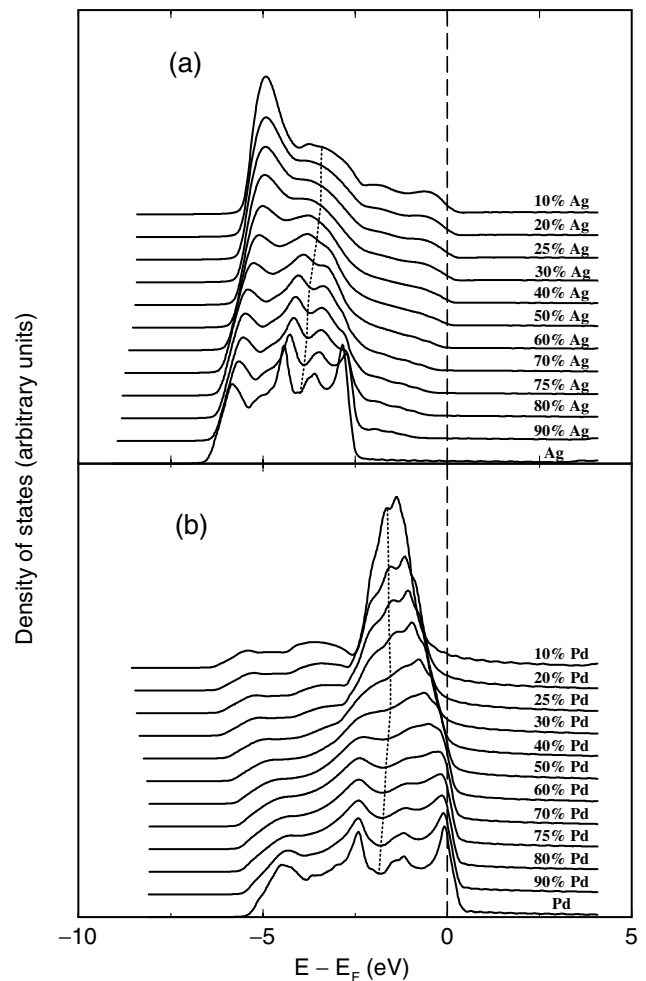


FIG. 2. The average local density of states of (a) Ag and (b) Pd in fcc Ag-Pd alloys with different concentrations as a function of energy (relative to the Fermi energy E_F). The centers of the d bands are shown by dotted lines.

As one can see from Fig. 2, pure fcc Pd has a wide d -band that is just partly filled, and therefore is located at the Fermi energy. However, the d band of Ag is completely filled, has a smaller width, and is removed from the Fermi level. Let us first consider alloys with low Pd concentrations. The Pd impurity in this case is surrounded mostly by Ag, leaving only a few electronic states that a Pd electron could jump to (the Ag DOS is very low around E_F). Thus, these electrons become virtually localized on the Pd sites, and this can be seen by the presence of the Pd virtual bound state close to E_F in the $\text{Ag}_{90}\text{Pd}_{10}$ alloy. Because of the substantial band narrowing, the center of the Pd d band shifts towards higher energy. Note that a similar effect takes place at surfaces for metals with more than half-filled bands. On-site potential which leads to this shift must be nonzero, and this leads to a shift of the one-electron eigenstates towards higher energies, or to negative initial state CLS on Pd atoms.

If one now looks at the Ag DOS, one notices (Fig. 2a) that the d -band width increases with decreasing Ag con-

centration. This is so because Ag in a dilute Pd-based alloy is surrounded mostly by Pd. Pd electrons with high energies (in the neighborhood of E_F) induce some new states on Ag due to hybridization effects. As a result of the widening of the Ag d band, its center also shifts towards higher energies, as is clearly seen in Fig. 2a. Note that both the Pd and Ag d bands shift in the same direction. This explains the fact that their initial state CLS have the same sign.

The discussion above establishes a relationship between the hybridization effects in the valence band and the shifts of the core one-electron eigenstates, or the initial state CLS. However, as was discussed earlier, the CLS calculated within the complete screening picture is much closer to experiment than those obtained by the model of initial state, especially for the Pd atoms. By examining the trend of the density of states in Fig. 2, one recognizes that for the final state effects the DOS at the Fermi level plays an important role. As was pointed out in Refs. [1,9,19], the orbital character of the screening charge plays an important role in the efficiency of the screening, and it determines the magnitude of the final state effects. Thus, one can expect a smaller effect due to the core-hole relaxation if the screening charge is of the same character in the metal and in the alloy, and vice versa if the screening in the pure metal and in the alloy originates from electrons with different orbital quantum numbers.

For pure Pd the DOS just above E_F is mainly determined by d electrons, while for a Pd impurity in a Ag host a virtual bound state is formed, and the amount of d electrons at the Fermi energy decreases. The screening charge in the alloy has more sp character, and the final state effects are very large. Note that the final state contribution is almost constant in the concentration interval $0 < c_{Pd} < 50\%$, and then substantially decreases. At about 50% of Pd, the electron topological transition takes place, and the d band crosses the Fermi level around point X of the fcc Brillouin zone [20]. For alloys with higher Pd concentrations the screening becomes closer to that of pure Pd metal, and the contribution of the final state effects to the CLS decreases.

The opposite situation holds for the Ag atoms. In pure Ag the d band is well below the Fermi energy, and the screening charge is of sp character. When Ag is alloyed with Pd, the situation does not change substantially, the DOS above the Fermi energy is of sp character, and the core-hole relaxation contribution is small. With increasing Pd concentration, some d states close to the Fermi energy are induced on Ag sites, and in dilute Pd-based alloys the contribution due to final state effects increases, as can be clearly seen from Fig. 1(b).

In conclusion we have carried out first-principles calculations of the core-level binding energy shift for $3d_{5/2}$ electrons of Ag and Pd in fcc Ag-Pd alloy over the whole interval of concentrations within the complete screening picture. We show that the behavior of the initial state shift

can be understood in terms of hybridization between valence electron states of Ag and Pd that induces a shift of the on-site electrostatic potential without intrasite charge transfer. The final state effects give a large contribution to the CLS, which is especially pronounced for Pd atoms. This effect is related to the character of the valence electrons that participate in the screening of a core hole.

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