

Electronic structure information of metals and alloys from auger and photoemission

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Abstract

We report some of the results of extensive experimental and theoretical studies by our group of the XPS and Auger spectra of the transition and noble metals and some of their alloys: we concentrate on those aspects of the spectra which regard the determination of electronic structure. Consideration of the Auger kinetic energies yields insight into screening mechanisms and suggests methods for extracting electronic structure changes in alloys from XPS and XAES shifts. We demonstrate that the charge transfer in a number of alloys (AuPd, CuPd, AgPd, AuCu, AgAu and CuNi) appears to be negligible (i.e., on the order of hundredths of electrons/atom). Examples (i.e., AuZn, AuMg, AuPd, AgPd and CuNi) of the results for the d- and sp-electron occupations are given.

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1. Introduction

In heterogeneous catalysis, information regarding the electronic structure of the catalyst, often in the form of a metallic alloy, is of fundamental importance in order to facilitate correlation of the reaction and catalyst characteristics. X-ray photoelectron spectroscopy (XPS) is one of the most commonly used experimental techniques in the field for characterization: the spectral peak energy positions permit chemical identification and the spectral peak intensities allow composition determination. It has long been recognized that another feature of the XPS spectra, the chemical shift of the peak energy, reflects the chemical environment of the corresponding atom. Nevertheless, extraction of quantitative electronic structure information from the shifts is hardly a routine procedure.

Although random metallic alloys, of great importance in catalysis, represent one of the simplest situations beyond that of perfect crystals, the problem of determining their electronic structure presents difficult challenges for electronic structure theory. Nevertheless, we shall show here that that

it is indeed possible to extract electronic structure of random alloys from the chemical shifts.

More specifically, in this paper, we review work by our group at Unicamp [1–3] on the use of shifts from XPS and X-ray excited Auger electron spectroscopy (XAES) to determine electronic structure changes in solid solution metallic alloys. In order to orient this discussion, we first describe the physical processes underlying the spectroscopies, as well as the essential features involved in achieving the objective of electronic structure determination. Since we have reviewed aspects of the physics of the photoemission and Auger recombination processes, especially in metals and alloys, and their experimental manifestations as well the complete screening model [4–7], we concentrate here on some results of the electronic structure determinations.

We present, in Fig. 1, a schematic representation of the photoemission process and of different types of Auger transitions. The one-electron energy spectrum of the sample is separated into discrete, spatially localized, core levels such as i, j, k or c with positive binding energy, B , with respect to the Fermi energy, E_F , and spatially delocalized valence bands, VB, represented by hatched boxes (valence band states are denoted v and V). We should note that, for both XPS and XAES, the final state contains core holes, which should be taken into

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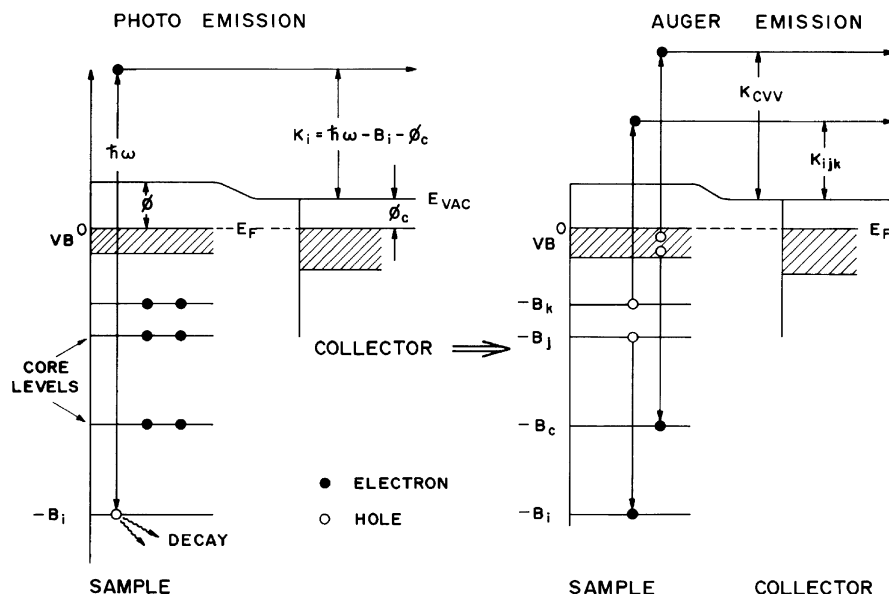


Fig. 1. Schematic illustration of Photoemission and Auger recombination. The quantities K_i and K_{ijk} denote the respective kinetic energies of the emitted photo- and Auger electron with respect to the vacuum level, E_{vac} . ϕ and ϕ_c are the work functions of the sample and the collector, respectively. The levels i , j , k and c are core levels of the sample with positive binding energy, B , with respect to the Fermi energy, E_F . Valence bands, VB, are represented by hatched boxes (valence states are denoted by v and V). In the case of Auger recombination, the cause of initial ionization is not specified, although we treat the case of X-rays of energy $\hbar\omega$. The initial core hole can decay.

account in describing the electronic structure. Since many of the same considerations are applicable to XPS, we shall concentrate on the Auger processes, which are more complicated.

The initial-state of the Auger process is one in which a hole is created in a core level, say i , or c . We assume that this excited state of the sample is produced through excitation by X-rays (XAES). In this discussion, we shall suppose that the measured lineshape resulting from the Auger process itself is independent of the excitation means.

The Auger transition is one in which an electron from a higher level, say j , fills the initial hole. The energy released in this transition is simultaneously transmitted to an electron in another level, say k , which is promoted to a continuum state. The Auger final-state, therefore, has two holes, in the j and k levels. The transition is denominated by the levels involved (usually in X-ray notation): when all three levels are core states the process is called an ijk transition, when one of the final holes is in the VB, it is an ijv transition and when both final holes are in the VB, it is an cvv transition (in Fig. 1, we depict ijk and cvv processes).

The Auger kinetic energy of, for example, the ijk process which we denote as K_{ijk} , is measured relative to the vacuum level near the collector. Since the sample and collector are in thermal equilibrium, we can derive ε_{ijk} , the Auger kinetic energy with respect to the Fermi energy. From energy conservation in a simple one-electron picture,

$$\varepsilon_{ijk} = K_{ijk} + \phi_c = B_i - B_j - B_k, \quad (1)$$

where ϕ_c is the work function of the collector. Because of the spatially localized nature of the core wave functions, the

core level shifts measure essentially the electrostatic potential energy at the position of the nucleus [8] so that all core level binding energy shifts with respect to the pure metal, ΔB , are equal. Consequently, the Auger energy shift is, in fact, a binding energy shift [4], as in Eq. (2),

$$\Delta\varepsilon_{ijk} = -\Delta B_k \quad (2)$$

One aspect of Fig. 1 deserves additional comment: the k electron feels the effect of the hole in the j state: that is, the final-state holes are correlated. Consequently, Eq. (1) is not really correct and we should write instead, for the experimental ε_{ijk} ,

$$\varepsilon_{ijk} = K_{ijk} + \phi_c = B_i - B_j - B_k^{(j)}, \quad (3)$$

$$\Delta\varepsilon_{ijk} = -\Delta B_k^{(j)}, \quad (4)$$

where $B_k^{(j)}$ is the binding energy of an electron in state k in the presence of a hole in state j [9].

Since we are considering binary alloys, in general, it is clear, from the outset, that we must determine the d- and sp-electron occupation changes of both alloy components; the charge transfer of each component is the sum of these d- and sp- changes (charge neutrality imposes another condition relating the charge transfers of the two components). In other words, we must determine five unknown quantities: the occupation changes and the Fermi energy in the alloy relative to that in the pure metal for each component (since the XPS and XAES shifts are defined with respect to the Fermi energy). Consequently, it is necessary to measure both the XPS and XAES shifts if we are to have any hope of extracting the electronic structure changes. A further point to make is that

Eq. (4) is valid only for core level transitions. Auger transitions involving spatially delocalized states, such as valence states, can have shifts which reflect the valence band density of states and which are not equal to the electrostatic potential energy at the atom's nucleus [10,11].

Eqs. (3) and (4) reflect the effect of correlation of the final state holes on the Auger kinetic energy. Correlation effects should be largest for holes in localized states: two holes localized in the same volume should display larger effects than two delocalized holes. Localization of the valence orbitals is not the whole story, however. Cini [12] and Sawatzky [13] have presented theories which determine that it is the competition between the effective Coulomb interaction between the final state holes, or Auger parameter, ξ [14], and the valence band width that determines the form of the iVV Auger spectrum. When the former is much larger than the latter, the spectrum is quasi-atomic in form; when the opposite situation holds, the spectrum is band-like. The question, therefore, is why is the Auger parameter so large in Cu that the LVV spectrum is atomic-like and so small in Ni that its spectrum is so different (the Ni LVV is strongly influenced by the valence band but deviates from purely band-like behavior [15] and has been interpreted as 'quasi-atomic') despite the similar degree of localization of the d-orbitals? The answer to the question involves the nature of the screening of the core hole by valence electrons [4,5].

A wide variety of XPS and XAES phenomena [9,15–17] have been interpreted successfully in terms of the complete screening model of the core hole [8]. In this model, the electronic valence band properties of a metal, such as the local density of states, correspond to the completely relaxed "ground state" of the core hole-metal system [8]. In its most usually applied form, the quasi-atomic model (QAM), the screening charge distribution resembles that of an additional atomic valence electron and the metal behaves as a structureless source of screening electrons. Usually, the core hole is treated as an extra proton and the valence electron is considered as being self-consistently added to a $z+1$ impurity in a metal with atomic number z [9,16–19]. In Fig. 2, we illustrate schematically the application of the QAM to a metal like Ni.

In order to illustrate the success of the QAM, we describe one application of the QAM: the determination of the nature of the screening of core and valence holes from the behavior of ξ in the 3d [9,20], 4d [20–22] and 5d [20,23,24] series. In all three series, ξ increases monotonically with increasing z (in the transition metal region) until it jumps between the corresponding members of the Pt and noble metal groups, after which (in the sp-metal region) it increases linearly. The jump is attributed in the QAM to the change from d- to s-electron screening. In open d-shell transition metals, the screening electrons reduce ξ because they go into d-states (which are effective because of the localized character of their orbitals); in the closed d-shell metals, only the much more delocalized s-orbitals are available for the screening electrons, so that ξ is reduced much less.

Application of the QAM ideas quantitatively [20–23] involves calculation of the binding energies in Eqs. (1) and (3) by utilizing the density functional formalism [25,26]. As a consequence, the Auger parameter can be written as the sum of a term involving only core electron wave functions, which is linear in z , and a valence electron term independent of i , j and k , which contains the screening contributions [20–23]. We can remove the core dependence and isolate the valence part of the experimental data. therefore, by subtracting from the experimental data the linear dependence of the Auger parameter measured in the sp-metal region [20–23]. From its definition, the resulting quantity represents the difference in screening from that of the sp-metals and reflects the greater screening effectiveness of the d-electrons with respect to the sp-electrons. The similarity among the data of all three series is striking, indicating the strong similarity of the screening mechanisms in all three series [21,22]. Another important observation is that the d-band holes appear to behave like core holes in relation to the screening [21,22].

It is possible to formulate a simple model that incorporates the two basic, interrelated, physical mechanisms of the QAM [20,21]: (i) the core hole modifies the local density of states by changing the valence electron wave functions and by pulling initially unoccupied states below the Fermi energy and (ii) it also attracts screening electrons to these states. The only parameters in the model are the difference in d- and s-electron effective Coulomb integrals, $U_{ds}(z) \equiv U_d(z) - U_s(z)$, assumed to vary linearly, and p_{nob} , the number of d-band holes in the ground state of the corresponding noble metal. For the 5d metals, we took these quantities from the literature [27]. For the 4d $L_3M_{4,5}M_{4,5}$ transitions, we derived the parameters from the data, permitting extraction of $U_{ds}(z) = 4.69 - 0.445(z-47)$ (in eV) and $p_{nob} = 0.1$ [20,21], which is consistent with literature findings [28,29]. The agreement between the model results and the experimental measurements is very good [20–23].

In this Introduction, we have described the physical processes controlling the measured spectroscopic XPS and XAES energies and the complete screening model, which describes these processes well. In Section 2, we discuss determination of the relative Fermi energies in alloys, a fundamental component of the shifts in Eq. (4), and, in Section 3, we report results for the d- and sp-electron occupation changes induced by alloying. In Section 4, we present our conclusions.

2. Relative fermi energies

The complete screening model can be applied to the determination of the relative Fermi energy in a number of alloys containing noble metal components from the Auger kinetic shifts of the noble metal atoms [1–5,30–32]. Even though the derivation is somewhat elaborate [30], we present a simplified explanation and rely on the literature for more details [1–5,30–32].

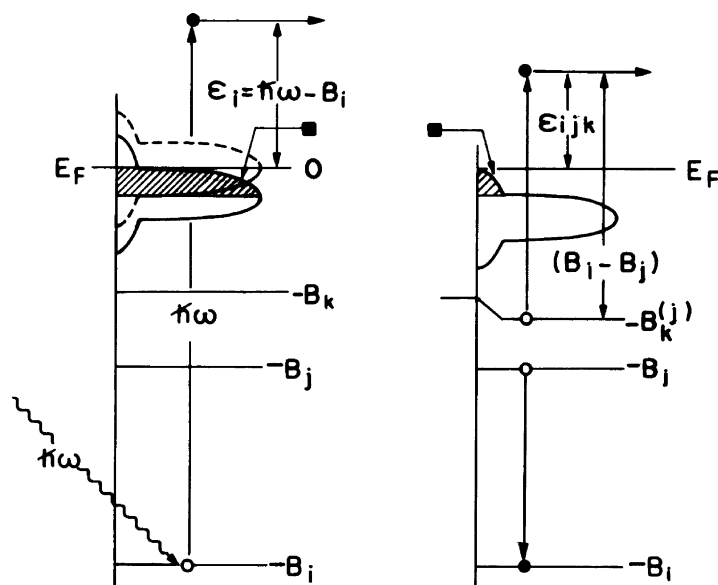


Fig. 2. Schematic application for a metal like Ni of the quasi-atomic screening model to an ijk process. During initial ionization, the core hole resembles an extra proton and the local valence band density of states changes from that of Ni to one resembling that of a Cu impurity, with an additional d-screening electron (full square) added. During Auger emission, the extra core hole makes the local VBDOS that of Zn (full d-band) and increases $B_k^{(j)}$, the binding energy of the emitted electron.

Consider two binary alloys containing low concentrations of Ag, such as Pd–Ag and Ag–Au, as in Table 1. Measurements of the shifts of the kinetic energies of the Ag core level Auger lines in these alloys (relative to that in pure Ag) from the second column of Table 1 indicate that the difference in the shifts (0.6 eV for Pd–Ag and 0.0 eV for Au–Ag), as in the third column, is equal (within experimental error of 0.15 eV) to the measured shift of the core level Auger line of Au in a Pd–Au alloy which is dilute in Au (0.7 eV), from the first column. The same result is achieved for Pd–Cu and Au–Cu alloys which are dilute in Cu (0.4 and –0.3 eV, respectively). In other words, the measured shifts behave as though they were mathematically transitive (i.e., $(A-\underline{B})-(\underline{B}-C) = (A-C)$ independent of \underline{B}).

From the complete screening model [1–5,30–32], such a result would be possible only if the charge transferred to the dilute noble metal component in the alloy were zero (within

0.01–0.02 electrons/atom). Concomitantly, the noble metal, say Ag, Auger shift would equal the negative of the relative Fermi energy, or, the difference between the Fermi energy in pure Ag and that in the alloy: note that the relative Fermi energy is not directly measurable, since it is a purely bulk quantity [4]. This result should be valid for all the alloys involved: Pd–Ag, Pd–Cu, Pd–Au, Au–Cu, and Ag–Au, all of which are solid solutions, as indicated in Table 1. Since one expects the charge transfer to be largest for a dilute alloy, the result could be extended to the whole concentration range.

That such a fundamental conclusion derived from such simple reasoning might be true is intriguing. Its first independent verification [30] is in the excellent agreement between theoretical results for the relative Fermi energy [33] and the shift of the measured Cu core level Auger energy in Pd–Cu. Another verification of the validity of the conclusion is in noting that, in a trimetallic alloy with two different noble metal components, the difference between their Auger shifts should be a constant (equal to the difference between the Fermi energies of the two pure noble metals), independent of the composition of the alloy, since the Fermi energy of the trimetallic alloy should cancel out of the shift difference. Measurements of the trimetallic alloys PdAuCu and PdAuAg [32] are consistent with this prediction.

These results suggest a method for determining the relative Fermi energy of an arbitrary metallic sample [4]: introduce low concentrations of two noble metal atoms in the sample and measure their Auger shifts. If the shift difference equals that between the pure noble metals, then it is consistent to

Table 1
Comparison of dilute binary alloy Auger shifts and the shift differences

BA	$\Delta\varepsilon(A)$	Pd–Au	Pd–Cu	Pd–Ag
<i>PdCu</i>	0.4	Cu 0.7	Au 0.5	Au 0.7
<i>AuCu</i>	–0.3	Ag 0.6		
<i>PdAu</i>	0.7			
<i>CuAu</i>	0.2			
<i>AgAu</i>	0.0			
<i>PdAg</i>	0.6			
<i>AuAg</i>	0.0			

The second column presents the Auger shifts of the dilute italicized component. The other columns represent the result of subtracting the shifts of the italicized component in two different alloys from the second column. For example, the second row of the third column corresponds to PdCu–AuCu.

conclude that each shift is equal to the negative of the Fermi energy of the matrix relative to that of the corresponding pure noble metal.

3. Electron occupation changes in alloys

Determination of the redistribution of valence d- and sp-electrons upon formation of the alloy requires measuring both XPS and XAES shifts. Expressions for the two XPS and two XAES shifts [1,3,20] involve five unknowns: the relative Fermi energy, and the d- and sp-electron occupation number changes of the two components. In addition, in the alloys containing noble metal components which we have considered, the reasoning in the previous section yields the relative Fermi energy, as well as the charge transfer, which relates the d- and sp-occupation changes of each component. Consequently, the occupation changes should be over determined if our reasoning is correct: in other words, the relative Fermi energy derived from the Auger shift of the noble metal component, applied to the expressions for the XPS and XAES shifts of the other component, should yield d- and sp-occupation changes of the other component that are consistent with the charge transfer derived from the noble metal Auger shifts. Such a procedure was applied to Pd–Au alloys [3,31] and the results do seem to be internally consistent. Improved calculations of the XPS and XAES shifts [2,3], incorporating the possibility of the change from d- to sp-screening between the initial- and final-spectroscopic states, do not change the preceding conclusions.

Two important additional developments might have an important impact on the fabric of reasoning underlying these results. The first of these is the derivation of site dependent extra-atomic charge induced on the neighbors in a random alloy through the correlated site model [34,35] and the other is the demonstration that induced valence charge modifies the atomic potential parameters significantly [36,37]. Analysis of these developments [1] indicates that the extra-atomic charge is easily accounted for and does not invalidate the reasoning leading to the derivation of the relative Fermi energy from the noble metal Auger shift; theoretical results [34,35] for the charge transfer are in fair agreement with our value of 0.01–0.02 electrons/atom derived above for the alloys considered. The second development is more serious in that it changes the expressions for the shifts [1] and introduces terms proportional to the average of the square of the appropriate occupation number, a term that is difficult to evaluate. These additional terms appear to be most important for the Auger shifts of Pd group metals and the XPS shifts of noble metals. In particular, they do not appear to invalidate the relationship between the relative Fermi energy and the noble metal Auger kinetic energy shift described above.

In Tables 2 through 7, we present examples of results for some solid solution alloys. Table 2 compares results of our analysis [3] of Au shifts in 50% AuZn and AuMg with those of Thomas and Weightman [27]. Although the magni-

Table 2
The change of Au d-occupation number in 50% Au–Zn and Au–Mg alloys

	This work	Ref. [27]
Au–Zn	$-0.08 \leq \delta n_d^{\text{Au}} \leq -0.04$	$0.00 \leq \delta n_d^{\text{Au}} \leq 0.01$
Au–Mg	$+0.07 \leq \delta n_d^{\text{Au}} \leq +0.15$	$+0.03 \leq \delta n_d^{\text{Au}} \leq +0.07$

Table 3
Pd occupation changes in $\text{Au}_{1-x}\text{Pd}_x$ alloys [3,21].

x	ΔB^{Pd} (eV)	ΔK^{Pd} (eV)	ΔE_F^{Pd} (eV)	δn_d^{Pd}	δ^{Pd}
0.25	–0.4	–0.34	0.7	+0.20	+0.03
0.50	–0.1	–0.2	0.1	+0.1	–0.02
0.75	–0.1	–0.15	0.0	+0.1	–0.02

The quantity δ represents the charge transferred to the Pd atom and δn_d denotes the d-electron occupation change. The calculations include site correlation [1] and assume 1.2 holes in the Pd ground state d-band.

Table 4
Au occupation changes in $\text{Au}_{1-x}\text{Pd}_x$ alloys [3,21]

x	ΔB^{Au} (eV)	ΔE_F^{Au} (eV)	δn_d^{Au}	δ^{Au}
0.75	–0.5	–0.7	–0.1	± 0.01
0.50	–0.4	–0.6	–0.1	± 0.01
0.25	–0.2	–0.1	+0.1	± 0.01

The quantity δ represents the charge transferred to the Au atom and δn_d denotes the d-electron occupation change. The calculations include site correlation [1] and assume 0.4 holes in the Au ground state d-band.

tudes of all occupation changes are small in Table 2, the results are considerably different because of the different treatments of screening.

In Tables 3 and 4, we exhibit the occupation number changes of Pd and Au, respectively, in AuPd alloys [3,21]: these results, as do the others we present, include site correlation [1], which changes the results little [3]. We should note that the value for the Pd charge transfer, δ , was derived from the shift data and is consistent (i.e., on the order of hundredths of electrons/atom) with that derived for Au from the transitivity relation discussed in Section 2. We should also observe that the sign of the Au d-occupation change, δn_d , changes in going from dilute to high concentrations of Au.

Table 5
Pd occupation changes in $\text{Pd}_{1-x}\text{Ag}_x$ alloys [1,3,38]

x	ΔB^{Pd} (eV)	ΔK^{Pd} (eV)	ΔE_F^{Pd} (eV)	δn_d^{Pd}	δ^{Pd}
0.05	± 0.1	–1.05	0.0	+0.2	–0.01
0.50	± 0.1	–0.5	0.46	+0.1	+0.03

The quantity δ represents the charge transferred to the Pd atom and denotes the d-electron occupation change. The calculations include site correlation [1] and assume 1.2 holes in the Pd ground state d-band.

Table 6
Ag occupation changes in $\text{Pd}_{1-x}\text{Ag}_x$ alloys [1,3,38]

x	ΔB^{Ag} (eV)	ΔE_F^{Ag} (eV)	δn_d^{Ag}	δ^{Ag}
0.05	–0.59	–0.79	–0.1	± 0.01
0.50	–0.50	–0.33	+0.2	± 0.01

The quantity δ represents the charge transferred to the Ag atom and δn_d denotes the d-electron occupation change. The calculations include site correlation [1] and assume 0.3 holes in the Ag ground state d-band.

Table 7
Cu occupation changes in Ni_{1-x}Cu_x alloys [1,3,38]

x	ΔB^{Cu} (eV)	$\Delta E_{\text{F}}^{\text{Cu}}$ (eV)	$\delta n_{\text{d}}^{\text{Au}}$	δ^{Cu}
0.10	-0.20	-0.3	-0.03	± 0.01

The quantity δ represents the charge transferred to the Cu atom and δn_{d} denotes the d-electron occupation change. The calculations include site correlation [1] and assume 0.7 holes in the Ag ground state d-band.

In Tables 5 and 6, we exhibit the occupation number changes of Pd and Ag, respectively, in AgPd alloys [1,3,38]. As in the case of AuPd, we should observe that the Pd charge transfer calculated from the XPS and XAES shifts are consistent with those from the noble metal shifts. It is clear that δn_{d} of Ag also changes sign as we vary the concentration [38].

Finally, in Table 7, we report the results for NiCu [38]. The Cu atom's electronic structure changes little upon alloying. In this case, the results are less reliable because the inaccessibility of the Ni core level XAES shifts: that is, the abovementioned consistency cannot be established. Nevertheless, we can calculate δn_{d} of Ni from the XPS shift: for a 10% Cu alloy, $\delta n_{\text{d}} \leq 0.1$ electrons/atom.

We feel that, at the present time, we can estimate only the orders of the charge transfer (hundredths of electrons/atom) and of the occupation number changes (tenths of electrons/atom) in these solid solution alloys. More accuracy than this does not seem justified because of the intrinsic experimental errors.

4. Conclusions

In this paper, we have briefly reviewed work on the determination of electronic structure changes in alloys by our group at Unicamp.

We discuss the extent to which the complete screening model can be used to extract electronic structure information from XPS and XAES energy data. Analysis of Auger parameter data reveals general systematics of screening and permits extraction of physically relevant parameters. Consideration of Auger kinetic energy shifts shows to what extent these shifts can be used to determine the relative Fermi energy in alloys containing noble metal components, as well the changes of d- and sp-occupations of the components. In the solid solution alloys considered (i.e., Pd–Au, Pd–Cu, Pd–Ag, Ag–Au, Ag–Cu, and CuNi), it seems that we can estimate the charge transfer to be on the order of 0.01–0.02 electrons/atom and the occupation changes to be on the order of tenths of electrons/atom.

We should emphasize, in a journal devoted to catalysis, that both XPS and XAES shifts of both components of an alloy should be measured when we consider determination of electronic structure changes, and the XAES spectra should involve only core levels. In addition, when the complete screening model is applicable, the XAES spectra of dilute noble metal components in alloy matrices without noble metals can be used to immediately give insight into the existence of size-

able charge transfer. In those cases when the charge transfer is negligible, XPS and XAES shifts of the majority components should yield information regarding rearrangement of the d- and sp-occupations.

Acknowledgments

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References

- [1] G.G. Kleiman, R. Landers, J. Electron. Spectrosc. Relat. Phenom. 88–91 (1998) 435.
- [2] G.G. Kleiman, R. Landers, S.G.C. de Castro, J. Electron. Spectrosc. Relat. Phenom. 72 (1995) 199.
- [3] G.G. Kleiman, R. Landers, J. Electron. Spectrosc. Relat. Phenom. 76 (1995) 319.
- [4] G.G. Kleiman, 11/12, Appl. Surf. Sci. (1982) 730.
- [5] George G. Kleiman, Phys. Status Solidi B 192 (1995) 503.
- [6] G.G. Kleiman, J. Electron. Spectrosc. Relat. Phenom. 100 (1999) 17.
- [7] G.G. Kleiman, J. Electron. Spectrosc. Relat. Phenom. 127 (2002) 53.
- [8] N.D. Lang, A.R. Williams, Phys. Rev. B 16 (1977) 2408.
- [9] N.D. Lang, A.R. Williams, Phys. Rev. B 20 (1979) 1369.
- [10] G.G. Kleiman, R. Landers, S.G.C. de Castro, P.A.P. Nascente, Phys. Rev. B 45 (1992) 13899.
- [11] G.G. Kleiman, R. Landers, S.G.C. de Castro, P.A.P. Nascente, Surf. Sci. 287/288 (1993) 794.
- [12] M. Cini, Solid State Commun. 24 (1977) 681; M. Cini, Phys. Rev. B 17 (1978) 2486.
- [13] G.A. Sawatzky, Phys. Rev. Lett. 39 (1977) 504.
- [14] The effect of correlation on ε_{ijk} is conveniently represented by ξ , the effective Coulomb interaction or Auger parameter, which is expressed as the difference between the uncorrelated expression in Eq. (1) (i.e., $B_i - B_j - B_k$) and the experimentally measured ε_{ijk} (see Ref. [9]).
- [15] N. Mårtensson, B. Johansson, Phys. Rev. Lett. 45 (1980) 482.
- [16] N. Mårtensson, P. Hedegard, B. Johansson, Phys. Scripta 29 (1987) 154.
- [17] N. Mårtensson, R. Nyholm, B. Johansson, Phys. Rev. Lett. 45 (1980) 754.
- [18] B. Johansson, N. Mårtensson, Phys. Rev. B 21 (1980) 4427.
- [19] A.R. Williams, N.D. Lang, Phys. Rev. Lett. 40 (1978) 954.
- [20] G.G. Kleiman, R. Landers, P.A.P. Nascente, S.G.C. de Castro, Phys. Rev. B 46 (1992) 4405.
- [21] G.G. Kleiman, R. Landers, S.G.C. de Castro, P.A.P. Nascente, Phys. Rev. B 44 (1991) 3383.
- [22] G.G. Kleiman, R. Landers, S.G.C. de Castro, P.A.P. Nascente, J. Vac. Sci. and Technol. A 10 (1992) 2839.
- [23] G.G. Kleiman, S.G.C. de Castro, J.D. Rogers, V.S. Sundaram, Solid State Commun. 43 (1982) 257.
- [24] J.D. Rogers, V.S. Sundaram, G.G. Kleiman, S.G.C. de Castro, R.A. Douglas, A.C. Peterlevitz, J. Phys. F 12 (1982) 2097.
- [25] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864.
- [26] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A113.
- [27] T.D. Thomas, P. Weightman, Phys. Rev. B 33 (1986) 5406.
- [28] C.D. Gelatt Jr., H. Ehrenreich, Phys. Rev. B 10 (1974) 398.
- [29] F.M. Mueller, Phys. Rev. 153 (1967) 659.
- [30] G.G. Kleiman, R. Landers, S.G.C. de Castro, J.D. Rogers, Phys. Rev. B 44 (1991) 8529.

- [31] P.A.P. Nascente, S.G.C. de Castro, R. Landers, G.G. Kleiman, *Phys. Rev. B* 43 (1991) 4659.
- [32] R. Landers, S.G.C. de Castro, G.G. Kleiman, *J. Electron. Spectrosc. Relat. Phenom.* 68 (1994) 145.
- [33] H. Winter, P.J. Durham, W.M. Temmerman, G.M. Stocks, *Phys. Rev. B* 33 (1986) 2370.
- [34] R. Magri, S.H. Wei, A. Zunger, *Phys. Rev. B* 42 (1990) 11388.
- [35] D.D. Johnson, F.J. Pinski, *Phys. Rev. B* 48 (1993) 11553.
- [36] R.J. Cole, D.A.C. Gregory, P. Weightman, *Phys. Rev. B* 49 (1994) 5657.
- [37] R.J. Cole, J.A.D. Matthew, P. Weightman, *J. Electron. Spectrosc. Relat. Phenom.* 72 (1995) 255.
- [38] P.F. Barbieri, A. de Siervo, M.F. Carazzolle, R. Landers, G.G. Kleiman, *J. Electron. Spectrosc. Relat. Phenom.* 135 (2004) 113.