Core level broadening at the surfaces of disordered systems

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Abstract

The “disorder broadening” of core level binding energies in disordered metallic alloys is considered. The origin and magnitude of the effect in bulk alloys is discussed, with particular reference to an intuitive charge model that emphasizes the underlying physics. The model is also used to simulate the core level photoelectron spectra derived from the surface region of various disordered systems.

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1. Introduction

It is well known that the binding energies of core electrons in atoms exhibit shifts according to local chemical environment. In molecules and compounds the magnitude of such shifts may be several eV [1–4] but is typically an order of magnitude smaller in metallic alloys [5]. In disordered alloys many distinct environments are present simultaneously, implying a broadening of their core photoelectron spectra. Surprisingly, “core disorder broadening” (CDB) was only identified relatively recently [6] in the experimental core photoelectron spectra of Cu$_x$Pd$_{1-x}$ alloys, but subsequent studies have shown the effect to be quite general [6–11], typically having magnitude of a few tenths of an eV.

In the present work we briefly discuss the description of the CDB effect by means of a simple physical model [12–14]. After a brief summary of recent results for bulk-sensitive core level spectroscopy, near-surface effects such as surface segregation are considered.

2. Core disorder broadening in bulk alloys

2.1. The electrostatic potential model

The earliest attempts to describe systematically the observed core level shifts in molecules and solids [1,2] used an electrostatic model of the form:

$$V^i = \frac{Q^i}{r^i} + \sum_{j \neq i} \frac{Q^j}{r_{ij}}$$  \hspace{1cm} (1)

where the first and second terms on the right-hand side are the intra-atomic, $V^i_a$, and Madelung, $V^i_M$, contributions to the total potential, $V^i$. $r_{ij}$ is the distance between sites $i$ and $j$ and $r^i$ is the effective radius of atom $i$. For systems where the atoms occupy the sites of an undistorted Bravais lattice, Eq. (1) can be written as a sum over shells:

$$V = \frac{1}{R} \sum_{m=0}^{\infty} \frac{1}{\rho_m} \sum_{j \in m} Q^j$$  \hspace{1cm} (2)

where $R$ is the nearest neighbor distance and $\rho_m$ is the radius of shell $m$ (in units of $R$). The physical picture behind these expressions is of a superposition of spherical charge distributions, the core electrons of each sphere residing well within the valence radius such that their eigenenergies all shift with $V$, as appears to be the case in real systems (to first approximation at least [1,2,4,15]). Although good overall consistency between measured shifts, the “potential model” and electronic structure calculations was achieved for a wide range of molecules and compounds [16], Eqs. (1) and (2) do not appear to be well suited to metallic alloys where charge transfer effects are rather modest and in competition with several other effects [17–20]. We will return to this point a little later.

2.2. The “single site” picture

Various types of disordered systems are illustrated in Fig. 1. While Fig. 1a shows the general case of an amorphous binary alloy, in this work we have in mind crystalline systems, such as those shown in Fig. 1b and c. The latter case, in which the underlying lattice is undistorted, is more amenable to theoretical description, but even this presents a major conceptual challenge since Bloch’s theorem does not pertain. Fig. 1d illustrates a mean field simplification: the disordered alloy is modeled by the combination of a single $A$ atom and a single $B$ atom each embedded in some effective medium whose properties must be determined by some appropriate aver-
Fig. 1. Schematic representation of (a) an amorphous binary alloy, (b) a crystalline alloy with random site occupation by mismatched constituents, and (c) a crystalline alloy with no size mismatch. (d) Illustrates the “single site” picture in which a single atom of each constituent is considered to be embedded in some otherwise periodic effective medium.

aging procedure, such as the “coherent potential approximation” (CPA) [21,22]. This “single site” picture, illustrated in Fig. 1d, can provide no information on the nature or distribution of particular environments.

While in principle one should concede that the site charges appearing in Eq. (2) could vary with local environment, such effects are beyond a strict single site picture, where all A and B sites must have charge $Q_A^{ss}$ and $Q_B^{ss}$, respectively. These charges are subject to the constraint of global electroneutrality: $c_A Q_A^{ss} + c_B Q_B^{ss} = 0$, where $c_A$ and $c_B$ are the concentrations of A and B atoms. Provided sites are occupied randomly by A and B atoms (i.e. with probabilities in accord with the global alloy composition), the average potential at an A site with $N_1$ unlike neighbours in its first neighbour shell is

$$\langle V(N_1) \rangle_A = \frac{Q_A^{ss}}{R} \left( \frac{1}{c_0} - \frac{N_1 - \bar{N}_1}{1 - c_A} \right).$$

(3)

Averaging over $N_1$ causes the Madelung potential to vanish (and hence the Madelung energy is zero), and the average A site potential shift is simply $Q_A^{ss}/c_0$. These results are illustrated in the lower panel of Fig. 2. It is apparent that within the single site picture compositional disorder in the nearest neighbour shell gives rise to considerable CDB (in fact the broadening is much larger than the shift). Underwood et al. [14] have shown that this statistical broadening effect does not diminish with shell radius, leading to a divergent variance in $V$, in defiance of all experimental evidence.

2.3. Charge correlation

The need, when seeking a reasonable description of electrostatics in disordered alloys, to go beyond the single site picture was pointed out some time ago by Magri et al. [12]. These authors noted that if the site charges vary with local environment then, even if the site occupations are random, the charges are correlated [12], giving rise to a non-zero Madelung energy. Magri et al. proposed a simple model in which site charges are linear in the local composition:

$$Q = 2 S_0 \lambda N_1$$

(4)

where $S_0$ is the sign of the charge at the central site (“shell 0”) and $\lambda$ sets the scale of the charges. It has been shown [14] that the resulting site potentials can be expressed:

$$V(N_1, N_2, N_3, \cdots) = \frac{2 \lambda S_0}{R} \sum_{\alpha=0}^{\infty} f_{\alpha} \left[ \bar{N}_\alpha - N_\alpha \right]$$

(5)

where $N_\alpha$ is the number of unlike neighbours in shell $\alpha$ and $f_{\alpha}$ decays rapidly with shell radius such that the CDB is dominated by compositional disorder in the nearest neighbour shell. $\tilde{V}_A$ and $\langle V(N_1) \rangle_A$ for the Magri charge model are illustrated in the upper panel of Fig. 2.

2.4. Ab initio results

Although Eq. (5) determines both the CDB and the chemical shift, comparison with experimental measurements has proved problematic. For example widely differing values of $\lambda$ (0.005 and 0.003) must be assumed to reproduce the measured chemical shift [23] and disorder broadening [6] of Cu50Pd50. The obvious explanation for such observations is that the formalism employed (i.e. Eqs. (1), (2) and (4)) is just too simplistic. In fact the results of ab initio electronic structure calculations performed for unit cells containing hundreds of atoms [24,25] have also revealed surprising simplicity and generality. In particular the extensive calculations (for different chemical species, crystal structures and compositions) by Ruban and Skriver [25] have shown that site charges appear to exhibit a
composition, and assumes the linear charge law proposed in Ref. [12]. A simple cubic lattice, 50/50 composition, and a continuous Gaussian distribution and with a universally linear relation (when \( Q \) and \( V_M \) are suitably normalized) to the corresponding Madelung potentials. To elucidate the origin of these observations, Ruban and Skriver computed the changes in site charges caused by “flipping” the identity of a single atom in an alloy supercell. Their calculations revealed universal and very short range screening of charges in metallic alloys. The Ruban–Skriver universal screening function, \( \phi_m \), defined as the change in site charge normalized to the charge perturbation, is shown by the dotted curve in Fig. 3. In contrast \( \phi_m \) is given by \(-\delta_{m1}/Z_1\) in the Magri model, i.e. charges are perfectly screened in the nearest neighbour shell. It is clear from Fig. 3 that the screening function implied by the Magri model (represented by symbols) is a reasonable approximation. The extent to which the model also reproduces the linear \textit{ab initio} \( Q \sim V_M \) “law” has been discussed several times in the literature [24,26,7,14]. Crudely put, it works surprisingly well, and Underwood et al. have shown recently that a simple multi–shell generalization of Eq. (4) improves its \( Q \sim V_M \) properties further, implying a more realistic screening function in the process [14]. For the present work, this multi-shell generalization can be considered an unnecessary detail.

It was pointed out some time ago [27,25] that the Magri model can be derived from the assumption of universal first neighbour screening. Placing “single site” charges \( Q^A \) and \( Q^B \) at \( A \) and \( B \) sites and distributing counter-charges among the nearest neighbours gives:

\[
Q^i = Q^A_1 \delta^i_A + Q^B_1 \delta^i_B + \frac{1}{Z_1} \sum_{j \in \text{n.n.}} \left[ Q^A_1 \delta^i_j + Q^B_1 \delta^i_j \right].
\]

(6)

It is straightforward to show that this expression has the form of Eq. (4). It is through consideration of metallic screening, rather than a chemical charge transfer argument, that the electrostatic potential model of Eq. (1) finds applicability to metallic systems.

Having reconciled model calculations (Eqs. (1), (2) and (4)) to \textit{ab initio} results, it is disappointing to discover that the CDB calculations from the latter approach do not necessarily give good agreement with experiment [10]. In seeking to resolve this issue, Newton et al. speculated that electronic relaxation following core ionization in the photoemission experiment could also be sensitive to local environment and that such “final state” disorder broadening could in principle either reinforce or cancel the initial state broadening [10]. This conjecture was substantiated in a landmark paper by Marten et al. [28]. Initial and final state broadenings were found to have comparable magnitude and were seen to reinforce for noble metal sites in \( \text{Cu}_{0.5}\text{Pd}_{0.5} \) and \( \text{Ag}_{0.5}\text{Pd}_{0.5} \) but to cancel for \( \text{Pd} \) sites [28].

Lattice distortion in alloys comprising constituents with significant size mismatch has also been identified as a complication to CDB calculations. \textit{Ab initio} supercell calculations for \( \text{Cu}_{0.5}\text{Ag}_{0.5} \) using both relaxed and unrelaxed lattices have both indicated a CDB effect [11], but lattice distortion reverses the slope of the linear dependence of \( \langle V(N_i) \rangle \) on \( N_i \) [11].

### 3. Surface and near surface effects

Though further systematic bulk studies would be welcome, particularly of the effects of electronic relaxation and lattice distortion, it appears that the CDB effect observed experimentally for bulk alloys is well understood and can be reproduced quantitatively by \textit{ab initio} calculations and qualitatively by model calculations. We now follow the latter approach to investigate CDB effects arising in the near surface region of various systems. Core level XPS spectra are simulated using the expression:

\[
P^0(\omega) = G_{\sigma_E}(\omega) \otimes \sum_{i \in \Gamma} e^{-\ell/d} L_F(\omega - V_i)
\]

(7)

where \( G_{\sigma_E} \) is the Gaussian function with standard deviation \( \sigma_E \), representing instrumental broadening (the experimental resolution corresponding to 2.35\( \sigma_E \)), \( L_F \) is a Lorentzian with full-width at half-maximum \( \Gamma \), representing lifetime broadening, and \( \otimes \) indicates the convolution operator. The exponential term accounts for the biasing of spectral weight towards surface atoms. \( d \) is the effective depth of atom \( i \) from the surface (and therefore the actual depth for detection of photoelectrons emitted perpendicularly from the surface) and \( \ell \) is the photoelectron escape depth.
3.1. Surface region of homogeneous alloys

Provided the occupation of sites in all layers is random, it can be shown that \( \langle V(N_1) \rangle \) is linear in \( N_1 \) but with layer dependent coefficients:

\[
\langle V(N_1) \rangle = \frac{2\lambda}{R} \sum_{0} X^p (1 - c_0) + Y^p N_1
\]

where \( c_0 = c_{B(A)} \) if we are considering \( A(B) \) sites, and we use the convention that the layer labeled by index \( p \) is separated from the vacuum region by \( p \) other layers. \( X^p \) and \( Y^p \) are given by

\[
X^p = \frac{Z_p (T^p - \Sigma^p)}{T_1}
\]

\[
Y^p = \Sigma^p - T^p + \frac{1}{\rho_0}
\]

where

\[
Z^p_{\alpha} = \sum_{q=0}^{\infty} Z^p_{\alpha q}
\]

\[
T^p = \sum_{q=0}^{\infty} Z^p q Z^q_{1}
\]

\[
\Sigma^p = \sum_{q=1}^{\infty} \sum_{q=0}^{\infty} \frac{Z^p_{\alpha q} L^p q q^p}{\rho_0 L^q q^q}
\]

and \( Z^p_{\alpha q} \) is the number of sites in shell \( \alpha \) of a site in layer \( q \) which are in layer \( r \), and \( K^p_{\alpha} \) is the number of shared nearest neighbours between two sites in layers \( q \) and \( r \) separated by distance \( R_{\alpha qr} \).

Values of \( \langle Z^p_{\alpha q} \rangle, T^p, \Sigma^p, X^p \) and \( Y^p \) are given in Table 1 for the (1 0 0) surface of the FCC lattice. It can be seen that \( \langle V(N_1) \rangle \) is bulk-like for \( p \geq 2 \), while the surface and first subsurface layers, \( p = 0 \) and \( 1 \) respectively, have distinct behaviour. A more subtle picture is revealed by the numerical results shown in Fig. 4 where \( V \) vs. \( N_1 \) data are plotted for various (1 0 0) planes of an \( A_{0.5}B_{0.5} \) alloy with an FCC lattice. Here we have chosen \( \lambda \) to be 0.1/12 (giving an average charge of 0.1e), and \( R \) to be 2.89 Å. It can be seen that the numerical results reproduce the analytical results for \( \langle V(N_1) \rangle \) (i.e. when averaging over the compositions of shells beyond the first), but it is interesting to note that the scatter of the site potentials about these averages increases as the surface is approached.

This observation is suggestive of increased disorder broadening when the photoelectron escape depth is short. Core-level XPS spectra simulated using Eq. (7) with \( \sigma_g = 0.12 \text{ eV}, \Gamma = 0.3 \text{ eV} \) are shown in Fig. 5. Although CDB is easily observed in each, there appears to be no discernible difference between the simulated spectra for \( \ell = 10 \text{ Å} \) (black solid curve) and \( \ell \rightarrow \infty \) (black dashed curve). It appears that the CDB effect is dominated by disorder in the nearest neighbour shell, i.e. the parameter \( Y^p \). Indeed, the simulation in Fig. 5 for an ultra-short escape depth of 2.5 Å shows a slightly reduced CDB on account of the shallower \( Y^p \) gradient for the surface and first subsurface layers, which contribute most of the spectral weight in this case. We find that for almost all practical purposes the effect on the core photoelectron spectra due to the modification of site potentials near the surface of homogeneous alloys can be ignored. In effect CDB in the core spectra of such systems is a bulk phenomenon.

Table 1: Structural parameters for the (1 0 0) surface of the FCC lattice. Note that \( \rho_0 \) in Eq. (10) has been set to the plausible valuable of 1/2.

<table>
<thead>
<tr>
<th>( p )</th>
<th>( Z^p_{\alpha q} )</th>
<th>( T^p )</th>
<th>( \Sigma^p )</th>
<th>( X^p )</th>
<th>( Y^p )</th>
</tr>
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<td>0</td>
<td>8</td>
<td>10</td>
<td>6.65</td>
<td>18.82</td>
<td>-1.35</td>
</tr>
<tr>
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<td>12</td>
<td>10.6</td>
<td>7.44</td>
<td>26.76</td>
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</tr>
<tr>
<td>( \geq 2 )</td>
<td>12</td>
<td>12</td>
<td>8.22</td>
<td>33.32</td>
<td>-1.78</td>
</tr>
</tbody>
</table>

![Fig. 4](image_url) (Colour online) V vs. \( N_1 \) for \( A \) sites near a (1 0 0) surface of a disordered \( A_{0.5}B_{0.5} \) alloy. The open circles in the upper and middle panels correspond to calculated potentials for sites in the surface and subsurface layers respectively. In the lower panel the open circles correspond to the \( p = 2 \) layer, the red (dark gray) squares to the \( p = 3 \) layer, and the cyan (light gray) diamonds to results of bulk calculations. In each case the solid lines indicate the corresponding analytic results for \( \langle V(N_1) \rangle \). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

![Fig. 5](image_url) (Colour online) Simulated core level photoelectron spectra from the A sites of a (1 0 0) surface of a disordered \( A_{0.5}B_{0.5} \) alloy with an FCC lattice. The solid black and red (grey) lines represent simulations using Eq. (7) with electron escape depths of \( \ell = 10 \) and 2.5 Å respectively. The black dashed line corresponds to the bulk limit (\( \ell \rightarrow \infty \)). For comparison \( G_{\text{ext}} \otimes I \) is shown by the dotted curve, representing the spectrum of a pure elemental solid. For ease of comparison the binding energies of all spectra have been aligned. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)
is greatly increased by segregation. This effect is less pronounced
version of the article.)

of the references to colour in this figure legend, the reader is referred to the web
ity of a photoelectron escaping from each layer when
all spectra have been aligned. The dashed line in the lower panel gives the probabil-
panel. The solid black and red (grey) lines correspond to species
Fig. 6. (Colour online) Simulated spectra (upper panel) from the (1 0 0) surface of a
disordered FCC $A_xB_{1-x}$ alloy with the concentration profile specified in the lower
layer $A$ and red (grey) lines correspond to species $A$ and $B$ respec-
Dashed and dotted lines are the spectra for a homogeneous alloy and an
panel. The solid black and red (grey) lines correspond to species
3.2. Surface segregation
It is well known that in the vicinity of a surface deviation from
bulk composition is observed in many alloys [29,30]. We now
consider the case of an oscillatory surface profile in which the com-
position of A atoms in layer $p$ is

$$c_A^p = Ce^{-\mu/p} \cos \left( \frac{2\pi p}{\nu} \right) + c_A^\infty.$$  (14)

The parameters $C$, $\mu$ and $\nu$ determine the amplitude, attenuation
length and wavelength of the oscillations respectively, the latter two being measured in units of the interplanar spacing. Simulated
core level photoelectron spectra are shown in Fig. 6 for $C = 0.4$,
$\mu = 2$, $\nu = 5$ and $\ell = 10\AA$. It can be seen that the CDB of species $A$
is greatly increased by segregation. This effect is less pronounced
in species $B$. In both cases however the CDB is larger than for the
homogeneous case.

4. Conclusions
Model calculations predict that systems exhibiting composition
variations with depth from the surface give rise to an exaggerated
core disorder broadening effect which is not present in surface-
sensitive photoelectron spectra of homogeneous alloys. It seems
likely that this effect could explain the anomalously large CDB effect
very recently observed for AgPd surface alloys by Medicherla and
Drube [31]. The results of the calculations reported here confirm
the recent claim by Holmstrom et al. [32] that CDB promises to
be an important tool for the characterization of nanodevices and
the materials and interfaces they comprise. The model approach
employed here offers an efficient framework for exploring the rich
phenomenology of such systems.

References
1969.
Springer, Berlin, 1975 (see, for example).