Probing atomic environments in alloys by electron spectroscopy

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In alloys exhibiting substitutional disorder, the variety of atomic environments manifests itself as a ‘disorder broadening’ in their core level binding energy spectra. Disorder broadening can be measured experimentally, and in principle can be used to deduce information about specific atomic environments within a sample. However, progress in this endeavor is hampered by the lack of a model for this phenomenon which can treat complex systems. In this work we describe such a model, which is simple enough to allow the concentration profile of a system to be deduced from its core level spectrum. We validate the model against detailed electronic structure calculations - which are capable of determining the spectrum for a known concentration profile, but not vice versa. The model is used to elucidate the relationship between charge transfer, atomic environment, and disorder broadening in complex systems, with a focus on the problem of characterizing the interface quality of metallic multilayers. Several counterintuitive aspects of the disorder broadening phenomenon are uncovered, an understanding of which is essential for the correct interpretation of experimental results. For instance, it is shown how in some systems a ‘disorder narrowing’ is possible.

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An atom’s core level binding energies depend on its chemical species. This fact has been exploited for decades in order to determine the proportion of different species within a given sample via core level spectroscopy - which provides the distribution of core electron binding energies within a sample. An atom’s binding energies also depend on its environment, i.e., the species of its surrounding atoms. For instance, in a Cu metal all atoms have the same environment, and hence the binding energies for a given Cu core level will be the same for all atoms. By contrast, in a CuZn alloy exhibiting substitutional disorder the Cu atoms exhibit a variety of environments, and hence also a variety of binding energies. Such a dispersion in the binding energies has been observed in many alloy systems, and in theory can be used to deduce information about specific environments within a sample, including the concentration profile on the atomic scale. The viability of achieving this via high kinetic energy photoelectron spectroscopy (HIKE) has recently been demonstrated. This is promising because HIKE, unlike other widely-used techniques, is both bulk-sensitive and non-destructive. Such environment-resolved spectroscopy would prove useful to the many research areas involving alloys in which segregation plays a crucial role, e.g. metal embrittlement, and nanocatalyst design. However, success in this endeavor hinges upon a solid understanding of the relationship between an atom’s environment, its electronic structure, and its core level binding energies in alloys.

Random alloys - the archetype of disordered alloys in which there are no correlations between the species of sites - are the most tractable system exhibiting substitutional disorder to treat theoretically, and have been the focus of both experimental and theoretical attempts to understand the dispersion phenomenon described above. In this context the phenomenon is known as ‘disorder broadening’ on account of the increase in width of, say, the Cu binding energy distribution for a CuZn random alloy compared to that for a Cu metal. Sophisticated ab initio models have provided insight into disorder broadening in these systems. However, most systems of practical interest cannot be idealized as random alloys, and unfortunately the complexity of these systems is such that an ‘exact’ description of their disorder broadenings using ab initio models is intractable: a less computationally-demanding model is desirable to treat these systems. While such models have been developed, their accuracy has been questioned. One criticism is that these models do not take into account ‘final state effects’ associated with changes in the valence electron density after photoemission. It has even been claimed that the complexity of the relationship between binding energies and environment in alloys precludes an accurate alternative to ab initio methods.

In this letter we present an accurate model which accounts for final state effects. The model, like previous approaches, is charge-transfer based, and provides a simple framework for rationalizing the disorder broadening phenomenon. Furthermore, the model is simple enough that it can be used to deduce a system’s concentration profile from its core level binding energy spectrum. After describing the model, we validate it against the results of ab initio calculations - which are capable of deducing the spectrum from a known concentration profile, but not vice versa. We then use the model to elucidate the relationship between charge transfer, core level binding energies, and atomic environment in alloys. As a testing ground for the model we consider the problem of characterizing the interface quality in metallic multilayers. This problem has received significant attention on account of its importance to nanotechnology, and
Figure 1: (Color online) Schematic illustration of [Ni$_5$/Cu$_5$] at various $\sigma$ (a), and the corresponding model spectra (b). In (b), each red bar corresponds to a different value of $N_{\text{Ni1}}$: the ordinate of the bar is the CLS corresponding to $N_{\text{Ni1}}$ according to Eqn. (5), and its height reflects the frequency of \( \sigma \) face roughening. The bars corresponding to $N_{\text{Ni1}} = 0, 6, 12$ are indicated. The dotted curves in (b) are spectra for $\sigma = 0$.

The CLSs can be restated as follows: what is the degree of ‘interface roughening’ $\sigma$ in a given sample$^{21,22}$. Fig. 1(a) provides an illustration of the multilayer system [Ni$_5$/Cu$_5$] with various $\sigma$ - where the square brackets signify that the system at $\sigma = 0$ consists of a 10 monolayer stack Ni$_5$/Cu$_5$ repeated throughout all space. Some of our results are counterintuitive, and an understanding of them is essential for the correct interpretation of experimental results: we show that inhomogeneous concentration profiles can yield larger disorder broadenings than is possible in random alloys, and that a ‘disorder narrowing’ is possible in some systems.

Our model is based upon the charge-excess functional model$^{22}$ within the non-random approximation$^{21,23}$ (NRA-CEFM), which has been shown to provide an accurate description of charge distributions and configurational energy differences in alloys$^{21,22,31}$. In the NRA-CEFM the alloy energy is postulated to take the form

\[
E = E_0 + \frac{1}{2} a \sum_i (Q_i - b_i)^2 + E_M,
\]

where $E_M$ is the inter-site electrostatic energy, $Q_i$ is the net charge on site $i$, $a$ and $E_0$ are composition-dependent constants$^{22}$ and $b_i$ is a composition-dependent quantity which takes the same value $b_X$ respectively for all sites belonging to species $X$. Minimizing $E$ leads to the following expression for the charge of an $X$ site$^{21}$:

\[
Q_i = \Lambda \sum_Y b_{YX} \sum_{\beta=1}^\infty g_{\beta} N_{Y\beta},
\]

where $N_{Y\beta}$ is the number of $Y$ sites in the $\beta$th nearest neighbor shell of site $i$; $b_{YX} = (b_Y - b_X)$; the quantities $\Lambda$ and $g_{\beta}$ for all $\beta$ are geometrical constants which depend only on $a$ and the underlying lattice$^{22}$, and the summation over $Y$ is over all chemical species. The free parameters $a$ and $b_{YX}$ (for all $X$, $Y$) can be obtained from ab initio calculations or by other means$^{21}$. Note that the quantities $N_{Y\beta}$ for all $\beta$ and $Y$ characterize the environment of $i$. Therefore Eqn. (2) explicitly relates $Q_i$ to the environment of site $i$. The above equation allows us to interpret an alloy’s charge distribution in terms of charge transfer between pairs of unlike sites as follows$^{21}$: an $X$ site gains a charge $\Delta b_{YX} b_{\beta}$ from each $Y$ site in its $\beta$th nearest neighbor shell, with the $Y$ site losing the opposite amount. This picture allows us to attribute the following physical significance to the quantity $b_Y$: it is a measure of the electropositivity of species $Y$ for the given composition.

By appealing to the complete screening picture$^{22}$ - in which final state effects are implicitly accounted for - it can be shown$^{23}$ that the metal-alloy core level shift (CLS) of an $X$ site $i$ within the NRA-CEFM is given by

\[
\Delta E^B_i = -a b_X \cdot Q_i + \Phi_X,
\]

where $\Phi_X$ is a composition-dependent constant, and $X^*$ denotes the chemical species corresponding to a photoionized $X$ site. Hence there is a species- and composition-dependent linear mapping between $Q_i$ and $\Delta E^B_i$. Therefore changes in the $X$ spectrum associated with configuration changes - such as an increase in $\sigma$ - directly reflect changes in the $X$ charge distribution. Furthermore the shape of the spectrum is the same as that of the charge distribution on account of the linear nature of the mapping between $Q_i$ and $\Delta E^B_i$. We will elaborate on these points later.

In Ref. [17] the mean Cu CLS $\langle \Delta E^B \rangle_{\text{Cu}}$ for each monolayer $l$ was calculated ab initio for Ni/Cu/Tr/Ni at various $\sigma$ and $T$. We will now illustrate the accuracy of the model by comparing its predictions for these systems to those of that study. Using Eqs. (2) and (3), expressions can be derived$^{22}$ for $\langle \Delta E^B \rangle_{\text{Cu}}$ and $\Gamma^l_X$ - the mean and full width at half maximum (FWHM) of the $X$ CLS distribution for monolayer $l$ - in terms of the concentration profile. Expressions can also be derived$^{22}$ for $\langle \Delta E^B \rangle_{\text{Ni}}$ and $\Gamma^l_X$ - the ‘total’ mean and FWHM of the $X$ CLS distribution. Using these expressions, we determined $\langle \Delta E^B \rangle_{\text{Cu}}$ and $\langle \Delta E^B \rangle_{\text{Ni}}$ for the Ni/Cu/Tr/Ni systems for various sets of model parameters, and found excellent...
agreement with Ref. [14] when \( a_R W_s \approx 2.6 \) (where \( R_W \) denotes the Wigner-Seitz radius), \( \Phi_{Cu} \approx 0.15 \text{eV} \), and \( b_{Cu-Cu} b_{NiCu} \approx -0.015 \text{eV} \), as is shown in Fig. 2. These values are similar to analogous quantities obtained from \textit{ab initio} calculations for other alloys [14, 21, 24, 33, 37]. However, the ‘exact’ values of these quantities are unknown: they are sensitive to the \textit{ab initio} method used to obtain them. Hence an interesting prospect is to use the model to determine their values experimentally.

The aforementioned expressions relating \( (\Delta E^B)^X \) and \( \Gamma^X \) to the concentration profile of the system under consideration can be implemented within a curve fitting procedure, which can be used to deduce a system’s concentration profile from its \( X \) core level spectrum. Details of this procedure are provided in Ref. [28]. A simpler approach is also possible: using the expressions for \( (\Delta E^B)^X \) and \( \Gamma^X \), one can quickly produce a ‘map’ of these quantities as a function of \( \sigma \) for a given system. Their experimentally determined values for, say, a given temperature can then be compared with this map in order to deduce \( \sigma \) at that temperature. Such maps for a variety of NiCu systems are illustrated in Fig. 3.

In Ref. [38] it was found that, in [Ni5/Cu5], the mean of the Cu CLS spectrum decreases with increasing temperature, and the width increases then decreases. The increases were attributed to an increase in \( \sigma \) with temperature. Fig. (1b) shows spectra simulated using the model for this system at various \( \sigma \). It can be seen from this figure and Fig. 3 that the model reproduces the trends observed experimentally. The model also provides a means of rationalizing these trends. Consider Eqn. (2).

An insightful approximation is to ignore the dependence of \( Q_i \) on environment beyond the nearest neighbor shell, in which case for Cu in NiCu the number of Ni nearest neighbors \( N_i^{Ni1} \) of site \( i \) wholly determines \( Q_i \). Specifically, \( Q_i \) is linear in \( N_i^{Ni1} \):

\[
Q_i \approx A g_1 b_{NiCu} N_i^{Ni1} . \tag{4}
\]

The same then applies to \( \Delta E_i^B \) (from Eqn. (3)):

\[
\Delta E_i^B \approx - a g_1 b_{Cu}\cdot Cu b_{NiCu} N_i^{Ni1} + \Phi_{Cu} . \tag{5}
\]

Using the above expression the Cu spectrum can be decomposed into, or constructed from, components associated with Cu atoms with each value of \( N_i^{Ni1} \). This is done in Fig. (1b), and allows us to equate changes in the Cu spectrum to changes in the system’s \( N_i^{Ni1} \) histogram for Cu. At \( \sigma = 0 \) Cu sites exhibit only two possible environments, \( N_i^{Ni1} = 0 \) or 4, with the former corresponding to the 3 ‘central’ monolayers of the 5 monolayer Cu stack and the latter corresponding to the 2 ‘edge’ monolayers. On the whole Cu sites exhibit higher values of \( N_i^{Ni1} \) as Cu diffuses into the Ni region, leading to a shift in the spectrum to low binding energies as \( \sigma \) increases. The width of the spectrum increases as the \( N_i^{Ni1} \) histogram becomes ‘flat’ near \( \sigma = 1.5 \), and then narrows again as \( \sigma \to \infty \) and the histogram tends to that corresponding to the random
alloy Ni$_{0.5}$Cu$_{0.5}$. Interestingly, the disorder broadening is not maximized at the random alloy configuration - which corresponds to the maximum substitutional disorder. An explanation for this is as follows. The $N_{Ni11}$ histograms for random alloys - substitutionally disordered systems with homogeneous concentration profiles - are binomial distributions. For inhomogeneous concentration profiles, such as those for [Ni$_5$/Cu$_5$] at $\sigma \neq \infty$, the histograms are not constrained to be binomial distributions - they are free to be ‘flatter’. Therefore systems with inhomogeneous concentration profiles can exhibit significantly larger disorder broadenings than random alloys.

The above ideas can be extended to ternary systems consisting of three species $A$, $B$, and $C$, where this time the evolution of the $A$ spectrum reflects the evolution of $A$’s $(N_{iB1}, N_{iC1})$ histogram’. This is illustrated in Fig. 3 for this system, which can be found in Ref. 28, along with an alternative explanation of the narrowing in terms of the evolution of the $(N_{iB1}, N_{iC1})$ histogram for species $A$ with $\sigma$.

In conclusion we have presented an accurate model for core level shifts in alloys, and have used it to add insight into the relationship between atomic environment, charge transfer and disorder broadening in complex systems. While we have focused on photoelectron spectroscopy, the model can be easily adapted to treat other core level spectroscopies, the most prominent of which is Auger electron spectroscopy. The model therefore should find widespread use as a framework in which to interpret experimental results.

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By composition here we mean a specification of the un
number of sites in any site’s
boundary conditions’ beyond the nearest neighbor shell,
third nearest neighbor shell,
for \( \beta > 1 \), where \( Z_\beta \) is the number of sites in any site’s \( \beta \)th nearest neighbor shell, and \( c_{Ni} \) is the global concentration of Ni. This would lead to better agreement between the histograms and model spectra in Fig. 1(b). However, we do not do this here for the sake of simplicity.