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Observation of disorder broadening of core photoelectron spectra of CuZn alloys

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Abstract. The distribution of site potentials in CuZn alloys is investigated using x-ray-excited photoelectron spectroscopy. A small ‘disorder broadening’ of the core-level photoelectron spectra is observed for the alloys. Experimental results are compared with results of model and first-principles calculations.

1. Introduction

The last decade has seen a resurgence of interest in disordered binary alloys, stimulated in part by a reassessment of quite fundamental concepts of electronic structure and bonding. In an attempt to investigate the Madelung energy of random systems, Magri, Wei and Zunger [1] suggested that the excess charge on each A site in an A_xB_{1-x} system is linearly proportional to its number of B neighbours. This model, which is consistent with chemical intuition and is supported by electronic calculations for small ordered cells [2], is referred to here as the ‘correlated charge model’ (CCM) since it follows that, even when lattice sites are randomly occupied by A and B atoms, the site charges will be correlated. Magri *et al* [1] have pointed out that although the CCM gives rise to rather large Madelung energies, such a contribution to the alloy total energy is usually neglected in single-site treatments of disorder. Abrikosov, Vekilov, Korzhavyi, Ruban and Shilkrot [3] and Johnson and Pinski [4] have shown how a Madelung correction can be built into a single-site formalism, but some physical insight is needed to guide the choice of the nature of these corrections. Subsequent improvements in computational power and the development of so-called ‘order- N ’ algorithms have enabled *ab initio* calculations to be performed for quite large (hundreds of atoms) pseudorandom supercells which in principle enable the CCM and predictions based on it to be assessed. Results of such calculations for Cu_xZn_{1-x} alloys have been used both to defend [5] and undermine [6] the CCM.

Core-level x-ray-excited photoelectron spectroscopy (XPS) probes the local potential at lattice sites in a solid and so should be able to provide information on both the conditionally averaged site potentials in a disordered alloy and fluctuations about those averages. Indeed, it has recently been shown that the broadening of core-level spectra of Cu_xPd_{1-x} alloys reveals a distribution of site potentials [7]. It was argued that the observed ‘disorder broadening’ of 0.21 eV (Gaussian FWHM) was consistent with a prediction based on the CCM and point charge electrostatics. *Ab initio* calculations of the core eigenvalues for random binary alloys have subsequently confirmed the existence (and proposed magnitude) of this effect, although results for $Cu_{0.50}Pd_{0.50}$ alloys indicated a broadening of only 0.05 eV [8]. In summary, we can say that

there is active debate rather than an accepted consensus of opinion on the validity and utility of simple models in describing the electrostatics of random alloys. It is clear that theoretical models and the results of calculations must be compared with experimental measurements for more alloy systems. The present paper makes such comparisons for $\text{Cu}_x\text{Zn}_{1-x}$ alloys.

2. Experimental results

Disordered specimens of $\text{Cu}_x\text{Zn}_{1-x}$ alloys in the α -phase (fcc) for $x = 0.90, 0.80$ and 0.70 and in the β -phase (bcc) for $x = 0.52$ were obtained from Metal Crystals and Oxides (Cambridge). The compositions were confirmed by x-ray fluorescence and XPS, and x-ray diffraction (XRF) gave results for the lattice constants of the α -phase alloys in agreement with the variation in lattice constant with composition reported previously [10, 11]. Following *in situ* mechanical cleaning, high-resolution core-level XP spectra were obtained for normal electron emission using a Scienta ESCA 300 spectrometer at the RUSTI facility at the Daresbury Laboratory. The Cu and Zn $2p_{3/2}$ photoelectron spectra for $\text{Cu}_{0.52}\text{Zn}_{0.48}$ and the corresponding elemental metals are shown in figures 1 and 2 respectively. It can be seen that in each case the alloy spectra are slightly broader. To quantify this observation we performed least-squares (LS) fitting of the spectra following a procedure described in detail previously [12] and briefly below.

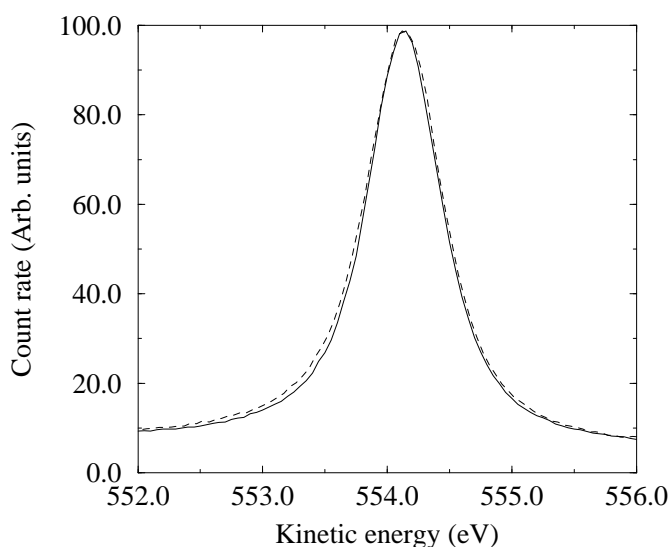


Figure 1. Experimental $\text{Cu } 2p_{3/2}$ photoelectron spectra for Cu (solid curve) and $\text{Cu}_{0.52}\text{Zn}_{0.48}$ (dashed curve). The spectra have been normalized according to peak height. In each case the photoelectron peaks have been aligned in kinetic energy.

We first performed an LS fit of the $2p_{3/2}$ spectrum of pure Cu using bulk and surface Doniac–Sunjic components $f^{\Gamma\alpha}$ where Γ and α are the usual lifetime and asymmetry parameters. The surface component was shifted to higher kinetic energy by an amount E_s relative to the bulk line and was given a weight $I_s = 0.12$, the value determined in an earlier and more surface-sensitive study [14]. The simulated lineshape was broadened by a Gaussian of FWHM W . Allowing E_s, Γ, W, α to vary freely, we obtained $\chi^2 = 0.55$ and the results shown in table 1. The fit quality as revealed by the residuals was found to be good. E_s, Γ and α were consistent with the previous results [7, 14] and the value of $W = 0.265 \pm 0.008$ eV was in excellent agreement with the broadening observed at the Fermi edge. Keeping I_s, Γ and W at their pure-Cu values, we then attempted to fit the experimental $\text{Cu } 2p_{3/2}$ spectrum of the

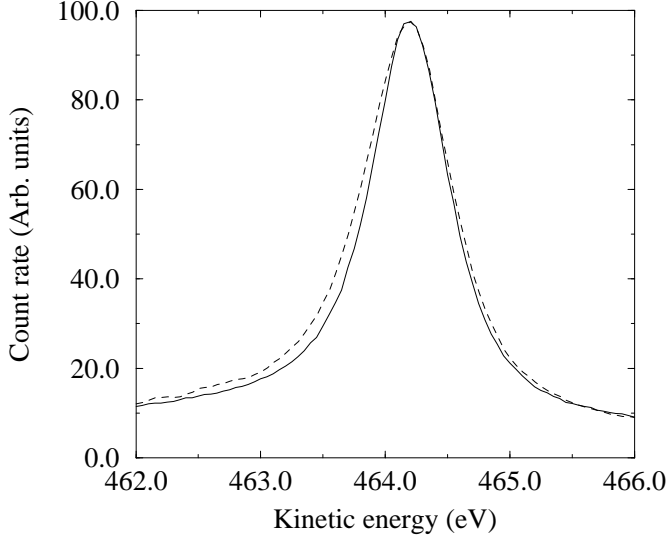


Figure 2. Experimental Zn $2p_{3/2}$ photoelectron spectra for Zn (solid curve) and $\text{Cu}_{0.52}\text{Zn}_{0.48}$ (dashed curve). The spectra have been normalized according to peak height. In each case the photoelectron peaks have been aligned in kinetic energy.

Table 1. LS fitting results for the Cu $2p_{3/2}$ photoelectron spectra of Cu and $\text{Cu}_{0.52}\text{Zn}_{0.48}$. Parameters without error bars are held fixed.

	Fit 1	Fit 2	Fit 3
Sample	Cu	$\text{Cu}_{0.52}\text{Zn}_{0.48}$	$\text{Cu}_{0.52}\text{Zn}_{0.48}$
E_s in eV	0.27 ± 0.07	0.32 ± 0.04	0.24 ± 0.04
I_s	0.12	0.12	0.12
Γ in eV	0.57 ± 0.01	0.57	0.57
W in eV	0.265	0.265	0.265
α	0.031 ± 0.008	0.056 ± 0.016	0.044 ± 0.007
λ/R in $e \text{ \AA}^{-1}$	—	—	$(0.88 \pm 0.23) \times 10^{-3}$
χ_r^2	0.55	1.72	0.72

$\text{Cu}_{0.52}\text{Zn}_{0.48}$ alloy. A poor fit ($\chi^2 \sim 1.72$) was obtained, with large systematics visible in the residuals. A satisfactory fit could only be obtained after increasing W to 0.34 eV, an additional Gaussian broadening of 0.21 eV. This indicates that there is an additional source of broadening not included in our simulation and that this is Gaussian in character. Very similar observations have recently been made for $\text{Cu}_x\text{Pd}_{1-x}$ alloys where the additional broadening was explained as an electrostatic disorder effect [7]. Following this earlier work, we now model the ‘disorder broadening’ by the range of potentials generated by a CCM lattice.

The charge on site i in the CCM has the form

$$Q^i = 2\lambda N_1^i S^i \quad (1)$$

where λ determines the ‘ionicity’ of the A_xB_{1-x} alloy system, N_1^i is the number of unlike neighbours in the first shell around site i , and $S^i = -1$ (1) if the site is occupied by an A (B) atom. Q and λ are measured in units of e with the following sign convention: $Q > 0$ ($Q < 0$) \Rightarrow loss (gain) of electrons. We assume that the potential at site i is given in volts by

$$V^i = \frac{2Q^i}{R_1} + \sum_{i \neq j} \frac{Q^j}{R_{ij}} \quad (2)$$

where R_1 is the nearest-neighbour distance in Å, and we have suppressed a factor of 14.4 on the right-hand side for brevity. The summed term is frequently referred to as the Madelung potential, while the first term on the right-hand side is intra-atomic in origin. Note that in equation (2) it is implicit that the excess charge on each site resides on the surface of touching spheres of radius $R_1/2$. Given equations (1) and (2), it can be shown [12] that the V^i depend linearly on the compositions of all shells. It follows that the site potentials for $c^A = c^B = 0.5$, where $c^{A(B)}$ is the global concentration of A (B) atoms, have an approximately Gaussian distribution for the random CCM lattice [13]. The disorder broadening predicted from the CCM is therefore consistent with our observation of increased Gaussian broadening of the Cu photoelectron lines in $\text{Cu}_{0.52}\text{Zn}_{0.48}$.

For a given global composition, V^i is determined primarily by N_1 (i.e. by disorder in the composition of the nearest-neighbour shell) and we can simulate the core-level XP spectra of disordered alloys with the expression [12]

$$I^X(\omega) = \sum_{N_1=0}^{Z_1} P(N_1, c^X) f^{\Gamma\alpha}[\omega, \langle V(N_1, c^X) \rangle_X] \quad (3)$$

where X can be either A or B, $P(N_1, c^X)$ is the probability of a site having N_1 unlike neighbours when the X concentration is c^X , and $f^{\Gamma\alpha}[\omega, \omega_0]$ is a Doniac–Sunjic lineshape with position ω_0 . $\langle V(N_1, c^X) \rangle_X$ is the average potential at X sites with N_1 unlike neighbours and is given by [12]

$$\langle V(N_1, c^X) \rangle_X = 2 \frac{\lambda}{R_1} S^X Z_1 (1 - c^X) + 2 \frac{\lambda}{R_1} S^X \{ Z_1 (1 - c^X) - N_1 \} (Z_1 - \Sigma_1) \quad (4)$$

where Z_1 is the total number of atoms in the first shell and Σ_1 is a constant determined by the underlying crystal structure [12].

LS fitting the Cu photoelectron spectra of $\text{Cu}_x\text{Zn}_{1-x}$ using equation (4) for the bulk component [15] with Γ , I_s , W at their values for pure Cu, we obtained $\lambda_{\text{Cu}}^{\text{BCC}} = (2.2 \pm 0.5) \times 10^{-3} e$ and $\lambda_{\text{Cu}}^{\text{FCC}} = (2.1 \pm 0.5) \times 10^{-3} e$. Repeating this procedure for the Zn 2p photoelectron spectra we deduced $\lambda_{\text{Zn}}^{\text{BCC}} = (2.8 \pm 0.8) \times 10^{-3} e$, $\lambda_{\text{Zn}}^{\text{FCC}} = (3.3 \pm 0.8) \times 10^{-3} e$. Comparison with values of the λ -parameters from *ab initio* calculations [5, 6] reveals that the broadening measured experimentally is smaller by a factor of 3–4 than expected on the basis of equations (1) and (2).

3. Discussion

To summarize, we now have high-resolution core-level XP spectra for three classes of disordered alloys, namely the BCC $\text{Cu}_{0.52}\text{Zn}_{0.48}$ and FCC $\text{Cu}_x\text{Zn}_{1-x}$ alloys studied here, and the FCC $\text{Cu}_x\text{Pd}_{1-x}$ alloys studied previously [7, 12]. In each case, alloy-induced core-level broadening has been observed and analysed in terms of the CCM. Very recently, Faulkner Wang and Stocks have calculated the distribution of core-level eigenvalues ϵ for $\text{Cu}_x\text{Zn}_{1-x}$ and $\text{Cu}_x\text{Pd}_{1-x}$ alloys [8]. Since we have *ab initio* and model-calculated results as well as experimental data, we are now in a position to answer the following questions:

- (i) Are the CCM potentials consistent with *ab initio* calculations?
- (ii) How do the CCM and *ab initio* results compare with experiment?

3.1. Validity of the model

As mentioned in section 1, the validity of equation (1) has already been investigated by two groups. It is reasonable to say that the model works rather well for FCC systems but less so

for the BCC structure, although Wolverton *et al* [5] and Faulkner, Wang and Stocks [6] have taken more extreme and opposing views on this point. However, even if the validity of the CCM is accepted, it does not follow that a random CCM point charge array will give a correct description of the electrostatics in a random alloy, since the CCM gives only the net charge transfer from site to site and does not describe the *distribution* of the charge within each atomic volume. This is an important distinction in seeking to compare the predictions of the CCM with the results of the large-pseudorandom-supercell calculations of Faulkner *et al* [8]. These authors used the muffin-tin approximation and unrelaxed Bravais lattices, defining equal-sized atomic volumes using the Wigner–Seitz construction. The charge density for the alloy is made up of a constant, independent of position, plus spherically symmetric concentrations of charge of radius R_{MT} , the muffin-tin radius, centred on the lattice sites. The net charge on a site is then given by the difference in charge within the muffin tin at the site of interest relative to a neutral site. The Madelung potential for the muffin-tin system is given by the potential generated if the site charges are collapsed to points. It follows that if the CCM gets the charges right, then it should also get the Madelung potentials right, where ‘right’ means in agreement with the muffin-tin results. This has already been shown to be the case by Wolverton *et al* [5].

The *ab initio* core-level eigenvalues ϵ^i calculated by Faulkner *et al* [8] and the CCM potentials V^i generated by equation (2) are not in good agreement with each other. Although a linear correlation is observed between ϵ^i and V^i , the slope $\delta\epsilon^i/\delta V^i \sim 0.55$ for BCC $\text{Cu}_{0.50}\text{Zn}_{0.5}$ and is almost zero for the FCC $\text{Cu}_x\text{Pd}_{1-x}$ alloys. Given the observations made above concerning the Madelung potential, we must attribute the disagreement between the CCM and *ab initio* calculations to the form of intra-atomic potential used in equation (2). We noted earlier that equation (2) is based on the assumption [7] that any excess charge on a site resides on a sphere with radius equal to half the nearest-neighbour distance. This is a plausible assumption, but not necessarily the optimum one for obtaining agreement with experiment. It has been shown previously [9] that the intra-atomic and Madelung contributions to $\langle V[N_1, c^X] \rangle$ in equation (4) have an opposite dependence on N_1 , with the result that the dependence of the total potential on N_1 is much weaker than that of either of its components. Thus small changes to the intra-atomic term can significantly reduce the spread in CCM potentials without producing large changes in the averages $\bar{V}_A(c^X)$, $\bar{V}_B(c^B)$. Thus the CCM is not necessarily incompatible with *ab initio* results, despite recent claims [8]. It would however be very helpful to know how the excess charge in *ab initio* calculations is redistributed within the muffin-tin (i.e. an estimate of $\int \delta\rho_{MT}(r)/r \, dr$).

We consider now the conditionally averaged eigenvalues and CCM potentials $\bar{\epsilon}_X$ and \bar{V}_X calculated in reference [8]. A systematic correspondence of $\bar{\epsilon}_X$ and \bar{V}_X was not observed, prompting further criticism of the CCM potentials. Although this point was overlooked by Faulkner *et al* [8], it is widely appreciated [17–19] that the difference in Fermi levels $\Delta\epsilon_f$ contributes to core-level shifts. Of course a comparison of shifts measured and calculated relative to the Fermi level is valid, but these quantities should be compared with $\Delta\bar{V} + \Delta\epsilon_f$. In this respect the analysis of Faulkner *et al* [8] was incomplete.

Given that large-scale *ab initio* electronic structure calculations can now be performed, one is entitled to doubt the need to discuss simple models. While *ab initio* approaches should offer the most accurate description of the electronic structure of alloys, model approaches (sometimes in their failure) can elucidate the important concepts. The fact that the CCM provided the initial stimulus for the consideration of Madelung effects in disordered alloys bears testament to this point of view. Just as it is wrong to say that equation (2) is *always* the basis for describing core-level shifts [17], we believe it is wrong to say that it *never* provides such a basis. The critique of our earlier work [7, 12] by Faulkner *et al* [8] is incomplete. Our objective here is to present a more balanced view and, more importantly, to offer new

experimental data against which all calculations and models must be judged. We turn now to the comparison with experiment.

3.2. Comparison with experiment

As discussed in section 2, our experimental measurements reveal a broadening in both FCC and BCC $\text{Cu}_x\text{Zn}_{1-x}$ alloys which is considerably smaller than predicted by equations (1) and (2) using the charge-transfer parameters λ determined by Wolverton *et al* [5]. Of course we could attribute the discrepancies to the uncertainty in our treatment of the intra-atomic potential, as discussed above, and we could easily improve agreement with experiment by introducing a parameter. Here, as previously [7, 12, 20], we explicitly choose not to do this.

The *ab initio* eigenvalue results from reference [8] overestimate the disorder broadening of the core lines in $\text{Cu}_{0.52}\text{Zn}_{0.48}$ by a factor of ~ 2 . The reason for this is not clear. One could argue that the calculations neglect relaxation shifts which could in principle be site dependent. That the site-averaged alloy–metal eigenvalue shifts for ordered CuZn calculated by Faulkner *et al* [8] are 62% and 45% larger than experiment for Cu and Zn sites respectively may be evidence for significant relaxation effects in the CuZn alloy system. Alternatively the discrepancy could be attributed to short-range order in the alloy specimens, particularly for the $\text{Cu}_{0.52}\text{Zn}_{0.48}$ composition which is prone to ordering.

4. Conclusions

New experimental data exhibiting the ‘disorder broadening’ of photoelectron lines have been presented for the $\text{Cu}_x\text{Zn}_{1-x}$ alloy system. Comparison of these data with model results and *ab initio* calculations has been made. In general there is qualitative agreement between experiment and the calculations. Possible shortcomings of both the experimental results and their theoretical description have been discussed.

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