Comment on "Core Level Shifts in Metallic Alloys"

Recently Faulkner, Wang, and Stocks (FWS) [1] gave results for the core level eigenvalues of substitutional alloys obtained from first-principles calculations. These results confirmed the existence and order of magnitude of site dependent fluctuations of core potentials observed previously for disordered CuPd using x-ray photoelectron spectroscopy (XPS) [2]. FWS compared their results with those of a "potential model" (PM), similar to that used to interpret the XPS results [2], and concluded that PM's are unreliable. We argue that the analysis of FWS was incomplete, and that their conclusions concerning the efficacy of PM's are overstated and misleading.

We consider first the distribution of potentials for a given disordered alloy. Following FWS, we adopt the muffin-tin approximation and assume equal sized Wigner-Seitz atomic cells. Within these assumptions the sample charge model proposed by Magri, Wei, and Zunger (MWZ) [3] (and used in Ref. [2] to construct site potentials) should give the "correct" distribution of Madelung potentials, and this has been demonstrated [4]. To get the total core potential one has to make an assumption about the intra-atomic contribution since the MWZ model gives the site charges but says nothing about the *distribution* of charge in each atomic cell. In Ref. [2] we assumed the excess charge on each site resides in a spherical shell with radius r_{eff} equal to half the bond length. This is a simple plausible assumption but not necessarily the optimum one. FWS make the same assumption and find poor agreement between the distribution of potentials given by their PM and the distribution of calculated core level eigenvalues. For $\mathrm{Cu}_{0.5}\mathrm{Zn}_{0.5}$ these quantities were found to be linearly correlated but with gradient 0.55 rather than unity. However, the Madelung and intra-atomic potentials in the PM both scale linearly with the nearest neighbor composition but with opposite sign, and so a small refinement of r_{eff} can significantly reduce the distribution of site potentials. Thus the PM is not inherently inconsistent with the first-principles results, rather its intra-atomic contribution is not implicitly calibrated. In Ref. [2] we did not "fine-tune" r_{eff} (contrary to the assertion made in Ref. [1]), but charge densities from first-principles calculations offer in principle a systematic means of determining it.

A much more serious problem is that the FWS results indicate that the core eigenvalues for Cu sites in $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ are broadened by 0.05 eV by disorder while experiment shows a broadening of $\gtrsim 0.26$ eV [2]. (The simple PM of Ref. [2] gives a core level broadening of 0.5 eV). Accounting for the possible presence of short range order in the specimens studied would worsen the comparison between experiment and the first-principles results. FWS concede that this poor result for CuPd may be due to the neglect of lattice relaxation. Extended x-ray-absorption fine structure results [5] show significant local relaxations in Cu-Pd and that the Cu-Pd distance is independent of composition contrary to the assumptions made in Ref. [1].

Turning now to site-averaged core level shifts with alloy composition, FWS found no systematic correlation between the average core eigenvalue shifts and the average PM shifts. However it is widely appreciated, though overlooked by FWS, that differences in Fermi levels contribute to core level shifts referenced to the "crystal zero" [6]. Of course this contribution cancels when comparing eigenvalue shifts and experimental binding energy shifts when both are referenced to the Fermi level, but must be included for a comparison with PM calculations. We note that good agreement is obtained between experimental core level shifts and PM shifts for CuPd systems when Fermi level shifts are included in the analysis [2,7] and contributions from the XPS final state are small.

In conclusion, we maintain that while it is wrong to always interpret core level shifts in terms of a simple potential model of charge transfer, it is not necessary to disregard models completely. Indeed, the recent wave of interest in Madelung effects in disordered alloys was stimulated by the results of MWZ. Clearly simple empirical models are not substitute for first-principles calculations, but much physical insight can be gained by carefully comparing experimental data, first-principles calculations, and model calculations.

P. Weightman[1] and R. J. Cole[2]
[1]Department of Physics and Surface Science
Research Centre
University of Liverpool
Liverpool, L69 3BX United Kingdom
[2]Department of Physics and Astronomy
University of Edinburgh
Edinburgh, EH9 3JZ United Kingdom

Received 29 January 1999
PACS numbers: 71.20.Be, 71.15.Mb, 71.23.−k, 82.80.Pv

[1] J. S. Faulkner, Y. Wang, and G. M. Stocks, Phys. Rev. Lett. **81**, 1905 (1998).
[2] R. J. Cole, N. J. Brooks, and P. Weightman, Phys. Rev. Lett. **78**, 3777 (1997); R. J. Cole and P. Weightman, J. Phys. Condens. Matter **10**, 5679 (1998).
[3] R. Magri, S. H. Wei, and A. Zunger, Phys. Rev. B **42**, 11 388 (1990).
[4] C. Wolverton and A. Zunger, Phys. Rev. B **51**, 6876 (1995).
[5] J. M. C. Thornton *et al.*, Europhys. Lett. **26**, 259 (1994).
[6] R. E. Watson in *Structure and Bonding*, Photoelectron Spectrometry Vol 24 (Springer-Verlag, New York, 1975).
[7] R. J. Cole, N. J. Brooks, and P. Weightman, Phys. Rev. B **56**, 12 178 (1997).