

Core Level Chemical Shifts in Metallic Alloys

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The average chemical shifts and the distribution of the shifts about the average are obtained for CuPd, CuZn, and AgPd alloys using supercells that contain hundreds of atoms. Density functional theory and local density approximation (DFT-LDA) calculations are carried out using the order- N locally self-consistent multiple-scattering method. The DFT-LDA calculations provide reliable predictions for the chemical shifts in the alloys, but the electron spectroscopy for chemical analysis potential model does not. [S0031-9007(98)06901-4]

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Charge transfer has always played a major role in theories of valence and bonding in condensed matter [1]. It is generally believed that charge transfer can be inferred from the shifts of core level binding energies in different chemical environments, and x-ray photoelectron spectroscopy, which can be used to measure such shifts, became an important tool under the appellation electron spectroscopy for chemical analysis (ESCA) [2]. The charge transfer in metallic alloys has always been of interest and is studied experimentally using ESCA, x-ray absorption near-edge structure (XANES), bremsstrahlung isochromat spectroscopy (BIS), and Auger electron appearance potential spectroscopy. It is reasonable to assume, and it has been demonstrated theoretically [3], that the charges on the atoms of a given species in a binary substitutional alloy with no short-range order take on a continuous distribution of values about their mean. The suggestion has been made that this distribution of charges should be reflected in a distribution of binding energies for a given atomic core level, and the resulting disorder broadening of the core level has been studied experimentally using a high-resolution ESCA spectrometer [4]. In the present paper, an order- N method for studying the electronic states of disordered alloys [3,5,6] will be used to calculate the chemical shifts and their distribution about their mean within the density functional theory and local density approximation (DFT-LDA) for three alloy systems. The experimental results and the DFT-LDA calculations will be compared with each other and with the predictions of the ESCA potential model that was used to analyze the experimental data in Ref. [4].

In the DFT-LDA, the binding energy of a core level $E_{n,i}^{A,i}(c)$ of an A atom on site i in an A - B alloy with a concentration c is the negative of the one-electron core level energy measured relative to the Fermi energy. The binding energy for the A atoms, $E_{n,i}^A(c)$, is the average of $E_{n,i}^{A,i}(c)$ over all the A sites. It is well understood that there are significant differences between this Koopman approximation to the binding energy and the measured

binding energy of a core electron because of the relaxation of the electrons around the core hole [7]. The chemical shift for an atom in an alloy, $\delta E_{n,i}^{A,i}(c)$, is the change in the binding energy relative to the pure metal. It has been proposed that the many-body relaxation corrections are approximately independent of concentration, so they are not very important in measurements of $\delta E_{n,i}^{A,i}(c)$ [8].

The alloys are modeled with supercells that contain several hundred atoms, and periodic boundary conditions are applied to them. An order- N method for which the computer time increases linearly with N must be used, and the one that is employed here is the locally self-consistent multiple scattering (LSMS) method, which has been described in the literature [9,10]. It differs from other order- N methods in that it is based on the multiple scattering method of Rayleigh [11], Korringa [12], and Kohn and Rostoker [13], and it is particularly well suited to calculations on transition metals. At the present stage of development of the LSMS, the core electrons are treated nonrelativistically or fully relativistically, and the conduction electrons are treated nonrelativistically or quasirelativistically. The calculations in this paper are nonrelativistic, and the muffin-tin approximation is used. The LSMS is an all-electron method, in that the core states are iterated to self-consistency.

Binary substitutional alloys are modeled by creating a Bravais lattice and placing A or B atoms on the sites with the probability c or $1 - c$. It might be thought that putting the atoms on the ideal lattice sites is a severe approximation. However, x-ray diffraction experiments on alloys show consistently that the static rms displacements of atoms from their ideal sites due to the size effect are less than a third of the rms thermal displacements at room temperature, even for alloys for which the sizes of the atoms are very different [14–17].

The results of calculations and experiments on three alloy systems are shown in Table I. All of the calculations for the CuPd alloys use supercells containing 256 atoms based on fcc Bravais lattices, the lattice constant for the

TABLE I. Experimental and calculated chemical shifts.

Alloy (source of experiment)	Atom level	Expt shift (eV)	Calc shift (eV)	FWHM (eV)	Charge (e)	ESCA shift (eV)
50% CuPd (Ref. [18])	2 <i>p</i> Cu	-0.70	-0.72	0.05	-0.18	-0.83
	3 <i>d</i> Pd	0.26	0.34	0.10	0.18	0.83
80% CuPd (Ref. [18])	2 <i>p</i> Cu	-0.25	-0.27	0.05	-0.08	-0.40
	3 <i>d</i> Pd	0.70	0.65	0.08	0.31	1.61
50% CuZn	2 <i>p</i> Cu	...	0.34	0.35	-0.10	-0.60
...	2 <i>p</i> Zn	...	-0.01	0.51	0.10	0.60
CuZn B2 (Ref. [19])	2 <i>p</i> Cu	0.35	0.57	0.00	-0.13	-0.17
	2 <i>p</i> Zn	-0.20	-0.29	0.00	0.13	0.17
50% AgPd (Ref. [20])	3 <i>d</i> Ag	-0.50	-0.48	0.31	0.05	0.26
	3 <i>d</i> Pd	0.00	-0.10	0.08	-0.05	-0.26

50% alloy being 6.9 a.u. and for the 80% alloy being 7.1 a.u. The disordered 50% CuZn alloy is in the β phase (bcc) with a lattice constant of 5.5 a.u. and is modeled with a supercell containing 432 atoms. The ordered β' phase of CuZn is in the B2 (CsCl) structure with the same lattice constant as the β phase. The 50% AgPd alloy is modeled with a supercell containing 256 atoms and a fcc Bravais lattice with a lattice constant of 7.61 a.u. The pure metals Cu, Pd, Ag, and Zn are all taken to be fcc with lattice constants 6.7677, 7.43, 7.2744, and 7.79 a.u. The experimental chemical shifts for CuPd are the most recent [18]. A number of technical problems were overcome in order to obtain the experimental data on CuZn shown in the table [19]. The shifts have been measured for AgPd for a wide range of concentrations [20]. The choice of the core levels listed in Table I is dictated by the availability of experimental data, which are, in turn, determined by the existence of peaks in the energy range that can be sampled using Al $K\alpha$ or Mg $K\alpha$ x rays that are well defined.

The calculated shifts in the fourth column of Table I agree with the experimental shifts in the third column to within experimental error. The shifts calculated for ordered and disordered CuZn are significantly different. The data indicate that the CuZn alloy used in the experiments is in the ordered β' phase, as expected. The agreement between theory and experiment in Table I lends further credence to the proposition that DFT-LDA calculations of chemical shifts for alloys are reliable because the many-body effects cancel to a large degree.

The distribution of binding energies about the mean can vary considerably from one alloy to another. A rough measure of this distribution is obtained by fitting the density in energy of the calculated data points to a Gaussian, the shape of which is measured by the full width at half maximum (FWHM). It appears that the only experiments designed to measure this distribution are the ones in Ref. [4] that focused on the 50% and 80% CuPd alloys, and the conclusion from these experiments is that the FWHM for the Cu 2*p* level must be less than 0.25 eV. The calculations in Ref. [4] are based on the ESCA potential model, and predict a FWHM of 0.5 eV. It

is clear from Table I that the DFT-LDA predicts a FWHM that is considerably smaller than that upper bound for both CuPd alloys. If anything, the DFT-LDA prediction for the FWHM is on the small side. Although we have argued that size effects are not a primary factor in this analysis, the size effects in CuPd used in a recent discussion of the Auger spectra in Cu-rich CuPd alloys [21] might serve to increase the calculated FWHM somewhat.

It would be interesting to see measurements of the distribution of the core level shifts about the average in other alloys systems. The DFT-LDA calculations predict that the FWHM for the Ag core level in the 50% AgPd alloy will be 3 times larger than for the Pd level. The calculations also indicate that the distributions are considerably broader for the core levels in the disordered CuZn alloy than for the other alloy systems studied. It will presumably be difficult to see this effect experimentally because it is not easy to quench CuZn in the disordered β phase, in addition to the other technical difficulties described in Ref. [19].

To this point, nothing has been said about the way that the charge in the alloys is assigned to the individual atoms. The reason for this is, of course, that such a concept does not enter into the calculations. If a first-principles DFT-LDA method is well converged, the way that space is divided up in the calculation is irrelevant. The argument has already been made for placing the nuclei of all the atoms in the disordered alloy on the sites of a Bravais lattice, so there is no compelling reason to divide space in any way other than equal volumes for the two atoms. The primary purpose of Refs. [3,5,6] was to calculate for disordered metallic alloys the net charges q^i within the standard Wigner-Seitz cells for the Bravais lattice, and from those charges to calculate the Coulomb potentials V^i at the sites. The net charges q^i are calculated for all the atoms in the alloys, and the averages of these charges for each of the atomic species, q^A and q^B , are shown in Table I. The units are the absolute value of the charge of an electron, so the number -0.18 for Cu in 50% CuPd means that, on the average, 0.18 electrons move from the Pd atoms to the Cu atoms.

The formula that is commonly used for interpreting ESCA measurements on molecules states that the potential shift for an A atom on site i is related to the charges on the atoms by $V_{n,i}^{A,i}(c) = k_{n,i}^A q^i + V^i$, where the q^i and V^i have been defined, and $k_{n,i}^A$ is roughly the Coulomb repulsion integral between the core electron and the valence electrons on the site [22]. The dependence of $k_{n,i}^A$ on the atomic species and the core level is ignored in Ref. [18], $k_{n,i}^A = k$, and the choice for k is discussed extensively. We use this version of the ESCA potential model with k set equal to 2 divided by the radius of the nearest-neighbor shell, as is also done in Ref. [4]. According to the ESCA potential model $\delta E_{n,i}^{A,i}(c) = V_{n,i}^{A,i}(c)$, so a plot of $\delta E_{n,i}^{A,i}(c)$ versus $V_{n,i}^{A,i}(c)$ should yield a straight line with a slope of 1.

The plot of the average chemical shifts for the CuPd alloys with $c = 0.5$ and $c = 0.8$ versus the corresponding average ESCA potentials in Fig. 1 yields a line that has a slope approximately equal to 1. This is in agreement with the calculations in Ref. [18], and the agreement could no doubt be made better by fine-tuning the value of k as those authors did. However, the points that correspond to the shifts of the individual atoms in the two alloys, the $\delta E_{2p}^{Cu,i}(c)$ versus $V_{2p}^{Cu,i}(c)$ and $\delta E_{3d}^{Pd,i}(c)$ versus $V_{3d}^{Pd,i}(c)$, do not fall on the line at all. The FWHM's from the statistical distribution of the ordinates of these points are listed in Table I. The FWHM's from the statistical distribution of the abscissas, $V_{2p}^{Cu,i}(c)$ and $V_{3d}^{Pd,i}(c)$, are approximately 0.7 eV for both constituents in both alloys. The difference between this and the FWHM of 0.5 eV that was obtained for the Cu $2p$ level in Ref. [4] from the ESCA potential model is not significant. Thus, the

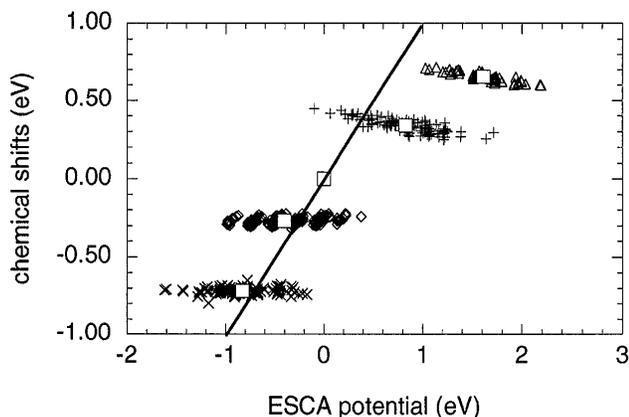


FIG. 1. The crosses show the chemical shifts of $\delta E_{2p}^{Cu,i}(0.5)$ versus the ESCA potentials $V_{2p}^{Cu,i}(0.5)$ for the 128 Cu atoms in the model of the 50% CuPd alloy. The plus signs show $\delta E_{3d}^{Pd,i}(0.5)$ versus $V_{3d}^{Pd,i}(0.5)$ for the 128 Pd atoms. The diamonds show $\delta E_{2p}^{Cu,i}(0.8)$ versus $V_{2p}^{Cu,i}(0.8)$ for the 204 Cu atoms in the model of the 80% CuPd alloy. The triangles show $\delta E_{3d}^{Pd,i}(0.8)$ versus $V_{3d}^{Pd,i}(0.8)$ for the 52 Pd atoms. The squares show the average chemical shifts versus the average ESCA potentials. The slope of the solid line is 1.

distribution of charges q^i that the authors of that paper assumed is not unreasonable and they calculated the Coulomb potentials V^i correctly. The reason that they obtained a FWHM that is outside the range that can be consistent with their experiment is simply due to the failure of the ESCA potential model.

The failure of the ESCA potential model is illustrated even more graphically by the fact that none of the points corresponding to the $\delta E_{2p}^{Cu,i}(0.5)$ versus $V_{2p}^{Cu,i}(0.5)$ and $\delta E_{2p}^{Zn,i}(0.5)$ versus $V_{2p}^{Zn,i}(0.5)$ for the 216 Cu and 216 Zn sites in the 50% CuZn alloy fall on the line with slope one in Fig. 2. The value of k was taken to be 2 over the nearest-neighbor radius as for CuPd, but there is no positive value of k that could be used to obtain agreement with the ESCA model. The fact that the points that correspond to the chemical shifts for alloy in the ordered B2 structure fall on the lines defined by the $\delta E_{2p}^{Cu,i}(0.5)$ and $\delta E_{2p}^{Zn,i}(0.5)$ for the disordered alloy is not surprising. The sites in the random alloy that they correspond to are the ones that have a fairly short-range environment that happens to be the same as in the ordered alloy. The plot of the $128\delta E_{3d}^{Ag,i}(0.5)$ versus $V_{3d}^{Ag,i}(0.5)$ and the $128\delta E_{3d}^{Pd,i}(0.5)$ versus $V_{3d}^{Pd,i}(0.5)$ for the 50% AgPd alloy in Fig. 3 is even more discouraging for this model. The $\delta E_{3d}^{Ag,i}(0.5)$ are distributed rather broadly about their mean, but the different values that they take on clearly have no relationship with the $V_{3d}^{Ag,i}(0.5)$.

It has been pointed out [8] that the failure of the ESCA potential model for metallic alloys can be demonstrated without any calculations by noting that there are alloys, such as CuNi, CuZr, PdZr, and PdTi, in which the sign of the chemical shift is the same for both constituents in the alloy. The present calculations show that CuZn and AgPd

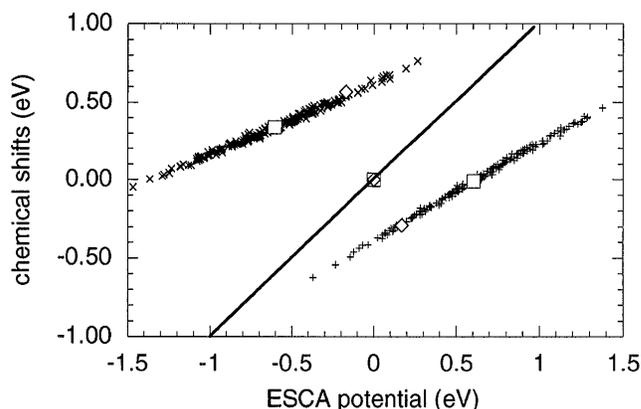


FIG. 2. The crosses show the chemical shifts $\delta E_{2p}^{Cu,i}(0.5)$ versus the ESCA potentials $V_{2p}^{Cu,i}(0.5)$ for the 216 Cu atoms in the model of the 50% CuZn alloy. The plus signs show $\delta E_{2p}^{Zn,i}(0.5)$ versus $V_{2p}^{Zn,i}(0.5)$ for the 216 Zn atoms. The squares show the average chemical shifts versus the average ESCA potentials. The diamonds show the chemical shifts versus the ESCA potentials for the ordered B2 alloy. The slope of the solid line is 1.

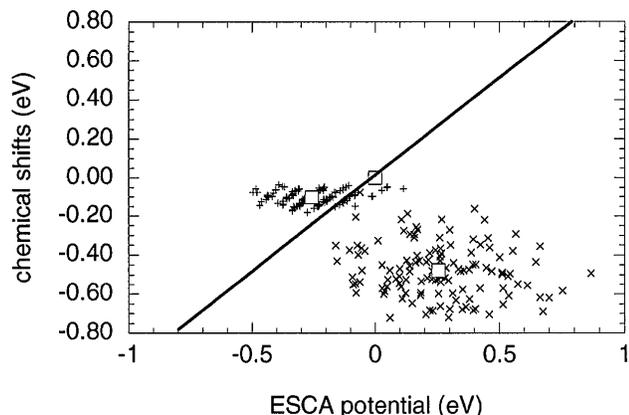


FIG. 3. The crosses show the chemical shifts $\delta E_{3d}^{\text{Ag},i}(0.5)$ versus the ESCA potentials $V_{3d}^{\text{Ag},i}(0.5)$ for the 128 Ag atoms in the model of the 50% AgPd alloy. The plus signs show $\delta E_{3d}^{\text{Pd},i}(0.5)$ versus $V_{3d}^{\text{Pd},i}(0.5)$ for the 128 Pd atoms. The squares show the average chemical shifts versus the average ESCA potentials. The slope of the solid line is 1.

must also be added to this category of alloys for which no value of k can be found that will give agreement with this simple model. At first sight, it would appear that CuPd is an exception, but, when the shifts for the individual atoms are considered, it is seen that the model fails again.

In conclusion, the primary results of this paper are the first principles of DFT-LDA calculations of the average chemical shifts and the FWHM's of the distributions about the averages that are shown in Table I. The ESCA potential model was brought up only because it has been used to analyze recent experiments. More sophisticated discussions of chemical shifts, and also Auger, BIS, and XANES measurements on alloys, make extensive use of the angular momentum decomposition of the charge density [23–26]. The information to evaluate this approach is generated in the process of doing our first-principles LSMS calculations, but we have never isolated it and stored it in a usable form. We plan to rewrite our computer codes to investigate it for disordered alloys. Some interesting correlations between the average core-level binding-energy shifts and cohesive energies in metals have been pointed out [27], and it would be interesting to see if these can be extended to the distributions of shifts about the average. Perhaps the differences between these distributions for the alloys considered here have to do with the differences in the relative binding and ordering energies of CuPd, CuZn, and AgPd.

[1] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1960), 3rd ed.

[2] K. Siegbahn *et al.*, *ESCA, Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy*, Nova Acta Regiae Soc. Sci. Upsaliensis, Ser. IV, Vol. 20 (University of Sweden, Upsala, 1967).

- [3] J.S. Faulkner, Yang Wang, and G.M. Stocks, *Phys. Rev. B* **55**, 7492 (1997).
- [4] R.J. Cole, N.J. Brooks, and P. Weightman, *Phys. Rev. Lett.* **78**, 3777 (1997).
- [5] J.S. Faulkner, Yang Wang, and G.M. Stocks, in *Alloy Modeling and Design*, edited by G.M. Stocks, C.T. Liu, and P.E.A. Turchi (The Minerals, Metals, and Materials Society, Warrendale, PA, 1995); in *Stability of Materials*, edited by A. Gonis, P.E.A. Turchi, and J.A. Kudrnovsky, NATO ASI, Ser. B, Vol. 355 (Plenum, New York, 1996); J.S. Faulkner, Yang Wang, Nassrin Moghadam, and G.M. Stocks, in *Proceedings of the First International Alloy Conference (IAC-1)*, edited by A. Gonis, A. Meike, and P.E.A. Turchi (Plenum, New York, 1996).
- [6] J.S. Faulkner, Yang Wang, and G.M. Stocks, *Phys. Rev. B* **52**, 17 106 (1995).
- [7] A.R. Williams and N.D. Lang, *Phys. Rev. Lett.* **40**, 954 (1978); *Phys. Rev. B* **16**, 2408 (1978).
- [8] M. Weinert and R.E. Watson, *Phys. Rev. B* **51**, 17 168 (1995).
- [9] G.M. Stocks, D.M.C. Nicholson, Y. Wang, W.A. Shelton, Z. Szotek, and W.M. Temmerman, in *Proceedings of the 1994 Simulation Multiconference*, edited by A.M. Tentner (The Society for Computer Simulation, San Diego, CA, 1994); D.M.C. Nicholson, G.M. Stocks, Y. Wang, W.A. Shelton, Z. Szotek, and W.M. Temmerman, *Phys. Rev. B* **50**, 14 686 (1994).
- [10] Yang Wang, G.M. Stocks, W.A. Shelton, D.M.C. Nicholson, Z. Szotek, and W.M. Temmerman, *Phys. Rev. Lett.* **75**, 2867 (1995).
- [11] Lord Rayleigh, *Philos. Mag.* **34**, 481 (1892).
- [12] J. Korringa, *Physica (Utrecht)* **13**, 392 (1947).
- [13] W. Kohn and N. Rostoker, *Phys. Rev.* **94**, 111 (1954).
- [14] F.H. Herbstein, B.S. Borie, Jr., and B.L. Averbach, *Acta Crystallogr.* **9**, 466 (1956).
- [15] D.I. Vadets, V.A. Val'chikovskaya, S.E. Naminskaya, and Yu.I. Perel', *Sov. Phys. J.* **16**, 1769 (1973).
- [16] X. Jiang, G.E. Ice, C.J. Sparks, L. Robertson, and P. Zschack, *Phys. Rev. B* **54**, 3211 (1996).
- [17] J.S. Faulkner, *Phys. Rev. B* **56**, 2299 (1997).
- [18] R.J. Cole, N.J. Brooks, and P. Weightman, *Phys. Rev. B* **56**, 12 178 (1997).
- [19] G.K. Wertheim, M. Campagna, and S. Hufner, *Phys. Condens. Matter* **18**, 133 (1974).
- [20] P. Steiner and S. Hufner, *Acta Metall.* **29**, 1885 (1981).
- [21] Yu. Kucherenko, A.Ya. Perlov, A.N. Yaresko, V.N. Antonov, and P. Weightman, *Phys. Rev. B* **57**, 3844 (1998).
- [22] U. Gelius, *Phys. Scr.* **9**, 133 (1974).
- [23] R.E. Watson, J. Hudis, and M.L. Perlman, *Phys. Rev. B* **4**, 4139 (1971).
- [24] M. Weinert and R.E. Watson, *Phys. Rev. B* **51**, 17 168 (1995).
- [25] T.K. Sham, Y.M. Yiu, M. Kuhn, and K.H. Tan, *Phys. Rev. B* **41**, 11 881 (1990); M. Kuhn and T.K. Sham, *Phys. Rev. B* **49**, 1647 (1994).
- [26] R.J. Cole and P. Weightman, *Metallic Alloys: Experimental and Theoretical Perspectives*, edited by J.S. Faulkner and R.G. Jordan (Kluwer, Amsterdam, 1994).
- [27] B. Johanson and N. Martenson, *Phys. Rev. B* **21**, 4427 (1980).