PHYSICAL REVIEW B **79**, 012201 (2009)

Suppression of disorder broadening of core-level photoelectron lines in CuAu alloys by inhomogeneous lattice distortion

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(Received 26 September 2008; published 20 January 2009)

Disorder broadening of core-level binding energies is a general effect observed in random alloys, and identifies an opportunity for studying specific local environments experimentally. Here we study it in an archetypical system: face-centered-cubic $Cu_{50}Au_{50}$. While the disorder broadening is clearly detectable at Au, at Cu it is below the detection limit. We supplement experiments by a theoretical study where we model the alloy by a large supercell constructed as a special quasirandom structure and calculate binding-energy shifts at all sites in the supercell. Theory shows that the suppression of the disorder broadening at Cu results from a delicate balance between the influence of local chemical environment and inhomogeneous lattice distortions on the site-resolved core-level shifts. Surprisingly, even larger relaxation-induced shifts are observed at Au sites.

DOI: 10.1103/PhysRevB.79.012201 PACS number(s): 79.60.Ht, 71.15.−m, 71.23.−k

Local environment effects represent a signature of disorder in a nonperiodic system. In an ideal periodic solid all atoms that occupy equivalent positions in the crystal unit cell have exactly the same properties. In a disordered system even chemically equivalent atoms are, strictly speaking, different. This is a fundamental property of nonperiodic solids. The presence of local environment effects has been largely ignored in earlier theories of disordered alloys. Also, experimental studies require extremely high resolution. However disorder broadening of core-level x-ray photoemission line shapes in alloys was observed by Cole *et al.*,[1] and it has since been detected in several alloy systems (see Ref. 2 and references therein). Its observation in high-resolution photoelectron spectroscopy promises insight into the number and nature of nearest neighbors, the dependence of the atomic core potential on the orbital character of the initial- and final-state charge distribution, and local lattice relaxation, as well as structural characterization of complex systems.[3,4]

The effect also attracted substantial theoretical attention. Early theoretical work analyzed core-level shift (CLS) and disorder broadening in terms of the so-called potential models.[1,5] This gave rise to some discussion on the reliability of the calculations.[6–8] Recently sophisticated methods have been developed which make it possible to calculate accurately CLS and disorder broadening of core-level photoelectron lines in alloys from first principles.[9,10] Thus, the disorder broadening of core-level photoelectron line shapes is currently understood to be a general effect of alloying.

In this work we present experimental core-level photoelectron spectra of disordered $Cu_{50}Au_{50}$, an archetypical system for studies of electronic structure and ordering effects in alloys. Our results show that, as expected, the core-level x-ray photoemission line shape for Au exhibits substantial disorder-induced broadening as compared to pure gold. However, our analysis indicates that the disorder broadening is smaller for Cu. We apply the complete screening picture and a supercell method to give a comprehensive theoretical analysis of these measurements. We show that the reduced broadening of the Cu lines in the alloy results from a delicate balance between the chemically induced local environment effects and inhomogeneous lattice distortions due to the large size mismatch between the alloy components.

A disordered specimen of $Cu_{50}Au_{50}$ was made from high-purity elemental material by comelting in an Ar arc furnace. To ensure homogeneity the sample was remelted a number of times followed by rapid quenching. X-ray diffraction gave a result for the lattice constant of the polycrystalline disordered alloy that agreed with previous measurements for this composition.[11]

X-ray photoelectron spectroscopy (XPS) measurements were performed on the alloy and on samples of the pure elements using the Scienta ESCA 300 spectrometer at the NCESS facility of the Daresbury Laboratory. Prior to the XPS experiments the specimens were cleaned by mechanical scraping in the specimen preparation chamber of the spectrometer and transferred to the measuring chamber without breaking the ultrahigh-vacuum environment. The scraping produced clean surfaces as shown by the absence of XPS peaks from the $1s$ core levels of O and C. High-resolution XPS spectra were taken of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ core levels of the specimens at near normal emission. The relative intensity of the Cu and Au core photoelectron lines was found to be consistent with the known bulk composition. Analysis of the XPS spectra in the vicinity of the Fermi edge showed the spectrometer to have a Gaussian resolution of 0.29 ± 0.02 eV full width at half maximum (FWHM).

The binding energies of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ core levels of the $Cu_{50}Au_{50}$ alloy were found to be shifted with respect to those of the pure elements. The observed CLSs are reported in Table I. They are in good agreement with earlier measurements.[12,13] The XPS profiles for these two core levels are shown in Figs. 1(a) and 1(b), respectively. In these

TABLE I. Experimental and theoretical XPS core-level binding shifts ($E_b^{\mathrm{alloy}}-E_b^{\mathrm{metal}}$) and core-level disorder broadening, all measured in eV. Theoretical results for the unrelaxed underlying lattice are given in parentheses.

	CLS		FWHM	
	Expt.	Theor.	Expt.	Theor.
Cu $2p_{3/2}$	−0.20	−0.13 (−0.14)	≲0.08	0.03 (0.09)
Au $4f_{7/2}$	0.25	0.28 (0.36)	0.12	0.09 (0.11)

figures the energy scales of the spectra have been shifted by the amounts shown in Table I in order to bring their peaks into alignment. It is clear from Fig. 1(a) that the Au $4f_{7/2}$ spectrum of $\mathrm{Cu_{50}Au_{50}}$ is broader than that of pure Au, demonstrating the disorder broadening effect observed previously for other alloy systems.[1,2] This effect was quantified by numerical analysis of the experimental data as described in detail previously.[1,5] This procedure begins by modeling the core spectra of the pure metals using the expression[14]

$$I(E) = G_W(E) \otimes \{I_b f(\Gamma,\alpha,E_b^b,E) + I_s f(\Gamma,\alpha,E_b^s,E)\}, \quad (1)$$

where $f(\Gamma,\alpha,E_b)$ is the Doniac-Sunjic function with lifetime broadening Γ, asymmetry parameter α, and binding energy E_b; G_W is a Gaussian of FWHM W, representing the instrumental broadening function; and $\otimes$ indicates the numerical convolution operator. While surface effects are not the prime concern in the present work, a good representation of the experimental core photoelectron spectra of the noble metals requires inclusion of distinct bulk and surface contributions with intensities I_b and I_s and binding energies E_b^b and E_b^s, respectively.[14] Least-squares fitting of the experimental Cu $2p_{3/2}$ and Au $4f_{7/2}$ spectra of the pure metals to the form of Eq. (1) yielded values of Γ, α, I_s/I_b, and $E_b^s-E_b^b$ that are in excellent agreement with those of Ref. 14. Least-squares fitting of the Au $4f_{7/2}$ spectrum of $\mathrm{Cu_{50}Au_{50}}$ revealed a shift in E_b^b and an increase in W with no significant changes to any other parameters. We conclude that the additional broadening of the Au $4f_{7/2}$ spectrum of $\mathrm{Cu_{50}Au_{50}}$ is Gaussian in character, as expected for the disorder broadening effect,[1,5] with FWHM of 0.12 ± 0.02 eV.

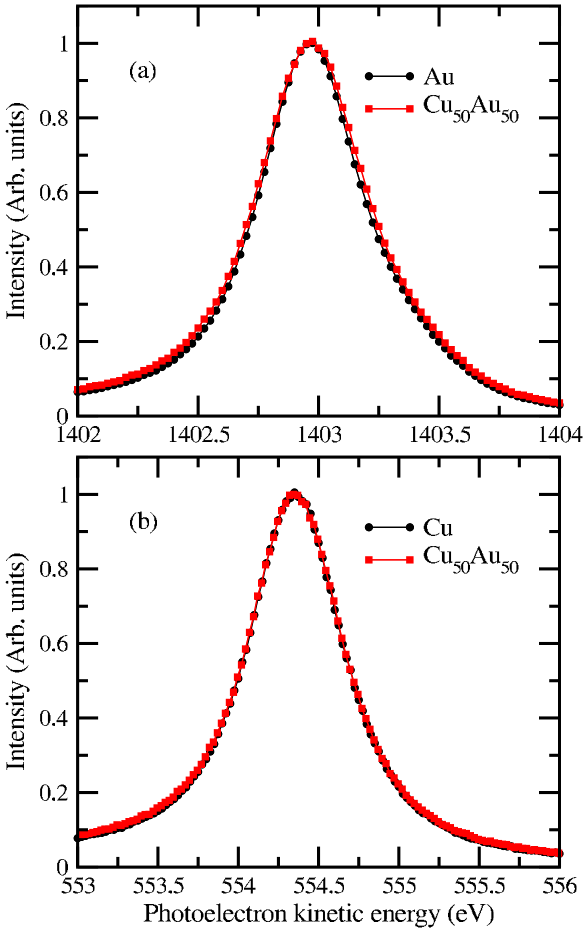

FIG. 1. (Color online) (a) Au $4f_{7/2}$ and (b) Cu $2p_{3/2}$ photoelectron spectra of $\mathrm{Cu_{50}Au_{50}}$ and the elemental metals. The binding energies of the alloy spectra have been shifted by the corresponding CLSs listed in Table I to emphasize line-shape differences.

Detection of disorder broadening in the Cu $2p_{3/2}$ spectrum of the $\mathrm{Cu_{50}Au_{50}}$ alloy presents a much harder challenge since the core hole lifetime is significantly shorter ($\Gamma=0.56$ eV, as opposed to 0.33 eV for the Au $4f_{7/2}$ hole state). Careful examination of the raw data in Fig. 1(b) suggests that the alloy spectrum is very slightly broader than that of pure Cu. However in consideration of synthetic spectra with the Cu $2p_{3/2}$ lifetime broadening and a series of different Gaussian widths, we have found that the disorder broadening needs to be at least $\sim$0.12 eV for the effect to be reliably quantified when the experimental resolution is $\sim$0.3 eV. Broadenings of $\sim$0.08 eV should be visible, but barely. We conclude that the disorder broadening of the Cu $2p_{3/2}$ spectrum of $\mathrm{Cu_{50}Au_{50}}$ is below the detection limit of $\sim$0.08 eV. Results obtained by numerical fitting of the experimental data (we obtained a disorder broadening effect with magnitude of 0.06 eV, but with an uncertainty of 0.06 eV) are consistent with this conclusion.

In order to understand the experimental observations, we carried out an *ab initio* simulation for the equiatomic Cu-Au alloy. The electronic structure was analyzed using a special quasirandom structure (SQS) technique, proposed first by Zunger *et al.*,[15] and discussed recently in detail in Ref. 16. The supercell SQS containing 64 atoms was constructed, and total energies were calculated using the projected augmented plane-wave method[17,18] as implemented in the Vienna *ab initio* simulation package.[19–22] Core-level binding-energy shifts at each site are obtained using the complete screening scheme[9,23] in conjunction with the $Z+1$ approximation in which a core-ionized atom with atomic number Z is simulated by the next atom in the Periodic Table, with atomic number $Z+1$. The energy cutoff was set to 300 eV in all calculations. Details of the calculations follow the scheme presented in Ref. 10, where the reliability of the present theoretical approach was also demonstrated.

Theoretical values of the CLS averaged over all the sites in the supercell are presented in Table I, where they are also compared to experiment. As one can see theory predicts the

CLS in good agreement with experiment. Two sets of theoretical values are given, for the supercell where all the atoms occupy the ideal sites of the fcc underlying crystal lattice (the unrelaxed system) and for the supercell where the ionic positions are optimized to zero forces acting on the atoms (relaxed calculations). The ionic displacements are induced by the large size mismatch for the alloy components, and represent the case of the so-called inhomogeneous lattice distortions.[16] The effect is known to be substantial for the Cu-Au system. We also notice that for Au the inclusion of local lattice relaxations substantially reduces the global average CLS, bringing it in closer agreement with experiment. In the case of Cu the theory slightly underestimates the average CLS, but is still in good agreement taking into account the experimental uncertainty of ±0.05 eV.

In order to estimate the disorder-induced broadening of the core-spectral lines, we proceeded as follows. Assuming a Gaussian distribution the FWHM of CLS about the mean may be calculated as $2\sigma\sqrt{2\ln 2}$, where σ is the standard deviation. Calculated values are presented in Table I. One can see that the estimated disorder broadening for the Au is in very good agreement with the experimental value. For Cu the theory predicts a very small value of the effect, just 0.03 eV, which is below the detection limit, in agreement with the experiment.

In order to understand the behavior observed experimentally we present in Fig. 2 calculated CLS at all the atoms in our supercell as a function of the number of their nearest neighbors of the opposite kind in the first coordination shell. In the figure the solid circles represent the CLSs at specific sites, while lines connect the CLSs, averaged over all sites with the same number of unlike nearest neighbors. The figure also compares the results obtained for unrelaxed supercell and relaxed supercell with fully optimized ionic positions. The inclusion of inhomogeneous lattice distortions has a dramatic effect on the predicted CLS for each local environment, and modifies the predicted disorder broadening and average CLS of both elements. The comparison between Cu [Fig. 2(a)] and Au [Fig. 2(b)] is striking.

Figure 2 demonstrates that there are two contributions to the total broadening: (i) an increase or decrease in the CLS as a function of number of unlike nearest neighbors, and (ii) a dispersion around this “average line.” In Fig. 2(a) we see that while there is still a dispersion of the CLS at individual Cu atoms, the averaged values turn out to be independent of the number of unlike atoms in the first coordination shell. This clearly reduces the total broadening, and takes it below the experimental detection limit. Moreover, the effect is clearly driven by the balance between two contributions. In calculations for the supercell with atoms at ideal lattice sites (unrelaxed supercell), the chemically induced local environment effects appear as an increase in the CLS at Cu atoms with increasing numbers of Au atoms in their first coordination shell. It should be possible to detect the predicted broadening, 0.09 eV from the unrelaxed supercell calculation. However, the inclusion of local lattice relaxations compensates for this increase almost exactly.

As a matter of fact, similar competition between the decrease in the CLS with increasing number of unlike neighbors in a supercell with ideal fcc underlying crystal lattice and its increase by the inhomogeneous lattice distortions is also seen for Au. But in this case the latter effect is even more pronounced than for Cu, to the extent that it completely reverses the trend seen for the unrelaxed supercell, leading to the overall increase in the CLS with increasing number of unlike nearest neighbors. Thus, in the case of Au the disorder-induced broadening is sufficiently strong to be detected in the XPS experiments.

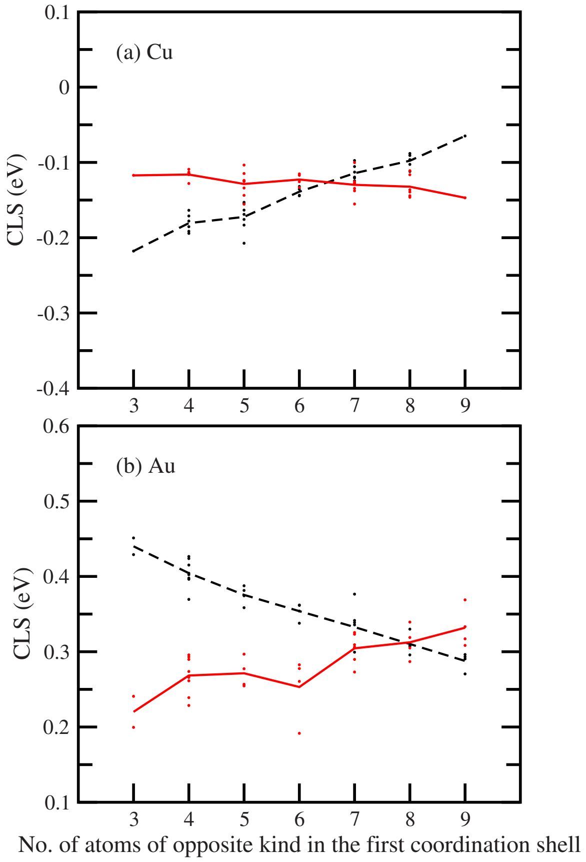

FIG. 2. (Color online) Dependence of core-level binding-energy shifts for sites in the unrelaxed (black dashed lines and symbols) and relaxed (red solid lines and symbols) geometries. Solid circles represent the CLSs at specific sites. Lines connect the average CLSs for all sites with a particular number of atoms of opposite kind in the first coordination shell.

The exploitation of core-level disorder broadening to probe specific local environments in disordered alloys is an exciting prospect, and efforts in this direction have recently begun. Jiang *et al.*[24] measured spectra of Auger electrons from $Ag_{50}Pd_{50}$ detected in coincidence with core-level photoelectrons. In principle varying the photoelectron selection energy allows environment-resolved Auger spectroscopy. We note that the very recent development of ultrahigh-resolution (0.05 eV) hard x-ray photoelectron synchrotron facilities[25] will take site-resolved spectroscopy to a new level, redefining the scope of electron spectroscopy of alloys. The computational results in Fig. 2 demonstrate that interpretation of such measurements could be qualitatively wrong if lattice relaxation is not accounted for.

In summary we have studied the effect of disorder-induced broadening of core-level photoelectron lines in a

$Cu_{50}Au_{50}$ alloy. As usual, we observe the disorder broadening for Au; it has a magnitude of 0.12 eV. On the contrary, the effect at Cu is below the detection limit of 0.08 eV. First-principles calculations of the site-resolved CLS in the alloy, modeled by a large supercell with a quasirandom distribution of Au and Cu at the sites of fcc underlying crystal lattice, reveal a much smaller broadening of Cu than Au. That is, a different behavior for two alloy components has been observed in this system. Based on the theoretical studies, we attribute the suppression of the disorder broadening of core-level photoelectron lines of Cu to the presence of a delicate balance between the dispersion of the CLS induced by the different local chemical environments of Cu atoms in a random alloy and the influence of inhomogeneous lattice distortions. For both Cu and Au sites in $Cu_{50}Au_{50}$, an approximately linear correlation between CLS and nearest-neighbor chemical composition remains, but lattice distortion reverses the sign of this relationship. Understanding this effect is vital to the development of environment-resolved experimental techniques based upon energy selection of core-level photoelectrons.

The EPSRC UK is acknowledged for support of NCESS and P.W. The Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF), and the Göran Gustafsson Foundation for Research in Natural Sciences and Medicine are acknowledged for financial support. Calculations were performed at Swedish National Infrastructure for Computing (SNIC).

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