Electronic structure of sputter-deposited alloy films: application to the Fe-Cu-Ag system

LETTER TO THE EDITOR

Electronic structure of sputter-deposited alloy films: application to the Fe–Cu–Ag system

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Abstract. We discuss the electronic structure of the FCC phase of sputter-deposited Fe–Cu–Ag ternary alloy films and determine theoretically their x-ray photoelectron spectra using the tight-binding linear muffin-tin orbital method and the coherent potential approximation. The calculated results are in good agreement with the experimental data.

There is an increasing interest in the study of artificially prepared compounds that do not exist in the equilibrium solid state. Important examples of such compounds are the metastable and homogeneous (not phase separated) alloy films prepared by vapour deposition on cold substrates [1–3]. This technique makes it possible to prepare the FCC and BCC phases of Fe–Cu [1–3] or Fe–Ag [3] binary alloy films over a wide range of composition despite negligible solid solubility of Fe in Cu or Ag. Recently, the FCC phases of the ternary Fe–Cu–Ag alloy films were also prepared [3] by the same technique and their valence electronic structure was studied by x-ray photoelectron spectroscopy (XPS).

In a recent paper [4], we have determined the electronic structure of binary Fe–Cu and Fe–Ag alloy films using the first-principles tight-binding linear muffin-tin orbital coherent potential approximation (TB LMTO CPA) method [5] and have successfully explained the XPS spectra from these alloys. In this letter we report similar calculations for the ternary Fe–Cu–Ag alloy films performed with suitable modifications in the TB LMTO CPA method necessary for substitutionally disordered ternary alloys. This letter presents the first application of the TB LMTO CPA method to disordered ternary alloy systems.

The TB LMTO CPA method can be straightforwardly generalised from the common case of binary [5] $A_{1-x}B_x$ or quasiternary [6] $A_{1-x}B_xC$ alloys to the case of ternary $A_{1-x-y}B_xC_y$ alloys. Below we summarise the basic equations. For details concerning the TB LMTO CPA method itself, we refer the readers to our recent papers [5, 7]. The Hamiltonian of the ternary alloy $A_{1-x-y}B_xC_y$ in the site representation, which describes the ferromagnetic phase, is

$$H^\sigma_{RL, R'L'} = C_{RL\sigma}\delta_{RR'}\delta_{LL'} + \Delta^{1/2}_{RL\sigma}(S^0(1 - \gamma_\sigma S^0)^{-1})_{RL, R'L'}\Delta^{1/2}_{R'L'\sigma}. \quad (1)$$

Here, R is the site index, $L = \{l, m\}$ is the orbital index ($l \leq 2$ for the transition and noble

metals), and σ is the spin index. The quantities $\mathbf{X} = \mathbf{C}, \mathbf{\Delta}, \boldsymbol{\gamma}$ are matrices diagonal with respect to the site, orbital and spin indices (R, L, σ), whose matrix elements $X_{RL\sigma}$ randomly take three different values $X^Q_{L\sigma}$ (Q = A, B, C) for each spin σ with probabilities

$$c^Q: \qquad c^A = 1 - x - y \qquad c^B = x \qquad c^C = y \left(\sum_Q c^Q = 1 \right).$$

The potential parameters $C^Q_{L\sigma}$, $\Delta^Q_{L\sigma}$ and $\gamma^Q_{L\sigma}$, obtained from the solution of the radial Schrödinger equation for the LDA (local density approximation) potential in the sphere centred at the lattice site R, can be combined to give the potential functions

$$P^Q_{L\sigma}(z) = (z - C^Q_{L\sigma})/[\Delta^Q_{L\sigma} + \gamma^Q_{L\sigma}(z - C^Q_{L\sigma})].$$

The potential functions have a direct physical meaning; they are proportional to cotangents of phase shifts of the corresponding LDA potentials. The structure of the lattice enters the theory via a non-random and spin-independent structure constant matrix, S^0, with elements $S^0_{RL,R'L'}$ known analytically [8]. The configurational averaging of the Green function is done in a suitably chosen LMTO basis, where it can be performed without limitations inherent to the empirical TB CPA method and, in the end, the results are transformed back to the original basis in which the Hamiltonian (1) is written [5, 7]. This procedure can be applied to ternary alloys, and the basic CPA equations, to be solved independently for each spin direction are,

$$\Phi_{L\sigma}(z) = \sum_Q c^Q (P^Q_{L\sigma}(z) - \Omega_{L\sigma}(z))^{-1} \qquad \Omega_{L\sigma}(z) = \mathcal{P}_{L\sigma}(z) - \Phi^{-1}_{L\sigma}(z)$$

$$(2)$$

$$\Phi_{L\sigma}(z) = \frac{1}{N} \sum_k [(\mathcal{P}(z) - S^0(k))^{-1}]_{L\sigma,L\sigma}.$$

The site-diagonal coherent potential function $\mathcal{P}_{L\sigma}(z)$ is, by symmetry of the lattice, diagonal also with respect to the orbital index L. The quantity $S^0_{LL'}(k)$ is the Bloch transform of $S^0_{RL,R'L'}$ and the sum runs over the k-vectors of the irreducible wedge of the Brillouin zone. Once the CPA equations (2) are solved, the local densities of states (DOS) on atoms of a given type Q, orbital symmetry L and with spin σ, as well as the total DOS are found from

$$g^Q_{L\sigma}(E) = -(\mathrm{d}P^Q_{L\sigma}(E)/\mathrm{d}E) \, \mathrm{Im}(P^Q_{L\sigma}(E) - \Omega_{L\sigma}(E + \mathrm{i}0))^{-1}$$

$$g(E) = \sum_Q \sum_L \sum_\sigma c^Q g^Q_{L\sigma}(E). \qquad (3)$$

The XPS photocurrent $I(E + \omega)$ can be written as [9]

$$I(E + \omega) \propto \sum_Q \sum_L \sum_\sigma c^Q M^Q_{L\sigma}(E + \omega) g^Q_{L\sigma}(E) \Theta(E_F - E) \qquad (4)$$

where $\Theta(x)$ is the Fermi factor: $\Theta(x) = 1$ for $x > 0$, $\Theta(x) = 0$, otherwise. E_F is the alloy Fermi level and $M^Q_{L\sigma}(E + \omega)$ is the photoionisation cross-section calculated over the energy range of the DOS functions for an incident photon energy ω (the Kα-line of Al with $\omega = 1486.6$ eV in our case). We approximate [4] $M^Q_{L\sigma}(E + \omega)$ by its atomic counterpart $M^Q_d(\omega)$, which is tabulated [10] and gives a reasonable description for transition and noble metals with a dominant d state contribution. Through its dependence on $M^Q_d(\omega)$, the XPS photocurrent may be very different from the total DOS given by equation (3).

The last remark concerns the choice of the potential parameters $X^Q_{L\sigma}$, where $\mathbf{X} = \mathbf{C}$, $\mathbf{\Delta}, \boldsymbol{\gamma}$. We use as an input the potential parameters corresponding to atomic sphere

potentials of pure constituents evaluated at their, generally different, equilibrium Wigner–Seitz radii. These 'frozen' atomic potentials are for approximately neutral spheres and are related to a common energy zero, thus allowing us to relate them properly on the energy scale without performing self-consistent calculations [11, 7, 4]. Such transferability of pure constituent potential parameters is generally not valid for the ferromagnetic case as the magnetic moments (and hence the level splitting) can change significantly on alloying. Fortunately, in the present case the magnetic moments on Fe atoms remain essentially constant over a broad concentration range in Fe–Cu or Fe–Ag films [2, 3]. The reason [2] for this is that Cu or Ag atoms, with their d states situated well below the Fermi level (E_F), only weakly affect the alloy electronic structure around E_F which is decisive for magnetic behaviour [8], as their d states are situated well below E_F. We thus use, as in our previous paper [4], the ferromagnetic potential parameters for Fe and the paramagnetic potential parameters for Cu and Ag, all evaluated at their equilibrium Wigner–Seitz radii.

We have evaluated the DOS as well as the XPS spectra for the Cu-rich and Ag-rich alloys with the FCC lattice structure. Particularly the alloys $Fe_{0.38}Cu_{0.09}Ag_{0.53}$ and $Fe_{0.44}Cu_{0.46}Ag_{0.10}$, which were both magnetic at the measurement temperature [3], were studied. The results are presented in figures 1 and 2. The ratios $M_d^{Fe} : M_d^{Cu} : M_d^{Ag} = 1 : 2.5 : 4.5$ used in the evaluation of the XPS spectra according to (4), are similar to those used in [4]. To make the comparison with the experiment as close as possible, we have simulated the effects of lifetime and resolution broadening by folding the theoretical $I(E + \omega)$ curves with a Lorentzian of full half-width Γ of 0.03 Ryd:

$$\tilde{I}(E) \propto \int_{-\infty}^{\infty} \frac{I(\eta)}{(E - \eta)^2 + \Gamma^2} \, d\eta. \tag{5}$$

Other quantities of interest are the d density of states

$$g_d(E) = \sum_Q \sum_\sigma c^Q g_{d\sigma}^Q(E)$$
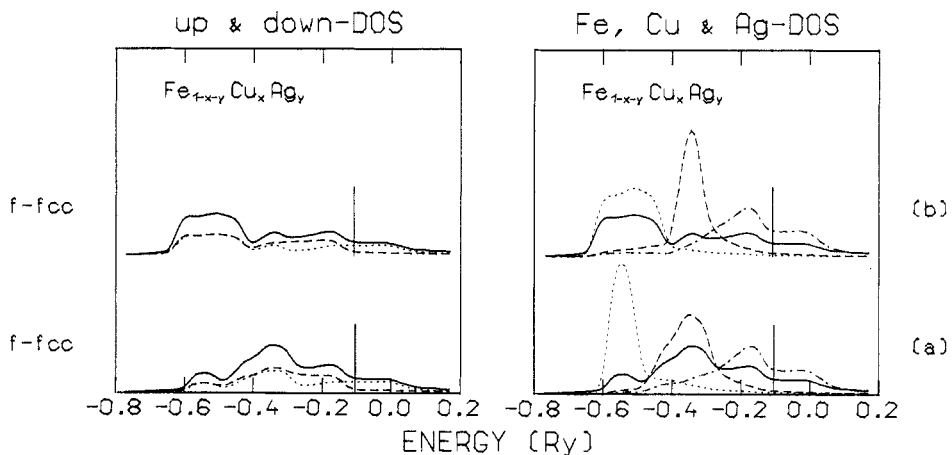

Figure 1. The total densities of states of sputter-deposited $Fe_{0.44}Cu_{0.46}Ag_{0.10}$ (*a*), and $Fe_{0.38}Cu_{0.09}Ag_{0.53}$ (*b*) alloy films (full curves) and their decomposition. Left-hand figure: the minority-spin (up) DOS (———) and the majority-spin (down) DOS (· · · ·). Right-hand figure: the local DOS on Fe (–·–·), Cu (———) and Ag (· · · ·) atoms, not concentration weighted. The lattice structure (FCC) and the magnetic state (f ferromagnetic) are indicated. The long vertical lines denote the position of the alloy Fermi levels. All densities of states are in arbitrary units.
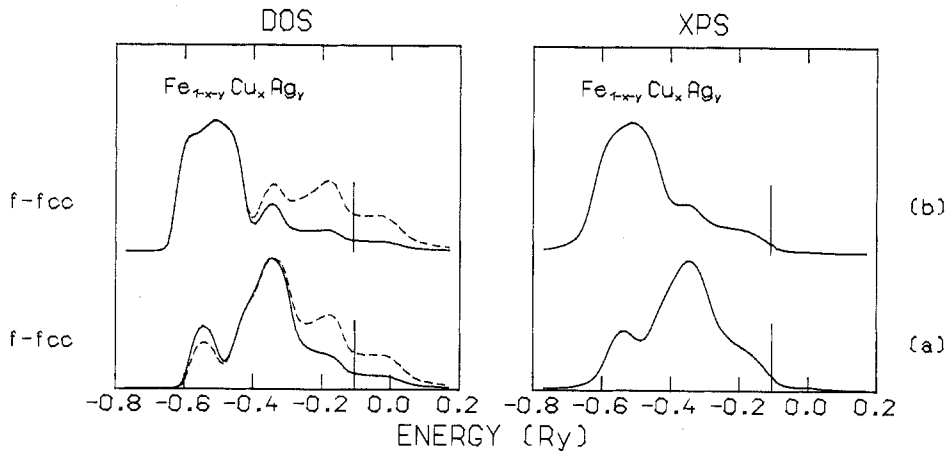
Figure 2. The xps spectra and related quantities of sputter-deposited $Fe_{0.44}Cu_{0.46}A_{0.10}$ (*a*), and $Fe_{0.38}Cu_{0.09}Ag_{0.53}$ (*b*) alloy films. Left-hand figure: the weighted d DOS (full curves) and d DOS (broken curves). Right-hand figure: the xps spectra broadened with a Lorentzian of full half-width 0.03 Ryd. The $M_d^{Fe} : M_d^{Cu} : M_d^{Ag}$ ratio is 1 : 2.5 : 4.5. All curves are normalised to a common maximum height 1 to facilitate their mutual comparison. The lattice structure (FCC) and the magnetic state (ferromagnetic) are indicated. The long vertical lines denote the position of the alloy Fermi levels.

and the weighted d density of states

$$g_d^w(E) = \sum_Q \sum_\sigma c^Q M_d^Q(\omega) g_{d\sigma}^Q(E)$$

which will be used to illustrate the effect of different values of the photoionisation matrix elements M_d^Q.

The d bands of pure Fe, Cu and Ag crystals extend over the energy regions $(-0.5, 0.1)$ Ryd, $(-0.55, -0.1)$ Ryd and $(-0.7, -0.35)$ Ryd, respectively. The minority- and majority-spin DOS nearly coincide in the energy region where the Ag or Cu d states dominate. This indicates negligible spin polarisations of these states in comparison with those on Fe atoms. We note that the local DOS on Fe atoms are similar in both cases, while the Cu and Ag DOS differ significantly, depending on which component, Ag or Cu, is the majority or the minority one. In other words, the Cu(Ag) atoms in $Fe_{0.38}Cu_{0.09}Ag_{0.53}$ ($Fe_{0.44}Cu_{0.46}Ag_{0.10}$) exhibit sharp, impurity-like behaviour. We also note that the Ag states are nearly separated from the Fe states on the energy scale, invoking the split-band regime of the alloy theory, which can be treated satisfactorily within the CPA. The other noticeable feature is the matrix element effect which destroys the similarity between the DOS and the xps spectra commonly seen in pure crystals and some transition metal (e.g. CuNi or AgPd) alloys [12]. Because the photoionisation matrix elements of both Cu and Ag atoms are much larger than those of Fe atoms [10], the contribution of the latter to the xps spectra manifests itself only as a shoulder below the Fermi level despite large Fe-concentrations (0.44 and 0.38). The theoretical xps curves agree reasonably well with the ones given in [3]. We note that for states below E_F, the weighted d DOS could be considered as the theoretical unbroadened xps spectra.

In conclusion, we have developed a simple theory of the xps of the FCC-based ferromagnetic ternary alloy films FeCuAg. Our treatment is based on the first-principles TB LMTO CPA method and takes into account the pronounced differences in the photoionisation cross-sections of the different types of atoms involved. Our computed xps spectra agree well with recent experimental results [3].

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