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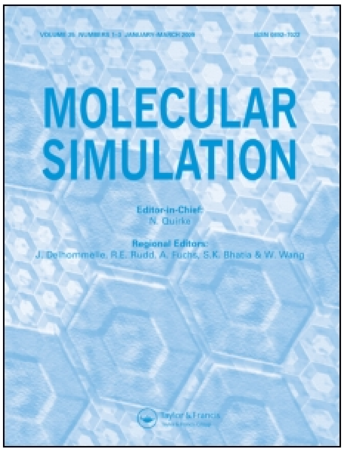

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EXPERIMENTAL INVESTIGATION OF THE ELECTRONIC STRUCTURE IN METALLIC SOLIDS

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The recent advances in calculational schemes involving density functional theory permit numerically accurate determinations of the electronic structure in ordered and disordered alloys. In order to establish the validity of the calculations and to investigate the electronic mechanism responsible for phase stability, for example, an experimental technique is required which probes the electronic spectral density in k-dependent detail. We demonstrate that angle-resolved photoemission measurements in association with photocurrent calculations based on a realistic model can provide such a technique.

KEY WORDS: Photoelectron spectroscopy, photocurrent calculations, electronic structure, alloys, order-disorder transformations

INTRODUCTION

Metallic alloys form a large class of scientifically interesting and technologically important materials. Since design engineers are usually constrained by the limitations of the materials available to them there is a strong motivation for the introduction and development of alloys with superior properties. In their efforts to create materials with higher strength to weight ratios, improved magnetic or electrical properties, for instance, metallurgists and materials scientists have tended to rely on, at best, empirical rules or, at worst, guess-work. However, it has been recognised for many years that the physical and metallurgical properties of metals and alloys are related directly to the underlying electronic structure (i.e., the distribution of electrons in space, energy and momentum). In order to understand such properties quantitatively, therefore, with the possibility of modifying and manipulating them to advantage, it is essential that realistic and parameter-free (i.e., first-principles) models be developed which describe the electron states. It is equally important, of course, that the results of such calculations are tested and verified experimentally.

During the past decade or so we have witnessed considerable progress in both the development of suitable experimental probes and in the theory of alloys. In the case of the former there has been the introduction of angle-resolved uv photoelectron spectroscopy (ARUPS)[1], in the case of the latter there has been the development of the KKRCPA[2]. Despite its mean field nature, the KKRCPA has proved to be rather more than adequate for first-principles calculations of electron states and the development of the statistical mechanics of compositional and magnetic configurations on the basis of the electronic structure. Furthermore, and conveniently, it provides a scheme for calculating, on the same footing, photocurrent spectra which greatly assists the interpretation of ARUPS measurements. Together, these advances provide an opportunity to investigate many of the central issues in metal-physics from a fully electronic point of view[3]. Potentially, such work can lead to a deeper understanding of the principles governing stability and the phase diagram, strength, transport properties, magnetism, etc. and can have, therefore, a considerable impact on the design and optimisation of alloys for specific applications.

There can be little doubt that ARUPS[1] can play an important role in the investigation of the electronic structure in metallic solids. Prior to its introduction in the 1970's, there was little detailed experimental information available about electron energy bands except in some ordered systems at the Fermi level principally through measurements of the de Haas-van Alphen effect. Most spectroscopies, such as soft x-ray, optical absorption and angle-integrated photoemission, produce spectra which are effectively an average over the Brillouin zone and reveal only the gross features of the density of states. In contrast, ARUPS provides data which can be interpreted, more or less directly, in terms of wave-vector (k) conserving transitions. By measuring the kinetic energies of the photoelectrons in a particular direction for different photon energies, for instance, one obtains information which is related to the spectral density of electrons as a function of energy and k, i.e., the electronic structure. Thus, in principle, theories and calculations can be confronted in a most direct and profound way.

The electronic spectral density plays a central role, therefore, in our approach towards a fundamental understanding of the properties of metals and alloys[3]. From the spectral density one can calculate the sum over the 1-electron eigenvalues, i.e., the structural dependent part of the total electronic energy, and determine a range of ground state properties such as the structure, lattice spacing, bulk modulus, magnetic moment, etc.; clearly, such information can have an important role to play in the design of alloys for specific applications[4]. In addition, one can determine the response of the electron system to external perturbations, e.g., the generalised susceptibility and the electrical conductivity. Furthermore, schemes have been developed which permit the calculation of concentration correlation functions[5] on the basis of the spectral function; these theories have application in studies of, for instance, short-range ordering, Guinnier-Preston zones and the subtle interplay between magnetism and composition and their role in phase stability.

Nowadays, nearly all electronic structure calculations are carried out within the framework of density functional theory (DFT), usually by invoking the local (spin) density approximation. The ground state properties of pure metals and ordered compounds with a few atoms per unit cell can be calculated with relative ease and are often in very good agreement with experimental measurements[6,7]. In the case of random alloys the KKRCPA method provides a (complementary) way of solving the Schrödinger equation that is of sufficient accuracy to permit its use in a global theory of alloys which treats the electronic structure and ground state properties on an equal footing. The 1-electron Bloch spectral function, $A_B(k,E)$[2], which represents the density of states at energy E and reduced wave-vector k, can be calculated reasonably straightforwardly within the KKRCPA, including charge self-consistency and, where appropriate, spin-polarisation and relativity[8,9,10].

In this paper we focus our discussion on probing the spectral function. We describe the photoemission process and show that the electronic spectral density can be probed more or less directly by ARUPS. Experimental spectra often contain a wealth of detail and quantitative interpretation is best achieved through comparisons with photocurrent calculations in which the many-body effects, the effect of the surface, etc., are taken into account. Accordingly, we indicate the calculational scheme and we demonstrate the effectiveness and potential of the combined experimental/theoretical approach by showing some results from a study of a *Cu*-Ni alloy. We conclude with a review of some recent results from studies of order-disorder transformations in CsCl-bcc and L12-fcc systems.

THE PHOTOEMISSION TECHNIQUE

In a photoemission experiment monochromatic photons of energy ω are incident upon the clean surface of a sample. Providing ω is greater than the work function of the sample photoelectrons are emitted through the surface; in an angle-resolved experiment the current of photoelectrons is measured as a function of energy, angle and, in the latest generation of experiments, spin. We shall not deal with details of the practical arrangement here but refer the reader to the other sources[1,3].

The Theoretical Model

(We have already alluded to the contribution that DFT has made in accurate calculations of the ground state properties of metals and alloys. However, DFT has little to say about electronic excitation energies and in using DFT eigenvalues or energy bands to interpret photoemission we are neglecting all final state interactions, relaxation, decay, etc. Nevertheless, one can still use DFT as a physically motivated approximation scheme and as we shall see in the examples we are concerned with it works rather well; in other systems it may well fail. When we use a single particle picture in our discussion we have DFT in mind and we shall refer to DFT bands as 1-electron bands or ground state bands more or less interchangeably.)

In a perfect (i.e., ordered) crystal the initial and final states correspond to definite crystal momenta k' and k, respectively. If the initial and final state energies are $E_n^0(k')$ and $\varepsilon(k)$, respectively, and q the photon momentum, the 1-electron approximation for the photocurrent into the detector in an angle-resolved experiment is given by the Golden rule and can be written[11], (we will use atomic units unless otherwise stated):

$$I^0(K_{\|},\omega,\varepsilon) = 2\pi\Sigma_{n,k'} \,|<\Psi(\varepsilon,k)|\,\Delta\,|\Psi(E_n^0, k')>|^2\, \delta(\varepsilon(k) - E_n^0(k') - \omega) \times \delta(k - k' - q) \;\ldots \tag{1}$$

where the electron-photon interaction $\Delta = -\alpha A.p = i\alpha A.\nabla v/\omega$ (α is the fine structure constant, A is the photon vector potential, p is the electron momentum and v is the potential in which the electron moves). For photon energies in the uv $|q|$ is negligible compared with the Brillouin zone dimensions and so the transitions from initial to final states are vertical (sometimes called direct) in the reduced zone scheme. We simplify eq. (1) by putting $E = \varepsilon - \omega$ so that

$$I^0(K_{\|},\omega,\varepsilon) \sim \Sigma_n \,|<m|\Delta|n>|^2\, A_n^0(k,E) \quad \ldots \tag{2}$$

where $|n>$ is an initial (occupied) state, $|m>$ is the final state of the system which propagates into the detector and

$$A_n^0(k,E) = \delta(E - E_n^0(k)),$$

where n is the band index. In crossing the sample surface the parallel component of the photoelectron wave-vector is conserved, mudulo a surface reciprocal lattice vector, i.e., $K_\parallel = k_\parallel + g_\parallel$. The electron state at the detector is a plane wave, $|K_\parallel, \varepsilon>$ with, if the detector is set at an angle θ to the surface normal,

$$|K_\parallel| = [2(\varepsilon - V_0)]^{1/2} \mathrm{Sin}\theta$$

where V_0 is the vacuum level. The final state inside the crystal can be expressed as a time reversed LEED state[12], i.e.,

$$|m> = G_2^- |K_\parallel, \varepsilon>$$

where G_2 is the Green function for the photoelectron. We put

$$A^0(k,E) = \Sigma_n A_n^0(k,E) = \Sigma_n \delta(E - E_n^0(k)) \quad \ldots \qquad (3)$$

and this expression, a sum of delta-function peaks whose loci in (E,k) space trace the band structure, is the ground state spectral function. If we ignore the band index n and wave-vector k dependence of the matrix elements then I^0 is proportional to the spectral function given by equation (3). Thus, equation (2) and (3) imply that the photoelectron spectrum from an ordered system will consist of a set of sharp peaks, modulated by matrix elements, at energies corresponding to the 1-electron eigenvalues of the system. In the case of a disordered alloy, the picture is a little more complicated since the spectral function is no longer a set of δ-function peaks[2], see Figure 1. Nevertheless, the approach is still valid.

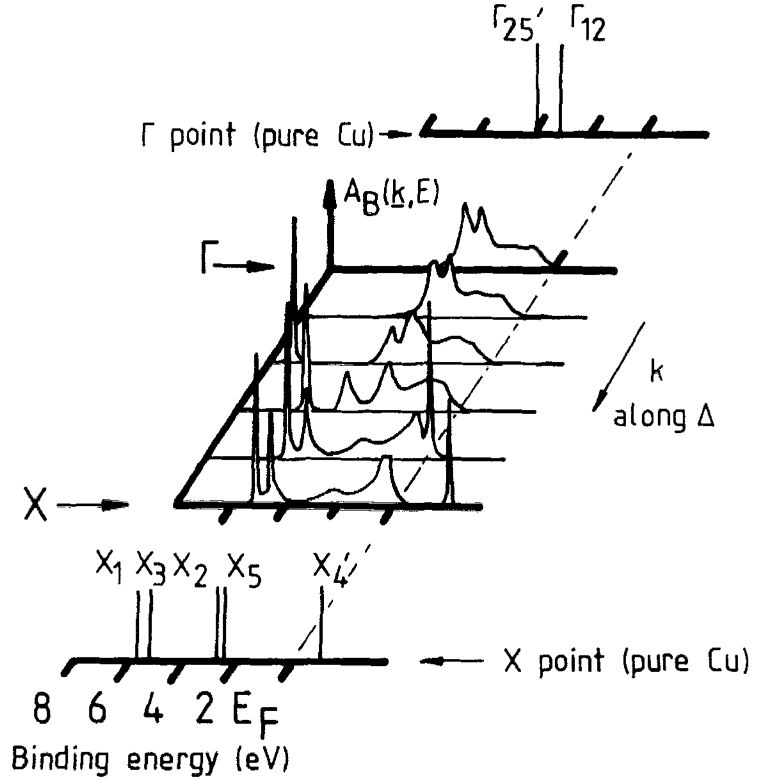

Figure 1 The spectral function for Cu-23%Ni along the ΓX direction calculated using the KKRCPA. Also shown are the corresponding features for pure Cu at the Γ and the X points.

It is now clear why photoemission can be such a powerful probe of the electronic structure in order and disordered systems. If we neglect the effect of the surface, i.e., replace $|m>$ by the plane wave that travels to the detector, to zeroth order the photocurrent given by equation (2) and (3) provides a direct picture of the spectral function modulated by simple electron-photon matrix elements. In fact, this result is valid beyond the non-interacting limit; it is still possible to derive the photoelectron spectrum from the 1-particle spectral function in the presence of interactions between the electron-hole pair produced in the photoemission process and the surrounding electrons, as we shall now show. For simplicity we continue with an ordered system.

Following the creation of the electron-hole pair many-body interactions will occur and the system begins to relax[13]. The key quantity for describing this behaviour is *the self-energy, $S_n(k,E)$, which represents the generalised correction to the 1-electron* eigenvalues. The spectral function for the non-interacting system given in equation (3) can be written in terms of the 1-electron Green function, i.e.,

$$A_n^0(k,E) = -(1/\pi)\, Im\{G_n^0(k,E)\}$$

where

$$G_n^0(k,E) = (E - E_n^0(k) + i\mu)^{-1}.$$

(When the limit $\mu \rightarrow 0^+$ is taken, $A_n^0(k,E) = \delta(E - E_n^0(k))$.) In the presence of interactions, the modified Green function becomes

$$G_n = G_n^0 + G_n^0 S_n G_n = (E - E_n^0(k) - S_n(k,E))^{-1}$$

The self-energy has real, $\Delta_n(k,E)$, and imaginary, $\Gamma_n(k,E)$, parts (related through a Hilbert transformation) and so the spectral function for the interacting system becomes, therefore,

$$A_n(k,E) = \frac{1}{\pi}\frac{|\Gamma_n(k,E)|}{[E - E_n^0(k) - \Delta_n(k,E)]^2 + [\Gamma_n(k,E)]^2} \qquad \ldots \qquad (4)$$

Providing Γ_n is not too large equation (4) will have resonance maxima whenever $E = E_n = E_n^0(k,E) + \Delta_n(k,E)$. The corresponding photoemission spectrum will now be peaked at energy E_n with FWHM $\sim 2|\Gamma_n|$. If Δ_n varies slowly near resonance then a single solution picks up most of the spectral strength and the main features of the 1-electron spectral function remain distinct, although broadened and shifted (by Δ_n) from their ground state values. Thus, comparisons between photoelectron spectra and band structure calculations are still possible, viz: the noble metals. However, if the self-energy disperses rapidly then the quasi-particle picture of a well defined hole breaks down and the spectral strength is spread over a number of excitations[13]. In this regime direct comparisons become very difficult.

If we unfold the square in equation (2) and use the identity

$$\Sigma_n |n> \delta(E - E_n^0(k)) <n| = -(1/\pi)\, Im\{G_1^+\},$$

where G_1 is the Green function for the initial state, we find that

$$I^0(K_\parallel, \omega,\varepsilon) = -(1/\pi) \;\; <K_\parallel, \varepsilon| G_2^+ \, \Delta Im\{G_1^+\} \Delta^* G_2^- |K_\parallel,\varepsilon> \qquad \ldots \qquad (5)$$

This expression forms the basis for photocurrent calculations. A scheme was developed by Pendry[12] using a layer multiple scattering formalism for a model consisting of a semi-infinite array of muffin-tin potentials separated from the vacuum by a surface barrier potential, represented by a step function. (The height of the latter is the sum of the Fermi energy and work function). The photocurrent, therefore, therefore includes contributions from the surface and the bulk layers. The many-body interactions are treated by simply taking into account the finite lifetimes of the hole and photoelectron states separately through the inclusion of (usually different) imaginary parts to the inner potential for the low and high energy states.

The first calculations using this approach were made for metals with the so-called PEOVER1 computer code[14]. Subsequently, the code was generalised to deal with ordered systems with more than 1 atom per unit cell – the NEWPOOL and NEWPOOLN codes[15] – and, by combining the KKRCPA ideas with the layer multiple scattering techniques, to disordered alloys[16]. Variations in composition normal to the sample surface can be taken into account within this scheme and so surface enrichment, for instance, may be included. During the past 12 months the codes for both ordered and disordered systems have been extensively modified to include relativistic effects[17].

Attempts have been made to calculate the self-energies in a number of 3d transition metals[18]. Although the various approaches are rather difficult they appear to show that for the d-bands $S_n(k,E)$ depends only on E, i.e., to a good approximation, $S_n(k,E) \rightarrow S(E) = \Delta(E) + i\Gamma(E)$. As a result, self-energy effects may be introduced into photocurrent calculations by renormalising the non-interacting spectrum, viz:

$$I(K_{\parallel},\omega,\varepsilon) = \frac{1}{\pi}\int \frac{|\Gamma(\varepsilon)|\, I^0(\omega,E')}{[\varepsilon - E' - \Delta(\varepsilon)]^2 + [\Gamma(\varepsilon)]^2}\, dE' \quad \ldots \qquad (6)$$

where $I^0(K_{\parallel},\omega,E')$ is given by equation (5). (A similar expression was derived by Durham[19] to include correlation effects in soft x-ray emission spectra.) However, it appears that only limited work has been carried out along these lines. We have not included self-energy effects in this way in the calculations in this paper although we have used 'realistic', but energy independent, values for the lifetimes of the hole and photoelectron states.

Comparisons With Experiment

We demonstrate the quality of the agreement between theory and experiment that can be achieved by selecting one example. We choose our study of the k-dependence of the disorder-broadening in a *Cu*-Ni alloy[20]. The calculated spectral function for Cu-23%Ni along the ΓX direction is shown in Figure 1. The Ni-related 3d-states, which lie about 0.5eV below E_F, appear as a broad feature at the Γ point because of considerable disorder-broadening. However, the feature sharpens up and moves slightly towards E_F as the X point is approached, where it is possible to resolve the Ni-related X_2 and X_5 states. According to our previous discussion such detail should be observable in an ARUPS experiment since in a direct transition picture varying the photon energy at normal emission from the (100) surface of a single crystal is equivalent to probing the spectral function along the Δ direction at a rate determined by the dispersion of the initial and final states. In such an experiment the changes are seen clearly in photoelectron spectra through variations of the ratio of the intensities of the Ni and Cu peaks (at ~ 0.5eV and ~ 2.5eV binding energies, respectively) with photon energy as shown in Figure 2a. The range $20\text{eV} < \omega < 140\text{eV}$ corresponds to scanning from near $X \rightarrow \Gamma \rightarrow X \rightarrow \Gamma$, etc. and there is excellent agreement between measurements and photocurrent calculations, not only in the positions of the maxima

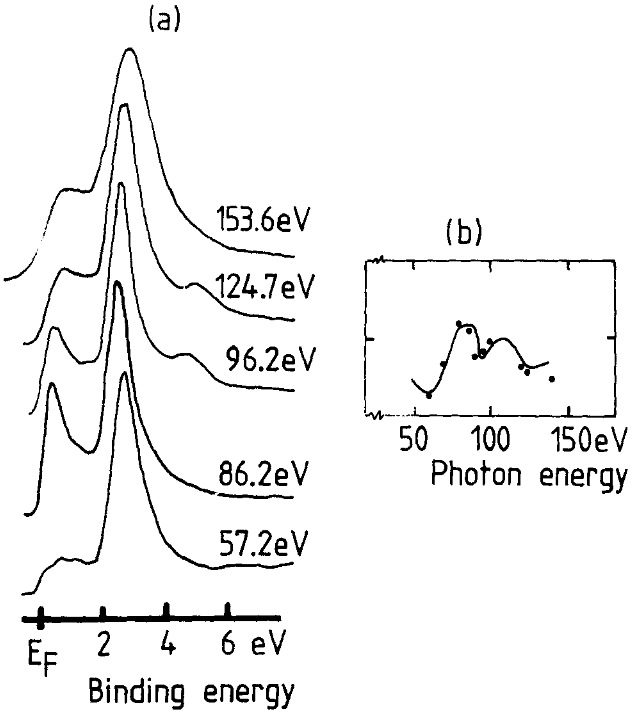

Figure 2 (a) Normal emission spectra from the (100) surface of a Cu-23%Ni alloy as a function of photon energy, p-polarisation, photon incidence angle = 20%. The Ni and Cu features occur at 0.5eV and 2-3eV binding energy, respectively. (b) Comparison between the measured and calculated ratios of the intensities of the Ni and Cu features in photoemission spectra as a function of photon energy.

and minima but in amplitude also[20], see Figure 2b. To achieve this level of agreement we assumed an alloy of uniform composition with a surface layer of pure Cu, as was indicated by independent AES studies. The minima at 60eV and at 125eV correspond to emission from near the Γ point and the maximum at ~90eV to emission from the *X* point. The dip in the data near 90eV, which is reproduced in the calculations, is due to a final state band gap at the *X* point some 90eV above E_F. In addition, the measurements confirm the small change in binding energy of the Ni-related feature referred to above. We believe this experiment, therefore, provides a dramatic demonstration of the combined power of angle-resolved photoemission measurements and proper theoretical analysis to test a key effect in electronic structure calculations in alloys. Furthermore, it shows that the effects of surface segregation can be treated quantitatively in the model.

RECENT STUDIES OF ORDER-DISORDER TRANSFORMATIONS

In the previous section we showed that photoemission measurements when combined with proper first principles analysis are an appropriate probe of the surface and bulk electronic structure in alloys. Since photoemission measurements can be carried out over a range of temperature we have the opportunity to address many of the interesting and complex issues in alloy physics directly in electronic terms. One such topic order-disorder transformations which, in contrast to the example above perhaps, are of particular interest to the materials scientist who is attempting to design alloys[3,4].

Order-disorder transformations in alloys arise because of competition between interatomic forces. The question concerning the origin of the driving force for the transformation has been addressed in three different ways. The first is the Landau theory of second order (continuous) phase transitions, based on symmetry and group theoretic arguments. In the second approach the configurational part of the energy of an alloy is described as a sum over pairwise interactions which permits the application of statistical mechanics of arbitrary complexity. The third approach is based on the fact that interatomic forces are determined by electrons and so the energies of ordering can be considered in terms of the total electronic energies of the ordered and disordered phases. However, the first two schemes are phenomenological with limited predictive power. As far as the third approach is concerned calculations along these lines are now a practicable proposition through the application of DFT. But ordering energies are very small (< 0.1eV) compared with total energies (10^4—10^5eV) and an accurate calculation of the total energy as a function of long range order parameter is a very stiff test of any theory of disorder, and, apart from some very recent calculations on AgZn (see below), little detailed work has been attempted along these lines. Furthermore, total energy calculations are rather 'brutal' in the sense that they give very little insight into the underlying mechanisms that drive order-disorder transformations.

In order to address the problem more quantitatively we need to consider a scheme which provides an accurate k-dependent description of the electronic structure. This immediately suggests an extension of the third approach that is based on determining the spectral function in the ordered, partially ordered and disordered states through a combination of calculation and experiment. We describe the electronic structure in the ordering system, therefore, in terms of a generalised Bloch spectral function $A_B(k,E,S)$ where S is the long-range order parameter[3,21]. (This quantity is of particular interest because it is related to the structure sensitive part of the total energy from which the thermodynamics of ordering can be derived, and it contains the information about the electronic driving forces behind the transformation—densities of states, Fermi surface mechanisms, etc.) When $S = 1$ the spectral function reduces to that of the ordered system, i.e. a sum of delta-functions at the Bloch eigenvalues. When $S = 0$ the spectral function corresponds to that of the random alloy, which as seen in Figure 1, comprises broadened peaks of different heights and widths that vary in a complex way with E and k. Furthermore, since the space groups of the two phases are different additional effects will arise because of the change in symmetry. Thus, it is clear that there may be substantial differences between $A_B(k,E,S = 1)$ and $A_B(k,E,S = 0)$. For $0 < S < 1$ we suppose that the spectral function will vary between these extremes in some complicated way. However, since the long range order parameter varies in a known way with temperature it would appear that photoemission spectra as a function of temperature might be a useful probe of the generalised spectral function. Some idea of the potential of this approach can be gained by recent studies of CuZn by Temmermann et al[22] and AgZn by Jordan et al[23] which undergo a transformation from a high temperature substitutionally disordered bcc (β) phase to a low temperature CsCl (β') phase.

Theoretical Study Of The Transformation In CuZn

In Figures 3a,b we show the electronic structures in ordered and disordered CuZn along the Σ direction. (Note that $|\Gamma M| = |\Gamma N|$ and so no folding back occurs in this direction.) The alloy exhibits extreme split-band behaviour and only the Cu d-states and states of s-p symmetry are shown in the Figure. Because the scattering in the d-channel on the Zn sites at these energies is very small, the topology of the dispersion of the Cu-d states in the β-phase resembles 'bcc Cu' with a reduced overall bandwidth. In contrast, the Cu d-states in the β'-phase are very similar to those of 'simple cubic Cu' with the lattice spacing of CuZn. These differences show up in the photocurrent calculations shown in Figures 4a,b for emission normal to the (110) faces. Changing the photon energy here corresponds to probing the initial states along the Σ direction, in the case of the β'-phase direct transitions occur near the Γ point for $\omega = 1.2\,H$ and at $k \sim 2/3$ of the ΓM distance for $\omega = 0.4\,H$. For the particular arrangement chosen initial states with Σ_4 symmetry are excited in s-polarisation (with the vector potential in the surface plane) while those with Σ_1 and Σ_3 symmetry are excited in p-polarisation (orthogonal to s-polarisation with components parallel and perpendicular to the sample surface). The positions of these states predicted by a direct transition model are shown. The spectra for s-polarisation are particularly simple and follow the dispersion of the Σ_4 band quite closely. The most prominent peak in the spectra for p-polarisation, however, is not a 'bulk' feature at all, but a surface state lying in the Σ_1 gap where a free-electron Fermi surface would push through the Brillouin zone face. The remaining features correspond to Σ_1 and Σ_3 bulk bands. The presence of the lower parts of the s-p band are faintly visible for the lower

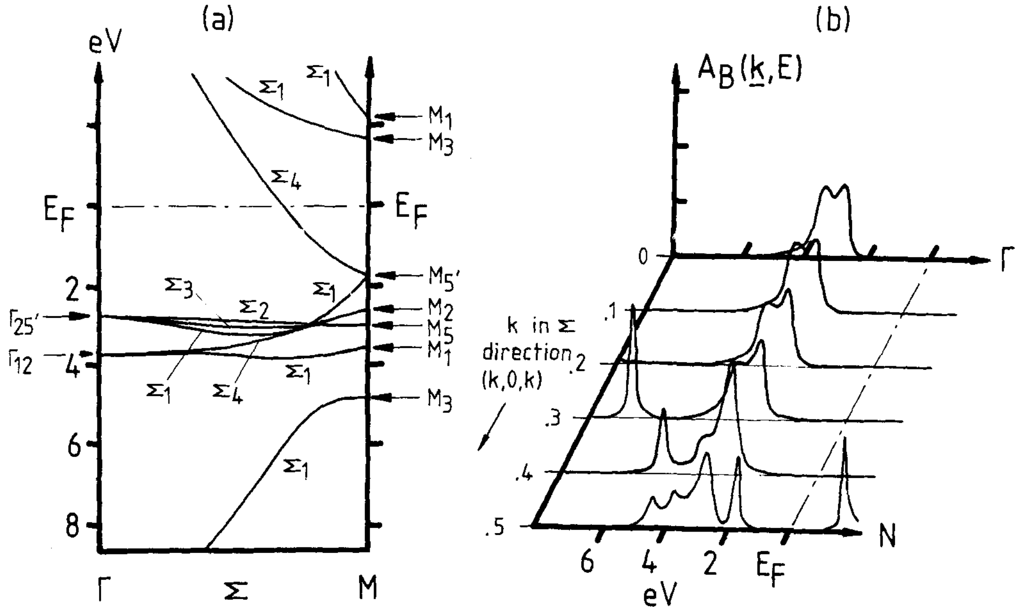

Figure 3 (a) The band structure for β'-CuZn (CsCl-structure) along the Σ direction calculated using the KKR. (b) The Bloch spectral function for β-CuZn (disordered bcc structure) along the Σ direction calculated using the KKRCPA.

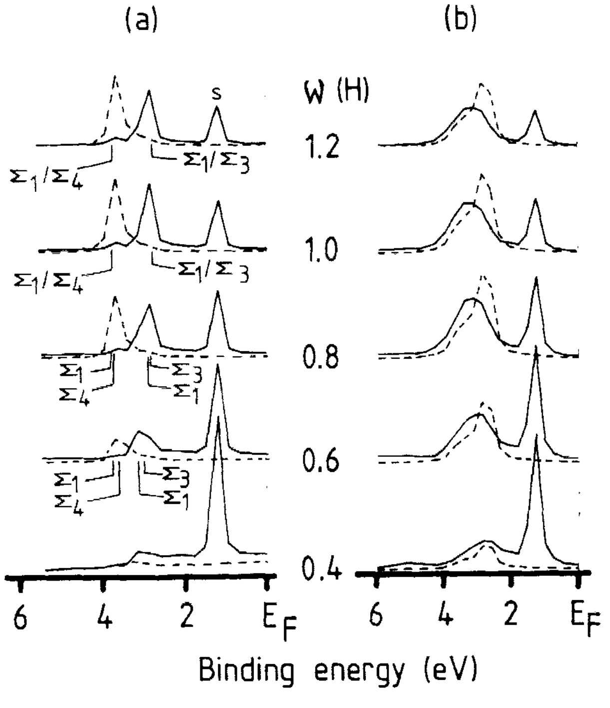

Figure 4 Calculated photocurrents at normal emission from the (110) surface of (a) ordered (β'-phase) and (b) disordered (β-phase), CuZn for different photon energies ω (Hartrees). The photon incidence angle = 45° in the $(1\bar{1}0)$ plane: the dashed curves are for s-polarisation and the solid curves are for p-polarisation. The initial and final state inverse lifetimes are 0.003H and 0.147H, respectively.

photon energies but they give rise to extremely broad peaks compared with the d-bands.

The spectral density in the (disordered) β-phase can be classified using the same symmetries as the corresponding ordered system and so the same polarisation-dependent selection rules can be applied. The surface state is still present as it is rather free electron like, and therefore, is little affected by disorder. However, this is not true for the Cu d-band features. Although disorder broadening is apparent the most obvious difference is the polarisation dependence, which is opposite to that for the β'-phase. The Σ_4 type states, for example, are shifted by about 1eV towards E_F and show signs of being split into two components. This effect is related simply to the change in symmetry. At the Γ point the Σ_4 states merge with the e_g or Γ_{12} states. In the bcc (and fcc) structure the e_g orbitals, which point along the cube edges, are directed towards next nearest neighbours which means that the e_g levels lie higher in energy than the t_{2g} levels. Such behaviour can be seen in the spectral function shown in Figure 3b. In contrast, in the β-phase the Cu atoms occupy a simple cubic sublattice and the e_g orbitals point towards nearest neighbour Cu atoms. The e_g states are now lower in energy than the t_{2g} states. Clearly, then, these calculations indicate that there are strong ordering effects on photoemission spectra which are related directly to the changes in the bulk electronic structure.

Order-Disorder Transformation In AgZn

Although CuZn would seem the most obvious alloy for an experimental study of CsCl-bcc order-disorder transformations, photoemission measurements at temperatures near the transformation (740K) are impossible due to the high vapour pressure of Zn. For the same reason it appears that measurements of the iso-electronic alloy AgZn (containing a few percent of Au) in the disordered state are also not possible, despite its lower transition temperature (600K). However, the electronic structure in the β'-phase has been studied by x-ray photoelectron spectroscopy[23]. XPS spectra do not provide the detail contained in angle-resolved measurements but they are closely related to the density of states[24], viz:

$$I_{XPS}(E) \propto \sum_{A,l} |M^{ll'}(E,\omega)|^2 \, n_{A,l}(E) \tag{7}$$

where $n_{A,l}(E)$ is the local density of states for angular momentum l and atom type A and $M^{ll'}(E,\omega)$ is an electron-photon matrix element. Although lacking the detail of ARUPS, XPS can provide a test of theory by monitoring changes in band centres and band-widths, etc. with alloying.

In Figure 5 we show experimental spectra from the valence band region in β'-Ag(+3%Au)Zn obtained at room temperature. In comparison with the spectra from Ag and Zn we observe two major differences. Firstly, the shape of the Ag-related d-band peak in the β'-phase is substantially different from that from pure Ag. Its binding energy is increased by ~ 1eV but there is a ~ 0.7eV reduction in the FWHM compared with the pure element. Secondly, although the Zn-related d-band peak for the β'-phase occurs at the same energy as in pure Zn the FWHM is smaller.

The electronic structure in β'-AgZn[25] resembles that in β'-CuZn, see Figure 3a,

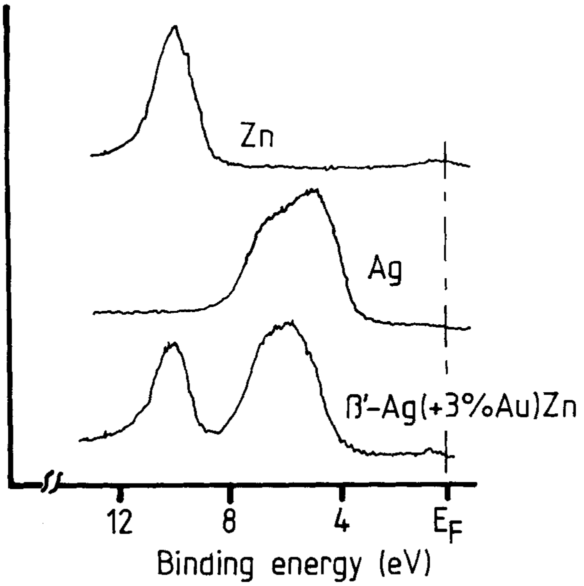

Figure 5 Experimental room temperature XPS valence band spectra from Ag, Zn and β'-Ag(3%Au)Zn using Al-Ka radiation (14.86.6eV).

except that in the former the Ag-Zn d-band separation is smaller. Calculations indicate that there is no shift of the Ag- nor Zn-related d-band centres on alloying relative to those in the pure elements, indicating no change transfer, although the band-widths are considerably smaller. This is because the latter are dominated by the overlap between d-orbitals of the same atomic species involving, therefore, next nearest neighbours. In addition, the order of the e_g and t_{2g} states in (fcc) Ag is reversed in (sc) β'-AgZn, cf the discussion on CuZn above.

These features in the density of states are reflected in the theoretical XPS spectra shown in Figure 6. The influence of the electron-photon matrix elements can be seen in the changes in the relative heights of the Ag- and Zn-related peaks and the skewed shape of the Ag peak in the β'-phase alloy. Indeed, the combination of the matrix elements effects and the narrowing of the Ag-related d-bands produces an apparent shift to increased binding energy. All the experimental observations noted previously are reproduced in these calculations except the Zn d-bands—and to a lesser extent the Ag d-bands—appear somewhat lower in energy compared with the calculated values. Similar discrepancies have been noted in pure Zn and are due to self-energy effects of the localised Zn hole[26]. This effect is difficult to treat quantitatively but does not affect our discussion.

The calculated density of states in β-AgZn still shows split-band character[25]. However, the band-widths of the two sets of d-bands are larger than in the β'-phase, because in a random bcc structure (i.e., the β-phase) an atom of one species has a 50% chance of having a like atom as a nearest neighbour. Indeed, the topology of the Ag

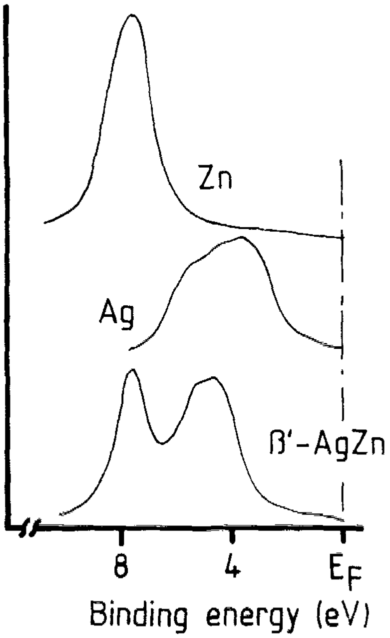

Figure 6 Calculated XPS photocurrents for Ag, Zn and β'-AgZn, Al-Kα radiation. The data have been folded with a Lorentzian broadening function of half-width 0.02H to take into account the lifetime of the initial state and the experimental resolution.

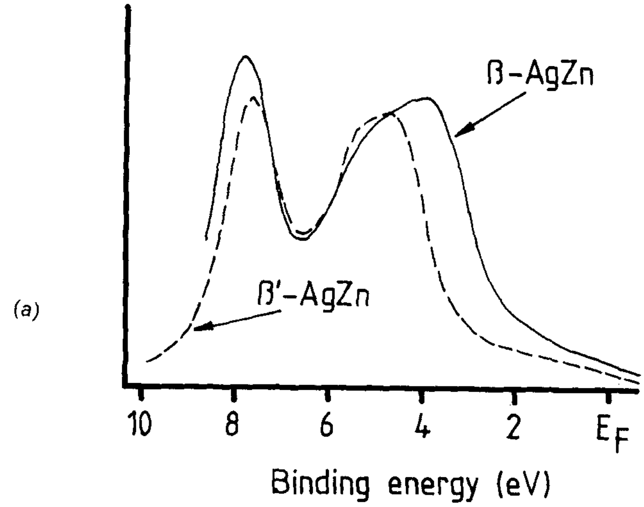

Figure 7 Calculated XPS photocurrents for ordered (β-phase) and disordered (β'-phase) AgZn. Same conditions as in *Figure 6.*

d-bands resembles 'bcc Ag' but with a reduced bandwidth. Calculated XPS photocurrents for β'- and β-AgZn are compared in Figure 8 and these differences are clear. The apparent shift and changes in shape of the Ag-related peak are due to the combined effects of disorder-broadening and the matrix elements.

(Very recently, KKRCPA calculations have been carried out for AgZn as a function of the long range order parameter, S, using a two-sublattice model. These calculations show in great detail how the band structure of the ordered compound evolves from the spectral density of the disordered (bcc) alloy. Furthermore, the corresponding 1-electron eigenvalue sums do indeed give a good description of the ordering energetics[27]).

Order–Disorder Transformation In Cu_3Au

In view of the practical difficulties referred to above only limited progress has been made on experimental studies of CsCl-bcc systems. However, we have carried out a more detailed photoemission investigation of the order–disorder in Cu_3Au which undergoes a first-order transformation from the L12 structure to (disordered) fcc at ~ 660K. Cu_3Au is a very suitable system as the temperatures required for dynamical studies are easily accessible in photoemission experiments. We have located regions in the Brillouin zone where it appears that large modifications in the electronic structure accompany the change in compositional order[21,28] and we include a selection of results here. We emphasise that our analysis and comparisons with recent electronic structure calculations[10] are at a very early stage.

The normal emission spectra from ordered and disordered $Cu_3Au(001)$ shown in Figure 8a,b correspond to scanning the spectral density along the Δ direction in the Brillouin zone. The overall picture is that the structure in the spectra from the ordered state is 'washed' out in the disordered state. However, closer inspection reveals that

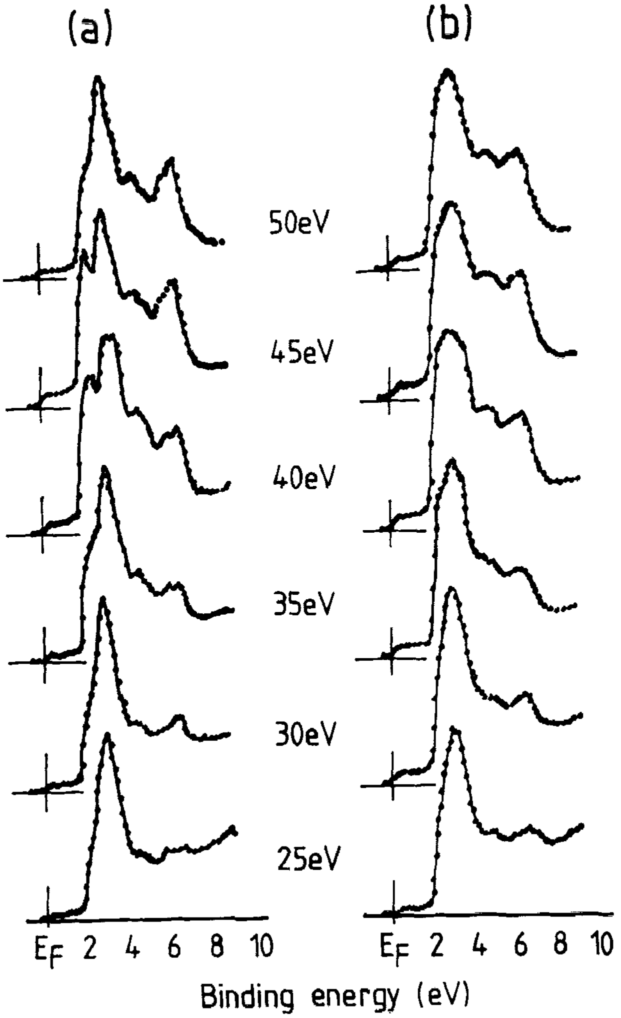

Figure 8 Angle-resolved photoemission spectra from the (100) surface of (a) ordered, and (b) disordered Cu_3Au at different photon energies. Normal emission, p-polarisation, angle of incidence = 30° in the $(0\bar{1}1)$ plane.

at certain photon energies (~ 25–30eV) there are only minor changes between spectra from the two phases, whereas at others (~ 40–50eV) there are substantial changes. At a photon energy of 40eV, for instance, the feature at 2-4eV binding energy in the ordered state is *broader* than the corresponding peak in the disordered state. Our preliminary explanation is that at this photon energy the emission is from initial states near the Γ point and, since $|\Gamma X|$ in the ordered phase is one-half that in the disordered phase, new states can be expected to occur at the Γ point when the symmetry changes; these new states will give rise to an increased width of the d-band complex. The changes in the spectral density are, therefore, *k*-dependent. Initial photocurrent

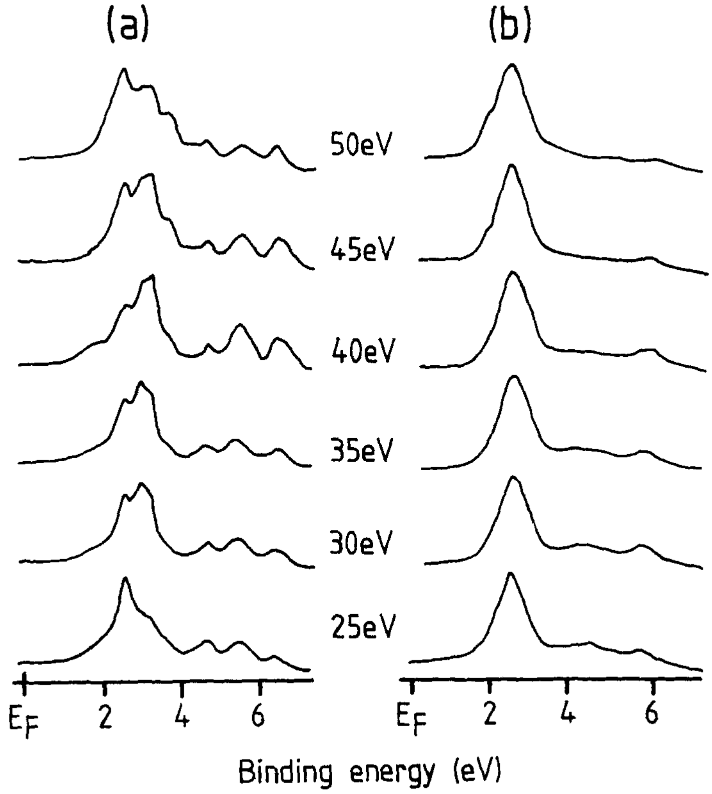

Figure 9 Calculated photocurrents from the (100) surface of (a) ordered, and (b) disordered Cu_3Au at different photon energies. Normal emission, p-polarisation, angle of incidence = 30°. The initial and final state inverse lifetimes are 0.05H and 0.150H, respectively.

calculations[29] for order and disordered $Cu_3Au(001)$, using the recently developed relativistic version of the photocurrent code[17] reproduce this behaviour reasonably well, see Figure 9a,b. However, it must be emphasised that these are preliminary data; for example, an improvement in agreement might be achieved with initial state lifetimes that are energy-dependent.

When the system starts to order the symmetry of the disordered phase is broken and new features associated with states of the ordered phase will appear in the spectral density whose weights will increase with the degree of order. We find evidence of this behaviour in the off-normal photoemission spectra at different temperatures [21] shown in Figure 10. Peaks A and B appear whose temperature dependence are such that they must be associated with ordering, and within the resolution limits of the analyser (± 0.15eV), they appear to be fixed in energy. The normalised intensity vs temperature variations are very similar which suggests that their weights in the spectral density increase at the same rate as a function of *S*. (We are unable to establish whether the curves are continuous or partly discontinuous but there does appear to be some weight above the transition. In fact, the variation is similar to that of the surface order parameter measured by LEED. Since the electron mean free paths

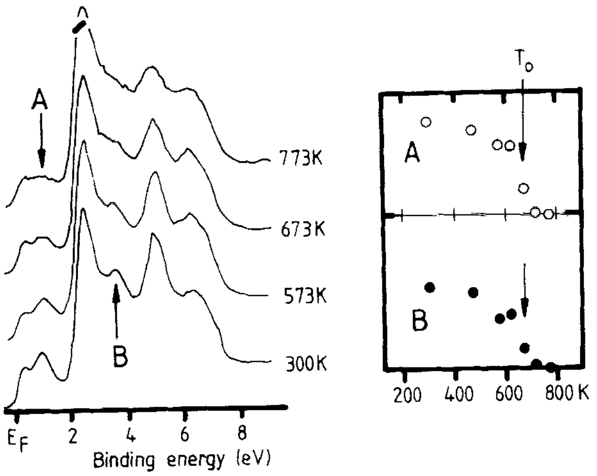

Figure 10 Photoemission spectra from the (100) surface of Cu_3Au at different temperatures. Photon energy = 40eV, incidence angle = 30°, emission angle = 25° in the $(0\bar{1}1)$ plane. The intensities of A and B were taken to be zero in the spectrum at 773K.

in these measurements are comparable with those in LEED studies this result may not be too surprising; however, it must be borne in mind that photoemission actually probes the spectral density and so only indirectly the degree of compositional order). Clearly, these measurements, and those in Figure 8, are rich in structure and detailed analysis and interpretation requires further calculations.

CONCLUDING REMARKS

Our goal is to achieve a detailed understanding of the physical properties of metals and alloys. Since these properties depend on the electronic structure we believe that it is important we gain a proper description of the electron states by combining experiment and theory. Sophisticated schemes exist for calculating the electronic spatial density in metals and alloys and the message we have attempted to relay in this paper is that ARUPS is an appropriate experimental probe of this quantity. In particular, in ordering systems photoemission measurements as a function of temperature reflect the dependence of the electronic spectral density on the long range order parameter. This generalised spectral function is related directly to the structure sensitive 1-electron part of the total energy, from which the thermodynamics of ordering can be derived, and contains all the elements of the electronic driving forces behind the ordering process, such as density of states arguments, the role of the Fermi surface, etc. It is an understanding of these mechanisms which will likely have an impact on the design of new and improved materials. Thus, ARUPS will play an important role in the future development of the electronic theory of alloys, particularly as the interests of solid state physicists and materials scientists draw ever closer together.

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