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Experimental determination of the Pd and Cu densities of states in $Cu_{75}Pd_{25}$

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The valence-band photoelectron spectra of $Cu_{75}Pd_{25}$ have been measured with the use of synchrotron radiation in the energy range 40 to 160 eV. By taking advantage of the Cooper minimum in the Pd photoelectron cross section, empirical results have been obtained for the Cu and Pd partial densities of states. These results show that the density of states of each element is distributed throughout the width of the band as predicted by recent self-consistent-field Korringa-Kohn-Rostoker coherent-potential-approximation calculations. The empirical results for the Cu density of states are in agreement with the calculations while those for the Pd density of states indicate that the calculations overestimate the Pd contribution at the bottom of the band.

INTRODUCTION

There is currently a lot of interest, both theoretically[1-4] and experimentally[1-11] in the band structures of Cu-Pd alloys. The band-structure calculations of Winter, Durham, Temmerman, and Stocks,[3] performed self-consistently within the self-consistent-field Korringa-Kohn-Rostoker coherent-potential approximation (SCF-KKR-CPA), predict that for the complete range of alloy compositions the Cu and Pd densities of states (DOS) are thoroughly mixed and that, contrary to previous interpretations, a Pd virtual bound state is not formed in Cu-rich alloys. Winter *et al.*[3] argue that their predicted DOS are consistent with x-ray photoelectron spectra of the Cu-Pd conduction band though it has proved difficult to reconcile the predicted Pd DOS with soft x-ray[9] and uv photoelectron measurements.[5,10] In alloys dilute in Pd, the Pd DOS predicted by the SCF-KKR-CPA calculations[3] have been shown to be incompatible with the experimental profile of Pd $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions[8] and with the profile of the valence band measured by uv photoelectron spectroscopy.[5]

In this work we have measured the conduction-band photelectron spectra of $Cu_{75}Pd_{25}$ using synchrotron radiation in the range $h\nu=40$ to 150 eV. By taking advantage of the Cooper minimum in the Pd photelectron cross section we are able to determine experimentally the Cu and Pd contributions to the $Cu_{75}Pd_{25}$ DOS.

EXPERIMENT AND RESULTS

The specimen of polycrystalline $Cu_{75}Pd_{25}$ alloy was prepared by melting high-purity elemental materials under argon in an arc furnace. No loss of weight occurred during alloy preparation. The valence-band spectra were taken at the Synchrotron Radiation Source (SRS) at Daresbury using a plane-grating monochromator.[12] The specimen was cleaned by Ar-ion bombardment and the experiments were performed in a vacuum of $\sim 8\times 10^{-10}$ Torr. The valence-band photoelectron spectra were measured using a double-pass angle-integrated cylindrical mirror analyzer. To achieve a high count rate at the Pd Cooper minimum the instrument was operated at less than optimum resolution. The resolution was determined from measurements of the Fermi edge of Au and varied from 0.5 eV at $h\nu=40$ eV to 1.1 eV at $h\nu=160$ eV. It is generally agreed,[1,5,6,13] that the surface regions of Cu-Pd alloys have compositions similar to the bulk compositions and that if surface enrichment does occur it does not have a large effect on the valence-band densities of states. This would seem to be true in these experiments since, after allowing for the difference in resolution, we obtained a similar spectrum using synchrotron radiation of $h\nu=40$ eV to that obtained from the same specimen using the He II radiation.[10] In the experiments using He II excitation the specimen was mechanically scraped in vacuum to give a surface composition equal to that of the bulk.

The experimental data are shown in Fig. 1. As can be seen from the figure the total intensity of the spectra vary markedly with $h\nu$. This variation is largely due to the transmission characteristics of the monochromator[12] which has a range of ~ 60 eV to 250 eV with a broad maximum in the transmission centered on $h\nu\sim 145$ eV, but there are also contributions from the variation in the beam current in the synchrotron which fell gradually during this series of experiments and from the energy dependence of the Cu and Pd photoelectron cross sections, the

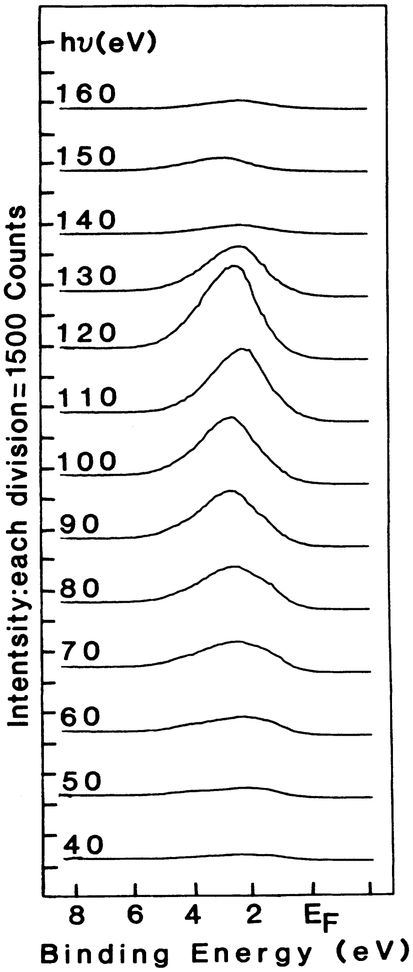

FIG. 1. This shows the photoelectron spectra of the conduction band of $Cu_{75}Pd_{25}$ excited by photons of different energies. The variation in the total intensity of the spectra with photon energy is due to a number of factors: the energy dependence of the transmission of the monochromator (Ref. 12) and of the photoelectron cross sections (Ref. 15) and the fall in the beam current in the synchrotron during the experiments which were not performed in an orderly sequence of increasing or decreasing $h\nu$.

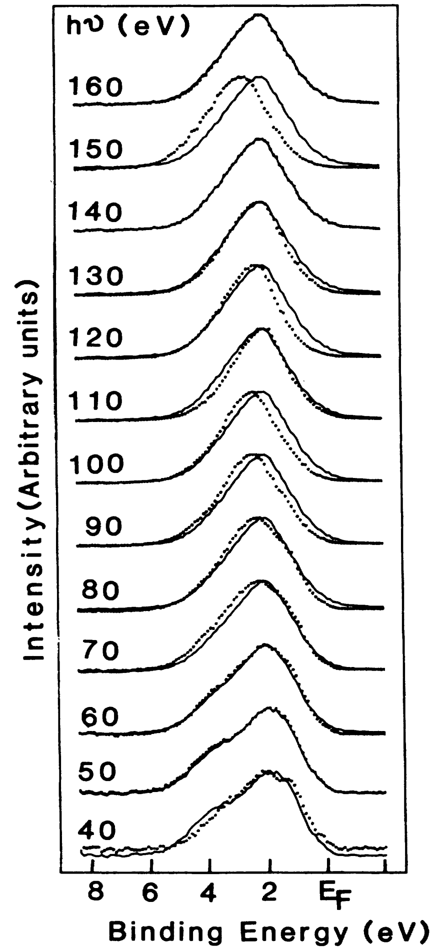

FIG. 2. The dots show the spectra of Fig. 1 after the subtraction of the background of scattered electrons as described in the text and normalized so that the vertical distance between the maximum and minimum count in each spectrum is the same. The curves are theoretical profiles generated from Eq. (1) using the photoelectron cross sections of Ref. 15 and the empirical DOS of Fig. 3.

latter having a Cooper minimum at $h\nu = 130$ eV.[14] We shall not be concerned with the total intensity of the spectra but with variations in the spectral shape with $h\nu$. The spectral shapes, after correcting for the background of scattered electrons, are shown by the dotted curves in Fig. 2. In this figure each spectrum has been normalized to give a constant height between the maximum and minimum recorded count. The correction to each spectrum for the background of scattered electrons has been made by assuming that at each kinetic energy the background is proportional to the total integrated intensity to higher energy. The constant of proportionality was found by requiring that after subtracting the background the residual count rate at energies above and below the valence band matched.

DISCUSSION

The aim of this work is to determine the separate contributions made by the Cu and Pd DOS to the $Cu_{75}Pd_{25}$ valence-band photoelectron spectrum. The contributions made by the two elements will be separated by exploiting the difference in the energy dependence of the Cu $3d$ and Pd $4d$ photoelectron cross sections[15] $\sigma_{Cu}(h\nu)$ and $\sigma_{Pd}(h\nu)$. The $3d$ wave function of a Cu atom does not have a node and $\sigma_{Cu}(h\nu)$ is expected to fall smoothly as $h\nu$ increases above the threshold energy.[15] The Pd $4d$ wave function has a node and $\sigma_{Pd}(h\nu)$ is expected to go through a minimum as $h\nu$ is increased above threshold. The atomic calculations of Yeh and Lindau[15] predict that $\sigma_{Pd}(h\nu)$ reaches a minimum of $h\nu \sim 110$ eV whereas measurements[14] on metallic Pd show a minimum at $h\nu \sim 130$ eV. This discrepancy is probably due to the neglect of relativistic and electron correlation effects in the calculations though it is possible that solid-state effects[16] also contribute. In the alloy the outer parts and, probably to a lesser extent, the inner parts of the conduction-band electron radial wave functions will differ from those of free atoms. We make a simplifying assumption that these changes in the atomic radial wave functions in the alloy at most cause a broadening of the Pd Cooper minimum.

We represent the valence-band photoelectron spectrum excited by radiation of energy $h\nu$ by

$$I(h\nu,E)=C(h\nu)[N_{\mathrm{Cu}}\sigma_{\mathrm{Cu}}(h\nu)D_{\mathrm{Cu}}(E) + N_{\mathrm{Pd}}\sigma_{\mathrm{Pd}}(h\nu)D_{\mathrm{Pd}}(E)] \ , \quad (1)$$

where N_{Cu} and N_{Pd} are the Cu and Pd concentrations in the alloy and $D_{\mathrm{Cu}}(E)$ and $D_{\mathrm{Pd}}(E)$ are the respective valence-band DOS of the two elements. These quantities are assumed to obey the sum rules

$$\sum_E D_{\mathrm{Cu}}(E)=\sum_E D_{\mathrm{Pd}}(E)=1 \ . \quad (2)$$

The variations in the total spectral intensity with $h\nu$ (Fig. 1) are represented by $C(h\nu)$. We assume that the escape depth is essentially constant for our experiments since the "universal escape depth curve"[17] shows a broad minimum for the energy range of photoelectrons excited by the radiation used in these experiments.

At the frequency of the Pd Cooper minimum the Pd photoelectron cross section will be small and we assume $\sigma_{\mathrm{Pd}}(h\nu_{\mathrm{min}})=0$, so Eq. (1) becomes

$$I(h\nu_{\mathrm{min}}\ ,E)=C(h\nu_{\mathrm{min}})N_{\mathrm{Cu}}\sigma_{\mathrm{Cu}}(h\nu_{\mathrm{min}})D_{\mathrm{Cu}}(E) \ . \quad (3)$$

This is an oversimplification of the situation since the Pd d states form a band and individual band states might be expected to go through a minimum in photoelectron cross section at slightly different values of $h\nu$. However, provided the Cooper minimum is fairly broad and $\sigma_{\mathrm{Pd}}(h\nu_{\mathrm{min}})$ is substantially lower than $\sigma_{\mathrm{Cu}}(h\nu_{\mathrm{min}})$ the assumption $\sigma_{\mathrm{Pd}}(h\nu_{\mathrm{min}})=0$ is a reasonable one. Since the alloy composition is known, and taking the Cu $3d$ photoelectron cross section from Yeh and Lindau,[15] it is possible to determine the instrumental factor $C(h\nu_{\mathrm{min}})$ from the total integrated intensity of the experimental spectrum by taking advantage of the normalization condition on $D_{\mathrm{Cu}}(E)$. The Cu DOS, $D_{\mathrm{Cu}}(E)$, can then be found from (3). This is shown in the upper part of Fig. 3, assuming $h\nu_{\mathrm{min}}=140$ eV.

We now choose a spectrum $I(h\nu';E)$ excited by radiation of energy $h\nu'$ sufficiently far from the Pd Cooper minimum that $D_{\mathrm{Pd}}(E)$ makes a significant contribution to the spectrum. We determine $C(h\nu)$ from the total integrated intensity of the spectrum and the sum rules (2) taking $\sigma_{\mathrm{Pd}}(h\nu)$ from Yeh and Lindau's[15] results. We can now determine the Pd DOS, $D_{\mathrm{Pd}}(E)$, from (1) and the earlier result for $D_{\mathrm{Cu}}(E)$. This result is shown in the lower part of Fig. 3, in which the experimental data for $h\nu=50$ eV were used.

If the experimentally determined Cu and Pd DOS are correct and if Yeh and Lindau's[15] calculations of the photoelectron cross sections are accurate, we should be able to reproduce the experimental spectra observed for all $h\nu$ using (1). There remains a single free parameter for each experimental spectrum, $C(h\nu)$, but this is essentially determined by the total intensity of the spectrum and not by its shape. The spectral profiles calculated at all $h\nu$ are shown by the curves in Fig. 2. Of course, very good agreement is obtained for the spectra excited by radiation of energy 140 eV and 50 eV since this data was used to determine the Cu and Pd DOS of Fig. 3. However, reasonably good agreement in spectral shape is obtained for most of the spectra, notable exceptions being that excited by $h\nu=40$ eV radiation, which indicates that the Pd DOS at the bottom of the band is slightly more intense than shown in Fig. 3, and with $h\nu=150$ eV radiation where the disagreement may arise from an incorrect setting of the monochromator and hence in energy referencing of the spectrum. The agreement between the predictions of our simple model and the experimental data (Fig. 2) is not perfect. Some of the disagreement could arise from our neglect of solid-state effects, since in pure Pd there are known to be marked differences in the response of bonding and antibonding states to excitation with radiation near the Cooper minimum.[16] If bonding and antibonding Pd states respond differently in the alloy we would expect our results for the Pd DOS to depend on the choice of $h\nu'$ used in our model. This is the case as is illustrated in Fig. 4 where the Pd DOS deduced for various choices of $h\nu'$ are shown. This figure shows that our model cannot determine the exact shape of the Pd DOS, and in particular it cannot determine whether or not there is a dip in intensity in the middle of the band. However,

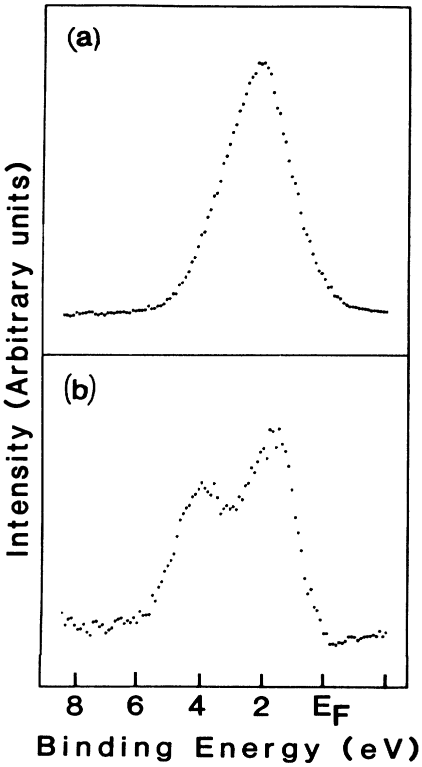

FIG. 3. (a) is the Cu DOS $D_{\mathrm{Cu}}(E)$ and (b) the Pd DOS $D_{\mathrm{Pd}}(E)$ deduced from Eq. (1) using the spectra of Fig. 2 excited by photons of energy 50 and 130 eV and the photoelectron cross sections of Ref. 14. The DOS obey the sum rules of Eq. (2).

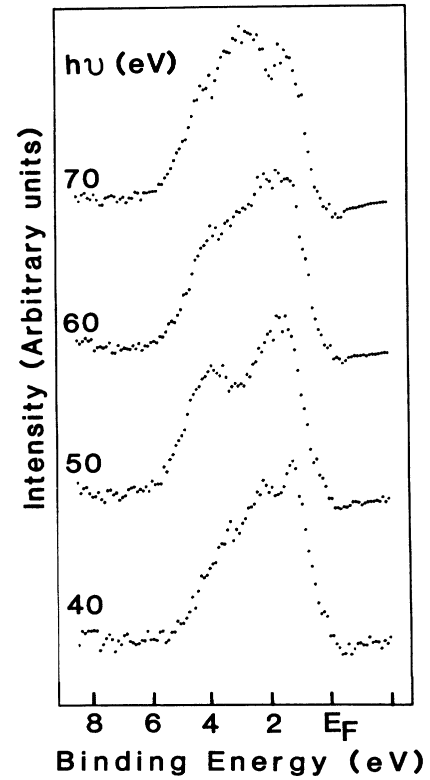

FIG. 4. These show alternative results for $D_{\mathrm{Pd}}(E)$ deduced from Eq. (1) by combining the spectra excited by photons of energy 40, 50, 60, and 70 eV, respectively, with the spectrum excited by photons of 130 eV.

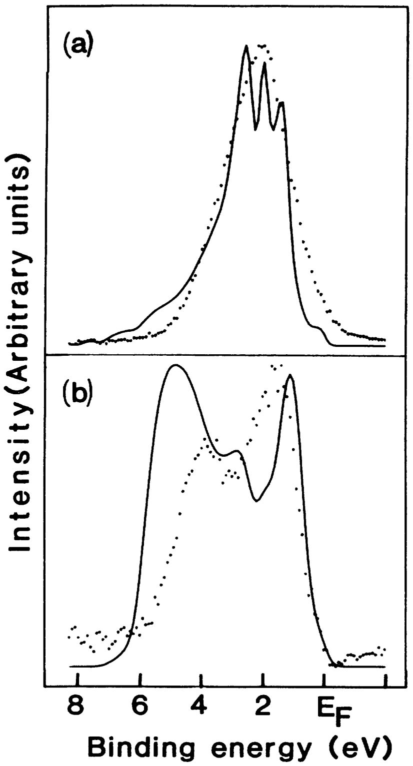

FIG. 5. The dots show $D_{\mathrm{Cu}}(E)$ and $D_{\mathrm{Pd}}(E)$ from Fig. 3. The curves are the results of Ref. 3 broadened by Gaussians of FWHM of 0.5 eV.

all the profiles agree that the Pd intensity is distributed over the whole bandwidth and that this intensity falls to very low values for binding energies greater than 6.0 eV.

The general agreement between the experimental results and the spectral profiles calculated using (1) and the Cu and Pd DOS of Fig. 3 indicates that the overall width and spread of intensity in the elemental DOS have been determined. The shape deduced for the Cu DOS is essentially the same as that of the observed spectrum at $h\nu_{\mathrm{min}}$. Inspection of the spectra show very similar shapes for $h\nu \sim 100$ eV to 160 eV, indicating that the minimum in $\sigma_{\mathrm{Pd}}(h\nu)$ is broad though it may occur at different energies for bonding and antibonding Pd states.

We turn now to a comparision (Fig. 5) of the empirical Cu and Pd DOS deduced for $Cu_{75}Pd_{25}$ in this work the SCF-KKR-CPA calculations of Winter *et al.*[3] We find that broadening the results of Winter *et al.*[3] for the Cu DOS of $Cu_{75}Pd_{25}$ by a Gaussian of width corresponding to the instrumental resolution with which our spectra were measured gives good agreement in the general distribution of intensity with the empirical results for the Cu DOS. However, Winter *et al.*[3] predict three sharp peaks in the Cu DOS which we do not observe. The agreement is less satisfactory for the Pd DOS in that the calculations of Winter *et al.*[3] predict a much higher DOS at the bottom of the band than our empirical result (Fig. 2). As a consequence of this, if we substitute the results of Winter *et al.*[3] for$D_{\mathrm{Cu}}(E)$ and $D_{\mathrm{Pd}}(E)$ into (1) and calculate the photoelectron spectrum of the $Cu_{75}Pd_{25}$ conduction band as a function of $h\nu$, we achieve good agreement with the observed spectra (Fig. 2) for $h\nu$ near the Cooper minimum in $\sigma_{\mathrm{Pd}}(h\nu)$ but progressively worse agreement as $h\nu$ is reduced. Winter *et al.*[3] were able to reconcile their calculated DOS with photoelectron spectra[18] of the $Cu_{75}Pd_{25}$ conduction band measured using Al $K\alpha$ excitation; $h\nu = 1486$ eV. However, to achieve this agreement they found it necessary to broaden the calculated DOS by up to 1 eV at the bottom of the band, a broadening they attributed to lifetime effects. Broadening the results of Winter *et al.*[3] by a Lorentzian of (FWHM) full width at half maximum of 1 eV fills in the peaked structures in the Cu DOS and gives very good agreement with our empirical results for the Cu DOS (Fig. 5), but the disagreement for the Pd DOS, particularly at the bottom of the band, is still very marked. Our empirical DOS (Fig. 3) are deduced from the experimental spectra and thus include any lifetime broadening. A possible explanation for the difference between our empirical DOS and the results of the calculations of Winter *et al.*[3] is that our results represent only the surface contribution and that the Pd DOS is significantly narrower at the surface than it is in the bulk.[3,19] This is a reasonable hypothesis since the spectra of Fig. 1 correspond to the minimum in the photoelectron escape depth which is ~3 Å. However, if the discrepancy is a surface effect it is much larger (Fig. 5) than the surface narrowing of the *d* bands of Cu, Ag, and Au.[20] An alternative explanation is that the use in the SCF-KKR-CPA calculations of average lattice constants to represent the expansion of the Cu lattice by the addition of Pd may hide a differential expansion of the lattice around a Pd site relative to a Cu site which would be expected to lead to a narrowing of the local Pd DOS.

CONCLUSIONS

By taking advantage of the Cooper minimum in the Pd 4*d* photoelectron cross section we have deduced empirical results for the Cu and Pd DOS's in $Cu_{75}Pd_{25}$ from conduction-band photoelectron spectra. The empirical results are shown in Fig. 2, and although our model does not yield the shape of the DOS within the band accurately (Fig. 3) it does show that the Pd DOS is spread roughly equally through the band and that the bandwidth is ~6 eV. Our empirical results agree with the calculations of Winter *et al.*[3] for the Cu DOS, provided the latter are corrected for lifetime broadening, but indicate that the calculations overestimate the Pd intensity of the bottom of the band. It is possible that the source of this disagreement is that our results correspond to the surface region of the alloy and that the Pd DOS is narrower at the surface than in the bulk. Alternatively, it may be due to a local expansion of the lattice around Pd sites.

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