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X-Ray Photoelectron Spectra of the Valence Bands of Some Transition Metals and Alloys

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Valence-band spectra of Cu, Ni, and Ag, obtained using x-ray photoemission, are compared with one-electron densities of states. Similar measurements on the CuNi and AgPd alloy systems are shown to be compatible with the predictions of the coherent-potential approximation.

I. INTRODUCTION

Many of the properties of solids can be derived from the dispersion relations of the electronic energy levels. For states very close to the Fermi energy these relations can be obtained with relative ease and precision by, for example, de Haas–van Alphen measurements. The determination of the energy bands at greater distances from the Fermi energy is much more difficult, and knowledge concerning them is relatively meager, even in seemingly simple systems such as the transition metals or their monoxides. Since some of the desired information about the energy bands is contained in the densities of states, the last few years have seen a large effort to determine them accurately for many materials of fundamental interest.[1–3] We have made measurements of a number of simple systems, namely, some transition metals, their alloys, and oxides, using x-ray photoemission with monochromatized radiation. The results on the metallic systems will be reported here.

II. COMPARISON OF METHODS

A number of methods have recently been used to determine densities of states. These include ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), soft-x-ray emission spectroscopy (SXS), ion-neutralization spectroscopy, and Auger-electron spectroscopy.[3] The most commonly used techniques are the first three. The UPS and the SXS methods have been in use for quite a number of years. It must therefore seem surprising that the valence bands of simple metals like Cu and Au are still being investigated. It is perhaps also not immediately apparent why a new method to investigate densities of states, namely, XPS, has received so much attention. Therefore it seems appropriate to compare briefly the UPS, SXS, and XPS methods, and especially to stress the shortcomings and advantages of the XPS technique (see also Ref. 4 for a discussion on these points).

Though the various steps in these experiments differ, the final states of the solid are the same: a hole in the valence band. Nevertheless there are subtle differences. In the XPS technique localized and itinerant electrons are excited, although the matrix element for their excitation may differ; therefore one may assume that the XPS technique measures a quantity correlated with the band density of states. In the SXS technique, on the other hand, the initial-state deep hole will be much more rapidly filled by an electron localized near that ion. As a result SXS may measure a quantity more closely related to a density of localized states. In all techniques, however, the transition matrix elements, which certainly are different for electrons having wave functions of different multipolarity, have to be taken into account.[5]

We next consider the unfolding processes required to derive a density of states from the experimental spectra. In the case of XPS (for a detailed discussion of this point see Ref. 4), the main deformation of the spectrum comes from inelastically scattered electrons, including effects of plasmon excitation, which result in a rising background starting at the zero-energy-loss line, shown dashed in Fig. 1. These contributions can be directly measured by looking at a core level near the valence band. This shows that inelastic scattering produces a featureless background on which the discrete losses due to collective excitations of the electrons are superimposed. These discrete energy losses have intensities very much dependent on the material under investigation,[6] but they are relatively weak in all materials considered in this paper. The generally accepted procedure for background correction in XPS spectra is to unfold from the measured valence band the background function determined experimentally from a core level. Second, the data require correction for the instrumental resolution, which is preferably determined by measuring the sharpness of the Fermi edge. A typical value for the resolution [full width at half-maximum (FWHM)] is about 0.55 eV for an instrument working with monochromatized Al $K\alpha$ radiation (see Sec. III of this paper for experimental details).[6] An inspection of Fig. 1 shows however, that the bulk of the information is already contained in the raw data and that the various unfolding processes do not produce severe changes in the shapes of the measured curves.

The unfolding process is more complex for SXS.

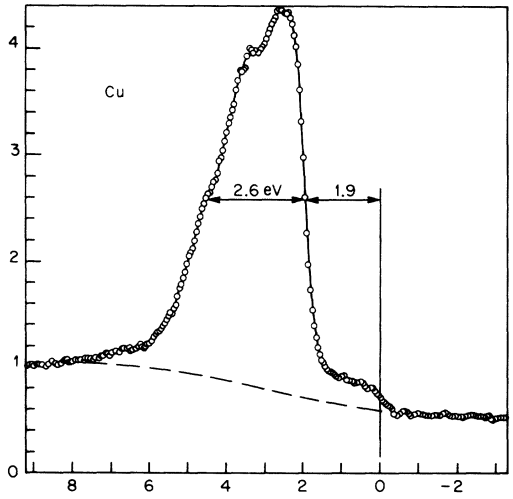

FIG. 1. X-ray photoemission spectrum of vacuum-evaporated copper film taken with monochromatized Al$K\alpha$ radiation on a HP spectrometer. Raw data are shown. The approximate background due to inelastically scattered electrons is indicated by the dashed line (for an exact background correction see Ref. 4).

For one thing it is generally hard to extract the core level width from the measured spectra. In addition, there may be difficulties due to overlapping spectra (see, e.g., the work on Cu[7]) and due to satellites. (To our knowledge, such satellites have so far not been observed in the XPS spectra of metallic samples.)[4] Nevertheless such unfolding has been successfully carried out for Cu M emission,[7] but no correction was applied for the width of the initial-state core hole. We have measured the width of this Cu $3p$ hole state in an XPS experiment and find a lower limit for the $3p$ linewidth of 1.4 eV. This limit is much greater than the 0.4–0.5 eV given in Ref. 7. The effect of the $3p$-level width may be responsible for the difference between the XPS valence band of Cu (based on the data of Fig. 1 after approximate correction for inelastic scattering) and the SXS valence band of the same material obtained by unfolding the $M_{2,3}$ emission spectrum[7] (see Fig. 2).

A further point worth noting is that the valence band obtained from the L_3 emission spectrum[8] is considerably narrower, and more like the XPS spectrum, than that obtained from M emission. This finding is in accord with the smaller 0.8 eV lower limit obtained by XPS for the width of the Cu $2p$ line. It therefore no longer seems necessary to account for the difference between the Cu valence-band structures derived from L and M emission only in terms of a transition-probability effect.

A comparison between UPS and XPS densities of states is much easier. UPS generally shows more structure, in part because the instrumental linewidth, 0.1–0.2 eV, is considerably better than that achieved in XPS. On the other hand, additional structure appears in UPS because this technique measures a folding between the occupied and empty band structure,[9] the so-called joint optical density of states (JODS) (for data on Cu see also Ref. 10). (In XPS the empty band structure is essentially featureless because of the high exciting energies.[4,11]) In UPS the spectra have been shown to vary greatly with exciting photon energy; see, for example, the data for Cu.[9,10,12] The changes found with variation of photon energy in UPS give additional information on the nature of the photoelectric process and on the empty band structure.[12] At exciting energies of about 40 eV, at least in certain instances (e.g., Au; compare data in Refs. 10 and, 13), the energy distributions measured by UPS and XPS become quite similar. To what extent this energy distribution corresponds to the actual density of states has to be checked carefully in each case.

The results of all three types of measurement (UPS, SXS, XPS) are subject to the question to what extent the valence-band hole influences the observed spectra. This problem has been dealt with in detail theoretically[14-17] but so far there is little definite experimental evidence for this effect in the results of UPS, SXS, or XPS.[18] These effects have been observed in x-ray absorption measurements and in Auger-electron-determined density of states.[19,20]

In one respect the SXS technique is definitely

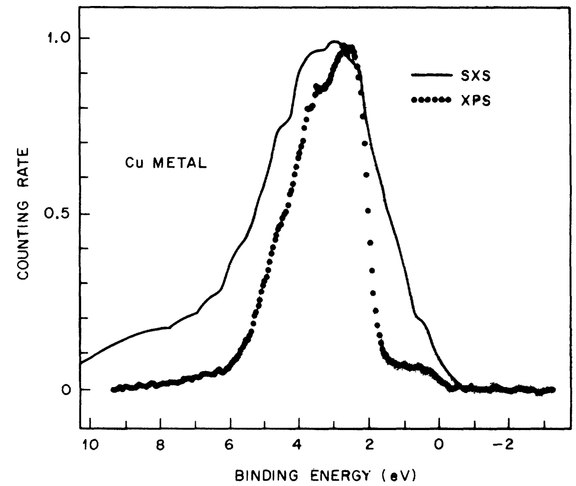

FIG. 2. Comparison of SXS and XPS Cu valence-band spectra. The points show the data of Fig. 1 corrected approximately for inelastically scattered electrons, but not for the instrumental resolution. Full curve from Ref. 7, based on an unfolding of the Cu M emission, but without correction for the $3p$ linewidth.

superior to UPS as well as XPS. X-ray emission is observed from an average depth of about 150 Å (see Ref. 7), and therefore it definitely measures bulk properties. Electron emission, with presently used exciting energies, is limited to a depth about an order of magnitude smaller.[21,22] Effects of the surface are therefore expected to be much more important in XPS and UPS spectra. This means that surface quality and chemical composition are of much more importance in UPS and XPS than in SXS. Second, as has been pointed out recently by Heine *et al.*,[23] the energy distributions measured by photoelectric methods may be narrowed owing to the small sampling depth. The bandwidth in a tight-binding approximation is proportional to the square root of the number of nearest neighbors. This number is smaller for a surface atom than for a bulk atom and, if the energy distributions are measured predominantly from the surface, an apparent narrowing in the energy distributions is observed.[24]

Finally, it is worthwhile to summarize the limitations of XPS: (i) The resolution at present is not better than ~0.5 eV.[13] (ii) The sampling depth when working with x-rays of ~1.5 keV is 15–20 Å.[21,22] The technique is consequently surface sensitive. Problems may arise from impurities deposited on the surface or chemically reacted with it, and from lattice defects created by sputtering. Changes in lattice constants or symmetry at the discontinuity can also affect the observed electron energy distributions, since k_z is then no longer necessarily a good quantum number in the first few atomic layers. This will presumably lead to a smearing of the structure corresponding to a perfect crystal. All these facts suggest that the experimentally observed electron energy distributions may differ from those expected under the assumption that they are a representation of the occupied density of states for an infinite crystal. (iii) It remains an open question whether any of the photoelectric techniques, including XPS, actually measure the one-electron band structure. It may well be that in certain cases collective excitations of the electronic system play an important role.[4,15–18,25] (iv) The extent to which matrix element modulation influences the observed spectra is hard to estimate. Careful comparison of experimental and theoretical densities of states[13] can shed some light here. (v) It is not yet clear to what extent the hole lifetime influences the observed spectrum.[4,25]

Until these latter questions are answered, the interpretation of XPS valence spectra should be approached with considerable caution. Henceforth the observed electron energy distributions will be called XPS densities of states. In comparing them with calculated band densities of states, the qualifications made above should always be kept in mind, although they shall not be reiterated in every case.

III. EXPERIMENTAL DETAILS

The XPS spectra used in this study were obtained with a Hewlett–Packard 5950A spectrometer with a resolution of 0.5 eV[13] (see also Fig. 11).

Since XPS samples only the first 15 Å[21,22] the quality of the surface is of prime importance in these experiments. Surface chemistry can be easily checked by measuring the core level emission of suspected contaminant. The main contaminants in these experiments were oxygen and carbon.

The vacuum in the measuring chamber of the instrument was in the 10^{-9}-Torr range. Samples were prepared by flash evaporation in a separate sample preparation chamber at a pressure of 10^{-6} Torr. This was done with the pure metals and the CuNi alloys and resulted in very small oxygen and carbon signals (about $\frac{1}{100}$ of the intensity of, e.g., the Cu 2*p* lines). For the evaporated alloys the final composition was deduced from the relative strength of the 2*p* lines of Cu and Ni using data on bulk samples for calibration. These data were obtained in a Varian IEE instrument, which was equipped with an argon-ion sputtering device.[26] In this instrument the bulk samples could be cleaned such that the O 1*s* line could not be observed in a 10-min run and the C 1*s* line gave an intensity roughly 5% of that of the Cu 2*p* lines. All data in which the concentrations were more than 15% different from those of the starting alloy material were disregarded. The AgPd alloys were mechanically cleaned directly before insertion. The general shape of the spectra compares very well with those taken on the Varian machine after sputtering, when the inherent difference in resolution is taken into account.

The metal samples were obtained from commercial sources. The alloys of CuNi and AgPd were prepared by induction melting high-purity constituents under argon. They were then cold worked to about half their thickness, annealed for one week in an evacuated quartz ampoule, and finally cold worked to 3-mil thickness. The composition of the AgPd series was checked by measuring the lattice constants, and agreed with the nominal composition to within a few percent.

It may be asked whether the composition of the surface is identical to that of the bulk, and whether preferential sputtering changes the composition at the surface. For the CuNi alloys there are good indications that sputtering does not severely alter the composition because prolonged sputtering does not alter the relative heights of the core level spectra of the two constituents. However, there is a phenomenon in both alloys which we cannot explain: The Ni and Pd spectra are always, respectively, ~30% and 50% weaker relative to the Cu and Ag spectra than anticipated from the nominal concentrations. The photoelectric cross section does indeed increase in going from Ni to Cu and Pd to Ag, but by less than the observed difference in intensity. There are two possible explanations for this phenomenon, neither of which we can rule out at present. First, there is the possibility that the surface composition is indeed different from that of the bulk material. Second, it is well known that molecules adsorb much more favorably on Ni and Pd than on Ag and Cu. Adsorbates would therefore tend to decrease the Ni and Pd signals with respect to the Cu and Ag signals. The compositions given for the alloys are bulk values which may differ from the surface concentrations applicable to the spectra.

A further question concerns the randomness of the alloys. Binary-solid solutions like CuNi or AgPd are known to exhibit varying degrees of short-range order, depending on the method of preparation. The bulk samples used were prepared such as to minimize clustering, by annealing at high temperatures and subsequent quenching and cold working. The evaporated samples were examined as deposited. The effect and extent of clustering, especially in the surface layer, remains a subject for future investigation. Typical data accumulation time was 4 h. During this time the O signal generally increased hardly at all, whereas the C signal increased by about a factor of 2.

IV. METALS Cu, Ni, AND Ag

The intent of the work discussed in this section is to determine to what extent XPS data give a direct view of the occupied band structure. This will be accomplished by comparing the XPS valence-band spectra with one-electron band structures adjusted to fit UPS experiments. The three metals mentioned have been investigated previously with unmonochromatized x rays.[4,11] The present results are in general agreement with these experiments although they show some more details.

After the original submission of this work Lindau and Wilson[27] published XPS work on the valence bands of Cu, Ag, and Au. The general conclusion of their work is that the structure observable in this type of experiment is a function of sample cleanliness rather than of resolution of the instrument employed. At least for the case of Au the available experimental evidence does not totally support this view. There is no reason to believe that the work on Au by Shirley[13] (with a resolution of ~0.55 eV) has not been done with considerable care. Nevertheless the rich structure of the Au XPS valence band of Ref. 27 (obtained with a resolution of 0.9 eV) does not show a one-to-one correspondence to the structure of the spectrum of Ref. 13. Therefore we tend to believe that the additional structure observed in the XPS valence-band spectra obtained with the Hewlett–Packard instrument is indeed due to the increased resolution.

Cu. The Fermi surface of Cu shows only slight effects caused by the *d* electrons.[28] Recent photoemission measurements of Smith[9] and Eastman[10] show good agreement with the calculated JODS.[12] To test the degree to which XPS gives a direct picture of the occupied density of states we compare in Fig. 3 the XPS density of states[29] with that calculated using the parameters given by Burdick.[30] The Hodges[31] interpolation scheme was used to perform the calculations. Burdick's calculation relied on the empirical Chodorow potential, modified to fit more recent experimental data. Spin-orbit coupling was inserted, but had only a minor effect. The calculated histogram was smoothed with a Lorentzian function of 0.5 eV width in order to approximate the effect of the spectrometer resolution function. It can be seen that there is quite gratifying agreement as far as width and shape of the density of states are concerned. There is even a rough correspondence between the position of some detailed features in the two curves, e.g., 4.5 eV below the Fermi energy. The comparison also confirms the value chosen for the resolution of the instrument. It is apparent from the figure that the measured intensities of all parts of the *d*

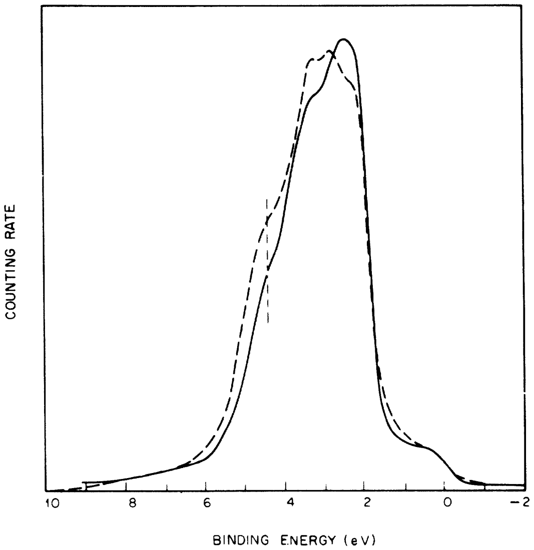

FIG. 3. Comparison of the valence-band structure of Cu obtained from XPS measurements of Fig. 1 (full curve) with density of states derived from Ref. 30 (broken curve). Background has been substracted from the XPS data, but no other corrections have been applied. The height of the theoretical curve has been normalized to facilitate comparison with the data. (From Ref. 29).

band cannot be simultaneously brought into agreement with those calculated.

Ag. The Fermi surface of Ag has been studied and can be well represented by band-structure calculations.[32] In this case as well, the UPS measurements of Smith[9] and Eastman[10] can be adequately represented by calculations using the band structure obtained by Snow.[33] A comparison between the XPS density of states and a density-of-states calculation based on Snow's band structure is shown in Fig. 4. This calculation was also performed in the Hodges interpolation scheme with spin-orbit splitting included. In order to match the experimental curve with the calculated one the *d* bandwidth was increased by 16%. The histogram was smoothed as above. Agreement between the two structures is satisfactory. Spin-orbit coupling turns out to be important in this case because the valley at 6 eV is reproduced by the theory only when it is included. Again no method of normalization will make the intensities of the experimental and theoretical curves agree everywhere.

The observations presented here for Cu and Ag and those of Shirley[13] for Au lend themselves to some general conclusions. The parameters used to fit the JODS obtained from UPS experiments yield a reasonable fit to these XPS density of states. However, the *d* bandwidths are in exact agreement only for Cu. In Ag the UPS parameters underestimate the width, while in Au they overestimate it. In addition, the finer details are also not too well reproduced by the calculations. In all three noble metals the intensities of the various parts of the measured bands could not be matched simultaneously with those of the calculated density of states. This may be a matrix-element-modulation effect due to increasing *s* admixture into the *d* band. Williams *et al.*[7] present estimates which show that owing to matrix element modulation the intensity of the observed *d*-band structure can vary by as much as 10% across the *d* band. The difference in matrix elements for electrons with different orbital character is most clearly apparent in the case of Ag, where the experimental *s*-band intensity falls well below the theoretical curve.

The XPS investigations on the noble metals, Cu, Ag, and Au, lead to the following conclusions: (i) The XPS density of states seems to correspond fairly well to that calculated in the augmented-plane-wave (APW) approximation, with the use of parameters deduced from other experiments. This means that XPS in these cases in fact measures a quantity related to the one-electron density of states. It should be emphasized that for Ag and Au relativistic effects are important. (ii) Correlation effects and effects due to the lifetime of the hole in the band, which have not been included in the theory, do not appear to have a very significant effect on the XPS data. (iii) Neither the expected narrowing of the *d* bands due to surface effects[23] nor any other effects due to the limited sampling depth have been detected in the data on the noble metals. A detailed comparison with theory remains to be presented, but will require a better understanding of the corrections that must be applied to the XPS data.

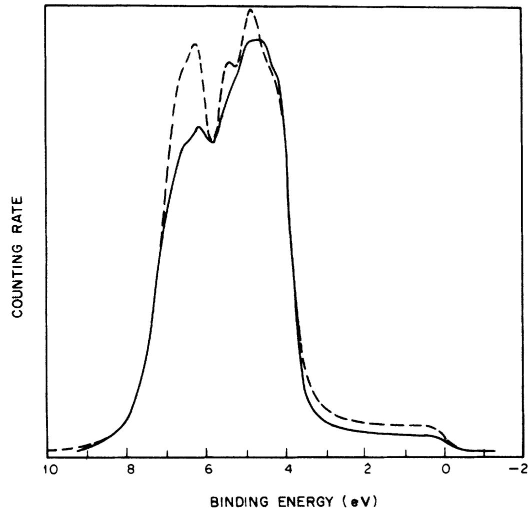

FIG. 4. Comparison of the XPS valence band of Ag (full curve) with a density of states derived from Ref. 33 (broken curve). (From Ref. 29.)

Recently Shirley *et al.*[34] have carried out similar investigations on Ir and Pt. Here again they find a strong correlation of the XPS densities of states with those calculated in the APW approximation.

Finally one may compare the XPS density of states with the JODS as measured by UPS. The systematic investigations of Eastman[10,35] show that, as anticipated by Shirley,[4] the curves measured by the two techniques for the materials considered so far look very similar for exciting energies higher than about 40 eV in UPS.

Ni. Eastman's[10] UPS measurements on the metal show a narrow asymmetrical (~1.5 eV FWHM) *d*-band peak without resolved structure just below the Fermi energy (the width at the bottom of the *d* band is about 3 eV). The XPS curve, Fig. 5, has a similar shape: it has a width of 2.7 eV (FWHM) and extends over about 5 eV at the bottom of the band. The broad peak at around 7 eV in the XPS data has been attributed to plasmon excitation,[11] but this assignment may be open for discussion. A peak at that energy is also clearly visible, in the 2*p* spectrum, indicating an energy loss due to a collective electron excitation of that energy. The compilation of Pines[36] lists energy losses in Ni below 10 eV. On the other hand Sickafus and

Steinrisser[36] in a recent energy-loss experiment do not find a loss below 10 eV. The nature of this 7-eV peak is therefore not clear. In addition, the early energy-loss experiments give a number of other discrete peaks of similar intensity which should also show up in the XPS spectra. This is, however not the case. The possibility that the observed peak is produced by the O $2p$ band of an oxygen contaminant is very unlikely, because in the Ni $2p$ spectrum no indication of a Ni species other than Ni metal could be detected. Also the O $1s$ line has less than 1% of the intensity of the Ni $2p$ line. Therefore the intensity of the 7-eV peak is too strong to be due to an oxygen contaminant.

A comparison with an APW calculation using the parameters given by Ehrenreich *et al.*[37] results in poor agreement. This finding can be anticipated from the very different XPS electron energy distributions for Ni and Cu. From a theoretical point of view the band parameters for these two elements should not be too different resulting in similar densities of states. One is therefore led to the suspicion that neither high-energy UPS nor XPS electron energy distributions give a good picture of the actual density of states in this case. This example may serve as a warning that one cannot necessarily regard the XPS electron energy distributions as a reasonable representation for the density of states. Rather, as pointed out before, each case has to be inspected with considerable care and caution. Heine *et al.*[23] have recently suggested that the observed band narrowing for Ni is due to the fact that one is predominantly measuring surface effects. This would indicate that the electron escape depth for Ni is considerably lower than that for Cu or Au. In the latter material it has been shown that the high-energy UPS electron distributions[35] are very similar to those obtained by the XPS technique,[13] which in turn show a quite close resemblance to the band density of states. Another point supports this view. The low-energy UPS electron energy distributions ($h\nu < 10$ eV) are quite similar for Cu and Ni.[10,38] In this regime, the electron escape depth is larger; the influence of surface effects should be correspondingly smaller. The similarity of the electron energy distributions is thus consistent with the expected similarity in their band-structure properties, supporting the conjecture of Heine *et al.*[23] Why Ni has a much smaller electron escape depth must remain an open question at this point. It also cannot, however, be excluded at this point that in Ni a many-electron theory is required for a theoretical description of the electron energy distributions.

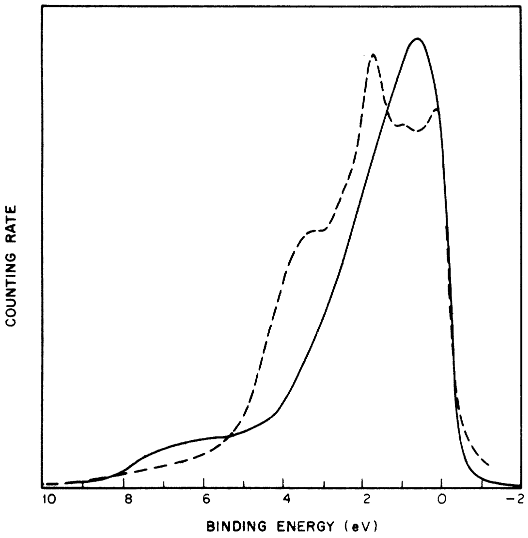

FIG. 5. Comparison of the XPS valence band of Ni (full curve) with a density of states derived from Ref. 38 (broken curve). (From Ref. 29.)

V. ALLOYS CuNi AND AgPd

A. General Remarks

From the discussion in Sec. IV and from similar investigations it is apparent that while the gross features of the electronic structure of the noble metals are understood, there are many details left to be studied, especially in the transition elements. The theoretical understanding of the electronic structure of simple alloys requires one further step of sophistication. From an experimental point of view the problem is also more difficult. For one thing, the possibility of short-range order provides an additional parameter which must be controlled. For another, phenomena, like the de Haas–van Alphen effect, which have been so valuable in uncovering the Fermi surface of metals, are not observable in most alloys. As a result the electron spectroscopic and related methods which directly provide information on the density of states should be of great importance.

Ultimately one may look forward to XPS studies of dilute magnetic impurities in diamagnetic hosts, such as Fe or Ni in Cu. The electronic properties of such systems have only recently been explained[39,40] but many problems remain. The results from photoelectric studies, such as XPS, may be of help for solving some of the remaining problems.

Much progress has been made in the theoretical description of the electronic properties of binary alloys. In the early days the rigid-band model was thought to be generally applicable.[41] It was believed that the density of states of an alloy could be obtained by taking a fixed density of states characteristic of the constituents and shifting the Fermi energy in such a way as to accommodate all the electrons. Although this model may provide a first-order approximation for alloys with much electron transfer it is clear that it cannot be applicable to systems like CuNi or AgPd. The *d* electrons in Cu or Ag are very well described by a tight-binding model, i.e., they experience a potential that is predominantly atomic, and only slightly modified by the effects specific to a metal. For adjacent elements like Cu and Ni or Ag and Pd the additional potentials superimposed on the atomic potentials can be assumed to be very similar. Therefore one may immediately conclude that a theoretical description is needed which leaves the positions of the *d* bands in the alloys at roughly the same position as in the pure metals. Changes in the shapes of the bands upon alloying will occur to the extent that they are influenced by scattering processes.

These considerations underlie a description of the electronic properties of binary alloys by the so-called coherent-potential approximation (CPA).[42,43] This is a scattering approach, in which only one scatterer is treated exactly and the rest are approximated by a medium through which the electrons travel unscattered (the coherent potential). (A basically equivalent method has been used to describe the phonon spectra of mixed crystals.) The predictions of the CPA can be nicely seen in a model calculation of Velicky *et al.*[43] or in the calculations of the band structure of CuNi alloys.[44–46] The alloys considered here both essentially fall into the so-called split-band regime in which the *d* bands of the two constituents overlap only slightly. For small impurity concentrations, e.g., Ni in Cu or Pd in Ag, the impurity forms a level roughly halfway between the top of the host *d* band and the Fermi energy. If one neglects the *s*-*d* scattering, this level is very narrow (see the model calculation); if *s*-*d* scattering is taken into account, the width of the level reflects largely the *s*-*d* scattering matrix element, although crystal field splitting and spin-orbit splitting may not always be negligible. As the impurity concentration grows, the width of the impurity band increases, and at the same time the host band loses structure. We may visualize these changes as the combined effect of two causes: First, the q vector ceases to be good quantum number, so that the structure is smeared out; and second, scattering becomes more intense. When the concentrations of the host and the impurity are equal, two bands appear roughly at the position of the bands in the pure metals, but their structure is much reduced. Finally, as the impurity concentration exceeds the host-atom concentration, the impurity band approaches the shape of the pure-metal band and the host-atom band narrows down to the single impurity band widened by the *s*-*d* scattering.

In the dilute-impurity limit the CPA agrees with the results of the Friedel–Anderson virtual-bound-state model.[47,48] In this approach, the impurity level is situated between the Fermi level and the host band and has a Lorentzian shape. This model is applicable to the low-impurity-concentration limit but is not readily extended to more concentrated systems.

B. CuNi Series

The CuNi alloy series is one of the classical binary systems. This is in part due to its simple metallurgical properties, namely, that the two constituents form a continuous solid solution with no change in crystal structure. The density of states of this system was originally thought to correspond to the rigid-band model, which seemed to explain many of the observed magnetic properties. Ehrenreich *et al.*[49,50] have shown, however, that this model fails to describe properties such as Curie temperature and the electronic specific heat. They suggested that a model which leaves the position of the Cu and Ni *d* bands essentially unchanged even in the alloy would be much more appropriate. The density of states of CuNi alloys has since been calculated by three groups using the CPA formalism, yielding very similar results.[44–46] The principal features of the results of these calculations have been outlined in Sec. V A.

We have measured the XPS density of states of CuNi alloys over the whole range of composition. Preliminary results[51] have been published and new high-resolution spectra are shown in Fig. 6. A comparison of the XPS density of states of this alloy series with theoretical density-of-states curves requires extreme care, because the XPS curves because, as has been shown above, the XPS curves of Ni obtained under the present experimental conditions do not seem to give a reasonable picture of the actual band density of states. The experimental curves in Fig. 6 do show, however, that a rigid-band model will not be applicable for their explanation. Comparing the experimental results with theoretical curves[44–46] one finds that some of the theoretical predictions are nevertheless adequately reproduced. One feature at low nickel concentrations is the formation of a narrow Ni band between the Fermi energy and the center of the copper band. As the concentration increases, the width of this band increases and finally, at about 50%, one sees essentially two peaks centered at the position of the *d* bands of the pure metals. A detailed comparison has, however, been postponed until the above reservations have been cleared up.

In order to show the present state of agreement between experiment and theory, a comparison of an XPS and a theoretical spectrum is made in Fig. 7. The calculated curve is taken from Stocks *et al.*,[45] and corresponds to the composition $Cu_{0.6}Ni_{0.4}$.

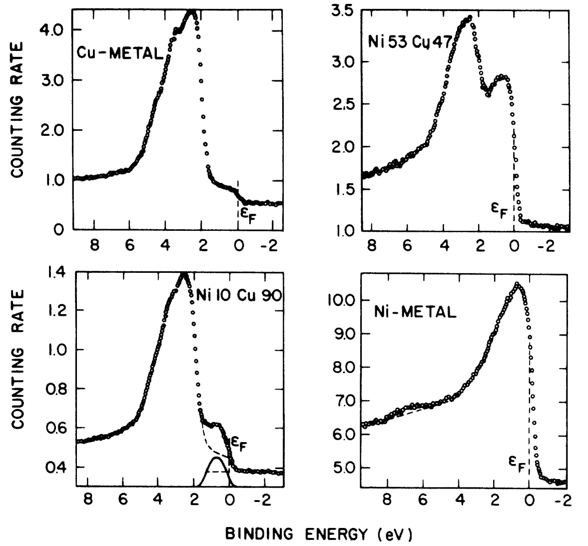

FIG. 6. Valence-band spectra of vacuum-evaporated Cu, Ni, and CuNi alloys. Uncorrected data taken with the HP spectrometer are shown; the alloy compositions refer to atomic fractions. The compositions were obtained by comparing the $2p$ core level intensities of the evaporated samples with those of bulk samples. These latter ones were measured in a Varian IEE 15 instrument.

The XPS data were taken on a sample prepared by vacuum evaporation of material with composition $Cu_{0.6}Ni_{0.4}$. A study of core level intensities suggests a shift toward the equiatomic composition ($Cu_{0.53}Ni_{0.47}$). In view of all the reservations that have been expressed this shift does not seem so severe as to invalidate some general conclusions. The data have been corrected for the inelastic components but not for instrumental resolution. The XPS density of states shows the double hump expected from the theoretical curve.

A comparison of the type just shown holds over the whole series. Figures 8 and 9 give a summary of our data concerning the width and the position of the copper and nickel d bands. The width has not been corrected for the instrumental resolution. Also shown in Fig. 8 is the theoretical concentration dependence of the nickel d bandwidth as determined from the calculations of Stocks *et al.*[45] A comprehensive UPS study of this system has been presented by Seib and Spicer[52] and has been compared with theoretical results for band density of states by Stocks *et al.*[45]; these latter authors[45] find good general agreement between their calculations and the experimental data. This comparison implies that the data taken with exciting energies $h\nu \leq 11.2$ eV do indeed lead to a good representation of the filled density of states. The systematic investigations of Eastman[10,35] show for pure metals that the extraction of the density of states from

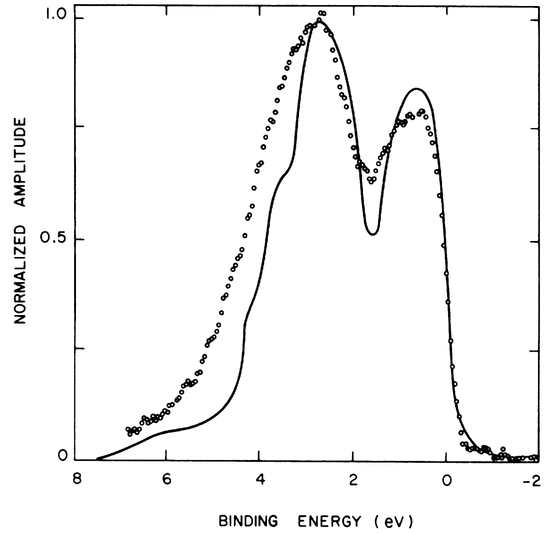

FIG. 7. Comparison of XPS valence-band spectrum for an evaporated CuNi-alloy sample with a density of states for $Cu_{0.6}Ni_{0.4}$ calculated in the CPA. The latter is from Ref. 45.

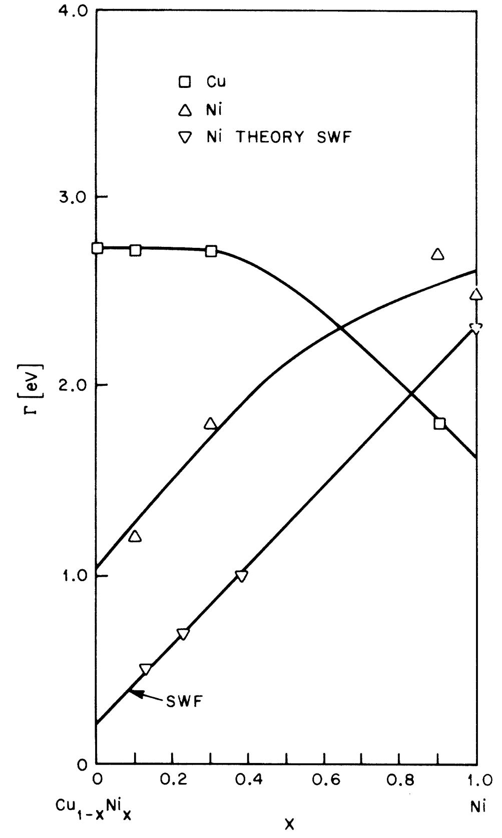

FIG. 8. Widths of the Cu and Ni derived d bands in CuNi alloys based on the data of Ref. 51. The theoretical Ni d bandwidths are from Ref. 45.

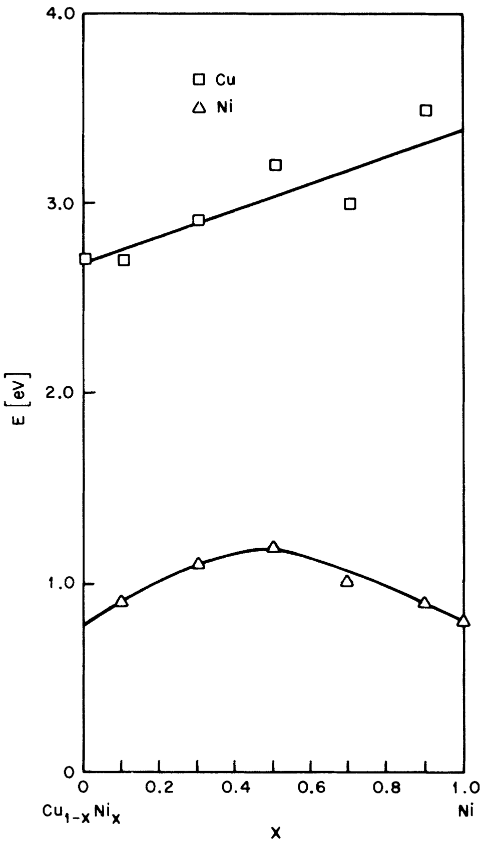

FIG. 9. Centroid positions of the Cu and Ni derived *d* bands in CuNi alloys.

data with a limited photon range may well pose a considerable, though in principle not insoluble, problem for a material as complicated as a binary alloy. It is nevertheless clear that UPS data taken over a limited photon energy range do show the general features of the density of states of the material under investigation.

At this point it seems useful to obtain the parameters that describe the behavior of dilute Ni in Cu, since these are important for our understanding of the formation of magnetic moments in metals. The procedure employed suffers from the uncertainty of the interpretation of the XPS density of states in terms of band density of states. The results must therefore be regarded with some reservations. The analysis is based on the Friedel–Anderson model.[47,48] The two parameters describing the virtual bound state are its position E_d below the Fermi energy E_F and, assuming a Lorentzian shape, the half-width at half-height Δ. We find $E_d = 0.9 \pm 0.1$ eV and $2\Delta_{\text{expt}} = 1.2 \pm 0.2$ eV for 10% Ni in Cu from the data in Fig. 6. It should be noted that these values are in good agreement with those obtained in the UPS experiment of Seib and Spicer[52] on a sample with 13% Ni. Since this experiment does have the advantage of a larger escape depth and is therefore not as sensitive to surface effects, one might conclude from this agreement that in the present experiment on the alloy the Ni results are also not too much influenced by surface effects. Extrapolating to zero concentration as indicated in Figs. 8 and 9, we find $E_d = 0.8 \pm 0.1$ eV and $2\Delta_{\text{expt}} = 1.0 \pm 0.2$ eV. Since the measured width is only twice the instrumental width, $\Gamma_{\text{inst}} = 0.5$ eV, the correction for instrumental broadening is important. The analysis of a great number of core lines (e.g., Ag 3*d*, Pd 3*d*) with the Hewlett–Packard instrument leads to the conclusion that its resolution function is neither completely Lorentzian nor completely Gaussian. Therefore it was decided to take the average value obtained after linear and quadratic subtraction of the instrumental linewidth from the experimental one. This yields $2\Delta = 0.7 \pm 0.2$ eV.

Table I summarizes the present status of results for the bound-state parameters for Ni and Cu. The most accurate results are certainly those of the very detailed recent optical investigation,[53] but on the whole the parameters agree surprisingly well, indicating $\Delta = 0.3$ eV and $E_d = 0.8$ eV for Ni in Cu. It should be pointed out that according to Yafet[56] crystal field splitting contributes only slightly to the width, so that the measured Δ is a very good representation of the *s*-*d* scattering matrix element. It is encouraging, considering our present state of understanding, that the 0.3-eV value for Δ derived by Yafet[56] from the spin-flip scattering amplitude is in good agreement with the direct spectroscopic measurements.

In the Anderson[47] model

$$\Delta = \pi \langle v^2 \rangle N_s(\epsilon),$$

where $\langle v^2 \rangle$ is the average *s*-*d* scattering matrix element and $N_s(\epsilon)$ is the conduction-electron state density at the position of the resonant bound state. Assuming that the bottom of the conduction band is 6–7 eV below the Fermi energy, one obtains $N_s(\epsilon) \sim 0.1\ \text{eV}^{-1}$. With $\Delta = 0.3$ eV, this leads to a value of $\langle v \rangle \sim 1.0$ eV, which is smaller than the original estimate by Anderson.[47] It is also worth pointing out that 2Δ is smaller than the width of the *d* band of Ni metal. This implies that a considerable portion of the *d* bandwidth is due to *d*-*d* overlap, while the width of the resonant bound state provides a measure of the *s*-*d* scattering.

Finally a brief comparison with x-ray spectroscopic investigations will be made. Clift *et al.*[57] have investigated the M_3 emission spectrum of CuNi alloys over the complete composition range. Their resolution was not sufficient to reveal any details of the conduction band, but they found that they could reproduce their alloy spectra by a linear

TABLE I. Resonant bound-state parameters for Ni in Cu;

$$E = \frac{g}{\pi} \frac{\Delta}{(E - E_d)^2 + \Delta^2}$$

(see Ref. 47).

Method	Δ (eV)	E_d (eV)	Composition (at.% Ni)	Ref.
Specific heat	0.3	0.93	10	55
Thermoelectric power	0.25 ± 0.10	0.70 ± 0.05	<1	54
UPS	0.55	0.95	13	52
Optical	0.27 ± 0.02	0.75 ± 0.02	1	53
XPS	0.35 ± 0.10	0.8 ± 0.1	0	this paper
CPA	0.23	0.8	13	45
Theory	0.3			56

superposition of the pure-metal spectra, with intensities proportional to the concentrations. This strongly suggests that there is very little sharing of electrons between the two constituents in this alloy series, as also found here. Gudat and Kunz[58] have performed an interesting x-ray absorption experiment in the region of the 3*p* transitions. They compared the x-ray absorption spectrum of a $Cu_{0.5}Ni_{0.5}$ alloy sample containing an equivalent of 150 Å of Ni and 150 Å of Cu with the spectrum obtained from a sample consisting of a sandwich of 150-Å Cu and 150-Å Ni separated by 80 Å of carbon and found no difference in the x-ray absorption spectra, showing again in an elegant way how little sharing of electrons occurs between Cu and Ni. Finally, Ertl and Wandelt[59] have determined the density of states at the Fermi energy by x-ray appearance-potential spectroscopy. They find a variation of that density of states with concentration which is in very good agreement with the results of the CPA calculations by Stocks *et al.*[45]

C. AgPd Series

From an electronic point of view, the AgPd system is very similar to the CuNi system just considered. It has the advantage that the centers of the *d* bands of the two constituents are more widely separated, so that the effects caused by changing the composition can be more easily resolved. It is of less general interest, however, because this system does not become magnetic.

High-resolution XPS spectra of the valence bands of a number of alloys, Figs. 10 and 11, exhibit features basically very similar to those of the CuNi series. A preliminary account of this work may be found in Ref. 60, where a comparison is made with the results of a CPA model calculation by Velicky *et al.*[43] This calculation does not use realistic band shapes, but contains all the other features characteristic of the CPA. The predictions of this model are in general agreement with the AgPd XPS density of states. Since no CPA calculations have been performed for the AgPd system, we cannot give a more detailed comparison.

Figure 11 shows selected spectra in greater detail. For low palladium concentrations, the Pd *d* band sits on top of the silver *sp* band well separated from the Ag *d* band. To determine the Pd *d*-electron contribution to the density of states at the Fermi surface in the dilute-alloy regime requires more detailed knowledge of the resolution function of the instrument than is currently available. We estimate the width of the impurity band in the low-concentration regime in the same way as for the Ni in Cu case. The position and width at 5-at.% Pd concentration are $E_d = 2.05 \pm 0.10$ eV and $2\Delta = 1.0 \pm 0.2$ eV; extrapolation to infinite dilution yields $E_d = 2.00 \pm 0.05$ eV and $2\Delta = 0.95 \pm 0.20$ eV, as can be seen from Fig. 12. Applying the resolution correction intermediate between a linear and quadratic subtraction of the instrumental resolution yields $2\Delta = 0.6 \pm 0.2$ eV. Band positions and uncorrected bandwidths are shown in Fig. 12. This figure reveals some interesting trends in the XPS density of states. The centers of the bands are almost independent of concentration for Ag as well as for Pd. This shows that the local potentials at the sites of Ag and Pd are roughly independent of concentration, an assumption which underlies also the CPA description of the binary-alloy systems. The variation of the bandwidth with concentration is very much more pronounced for Pd than for Ag. Band effects are expected to be more important in Pd than in Ag.[61] At low Pd concentrations the width of the XPS Pd band (except for instrumental effects) is caused by spin-orbit split-

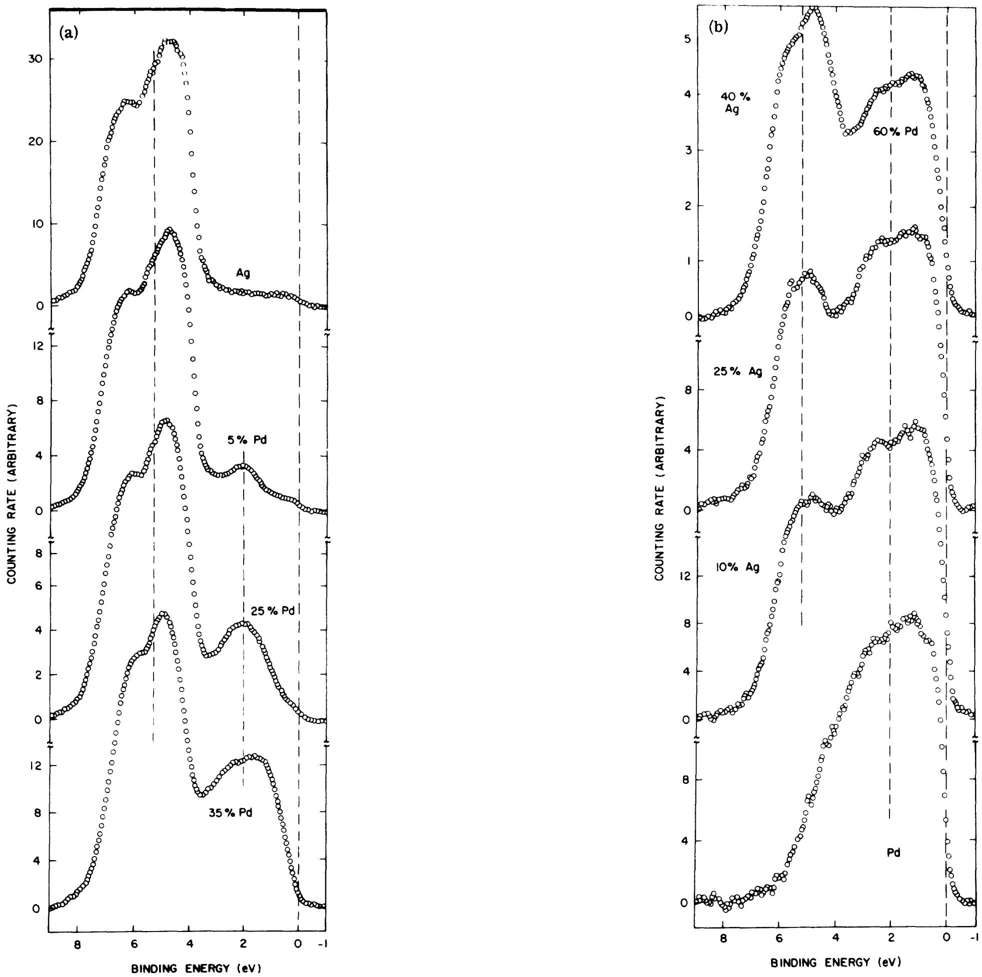

FIG. 10. Valence-band spectra of AgPd alloys obtained with monochromatized x rays. The inelastic component as well as the background has been subtracted. (a) Silver-rich alloys and (b) palladium-rich alloys; the alloy compositions refer to atomic fractions.

ting, crystal field splitting, and *s*-*d* overlap. With increasing concentration *d*-*d* overlap becomes important, and in pure palladium constitutes the major source of the bandwidth. The concentration dependence of the XPS bandwidth is much less pronounced for Ag. The infinite-dilution limit of about 1.8 eV is quite close to that found by Pollak *et al.*[61] in In and Cd, where, according to their analysis, the "4*d* bands" are basically atomiclike. In the latter material band effects start to become quite noticeable. The above shows that the screening of the *d* electrons is considerable and that the nature of an isolated Ag ion in a Pd matrix is still quite atomiclike as far as the 4*d* electrons are concerned.

This system suffers even more than the CuNi system from an uncertainty regarding the actual concentrations. It is evident that the relative intensity of the palladium peaks is lower by up to 50% as compared to that expected on the basis of the bulk composition. The XPS spectra for palladium alloys show oxygen and carbon signals which are larger than in the CuNi alloys. These signals have about $\frac{1}{20}$ of the intensity of the Pd 3*d* signal. It is known[62] that Co absorbs especially strongly on Pd, and in a AgPd alloy preferentially on Pd ions. It is possible that the reduction in palladium signals is actually due to this selective absorption on surface palladium atoms. Samples measured directly after mechanical cleaning show the same intensity ratios of the Pd and Ag signals as samples which have been extensively sputtered by argon-ion bombardment. In no case was it possible to detect additional lines due to some oxidized form of Pd in any of the Pd core level spectra. (The Pd 3*d* lines with a width of less than 1 eV are especially sensitive to this test.) It is therefore very likely that the observed Pd signal in the valence-band region is also due to metallic

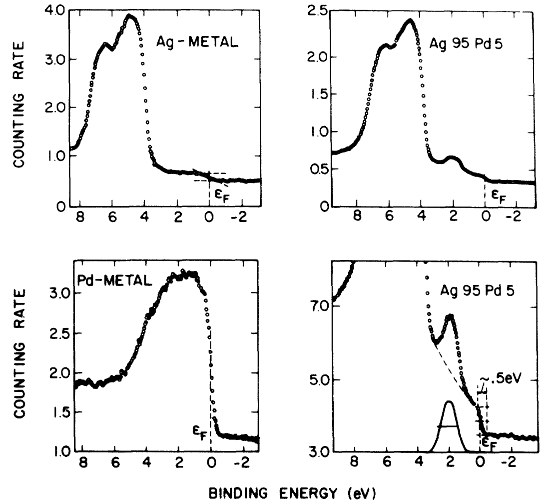

FIG. 11. Valence-band spectra of Ag, Pd, and $Ag_{0.95}Pd_{0.05}$, showing the Fermi energy and Pd virtual bound state; the alloy compositions refer to atomic fractions.

Pd, and that the main deformation in the spectra is a distorted intensity ratio between the Ag and Pd bands.

Detailed UPS measurements[63] have recently been reported for the AgPd system. The main limitation in these measurements arises from the use of a photon energy of $h\nu \leq 11.2$ eV. This makes it impossible, to obtain a complete picture of the silver and palladium *d* bands because they extend too far below the Fermi energy. In addition, as in every UPS measurement, there is the question as to the extent to which the measured electron energy distributions really represent the occupied density of states. On superficial inspection, at least, the UPS and XPS silver spectra look surprisingly similar, but the UPS spectrum shows only half of the *d* band, which at 11.2-eV energy happens to have structure similar to that of the complete band (the width being of course only half of that seen in the XPS spectrum). In the low-palladium-concentration range the UPS data concerning the width of the palladium *d* band appear quite similar to the XPS measurements. The *d* band falls 2.1 ± 0.1 eV below E_F in both experiments. The measured width of the *d* band in the very-dilute-palladium regime is 1 eV in both the UPS and XPS measurements. This is surprising in view of the fact that the UPS experiment appears to have a resolution considerably better than the XPS measurement, and suggests either that the instrumental resolution in the UPS experiment has been underestimated, or that differences in the preparation of the sample surface play an important role.

The XPS measurement, corrected for the instrumental resolution, as in the case of Ni in Cu, yields a width of 0.6 eV. Correction for spin-orbit splitting should reduce this value slightly. In the UPS case the authors[63] assumed that the instrumental broadening is negligible and that there is a 0.5-eV contribution due to spin-orbit splitting which they subtract from the measured width to obtain $2\Delta = 0.5$ eV. The subtraction of the full free-atom spin-orbit splitting does, however, seem hard to justify. We are thus left with the conclusion that the width of the palladium 4*d* band after correction for instrumental broadening seems to be slightly smaller in the XPS than in the UPS measurement. The extraction of the *s*-*d* scattering matrix element is complicated by the unknown magnitude of the spin-orbit splitting.

Low-resolution XPS and SXS spectra for $Ag_{0.7}Pd_{0.3}$ have recently also been reported by Hedman *et al.*[64] It is again evident that the SXS spectrum shows much less structure than the XPS spectrum. Finally it should be pointed out that the first interpretation of UPS data in terms of the CPA was that by Nilsson[65] on the AuAg system.

VI. SUMMARY

The XPS investigations on the noble metals have shown that there is some correlation between the XPS density of states and calculated one-electron band structures; the failure of Ni in this respect is a clear warning against generalization of this statement. Higher resolution for the XPS measurements is clearly desirable in order to detect more detailed structure. But again, some warning

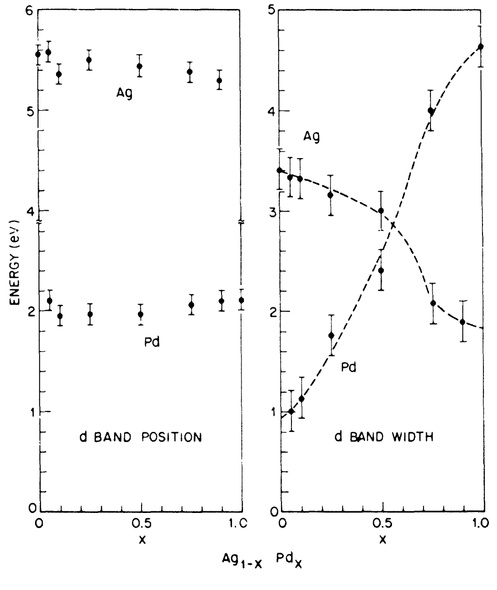

FIG. 12. Ag and Pd *d* bandwidths and positions in the AgPd alloys from Ref. 60.

seems to be in order. UPS experiments with a resolution of around 0.1 eV often fail to show much more structure than the XPS requirements with a fivefold worse resolution. This may indicate that lifetime effects smear out much of the structure expected from a one-electron band-structure calculation. The investigation by photoelectric methods of the CuNi and AgPd alloy systems show that the over-all prediction of the CPA is verified in systems which fall into the split-band regime. In the low-impurity limit the Friedel–Anderson model[47,48] is applicable. A number of problems remain. There is also the need for an independent determination of the surface composition. The systematic investigation of alloy systems may still help to shed some light on another problem, namely, whether UPS data are best described by direct transitions or by indirect transitions. Upon alloying, the k vector ceases to be a good quantum number and transitions which have been forbidden by the k selection rule in the pure metal should now be observable.

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