

Valence-band photoemission and Auger-line-shape study of $\text{Au}_x\text{Pd}_{1-x}$

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We report an experimental study of the electronic structure of the alloy system $\text{Au}_x\text{Pd}_{1-x}$. Valence-band photoemission spectra were recorded using synchrotron radiation, exploiting the different photoionization cross sections of the Au and Pd d bands to identify the spectral features. We find that recent electronic-structure calculations using the Korringa-Kohn-Rostoker method with the coherent-potential approximation (KKR-CPA) give good agreement with our results, whereas earlier calculations using other methods show serious discrepancies. In addition we measured the Au $N_{6,7}VV$ and Pd $M_{4,5}VV$ Auger line shapes. We find that one-electron calculations using the KKR-CPA results give reasonable qualitative agreement for the Au line shapes across the alloy series. Similar agreement is found for the Pd Auger line shapes at high Pd concentrations, but this breaks down for low Pd concentrations. We suggest that this disagreement results from a neglect of many-body interactions rather than a problem with the KKR-CPA calculations.

I. INTRODUCTION

The electronic structure of disordered alloy systems is an area in which much understanding has been gained in the last 15 years. The coherent-potential approximation (CPA),¹ in which the alloy is treated as an effective medium subject to zero average scattering, has been widely employed to calculate Bloch spectral functions and densities of states (DOS) for a wide range of random substitutional alloy systems. Initially used with a semiempirical tight-binding formalism (TB-CPA),² most recent work emphasizes the first-principles Korringa-Kohn-Rostoker method (KKR-CPA),³ although there is also some interest in the tight-binding muffin-tin-orbital approach (TB-MTO-CPA),⁴ also a first-principles method. Interest in these alloys is not only due to their intrinsic physics, but also to the fact that many disordered noble-metal alloy systems, including $\text{Au}_x\text{Pd}_{1-x}$, have important catalytic properties.⁵

The alloy system $\text{Au}_x\text{Pd}_{1-x}$ forms a continuous series of face-centered-cubic solid solutions over the entire compositional range. The earliest complete set of calculations are the TB-MTO-CPA results of Kudrnovsky and Drchal.¹⁶ There have also been several calculations for part of the series, employing the TB-CPA (Ref. 7) and KKR-CPA schemes.⁸ Recently Weinberger, Szunyogh, and Bennett⁹ calculated the electronic structure of the whole series using the fully relativistic KKR-CPA method. In addition they calculated spectra from three band-structure spectroscopies: valence-band photoemission, Au $N_{6,7}$ x-ray emission, and Au and Pd core-valence-valence (CVV) Auger line shapes.

The literature contains relatively little experimental band-structure spectroscopy of $\text{Au}_x\text{Pd}_{1-x}$. The Au-rich end of the series was studied with Au $N_{6,7}$ x-ray emission

by Muller *et al.*,⁸ and the Pd $M_{4,5}VV$ Auger line shape of $\text{Au}_{0.5}\text{Pd}_{0.5}$ was reported by Kleiman *et al.*¹⁰ as part of a more general study of alloy core-level shifts. The He I spectrum of dilute (4.5 at. %) Pd in Au was shown by van der Marel, Jullianus, and Sawatzky¹¹ in their study of dilute Pd and Pt alloys, together with calculations based on a model Hamiltonian which showed good agreement with their data. Only one set of experiments, the low-resolution He II photoemission date of Nicholson *et al.*,¹² covers the whole compositional range. There has been only one angle-resolved photoemission study,¹³ of $\text{Au}_{0.7}\text{Pd}_{0.3}$ (100), and this also employed a resonance lamp as the photon source. To date synchrotron radiation has not been used to study the $\text{Au}_x\text{Pd}_{1-x}$ system. This is somewhat surprising, since synchrotron radiation is particularly suited to the study of alloys, especially those of $4d$ and $5d$ metals. For these metals the Cooper minimum in the photoemission cross section of their respective d bands allows unambiguous identification of the main spectral features. In this paper we report valence-band photoemission spectra of $\text{Au}_x\text{Pd}_{1-x}$. In addition we have measured x-ray-excited Auger electron spectra (XAES) of both the Pd $M_{4,5}VV$ and Au $N_{6,7}VV$ transitions, again using synchrotron radiation. The advantage of using x-ray excitation is that the background of inelastic electrons is very much smaller compared to that from electron excitation, commonly used in Auger elemental analysis.

II. EXPERIMENT

Polycrystalline samples were prepared by arc-melting high-purity materials in the required ratios, giving sample of $\text{Au}_x\text{Pd}_{1-x}$ with $x = 0.2, 0.4, 0.8$, and 1. The photoemission and XAES experiments were performed using

Los Alamos beamline U3C (Ref. 14) at the National Synchrotron Light Source at Brookhaven National Laboratory. The beamline endstation was a Vacuum Science Workshops (VSW) ultrahigh-vacuum chamber, with a base pressure of $\sim 10^{-10}$ mbar. A VSW HA50 hemispherical analyzer, fitted with a multichannel detection system, was used to acquire the spectra. For the photoemission measurements the overall resolution varied from ~ 100 meV at $h\nu=40$ eV, to ~ 400 meV at $h\nu=200$ eV. For the XAES measurements we used exciting photons of energy 200 and 450 eV for the Au and Pd Auger lines, respectively, with an analyzer resolution of ~ 200 meV. Clean surfaces were obtained by scraping the sample *in situ*.

III. PHOTOEMISSION RESULTS

To demonstrate the photon energy dependence of the Au $5d$ and Pd $4d$ bands we show in Fig. 1 a series of valence-band spectra from $\text{Au}_{0.4}\text{Pd}_{0.6}$. The Pd Cooper minimum was calculated to be 110 eV by Yeh and Lindau,¹⁵ but was found experimentally for Pd metal to be 130 eV.¹⁶ In Fig. 1 we see that the peak near the Fermi level (E_F) is strongly suppressed at a photon energy of 120 eV while the other two peaks remain strong. Close to the Au Cooper minimum of 210 eV,¹⁵ we see that these two peaks are suppressed while the E_f peak remains strong. On the basis of these data it seems reasonable to assign the near- E_F peak to Pd $4d$ states and the other two peaks to the Au $5d^{3/2}$ and $5d^{5/2}$ states. The same three-peak structure showing the same trends in photon energy dependence is also exhibited by the other alloy concentrations, and so we conclude that these peak assignments are valid throughout the series. Note also that the apparent change in the Au $5d$ line shape at $h\nu=80$ eV is not in-

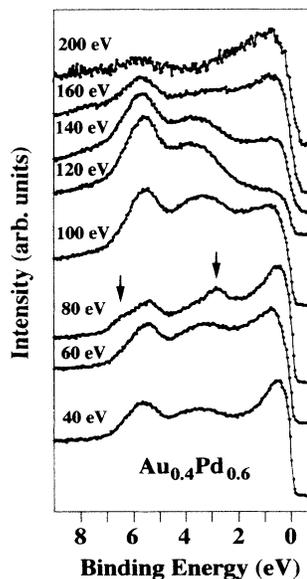


FIG. 1. Valence-band photoemission spectra of $\text{Au}_{0.4}\text{Pd}_{0.6}$ as a function of photon energy. The arrows in the spectra taken by $h\nu=80$ eV indicate the positions of the Au $4f$ levels in second order.

trinsic, but due to the Au $4f$ levels excited by second-order light of $h\nu=160$ eV. To quantitatively follow the binding-energy (BE) trend of the Pd $4d$ peak it might be considered preferable to measure the alloy series at a photon energy around the Au Cooper minimum. However the beamline resolution and Pd $4d$ photoemission cross sections around 200 eV are rather poor, so in Fig. 2 we compare the spectra taken at $h\nu=40$ eV, where the Pd peak is well resolved. These results are entirely consistent with the He II ($h\nu=40.8$ eV) results of Nicholson *et al.*,¹² although our resolution is somewhat higher. As the Pd concentration is reduced the Pd $4d$ band narrows and moves toward higher binding energy, though at all concentrations it remains distinct from the Au d bands, indicating split-band rather than mixed-band behavior. To follow the trends in Au $5d$ binding energies we show in Fig. 3 the alloy spectra taken at $h\nu=120$ eV. Here the Au $5d^{1/2}$ peak moves toward lower binding energies as the Au concentration is reduced, while the $5d^{5/2}$ peak moves toward higher binding energies. The use of the Pd Cooper minimum shows that the Au d bands do not converge to a single virtual bound state, as suggested by Nicholson *et al.* on the basis of their He II data. At $h\nu=40$ eV the tail of the Pd $4d$ state tends to mask the Au $5d^{5/2}$ peak, especially in low-resolution spectra, thus only one Au peak is apparent at low Au concentrations.

In Fig. 4 we plot the binding energies of the Pd $4d$ peak (from Fig. 2) and Au $5d$ peaks (from Fig. 3), together with those determined by Nicholson *et al.*,¹² and the theoretical binding energies from the two available complete sets of calculations. Comparing first the two sets of experimental data, we note that the binding energies of the Au $5d^{3/2}$ peak are in excellent agreement. The two experiments also agree on the BE trend of the Pd $4d$ peak, although we find consistently lower binding energy. This is almost certainly due to the poorer resolution of the He II spectra of Nicholson *et al.* For the Au $5d^{5/2}$

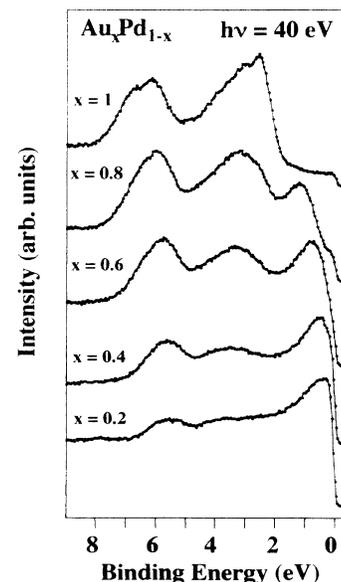


FIG. 2. Valence-band spectra of $\text{Au}_x\text{Pd}_{1-x}$ at a photon energy of 40 eV.

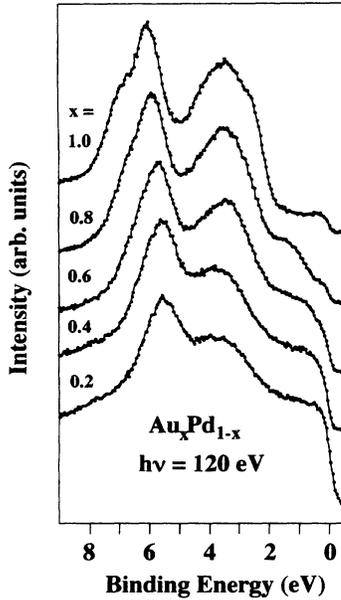


FIG. 3. Valence-band spectra of $\text{Au}_x\text{Pd}_{1-x}$ near the Pd 4d Cooper minimum.

peak there is also some discrepancy between the two experiments. This is probably due to the influence of the Pd 4d peak on the Au line shape in the He II spectra, as the presence of the Pd peak pulls the apparent position of the Au $5d^{5/2}$ peak to lower binding energy. For our result, utilizing the Pd Cooper minimum, such effects

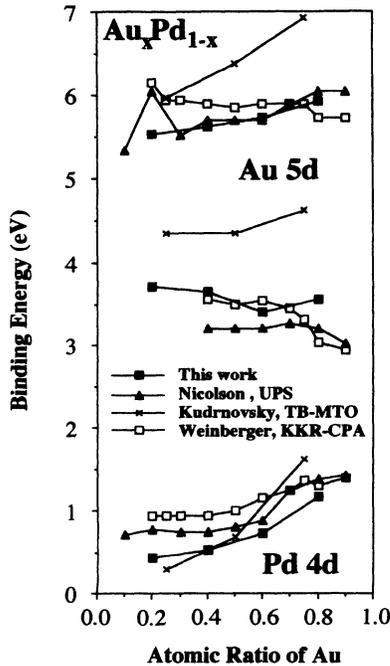


FIG. 4. Comparison of the d -band binding energies determined from experiment (this work and Ref. 12) with those calculated by Weinberger, Szunyogh, and Bennett (Ref. 9) and Kudrnovsky and Drchal (Ref. 6).

should be much reduced; hence we find the Au $5d^{5/2}$ peak consistently at higher binding energy. This effect can be seen in Fig. 1, where the apparent Au $5d^{5/2}$ binding energy is higher at $h\nu = 120$ eV than at all other photon energies, all of which have appreciable Pd 4d peaks. In general the KKR-CPA calculations of Weinberger, Szunyogh, and Bennett⁹ seem to provide good quantitative agreement with the experimental data. This suggests that self-energy effects are minimal in this system, which is not always the case with gold alloys. The only discrepancy of note here concerns the binding-energy trend of the Au $5d^{3/2}$ peak: the experiments show a trend toward higher binding energy as the Au concentration is increased, whereas the opposite trend is predicted by the calculations. The discrepancies with the TB-MTO calculations of Kudrnovsky and Drchal⁶ are rather more serious: the calculated Au binding energies are significantly higher than experiment, with both shifting to higher binding energy as Au concentration is increased. The shift in the Pd binding energy, while in the right direction, is also overestimated, by about a factor of 2. Kudrnovsky and Drchal⁶ also find an extra Pd peak at ~ 4.5 eV binding energy: we find no evidence for such a peak in the experimental results. Weinberger *et al.* show a second Pd peak at around 3 eV for high Pd concentrations. In Fig. 5 we show a spectrum of $\text{Au}_{0.2}\text{Pd}_{0.8}$ taken near the Au 5d Cooper minimum, in which the Pd peak can be seen to have a shoulder at around 2.6 eV. This may well have the same origin as the theoretical peak, but if so its intensity is clearly overestimated by the calculations. The TB-CPA calculations of Laufer and Papaconstantopoulos⁷ do not include spin-orbit interaction and so even the qualitative behavior of the Au d bands is not reproduced in their calculations.

IV. AUGER SPECTRA

In 1953 it was proposed¹⁷ that the line shape of CVV Auger transitions should be proportional to a self-convolution of the valence-band density of states. Many

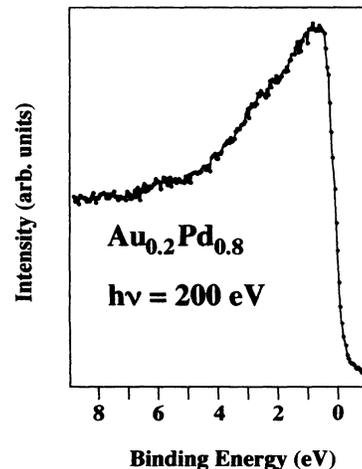


FIG. 5. Valence-band spectrum of $\text{Au}_{0.2}\text{Pd}_{0.8}$ near the Au 5d Cooper minimum.

years later it was found¹⁸ that while some materials had bandlike spectra, qualitatively consistent with the theory in Ref. 17, narrow-band materials had quasiautomatic spectra, which were in no way consistent with the theory. In the late 1970s Cini^{19,20} and Sawatzky²¹ considered the effect of the Coulomb repulsion U between two holes localized on the same atomic site on the Auger line shape. They found that in the limiting case $U \ll W$, where W is the local one-hole density of states, the spectra were bandlike, with the line shape given by the self-convolution of the DOS. However, once U/W exceeded a critical value of order unity a quasiautomatic peak developed outside the continuum. As U/W increased, so the bandlike part of the spectrum lost weight, and as the limit $U \gg W$ approached the spectrum became entirely atomic. Thus in the Cini-Sawatzky model the CVV Auger spectrum consists of both a bandlike and an atomiclike component, the relative intensities being controlled by the ratio of U to W . The $M_{4,5}VV$ transition, if we assume the two final-state holes are in the $4d$ band, has two states M_4 and M_5 each of which decays into the final state 1S , 3P , 1D , 3F , and 1G . The U value for each final state will be different, so the bandlike/atomiclike balance will similarly be different for each state, with the final Auger spectrum being a superposition of all the components. The validity of this model was confirmed largely by a series of experiments on Ag (Ref. 22) and Pd (Refs. 23 and 24) alloys by Weightman, Andrews, and co-workers. In particular they found²³ that for a series of Pd alloys the almost bandlike spectrum of pure Pd underwent a transition to an almost atomiclike line shape, in the case of $Mg_{0.75}Pd_{0.25}$, as the Pd $4d$ -band width was reduced.

Weinberger, Szunyogh, and Bennett⁹ calculated the Pd $M_{4,5}VV$ and Au $N_{6,7}VV$ Auger spectra using a fully relativistic one-electron formalism, which in the language of the Cini-Sawatzky model assumed $U \ll W$. For pure Pd this approach has been shown²⁵ to yield results very similar to that of a full Cini-Sawatzky calculation.²⁶ The calculations of Weinberger, Szunyogh, and Bennett⁹ show that as the Pd concentration is reduced the Pd $M_{4,5}VV$ spectrum resolves into two narrow peaks separated by the Pd $3d$ spin-orbit splitting of 5.3 eV. In Fig. 6 we show our experimental results. Clearly we are not seeing the behavior predicted by Weinberger, Szunyogh, and Bennett. For $Au_{0.2}Pd_{0.8}$ the agreement is still tolerable but becomes progressively worse as the Pd concentration reduces. Figure 7 shows the experimental and calculated spectra for $Au_{0.8}Pd_{0.2}$. Given that the Pd bandwidth is narrowing as the Pd concentration is reduced it is not surprising that the one-electron approach might fail at low Pd concentrations, as a transition to a quasiautomatic line shape might be expected. However, the quasiautomatic line shape for the Pd $M_{4,5}VV$ Auger spectrum, as shown by the $Mg_{0.75}Pd_{0.25}$ spectrum in Fig. 7, is clearly quite different. This behavior, a transition to a spectral line shape that appears to be neither quasiautomatic nor quasi-bandlike, an apparent failure of the Cini-Sawatzky model, was also seen for AgPd alloys²⁷ (see again Fig. 7) and at the time was regarded as anomalous. This was resolved

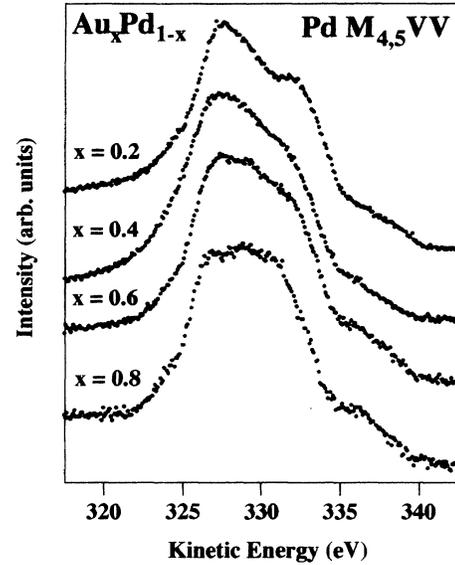


FIG. 6. Pd $M_{4,5}VV$ Auger spectra of Au_xPd_{1-x} . The energy scale is referred to the Fermi level.

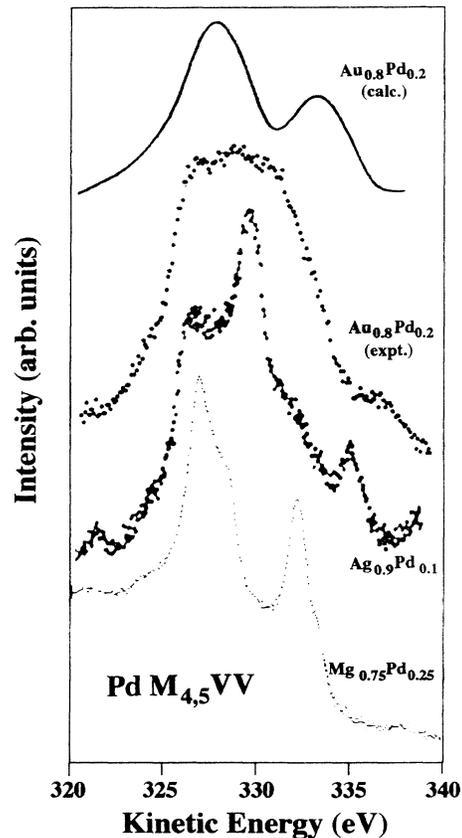


FIG. 7. Experimental (this work) and calculated (Ref. 9) Pd $M_{4,5}VV$ Auger spectrum of $Au_{0.8}Pd_{0.2}$, together with those of $Ag_{0.9}Pd_{0.1}$ (Ref. 26) and $Mg_{0.75}Pd_{0.25}$ (Ref. 22). The energy scale is referred to the Fermi level.

by Vos and co-workers,²⁸⁻³⁰ who pointed out that the lineshape of the i th quasiatomic component is determined by the one-hole DOS at a binding energy $E_b(4d) + U_i$, where $E_b(4d)$ is the binding energy of the Pd $4d$ band and U_i is the U value for the particular final state. If there is a structure in the DOS at this energy the narrow quasiatomic peak will be subject to considerable broadening. A clear theoretical example can be seen in Figs. 6 and 7 of Ref. 29. For $\text{Ag}_{0.9}\text{Pd}_{0.1}$ most of the binding energies $E_b(4d) + U_i$ coincide with the Ag d bands; hence the spectral components are broadened. However, the binding energies $E_b(4d) + U_i$ corresponding to the 1S_0 and 1G_4 components are clear of the Ag d band and so produce the sharp peaks seen in the otherwise broad $\text{Ag}_{0.9}\text{Pd}_{0.1}$ spectrum. Taking account of this effect, the Cini-Sawatzky model is able to produce excellent agreement²⁷ with the $\text{Ag}_{0.9}\text{Pd}_{0.1}$ spectrum of Fig. 7. To determine if this effect could also account for the broad $\text{Au}_{0.8}\text{Pd}_{0.2}$ spectrum we took the U_i values for $\text{Ag}_{0.9}\text{Pd}_{0.1}$ from Ref. 28 as an approximation for those of $\text{Au}_{0.8}\text{Pd}_{0.2}$. This seems a reasonable approximation since $U(^1G_4)$ has been found not to vary widely, having values of 2.95 ± 0.15 eV, for a wide range of Pd alloys.³¹ Taking $E_b(4d)$ to be the centroid of the Pd $4d$ peak in the photoemission spectra, we determined $E_b(4d) + U_i$ for the possible final states. The results are shown in Fig. 8. Unlike in $\text{Ag}_{0.9}\text{Pd}_{0.1}$, here all the energies $E_b(4d) + U_i$ coincide with the Au d band, and so we would expect each contribution to be broadened, producing an absence of sharp peaks in the Auger spectrum, as we observe. Vos *et al.*²⁸ in fact predicted that the Pd $M_{4,5}VV$ Auger spectrum in $\text{Au}_x\text{Pd}_{1-x}$ would behave in this fashion for low Pd concentrations, although they did not perform an explicit calculation.

The $N_{6,7}VV$ Auger spectrum of pure Au (Refs. 32 and 33) appears to be well explained on the basis of the Cini-Sawatzky model.^{32,34} Aside from $U(^1S_0)$ all the U_i

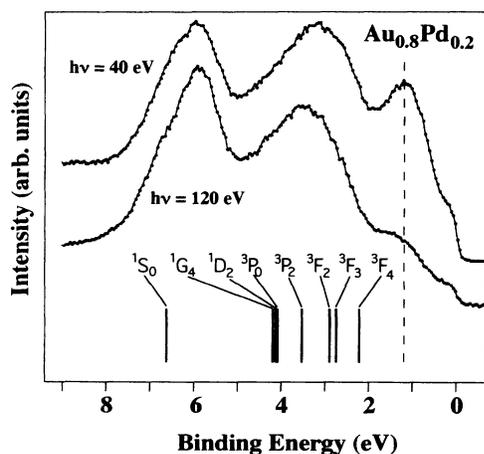


FIG. 8. Energy positions $E_b + U_i$ of the d^8 final-state terms for the Pd $M_{4,5}N_{4,5}VV$ Auger process. E_b is taken to be the centroid of the Pd d band (dashed line). For comparison with the Au d band the $\text{Au}_{0.8}\text{Pd}_{0.2}$ spectrum taken near the Pd Cooper minimum is also shown.

values were found to be small enough to yield bandlike spectral components³³ and so it seems reasonable to expect a one-electron calculation for Au to yield tolerable agreement with experiment, except for the presence of the quasiatomic 1S_0 component. Since our photoemission spectra and the DOS calculations of Weinberger, Szunyogh, and Bennett⁹ agree that the total Au $5d$ -band width does not significantly decrease across the $\text{Au}_x\text{Pd}_{1-x}$ series, the calculated Au $N_{6,7}VV$ spectra⁹ should give better agreement with experiment for dilute Au concentrations than is the case with the Pd spectra of dilute Pd.

Due to its low kinetic energy the Au $N_{6,7}VV$ spectrum lies on a sloping background of inelastic electrons. This background is smooth and can be subtracted by fitting a parametrized expression to the low and high kinetic energy sides of the spectrum and subtracting the result. An example of this procedure is shown in Fig. 9. The background-subtracted Au $N_{6,7}VV$ spectra of $\text{Au}_x\text{Pd}_{1-x}$ are shown in Fig. 10. The peak at ~ 66 eV is that which has been identified as the 1S_0 component in pure Au.³³ The principal features in the Auger spectrum are peaks at ~ 70 and 74 eV. As the Au concentration is reduced the relative intensities of these peaks changes: in pure Au the 74-eV peak is higher, but by $\text{Au}_{0.2}\text{Pd}_{0.8}$ the 70-eV peak is higher. The same trend is seen in the calculations of Weinberger, Szunyogh, and Bennett⁹ although the peaks are not well resolved, due presumably to the large broadening (1 eV) applied to the calculations to simulate experimental resolution (in our case the resolution was of order 200 meV). In both calculation and experiment the overall width remains essentially constant. There is little evidence of sharpening of spectral features in the experimental spectra, as would be expected if a transition to quasiatomic behavior were occurring. [For Au in AuPd alloys the energies $E_b(5d) + U_i$ all lie in a region with low DOS, thus any atomiclike contributions will be sharp peaks.]

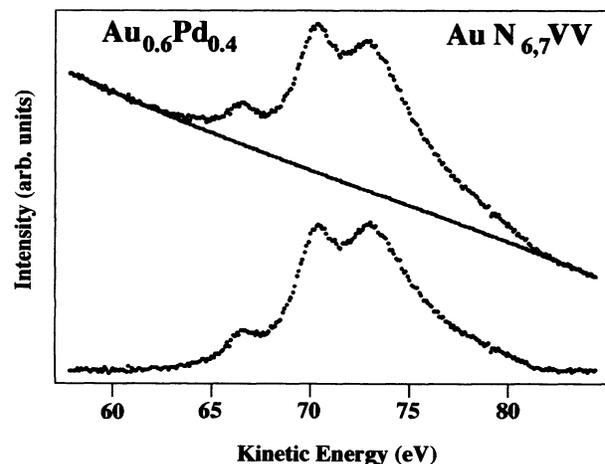


FIG. 9. Example of the subtraction procedure used to remove the inelastic background from the Au Auger spectra: (a) Raw data (points) and polynomial fit (solid line) to the background. (b) Data after subtraction of background.

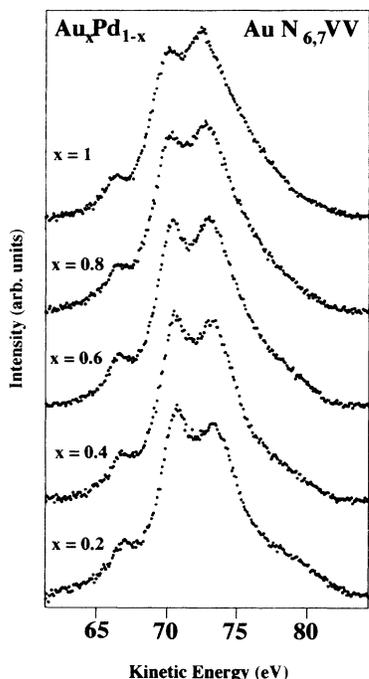


FIG. 10. $Au N_{6,7}VV$ Auger spectra of Au_xPd_{1-x} . The inelastic background has been subtracted from each spectrum using a polynomial fit (see Fig. 9). The energy scale is referred to the Fermi level.

V. CONCLUSIONS

The KKR-CPA calculations of Weinberger, Szunyogh, and Bennett⁹ appear to give a good description of the electronic structure of Au_xPd_{1-x} . There are some discrepancies—the binding-energy trend of the $Au 5d^{3/2}$ peak and the overestimation of the intensity of the Pd 3-

eV peak—but in general the agreement with the photoemission data is extremely good. The agreement between these calculations and our photoemission data is clearly better than that for the TB-MTO-CPA (Ref. 6) and TB-CPA (Ref. 7) calculations, and is comparable to that between the angle-resolved photoemission data of Arola *et al.*¹³ and their KKR-CPA calculation for $Au_{0.7}Pd_{0.3}$. We also note that the calculated x-ray emission spectra of Weinberger, Szunyogh, and Bennett⁹ show better agreement with the experimental data of Muller *et al.*⁸ than the early KKR-CPA calculations.⁸

The Auger spectra show less good agreement with the calculations of Weinberger, Szunyogh, and Bennett.⁹ The trends in the $Au N_{6,7}VV$ spectra are correctly predicted although it is difficult to judge the line-shape agreement further due to the large broadening applied to the calculated spectra. For the $Pd M_{4,5}VV$ spectra at low Pd concentrations the agreement is extremely poor but this seems very likely due to the neglect of many-body interactions in the calculated spectra. The Cini-Sawatzky model may well be able to describe the behavior of the Pd spectrum, but in the absence of a full calculation it is not possible to determine this with any quantitative accuracy. It is important to note that the discrepancy between our results and those of Weinberger, Szunyogh, and Bennett,⁹ for the Pd Auger spectra at low Pd concentrations, is not due to any intrinsic fault in the calculated electronic structure, but to an inadequate description of the Auger process.

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