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Unoccupied states and charge transfer in Cu-Pd alloys studied by bremsstrahlung isochromat spectroscopy, x-ray photoelectron spectroscopy, and L_{III} absorption spectroscopy

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We have observed the unoccupied partial Pd $4d$ density of states in Cu-Pd alloys by bremsstrahlung isochromat spectroscopy (BIS). It shows the filling of the Pd $4d$ band upon alloying, which is consistent with the Pd L_{III} absorption spectroscopy measurements. We have also determined the total charge transfer between Pd and Cu atoms from the binding energy shifts in the core-level x-ray photoelectron spectroscopy and the intensity of unoccupied Pd d states in the BIS spectra. This is compared with the result from the Pd L_{III} absorption spectroscopy.

I. INTRODUCTION

Alloy systems have attracted much attention recently both because of their interesting physical properties and the potential technological applications such as shape memory alloys, invar alloys, and new magnetic materials. In particular, their electronic structure has been the subject of many investigations since it is the first step in understanding the basic physical properties of alloys. However, the electronic structure study of disordered alloys has been hampered by the lack of the periodicity of the lattice, which makes Bloch theorem inapplicable. Many calculational methods such as the rigid-band model, the coherent potential approximation, and the supercell approximation were proposed to overcome this difficulty. On the experimental side, much effort has been directed to determine whether any of these theoretical models give correct electronic structures of alloys. Photoelectron spectroscopy has been instrumental in this effort, and naturally the occupied part of the electronic states were intensively studied. However, the study on the unoccupied level has been relatively rare so far.

Some years ago Fuggle *et al.*[1] reported that the Ni or Pd valence d band centroid shifts to the higher binding energy with respect to the Fermi level (E_F) when it forms binary alloys with electropositive metals. Their photoemission spectra also showed that the d density of states (DOS) at E_F reduces severely and the Ni or Pd d bandwidth tends to become narrow with alloying. These facts led them to propose that the Ni or Pd valence "d band" is being filled when alloyed with electropositive metals. The reduction of the DOS at E_F is also consistent with the drop of electronic specific heat[2] as well as the disappearance of magnetism in numerous such alloys, because both the electronic specific heat and magnetism depend on the DOS at E_F.

However, it is still a very controversial question whether or not the Ni or Pd d level is completely filled so that there exists no d state in the unoccupied level in these alloys. In theoretical aspects, the authors of Ref. 1 argued that the unoccupied d states can exist since the hybridization between Ni $3d$ and Ni $4s,4p$ occurs as alloying.[1,3] In other words the Ni unoccupied sp band retains some d character as alloying due to the hybridization, although the Ni "$3d$ band" is filled completely. In this regard, it may be noted that the calculation of the charge transfer to or from the Ni $3d$ states revealed only small changes in the number of d electrons of the order of 0.3 electron in alloys.[4] This fact supports the above argument since Ni metal has 1.2 holes of d character as determined by the population analysis of the linear combination of atomic orbital wave function,[5] so that there still remain about 0.9 hole of the d character in alloys.

The observation of the unoccupied density of states will be the direct test of this picture. Yet, there have been few studies on the unoccupied level in contrast to abundant theoretical and experimental studies on the occupied level. In this study, we have performed the bremsstrahlung isochromat spectroscopy (BIS), Pd L_{III} x-ray absorption spectroscopy (XAS) and core-level x-ray photoelectron spectroscopy (XPS) measurements on Cu-Pd alloys. We chose Cu-Pd alloys as our samples because their electronic structures of the occupied level are well known[6–9] but very little is known about the unoccupied level so far. We have measured BIS and XAS spectra to observe whether or not the unoccupied d state exists. We have also measured binding energy shifts of Cu $2p$ and Pd $3d$ core levels by XPS to determine the amount of the charge transfer to the Pd $4d$ level.

II. EXPERIMENT

The polycrystalline $\mathrm{Cu}_{1-x}\mathrm{Pd}_x$ (x = 0.00, 0.10, 0.25, 0.50, 0.75, 0.90, and 1.00) alloys were made by melting high-purity metallic Cu and Pd wires under argon atmosphere in arc furnace. Their elemental weights were exactly measured according to the composition of alloys. We checked weight loss after the arc-melting process and found that there was no severe change of the total weight.

According to the phase diagram of the Cu-Pd alloys,[10] the formation of the ordered phase is possible in the range 7–27 at. % Pd below 500 °C (fcc structure, i.e., α phase) and 29–55 at. % Pd below 600 °C (bcc structure, i.e., $\beta 4$ phase). To obtain randomly disordered alloys of the fcc structure, the quartz tubes containing samples were rapidly quenched in cold water after the homogenization anneal of about 20 h at the temperature of 600 °C.

The compositions of alloys in this work were mainly determined from the elemental weights before and after the arc melting. To check for the homogeneity of alloy samples, x-ray diffraction was measured and it was found that no additional different phases exist. The alloy compositions was also confirmed from XPS core-level spectra, which showed that the intensity ratios of the Pd core level to Cu core levels follow the composition of the sample.

BIS and XPS experiments were performed in an ultrahigh vacuum photoelectron spectrometer manufactured by VSW Scientific Instruments Ltd. It is equipped with a 150-mm-radius hemisphere analyzer and multichannel detector system. In the BIS experiment we used an x-ray monochromator that was set at 1486.6 eV to detect a fixed frequency of photons. The incident electron beam energy was varied from 1480 to 1500 eV. The total resolution [full width at half maximum (FWHM)] was 1.0 eV as measured by the width of the recorded step in the Ag metal BIS spectrum at E_F.

In the XPS experiment the Al $K\alpha$ line ($\hbar\omega$ = 1486.6 eV) was used as the photon source. Total spectrometer resolution (FWHM) was determined to be about 1.1 eV. The base pressure of the main chamber where BIS and XPS experiments were done was maintained in the low 10^{-10}-torr range. The samples were cleaned by sputtering with an Ar ion beam. The cleanness of the samples was checked by measuring oxygen $1s$ and carbon $1s$ peaks in XPS. During the course of study very little carbon and oxygen contamination was detected. In the case of alloys, care must be exercised regarding the composition change due to the surface segregation effect. Fortunately, it was shown for Cu-Pd alloys[11] that this effect is almost nonexistent or only leads to a very slight Pd enrichment at most, which was also confirmed in our experiments.

Pd L_{III} edge x-ray absorption near-edge spectroscopy (XANES) spectra of $\mathrm{Cu}_{1-x}\mathrm{Pd}_x$ alloys were obtained at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory on beamline X-19A. X-ray energy was varied using a Si(111) double-crystal monochromator that was detuned by ca. 50% to minimize higher-order harmonics in the x-ray beam. The X19-A beamline is maintained at ultrahigh vacuum (UHV) by up to 10-mil-thick beryllium window located inside the hutch. Since the monochromator is installed in a UHV condition, X19-A is suitable to measure L_{II}, L_{III} absorption spectra on $4d$-row transition metal compounds. To avoid thickness effect, the spectra were collected in the total electron yield mode.

III. THEORY OF THE CORE-LEVEL SHIFT

The theory of the core-level binding energy shift and the method to extract the amount of the charge transfer from the experimental core-level shift measured by XPS are described in detail in Ref. 12. Here we will briefly summarize the formula, mainly to define the notation. Experimental binding energy shift $\Delta E(i)$ of the core level i between pure metal and the alloy measured relative to the Fermi level in XPS experiments can be written as follows:[12,13]

$$\begin{aligned}\Delta E(i) &= E_B(i,\mathrm{alloy}) - E_B(i,\mathrm{metal})\\ &= -\Delta\epsilon(i) + \Delta E_F - \Delta E_r,\end{aligned} \tag{1}$$

where $\Delta\epsilon(i)$ is the change of the Hartree-Fock one-electron energy of the core level i, ΔE_F is the change of the Fermi energy, and ΔE_r is the change of relaxation energy in the presence of the core hole between pure metal and alloy.

The change of the Hartree-Fock one-electron energy level $\Delta\epsilon(i)$, which is directly related to the charge transfer in the initial ground state, can be written as

$$\Delta\epsilon(i) = \sum_j^{\mathrm{val}}[\Delta n_j F^0(i,j)] - \left[\sum_j^{\mathrm{val}}\Delta n_j\right] F^0_{\mathrm{latt}}, \tag{2}$$

where $F^0(i,j)$ is the Coulomb repulsion energy between the core electron i and the valence electron j, and Δn_j is the change in the number of the valence electron j. The first term in the right-hand side of Eq. (2) arises from the redistribution of valence electrons, and the second term is associated with the charge changes on other lattice sites due to the total charge transfer

$$\delta n = \sum_j^{\mathrm{val}}\Delta n_j, \tag{3}$$

in or out of the parent atomic site. In the case of Cu (or Pd) atom, the valence electrons are composed of $3d$ electrons ($4d$ for Pd) and $4s$ electrons ($5s$ for Pd). There may be the contribution from p electrons, but it is not necessary to distinguish s and p electrons for the present discussion. Then Eq. (2) can be rewritten as

$$\Delta\epsilon(i) = \Delta n_d F^0(i,d) + \Delta n_s F^0(i,s) - \delta n F^0_{\mathrm{latt}}, \tag{4}$$

with

$$\delta n = \Delta n_d + \Delta n_s. \tag{5}$$

To deduce $\Delta\epsilon(i)$ from the experimentally measured value $\Delta E(i)$ using Eq. (1), we have to know the values of ΔE_F and ΔE_r. We first assume that $\Delta E_F = -\Delta\Phi$, the difference of the experimental work functions of the metal and the alloy. This is equivalent to assuming that the surface dipole barrier potential contribution to the work function does not change between pure metal and the alloy. The term ΔE_r is the difference of the relaxation energy in the presence of the core hole between alloy and metal, so it is related to the final-state screening effect. A theoretical calculation[14] on alloy systems based on the pseudopotential linear response method in the presence of the core hole reveals that ΔE_r can be as large as 2 eV, which is the same order of magnitude as the initial-state effect $\Delta\epsilon(i)$ and therefore cannot be neglected. Here we will make use of the result of this calculation in Ref. 14.

Putting these all together we get the following relation between the experimental binding energy shift $\Delta E(i)$ and the amount of the charge transfer:

$$\begin{aligned}\Delta E(i) + \Delta\Phi + \Delta E_r &= -\Delta\epsilon(i)\\ &= -\Delta n_d[F^0(i,d) - F^0(i,s)]\\ &\quad + \delta n[F^0_{\text{latt}} - F^0(i,s)]. \end{aligned}\tag{6}$$

Furthermore, the total charge neutrality condition for the $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloy implies

$$x\delta n^{\mathrm{Cu}} + (1-x)\delta n^{\mathrm{Pd}} = 0. \tag{7}$$

IV. EXPERIMENTAL RESULTS

A. Unoccupied band spectra with BIS

BIS spectra of alloys shown in Fig. 1 reveal the reduction of the unoccupied DOS at E_F upon alloying clearly, which is consistent with the result of XPS and synchrotron radiation soft x-ray photoemission spectra of the occupied valence band.[7,9] These BIS spectra are normalized to have the same height at 6 eV above E_F, since Cu or Pd d states are not expected to exist at that high energy and therefore the BIS intensity is mostly due to Cu 4s and Pd 5s levels. It turns out that the photoionization cross section of the Cu 4s state is similar to that of Pd 5s,[15] so that the BIS intensity due to Cu 3s and Pd 5s states should remain almost the same regardless of the alloy composition.

We are interested in whether or not the unoccupied 4d state of the Pd atom exists at some eV above E_F. So, we need to obtain the unoccupied Pd partial density of states from the BIS spectra. For this purpose, we use a simple subtraction procedure by assuming that the partial DOS of Cu does not change upon alloying. This assumption is certainly good for Cu-rich alloys, although it will become questionable for Pd-rich alloys. But since the cross section of Pd 4d states is more than 50 times larger than that of Cu 4s,[15] a slight inaccuracy in the Cu 4s DOS would not have serious consequences. Hence to obtain the Pd partial BIS spectra of the $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloy, we subtract x fraction of pure Cu BIS spectra from the alloy BIS spectra. Figure 2 illustrates this subtraction procedure for the $\mathrm{Cu}_{0.75}\mathrm{Pd}_{0.25}$ alloys.

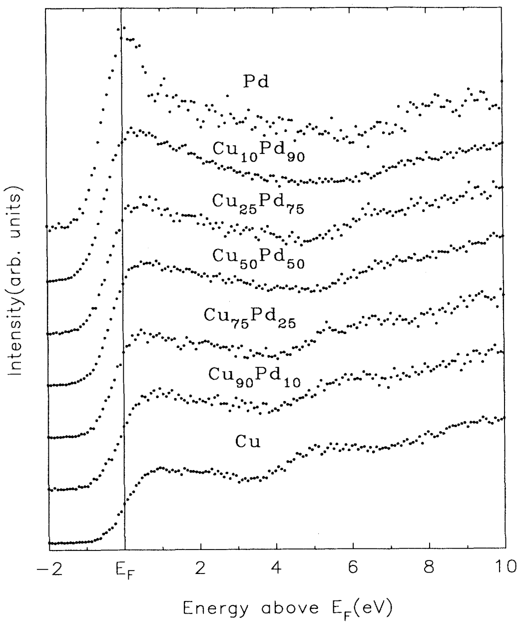

FIG. 1. BIS spectra of $\mathrm{Pd}_{1-x}\mathrm{Cu}_x$ alloys (x = 0.0, 0.10, 0.25, 0.50, 0.75, 0.90, and 1.0).

Figure 3 shows the Pd partial BIS spectra of $\mathrm{Cu}_x\mathrm{Pd}_{1-x}$ alloys obtained by the method mentioned above. We can see that the Pd unoccupied band consists of a sharp peak near the Fermi level and a broad band extending to about 6 eV above the Fermi level. Considered a Pd 4d band character (the cross section of the Pd 5s state is much smaller[15] than that of Pd 4d), the sharp peak near the Fermi level can be assigned to the pure Pd "4d band,"

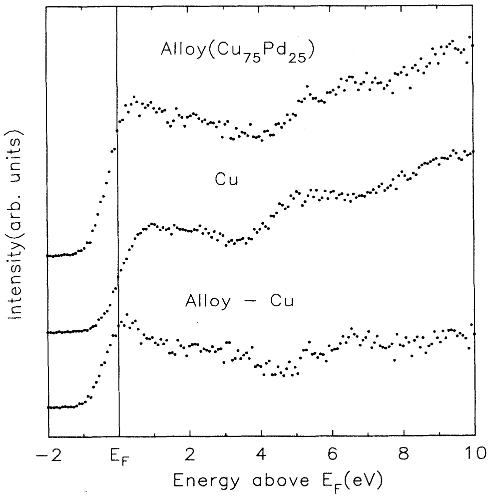

FIG. 2. Subtraction procedure to obtain Pd partial BIS spectrum.

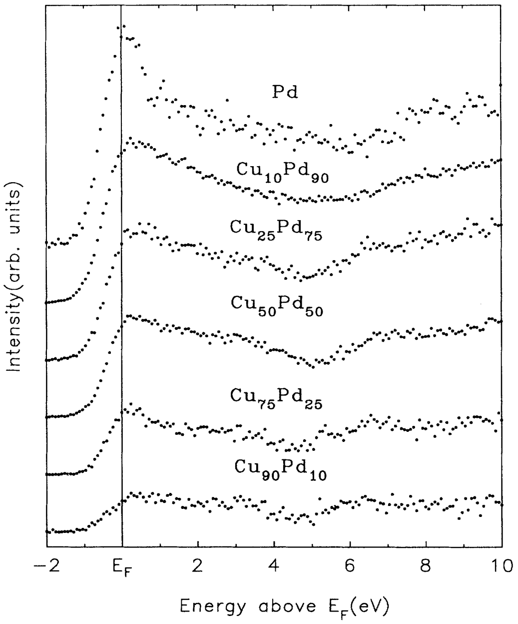

FIG. 3. Pd partial BIS spectra of $Pd_{1-x}Cu_x$ alloys after subtraction.

and the broad band from the Fermi level to about 6 eV above the E_F can be assigned as the contribution from the Pd 4*d* state to the hybridized band between Pd 4*d* and Pd 5*s*,*p* electrons. We can see from Fig. 3 that the unoccupied Pd 4*d* bands are reduced very clearly as the Pd content is decreased by alloying.

In order to determine quantitatively how much the number of unoccupied Pd 4*d* electron states (4*d* holes) is reduced as alloying, we obtain the weight of Pd 4*d* unoccupied states by subtracting pure the Ag BIS spectrum

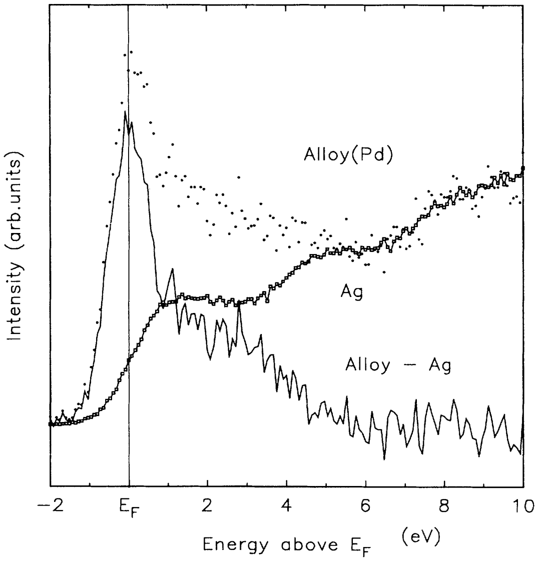

FIG. 4. The procedure to obtain the unoccupied Pd 4*d* band from Pd (alloy) BIS spectra by subtracting Ag metal BIS spectrum. Dots and squares are BIS data of Pd and Ag metals respectively, and the line represents Pd 4*d* unoccupied density of states obtained by the subtraction of the two.

from the alloy Pd partial BIS spectra of Fig. 3. This assumes that 5*s* bands for Ag and Pd are similar since Ag is next to Pd in the periodic table and the Ag 4*d* band is full. The procedure is shown in Fig. 4 for pure Pd metal, where the two spectra are aligned at 6 eV above the Fermi level. A similar subtraction procedure is carried out for other alloys. From the area of the difference curve we obtain the weight of the unoccupied Pd 4*d* levels, which in turn is converted to the number of Pd 4*d* holes n_d in

TABLE I. The values (in units of eV) of the measured core-level binding energy shift $\Delta E(i)$, the work function change $\Delta\Phi$, the final-state relaxation energy shift ΔE_r, and the change of the one-electron energy of the core-level i $\Delta\epsilon(i)$ for the (a) Cu $2p_{3/2}$ and (b) Pd $3d_{5/2}$ core levels in Cu-Pd alloys at several compositions. δn^{Cu} (δn^{Pd}) is the amount of the total interatomic charge transfer into the Cu (Pd) atom calculated by Eqs. (6) and (7). Δn_d(BIS) is the change of the *d*-state occupation number relative to the pure metal as determined by BIS spectra, while Δn_d(XAS) is that obtained from the x-ray absorption experiment. Δn_d for Cu is obtained from the calculation as described in the text. (*e* is the magnitude of the fundamental charge.)

(a) Cu $2p_{3/2}$ level

Cu (at.%)	$\Delta E(i)$ (eV)	$\Delta\Phi$ (eV)	ΔE_r (eV)	$-\Delta\epsilon(i)$ (eV)	δn^{Cu} (BIS)	Δn_d (BIS)	δn^{Cu} (XAS)	Δn_d (XAS)
100	0.00	0.00	0.00	0.00	0.00*e*	0.00*e*	0.00*e*	0.00*e*
90	-0.01	0.09	0.04	0.12	0.0021	-0.011	-0.021	-0.0048
75	-0.20	0.23	0.11	0.14	0.0049	-0.013	-0.026	-0.0053
50	-0.42	0.45	0.18	0.21	0.025	-0.024	-0.021	-0.013
25	-0.53	0.67	0.28	0.42	0.24	-0.097	0.11	-0.064
10	-0.77	0.81	0.30	0.34	0.43	-0.14	0.23	-0.087

(b) Pd $3d_{5/2}$ level

Pd (at.%)	$\Delta E(i)$ (eV)	$\Delta\Phi$ (eV)	ΔE_r (eV)	$-\Delta\epsilon(i)$ (eV)	δn^{Pd} (BIS)	Δn_d (BIS)	δn^{Pd} (XAS)	Δn_d (XAS)
100	0.00	0.00	0.00	0.00	0.00*e*	0.00*e*	0.00*e*	0.00*e*
90	0.04	-0.09	-0.11	-0.16	-0.048	0.05	-0.025	0.040
75	0.07	-0.23	-0.25	-0.41	-0.081	0.11	-0.035	0.090
50	0.16	-0.45	-0.53	-0.82	-0.025	0.16	0.021	0.14
25	0.33	-0.67	-0.89	-1.23	-0.015	0.23	0.077	0.19
10	0.65	-0.81	-1.28	-1.44	-0.019	0.27	0.18	0.18

alloys by assuming that the number of Pd 4*d* holes in pure Pd metal is 0.36 electron.[1] The *change* of the Pd 4*d* electron number for each alloy composition compared with pure Pd metal deduced from this analysis is written in the seventh column of Table I(b) as Δn_d(BIS).

B. Pd $L_{\rm III}$ x-ray absorption near-edge spectra

The Pd $L_{\rm III}$ x-ray absorption spectra have been background subtracted and normalized as follows. Since the total electron yield is an increasing function of the incident photon energy, the linear fit of the pre-edge region representing the absorption coefficient for photons of energy less than the absorption threshold is subtracted for each raw spectrum. The resulting curve is normalized by multiplying a factor that makes the continuum step equal to unity at the higher energy. The zero of the (relative) photon energy is assigned to the maximum point of each absorption spectrum.

Figure 5 shows the Pd $L_{\rm III}$ XANES for various Cu-Pd alloys. As shown in Fig. 5, the strength of the Pd white line feature reduces dramatically compared to that of pure Pd with increasing Cu concentration. The reduction of white line strength indicates that the unoccupied density of *d* states projected onto the Pd atomic sphere is reduced upon alloy formation with Cu.

In order to calculate the change of the number of the Pd *d* hole, the $2p \rightarrow 4d$ related white line area, which should reflect directly the *d*-hole count, has been calculated as follows. The white line feature rides on top of the continum step feature, hence this background continum feature must be subtracted from the $L_{\rm III}$ XANES spectra to estimate the white line strength.[16] Since pure Ag has almost no *d* hole, we use the pure Ag $L_{\rm III}$ XANES spectrum to approximate the continum background. To extract the white line area the pure Ag XANES spectrum is first shifted in energy so that its inflection point aligns with the white line maximum peak of the Pd XANES spectrum in each alloy. The pure Ag XANES spectrum is then subtracted from each Pd $L_{\rm III}$ XANES spectrum and the resulting area of the difference spectrum yields an estimate of the number of Pd *d* holes. The area of the difference spectrum is integrated up to an energy 4.5 eV above the maximum peak of the Pd $L_{\rm III}$ XANES spectrum. The results thus obtained are written as the *change* of the Pd 4*d* electron number Δn_d(XAS) relative to the pure Pd metal in the last column of Table I(b). Comparing this with Δn_d(BIS) of the seventh column obtained from the BIS analysis, we find that these two numbers are in fairly good agreement except for the $\mathrm{Cu_{90}Pd_{10}}$ alloy. For this Pd dilute alloy these numbers are probably not so reliable since the signal-to-noise ratio is low and some of the simplifying assumptions above can become questionable. Similar agreement between the Pd 4*d* unoccupied densities of states obtained by BIS and those from XANES was also found for the Pd-Al alloy system.[17]

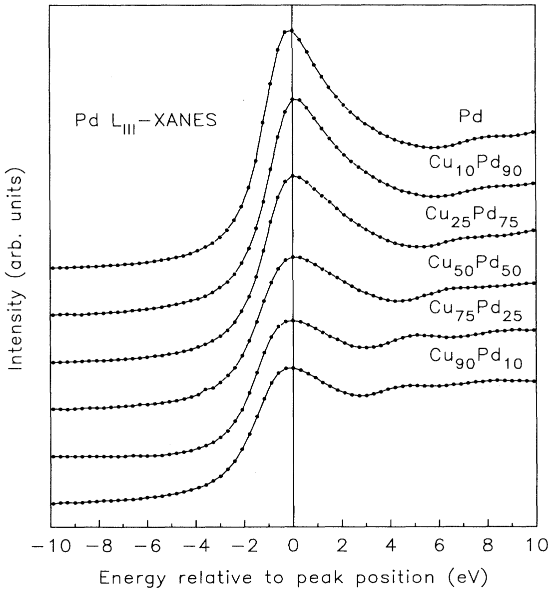

FIG. 5. Pd $L_{\rm III}$ x-ray absorption near-edge spectra of $\mathrm{Pd_{1-x}Cu_x}$ alloys.

C. Core-level spectra with XPS

XPS core-level spectra of Cu $2p_{3/2}$ and Pd $3d_{5/2}$ levels for $\mathrm{Cu_xPd_{1-x}}$ alloys (x = 0.00, 0.10, 0.25, 0.50, 0.75, 0.90, and 1.00) are shown in Fig. 6. We can see that

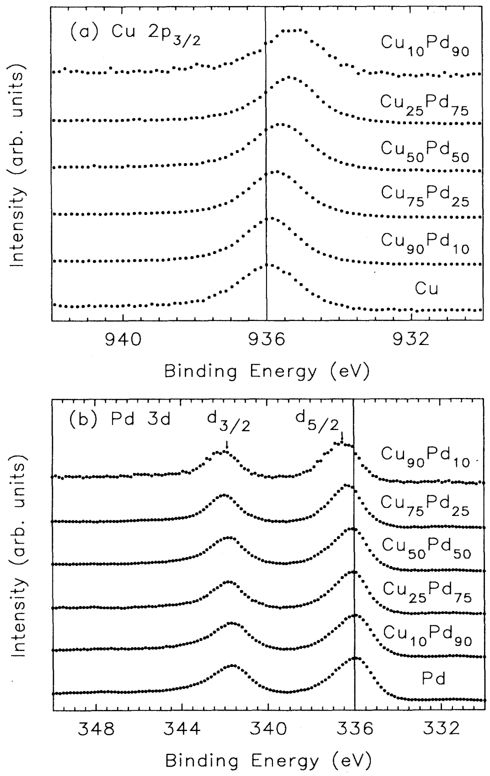

FIG. 6. (a) Cu $2p_{3/2}$ core-level binding energy shift and (b) Pd 3*d* core-level binding energy shift of $\mathrm{Pd_{1-x}Cu_x}$ alloys measured by the x-ray photoelectron spectroscopy.

the Cu $2p_{3/2}$ peak moves to the lower binding energy as alloying with Pd, while the Pd $3d_{5/2}$ peak moves to the higher binding energy as alloying with Cu.

The binding energies of Cu $2p_{3/2}$ and Pd $3d_{5/2}$ core levels are determined by the curve fitting of these experimental spectra. In the case of the Cu $2p_{3/2}$ peak, we have performed the curve fitting by the Doniach-Šunjić line shape convoluted with the Gaussian instrumental broadening whose half width at half maximum (HWHM) is 0.6 eV. The Doniach-Šunjić line shape combines the effects of the electron-hole pair production near the Fermi level and the finite core-hole lifetime, and is given by the convolution of $1/E^{1-\alpha}$ with a Lorentzian function of HWHM γ:[18]

$$f(E) = \frac{\Gamma(1-\alpha)\cos[\pi\alpha/2 + (1-\alpha)\arctan(E/\gamma)]}{(E^2+\gamma^2)^{(1-\alpha)/2}}, \quad (8)$$

where Γ and α denote the γ function and the asymmetry parameter due to the electron-hole production near the Fermi level, respectively.

However, for the Pd $3d_{5/2}$ peak the curve fitting by the Doniach -Šunjić line shape does not give a good fit, presumably because the DOS of the valence level at E_F is very sharp contrary to the assumption of the flat valence band in the Doniach-Šunjić line shape. Thus we convolute the Mahan function[18] $g(E)$ given as follows instead of $1/E^{1-\alpha}$ with the Lorentzian.

$$g(E) = \frac{\exp(-E/\xi)}{E^{1-\alpha}}, \quad (9)$$

where ξ and α denote the Mahan parameter and the asymmetry parameter, respectively. The Mahan parameter is determined to be 1.0 eV for pure Pd and increases monotonically as alloying, so that the shape becomes close to that of Doniach-Šunjić type for Cu-rich alloys. This is as expected since we have already seen that the Pd DOS of the valence band at E_F becomes flatter upon alloying with Cu.[7,9] The results of the curve fitting for pure Pd and Pd-diluted $Cu_{90}Pd_{10}$ alloys are shown in Fig. 7. In this figure, dots and solid lines are raw data and fitted curves respectively, and the assumed inelastic background and weak Pd core-level satellites[3,8] are also shown.

In this way, we obtain the binding energy shifts $\Delta E(i)$ of Cu $2p_{3/2}$ and Pd $3d_{5/2}$ core levels relative to pure metals as shown in Table I. In the same table, we also list the values of the quantities $\Delta\Phi$ and ΔE_r of Eq. (6), which are necessary to determine the amount of the charge transfer. The work function change $\Delta\Phi$ is calculated assuming a linear behavior with the composition x. The work functions (averaged over the crystal planes) of Cu and Pd metals are known to be 4.65 and 5.55 eV, respectively.[19] The final-state relaxation energy term ΔE_r is quoted from the result of the recent theoretical calculation.[14] In the case of Pd $3d$ core level, we notice that ΔE_r is much bigger than the experimental binding energy shift $\Delta E(i)$. This implies that the final-state shift is nearly as important as the initial-state shift. Adding all three terms we obtain the initial-state binding energy shift $\Delta\epsilon(i)$ in the fifth column of Table I.

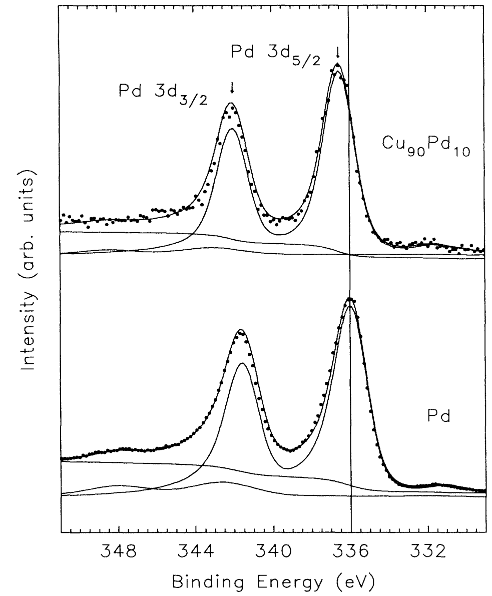

FIG. 7. Curve fitting of the Pd $3d$ core-level spectra in pure Pd metal and $Pd_{10}Cu_{90}$ alloy using the Mahan function. Dots and solid lines are raw data and fitted curves, respectively. Inelastic backgrounds and the weak Pd core-level satellites are also shown.

V. DISCUSSION

A. Charge transfer in Cu-Pd alloys

To estimate the amount of the charge transfer from $\Delta\epsilon(i)$ in Table I, we have to determine the parameter values of the right-hand side of Eq. (6). The Coulomb repulsion energy $F^0(i,j)$ can be estimated from the atomic Slater integral

$$F^0(i,j) = \int\int P_i(r_1)^2\left[\frac{1}{r_>}\right]P_j(r_2)^2 r_1^2 dr_1 r_2^2 dr_2, \quad (10)$$

where the $P_i(r)$ is the one-electron radial function normalized such that $\int P(r)^2 r^2 dr = 1$, and $r_>$ is the greater of the two radial coordinates r_1 and r_2. In the case of Cu and Pd atoms, we obtained the following values of Slater integrals from the atomic Hartree-Fock calculation. For the Cu atom ([Ar]$3d^{10}4s^1$ configuration), $F^0(2p,3d) = 37.3$ eV, $F^0(2p,4s) = 10.2$ eV. For the Pd atom ([Kr]$4d^9 5s^1$ configuration), $F^0(3d,4d) = 23.7$ eV, $F^0(3d,5s) = 8.6$ eV.

In the case of solid, or metal, the value of $F^0(i,j)$ changes mainly due to two effects.[13] One is the renormalization of the valence electron wave functions inside the Wigner-Seitz cell of each atom, which tends to increase the $F^0(i,j)$ value. The other is the modification of the valence shell wave function when a core electron is removed, which tends to decrease the $F^0(i,j)$ value. For example, in the case of Au these two effects reduce $F^0(4f,5d)$ from the free atomic value of 21.2 eV to 16.1 eV, whereas they increase $F^0(4f,6s)$ from 11.5 eV to 12.8 eV in solid.[13]

In order to estimate the $F^0(i,j)$ value in Cu and Pd metals, we make the following assumptions. For the case of Cu $F^0(2p,3d)$, we recall that the value of Ni $F^0(3d,3d)$ is reduced from 24.7 eV to 13.5 eV mainly due to the valence wave-function modification in the presence of the core hole and the electron correlation effect.[20] The wave-function renormalization effect is not important here since the Ni $3d$ wave function is already almost inside the Wigner-Seitz cell. Since Ni and Cu are next to each other in the periodic table, it is reasonable to assume that Cu $F^0(2p,3d)$ is reduced by the same amount as Ni $F^0(3d,3d)$. In the case of Cu $F^0(2p,4s)$, we can make use of the interpretation of the 11.8-eV satellite in the core-level spectra of Cu metal[8] as $F^0(2p,3d) - F^0(2p,4s) = 11.8$ eV. For Pd F $(3d,4d)$ and F $(3d,5s)$, we use the calculated values based on the renormalized scheme quoted in Ref. 21. These values are consistent with the interpretation of the core-level satellite in the XPS spectra of Pd metal.[3,8] Summarizing all these results, we have the following. For Cu (solid), $F^0(2p,3d) = 26.1$ eV, $F^0(2p,4s) = 14.3$ eV. For Pd (solid), $F^0(3d,4d) = 18.4$ eV, $F^0(3d,5s) = 12.9$ eV.

Now we consider the Madelung-like potential $F^0_{\rm latt}$ term. There exists a reasonable approximation to estimate $F^0_{\rm latt}$ by assuming that the transferred charge δn resides on the surface of the atomic sphere after the manner of the Friedel theory.[22] Using the metallic radii of Cu and Pd ($r_{\rm Cu} = 1.28$ Å and $r_{\rm Pd} = 1.38$ Å)[23] we can estimate as follows. For the Cu atom, $F^0_{\rm latt} = e^2/r_{\rm Cu} = 11.3$ eV. For the Pd atom, $F^0_{\rm latt} = e^2/r_{\rm Pd} = 10.5$ eV.

Since all the parameters such as Δn_d, $F^0(3d,4d)$, $F^0(3d,5s)$, and $F^0_{\rm latt}$ for the Pd metal, which are required to determine the interatomic charge transfer δn using Eq. (6), have been obtained, we can now calculate $\delta n^{\rm Pd}$ from Eq. (6). The results of $\delta n^{\rm Pd}$ thus obtained are tabulated in the sixth column of Table I(b). With the charge conservation relation Eq. (7), we can then calculate the amount of the interatomic charge transfer into the Cu site $\delta n^{\rm Cu}$. The results of this calculation for $\delta n^{\rm Cu}$ are listed in the sixth column of Table I(a). The change of Cu $3d$ holes $\Delta n_d^{\rm Cu}$ can also be calculated with Eq. (6), the results of which are summarized in the seventh column of Table I(a).

We can note several facts from this table. First, the amount of the charge transfer is in general very small, less than 0.3 electron in all alloys, except for the case of $\rm Cu_{10}Pd_{90}$ where the numbers are somewhat unreliable because a small change of $\delta n^{\rm Pd}$ can introduce a large variation of $\delta n^{\rm Cu}$ via Eq. (7). Second, in the case of Pd, the total charge transfer $\delta n^{\rm Pd}$ is smaller than the change of $4d$ electron number Δn_d. That is, the intra-atomic charge transfer $s \to d$ is more important than the interatomic charge transfer between Pd and Cu atoms. Third, the interatomic charge transfer occurs from Pd atom to Cu atom. Since the electronegativity[24] of Cu is 1.8 which is smaller than the 2.0 for Pd, this direction of the charge flow cannot be simply explained by the electronegativity difference. However, this is consistent with the results of the Korringa-Kohn-Rostoker coherent-potential-approximation calculation.[6]

B. Electronic structure of Cu-Pd alloys

We can see in Table I that the change of the Pd $4d$ occupation number Δn_d determined by BIS or XANES is positive and increasing with the Cu concentration, meaning that the $4d$ band is being gradually filled upon alloying with Cu. However, even in $\rm Cu_{90}Pd_{10}$ where Δn_d is largest, it is less than the number of d holes ($0.36e$) for pure Pd. Therefore the Pd $4d$ band is not completely filled, at least for alloy compositions studied here. This is consistent with the Pd partial spectral weights determined by the recent synchrotron radiation valence-band photoemission study.[9] This study showed that Pd $4d$ density of states becomes narrow and its centroid moves toward the high binding energy side as Pd is diluted, but still the Pd DOS extends up to the Fermi level. Hence Pd $4d$ levels are filled as Pd is diluted, but not completely.

We also see in Table I(a) that Δn_d for Cu is negative, that is, the number of Cu $3d$ electrons decreases upon alloying with Pd. This is also consistent with the synchrotron radiation photoemission study mentioned above,[9] which shows that Cu $3d$ partial spectral weights become broadened and extend toward the Fermi level in the Pd-rich alloys.

VI. CONCLUSION

In this paper we have studied the unoccupied partial Pd $4d$ density of states in Cu-Pd alloys by bremsstrahlung isochromat spectroscopy, Pd $L_{\rm III}$ x-ray absorption near-edge structure, and the core-level shifts in the x-ray photoelectron spectroscopy. They all show the gradual filling of the Pd $4d$ band upon alloying with Cu, but the unoccupied $4d$ states of the Pd atom is not completely filled even in the $\rm Cu_{90}Pd_{10}$ alloy. The Cu atom loses some $3d$ electrons in the Cu-diluted alloys. These results are consistent with the partial spectral weights determined by the recent synchrotron radiation valence-band photoemission study.

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