Partial densities of states in amorphous $Pd_{0.81}Si_{0.19}$

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Photoemission and Auger spectra involving both core and valence electrons have been measured for Pd, Si, and a-$Pd_{0.81}Si_{0.19}$. Partial Pd $4d$, Si $3p$, and Si $3s$ densities of states (PDOS) have been derived from these measurements. The Pd $4d$ PDOS shows a filling of the $4d$ shell in the amorphous alloy which is accompanied by characteristic changes in the spectral shape of the $4d$ bands when compared to Pd. The Si PDOS can be divided into $3p$ derived states that overlap the Pd $4d$ PDOS and a corelike $3s$ portion that is located ~ 7 eV below the center of the Pd $4d$ PDOS. The Si $3p$ PDOS is bifurcated as a result of Pd $4d$-Si $3p$ hybridization with a local maximum at E_F. The Si PDOS is well described by an extension of the virtual-bound-state model of Friedel and Anderson owing to Terakura. Core-level shifts of the order of 0.35 eV reflect changes in relaxation rather than a charge transfer from Si to Pd.

I. INTRODUCTION

Nagel and Tauc[1] have recently discussed the possibility of an electronic contribution to the stability of metallic glasses. They invoke an isotropic free-electron model not unlike that of Penn[2] and argue that a pseudogap at the Fermi energy E_F will develop when the position k_p of the maximum in the structure factor equals the diameter $2k_F$ of the Fermi sphere. This isotropic pseudogap lowers the electronic energy of the amorphous system compared to a crystalline system with unisotropically distributed gaps which might not coincide with E_F.

The condition $2k_F = k_p$ is indeed met for a number of transition-metal–metalloid alloys which can be made amorphous when quenched rapidly from the melt. The proposal of Nagel and Tauc gains further support from a number of workers who explain the negative temperature coefficient in the resistivity observed for many metallic glasses through an extension of the Faber Ziman theory of liquid metals.[3-5] Here again it is the near coincidence of $2k_F$ and k_p that helps to lower the resistivity with temperature in the amorphous phase. In estimating k_F one has to rely on the simplest model of a free-electron-like conduction band in lieu of a more realistic picture of the conduction band in these alloys.

A photoemission study[6] on a-$Pd_{0.775}Cu_{0.06}Si_{0.165}$ did indeed reveal a low density of states $N(E_F)$ at the Fermi energy when compared to $N(E_F)$ for Pd. The similarity of the spectrum with that of Cu and the known diamagnetism[7] of the amorphous Pd-Cu-Si alloy suggests, however, that the low $N(E_F)$ is due to a transition of E_F from the high Pd $4d$ density of states (DOS) in Pd to the low DOS of the s-p

bands in the alloy. These measurements confirm therefore the idea that the addition of the fourvalent Si to the monovalent Pd shifts E_F to higher values; they cannot, however, prove or disprove the model of Nagel and Tauc as long as no reliable picture of the *partial* s-p density of states in the alloy is available.

It is the purpose of the present investigation to provide this partial density of states by combining photoemission measurements at different energies of the exciting radiation with Auger emission spectra. The system studied is a-$Pd_{0.81}Si_{0.19}$ which avoids the added complication of the copper component. The experimental results are augmented by a model calculation which reproduces the partial densities of states so obtained and aids in their interpretation.

II. EXPERIMENTAL

The $Pd_{0.81}Si_{0.19}$ alloys were prepared by splat cooling from the melt in both an air and an argon atmosphere. No difference was observed in the spectra of the differently prepared samples and no further distinction will therefore be made between them. The samples were obtained as disks about 1 cm in diameter and several hundredths of a millimeter thick. The noncrystallinity was checked using x rays. X-ray-induced photoemission spectra (XPS) were obtained at a resolution of 0.6 eV using monochromatized Al $K\alpha$ x rays ($h\nu = 1486.6$ eV). uv-induced spectra (UPS) were taken with He I ($h\nu = 21.22$ eV) radiation at a resolution of 0.2 eV. Undifferentiated Si Auger spectra were measured using an electron-beam modulation technique and a double-pass cylindrical-mirror analyzer. The resolution so achieved was 1 eV. Undifferent-

iated Auger spectra from palladium excited by x rays could also be obtained simultaneously with the XPS measurements.

All spectra were recorded in UHV systems with pressures well below 10^{-9} Torr. The samples were cleaned by scraping them in vacuum with a diamond file. This yielded clean surfaces except for a few atomic percent of adsorbed oxygen as monitored by the intensity of the O $1s$ line but no trace of oxidation of either silicon or palladium.[8] This mode of cleaning the surface was chosen because it ensures a surface composition of the alloy identical to that of the bulk without the need to anneal the sample which would lead to a recrystallization of the a-$Pd_{0.81}Si_{0.19}$ alloy. A subsequent mild argon-ion bombardment (1 kV, 12 μA h) was sufficient to remove the residual oxygen signal completely. XPS spectra taken before and after the argon-ion bombardment ensured that this treatment had not resulted in a change of composition at the surface. No subsequent oxygen buildup was detected on any of the samples for at least 8 h under the vacuum conditions referred to above. Energies are measured relative to the Fermi level E_F of the metallic samples. The position of E_F was determined in the usual way using gold as a standard and adopting a binding energy of 84.0 eV for the $4f_{7/2}$ level of Au. In order to make a meaningful comparison of the alloy binding energies with those of the elements we had to refer all energies to the vacuum level. The work function ϕ was therefore measured by combining the low-energy threshold E_T and the position of E_F in the UPS spectra with the photon energy $h\nu$ according to

$$\phi = h\nu - (E_F - E_T).$$

The samples of pure Pd which were used for comparison were treated similarly in all respects.

III. RESULTS

A. Valence bands

In Fig. 1 we compare the XPS valence-band spectrum of a-$Pd_{0.81}Si_{0.19}$ with that of pure polycrystalline Pd. The Pd sample was merely scraped to avoid the formation of an amorphous surface layer that occurs as a result of intense argon bombardment.[9] Both spectra are dominated by the ~6-eV-wide contribution of the Pd $4d$ electrons. In pure Pd this distribution intersects the Fermi level to give a high density of states $N(E_F)$ at E_F. Four pieces of fine structure (labeled 1–4 in Fig. 1) can be distinguished. They correspond to peaks in the density of states from critical points in the band-structure of Pd. The number and position of these features are virtually identical with those reported by others.[9] In the a-$Pd_{0.81}Si_{0.19}$ alloy critical points

are, of course, absent and so is the fine structure. Instead we observe a single peak labeled B in Fig. 1 at $E_F - 2.2$ eV and a shoulder C at $E_F - 4.0$ eV. The Fermi level intersects a region of low density of states, which agrees with the observation made by Nagel et al. for the a-$Pd_{0.775}Cu_{0.06}Si_{0.165}$ alloy.[6] The lowering of $N(E_F)$ is reflected in the almost symmetrical Pd $3d$ and $3p$ lines of the alloy whereas these lines are asymmetric in Pd as a result of electron-hole excitations across the Fermi surface.[10] The width of the Pd $4d$ band is slightly smaller in a-$Pd_{0.81}Si_{0.19}$ than in Pd.

At $E_F - 9.8$ eV a weak peak (E in Fig. 1) can be distinguished in the spectrum of the alloy which we identify with emission from the Si $2s$ electrons. The position of E agrees quite well with the lowest peak in the density of states of pure Si.[11] The area under peak E amounts to 2% of that under the Pd $4d$ region. Assuming that ten Pd $4d$ and two Si $3s$ electrons contribute to the two structures, respectively, we calculate an intensity ratio of 3% using the appropriate theoretical cross sections of Nefedov et al.[12] This agreement lends further support to our assignment. The Si $3p$ contribution is hidden under the Pd $4d$ emission with a relative intensity of less than 1%, a value we arrive at by combining $\sigma(3s)/\sigma(3p) = 3.4$ from the work of Cavell et al.[13] with our estimate of the Si $3s$ intensity. These intensity relations are changed in favor of the Si $3p$ electrons in the UPS spectra shown in Fig. 2. From uv-photoemission studies by Wehking et al.[14] of Ag layers on Si we estimate a cross section ratio $\sigma(Si\ 3p)/\sigma(Ag\ 4d)$ of about one at 21.2 eV, a value we expect to be similar for Si and Pd.

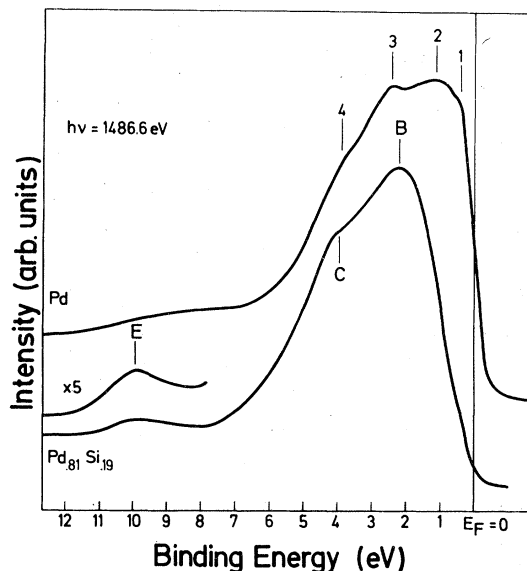FIG. 1.   XPS spectra of Pd and a-$Pd_{0.81}Si_{0.19}$.

The spectrum of pure Pd in Fig. 2 differs from that taken at x-ray energies due to the direct (i.e., k-conserving) nature of the electronic transitions which introduce a duplicate of the joint density of states at $h\nu = 21.2$ eV rather than the density of states (DOS) as is the case at 1486.6 eV.[15] Consequently only the critical points 1 and 3 of the DOS show up in Fig. 2, and 2 and 4 are suppressed. The k-conserving selection rule is a result of the long-range order in Pd and it does therefore not apply to the amorphous alloy. The d portion of the UPS spectrum of a-$Pd_{0.81}Si_{0.19}$ is indeed very similar to the corresponding part of the XPS spectrum with peak B and shoulder C at identical energies. New features are the foot A extending from the top of the d emission to E_F and a peak D at a binding energy of 5.8 eV. In view of the cross sections given above we argue that these new features are predominantly Si $3p$ derived states. The Si $3s$ electrons at $E_F - 9.8$ eV do not show up in the UPS spectrum due to their low cross section which amounts to only 2% of that of the Si $3p$ electrons at $h\nu = 21.2$ eV and the steeply rising background of secondary electrons.[16]

The work function of Pd was determined as $\phi = 5.55 \pm 0.05$ eV and that of a-$Pd_{0.81}Si_{0.19}$ as $\phi = 4.95 \pm 0.10$ eV, respectively. Our value for Pd agrees with the value of 5.55 ± 0.1 eV measured earlier by Eastman.[17]

B. Auger spectra

Auger transitions that involve two holes in the valence band as the final state carry information about the local density of states of the ionized atom provided the Coulomb interaction between the two holes is small compared to the bandwidth.[18]
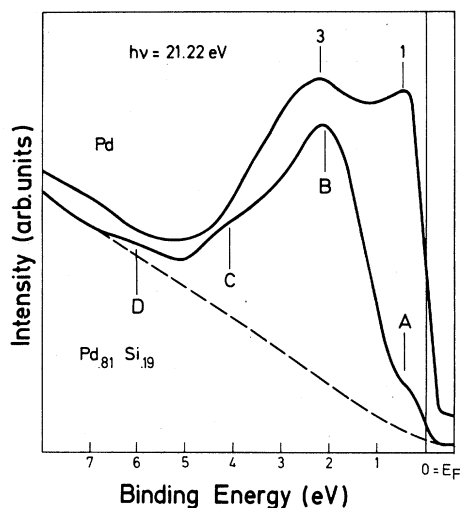
This condition is met by silicon and the Si $L_{23}VV$ Auger transition in elemental Si is properly interpreted as the self-convolution of the valence density of states. As shown by Feibelman et $al.$[19] and elaborated upon by Jennison[20] the Si $L_{23}VV$ Auger decay is heavily weighted in favor of transitions that involve the $3p$ electrons so that the one peak structure observed experimentally at 91 eV for this transition[21] represents essentially the self-convolution of the partial p density of states of Si (see Fig. 3).

The same transition in a-$Pd_{0.81}Si_{0.19}$ consists of three equidistant peaks as shown in Fig. 3. The separation between peaks is 5.5 eV and the kinetic energy of the central line is 91 ± 2 eV. The three peaks represent the self-convolution of two peaks in the partial density of states of Si in the Pd-Si alloy which are separated by 5.5 eV. This is also the separation of features A and D in the 21.2-eV spectrum (Fig. 2) which we already associated with Si $3p$ derived states.

The Pd Auger transitions involving the $4d$ (N_{45}) valence electrons represent the case in which the on-site Coulomb interaction exceeds the bandwidth, a situation familiar in Cu and Zn. These spectra are well described in terms of the atomlike two-hole final states and band-structure effects are largely absent.[22,23] The most intense Pd Auger line is the $M_{45}N_{45}N_{45}$ transition shown in Fig. 4. Aside from a 1-eV shift in energy the spectra of pure Pd and of a-$Pd_{0.81}Si_{0.19}$ are virtually identical. The two
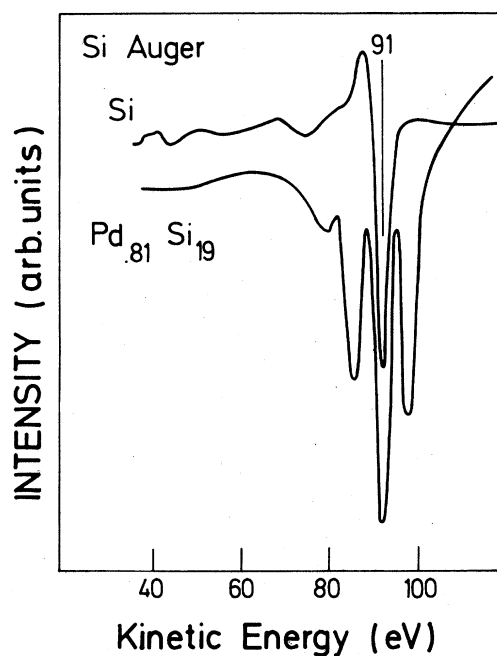

FIG. 2. UPS spectra of Pd and a-$Pd_{0.81}Si_{0.19}$.

FIG. 3. Electron-excited Si $L_{23}VV$ Auger spectra of Si and a-$Pd_{0.81}Si_{0.19}$.

components reflect the 4.7-eV spin-orbit splitting of the 3d (M_{45}) level.

C. Core levels

A number of core levels in a-$Pd_{0.81}Si_{0.19}$ have been recorded and their binding energies together with those of the elements are listed in Table I. All energies are referred to the vacuum level. The binding energies of both Pd and Si core levels increase by an average of 0.35 ± 0.05 eV compared to the elements.

In order to extract the desired information about a possible charge transfer between the components of the alloy from these changes in binding energy (ΔE_B) we partition ΔE_B according to

$$\Delta E_B = \Delta \epsilon + \Delta E_R + E_M . \qquad (1)$$

$\Delta \epsilon$ is the shift in orbital energy ϵ which is proportional to the charge transfer q with a proportionality constant α. ΔE_R is the change in relaxation energy E_R, and E_M is the Madelung contribution to ΔE_B. We estimate ΔE_R using the change in relaxation energy encountered in an Auger transition.[22] The kinetic energy of the Pd $M_{45}N_{45}N_{45}$ Auger transition is written according to this model[22]:

$$E_A(M_{45}N_{45}N_{45}) = E_B(M_{45}) - E_B(N_{45}) - E_B(N_{45})$$
$$+ F(N_{45}, N_{45}) + 2E_R . \qquad (2)$$

F represents the two-electron integral between the two holes in the final state which we assume to be equal in Pd and a-$Pd_{0.81}Si_{0.19}$. Evaluating Eq. (2) for the element and the alloy using the binding energies of Table I and the Auger energy shift of 1.0 eV, we obtain $\Delta E_R = -0.3$ eV, i.e., the relaxation energy for Pd core levels in a-$Pd_{0.81}Si_{0.19}$ is 0.3 eV smaller than in Pd. This reduction is reasonable in view of a filled 4d shell in the alloy. It eliminates the most effective transfer of screening charge into the 4d band, a transfer that is at least partially
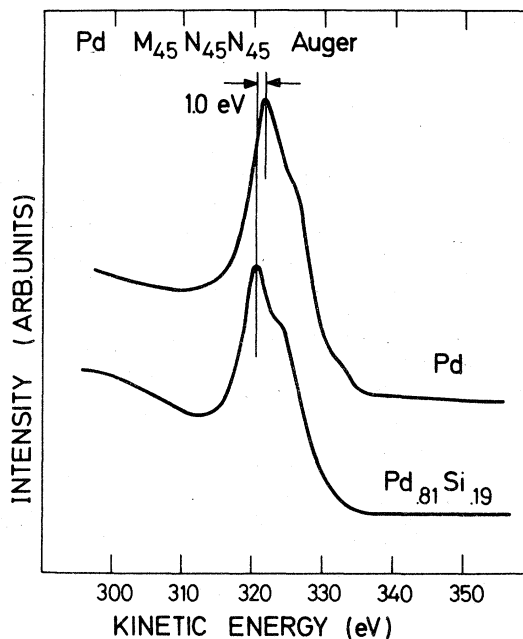

FIG. 4. X-ray-excited Pd $M_{45}N_{45}N_{45}$ Auger spectrum in Pd and a-$Pd_{0.81}Si_{0.19}$.

possible in Pd metal with its unfilled 4d shell. Inserting ΔE_R into Eq. (1) gives a value for $\Delta \epsilon + E_M$ of essentially zero. This result is compatible with negligible charge transfer to or from Pd in the alloy which would render $E_M = 0$. Symmetry requires, of course, the same to hold for Si even though the considerable differences in the Si Auger spectra of the element and the alloy defy a similar reduction of ΔE_B(Si). As crude as the analysis admittedly is, it precludes under all conceivable circumstances an electron transfer of 0.36 electrons which requires an $\Delta \epsilon$ of 4.4 eV using for α the expectation value of the inverse of the Pd 4d valence shell radius $\langle 1/r_{4d} \rangle$ as calculated by Mann.[24] A

TABLE I. Binding energies (in eV) of core levels in Pd, a-$Pd_{0.81}Si_{0.19}$ and Si relative to the vacuum level.

Pd level	Pd binding energy	Shift	$Pd_{0.81}Si_{0.19}$ binding energy	$Pd_{0.81}Si_{0.19}$ binding energy	Shift	Si binding energy	Si level
Fermi level	5.55 (5)	−0.6 (2)	4.95 (10)			5.15 (5) [a]	
First moment of the d band	7.75 (10)	0.25 (10)	8.0 (1)				
$4p_{3/2}$	57.75 (40)	0.4 (2)	58.15 (40)				
$4p_{1/2}$	61.45 (40)	0.3 (2)	61.75 (40)				
$4s$	92.95 (20)	0.2 (2)	93.15 (20)	104.95 (25)	0.35 (20)	104.6 (1)	$2p$
$3d_{5/2}$	340.65 (15)	0.45 (20)	341.1 (3)	156.15 (25)	0.35 (20)	155.8 (1)	$2s$
$3d_{3/2}$	345.85 (15)	0.45 (20)	346.4 (3)				
$3p_{3/2}$	537.25 (25)	0.9 (6)	538.15 (30)				
$3p_{1/2}$	565.15 (25)	0.8 (6)	565.95 (30)				

[a] Photoemission threshold, from G. W. Gobeli and F. G. Allen, Phys. Rev. **127**, 141 (1962).

charge transfer of 0.36 electrons is at least neces-sary to fill the Pd $4d$ shell in the alloy if one were to adopt the simplistic view of the rigid band model for the Pd-Si alloy.[25] The Madelung correction E_M to the value of $\Delta\epsilon$ is expected to be small because the $4d$ valence radius $\langle 1/r_{4d} \rangle^{-1}$ of 0.6 Å is small compared to the mean Pd-Si distance of 2.4 Å (Ref. 26) to 2.5 Å.[27]

IV. DISCUSSION

A. Partial densities of state

From the photoemission and Auger spectra pre-sented in Sec. III we have constructed "spectro-scopic" partial densities of state (PDOS) for the Pd $4d$ electrons and the $3s$ and $3p$ electrons of Si. The term spectroscopic implies that the densities of states are still weighted by transition probabil-ities which render a direct comparison of the am-plitudes of PDOS originating from different atomic levels meaningless. The emphasis will therefore be on the energies and structures rather than on their intensities.

As mentioned earlier, the XPS spectra are dom-inated by the emission from the Pd $4d$ electrons with the Si $3p$ derived states contributing less than 1%. The Pd $4d$ PDOS, n_d, in Fig. 5, is therefore taken directly from the XPS spectra after a cor-rection for a background of inelastically scattered electrons. Peak E in Fig. 1 which was already at-tributed to Si $3s$ states is well separated from the $4d$ emission and has, of course, been omitted in n_d of Fig. 5. In Pd ~4% of n_d(Pd) lies above E_F as indicated by the dashed line to account for the 0.36 holes in the $4d$ shell.[25] The first moment E_d of the occupied portion of n_d in a-$Pd_{0.81}Si_{0.19}$ lies 0.25 ± 0.10 eV lower than E_d for the occupied portion of n_d in Pd. The width as measured by the second moment decreases upon alloying from 2.43 to 2.36 eV^2. This decrease is largely due to a recession of the leading (i.e., low-binding-energy) edge of n_d. The Fermi level has at the same time moved upwards by 0.6 eV so that the Pd $4d$ shell is filled in the alloy. That supports the explanation given by Güntherodt et al.[28] for the diamagnetism of the closely related a-$Pd_{0.775}Cu_{0.06}Si_{0.165}$. The recession of the leading edge and the altered shape of n_d ex-clude, however, an interpretation of this filling of the $4d$ shell in terms of a simple rigid-band model. The required charge transfer from Si to Pd has furthermore been excluded on the basis of the anal-ysis of the binding energy shifts. We are thus led to invoke as an explanation of the filled $4d$ shell a rehybridization between the $5s$-$5p$ and the $4d$ elec-trons on the Pd site brought about by the presence of the strong s-p scatterer Si.

A neutral Pd with a filled $4d$ shell has the formal configuration $4d^{10}5s^0$ and the s-p contribution of states in the alloy must therefore predominantly originate on the Si atoms. The local $s(n_s)$, and $p(n_p)$ DOS of Si are therefore representative of the partial s-p conduction band DOS of the alloy as it is shown in the lower part of Fig. 5. At 15 eV below the vacuum level we have placed peak E of the XPS spectrum. This peak is largely derived from Si $3s$ electrons and represents therefore n_s, the s por-tion of the PDOS. The symmetrical shape of n_s with a width of about 1.5 eV (full width at half max-imum) alludes to the rather atomiclike nature of n_s.

Information about n_p (Si), the Si $3p$ derived part of the PDOS comes from the Si $L_{23}VV$ Auger spec-trum and from features A and D in the UPS spec-trum. As discussed earlier, the three line struc-ture of the Si $L_{23}VV$ Auger spectrum implies a two-peaked structure for n_p(Si) with a separation of 5.5 eV between the two components. A reliable deter-mination of the absolute energy of n_p(Si) based on the Auger energy alone is not possible without a value for the relaxation energy E_R [compare Eq. (2)]. If we place the two peaks in n_p(Si) as indicated by the vertical bars in Fig. 5, however, they coin-cide in energy with the shoulders A and D of the UPS spectrum (Fig. 2) which we have identified al-ready with Si $3p$ derived states in Sec. III A. As to
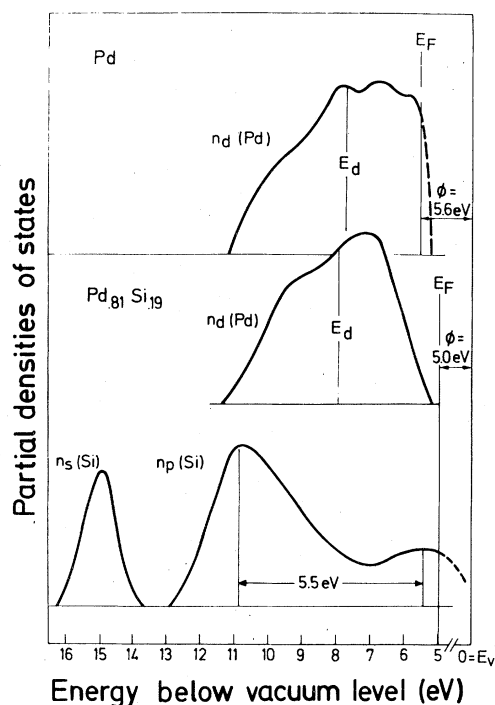

FIG. 5. Partial densities of states for Pd and Si in Pd and a-$Pd_{0.81}Si_{0.19}$ as derived from the photoemission and Auger spectra.

the exact width and intensities of the two peaks in n_p we must rely on estimates. From both the UPS and the Auger spectra equal intensities may be inferred neglecting any modulation in the transition probabilities. It is, however, reasonable to assume that the $3s$ character increases towards higher binding energies due to hybridization with the Si $3s$ electrons. Since both the Auger spectrum and the UPS spectrum emphasize the states with p character they will overestimate the intensity of the upper peak. The true intensity ratio will therefore be more like that given by the continuous curve in Fig. 5 which is based on a model calculation for the electronic structure of Si in Pd which will be discussed in Sec. IV B. The widths of the two components in Fig. 5 are also taken from these calculations.

In spite of the uncertainties in the relative intensities it is apparent from the preceding discussion that the conduction band of a-$Pd_{0.81}Si_{0.19}$ is far from free-electron-like and that we find a local maximum in the s-p portion of the density of states near E_F rather than a minimum as proposed by Nagel and Tauc. The split-off Si $3s$ contribution lies well below the bottom of the s-p band of pure Pd which falls at ~11.5 eV on the scale of Fig. 5.[15] It is therefore not clear how the two Si $3s$ electrons are to be included in a calculation of k_F which is based on the prescriptions of Refs. 3–5.

B. Model calculation for the partial densities of state of Si

The filling of d bands and changes in the densities of state at E_F are a common phenomenon encountered when nontransition elements are dissolved as impurities in transition metals. Terakura et al. have developed a formalism which is capable of explaining many of the experimentally observed features related to these two mechanisms, such as variations in the magnetic moment, the linear part of the specific heat and spin relaxation times.[29-32] In this formalism the impurity atom is imbedded into the otherwise perfect metal matrix and the scattering properties of the impurity are expressed in terms of a muffin-tin potential constructed using Hartree-Fock-type wave functions. A constant potential ΔV is added to ensure charge neutrality on the impurity site. The local densities of states are calculated using a Green's-function formalism.[29]

We have adopted this approach to the a-$Pd_{0.81}Si_{0.19}$ alloy. X-ray and neutron diffraction studies[26,27] indicate that there are no Si-Si nearest neighbors and we therefore expect the impurity model to be a reasonable first approximation. Figure 6 shows $n_s(Si)$ and $n_p(Si)$, the partial Si $3s$ and Si $3p$ densities of states thus obtained for one Si atom in a Pd

matrix. Since the atomic volume of Pd in a-$Pd_{0.81}Si_{0.19}$ differs by only 1% from that in pure Pd,[33] we believe the result to be representative for Si in the alloy. The Fermi level in Fig. 6 has been shifted, however, by 0.6 eV to bring it in agreement with E_F of a-$Pd_{0.81}Si_{0.19}$ and n_s and n_p have also been broadened to allow for a finite experimental resolution and second neighbor Si-Si interaction.

The calculated Si PDOS agrees in all essential features and energies with the spectroscopically determined one. The strong phase shift at the Si site pulls the bound state n_s out of the continuum of the surrounding conduction states to form the quasiatomic Si $3s$ state observed at 15 eV below the vacuum level. The p density of states shows a distinct minimum around 6 eV. This minimum reflects the Fano-type antiresonance in the conduction band due to its hybridization with the sharp Pd $4d$ resonance.[34] This antiresonance is already present in the absence of the Si atom. The resonances below and above are, however, emphasized in the presence of the Si atom due to the strong s-p scattering potential of the impurity. The local density of states at the Si site gives thus an enhanced replica of the s-p conduction band of the Pd matrix. The general shape of n_p is therefore rather insensitive to the details of the potentials involved as long as a sharp d resonance interacts with a wide s-p conduction band. Densities similar to
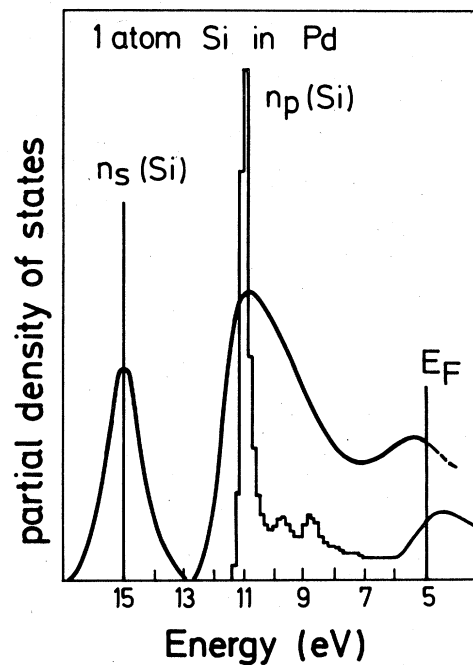

FIG. 6. Local density of states of a Si impurity in a Pd matrix as calculated (histogram) and broadened by a Gaussian of 2 eV width. The Fermi-level E_F is that of the a-$Pd_{0.81}Si_{0.19}$ alloy.

those of Fig. 6 have been obtained for Si in Cu[32] and they have been confirmed experimentally in the Si $K\beta$ soft-x-ray emission spectrum.[35]

Furthermore, our results provide a natural explanation for the recent low-temperature specific-heat data of Mizutani et al.[36] on amorphous $Pd_{1-x-y}Si_xCu_y$ alloys. They find that the linear term temperature coefficient γ changes with alloy composition and shows a distinct maximum near an electron-atom ratio of 1.6. Since γ is essentially proportional to $N(E_F)$ it follows the shape of n_p (Si) as the number of electrons is changed. For our alloy the electron-atom ratio is 1.57, slightly below the maximum as expected from Fig. 6.

Let us finally comment on the wave functions that contribute to the PDOS. The two peaks in n_p are derived from bonding and antibonding combinations of Si $3p$ and Pd $4d$ electrons, respectively. There is also some s-p hybridization between n_s and the lower peak in n_p. This is, incidentally, the reason why the two peaks in n_p show up with equal intensity in the Si Auger spectrum: the s admixture strongly reduces the Auger transition probability from the states around $E_v - 11$ eV.

About two months after the manuscript was submitted for publication, calculations of the electronic structure of model structures for a-$Pd_{0.80}Si_{0.20}$ as well as for crystalline Pd_3Si by Kelly and Bullett[37] came to our attention. The partial densities of states calculated for the Boudreaux-Gregor model are in virtually quantitative agreement with our experimental results. The authors find in particular the two-peaked structure in n_p (Si) with a mean separation of 5.5 eV and the atomiclike Si $3s$ level

at 15.5 eV below the vacuum level.

V. CONCLUSION

A combination of XPS, UPS, and Auger studies has permitted the experimental construction of the partial densities of states of the s and p derived bands in the amorphous $Pd_{0.81}Si_{0.19}$ alloy. They are in agreement with calculations using a modified Friedel-Anderson model for an isolated Si atom in a Pd matrix. These partial densities of state are very different from a free-electron band structure, so that the success of the free-electron model in accounting for resistivity data must, as yet, be regarded as unexplained.

The results cannot support the theory of Nagel and Tauc to account for the stability of amorphous alloys. This model requires a pseudogap to appear at E_F in a free-electron-type band whereas a local maximum in the DOS is actually observed. The shape of the partial p density of states is indicative of considerable hybridization between the Pd $4d$ and the Si $3p$ electrons. The position of the Fermi energy is such that the antibonding states are only partially filled. We thus expect an electronic contribution to the stability of this alloy that is reminiscent of covalent bonding.

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