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High-energy-spectroscopy study of the Pd-Ce system

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We report x-ray-absorption and photoemission measurements on crystalline and amorphous $Pd_{1-x}Ce_x$ alloys. In this system, cerium ions present a valence change induced by concentration and a correlation between the cerium electronic configuration and the density of occupied states. The centroid of the Pd $4d$-related band moves away from the Fermi level with increasing cerium content, leading to a decrease in the mixing between $4f$ and conduction electrons and then to the stabilization of the cerium trivalent state. The effect of structural disorder on the cerium valence anomaly in amorphous alloys is also discussed.

I. INTRODUCTION

In many compounds, cerium exhibits fascinating physical properties which reflect the importance of the hybridization between the $4f$ and the conduction electrons.[1] This situation, which is rather unique in the lanthanide series, leads to interesting phenomena such as the Kondo effect, heavy-fermion behavior, or valence instabilities. High-energy spectroscopies such as x-ray-absorption (XAS) or photoemission [x-ray photoemission spectroscopy and ultraviolet photoemission (XPS) and UPS)] spectroscopy are powerful techniques for the study of such materials and considerable work has been done in that field in the last few years.[2-4] For instance, such techniques have clearly shown that, even in the so-called "tetravalent" systems, the $4f$ character was still present.[5] However, as we consider highly correlated systems, it is necessary to take into account the interaction, in the final state, between the core-hole and the conduction electrons to explain the spectroscopic results. Indeed final-state effects can obscure the ground-state properties.[6] Recently Gunnarsson and Schönhammer[7] have proposed a modified Anderson impurity model which explains consistently the XPS, UPS, XAS, and bremsstrahlung isochromat (BIS) spectroscopy spectra recorded for many cerium intermetallic compounds.

The aim of the present study is to follow the behavior of the cerium valence, i.e., the amount of $4f$ character, in a system where the electronic parameters can be changed continuously. Particularly we are interested in the correlation between valence and band structure which is not clear yet. The $Pd_{1-x}Ce_x$ system is well suited for such a study. Previous XAS (Ref. 8) and perturbed angular γ-ray distribution[9] results on dilute Pd-Ce alloys have shown that Ce is in a saturated mixed-valence state whereas crystalline $CePd_3$ is known to be a typical weak intermediate-valence compound ($v=3.15$).[10] Moreover, Pd and Ce form a binary solid solution on a broad concentration range (up to $x=0.125$) and it is possible to extend this limit up to $x=0.3$ by the formation of amorphous alloys. XAS and XPS results are used to obtain the average cerium valence which goes from trivalent to saturated mixed valent when x decreases from 0.3 to 0. The evolution of the density of states in the $Pd_{1-x}Ce_x$ alloys is deduced from UPS results (Sec. III). The role of the d-band filling and the influence of structural disorder on the valence instabilities will be analyzed in Sec. IV.

II. EXPERIMENT

The $Pd_{1-x}Ce_x$ alloys have been prepared by the coevaporation technique in ultrahigh vacuum conditions (10^{-8} Torr during evaporation) onto a liquid-nitrogen-cooled substrate. The crystallographic state has been investigated by electron microscopy. Palladium and cerium form a binary solid solution for $x<0125$ and the samples are in the amorphous state for $x>0.125$. For the XAS experiments, samples of about 1 μm thickness are protected from oxidation by a 1000-Å Si coating.

XAS experiments have been carried out at Laboratoire pour l'Utisation du Rayonnement Electromagnétique (Orsay, France) on the EXAFS II (EXAFS denotes extended x-ray-absorption fine structure) station, using the synchrotron radiation delivered by the D.C.I. storage ring which was operated at 1.8 GeV and 150 mA. The experimental resolution in the cerium L_{III} energy range (5700 eV) is approximately 1 eV. XPS and UPS experiments were carried out on a VG apparatus (ESCALAB MARK II) at the "Service Commun de Photoémission de l'Université de Nancy I." The vacuum was typically in the 10^{-10}-torr range. The sample surfaces were cleaned up by argon sputtering and the oxygen contamination was followed by monitoring the oxygen KVV Auger intensity. As previously found for cerium compounds,[11] we also did not observe any significant difference between surface and bulk in our $Pd_{1-x}Ce_x$ alloys. Particularly the surface composition, deduced from XPS, is in good agreement with the nominal one.

III. EXPERIMENTAL RESULTS

A. L_{III}-edge spectroscopy

The L_{III} edges of cerium are reported in Fig. 1 for several alloys. The mixed-valence character of the Ce

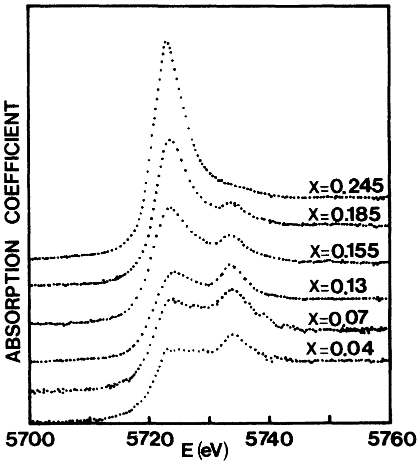

FIG. 1. Ce $L_{\rm III}$-edge absorption spectra for several $Pd_{1-x}Ce_x$ alloys of different composition.

ions is clearly demonstrated by the typical two-bump structure observed in the low-x range. No significant change of the $L_{\rm III}$-edge shape is observed in the crystalline alloys ($x \leq 0.125$) and growth of the low-energy bump is shown with increasing Ce content in the amorphous range. Up to now, there has been no theoretical description for the $L_{\rm III,II}$ edges ($2p_{5/2,3/2} \rightarrow \varepsilon d$). Then experimentalists use a phenomenological approach to extract the valence state. As, unlike $3d$ XPS experiments, the $L_{\rm III}$ spectra are relatively free of final-state effects,[12] they are interpreted by a superposition of two white lines separated by about 10 eV (Fig. 2). This separation is thought to be due to the different screening channels of the $2p$ hole. Then the bump of the high-energy side is attributed to the $4f^0$ final state and the low-energy one to the $4f^1$ configuration. Each white line is assumed to be the superposition of a step function describing the transitions into the continuum states and a function representing the transition into the $5d$ unoccupied states. Both contributions are convolved with a Lorentzian (3-eV width) to take into account the finite core-hole lifetime. The width and shape of the density of $5d$ final states are free parameters and are adjusted to reproduce each resonance at the threshold. Finally, the average valence is simply obtained by weighting the relative intensities of these two contributions.

The concentration dependence of the cerium valence is shown in Fig. 3. Two regimes can be underlined.

(i) In the crystalline alloys, the valence of cerium is saturated to a $V = 3.3$ value. Such a saturation effect has previously been observed in pseudobinary compounds[13,14] and in binary amorphous alloys.[15]

(ii) In the amorphous phase, the average valence of the sample decreases progressively with increasing cerium content. The amorphous counterpart of the $CePd_3$ compound is trivalent.

In the range where the valence is saturated, we can notice that the shape of the $L_{\rm III}$ edge changes with composition. Whereas the high-energy peak ($4f^0$) is quite narrow and symmetric, the low-energy one ($4f^1$) becomes more and more asymmetric and broad as the cerium content decreases. This effect and its correlation with the electronic parameters will be discussed in Sec. IV.

B. XPS and UPS measurements

As pointed out above and in contrast to divalent rare-earth elements (Sm, Eu, and Yb), cerium exhibits the same valence both at the surface and in the bulk.[16] Then, reliable information about the electronic configuration of cerium can be deduced from such XPS experiments. We shall now present the XPS results we have obtained for the cerium $3d$ (Sec. III B 1) and palladium $3d$ (Sec. III B 2) core-level spectra. Finally, the UPS valence-band spectra are presented in Sec. III B 3.

1. Cerium 3d core-level spectra

The cerium $3d$ core-level spectra, for several concentrations, are shown in Fig. 4. The intensity of the high-energy structure ($E_B = 914.5$ eV), which is associated with $4f^0$ final states, qualitatively reproduces the compo-

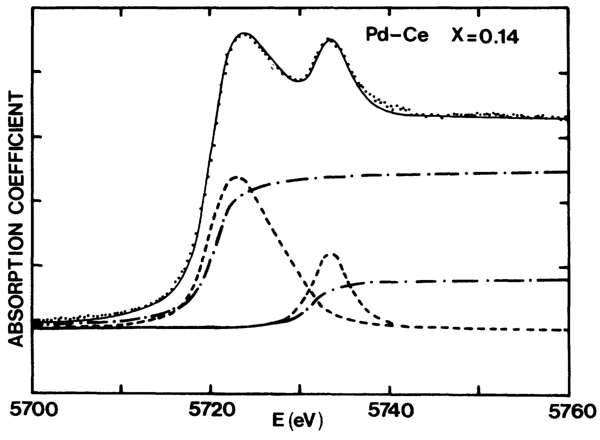

FIG. 2. Deconvolution of a Ce $L_{\rm III}$ spectrum. Dotted lines represent the different contributions (transition into the $5d$ states and into the continuum).

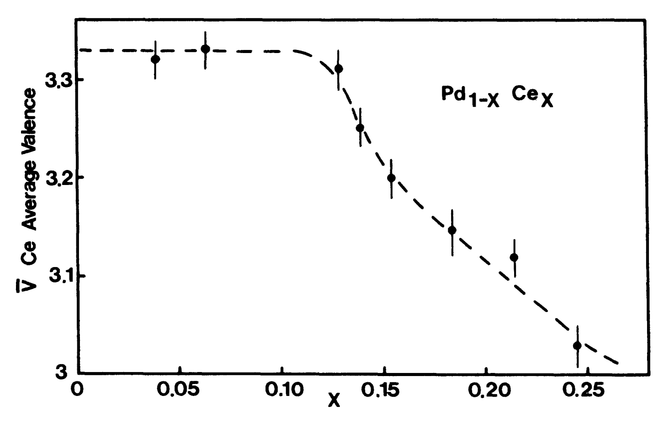

FIG. 3. Average Ce valence vs composition in the $Pd_{1-x}Ce_x$ alloys.

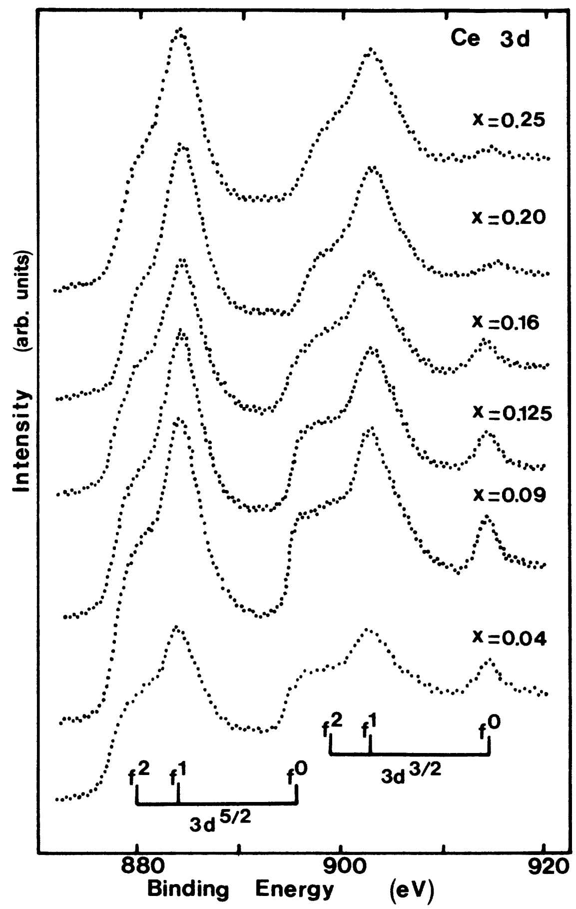

FIG. 4. Cerium $3d$ core level for several $Pd_{1-x}Ce_x$ alloys of different concentration.

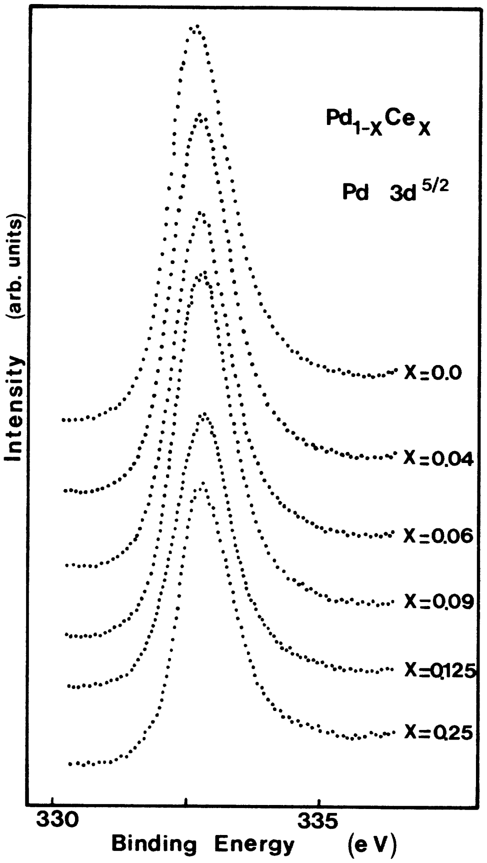

FIG. 5. Palladium $3d$ core levels for several $Pd_{1-x}Ce_x$ alloys of different concentration.

sition dependence of the cerium valence deduced from the L_{III} edges. In addition, we observe in all spectra the well-known shakedown structure which reflects the $4f^2$ final state. The intensity of this satellite structure exhibits roughly the same concentration dependence as for the $4f^0$ structure. Similar behavior has previously been reported in the XPS study of crystalline Ce_mPd_n compounds.[17] As explained by Gunnarsson and Schönhammer,[18] these $4f^2$ features are a direct signature of the hybridization strength between the $4f$ and the conduction electrons whose typical value is about 0.1 eV.

As already observed in the XAS spectra, two concentration ranges can be clearly distinguished.

(i) In the crystalline state no significant changes occur, neither on the $4f^0$ intensity (reflecting the valence saturation) nor on the $4f^2$ intensity, which means that the hybridization remains roughly constant.

(ii) In the amorphous state, in contrast, the $4f^0$ intensity decreases with increasing Ce concentration, confirming the progressive stabilization of the trivalent state. Let us remark that the $4f^2$ structure does not completely disappear, suggesting that hybridization should be important even in the trivalent alloy $Pd_{0.75}Ce_{0.25}$.

2. *Palladium 3d core-level spectra*

These core levels are reported in Fig. 5. For dilute alloys, we observe the same asymmetry of the $3d$ line shape as in palladium metal itself. This asymmetry progressively decreases with increasing Ce content and, for higher concentrations ($x > 0.125$), we obtain quite symmetric line shapes. It is well known that the asymmetry of core-level spectra results from many-body interactions between the core hole and the conduction electrons[19–21] and that it can be related, quantitatively, to the divergence power of the cross section at the threshold and then to the partial density of states at the Fermi level.[22,23]

In Fig. 6, we report the concentration dependence of the asymmetry parameter defined as the ratio between the high- and low-energy half-widths at half maximum of the Pd $3d$ core-level spectra. This dependence clearly reflects a strong decrease in the density of states at the Fermi level and, therefore, the progressive filling of the "Pd $4d$" band. This modification occurs while the cerium configuration remains unchanged (Fig. 3).

We shall now consider the UPS results which give direct information on the valence bands.

3. *Valence-band spectra*

Direct information about the $4f$ spectral distribution is difficult to obtain from usual (Al $K\alpha$ and Mg $K\alpha$) XPS measurements, especially in rare-earth–transition-metal compounds, because of the high transition element d contribution arising near the Fermi level (E_F). Moreover,

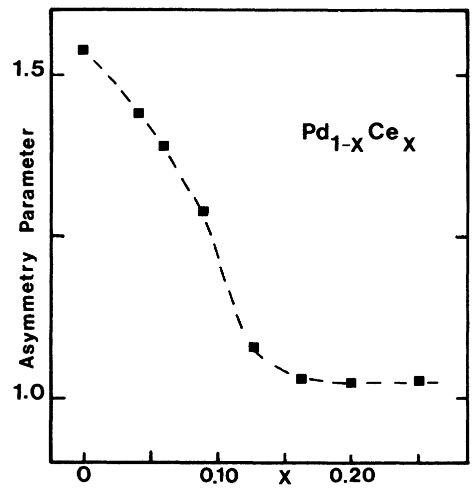

FIG. 6. Asymmetry parameter of the palladium $3d$ core level vs composition in the $Pd_{1-x}Ce_x$ alloys.

relaxation effects and joint density of states can modify the results we expect from a theoretical calculation of the density of states DOS. Nevertheless, such difficulties do not prevent the qualitative study of the DOS modifications using valence-band photoemission as shown in several studies of transition-metal binary solutions.[24–27]

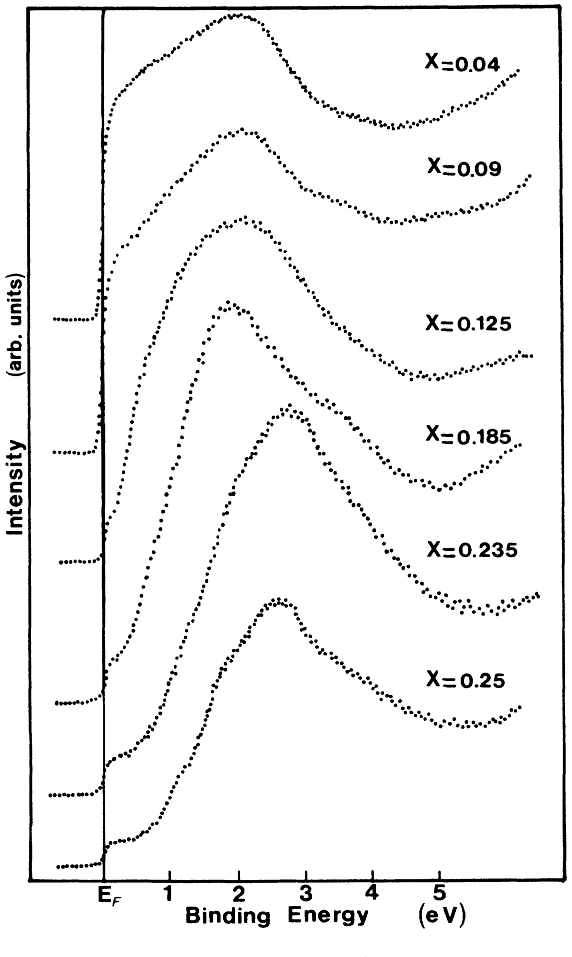

FIG. 7. UPS valence-band spectra for different $Pd_{1-x}Ce_x$ alloys.

The He I ($h\nu=20.1$ eV) UPS spectra are reported in Fig. 7. These spectra clearly show that the DOS at the Fermi level strongly decreases with increasing cerium content in the solid solution range, but remains roughly constant for the amorphous alloys. This behavior can be qualitatively explained by a charge transfer from cerium to palladium and thus by the progressive filling of the palladium $4d$ band which is filled up at $x=0.125$, the upper limit of the solid solution range. The shoulder which appears at E_F for larger concentration (see Fig. 7) results from the extended s band, whereas the narrow palladium d band progressively moves away from E_F when the cerium content increases. This behavior and the L_{III} or core-level results suggest that a correlation exists between the cerium average valence and the density of states. This will be discussed in the following section.

IV. DISCUSSION

Before discussing the variations of the cerium average valence and the density of states with composition in Pd-Ce alloys (Sec. IV B), we briefly comment upon the effect of structural disorder on the cerium electronic configuration (Sec. IV A).

A. Influence of structural disorder on the cerium electronic configuration

The amorphous phase yields the possibility to study continuously the composition dependence of electronic parameters in binary systems. Nevertheless, structural disorder may induce some modifications in the electronic properties. Therefore comparison between the amorphous alloys and their crystalline counterparts (if they exist) is useful to understand the possible role of long-range order (LRO) and short-range order (SRO) on the mixed-valence ground state. From earlier studies on dilute rare-earth (RE) compounds such as Ce in La-Th alloys[28] or Tm in YSe,[29] the mixed-valence behavior seems to be a single-ion property, suggesting that LRO does not play the important role.[28,29] However, in these pseudobinary systems, the short-range order around RE ions is basically preserved. In contrast, in amorphous alloys, topological and chemical disorders strongly affect the local environment around RE ions. As we showed in a previous paper,[15] two different situations are encountered for Ce compounds.

(i) If the valence of cerium is either 3 (e.g., $CeAu_3$, $CeAg_2$, $CeGe_2$, etc.) or weakly mixed valent (e.g., $CeSi_2$, $CeSn_3$, etc., i.e., in the α phase) the structural disorder stabilizes the trivalent magnetic state.[30,31]

(ii) If Ce is in the so-called strong mixed-valence state ($CeCo_5$, $CeNi_5$, $CeRh_3$, etc.), no effect of structural disorder can be evidenced.[15]

The present results we obtained for the Pd-Ce alloys confirm this general tendency. Indeed, the $Ce_{0.25}Pd_{0.75}$ amorphous alloy is trivalent, whereas the $CePd_3$ compound is known to be in a weak mixed-valence state ($\bar{V}=3.15$). At the same time, we observe a modification of the valence-band spectrum as shown in Fig. 8. The

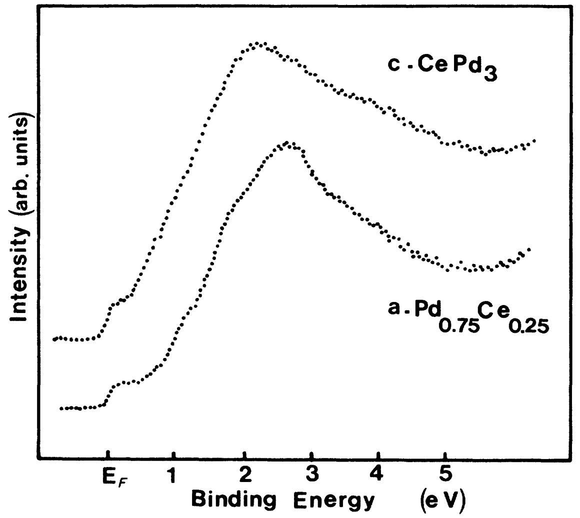

FIG. 8. Comparison between the UPS valence-band spectra of the crystalline $CePd_3$ compound and the amorphous $Pd_{0.75}Ce_{0.25}$ alloy.

Pd 4*d*-derived feature in the crystalline $CePd_3$ compound is closer to the Fermi level than that in its amorphous counterpart. Moreover, the band is narrower in the amorphous alloy, reflecting probably the more localized character of the palladium *d* orbitals in the disordered phase. As we shall discuss in the following subsection, this modification of the occupied density of states is correlated to the stabilization of the trivalent state by structural disorder.

B. Relation between valence and DOS

Comparison between XAS and XPS measurements shows the contrasted effects of the composition on the Ce average valence and the band structure. In the crystalline binary solid solution ($0 \leq x \leq 0.125$) alloys, the average valence of cerium remains saturated ($V = 3.3$), whereas the DOS at E_F deduced from XPS and/or UPS valence-band spectra and core-line asymmetry strongly decreases. On the contrary, in the amorphous alloys ($0.125 \leq x \leq 0.30$) the trivalent configuration of cerium is progressively stabilized whereas no significant change of the DOS at E_F is observed. In this concentration range, the conduction electrons have mainly an *s* character; meanwhile the *d* band is moving away from E_F as *x* increases.

Let us first discuss the important modifications we observe on the L_{III} line shape in the crystalline range. The high-energy $4f^0$ final-state structure is much more narrow and symmetric than the low-energy $4f^1$ structure. This effect has been previously observed for $Ce(Pd_{1-x}Rh_x)_3$ compounds[13] and was phenomenologically reproduced by using two final 5*d* spectral distributions with different width and shape. A systematic study of x-ray-absorption spectra in RE and uranium intermetallics led Lawrence *et al.*[32] to the conclusion that the core-hole potential tends to localize the final 4*f* or 5*d* photoelectron state (Kotani-Toyozawa-like mechanism[33]). We think that the difference between the line shapes of the two structures arises from the screening mechanisms of the 2*p* hole. Indeed, screening by a 4*f* electron is more efficient than by a 5*d* electron. Thus in the $4f^1$ channel, the 5*d* states should be less localized than in the $4f^0$ channel and therefore the $4f^1$ feature should be broader. Moreover, the concentration dependence of the low-energy peak line shape suggests a modification of the final 5*d* energy distribution.

This fact is supported by the strong decrease in $n(E_F)$ observed both on valence-band and core-level spectra. In a rigid-band model, this effect may be interpreted by a charge transfer from cerium to palladium. Such a charge transfer has been invoked to explain the evolution of magnetic properties in several palladium solid solution alloys.[34] The room-temperature susceptibilities have been correlated with the effective valence of the solute element. When the room-temperature susceptibilities of Pd-Ag and Pd-Y systems are plotted against $V_S C_S$, where V_S is the effective valence ($V_{\mathrm{Ag}} = 1$ and $V_{\mathrm{Y}} = 3$) and C_S is the concentration, a common curve is found. The crystalline Pd-Ce alloys can also be reported on this common curve by taking a Ce effective valence of 4. This result suggests that the 4*f* electron also contributes to the Pd band filling and, then, that there is a strong hybridization between 4*f* and Pd 4*d* states. Nevertheless, this description in terms of charge transfer towards the Pd *d* orbitals is somewhat misleading. Indeed, band-structure calculations[35] have indicated that charge transfer is rather weak in intermetallic compounds. Then, Fuggle *et al.*[36] have shown that the Pd *d*-band filling observed in several Pd-*M* systems (where *M* is an electropositive metal like Al, V, or RE metals) is dominated by a mixing of the Pd and *M* states. Therefore, the so-called *d*-band states are actually hybridized states involving Pd 4*d* and Ce 5*d*,4*f* states. Besides, a Pd 4*d* character is present above the Fermi level as clearly demonstrated in band calculations[37] and BIS measurements.[38]

In the model recently developed by Fujimori[39,40] to describe the XPS and XAS spectra of CeO_2 and extended to intermetallic compounds, the ground state is represented by a mixing between two configurations: $4f^0$ and $4f^1L^{-1}$ (where L^{-1} stands for a hole in the ligand). Then, cerium remains strongly mixed valent when the Pd 4*d* orbitals are not completely filled because of the strong hybridization between 4*f* electrons and Pd 4*d* ligand state. For $x > 0.125$, the Pd 4*d* band is full; thus no transfer is possible and the trivalent configuration is stabilized. In Fujimori's picture, one expects the lowering of the 4*f* ligand state mixing, and consequently, a reduction of the valence anomaly. The role of band filling on mixed-valence properties has been discussed in the case of europium intermetallic compounds. Eu intermetallics exhibit the same systematic trend as Ce compounds; i.e., for "*s*"-band-like character, Eu ions are divalent (Ce ions are trivalent) whereas for strong "*d*" character at E_F, a mixed-valence state is stabilized. This behavior was explained in a one-impurity model by screening considerations.[41] The $4f^{n-1}$ configuration is more stable than the $4f^n$ if the screening of the 4*f* hole can be achieved. Thus if the Fermi level lies in a region of available *d* states such a screening will be possible, whereas if it lies in a region of mainly s character the local screening cannot be achieved at all and the normal valence state should be stabilized. In this model, the valence state is fixed by the DOS at E_F.

However, as shown by our experiments on the Pd-Ce alloys, the average valence cannot be directly related to $n(E_F)$. No significant change in $n(E_F)$ is observed at the valence transition. Therefore, the screening mechanism is not suitable to explain the configuration change we observed in the Pd-Ce alloys. We believe that our results can be explained more simply by the filling of the so-called $4d$ band and its moving away from E_F. In the Gunnarsson and Schönhammer (GS) model, the ground state is built as follows:[7] they first introduce a state where all the conduction states below E_F are occupied and the $4f$ level is empty. Then, they introduce a set of states with one electron in the $4f$ level and a hole below E_F. They show that, in first order, the ground state is obtained by a mixing of these states. The other states weakly contribute to the ground state in the limit of high degeneracy. Besides, the mixing between $4f$ and conduction electrons is important for band states close to the Fermi energy. Then, the $4f$-electron–conduction-band mixing is maximized if the conduction band has most of its weight near the Fermi level. Thus, in the crystalline solid solution alloys, the d band is partially unoccupied and the high density of states just below E_F allows a strong mixing between $4f^1$ and conduction electrons; hence the valence anomaly is maximum. On the contrary, in the amorphous range, when cerium content increases the Pd d band centroid moves to larger binding energies. This moving of the $4d$ band induces a decrease in the density of states just below the Fermi level. Therefore the mixing between $4f$ and conduction electrons is strongly reduced and the mixed-valence state is progressively suppressed. Such a decrease in the transition-metal-derived DOS has been observed in going from $CeRh_3$ to $CePd_3$ and has already been invoked to explain the valence variation in the pseudobinary $Ce(Pd_{1-x}Rh_x)_3$ system.[12]

In the amorphous phase, the decrease in the sample average valence is the result of the appearance of trivalent cerium ions as indicated by magnetic measurements.[42] The fluctuations of SRO in the amorphous alloys induce related fluctuations of local density of states and then distribution of mixing between $4f$ and conduction electrons. Then inequivalent sites of cerium appear and the valence state is determined by the local environment, leading to an inhomogeneous admixture of Ce ions. Such a behavior has already been observed in the crystalline disordered system $Ce(Cu_{1-x}Ni_x)_5$ (Ref. 43) where the physical properties are interpreted by an admixture of trivalent and saturated mixed-valence Ce ions. Therefore, if XAS and XPS clearly show a decrease in valence with increasing Ce content in the amorphous alloys, this *sample average information* reflects the stabilization of the two electronic configurations which are compatible with the structural disorder: the trivalent and saturated mixed-valence states.

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