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Electronic structure of Pr in $PdPr_{0.014}$

A. Ślebarski,* M. Neumann, and S. Mähl
Universität Osnabrück, Fachbereich Physik, 49069 Osnabrück, Germany
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We report the Pr $3d$ core-level x-ray photoelectron-spectroscopy (XPS) spectra of $PdPr_{0.014}$. The Pr $3d$ spectra show a satellite structure, comparable with the satellite structure of Ce $3d$ XP spectra. We attempt an analysis of this core-level spectra using the Gunnarsson-Schönhammer model. It seems that Pr in a Pd matrix exhibits mixed valence.

I. INTRODUCTION

The aim of the work reported in this paper is to study the electronic structure of dilute Pr impurities in Pd and to ascertain whether these Pr impurities show valence instabilities. It is well known that valence instabilities occur for Ce. The large valence of Ce impurities in Pd is consistent with the tendency of Pd to absorb all valence electrons of impurities dissolved in Pd in the Pd d shells.[1] Because of the extreme value of the fractional valence of Ce impurities in Pd,[2] it seemed to us that there was a good chance that we could observe a considerable fractional valence effect of Pr in Pd.

There are several experiments which indirectly point to a valence instability of Pr. Fisk and Matthias[3] found a large depression of the superconducting transition temperature of ZrB_{12} in dilute alloys of the type $Zr_{1-x}Pr_xB_{12}$. Wittig[4] found a similar effect with dilute Pr in La, at an external pressure exceeding 200 kbar. Pr impurities in $LaSn_3$ resulted in resistivity behavior which was interpreted in terms of the Kondo effect due to hybridization of the f electrons with the conduction-band states[5] which can lead to valence instability for strong enough hybridization. Similar resistance anomalies were observed with Pr impurities in Pd.[6,7] One observes a small drop of the resistivity increment $\Delta\rho = \rho_{\text{alloy}} - \rho_{\text{Pd}}$ of Pr between 1.5 and 25 K, which is clearly independent of the concentration of Pr, and is proportional to $-\ln T$ between 4 and about 20 K. Qualitatively this type of behavior is expected from the Kondo effect and predicts an incipient valence instability of Pr due to hybridization effects.

In Ref. 8, L_{III} x-ray-absorption measurements and the effective moment of Pr in $PdPr_{0.014}$, at low temperatures, show again that the Pr instability does not lead to a strongly fractional valence, as for Ce impurities in Pd (i.e., the valence of Pr impurity is close to 3). However, the ground state of the Pr impurity[8] is nonmagnetic, as expected for fractional valence or the Kondo effect. In Ref. 9 the electrical and thermal transport properties of $PdPr_{0.014}$ are successfully described using the phenomenological "dynamic alloy" model.[10]

The main idea of this model is that a periodic intermetallic compound with unstable ions can be regarded as a dynamic alloy: the minority configuration of the two configurations $4f^1$ and $4f^2$ produces a scattering potential which, however, is not static but fluctuates with some fluctuation time $\tau_f = h/k_BT_f$. The second time scale in the model is an inelastic lifetime $\tau_e = h/k_BT$. At high T, $\tau_e \ll \tau_f$ and conduction electrons (CE's) see the full scattering potential coming from the minority configuration (fully incoherent scattering), but at very low T, when $\tau_e \gg \tau_f$, CE's average over the fluctuating potential and it is seen as a mean-field potential, i.e., fully coherent scattering. At the intermediate temperature range, the scattering is partly coherent and only the last one is seen in the resistivity. For diluted Pr (Ce) in the alloy $\Delta\rho$ at T=0 reflects in this model the charge density contrast between the impurity with valence $(3 + \nu)$ and the Pd matrix and is proportionate to $1/T_f$.[9] According to the model, one is not surprised to see that the unstable Pr diluted in Pd scatters less than stable trivalent Lu impurities, especially near T=0.

Contrary to the above arguments, we have observed in $PdPr_{0.014}$, through inelastic neutron scattering,[11] evidence for the dynamical spin instability of Pr, similar to that of a typical Ce-Kondo system. There is a $T^{\frac{1}{2}}$ law for the quasielastic linewidth.

In this paper we suggest the f electron instability of Pr in $PdPr_{0.014}$ from the Pr $3d$ XP spectra. In addition to the main Pr $3d$ XPS peaks due to the $3d_{\frac{5}{2}}$ and $3d_{\frac{3}{2}}$ doublet, there are additional satellites which are interpreted in the same way as the respective satellite peaks of α-Ce $3d$ XP spectra. As a proof we try to use the Gunnarsson and Schönhammer model[12] for interpretation of the data.

II. EXPERIMENT

The sample of 1.4% Pr in Pd was arc melted on a cooled copper crucible in a high-purity argon atmosphere. The elemental purity was Pd 99.9999% and Pr 99.99%. In order to avoid segregation and still be able to use the concentrations mentioned above, we eventually worked with unannealed samples as quenched from the melt. It was shown in Ref. 13 that for rapidly quenched alloys, the limit of solubility of Pr in Pd approaches 4% .

We used the same sample before for measurements of magnetic susceptibility, resistivity, thermopower, L_{III} x-ray-absorption edge at the room temperature,[8] neutron

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inelastic scattering,[11] Hall resistivity, thermal lattice expansion, and the specific heat.[9]

X-ray analysis and metallographic optical analysis show no evidence for phase segregation in unannealed alloys of Pr. The resistivity and susceptibility measurements, which can detect phase segregation on a much finer scale than the x-ray analysis, indicate rather good solution of Pr in Pd up to 3%.[8,9]

For the XPS measurements of $PdPr_{0.014}$ the same sample was used. The spectra were excited with monochromatic AlKα radiation ($\hbar\omega$ = 1486.6 eV). The energy spectra of the electrons were analyzed by a hemispherical mirror analyzer with an energy resolution better than 0.4 eV. All the spectra were measured in vacuum below 6×10^{-10} Torr. Calibration of the spectra was performed according to Ref. 14. The $4f$ levels of gold were found at 84.0 eV and the observed energy spread of electrons detected at the Fermi energy (ϵ_F) was about 0.4 eV.

III. RESULTS AND DISCUSSION

Figure 1 compares the XPS spectra of the valence bands of pure Pd and a $PdPr_{0.014}$ alloy. The valence-band (VB) XP spectra of Pd compare well with the literature data,[15,16] whereas a satellite structure is observed at binding energies (BE) of 7.3 eV and 9 eV for $PdPr_{0.014}$. The peak at 7.3 eV can be related to the electronic configuration fd^2s^2 of the Pr ions, calculated by Brever in Ref. 17.

In Fig. 2 the $3d$ core-level XPS spectra are presented for Pr in a Pd host. The figure also contains theoretical curves fitted to the main peaks of the data with shapes given by the theory of Doniach and Šunjić.[18] The theoretical line shapes were convoluted with the experimental resolution which is represented by a Gaussian of 0.4 eV FWHM (the full width at half maximum).

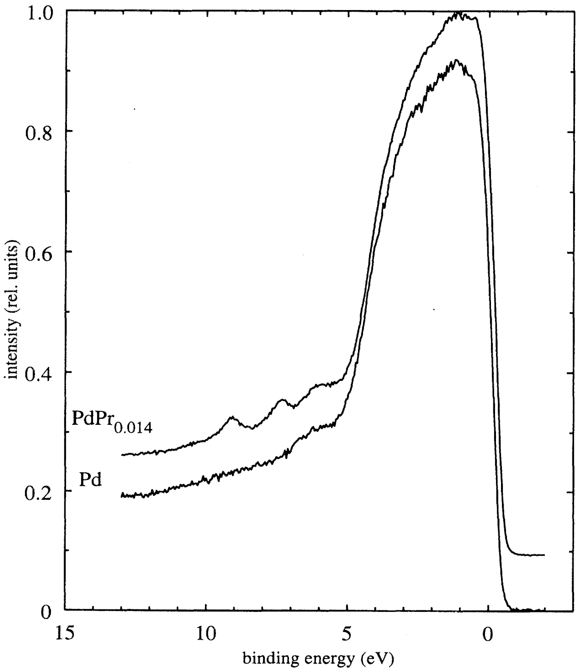

FIG. 1. The valence band XPS spectra of $PdPr_{0.014}$ and Pd.

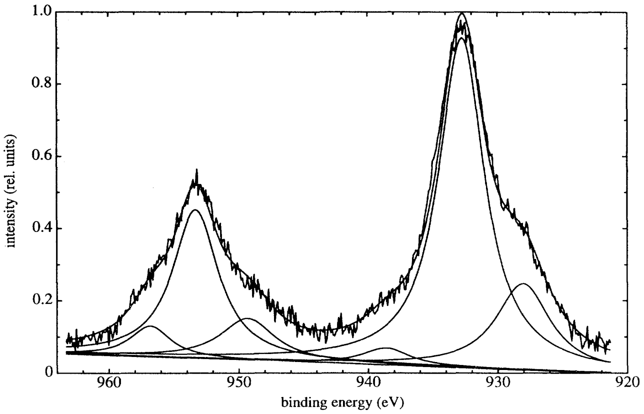

FIG. 2. Experimental result of Pr $3d$ XPS for $PrPd_{0.014}$. The spectra consist of $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ components with higher and lower energies, respectively. Two satellites in every $3d$ component are observed. Solid lines are fits to the experimental data assuming Doniach-Šunjić lines in Pr.

In Table I we present the energies and the relative intensities of the $3d$ XPS peaks as fitting parameters which correspond to the final states for $PdPr_{0.014}$. The Pr $3d$ spectra for $PdPr_{0.014}$ alloys show a subtle difference in comparison with the related $3d$ spectra of pure Pr.[19,20] The $PdPr_{0.014}$ XP spectra presented in Fig. 2 show intensities due to the $3d^9 4f^2$ final states, moreover, the two satellites for both $3d_{\frac{5}{2}}$ and $3d_{\frac{3}{2}}$ components are observed. The shape of the Pr $3d_{\frac{3}{2}}$ peak of $PrPd_{0.014}$ is similar to the Pr $3d_{\frac{3}{2}}$ peak in Pr_2O_3, which exhibits satellites on both sides of the main peak.[21] The Pr $3d_{\frac{5}{2}}$ spectrum of $PdPr_{0.014}$, however, differs from the corresponding $3d_{\frac{5}{2}}$ peak of Pr_2O_3. For the trivalent praseodymium ions in Pr_2O_3 the satellite located at the higher binding energy (BE) is not observed in the $3d_{\frac{5}{2}}$ component, but it is clearly seen at higher binding energies of the $3d_{\frac{5}{2}}$ component of Pr $3d$ spectra for PdPr. We note that Pr $3d$ spectra for $PdPr_{0.014}$ qualitatively are similar to $3d$ XP spectra of α-Ce.

The structure in the XPS-Ce spectra is usually interpreted in terms of the Gunnarsson-Schönhammer theory.[12] Multiplet effects due to the coupling of the $3d$ hole with the open $4f$ shell are clearly visible in the $3d_{\frac{3}{2}}$

TABLE I. $3d$ XPS peak binding energies (E) and the relative intensities (I) for Pr in $PdPr_{0.014}$. All energies are in eV with respect to ϵ_F.

		$3d_{\frac{3}{2}}$			$3d_{\frac{5}{2}}$	
E	957	953	949	939	933	928
I	0.09	0.45	0.13	0.05	1.0	0.26

peak and have been tentatively assigned to the underlying multiplet structure of the $3d^9 4f^1$ configuration.[22] In the $3d$ core-hole spectra of Ce, one observes in addition to the main feature ($3d4f^1$) a shakedown satellite ($3d4f^2$) at a smaller BE. In this work, we identify the peaks at 928 eV and 949 eV (Fig. 2) as Pr satellites $3d_{\frac{5}{2}}4f^3$ and $3d_{\frac{3}{2}}4f^3$, respectively. Note that for praseodymium, the $3d_{\frac{5}{2}}4f^3$ satellite in the XP spectra correlates with the center of gravity of the $3d$ x-ray-absorption line.[23] In Ref. 20 it has been shown that the dominant final state in XPS from the $3d$ levels of the light rare earths is produced by screening the core hole within the $5d$ conduction electrons, whereas the shakedown satellite corresponds to screening by f electrons. The creation of the core hole pulls an empty $4f$ level below ϵ_F. The probability that a conduction electron will fill this hole, which determines the intensity of the satellite, is proportional to Δ. In the Anderson model,[24,25] the degree of the $4f$ instability (mixed valence) depends on the hybridization energy Δ, between the $4f$ and the conduction electrons and the energy separation between the $4f$ level and ϵ_F.

Gunnarsson and Schönhammer,[12] using a slightly modified version of the Anderson impurity Hamiltonian and taking into account the degeneracy N_F of the f level, calculated XPS Ce spectra and discussed how experimental spectra can be used to estimate the f occupancy n_f, and the coupling Δ, between the f level and the conduction states. In Ref. 26, Fig. 6, the intensity ratios $I(f^2)/I(\text{total})$ of Ce ($I(f^1)/I(\text{total})$ of La) are calculated as a function of the hybridization parameter Δ. It is possible to determine the Δ parameter when the intensity of the final $3d^9 f^1$ and $3d^9 f^2$ states of Ce or Ce in an alloy is measured. For most of the α-type Ce intermetallic compounds (Ce in the mixed valence state) Δ is of the order of 100 meV.

Unfortunately, this function of the intensity ratio vs Δ has not yet been calculated for Pr, which shows often the typical mixed valence state behavior.

We assumed that the calculated variation of the ratio $r(r = I(f^3)/[I(f^2) + I(f^3)])$ vs Δ of Pr is similar to the function calculated for Ce. The intensity ratio experimentally determined from XPS of $\mathrm{PdPr}_{0.014}$ gives the value 0.21 and a very crude analysis gives $\Delta \cong 100$ meV. We may suggest that the Pr f levels are in the so-called mixed-valence state in $\mathrm{PdPr}_{0.014}$. In this alloy Pr is under a high lattice pressure of about 200 kbar. In the simple phenomenological model of valence fluctuations,[9,10] it is possible to calculate the mixing matrix element Δ, between the states of different f configurations, based on the resistivity and magnetic susceptibility measurements, when the crystal field splitting is well known. This model of the valence fluctuation predicts a Pr valence in a Pd host which is 0.5% larger than 3 with an order of magnitude for Δ of 1000 K (about 80 meV).

In α-Ce there is also clear evidence of a $3d^9 4f^0$ component for both $3d_{\frac{3}{2}}$ and $3d_{\frac{5}{2}}$ multiplets, which are not present in γ-Ce (e.g., Ref. 27).

The peaks in the XPS $3d$ spectrum of $\mathrm{PdPr}_{0.014}$ at 939 eV and 957 eV were attributed to $3d^9 4f^1$ final states of tetravalent praseodymium.

Previously a valence, larger than 3, for Pr in Pd was determined from L_{III} x-ray-absorption measurements.[8] The distance in energy between $\mathrm{Pr}^{3+}(4f^2)$ and $\mathrm{Pr}^{4+}(4f^1)$ lines observed for $\mathrm{PdPr}_{0.014}$ in L_{III} spectra is about 7 eV. The XPS $3d$ spectra for $\mathrm{PdPr}_{0.014}$ correlate with the L_{III} x-ray-absorption results, in that the average distance between the $3df^1$ and $3df^2$ XPS peaks is about 5 eV.

The relative intensities of the $3df^1$ final states in the $3d$ XP spectra of $\mathrm{PdPr}_{0.014}$ are weak (about 5%: see Table I), so we conclude that Pr might exist in the mixed valence state.

The investigations of the electric and thermal transport properties and magnetic susceptibility indicate anomalies associated with the $4f$ instability of Pr in Pd. The L_{III} measurements and the effective magnetic moment of Pr show at helium temperatures a fractional valence of the Pr impurities much closer to 3[8] (i.e., the valence instability of Pr does not lead to a strongly fractional valence, as observed for Ce impurities in Pd).

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[*] Permanent address: Institute of Physics, Silesian University, 40-007 Katowice, Poland.

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