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$3d$ and $4d$ resonant photoemission in Pr and Nd metal

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Resonant photoemission experiments around the $3d$ and $4d$ thresholds are presented for Pr and Nd metal. The behaviors at the two thresholds are different, in that the data at the $4d$ edge show a prethreshold enhancement. In addition to the strong enhancement of the f^1 and f^2 final state structure for Pr (f^2 initial state) and Nd (f^3 initial state) metals, respectively, a weak f^2(Pr) and f^3(Nd) final state structure is observed, starting at E_F.

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I. INTRODUCTION

Photoemission spectroscopy (PES) measures a state with one electron missing relative to the initial state. This often results in complicated spectra, which are difficult to interpret.[1] There are two limiting cases that can be used to analyze experimental data.[2] One is the independent (one-) electron model (thought to be applicable to, e.g., the free electron metals), where one has very many (N) electrons, that do not interact with each other, and where the $(N-1)$ final state can be safely assumed to equal the N-electrons initial state. On the other side there is the independent orbital model, where one has an orbital not interacting with other ones (holding, e.g., for many though not all core orbitals of atoms, and to a lesser degree for those of solids and molecules) where the $(N-1)$ final state can be calculated from the N-particle initial state with a high degree of accuracy, because N is a relatively small number. In most practical cases these simple approaches are not sufficient and one has to employ many electron schemes for an interpretation of the data. A particularly successful one is the Gunnarsson-Schönhammer[3–8] approach, which has been used to analyze data from Ce (and Yb) systems where one has one localized $4f$ electron, which couples to the system of conduction electrons. In a simplified version of this model the conduction electron system is replaced by a valence orbital.[9–11] While some authors have stressed the success of the Gunnarsson-Schöhammer model,[12,13] others have questioned its validity.[14–20]

In principle this model should not only apply to Ce systems but also to those containing other rare earth elements. Some works for Pr and Nd compounds have been performed to test the extension of the Gunnarsson-Schönhammer model.[6,21] On the theoretical side it was shown that in Pr systems, in addition to the f^1 final state, a second state nearer to (but not at) the Fermi energy can be produced by the mixing of the f electrons and the conduction electrons. On the experimental side, a number of Pr and Nd intermetallics[22–24] show, in addition to the f^{N-1} peak, a structure with approximately 2-eV smaller binding energy the interpretation of which is not established. Note that in these intermetallic compounds, there is a strong contribution of the d electrons to the valence band spectra, which makes the extraction of the f contribution for the spectra difficult. The data on $Pr_{0.9}Th_{0.1}$, on the other hand,[22] have only been measured up to a photon energy of $\hbar\omega = 80\,\mathrm{eV}$, which is below the $4d$ threshold at 133 eV and therefore allows one not to deduce the $4f$ contribution with confidence.

Here PE data for Pr and Nd metals around the $4d$ and $3d$ thresholds are reported. The data differ for the two thresholds qualitatively. The spectra at the $3d$ threshold show the expected behavior, with a clear separation of the valence band and the f^{N-1} final state below the resonance. At the resonance the f^{N-1} structure is strongly enhanced and additional structure is recovered. We give evidence that this additional structure is due to f^N (f^2 for Pr and f^3 for Nd) final states. In approaching the $4d$ resonance structure in the spectra extending to the Fermi energy gets enhanced, indicating its f character, however, there is no clear distinction between the ‘‘on-resonance’’ spectra and the ‘‘off-resonance’’ spectra. The data presented emphasize the importance of the $f-(ds)$ hybridization for the interpretation of PE spectra from rare earths.[25–28]

II. EXPERIMENT

The experiments were performed at beamline 7.0.1 at the Advanced Light Source in Berkeley. The samples were films evaporated on a W(110) single crystal. Although the vacuum was in the 10^{-11}-Torr range, an oxygen signal was always visible in the spectra taken around the $4d$ edge, while it was barely detectable in the spectra from around the $3d$ edge, signaling the much reduced surface sensitivity in the kinetic energy range obtained with the latter photon energies. For Pr metal the $3d$ ($4d$) absorption maximum is at 931 eV (133 eV) and for Nd metal the corresponding numbers are 979 eV (137 eV).

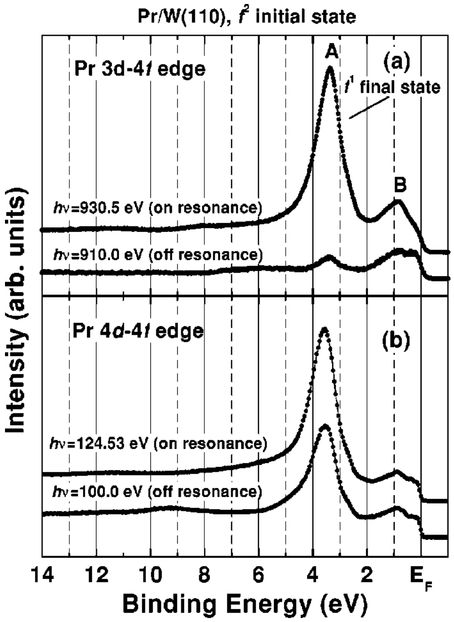

FIG. 1. (a) On-resonance ($\hbar\omega = 930.5\,\mathrm{eV}$) and off-resonance spectra ($\hbar\omega = 910.0\,\mathrm{eV}$) of Pr metal for the $3d \rightarrow 4f$ absorption resonance. A large enhancement of the intensity is observed in the f^2 final state structure but to a lesser degree also in the energy interval between the f^2 resonance and the Fermi energy (E_F). (b) On-resonance ($\hbar\omega = 124.53\,\mathrm{eV}$) and off-resonance spectra ($\hbar\omega = 100.0\,\mathrm{eV}$) of Pr metal for the $4d \rightarrow 4f$ absorption resonance. There is an enhancement in the f^1 final state structure and also in the energy interval between the f^1 structure and E_F. Adjusting the intensities in this second regime one notices that, in contrast to the behavior near the $3d \rightarrow 4f$ resonance, now the shape of the spectra on and off resonance stays similar.

III. RESULTS

A. Pr metal

Figure 1(a) shows the ''on-resonance'' (and ''off-resonance'') spectra of Pr metal at the $3d$ resonance. They exhibit the anticipated features. The off-resonance spectra give a valence band ($5d6s^2$) with a width of slightly over 2 eV and at 3.5 eV the $4f^1$ final state structure expected from the f^2 initial state of Pr in Pr metal.[29] The on-resonance spectrum gives an enhancement of the f^1 structure but also additional intensities between E_F and the f^1 structure. A and B mark the two final state structures observed in resonance photoemission experiments on Pr intermetallics.[22–24]

In the simplest approach one assumes that to analyze the resonant photoemission of Pr metal, there are two channels at resonance that contribute to the spectra.

(1) Direct PES:

$$3d^{10}4f^2(5d6s)^3 \xrightarrow{\hbar\omega} 3d^{10}4f^1(5d6s)^3[5d].$$

(2) Resonance PES:

$$3d^{10}4f^2(5d6s)^3 \xrightarrow{\hbar\omega(3d)} 3d^9 4f^3(5d6s)^3$$

$$\xrightarrow{\text{Auger}} 3d^{10}4f^1(5d6s)^3[5d].$$

Here the screening electron in the valence band has been indicated by square brackets. The two equations indicate that an enhancement in the $4f^1$ final state structure should be observed at the resonance, as is actually the case.

The additional structure in the on-resonance spectra is mot likely produced by a $4f^2$ final state, which can occur via three mechanisms. (I) Because the correlation energy (U) of the $4f$ electrons is finite,[21] there is a mixing of the f^3 configuration into the f^2 ground state configuration of Pr. This, via direct photoemission, results in a f^2 final state configuration. (II) There is a second decay channel from the resonant photoemission intermediate state into the final state in the resonant channel, namely:

$$3d^9 4f^3(5d6s)^3 \rightarrow 3d^{10}4f^2(5d6s)^2[5d].$$

It is difficult to determine the relative strength of the two processes. (III) There is a (small) hybridization between the $(5d6s)^3$ configuration and the $4f^N$ configuration. Therefore the $(5d6s)$ photoemission leads to a f^2 final state (and its excitation).

Figure 1(b) shows on- and off-resonance spectra of Pr metal at the $4d$ threshold. In the off-resonance spectrum an oxygen signal around 6 eV has been removed, which is just barely visible in the on-resonance spectrum (for them the raw data are shown). If one normalizes the spectra at the valence band edge one makes the striking observation that the two spectra are surprisingly similar to contrast to the situation at the $3d$ resonance as documented in Fig. 1(a) (the same behavior will be seen in the Nd data).

The most likely reason for this observation is the energy dependence of the $4f$ photoionization cross section. For Pr (and Nd) this rises from low photon energies to a maximum at slightly below 100 eV, and decreases slowly from then on, having decreased by two orders of magnitude between the $4d$ and the $3d$ thresholds. This also explains that off resonance at the $4d$ threshold the $4f^1$ peak is substantially larger than the valence band, while at the $3d$ threshold the reverse is true.

In order to discuss the on-resonance spectra it is important to have a knowledge of the off-resonance spectra, which we display, using energies smaller than those of the $3d$ edge for Pr and Nd metals in Fig. 2. The two valence bands are quite similar with little structure, except for peaks at E_F and about 1 eV, and a width of about 2 eV. In addition the spectra show the $4f^{N-1}$ structure at 3.5 eV in Pr and at 5 eV in Nd. Comparison will be made with on-resonance data at the $4d$ edge, because these data have a higher resolution compared to those taken at the $3d$ edge.

Figure 3(a) gives an on-resonance spectrum of Pr metal at the $4d$ threshold, which shows (although only barely visible in the raw data) additional structure. The structure was made more visible by subtracting from the raw data a set of smoothed data (15 channels). This procedure enhances the structures of the raw data, producing also the usual undershoot at the Fermi energy. Enhancing the structures by a division through the smoothed data leads to similar results [Fig. 3(b)] indicating the consistency of the procedure.[30]

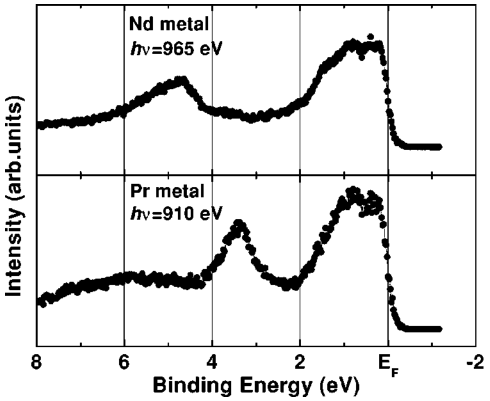

FIG. 2. Off-resonance spectra near the $3d\rightarrow4f$ absorption for Pr and Nd metals showing a gap between the valence band and the $4f^{N-1}$ final state structure for both metals.

In order to analyze the structure it was assumed that it is derived from a $4f^2$ final states structure. If this interpretation is correct the additional peaks should correlate with the known $4f^2$ multiplet structure.[31–33] We have indicated this structure weighted with their optical transition probabilities by a bar diagram with no extension or contraction as used for the analysis for the f^{N-1} and f^{N+1} structures[29] because now a situation close to that of the ground state is encountered.

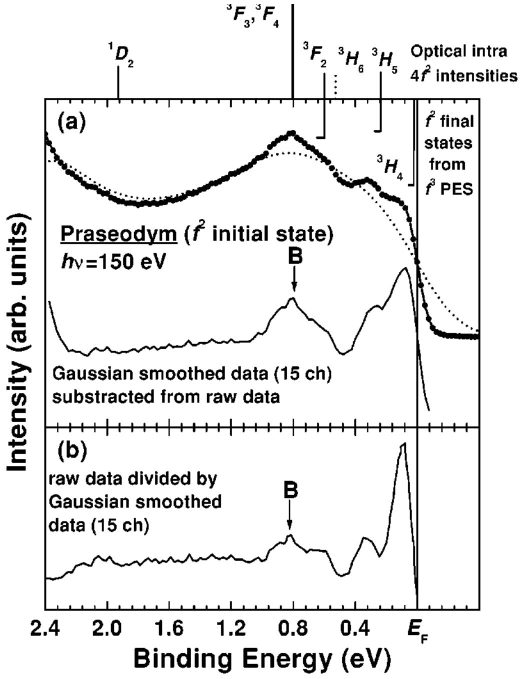

FIG. 3. (a) High resolution spectrum of Pr metal at the $4d\rightarrow4f$ resonance (note that this resonance covers a large energy interval between 120 and 160 eV). The data are also shown with a 15-point smoothed curve and a difference curve of the raw data and the smoothed curve in order to enhance the contrast. Bar diagrams give the position of the $4f^3\rightarrow4f^2$ final state structure and the position and intensities calculated for optical absorption spectra of Pr^{3+} ions in solution. (b) Division of the raw data by the smoothed data from (a).

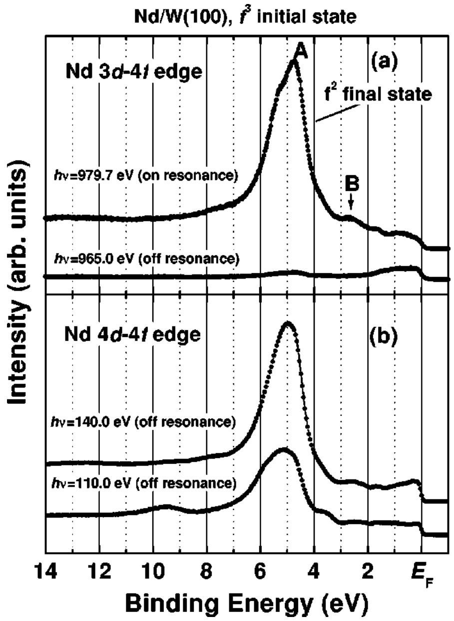

FIG. 4. (a) On-resonance ($\hbar\omega = 979.7\,\mathrm{eV}$) and off-resonance spectra ($\hbar\omega = 965.0\,\mathrm{eV}$) of Nd metal for the $3d\rightarrow4f$ absorption resonance. (b) On-resonance ($\hbar\omega = 140.0\,\mathrm{eV}$) and off-resonance spectra ($\hbar\omega = 110.0\,\mathrm{eV}$) of Nd metal for the $4d\rightarrow4f$ absorption resonance.

In addition, the final states are indicated, that are expected from a direct photoemission out of a $4f^3$ initial (mixed into the basic $4f^2$ initial state) state leading to a $4f^2$ final state.[34]

B. Nd metal

The results for Nd metal are similar to those for Pr metal. Figure 4(a) compares off- and on-resonance spectra at the 3d resonance and the general features are similar to those observed for Pr [Fig. 1(a)]. The off-resonance spectrum shows, clearly separated, the $4f^2$ final state and the valence band, while in the on-resonance spectrum, additional structure is created between these two features, with a large increase of intensity of the f^2 structure. A and B indicate the two final state features observed in the spectra of the intermetallics.[22–24] Figure 4(b) compares the off- and on-resonance spectra at the 4d edge and as for Pr, they are similar indicating again that the resonance processes for the 3d and 4d absorption regions are not completely identical.

In Figs. 5(a) and 5(b) the 4d resonance spectra of Nd metal of two samples are compared. The shapes are not identical, however, the positions of the weak structures remain the same.

In order to come to an understanding of the data we proceed as in the case of Pr (Fig. 3). A smoothed version of the spectra from both samples is produced and subtracted from the raw data in order to enhance the contrast (a division like in Fig. 3 produces identical results). We compare these curves which reveal structures, again with the bar diagram of the optical ($4f^3$) data[31–33] and the $4f^3$ final states, determined from PE out of a $4f^4$ initial state, calculated by Cox.[34]

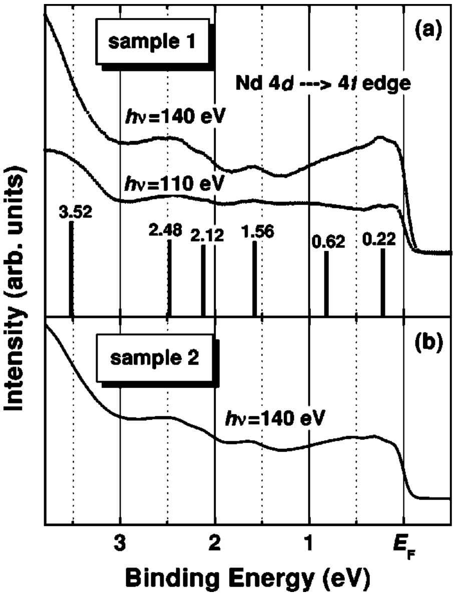

FIG. 5. (a) On- and off-resonance spectra of Nd metal at the $4d \rightarrow 4f$ absorption edge. (b) On-resonance spectra of Nd metal at the $4d \rightarrow 4f$ absorption edge of a second sample.

IV. DISCUSSION

The observation of a f^N final state in addition to the common f^{N-1} final state in the photoemission of rare earth metals has so far been restricted to Ce (and Yb) systems, where, in addition to the f^0 final state at 2-eV binding energy, a f^1 final state at the Fermi energy with its spin orbit excited state at 280 meV has always been observed. The data from the intermetallic compound (RE–Ru_2, –Pd_3, –Rh_2, –Ir_2 with RE=Pr, Nd, and $Pr_{0.9}Th_{0.1}$),[22–24] which showed two final states, provides evidence that in addition to the common $4f^{N-1}(5d6s)^3[5d]$ final state observed in rare earth systems, there should be another one containing the $4f^N$ initial state configuration. The position of these two previously observed final states are indicated by A and B in Figs. 1(a) and 4(a). On the theoretical side a simple screening model, put into mathematical form, e.g., with a two-level molecular orbital picture,[9–11] gives for any finite $f-(ds)$ hybridization two valence band final states, one with predominantly f^{N-1} character with some (ds) admixture and one with predominantly (ds) character and some f^N admixture. Also a more sophisticated theory[6,21] could reproduce the experimental two-peak structure in the earlier Pr data. It seems from these calculations that the second peak (beyond the f^{N-1} peak) is produced by the $f-(ds)$ hybridization, enhancing the structure in the (ds) valence band at the resonance. No attempt was made to incorporate any f^N excited state structure, because this had not been observed at that time.

So far only the origin of peak A in the Pr and Nd intermetallic compounds has been analyzed in detail. It is obvious to correlate structures A in Figs. 1(a) and 4(a) with similar structures in the intermetallics (and previous results in the metal) and therefore assign them to a f^{N-1} final state. The interpretation of structure B is less obvious because contrary to the case of the intermetallics, in the present metal spectra, in addition to structure B, there are other structures present.

Here no detailed theoretical analysis of the data (beyond the f^{N-1} structure) will be presented, only some suggestions can be given. Since the additional structure between the f^{N-1} final state and the Fermi energy is weak, it has to be assured that it is not due to impurities. To that purpose three series of data were taken at time intervals of several months with different samples. In Figs. 5 and 6, data of two samples of evaporated Nd metal are compared and while the intensities do not agree in every detail, the position of the (weak) peaks agree at 0.22, 0.62, 1.56, 2.12, 2.48, and 3.52 eV below E_F. This is evidence that the structures are genuine. The enhancement of these weak structures as given in Fig. 6 demonstrates again the strong similarity of the two data sets (except for different statistics).

An unhybridized $4f^N(5d6s)^3$ configuration leads only to two structures in the valence band, namely

$$4f^{N-1}(5d6s)^3[5d] \quad (4f^{N-1}\text{state})$$

and

$$4f^N(5d6s)^2[5d] \quad (\text{valence band}),$$

where $[5d]$ is a screening electron.

For zero $f-(ds)$ hybridization near the Fermi edge only the $5d6s$ valence band is observed and at the $4f^{N-1}$ excitation energy, the multiplet structure of this configuration. A finite $f-(ds)$ hybridization leads, in Ce systems near E_F, to a structure reflecting the $4f$ occupancy of the initial state, sometimes called the Kondo peak. In Pr and Nd metals the $f-(ds)$ hybridization will in an analogous way lead to a $4f^2$ and $4f^3$ structure, respectively, with the corresponding excited states. These should equal those derived, e.g., from optical spectroscopy.

In optical absorption (or emission) experiments the intra-$4f$ transitions are in principle not allowed for electric dipole radiation, because of the parity selection rule (weak magnetic dipole and electric quadrupole transitions are allowed). The observed electric dipole radiation strength in optical intra-$4f$ transitions originates from the mixing of $5d$ states into the $4f$ states via the crystal field or lattice vibrations.[31,32] The intensity of the various multiplets reflects the amount of $5d$ mixing. If the photoemission data are explained in terms of $f-ds$ hybridization, likewise the intensity of the observed $4f$ excited multiplets can reflect the $5d$ admixture produced by the $f-(ds)$ hybridizations. Thus the intensity of the optical intra-$4f$ transitions and the intensity of the $4f^N$ excited states in a photoemission experiment (in a $4f^N$ system) may have the same origin, namely the admixture of the $5d$ wave functions. This is the reason why in Figs. 3 and 6 the optical intensity modulated $4f$ energies are used in comparison with photoemission data, and not the bare $4f$ energies.

Another possibility attributes the observed $4f^N$ structure to photoionization of $4f^{N+1}$ states mixed into the ground state by the correlation energy U. To that purpose for Pr metal and Nd metal (Figs. 3 and 6) also the f^2 final states and f^3 final states produced out of a $4f^3$ and $4f^4$ initial state are indicated, with intensities as given by Cox.[34]

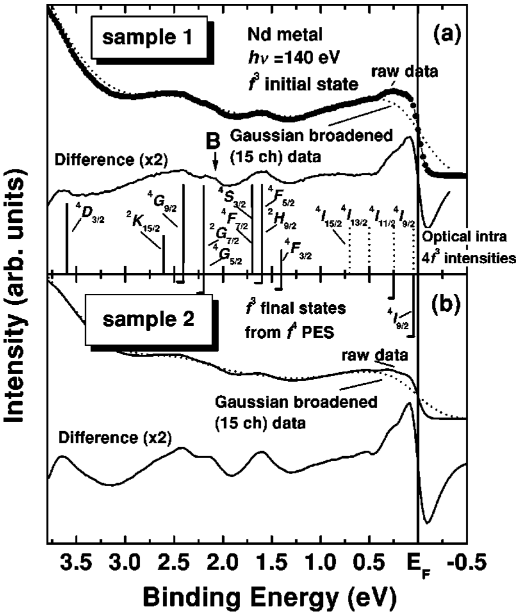

FIG. 6. (a) and (b) High resolution on-resonance photoemission spectra, smoothed data, and a substraction of raw and smoothed data for Nd metal for two different samples. Bar diagrams are the energies of the optical absorption maxima of Nd^{3+} ions in solution, where in many cases a number of transitions have been summed to make the general picture clearer (Ref. 32); also shown are the $4f^3$ final states obtained by photoemission from a $4f^4$ initial state (Ref. 34).

The final state at ~ 2 eV ($^1D_2$) in Pr metal and at ~ 3.6 eV ($^4D_{3/2}$) in Nd metal does not appear in the bare $4f$ calculations of Cox[34] but can be interpreted by invoking $f-(ds)$ hybridization, stressing its importance.

The question arises whether the present data can be used to contribute to the ongoing debate about the validity of the single impurity Anderson model (SIAM) for the interpretation of photoemission spectra of cerium (and ytterbium) compounds.[12–21] The SIAM can be successfully used to describe this qualitative nature of the spectra in some quantitative detail. Whether all the fine points come out correctly seems to be a matter of controversy. This discussion seems to be about quantitative matters rather than qualitative ones. With respect to the qualitative nature of the problem, there seems to be general agreement that the final state of a PE experiment in a RE compound, and hence also in a Ce or Yb compound, consists of a f^{N-1} final state (where N is the number of $4f$ electrons in the ground state) and in addition, due to the (small) mixing of the f electrons with the (ds) conduction electrons, there is also a f^N final state visible in the spectra. The SIAM has computational difficulties in dealing with f^2 or f^3 initial states in the same kind of detail, as it has done for f^1 initial states. In this respect a molecular orbital model has certain advantages, although it must also be stretched to account for all the excited states as observed in the present experiment. Therefore taking into account the admittedly low statistical accuracy of the present data, we think that it is very encouraging that one has been able to identify the f^N final state structure in some detail for Pr and Nd metals.

There remains the questions of the nature of the second peak in spectra of some rare earth intermetallic, at ~ 2 eV nearer to the Fermi energy (peak B). These 2 eV are the energy needed to convert a $5d$ electron into a $4f$ electron. Therefore, the most likely interpretation of this peak seems to be an intermediate state in the decay of the photoexcited $4f^{N-1}$ state to the $4f^N$ ground state. The question why this state shows up with large intensity in the intermetallic compounds, but only barely in the metals, is hard to answer. It may have to do with the large d density of states in these materials (RE Pd_3, $-Ru_2$, $-Rh_2$, and Ir_2), which overlaps the $4f^{N-1}$ energy and therefore can lead to a resonant process exchanging a f electron with a d electron.

In summary, $4f^2$ and $4f^3$ final state structures have been observed in the photoemission spectra of Pr ($4f^2$, initial state) and Nd ($4f^3$, initial state) metals. This is analogous to the $4f^1$ final state structure found in Ce systems. Since both Pr metal and Nd metal to the best of our knowledge are not Kondo systems, the interpretation of these data in terms of the Kondo model seems hardly possible. The more general view seems to be one where this $4f^N$ final state structure in photoemission from $4f^N$ initial state systems is interpreted in terms of hybridization between the (ds) conduction electrons and the $4f^N$ quasilocalized electrons. A special case in this picture is the Kondo model, which was used successfully to describe the spectral features of the Ce and Yb systems.

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