



Anomalous temperature behaviour of the mixed valence state of CePd 3 studied by XPS

G. Krill, L. Abadli, M.F. Ravet, J.P. Kappler, A. Meyer

► To cite this version:

G. Krill, L. Abadli, M.F. Ravet, J.P. Kappler, A. Meyer. Anomalous temperature behaviour of the mixed valence state of CePd 3 studied by XPS. Journal de Physique, 1980, 41 (10), pp.1121-1125. 10.1051/jphys:0198000410100112100 . jpa-00208937

HAL Id: jpa-00208937

<https://hal.science/jpa-00208937>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
79.60

Anomalous temperature behaviour of the mixed valence state of CePd₃ studied by XPS (*)

G. Krill, L. Abadli, M. F. Ravet, J. P. Kappler and A. Meyer

Laboratoire de Magnétisme et de Structure Electronique des Solides (**)
4, rue Blaise-Pascal, 67070 Strasbourg Cedex, France

(Reçu le 18 mars 1980, accepté le 30 mai 1980)

Résumé. — Nous avons étudié par spectroscopie de photoémission X (XPS) l'évolution en température des niveaux internes du cérium (Ce 3d et Ce 4d) dans le composé CePd₃. Alors que les expériences intéressant le volume (paramètre du réseau, absorption X, diffusion inélastique de neutrons...) indiquent une augmentation du nombre d'atomes de cérium en configuration Ce⁴⁺ (4f⁰ 5d²), les résultats de photoémission montrent une disparition totale de cette configuration Ce⁴⁺ lorsque la température décroît.

Abstract. — The evolution with temperature of the cerium 3d and 4d core levels in CePd₃ has been studied by X-rays Photoemission Spectroscopy (XPS). Whereas the bulk experiments (lattice parameter, X-rays absorption, inelastic neutron scattering...) indicate an increase in the cerium 4⁺ (4f⁰ 5d²) configuration as the temperature decreases, our XPS results show on the contrary a complete disappearance of this cerium 4⁺ configuration.

1. Introduction. — The intermetallic CePd₃ compound presents physical properties which are typical of the so-called intermediate valence state (I.V.) [1, 2, 3]. From the value of the lattice parameter at $T = 300$ K a mean value $\bar{V} \simeq 3.54$ can be deduced for the valence of cerium and the temperature behaviour of this lattice parameter agrees with the hypothesis that the number of Ce⁴⁺ (4f⁰ 5d²) configuration increases in the bulk when the temperature is lowered (at $T = 100$ K, $\bar{V} \sim 3.64$). Recently we studied the similar behaviour of CeBe₁₃ and we show in this case that a surface technique like XPS yields the same results as the bulk experiments [4]. In this paper we report the first XPS results on CePd₃ and we demonstrate that at the surface the mixing between Ce³⁺ and Ce⁴⁺ presents a temperature behaviour completely different as for the bulk. Indeed below $T = 200$ K, the contribution of the Ce⁴⁺ configuration to the XPS spectra vanishes and only the Ce³⁺ configuration is observed. At our knowledge this is the first time that such an effect is observed; we discuss briefly the possible existence of surface effects in order to explain this unusual behaviour of CePd₃.

2. Experimental. — The samples have been prepared by H.F. melting in a cold copper crucible under pure argon starting from 3N cerium and 5N palladium. All samples were found to be polycrystalline and single phased after melting and were studied in the as cast state. The XPS studies were performed on highly polished plane surface of bulk sample.

All the experimental details, both concerning the photo-emission and X-rays experiments, have been extensively discussed in our previous papers [4, 5].

Let us just remember (i) that XPS experiments are essentially devoted to the study of surfaces. This is due to the fact that the escape depth of a photoelectron in the energy range we used ($AlK\alpha \sim 1\,500$ eV) is less than 15 Å; (ii) that for the XPS experiment on rare earth compounds the main problem encountered is the oxygen affinity of the rare earth atoms which yields, even in ultra high vacuum ($< 10^{-10}$ torr), to a rapid contamination of the surface layer. In our previous papers [4, 5] we discussed how by argon ion bombardment (A.I.B.) such an effect can be considerably reduced.

3. Use of XPS in the intermediate valence rare earth compounds. — Recently Campagna *et al.* [6] have given a general review about the use of XPS in the area of rare earth compounds research. Considering

(*) Communication présentée lors des 3^e Journées R.C.P. 520, Grenoble 1980.

(**) LA 306.

the particular case of the I.V. compounds, the interesting point is that both $4f^n$ and $4f^{n\pm 1}$ configurations are simultaneously present and both valence electrons or core levels spectra will be affected by the presence of these two configurations. In the case of cerium, we restricted ourselves to the internal core

levels (3d and 4d) because it is difficult to observe the final states of $Ce^{4+}(4f^0 5d^2)$ in the valence band. Recently Herbst and Wilkins [7] have calculated the position in energy (Δ_-) as referred to the Fermi level of the 3d and 4d internal core levels of cerium in the Ce^{3+} and Ce^{4+} states :

$$\begin{aligned} Ce^{3+}(4f^1 5d^1) & \left\{ \begin{aligned} \Delta_-(4f^1 3d) &= E[3d^9 4f^1(5d 6s)^4] - E[3d^{10} 4f^1(5d 6s)^3] \simeq 892.5 \text{ eV} \\ \Delta_-(4f^1 4d) &= E[4d^9 4f^1(5d 6s)^4] - E[4d^{10} 4f^1(5d 6s)^3] \simeq 110.8 \text{ eV} \end{aligned} \right. \\ Ce^{4+}(4f^0 5d^2) & \left\{ \begin{aligned} \Delta_-(4f^0 3d) &= E[3d^9(5d 6s)^5] - E[3d^{10}(5d 6s)^4] \simeq 902.8 \text{ eV} \\ \Delta_-(4f^0 4d) &= E[4d^9(5d 6s)^5] - E[4d^{10}(5d 6s)^4] \simeq 118.6 \text{ eV} . \end{aligned} \right. \end{aligned}$$

For our study the main points can be summarized as follows :

(i) The Ce^{3+} and Ce^{4+} contributions are separated by an energy

$$\rho_{3d} = \Delta_-(4f^1 3d) - \Delta_-(4f^0 3d) \simeq 10 \text{ eV}$$

and

$$\rho_{4d} = \Delta_-(4f^1 4d) - \Delta_-(4f^0 4d) \simeq 8 \text{ eV} .$$

As mentioned by Herbst and Wilkins [7] the observation of these 3d and 4d replicate spectra is evidence that two different 4f configurations are present for times longer than that of the XPS measurements process ($\tau \sim 10^{-16}$ s).

(ii) The Δ_- values are an average between the $d_{5/2}$ and $d_{3/2}$ contributions which result from the spin orbit coupling acting on the d levels when one d electron has been ejected. In the case of the 3d levels of cerium this energy splitting $\delta_{3d} \simeq 19 \text{ eV}$.

(iii) Each cerium configuration (Ce^{3+} or Ce^{4+}) can be characterized by the final states arising from the photoemission process : for instance in the case of the cerium 4d level the final states associated with a $4d^9 4f^1$ configuration will be observed for Ce^{3+} whereas those associated with $4d^9$ (i.e. roughly the same as for lanthanum) will be observed for Ce^{4+} . As an illustration of this effect we report on figure 1 our results obtained for cerium metal (they are similar to those previously reported by Kowalczyk *et al.* [8]). We notice that the 4d level well agrees with the $4d^9 4f^1$ final states of cerium 3^+ as calculated by Signorelli and Hayes [9] except for the small component observed near 122 eV. This can be due either to the fact that this small component has not been taken into account in the calculations or to the presence of a slight proportion of Ce^{4+} . The 3d core level spectrum is less complicated and as shown on figure 1 it is essentially built by the $3d_{5/2}$ and $3d_{3/2}$ contributions. The position in energy of the various levels well agree with the hypothesis that only the trivalent configuration is present.

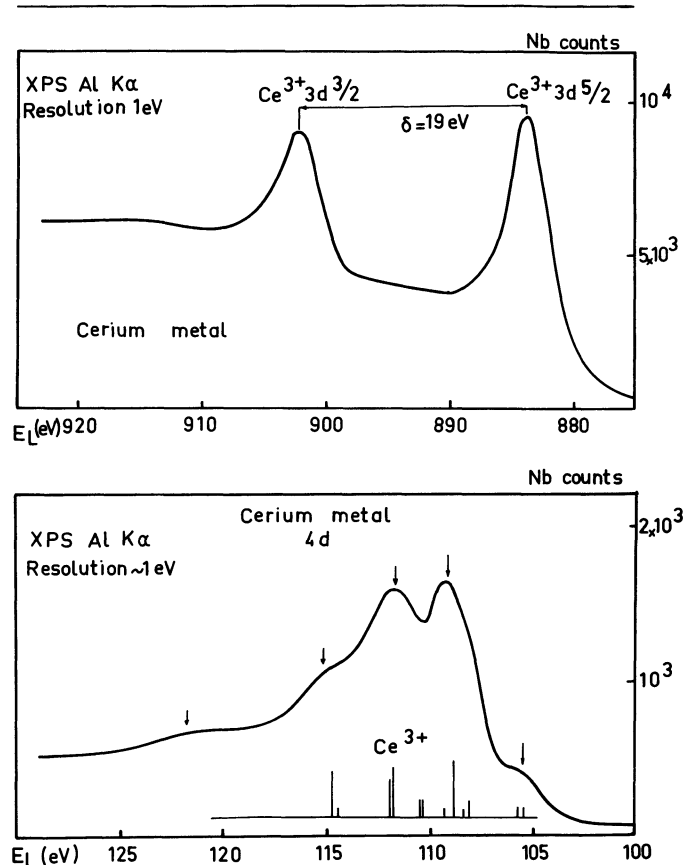


Fig. 1. — Cerium 3d and 4d XPS core level spectra of cerium metal.

4. Experimental results. — **4.1 INFLUENCE OF SURFACE CONTAMINATION.** — On figure 2 we report the 3d core level of cerium in a highly oxidized surface of $CePd_3$. We notice that the cerium atoms in chemical bonding with oxygen atoms contribute to the low energy side of the spectra and the observed shift in energy is $\Delta E \simeq -2.5 \text{ eV}$. This negative value for ΔE implies that the oxide layer which grows at the surface is not the tetravalent $Ce^{4+}O_2$ but rather the trivalent sesquioxide $Ce_2^{3+}O_3$. Similar conclusion can be drawn from our experiments on pure cerium metal and several compounds like $CeRu_4B_4$ (Krill *et al.*, to be published). A slight argon ion bombardment (5' for 2 kV and 50 μA) is sufficient to reduce consi-

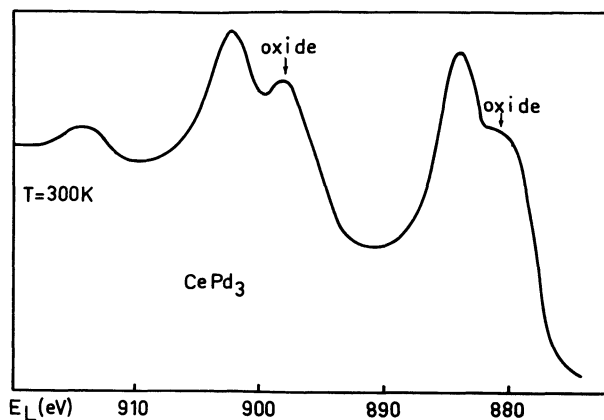


Fig. 2. — Cerium 3d core level spectrum for a highly oxidized CePd_3 compound.

derably the contribution of oxygen, however in the case of CePd_3 as the O_{1s} and $\text{Pd}_{3p_{3/2}}$ coincide the complete disappearance of O_{1s} cannot be directly observed. Therefore we follow the evolution of the XAES (X-ray Auger Electron Spectroscopy) signal of O_{1s} which takes place at $E_L \sim 950$ eV with the $\text{AlK}\alpha$ radiation. Under these conditions we conclude that immediately after the A.I.B. no oxygen can be detected at the surface of the sample and such conclusion is supported by the fact that the intensity ratio between the cerium and palladium core levels, taking into account the photoemission cross section of each individual level, is in good agreement with the expected nominal concentration : $\text{Ce/Pd} \sim 1/3$.

4.2 VALENCE ELECTRONS SPECTRA. — On figure 3 the photoemission spectra of valence electrons in CePd_3 at $T = 300$ K is reported. Near the Fermi level the shoulder observed on the electrons density curves can be associated to the 4f electrons of cerium and except this small contribution the valence band is very similar to that of pure palladium [10]. Let us notice that no modification of this spectra has been observed when temperature was lowered down to 100 K.

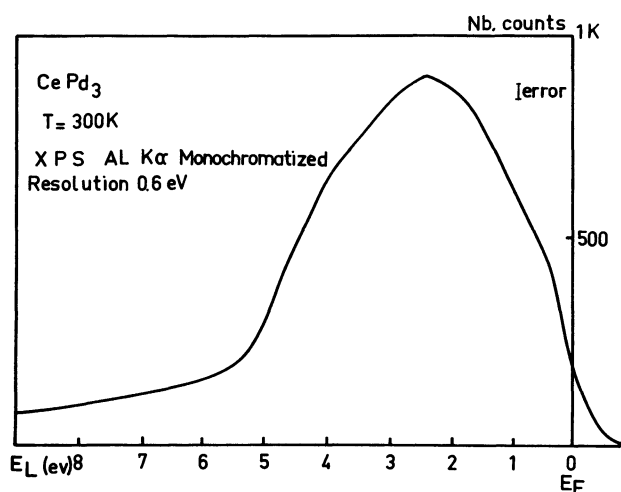


Fig. 3. — XPS valence band spectrum of CePd_3 .

4.3 3d AND 4d CORE LEVELS SPECTRA. — The cerium 3d and cerium 4d core levels spectra in CePd_3 taken between $T = 500$ K and $T = 100$ K are reported respectively on figures 4 and 5. Let us firstly consider the 3d spectra at high temperatures $T > 300$ K. The main point is that there exist undoubtedly two additional peaks shifted to higher binding energy by

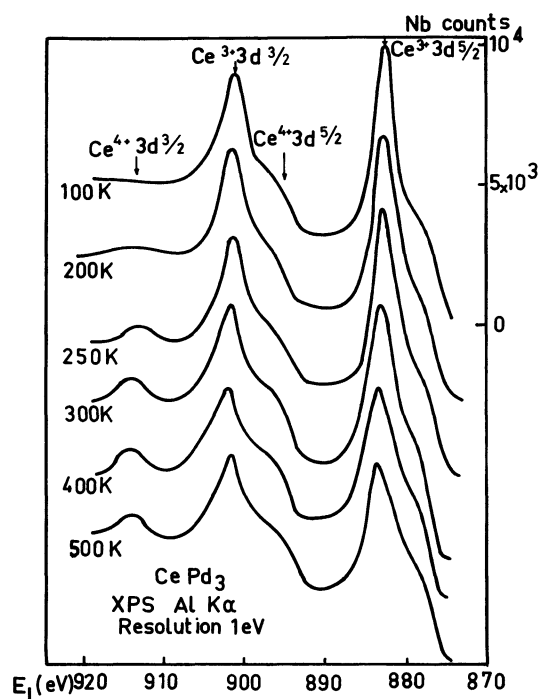


Fig. 4. — Temperature behaviour of the Ce 3d core level spectra in CePd_3 .

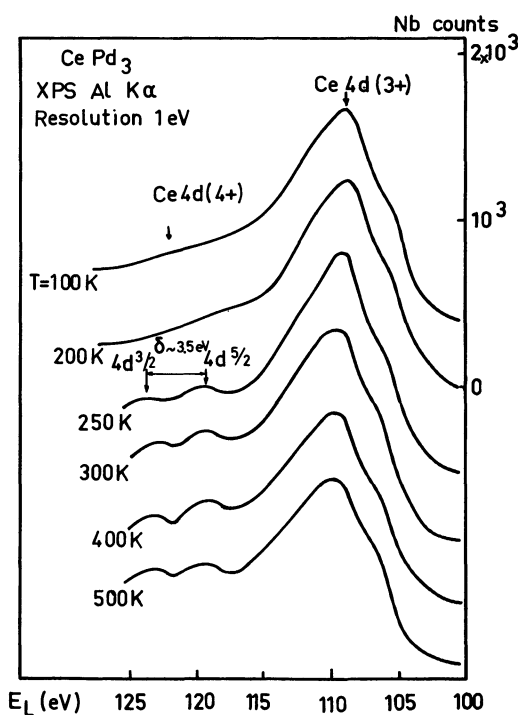


Fig. 5. — Temperature behaviour of the Ce 4d core level spectra in CePd_3 .

about 10 eV as we observe previously on CeBe_{13} [4]. As discussed in section 3, this replicate is representative of the tetravalent cerium atom. It is clearly shown when the temperature is lowered down to 100 K the peak at about 914 eV is completely disappeared, i.e. the contribution associated to the cerium $4+$ is disappeared. A still more convincing demonstration for the existence of this phenomenon is shown on figure 5 if we consider the Ce 4d spectra : for $E_L \sim 120$ eV we observe the very simple spectra given by the $4d^9 4f^0(\text{Ce}^{4+})$ final state (the $4d_{5/2}$ and $4d_{3/2}$ lines splitted by a ~ 3.5 eV spin orbit coupling) and when the temperature is lowered down to 100 K this contribution is disappeared. This transition is completely reversible and therefore cannot be due to spurious effects related to surface contamination.

As compared to cerium metal it still exists a non negligible contribution on the low energy side of the 3d lines at low temperatures, too (see Fig. 4); this can be due either to a small amount of oxide at the surface or to a final state containing one 4f electron (as previously observed on CeN by Baer *et al.* [11]). Concerning the 4d lines of cerium in CePd_3 , we can notice that the Ce^{3+} spectra ($E_L \sim 110$ eV, Fig. 5) is not well resolved as compared to the case of cerium metal (see Fig. 1). A similar lack of resolution has been previously observed on the mixed valence CeN compound by Baer *et al.* [11] and in our opinion this effect may be correlated with the existence of an intermediate valence state.

5. Discussion. — From XPS experiments it appears that below $T \sim 200$ K the cerium atoms at the surface of CePd_3 are essentially in the trivalent state. This is a puzzling result because if we consider our lattice parameter measurements with temperature (which agree with those previously reported by Harris *et al.* [1]), it appears that in the bulk the valency of cerium atoms goes towards $4+$ when the temperature decreases (see Fig. 6); similar conclusions can be deduced from our preliminar X-rays absorption measurements which show also the increase of Ce^{4+} configuration when T is lowered down to 100 K. Therefore we can conclude that at the surface the mixed valence state of CePd_3 does not present the same behaviour with temperature as in the bulk. Wertheim *et al.* [12] have demonstrated that at the surface of samarium metal the valence state was not the same as in the bulk (Sm^{2+} at the surface and Sm^{3+} in the bulk) and recently similar effects have been found on amorphous $(\text{La}_{1-x}\text{Sm}_x)_{80}\text{Au}_{20}$ compounds [13]. Because of the absence of several nearest neighbours, it seems possible that the rare earth atoms

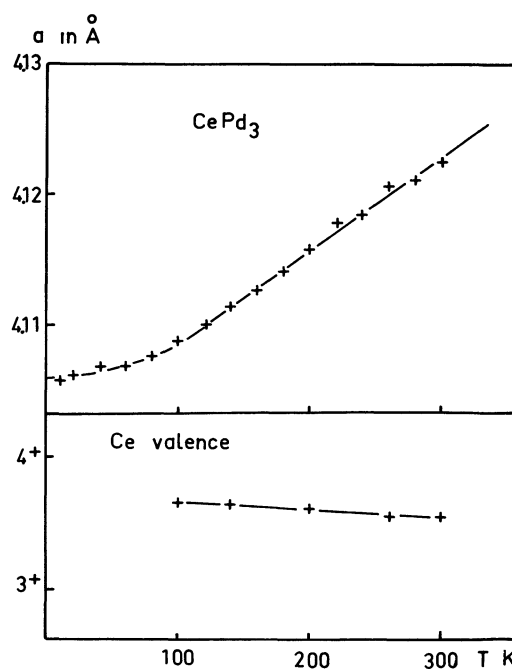


Fig. 6. — Behaviour of the lattice parameter of CePd_3 with temperature and variation of the valence of cerium deduced from these experiments.

at the surface stay in the valency corresponding to the highest 4f occupancy [12, 14] and this could explain for instance why the valence deduced from the XPS spectra is quite different from the valence deduced from the lattice parameter measurements (for CePd_3 at $T=300$ K, $\bar{V}=3.3 \pm 0.1$ (XPS) and $\bar{V} \simeq 3.55 \pm 0.05$ (X-rays)). Nevertheless if such surface effects can well explain an absolute difference between surface and bulk valences, it seems to us more difficult to understand in this way the results we obtained on CePd_3 . It will be perhaps very useful to discuss how the physical mechanisms which are supposed to be at the origin of the intermediate valence state (fast charge fluctuations, concentrated Kondo lattice, spin fluctuations...) behave as we approach the surface; however, at this time we think that such a discussion is still not possible. Further experimental details on these intermetallic cerium compounds are needed in order to show if the anomalous behaviour of CePd_3 is only an exception or if other I.V. compounds could present similar properties.

Acknowledgments. — The authors are grateful to Professor F. Gautier for his constant support and encouragement.

References

- [1] HARRIS, I. R. and RAYNOR, G. V., *J. Less Common Metals* **9** (1965) 263.
- [2] GARDNER, W. E., PENFOLD, J., SMITH, T. F. and HARRIS, I. R., *J. Phys. F* **2** (1969) 133.
- [3] HOLLAND-MORITZ, F., *Spez. Ber. Kernforschungsanlage Jülich*, n° 14, June 1978.
- [4] KRILL, G., KAPPLER, J. P., RAVET, M. F., AMAMOU, A. and MEYER, A., accepted for publication in *J. Phys. F*, 1980.
- [5] KRILL, G., SENATEUR, J. P. and AMAMOU, A., accepted for publication in *J. Phys. F*, 1980.
- [6] CAMPAGNA, M., WERTHEIM, G. K. and BAER, Y., *Photoemission in Solids* (Springer Verlag, Berlin) Vol. 2, p. 217-260.
- [7] HERBST, J. F. and WILKINS, J. W., *Phys. Rev. Lett.* **43** (1979) 1760.
- [8] KOWALCZYK, S. P., EDELSTEIN, N., MC FEELY, F. R., LEY, L. and SHIRLEY, D. A., *Chem. Phys. Lett.* **29** (1974) 491.
- [9] SIGNORELLI, A. J. and HAYES, R. G., *Phys. Rev. B* **8** (1973) 81.
- [10] HOLL, Y., KRILL, G., AMAMOU, A., LEGARE, P., HILAIRE, L. and MAIRE, G., *Solid State Commun.* **32** (1979) 1189.
- [11] BAER, Y., HAUGER, R., ZÜRCHER, Ch., CAMPAGNA, M. and WERTHEIM, G. K., *Phys. Rev. B* **18** (1978) 4433.
- [12] WERTHEIM, G. K. and CRECELIUS, G., *Phys. Rev. Lett.* **40** (1978) 813.
- [13] KRILL, G., BERRADA, A., RAVET, M. F. and DURAND, J., to be published.
- [14] BROUERS, F., DE MENEZES, O. L. T. and BENNEMANN, K. H., to be published.