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On the edge of tetravalent Ce in CePd₇

J G Sereni†, O Trovarelli†, A Herr†, J Ph Schillé†, E Beaurepaire‡ and J P Kappler†§

† Centro Atómico Bariloche and Consejo Nacional de Investigaciones Científicas y Técnicas, 8400 S C de Bariloche, Argentina

‡ IPCMS, GEMME, 4 rue Blaise Pascal, 67070 Strasbourg, France

§ Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bâtiment 209D, Université de Paris-Sud, 91405 Orsay, France

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Abstract. Data on the magnetic susceptibility, low-temperature specific heat and x-ray absorption spectroscopy (Ce L_{III} and M_{IV,V} edges) for CePd₇ and its reference compound YPd₇ are presented. The respective Pauli susceptibilities χ_0 of 0.11×10^{-3} emu mol⁻¹ and 0.50×10^{-3} emu mol⁻¹ and the respective Sommerfeld coefficients γ of 9.8 mJ K⁻² mol⁻¹ and 35.8 mJ K⁻² mol⁻¹ are much smaller (per atom) than those of the corresponding components (Ce, Y and Pd). The valence extracted from the Ce L_{III} edge is 3.5. The χ_0/γ -ratios are found to be 0.012 emu K² J⁻¹ and 0.014 emu K² J⁻¹ for CePd₇ and YPd₇, respectively. Such a value for CePd₇ corresponds to that of a free-electron system instead of an intermediate-valence system (0.035 emu K² J⁻¹).

1. Introduction

The main characteristics of Ce in its intermediate-valence (IV) state can be assumed to be as follows:

- (i) an enhanced Pauli-like susceptibility χ_0 in the range $0.5\text{--}1 \times 10^{-3}$ emu/Ce atom [1, 2];
- (ii) a linear specific-heat coefficient γ in the range 60–12 mJ K⁻²/Ce atom [1, 3];
- (iii) a χ_0/γ -ratio of 0.035 emu K² J⁻¹ [4];
- (iv) a significant volume contraction with respect to the trivalent isotopic compounds [5];
- (v) a spectroscopic L_{III} valence which does not exceed 3.3 [6].

These features are associated with partial delocalization of the 4f electron of Ce due to strong hybridization of that orbital with the conduction band and, in the limit, to partial charge transfer to the partner element. Although the large energy required for the $(6s5d)^3 4f^1 \rightarrow (6s5d)^4$ excitation (49 Kcal mol⁻¹ \simeq 2 eV [7]) can only be provided by a chemical reaction (as in CeF₄, Ce(SO₄)₂ or CeO₂), in intermetallic compounds the large electronegativity difference combined with structural symmetries of high coordination is able to induce significant 4f delocalization [8, 9].

The best example for pure 4f-band hybridization is given by the α -Ce phase, for which no charge transfer is expected [10]. Nevertheless, this is not the case when the Ce atom has its minimum size and, consequently, its maximum valence within the intermetallic systems.

The extreme IV examples are given by the cubic Laves phases AB_2 with a large coordination number and a 'hole-like' partner element. Owing to the small Ce–Ce spacing [11], direct f–f hybridization could be expected in these compounds; however, it was observed that in the Ce Laves phases the onset of IV behaviour coincides with the onset of the overlap between A and B atoms (taken as atomic spheres) [12]. Band calculations have confirmed the basic role of the f–ligand hybridization, which overshadows the direct f–f hybridization [13].

In the region of heavy-fermion behaviour where the Ce–Ce spacing is usually large, the f-band hybridization controls the formation of a 'narrow band' with a strong f character. This and the above-mentioned IV characteristics indicate that at any strength of the f-band hybridization the common feature of the Ce compounds is the f character of the band. This may be the reason for the empirical limit of the lower values of χ_0 and γ , and for the predicted χ_0/γ -ratio. Nevertheless, the extremely low values of χ_0 , γ and the χ_0/γ -ratio recently reported for CePd₇ [14] renews the question about the dominant f character of the band and the role of charge transfer in the marked change in Ce valence above the α -Ce limit. In order to elucidate the band character in CePd₇, we have performed further magnetic, thermal, transport and x-ray spectroscopy measurements on that compound and on its isotopic reference YPd₇.

2. Experimental details

The samples were prepared by arc melting the appropriate amounts of components in a Zr-gettered argon atmosphere, with negligible weight loss. The starting elements were 99.9% pure Ce and Y, and 99.99% pure Pd. The samples were annealed for 96 h at 1000 °C and then quenched to 20 °C. The structural studies on both compounds indicate that they form in the CuPd₇-type structure, with respective lattice parameters a of 8.096 Å and 7.940 Å for CePd₇ and YPd₇, in good agreement with the values in the literature [15, 16]. The magnetic measurements were carried out over the temperature range 4.2–300 K, in fields of up to 8 T, by means of a SQUID magnetometer and a Faraday magnetometer in an applied field of 0.5 T. The specific-heat measurements were performed in a semi-adiabatic ³He calorimeter, using the heat pulse technique. The Ce L_{III} and M_{IV,V} absorption edge measurements were performed at the French synchrotron radiation facility at the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique.

3. Experimental results

The temperature dependences of the magnetic susceptibility $\chi(T)$ of CePd₇ and its reference YPd₇, measured in a magnetic field of 1 T, are shown in figure 1. The $\chi = f(T)$ dependence can be described by a $\chi(T) = \chi_0 + C_1/T$ function or, as shown in the inset, by a $\chi T = \chi_0 T + C_1$ one. From these plots we obtain the following values: $\chi_0 = 0.116 \times 10^{-3}$ emu mol⁻¹ for CePd₇ and $\chi_0 = 0.506 \times 10^{-3}$ emu mol⁻¹ for YPd₇. The coefficient C_1 accounts for the paramagnetic impurities, which can be compared with the effect of 100 ppm Fe in Pd [17] or a few per cent of Ce oxide in CePd₇. The downturn in $\chi T = f(T)$ for $T < 10$ K (see inset of figure 1) is expected from the effect of the non-zero value of the paramagnetic temperature of the impurities. In the case of YPd₇ the C_1 -term is negligible. The χ_0 -values are in agreement with those reported in the literature [14, 18]. The χ_0 -values were checked at room temperature, where the magnetic impurities

give a lower contribution, by measuring the magnetization dependence in a magnetic field. As shown in figure 2, a linear M versus H dependence is observed up to 8 T at 300 K for CePd₇, whereas the magnetic field dependence at 2 K illustrates the paramagnetic character of the isolated impurities. The value of χ_0 extracted from the M versus H slope at 300 K (0.12×10^{-3} emu mol⁻¹) is in very good agreement with the susceptibility measurement.

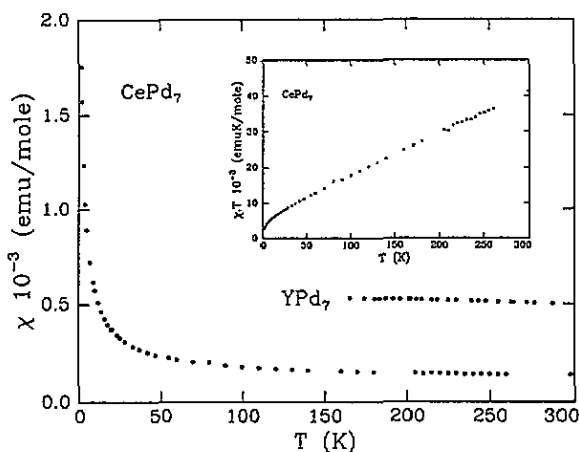


Figure 1. Temperature dependences of the magnetic susceptibilities of CePd₇ and YPd₇. The inset shows a χT versus T plot for the CePd₇ data.

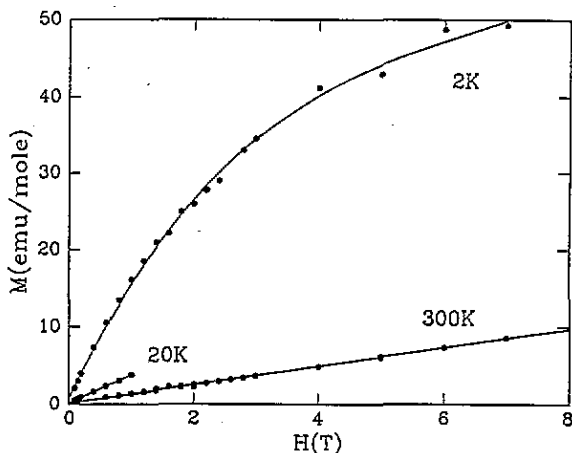


Figure 2. Magnetization versus magnetic field of CePd₇ at various temperatures. The lines are a guide for the eye.

The low-temperature specific heat ($1.5 \text{ K} < T < 10 \text{ K}$) is shown in figure 3 in a $C_p/T = f(T^2)$ plot for the compounds studied. Here, the experimental data can be fitted by a $C_p/T = \gamma + \beta T^2$ function, where the electronic contributions are found to be $\gamma = 9.8 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $35 \text{ mJ mol}^{-1} \text{ K}^{-2}$ for CePd₇ and YPd₇, respectively. The

phonon contributions are similar in both cases, $\beta = 0.53 \text{ mJ mol}^{-1} \text{ K}^{-4}$ and $0.60 \text{ mJ mol}^{-1} \text{ K}^{-4}$, which correspond to a Debye temperature Θ_D of $300 \pm 6 \text{ K}$. Such a temperature can be compared with that of pure Pd ($\Theta_D = 283 \text{ K}$ [19]) and CePd₃ ($\Theta_D = 306 \text{ K}$ [20]). For $T < 3 \text{ K}$, CePd₇ shows an increase in C_p , which has to be attributed to the paramagnetic impurities, in agreement with the magnetic measurements at that temperature. This increase in C_p , together with the lack of any anomaly around 6 K, suggests that the impurities in CePd₇ are paramagnetic (e.g. Fe) instead of Ce oxide.

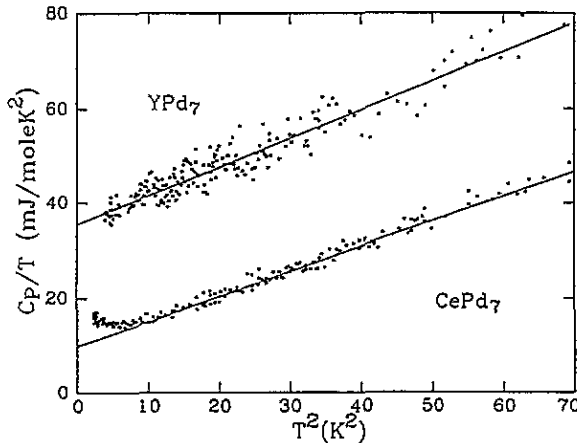


Figure 3. Low-temperature specific heats of CePd₇ and YPd₇ in C_p/T versus T^2 plots.

The measured L_{III} x-ray absorption edge of Ce in CePd₇ is presented in figure 4. The spectrum, characteristic of the IV Ce systems, exhibits a double-peaked structure (with a difference in energy of 9 eV) corresponding to two possible screening mechanisms of the 2p core hole and the intensity ratio of these structures, leading to the valence. The standard least-squares fit [6] gives a valence of 3.5. Note that the L_{III} spectrum of CePd₇ is very similar to that reported for the diluted alloy Pd-2% Ce [21] characterized by the largest chemical pressure and consequently by the highest L_{III} valence measured in intermetallic systems.

Figure 5 shows the Ce $M_{IV,V}$ spectra representative of the well separated intense resonances $3d_{5/2}$ (M_V) and $3d_{3/2}$ (M_{IV}). In addition to the main resonances assigned to the $3d^{10}4f^1 \rightarrow 3d^9 4f^2$ transition, satellite lines are observed at energies about 5 eV higher. These structures, which are due to the $3d^9 4f^1$ final states, are related to the IV character of Ce [22]. For comparison, figure 5 illustrates also the Ce $M_{IV,V}$ of Ce₃Al₁₁, the archetype of a γ -like Ce compound. Note that the multiplet structures in CePd₇ are far less resolved than in Ce₃Al₁₁. All these features bear witness to the strong 4f-conduction band hybridization in CePd₇.

A further experimental characteristic of CePd₇ is the positive slope of the temperature dependence of the electrical resistivity $\rho(T)$ which is typical of a metallic system and avoids the possibility of gap formation in the conduction band. However, its large residual resistivity $\rho(4 \text{ K}) = 20 \mu\Omega \text{ cm}$ and the $\rho(300 \text{ K})/\rho(4 \text{ K}) = 2$ ratio indicate significant disorder in the atomic positions in the lattice. Such disorder has already been reported in high-temperature [23] and low-temperature [24] studies.

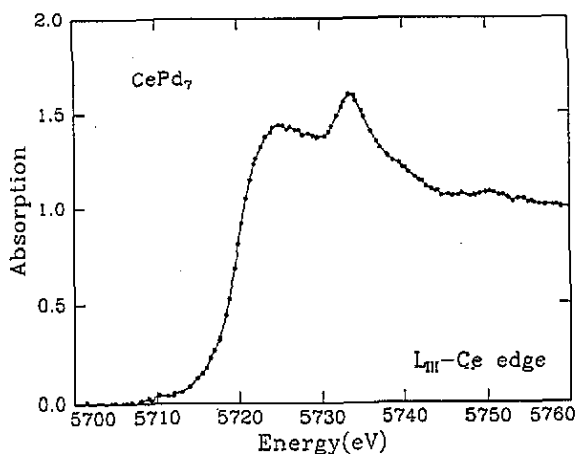


Figure 4. Ce L_{III} edge in CePd₇ at $T = 300$ K.

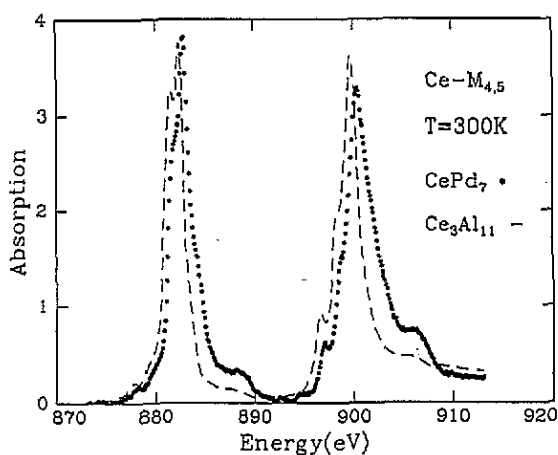


Figure 5. Ce M_{IV,V} edges for CePd₇ and Ce₃Al₁₁ at $T = 300$ K. The energy scale for Ce₃Al₁₁ is shifted 2 eV for clarity.

Some experimental results are summarized in table 1. In order to compare them with the results for pure Pd and α -Ce they are given in gram-atom units (remember that in the CePd₇ formula unit there are eight atoms per mole). Also for comparison, the lattice parameters of the CePd₇ compounds are divided by two.

4. Discussion

From the analysis in table 1, it becomes evident that in both CePd₇ and YPd₇ the densities of states in their conduction bands are much lower than those of their respective components. Although the enhancement factors $\lambda = \lambda_{e\text{-ph}} + \lambda_{\text{sw}}$ (due to the electron-phonon and spin-wave interactions) are quite large (for Pd, $\lambda = 0.76$ [25,27] and, for Y, $\lambda = 0.8$ [26]),

Table 1. Pauli susceptibilities, Sommerfeld coefficients, their respective ratios and the lattice parameters of CePd₇, YPd₇ and their respective components.

	χ_0 (10^{-3} emu (g-atom) ⁻¹)	γ (mJ K ⁻² (g-atom) ⁻¹)	χ_0/γ (emu K ² J ⁻¹)	a (Å)
CePd ₇	0.0145	1.22	0.012	4.048
YPd ₇	0.063	4.42	0.014	3.970
α -Ce	0.51 [1]	12.8 [1]	0.039	4.824 [1]
Pd	0.58 ^a	9.4 [25]	—	3.883 [15]
Y	0.19 ^a	7.9 [26]	—	Hexagonal

^a At room temperature.

their respective bare densities of states exceed the experimental γ -values observed for these compounds.

The drastic reduction in χ_0 for the systems under study with respect to that of their components was interpreted by Harris and Norman [18] in terms of a simple rigid-band model 'as the conduction electrons of Ce and Y being donated to the holes in the 4d band of Pd'. The same picture was applied to the Pd-Ag alloys to explain a similar reduction in γ and χ_0 [18]. The Ce valence extracted from such an electron-hole compensation mechanism was found to range between 3.7 and 4.0. Such a valence depends, however, on exact knowledge of the number of holes in Pd (between 0.6 [18] and 0.36 [27]) and on the number of remanent electrons in the conduction band of the 'metallic' CePd₇ and YPd₇ compounds. For comparison, one can say that the χ_0 -value observed in CePd₇ equals that of monovalent alkaline metals, such as Li, Na, K and Rb [28].

Concerning the eventual f character of the band, as evidence that the f-band hybridization mechanism controls the IV formation, we can compare the χ_0/γ -ratio of CePd₇ with that of other Ce IV compounds. As mentioned in the introduction, the experimental χ_0/γ -ratio is found to be 0.035 emu K² J⁻¹ [4], in agreement with the Wilson ratio R of 1.2, predicted in the Fermi liquid picture [29] for Ce IV compounds with a sixfold ground-state degeneracy. The observed χ_0/γ -ratio of 0.012 emu K² J⁻¹ for CePd clearly differs from that of the Ce IV compounds but resembles that of free electrons: $3(\mu_B/\pi k_B)^2 = 0.0137$ emu K² J⁻¹. Such a ratio is obviously observed in light alkaline metals [28, 30]. Further evidence of the non-f character of the conduction band can be obtained by comparing the χ_0/γ -ratio of CePd₇ with that of its isotopic compound YPd₇ (0.014 emu K² J⁻¹) (see table 1), where there are no chances for any f character.

This conclusion apparently conflicts with the spectroscopic result. In fact, if final-state effects are taken into account, a large 4f-conduction band hybridization (involving an appreciable number of 4f electrons) is necessary to produce the 4f⁰ contribution in the L_{III} edge [31]. In terms of a characteristic energy scale of the system, the 4f contribution to the magnetic susceptibility is related to the characteristic temperature T_K , which depends on the hybridization strength and the energy of the 4f level. This temperature was found to be about 100 K for Ce compounds showing spin fluctuation effects and up to a few thousand kelvins for compounds showing spin and charge fluctuations. Using reasonable parameters, a χ_{4f} -value of the order of 10⁻⁴ emu/Ce mol can be achieved using the theory with a Ce valence of 3.5 [32]. Since that value could be of the same order of magnitude for conduction electron paramagnetism and core electron diamagnetism, distinguishing between those contributions is difficult. A similar conflicting situation was observed for CeN [33] and for other Ce compounds formed with a 'p' element, such as CeSn₃ and CeBe₁₃ (see, e.g., [3, 6]).

To conclude, we note that CePd₇ is certainly exceptional in the sense that, in this compound, χ_0 and γ are particularly low when compared with other Ce intermetallics [3]. Therefore, the existence of localized 4f states can be reasonably rejected, although some 4f character in the band cannot be excluded from the x-ray absorption measurements.

A systematic study of the spectroscopic properties of CePd₇ is now in progress in order to achieve better understanding of the Ce electronic structure in this new state. Certainly band-structure calculations are highly desirable for this cubic compound, which resembles the well known CePd₃.

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