MAGNETIC TO NON-MAGNETIC TRANSITION OF Ce INDUCED BY VOLUME IN Ce(Pd, Ni) AND ELECTRON CONCENTRATION IN Ce(Pd, Rh)

J. Kappler, E. Beaurepaire, G. Krill, C. Godart, G. Nieva, J. Sereni

JOURNAL DE PHYSIQUE
Colloque C8, Supplément au n° 12, Tome 49, décembre 1988

MAGNETIC TO NON-MAGNETIC TRANSITION OF Ce INDUCED BY VOLUME IN Ce(Pd, Ni) AND ELECTRON CONCENTRATION IN Ce(Pd, Rh)

J. P. Kappler ([1]), E. Beaurepaire ([1]), G. Krill ([2]), C. Godart ([3]), G. Nieva ([4]) and J. G. Sereni ([4])

([1]) *I.P.C.M.S., Groupe d'Etude des Matériaux Métalliques, 3 rue de l'Université, 67084 Strasbourg, France*
([2]) *U.A. 155, Université de Nancy I, 54056 Vandœuvre les Nancy, France*
([3]) *C.N.R.S., E.R., 209 Place A. Briand, 92190 Meudon, France*
([4]) *Centro Atomico Bariloche, 8400 Bariloche, Argentina*

Abstract. – Unit cell volume, magnetic properties and L_{III} X-ray absorption edge studies in Ce(Pd, M) with M = Ni or Rh show that the Ce demagnetization is mainly driven by volume reduction in Ce(Pd, Ni) and essentially due to the reduction of the d electron number in Ce(Pd, Rh).

The possibility for inducing a continuous change from a magnetic to a non-magnetic ground state of Ce by alloying was the subject of many recent investigations [1]. It is well known that the effect of external pressure on Ce valence can be also produced by substitution of Ce by iso-electronic and smaller atoms, as for example in (Ce, Y)Pd_3 [2]. But the driving force for reaching the thermodynamical equilibrium of the system is the chemical potential, which depends not only on the volume but also on the occupation number of the open shell. The (Th, Y)Ce alloys [3] provide an example where there is no volume effect (Th and Y have the same atomic volume), but a difference in the number of electrons (Z) between the tetravalent Th and trivalent Y.

In the aim to provide an example where volume and Z are, independently, mainly responsible for the Ce change of valence, we have studied the $Ce(Pd_{1-x}M_x)$ systems, where M = Ni or Rh. Within these systems, the orthorhombic CrB structure and the Ce local symmetry is kept in the whole range of concentration. As pure metals, Pd and Ni have a similar electronic structure in their open shell, while their atomic volume is 35 % different. In the case of Pd and Rh, with one electron difference in their external shell, the atomic volume is practically the same. The CePd compound orders ferromagnetically at T_c = 6.6 K and does not show any volume anomaly with respect to the RE-Pd series [4]. From their reduced volume and nearly temperature independent susceptibility, both CeNi [5, 6] and CeRh [5, 7, 8] are good examples of Intermediate Valence systems.

The volume of the unit cell V_c is reduced as Pd is substitued by Rh or Ni (Fig. 1). For comparison, the Ce(Pt, Ni) system [9] is also included in this figure. In these systems there are two regions in the $V_c(x)$ concentration dependence. Within the experimental dispersion, the volume of the $Ce(A_{1-x}Ni_x)$ compounds (A = Pd or Pt) follows a linear dependence on x up to $x \simeq 0.7$, then it drops down just where there is a strong change in the magnetic character of

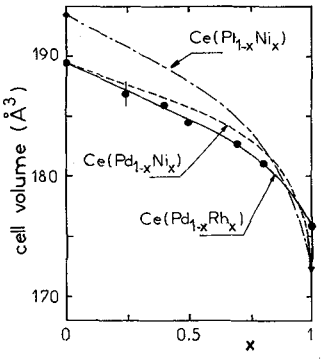

Fig. 1. – Concentration dependence of the unit cell (V_c) of the $Ce(A_{1-x}M_x)$ system, with A = Pd or Pt and M = Ni (taken from Refs. [1, 9]) or Rh.

Ce (see Refs. [1, 9]). Similar behaviour is shown in the Ce(Pd, Rh) system, but with a softer curvature.

In the $Ce(Pd_{1-x}Rh_x)$ system, the substitution of Pd by Rh, up to $x = 0.3$, leads to a smooth decrease of the Curie temperature (T_c), which drops down for $x > 0.3$ reaching an extrapolated $T_c = 0$ value at $x \simeq 0.7$. On the contrary the substitution of Pd by Ni increases T_c up to 10.6 K at $x = 0.6$ [1].

The saturation magnetisation (M_s) is nearly constant ($M_s \simeq 0.8\ \mu_s$) up to x = 0.4 of Rh, for larger concentration it decreases as T_c does. In Ce(Pd, Ni) the $M_s(x)$ variation follows a similar behaviour.

The Ce valence, extracted from the L_{III} X-ray absorption spectra, as a function of Rh and Ni concentration, is presented in figure 2. The valence is evaluated from the relative intensity of the $4f^1$ and $4f^0$ configuration resonances. The reference for the resonant line shape is taken from the L_{III} edge of LaNi, LaPd and LaRh compounds.

In order to compare the magnetic behaviour of both systems we have looked for a parameter able to relate the effect of volume (V_{at}) and the number of electrons of the Ce partners. One of the simplest approaches is

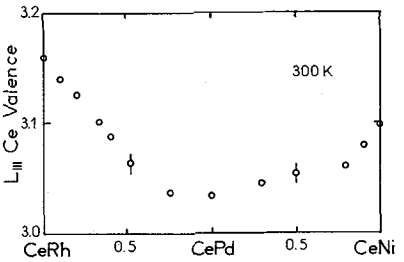

Fig. 2. – Concentration dependence of L_{III} Ce valence of the $Ce(Pd_{1-x}M_x)$ system, with M = Ni or Rh.

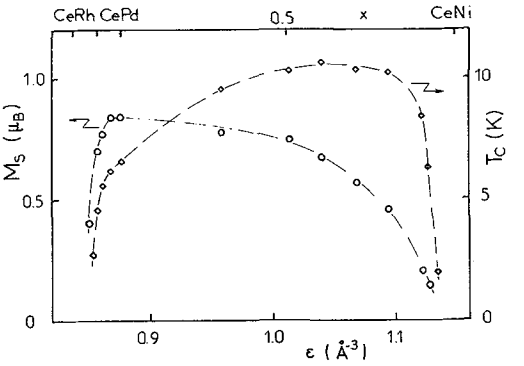

Fig. 3. – Curie temperature (T_c, (◇)) and saturation magnetization (M_s, (○)) as a function of the parameter ε for the Ce(Pd, M) system, with M = Ni or Rh.

to use the ratio between these two parameters: $\varepsilon = Z/V_{at}$, where $Z = 10 - h$ (h is the number of holes in the d shell). From Mott and Jones [10] we obtain Z (Ni = 9.4,) Z (Pd) = 9.45 and Z (Rh) = Z (Pd) −1 = 8.45. With this definition of the ε parameter, T_c and M_s show a continuous concentration dependence from Rh to Ni through Pd, as shown in figure 3.

In a more careful analysis of the figure 1, in the $x \leq 0.6$ region, one can observe that, although the atomic volume of Rh is larger than that of Ni, the measured V_c of Ce(Pd, Rh) decreases faster than that of Ce(Pd, Ni). This feature suggests that, in this concentration range, the electronic effect of Rh is stronger than the volume effect produced by Ni. The fact that the Ni substitution in the Ce(Pd, Ni) and in Ce(Pt, Ni) systems produces a weak effect on the Ce valence is confirmed by the linear variation of $V_c(x)$ for $0 \leq x \leq 0.5$. The extrapolated value at $x = 1$ ($\simeq$ 183 Å^3) is that of an hypothetical γ-CeNi. For $x \geq 0.6$ the relative strength of both effects is reversed, as indicated by the volume and the magnetic properties. In this concentration region the change in the Ce ground state is drastically reflected in all the measured parameters, i.e. V_c, T_c, M_s and L_{III} Ce valence.

Finally, we can remark that regardless the difference in concentration of Rh and Ni where T_c and M_s drop down, this effect occurs at similar volume V_c ($\simeq$ 182 Å^3) and Ce valence ($\simeq$ 3.08). For this value of V_c the Ce-Ce distances are close to 3.7 Å, which is twice the trivalent Ce atomic radius. In a rigid-sphere schema, such "critical" concentration is reached when the Ce atoms have a direct contact with each other.

[1] Nieva, G., Sereni, J. G., Afyouni, M., Schmerber, G. and Kappler, J. P., *Z. Phys. B* **70** (1988) 181 and references therein.

[2] Beaurepaire, E., Krill, G., Kappler, J. P. and Röhler, J., *Solid State Commun.* **49** (1984) 64.

[3] Sereni, J., Huber, J. G., Luengo, C. A. and Maple, M. B., *J. Low Temp. Phys.* **30** (1978) 729.

[4] Kappler, J. P., Besnus, M. J., Lehmann, P., Meyer, A. and Sereni, J. G., *J. Less-Common Met.* **111** (1985) 261.

[5] Dwinght, A. E., Conner, R. A. and Doroner, J. W., *Acta Crystallogr.* **18** (1965) 837.

[6] Walline, R. E. and Wallace, W. E., *J. Chem. Phys.* **41** (1964) 1587.

[7] Capena, F., Minguzzi, M. and Olcese, G. L., *J. Magn. Magn. Mater.* **63-64** (1987) 591.

[8] Kappler, J. P., Lehmann, P., Schmerber, G., Nieva, G. and Sereni, J. G., this conference.

[9] Gignoux, D. and Gomez-Sal, J. C., *Phys. Rev. B* **30** (1984) 3967.

[10] Mott and Jones, The theory of the properties of Metals and Alloys, chapter VI (Dover Publ.) 1958.