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# Magnetic behaviour of $Ce(Pd_{1-x}M_x)$ compounds (M = Rh, Ni and Ag) within the LDA approximation ☆

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**Abstract**

Ce intermetallic compounds have been intensively studied in the last few decades due to the large variety of behaviours they exhibit. In particular, two ways of demagnetizing Ce have been experimentally tried within the ferromagnetic systems $Ce(Pd_{1-x}M_x)$, namely through electronic concentration variations (M = Rh) and volume reductions (M = Ni). On the other hand, when Pd is substituted by Ag, a transformation from a ferromagnetic to an antiferromagnetic ground state has been observed. In this work, we analyse the evolution of the magnetism of Ce in the above-mentioned family of compounds by calculating the spin contribution to magnetism that results from spin polarised LDA calculations. 

*Keywords:* Rare earth-transition metal compounds; Intermediate valence; Band calculation

The study of the magnetic properties of Ce compounds in terms of the competition between the quenching of the local magnetic moment (Kondo effect) and the intersite magnetic interactions (RKKY interaction) has received great attention both in theory and experiment [1,2]. Another approach to understand the magnetic properties of these systems is based on an itinerant picture which can describe, in a qualitative way, the different magnetic ground states taking into account the strength of hybridisation and the chemical environment [3].

Of particular interest is to compare the effects of volume and electronic concentration on $Ce(Pd_{1-x}M_x)$ compounds (M = Rh, Ni and Ag) within the same structural symmetry. The available experimental information [4] shows that (i) Pd substitution by a hole-like metal (Ni or Rh) induces Ce demagnetization mainly by two different mechanisms, electronic concentration variations ($\Delta Z$, for M = Rh) and volume reduction ($\Delta V$, for M = Ni) [5]; (ii) Pd substitution by an electron-like metal (Ag) induces a ferromagnetic (F) to antiferromagnetic (AF) transition. This last result has been associated to a variation in charge screening at the nonmagnetic site [4].

The compounds CePd, CeNi, CeRh and their respective alloys, crystallize in the CrB-type structure, while in the case of Ce(Pd, Ag) such structure is kept almost up to 20% of Pd substitution by Ag. CePd is a ferromagnet, with $T_C = 6.5$ K, while CeNi and CeRh show the characteristic behaviour of intermediate valence systems [6]. Pd and Ni can be considered as isoelectronic (hole-like) elements, while Rh, Pd and Ag have similar volumes with different electronic concentrations.

In a recent contribution [3], we find a criterion for characterizing the magnetic ground state of Ce intermetallic compounds by analysing their LDA-spin contribution to the magnetic moment. Based on the comparison of experimental data with LDA results, we propose that, depending on the LDA magnetic moment, a Ce compound can be considered as nonmagnetic if $\mu_{Ce} = 0$, intermediate valence if $\mu_{Ce} < 0.5\mu_B$ or magnetic if $\mu_{Ce} > 0.5\mu_B$.

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In the present contribution, we analyse the evolution of Ce magnetism and the effects of volume and electronic concentration on $Ce(Pd_{1-x}M_x)$ compounds (M = Rh, Ni and Ag) using the above-mentioned criterion. The aim of this work is to check the extent to which an itinerant picture can provide a qualitative description of the experimentally observed magnetic phenomena driven by the variation of volume and electron concentration.

The ab-initio calculations are performed using the FP-LAPW WIEN97 code [7] with the exchange and correlation potential of Perdew and Wang [8]. In general, from 75 to 90 k-points in the irreducible Brillouin zone is enough to attain the desired precision. The considered muffin tin radii, $R_{mt}$, are 2.6 au for Ce atom, for 4d transition metals 2.2 au and for Ni 2.0 au. The cutoff parameter is taken as $R_{mt}K_{max} = 8$, where $K_{max}$ is the maximun value of the reciprocal lattice vector used in the plane wave expansion. The total energy is converged up to $10^{-4}$ Ry.

We do the calculations with M = Rh and Ni, and for different ordered structures with $x = 0$, 0.25, 0.5, 0.75 and 1. To study the magnetic behaviour when M = Ag, we consider fictitious structures with $x = 0.25$ and 0.50. Even if for $x > 0.2$ the underlying structure is no longer of the CrB type, the last calculations allow us to draw information on the magnetic interactions at smaller concentrations.

We perform the electronic calculations at the corresponding experimental volumes for each concentration in Ce(Pd, Rh) and Ce(Pd, Ni) alloys. The results obtained are given in Fig. 1 (a), and should be compared with the experimental ones in Fig. 1(b).

Experiments show that, in the case of Rh, the system becomes intermediate valent for $x > 0.6$ and in Ni alloys for $x > 0.9$. Besides, Ce magnetic moments are larger for the Ni systems along the whole range of $x$.

In the calculations, we obtain the same trends. The systems containing Ni also show larger magnetic moments than the ones with Rh (for $x = 0.25$, 0.5, 0.75). Both types of alloys become intermediate valent in the limiting case $x = 1$, because the calculated magnetic moments are less than $0.5\,\mu_B$ [3]. In the experiments, the systems with Rh reach this regime at a lower concentration.

To elucidate the mechanism which induces these phenomena, we do a calculation for the case $x = 0.75$ at a smaller cell volume than the experimental one (a volume reduction of 2.2%) for both alloys. The result is that the Ce(Pd, Rh) system suffers a decrease of 11.1% in the magnetic moment of Ce while for the Ce(Pd, Ni) system, the decrease is of 2.7%. This indicates that Rh–Ce hybridization is stronger than Ni–Ce one and a larger amount of Ni (as compared to Rh) is needed to make the Ni–Ce hybridization effective. This in turn leads to a volume decrease and to a subsequent

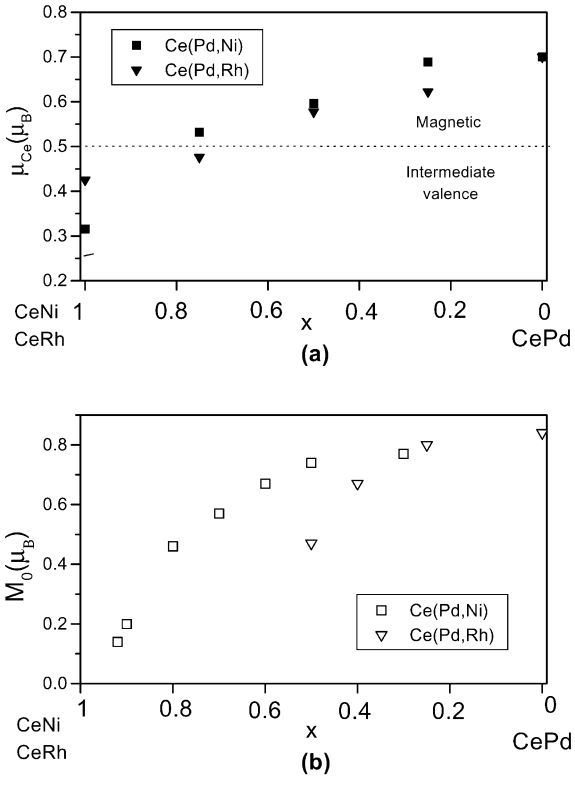


Fig. 1. (a) Spin contribution to the Ce magnetic moments, $\mu_{Ce}$, calculated for $x = 0$, 0.25, 0.5, 0.75 and 1; (b) Experimentally extrapolated zero-field magnetization, $M_0$, at 4.2 K from Refs. [4,5]. Both plots show the corresponding results for the Ce(Pd, Rh) and Ce(Pd, Ni) systems.

disappearance of the magnetic order, as suggested in Refs. [1,2]. This important difference in hybridization strength stems from the fact that Ni atoms are smaller than Rh ones and more Ni is needed for an efficient interaction.

On the other hand, it is experimentally observed that when Pd is substituted by Ag, even for very small concentration values ($x > 0.02$), the magnetic interaction between Ce atoms is no more ferromagnetic, the presence of Ag giving rise to nonsimple antiferromagnetism [4].

We consider several ordered-AF configurations and compare their total energies with the respective F arrangements. The energy differences among magnetic configurations are very small (of the order of $10^{-4}$ Ry for the whole unit cell) so that we can only be sure of the sign of such differences. In any case, we can say that the tendency (when Ag is present) is towards antiferromagnetism. For CePd and $CePd_{0.75}Rh_{0.25}$, the preferred magnetic configuration is always F. We attribute this transition not to an impurity effect but to a variation in

the density of conduction electrons which mediate Ce–Ce interactions. This is clear from the fact that we consider ordered structures in the calculations and, also, because this AF configuration persists for unphysically larger concentrations ($x = 0.5$) in which Ag atoms cannot be considered as impurities.

It is worth mentioning that the AF couplings do not take place among nearest neighbours (nn) Ce atoms. Actually, nn coupling results being ferromagnetic. This explains, in part, the small energy differences and the nonsimple AF ground state observed in the experiments.

Summarizing, we show that it is possible to understand qualitatively the evolution of magnetism in $CePd_{1-x}M_x$ compounds within an itinerant description. We obtain the experimentally observed trends for the F–NM transition as a function of Ni/Rh concentration and also the F–AF switch when replacing Pd by Ag.

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