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Systematics on the cerium magnetic transformations induced by alloying

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Abstract

A systematic study on the competition between on-site and inter-site magnetic interactions is performed on Ce intermetallics through magnetic, thermal, transport, structural and spectroscopic measurements analyses. It is shown that the volume and the electronic concentration variation produced by alloying the Ce-ligand, are not equivalent and only the volume reduction produces the maximum in the ordering temperature predicted by theory. For the magnetic to intermediate valence transformations, a change of regime is observed at a critical Ce-ligand substitution, which corresponds to a change in the substitution dependence of the experimental parameters. On the contrary, no change of regime is detected for the magnetic to heavy fermion transformation. The different regimes are correlated with the respective hybridization strengths of the ground and excited crystalline field states through the temperature dependence of the electrical resistivity. Such a correlation allows us to draw a generalized phase diagram containing these types of transformation.

1. Introduction

Within the physical properties of the Ce atom, the tendency for hybridization of its localized 4f state with the conduction band states is well known, resulting in an "on-site" screening of the magnetic moment through local spin fluctuations, known as the Kondo impurity effect. In the limit of very strong hybridization, charge fluctuations also contribute to the demagnetizing mechanism, inducing an intermediate valence (IV) state. When the Ce atoms are placed in a periodic arrangement the "inter-site" interactions, such as the electron-mediated magnetic exchange (RKKY), compete with the Kondo mechanism for the ground state (GS) formation. By decreasing the temperature, the Kondo effect tends to screen the Ce magnetic moment, while the RKKY interaction develops an intersite magnetic coupling, with a tendency to order the Ce lattice magnetically. The competition between the binding energy of the non-magnetic Kondo singlet (k_BT_K) and the magnetic coupling energy (k_BT_R) determines the nature of the ground state of the system [1]. Both energies depend on the same coupling constant for the exchange between the local spin and the conduction-electron spins, $g=n_FJ$ (n_F is the density of states and J the exchange integral), as: $T_K \sim \exp(1/g)$ and $T_R \sim g^2$. For small values of g, $T_R > T_K$ and the system orders magnetically. On the other limit, $T_K > T_R$ and the system becomes non-magnetic. In the intermediate case, both mechanisms compete, leading the system to a mixed state (MS) where part of the entropy condenses into a magnetic state and part in a non-magnetic singlet. Here, the magnetic moment, μ_s, is reduced by the Kondo effect and consequently the ordering temperature, $T_m \sim \mu_s{}^2T_R$, is also reduced. Therefore, the model predicts that the ordering temperature T_m first (for $g<g_{max}$) must increase, to reach a maximum around g_{max}, and then to drop to zero for $g \rightarrow g_0$. The resulting phase diagram is shown in Fig. 1(a).

There is, however, an increasing number of systems in which T_m decreases continuously by alloying the Ce-ligand. In such a case it is usually argued that those compounds lie in the range of g between g_{max} and g_0. The lack of a quantitative (or directly measurable) parameter makes it difficult to compare different systems and therefore to establish whether they are in the $g<g_{max}$ or in the $g>g_{max}$ region. Nevertheless, there is a system able to provide a direct comparison between these two possible behaviours, showing up the limitations of the g parameter for describing real systems. That system is $Ce(Pd_{1-x}M_x)$, where M = Ni and Rh. While CePd is a ferromagnetic (F) compound with T_c (*i.e.* T_m) = 6.5 K, CeNi and CeRh are IV compounds. Ce(Pd,Ni) undergoes the F to IV transformation with T_c passing through a maximum value, while for Ce(Pd,Rh), T_c decreases continuously despite the fact

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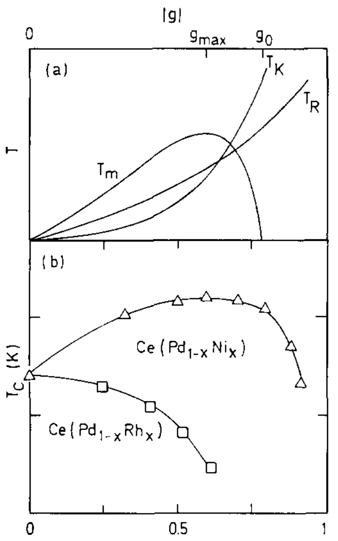

Fig. 1. (a) Comparative diagram of the Kondo (T_K), magnetic (T_R) and measured (T_m) ordering temperatures as a function of the coupling parameter g. (b) Curie (T_c) temperature as a function of Pd substitution.

that a similar F to IV transformation is induced [2]. Here the CePd as a "matrix" compound confronts two different behaviours with a single starting g value.

The aim of this work is to make a systematic comparison of the physical properties of the Ce systems, in which this atom undergoes a magnetic (M) to non-magnetic (NM) transformation driven by volume and electronic concentration variation through the Ce-ligand alloying. Some representative concentrations are analyzed and different behaviours induced by the alloying effect are discussed.

2. Comparison between volume and electronic concentration effects

The g parameter cannot be experimentally controlled in any direct manner, because the driving experimental parameters are the external pressure or the chemical potential variation (by alloying). Although these two external forces may induce variation in all the thermodynamic parameters, they can be considered as producing effects mainly on the volume (ΔV) or on the electronic concentration (ΔZ). Then, one has to ask whether ΔV and ΔZ are equivalent for describing the phase diagram of Fig. 1(a). Such effects can be quite independently induced in $Ce(Pd_{1-x}M_x)$, because for M = Ni, the dominant effect is the volume reduction (ΔV) and for M = Rh the electronic change (ΔZ) is dominant [2].

The comparison of the ordering temperature dependence on the Pd substitution by Ni or Rh is shown in Fig. 1(b), where a clear difference is observed. Although for both substitutions the F character is kept up to $x = x_0$ (where $T_c = T_m \rightarrow 0$), only Ni induces a maximum in $T_m(x)$ at x_{max} while Rh continuously depresses T_m.

Besides T_m, the temperature dependence of the electrical resistivity, $\rho(T)$, also shows a different behaviour depending on the Ce-ligand substitution. A qualitative description of $\rho(T)$ can be made by looking at some of its characteristic extrema values such as: the low temperature resistivity (ρ_{LT}), the maximum at high temperature (ρ_{HT}) and the temperature at which ρ_{HT} occurs (T_{max}). The differences concern not only the x dependence, but also their relative values. Under ΔV there is only one maximum (ρ_{HT}) and therefore $\rho_{HT} > \rho_{LT}$. On the contrary, under ΔZ effects, there are two maxima and $\rho_{LT} > \rho_{HT}$ [2]. For large x values, $\rho(T)$ behaves as for an IV system in both cases. From the comparative analysis of the transport properties, we can infer that the excited CF levels show hybridization effects at any concentration, while the GS behaves in a different manner depending on the ΔV or ΔZ effect. In the case of an Ni substituent, the onset of the GS hybridization coincides with the mixing with the CF levels, due to the fact that the width of the excited CF level overcomes the CF splitting around $x(\mathrm{Ni}) = 0.9$. In the second case, the hybridization of both levels rises independently, overlapping each other when the system becomes IV, around $x(\mathrm{Rh}) = 0.8$.

The volume of the unit cell (V) also depends on the substitution of the Ce-ligand. In the case of Ce(Pd,Ni) the $V(x)$ dependence has the slope which, up to $x \approx 0.8$, extrapolates to a hypothetical "$Ce^{3+}Ni$" compound. Above that concentration $V_{Ni}(x)$ practically collapses as the hybridization of the GS increases. On the contrary, $V_{Rh}(x)$ decreases faster than an estimated Végard'slaw between CePd and a hypothetical "$Ce^{3+}Rh$". At high concentration ($x > 0.7$), the slope of $Ce(Pd_{1-x}Rh_x)$ increases gradually [2]. The most striking feature in this comparative analysis comes from the fact that, regardless of the fact that the Ni atomic volume is 20% smaller than that of Rh, for $x \leqslant 0.7$ the dV/dx slope is smaller for Ce(Pd,Ni) than for Ce(Pd,Rh). Therefore, one concludes that the hybridization effect is present at any Rh concentration, while in the case of Ni it occurs only above a certain characteristic x value.

This experimental information shows that the ΔV and ΔZ effects on the valence evolution of Ce are different in these compounds. The structural pressure produced by the substitution of Pd by a smaller (Ni) atom is effective at large concentration. At intermediate Ni concentration the average Ce–Ce distance is reduced, increasing T_m as expected for a RKKY interaction. Within this picture, the maximum T_c represents the x value for which the Ce–Ce distance has the lower value before the Ce–Ni contacts become able to turn on the hybridization mechanism on the GS. Thus, the maximum in $T_m(x)$ is observed within a range of x in which the magnetic GS is still not affected by the hybridization mechanism.

On the other hand, the ΔZ changes produced by the Rh presence, immediately induce hybridization effects in the ground and CF excited states. Here the shortening of the Ce–Ce distance is not caused by the difference in size of the Ce-ligand, but by the reduction of the Ce volume itself due to the valence increase. Such a reduction of Ce volume is related to the early quenching of its magnetic moment and therefore no maximum in T_c is expected.

From the fact that Ce(Pd,Ni) and Ce(Pd,Rh) have the same "matrix" compound, CePd, but their respective behaviours are qualitatively different depending on the driving parameter (ΔV or ΔZ), one concludes that g cannot be taken as a "universal parameter" for comparing different systems in the form presented in the theoretical model.

Once the difference between ΔV and ΔZ effects was recognized in one case, one should ask whether such a difference is indeed a general rule or not. A number of binary and ternary Ce systems undergoing the M to NM transformation are listed in Table 1, mainly driven by one of these two effects: ΔV or ΔZ variation. It can be seen that they are correlated with the occurrence or not of a maximum in $T_m(x)$. As before, ΔV is obtained by substituting isoelectronic elements and ΔZ by elements having similar size. The conclusion extracted from the analysis of the 13 families of Ce compounds presented in Table 1, is that the occurrence of a maximum in $T_m(x)$ is directly related to the reduction of the Ce–Ce spacing, in agreement with the nature of the RKKY interaction.

TABLE 1. Correlation between the occurrence (or not) of a maximum in T_m (at x_{max}) and the dominant effect: volume (ΔV) or electronic concentration (ΔZ); x_0 corresponds to $T_m \to 0$; n.i., no information

Compound	Effect	x_{max}	x_0	Ref.
Ce(Pd, Ni)	ΔV	0.6	0.95	2
Ce(Pt, Ni)	ΔV	0.5	0.95	3
Ce(Pd, Rh)	ΔZ	–	0.7	2
Ce(In, Sn)$_3$	ΔZ	–	0.15	4
Ce(Tl, Sn)$_3$	ΔZ	–	0.8	5
Ce(Ge, Si)$_2$	ΔV	0.5	0.7	6
Ce(Pt, Ir)$_2$	ΔZ	–	n.i.	7
Ce(Pd, Ni)Sn	ΔV	0.25	0.8	8
Ce(Pt, Ni)Sn	ΔZ	–	0.8	9
CeIn(Ag, Cu)$_2$	ΔV	0.75	>1	10
CeRh$_2$(Ge, Si)$_2$	ΔV	0.88	>1	11
Ce(Rh, Ru)$_2$Si$_2$	ΔZ	–	0.4	12
Ce(Os, Ru)$_3$B$_2$	ΔV	0.1	>1	13

3. Analysis of the ground state evolution

When a M to NM transformation is studied, the heavy fermion (HF) or intermediate valent (IV) character of the non-magnetic GS is recognized from the values of the specific heat γ coefficient ($\sim 1/T_K$) or the paramagnetic temperature $|\theta_P|(\sim T_K)$. For the first parameter, a boundary was empirically established around 100 mJ Ceat^{-1} K^{-2} [14]. For the second one, it was observed that usually $\theta_P < 30$ K for the HF and $\theta_P > 100$ K for the IV compounds. It is known that the systems undergoing this transformation can have a two- ($N=2$, HF) or a sixfold degenerated GS ($N=6$, IV) in their respective non-magnetic limits. The fact that the initial state (magnetic at $x=0$) is always related to a Kramer's doublet CF ground state, gives a good reference point for searching whether there is any phenomenological difference in undergoing an HF or IV final state. The degeneracy difference between these states is large enough to expect some difference in the evolution of the thermodynamical parameters as a function of x. By taking into account that the formation of an IV ground state will imply the onset of charge fluctuations, one should expect that at a critical x value (x_{cr}), a change of regime should occur as a replica of the Ce($\gamma - \alpha$) phase transformation.

3.1. Concentration dependence of volume and paramagnetic temperature

In order to analyze the eventual change of slope in the $V(x)$ evolution in these systems, a number are listed in Table 2, which undergo a M to NM transformation, having a HF or IV compound as non-magnetic limit. The correlation between the $V(x)$ dependence and the nature of the "final" GS (or $x \to 1$) emerges clearly; the M to HF transformation follows Végard's law (*i.e.* $dV/dx = \text{constant}$), but there is a change of slope (at an x value identified as x_{cr}) for the M to IV transformation.

If the effect of the so-called "chemical pressure" is described as Végard's law, it is supposed that the electronic effects occur only on the band states driven by the continuous variation of the chemical potential. Such is also the case for $x < x_{cr}$ in the systems where a change in dV/dx is observed. But for $x > x_{cr}$, there is an extra reduction in volume indicating that the Ce-4f shell occupancy is affected. There, the $V(x)$ dependence can be described as: $dV/dx = (dV_g + dV_v)/dx$ where dV_g/dx denotes the Végard component and dV_v/dx the variation due to the charge fluctuation, related to the increase in the Ce valence. As expected $dV_v/dx = 0$ for an HF system.

Comparing the $T_m(x)$ and $V(x)$ evolution, one observes that $T_m(x)$ shows a maximum at x_{max}, a drop down at x_{cr} and becomes zero at x_0. But $V(x)$ is only sensitive

TABLE 2. Correlation between the type of transformation with the change (or not) of the $V(x)$ (or $\ln|\theta_P(x)|$) slope at x_{cr} (or x_p)

Compounds	Type			x_{cr}	x_p	Ref.
Ce(Pd, Ni)	F	–	IV	0.8	0.7	2
Ce(Pt, Ni)	F	–	IV	0.8	0.7	3
Ce(Pd, Rh)	F	–	IV	0.6	0.6	2
$Ce(In, Sn)_3$	AF	–	IV	0.65	0.65	4
$Ce(Ge, Si)_2$	AF	HF	–	–	–	6
$Ce(Pt, Rh)_2$	AF	–	IV	0.5	0.45	7
$CeSi_{2-x}$	F	–	IV	0.2[a]	0.18	16
CePt(Ge, Si)	AF[b]	HF	–	–	n.i.	17
Ce(Pt, Ni)Sn	AF	–	IV	0.6	n.i.	9
Ce(Rh, Ir)Ge	AF	–	IV	0.28	0.30	18
$CeIn(Ag, Cu)_2$	AF	HF	–	0.75[c]	–	10
$CeRu_2(Ge, Si)_2$	AF	HF	–	–	–	19
$Ce(Cu, Ni)_2Ge_2$	AF[d]	HF	–	–	–	20
$CeCu_2(Ge, Si)_2$	AF	HF	–	–	n.i.	21
$Ce(Pd, Cu)_2Si_2$	AF	HF	–	–	n.i.	22
$Ce(Os, Rh)_3B_2$	F	HF	–	–	n.i.	13
$Ce(Cu, Ni)_2Si_2$	–	HF	IV	0.4	0.35	23

[a] Range of existence of this compound: $0.1 < x < 0.3$.
[b] Continuous alloy for $x > 0.4$.
[c] A similar change of $V(x)$ slope is observed in the reference compound.
[d] Change in the AF structure at $x \simeq 0.15$.
n.i., no information.

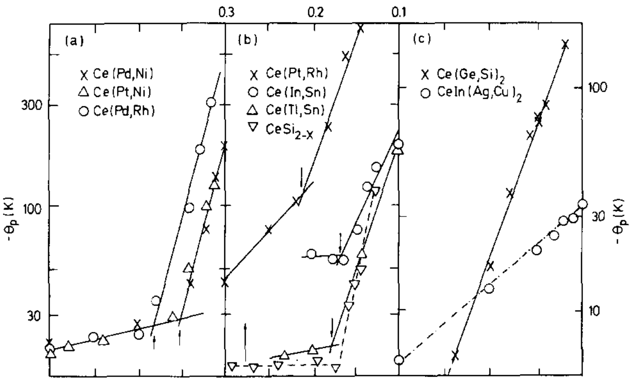

Fig. 2. Substitution dependence of the paramagnetic temperature (θ_P) in a semilogarithmic scale, (a) and (b) for systems undergoing a M to IV transformation and (c) for systems undergoing a M to HF transformation. The small arrows indicate the $x_p = x_{cr}$ concentration.

to the x_{cr} value through a change of its derivative. Here x_{cr} appears to be the most significant value in the concentration variation related to the transformation under study. The validity of the x_{cr} value as representative of a change of regime requires to recognize its role in the evolution of other physical parameters. One of those is θ_P. As described in the introduction $T_K \sim \exp(1/g)$, then if $\theta_P \sim T_K$, it should be a qualitative relationship of the type $-\ln \theta_P \sim x$ between these two measurable parameters. Such a relationship is shown in Fig. 2, in a semilogarithmic representation for nine systems undergoing a magnetic to IV or HF transformation. The $\ln \theta_P = f(x)$ dependence confirms the conclusion extracted from $V(x)$: There is a clear change of slope at $x = x_p$ in the magnetic to IV transformation and x_p coincides with x_{cr} (see Table 2). On the contrary, no change of slope is observed for the systems undergoing a magnetic to HF transformation. The existence of a change of regime at x_{cr} implies that the HF and IV ground states are qualitatively different and not only different from their respective T_K values.

3.2. Concentration dependence of other parameters

Further experimental information is required to confirm the role of x_{cr} in the evolution of the system. The Ce–L_{III} X-ray absorption spectrum becomes relevant information here because we have associated the critical concentration ($x_{cr} = x_p$) to the onset of the charge fluctuations. Therefore, a measure of the Ce valence (ν) as a function of x allows a direct "observation" of a change from the local moment regime to a the charge fluctuation regime. The $\nu(x)$ dependence in five families of compounds: Ce(Pd,Ni) and Ce(Pd,Rh) [2], $Ce(Pt,Rh)_2$ [7], Ce(Rh,Ir)Ge [18] and $Ce(Cu,Ni)_2Si_2$ [24] was analyzed. The first four undergo a magnetic to IV transformation, while the last one transforms from HF to IV. In the first four systems, the change of the $\nu(x)$ slope practically coincides with the x_{cr} concentration and in the last system, no change of slope is observed.

The characteristic parameters for the electrical resistivity have already been introduced in Section 2 for the $\rho(T)$ description of Ce(Pd,Ni) and Ce(Pd,Rh). In Fig. 3, we have plotted ρ_{LT} and T_{max} as functions of x for a number of systems, covering all the transformations discussed up to now. We have chosen only these two characteristic values for simplicity in comparing a large number of parameters and systems. The common feature in the systems, for which this information is available, is that $\rho_{LT}(x)$ shows its maximum value at $x = x_{cr}$, coincidentally with the concentration at which $T_{max}(x)$ starts to rise. The other characteristic values of x, such as x_0 or x_{max}, seems not to be relevant in the transport properties. Notice that these properties are sensitive for describing simultaneously the strength of hybridization of the ground and excited levels.

From specific heat measurements, one can extract two parameters to define the character of the GS of these systems: the entropy, ΔS and γ. The entropy related to the Kramer's doublet GS of Ce is $\Delta S = R\ln 2$. The evaluation of the entropy gain of the magnetically ordered phase, ΔS_m, gives a measure of the degrees of freedom involved in the RKKY intersite coupling when the phenomenological two-component picture [25] is applied. Therefore, $\Delta S_m = R\ln 2$ becomes a necessary and sufficient condition for a "full magnetic" (Ce^{3+}) compound. ΔS_m below that value indicates that some

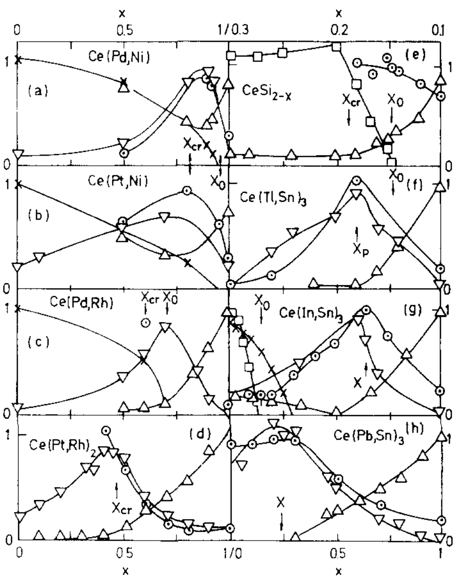

Fig. 3. Substitution dependence of some normalized characteristic parameters, defined in the text, of systems undergoing a M to IV transformation: ρ_{LT} (▽); T_{max} (△); γ_{HT} (○); $\Delta S_m/R\ln 2$ (×) and $T_m/10K$ (□). The respective values for the normalization of ρ_{LT} ($\mu\Omega$-cm), T_{max} (K) and γ_{HT} (mJ mol^{-1} K^{-2}) are: (a) 50, 200 and 200; (b) 15, 200 and 200; (c) 100, 300 and 200; (d) 200, 400 and 200; (e) 60, 300 and 260; (f) 100, 200 and 300; (g) 150, 300 and 300; (h) 60, 300 and 260.

degrees of freedom have been transferred to the non-magnetic (HF or IV) component, which should start to increase the band contribution (as a Kondo-like contribution). Therefore, the electronic contribution to the entropy can be written as $\Delta S(T)=\Delta S_K(T)+\Delta S_m(T)$. Also in Fig. 3 we have plotted the $\Delta\ S_m(x)$ and $\gamma(x)$ values for the systems where such information is available. As expected, $\Delta S_m = R\ln 2$ for the few "fully magnetic" compounds and decreases towards zero as $x \rightarrow x_0$. On the other hand, $\gamma(x)$ shows its maximum value around x_{cr} as further evidence that such a value marks a change in the GS character.

In order to make a quantitative comparison among different compounds, one can use the characteristic values of x which allows the respective "concentration" variables to be scaled. For such a purpose, we define $y=(x-x_{cr})/(x_0-x_{cr})$, with $y=0$ at $x=x_{cr}$ and 1 at $x=x_0$. The ΔS_m and the specific heat jump at $T_m(\Delta C_p)$ measured in Ce(Pd,Ni), Ce(Pt,Ni), Ce(Pd,Rh) and $Ce(Tl,Sn)_3$ fall in a unique curve. From this comparison one sees that a system may behave as purely magnetic up to a certain value of substitution and then some degrees of freedom begin to be transferred to the non-magnetic component. We note that the onset of the transference coincides with the concentration where $T_m(x)$ stops increasing in systems driven by ΔV effects.

4. Other types of transformations

There are some systems which undergo a transformation in their magnetic structure as a function of x, without losing the magnetic character of their GS. In these systems, their $T_m(x)$ drops rapidly and is overtaken by another type of magnetic order represented by $T_m'(x)$. Some examples of this behaviour are: $Ce(Tl,Pb)_3$, $Ce(In,Pb)_3$ [26] and $Ce(Cu,Ni)_2Ge_2$ [27], which undergo a transition from local magnetic moment antiferromagnetism (AF) to itinerant (or band) heavy fermion, also AF. Another example is Ce(Pd,Ag), which shows a transition from F to a complex AF-like magnetic order with only 2% of Pd substitution [2]. The characteristics of these systems can be resumed by: (i) the drastic reduction of $T_m(x)$; (ii) in the region where T_m and T_m' compete, the specific heat shows a structure around the ordering temperature, probably due to a mixture of phases; (iii) the entropy of the magnetically ordered phase is reduced when the order is related to a band magnetism, but not when T_m' is related to an order of local moment character as in Ce(Pd,Ag); (iv) as expected, no anomalies in the $V(x)$ slope are reported. The detailed analysis [28] of the criteria for the occurrence of local moment and band (itinerant) magnetism in narrow-band metals is an important tool for recognizing the nature of the magnetic GS of these systems.

On the other hand, there are systems which undergo non-magnetic transitions. In Table 2 we have included the $Ce(Cu,Ni)_2Si_2$ system as an example for the $V(x)$ change of slope (at $x=x_{cr}$) when the system transforms from a HF to an IV state. Further examples are $Ce(In,Sn)_3$ (in the $0.4<x<1$ range) and $Ce(Ru,Os)_2Si_2$ [29] which also transform from HF to IV.

It is generally accepted that the IV state of Ce is a limit for the increase of the Ce valence (fixed around $v=3.3$ by the L_{III} spectrum) and therefore a limit for the reduction in the Ce volume. The power of the dV/dx behaviour in denouncing changes in the Ce behaviour is put in evidence again in systems belonging to the limit where the demagnetized Ce has its smallest atomic volume. The intermetallic systems where Ce shows its maximum valence value are: $Ce(Pd,Rh)_3$ [30], $Ce(Ni,Fe)_2$, $Ce(Ni,Co)_2$ [31] and $Ce(Rh,Ru)_2$ [7]. These systems show a further change in the slope of dV/dx (at $x=x_{cr}'$) in coincidence with the concentration at which the Pauli-like susceptibility (χ_0) stops decreasing. A common feature for the compounds (placed at the $x>x_{cr}'$ limit) is that their electronic structure is such that Ce can be substituted by a tetravalent atom like Zr or Hf, but not by a trivalent one such as La [32]. The contrary is valid for systems that do not reach the x_{cr}' value.

5. Discussion

Before analyzing the features that have to be taken into account for a further improvement in a model applicable to the new experimental evidence, we will try to sort the different evolutions of the Ce systems produced by ligand substitution.

As expected, the ΔV effect reduces the Ce–Ce spacing and, below a certain value, affects the available volume of the Ce atom itself. A schematic phase diagram for this case is presented in Fig. 4(a). For $x < x_1$, the system behaves as "full magnetic" increasing its ordering temperature due to the reduction in the Ce–Ce spacing. Notice that in this group we have only registered F compounds. Between x_1 and x_{cr} there is a transference of degrees of freedom from the magnetic to the IV component. But the intensive parameters, like T_m and θ_P, are practically not affected. Here the x_{max} concentration does not seem to be significant for the description of the system. Right above x_{cr}, the intensive parameters change rapidly and the magnetically ordered component disappears as $x \rightarrow x_0$. Concerning the hybridization effects, the electrical resistivity indicates that the CF levels are more hybridized (Γ_{CF}) than the GS: $\Gamma_{GS} \gg \Gamma_{CF}$. The hybridization mechanism affects the GS only when Γ_{CF} becomes of the order of the CF splitting, *i.e.* $\Gamma_{CF} \approx \Delta_{CF}$. The Γ parameter is directly connected with g, but we will use the first one in this section in order to distinguish between the ground (Γ_{GS}) and the first excited state (Γ_{CF}) hybridization.

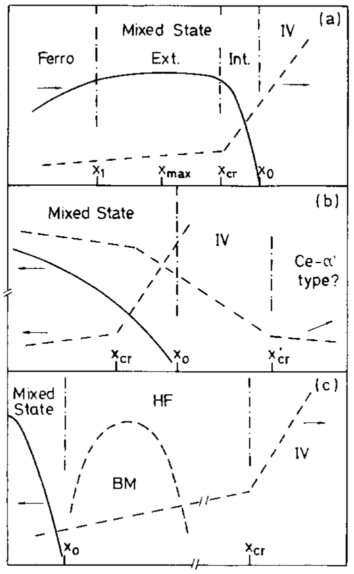

Fig. 4. Schematic phase diagrams for systems undergoing different types of transformation: (a) M to IV, driven by ΔV effect, "Ext." and "Int." indicate the regions where the respective extensive or intensive parameters are affected. (b) M to IV, driven by ΔZ effect and (c) M to IV through a HF state. The abbreviations are defined in the text.

The schematic phase diagram for the case where ΔZ drives the Ce magnetic behaviour is pictured in Fig. 4(b). In this group, the mixed state begins with the substitution of the Ce-ligand, as in the case of Ce(Pd,Rh), but it could happen that the magnetic compound itself (for $x = 0$) exhibits a mixed state, as in $Ce(Tl,Sn)_3$. Here it is not possible to recognize the regions where the extensive or intensive parameters, respectively, are affected because $T_m(x)$ decreases significantly when $\ln \theta_P$ still does not change significantly. On the IV side ($x > x_0$), another transformation is suggested by the change of the dV/dx slope at $x = x_{cr}'$, which is reached by the systems whose $x = 1$ compounds form isotopic compounds with tetravalent Zr and Hf. This transformation may be related to the Ce($\alpha - \alpha'$) change of phase. The electrical resistivity measured in these systems (for $0 < x < x_0$) suggests that the hybridization strength is similar for the GS and the CF levels ($\Gamma_{GS} \approx \Gamma_{CF}$) and the transformation of the system to an IV state occurs when $\Gamma_{GS}(+)\Gamma \approx \Delta_{CF}$.

The rest of the behaviour shown by the Ce systems is related to transformations from local magnetic moment (LMM) to band magnetism (BM) or to a HF state, as summarized in Fig. 4(c). The ordering temperature (typically AF) originating in the LMM decreases rapidly as $x \rightarrow x_0$. For $x > x_0$, the systems behave as a HF, which may eventually exhibit BM. At higher substitution, some of them transform to IV for $x > x_{cr}$. Distinctive for this group are the facts that $x_0 < x_{cr}$, and that the electrical resistivity shows a maximum (related to the hybridization effects) at low temperature. This means that $\Gamma_{GS} > \Gamma_{CF}$ and the transformation to an IV state occurs when $\Gamma_{GS} \approx \Delta_{CF}$. The representative examples for this group of systems are: $Ce(Cu,Ni)_2Ge_2$ [27], $Ce(Pb,Sn)_3$ [33] and $Ce(Au_{1-x},Cu_{5+x})$ [34].

From the experimental data shown in Fig. 3 and the different types of transformations analyzed in the previous section, one finds that T_{max} is the best phenomenological parameter for comparing the different hybridization strengths of the CF levels with those of the GS. There are three possible cases:

(A) Systems where $\Gamma_{GS} \ll \Gamma_{CF}$. They show only one maximum in $\rho(T)$ at low x, which appears around $T_{max} \approx \Delta_{CF}/k_B$. At higher substitution rate, T_{max} decreases to reach its minimum value at $x \approx x_{cr}$. For $x > x_{cr}$, T_{max} increases giving to $\rho(T)$ the characteristic dependence of an IV. Examples for this case are Ce(Pd,Ni) [2], Ce(Pt,Ni) [3] and under pressure, CeAg [35] and CePd [36]. All these systems show a maximum in T_m and are driven by ΔV effects.

(B) For $\Gamma_{GS} \approx \Gamma_{CF}$ two maxima appear in $\rho(T)$, related to the GS and the excited CF levels, respectively. Both maxima come together at around x_{cr} because of the decrease in T_{max} and then the single T_{max} starts to increase as in the first case. Examples for this case

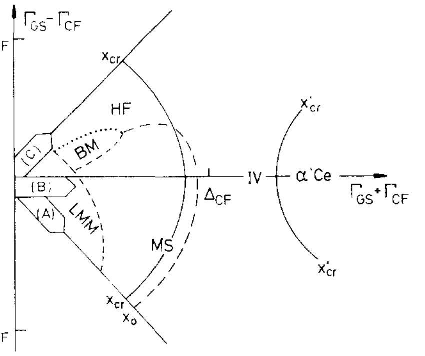

Fig. 5. Generalized diagram including three different routes for the M to NM transformation as a function of the relative hybridization strength of the ground and the excited sates. (A) $\Gamma_{GS}<\Gamma_{CF}$; (B) $\Gamma_{GS}=\Gamma_{CF}$; (C) $\Gamma_{GS}>\Gamma_{CF}$. The abbreviations are defined in the text.

are: Ce(Pd,Rh) [2], Ce(Tl,Sn)$_3$ [5] and CeSi$_x$ [16]. All these systems do not show a maximum in $T_m(x)$ and are driven by ΔZ effects.

(C) When $\Gamma_{GS}>\Gamma_{CF}$, a maximum at low temperature develops for low values of x being connected with the HF ground state formation. Approaching x_{cr}, a second maximum develops at higher temperatures (related to the CF excited levels). Both maxima come together around x_{cr} to follow the typical IV behaviour for higher x values. Examples for this case are: CeIn(Ag,Cu)$_2$ [10], Ce(Pt,Rh)$_2$ [37], Ce(In,Sn)$_3$, Ce(In,Pb)$_3$, Ce(Pb,Sn)$_3$ [38] and Ce(Au$_{1-x}$,Cu$_{5+x}$) [34].

In Fig. 5, we resume all the possible cases within a single diagram by taking as coordinates the sum and the difference of the hybridization strengths of the ground and the excited states (*i.e.* $\Gamma_{GS}+\Gamma_{CF}$ and $\Gamma_{GS}-\Gamma_{CF}$), respectively. Notice that the x_{cr} concentration represents a sort of boundary phase, corresponding to a hybridization strength comparable in energy to the CF-splitting, which here plays the role of unity of measure.

6. Conclusions

We have shown that although the early model proposed by Doniach [1] contains the basic ingredients for the description of a system undergoing a M to NM transformation, it is not able either to describe many of the real systems or to allow a comparison between them. Such a comparison can be achieved by scaling the characteristic concentrations related to the change of regime. The most significant concentration value was found to be x_{cr} where most of the physical parameters describing the real systems show some kind of anomaly related to a change of regime. This fact makes it evident that a single parameter, like the Kondo temperature, is not able to describe completely the evolution of the system from a LMM to an IV behaviour. Contrary to what was expected, the concentration at which the maximum of $T_m(x)$ is observed in some compounds, appears to be not related to any change of regime in the system.

By using the temperature dependence of the electrical resistivity, it was possible to sort the large number of systems reported up to now into three groups characterized by the relative strength of hybridization of their GS and CF levels. Therefore, a more realistic description of the systems should be reached by including the hybridization effects on the excited CF levels into the models, because the symmetries which determine the splitting of the Ce ground state given by Hund's rules, seems to be also important for the strength of the hybridization of each level. Once a pattern for a classification of the different systems is obtained, one should expect an easier description for the forthcoming results, which will thus become a test for the criteria followed in this work.

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