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A comparison between volume and electronic concentration effects in Ce transformations

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Abstract. The crossover from magnetic to non-magnetic ground states in Ce compounds is analysed within the competition between the on-site and inter-site interactions proposed by Doniach. The comparison of the evolution of the ordering temperature, as a function of pressure and alloying, was performed in more than twenty Ce systems. This systematic shows that volume (ΔV) and electronic concentration (ΔZ) effects, as the driving forces for such a transformation, present different characteristics. The maximum in the ordering temperature (T_0), predicted by the model, is only observed under ΔV effects (induced by alloying or by pressure) and not under ΔZ variations. This study leads to the conclusion that the maximum in T_0 cannot be considered intrinsic to a complete magnetic to non-magnetic transformation, but rather is a consequence of the Ce–Ce spacing decrease, before the wavefunction overlap turns on the hybridization mechanism.

1. Introduction

The Ce magnetic transformations in intermetallic compounds, induced by pressure or by alloying the Ce ligand, have been intensively studied in order to compare the degree of hybridization of the Ce 4f state with the band states in different environments. A relative evaluation of the hybridization strength can be obtained by comparing the binding energies of the respective Kondo singlet ground states, characterized by the so-called Kondo temperature ($k_B T_K$). However, such a procedure is distorted by the fact that a large number of Ce compounds show a coexistence of 4f-band hybridization with long-range magnetic order. In that case, another energy scale ($k_B T_R$) related to the magnetic interactions (usually of RKKY type) competes in the Ce ground-state (GS) formation, which in many cases results in a shearing of degrees of freedom between the two components [1]. The experimental evidence for such a coexistence is given by the fractional entropy of the magnetically ordered phase (expected to be $R \ln 2$ for a typical Ce^{3+} doublet GS), a reduced specific-heat jump at the ordering temperature (T_0) with respect to the value predicted by the mean field theory ($12.5 \text{ J mol}^{-1} \text{ K}^{-1}$) [2] and a reduced magnetic moment of the magnetically ordered GS [3].

Although the $k_B T_R$ energy is well defined by the magnetic phase transition, the Kondo energy ($k_B T_K$) strongly depends on fitting parameters and a model-mediated interpretation of the experimental results. Under these circumstances, a strict comparison between two systems can only be achieved through the experimental observation of the evolution of their characteristic parameters, when they can be continuously alloyed. The competition of these two energies was successfully described by Doniach [4], taking into account that

both depend on the same coupling constant between the local and the conduction-electron spins: $g = n_F J$, where n_F is the band density of states and $J (< 0)$ is the classical exchange integral. Their respective g dependences are $T_K \sim \exp(1/g)$ and $T_R \sim g^2$. For small values of $g \rightarrow T_R > T_K$ the system orders magnetically. In contrast, for large values of $g \rightarrow T_K > T_R$ the system becomes non-magnetic. At intermediate values (when T_K and T_R are comparable) both mechanisms compete, leading the system to a mixed state [5], where part of the entropy condenses into a magnetic state and part into a non-magnetic singlet. Here the effective magnetic moment, μ_{eff} , is reduced by the Kondo effect and consequentially the observed ordering temperature, $T_o \sim \mu_{\text{eff}}^2 T_R$, is decreased [6]. The classical example of this situation is the antiferromagnet (AF) CeAl_2 [1] which, with $T_N (= T_o) = 3.8$ K and an estimated $T_K = 5$ K, reaches an entropy $\Delta S \simeq 0.5 R \ln 2$ at T_N . The Doniach model for a one-dimensional Kondo lattice predicts a continuous transition (at zero temperature) from an AF GS to a Kondo-like state as a function of g . Because $T_R \sim g^2$, T_R is expected to increase faster than T_K for small values of g and therefore the observed ordering temperature T_o first has to increase (i.e. $dT_o/dg > 0$ when $g < g_{\text{max}}$), then reach a maximum at g_{max} and finally drop to zero as $g \rightarrow g_0$. The resulting phase diagram, shown in figure 1, is presented as a universal feature, i.e. $T_o(g)$ should always have to undergo a maximum value in a complete magnetic to non-magnetic transformation.

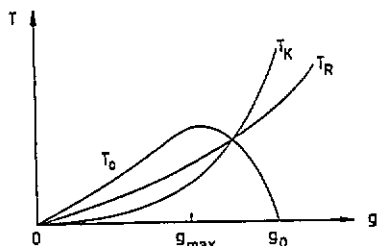


Figure 1. Comparative diagram of the Kondo (T_K), magnetic (T_R) and measured order (T_o) temperatures as a function of the coupling parameter g .

The usual procedure for studying the competition between two mechanisms is given by changing their relative strength through the variation of an appropriate physical parameter. In this case we have to change the chemical potential of the system. This can be done by changing the relative concentration of the components or by applying external pressure (see figure 2). For isostructural compounds which show continuous solid solution, the Ce-ligand substitution, $\text{Ce}(X_{1-x}Y_x)_j$, is related to the g variation ($g \sim x$), while in those compounds studied under pressure the g parameter was considered to be proportional to the applied pressure ($g \sim P$). In both cases, remarkable success in the qualitative description of the magnetic to non-magnetic transformation was obtained from the theory for a large number of systems [7].

By looking deeper into the T - g phase diagram of figure 1, one may ask how one distinguishes a system belonging to the 'full magnetic' region from a system belonging to the 'mixed' region. In terms of entropy, there should be a value of g (or a concentration 'x' in a given $\text{Ce}(X_{1-x}Y_x)_j$ system) where the degrees of freedom from the magnetically ordered phase begin to be transferred from the magnetic to the non-magnetic component. There, the entropy of the magnetically ordered phase should start to decrease from the expected $R \ln 2$ value as an enhanced density of electronic states ($\sim \gamma$) should start to rise.

As well as systems showing a maximum in $T_o(x)$, there is an increasing number of systems in which $T_o(x)$ decreases continuously by alloying the Ce ligand, as shown in figure 2. In such a case it is usually argued that those compounds belong to the

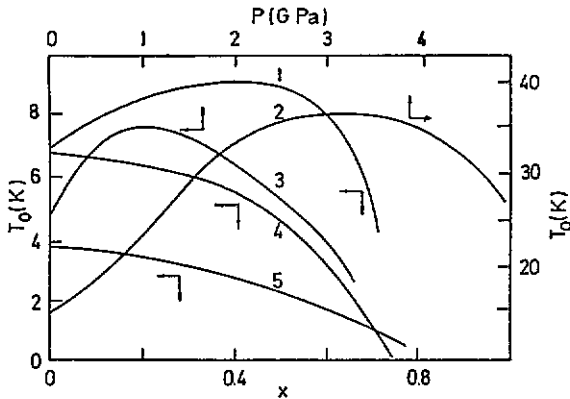


Figure 2. Dependence of the ordering temperature (T_0) on pressure (upper scale) or alloying (lower scale). Pressure dependence: curves 2 (CeP) and 3 (CeAg); alloying: curves 1 (Ce(Ge_{1-x}Si_x)₂), 4 (Ce(Pd_{1-x}Rh_x)) and 5 (Ce(Tl_{1-x}Sn_x)₃). The respective references are given in table 1.

$g_{\max} < g < g_0$ region [8]. However, the $x \rightarrow 0$ limit for some of them corresponds to a 'full ferromagnetic' compound, with total $R \ln 2$ entropy, large magnetization and specific heat jump at T_0 and consequentially a low γ value [3]. In other words, there is no indication for a Kondo-like component even though $dT_0/dg < 0$ at $x \sim 0$. Such is the case in Ce(Tl_{1-x}Sn_x)₃, which undergoes an AF to non-magnetic transformation without showing any maximum in the $T_N(x)$ dependence [9]. In this case it would be expected that CeTl₃ belongs to the $g_{\max} < g(x) < g_0$ region. However, this compound has the entropy gain, the specific heat jump at T_N and the saturation magnetization as predicted for the Γ_7 GS. Furthermore, practically no γT contribution to the specific heat is observed at low temperatures [10]. All this evidence places CeTl₃ (which is the $x \rightarrow 0$ limit of the Ce(Tl_{1-x}Sn_x)₃ system) on the $g(x) < g_{\max}$ region. The same features are observed in Ce(Pd_{1-x}Rh_x) [11]. An apparent contradiction emerges here from the fact that, from their $dT_0/dg < 0$ slope, these two systems are expected to belong to the g region with a mixed regime, while their $x \rightarrow 0$ limit corresponds to a 'full magnetic' one.

Such a contradiction has a cruder example in the Ce(Pd_{1-x}M_x) family of compounds, where M = Ni or Rh [12]. In both cases the $x \rightarrow 1$ limit corresponds to an intermediate valent (IV) behaviour and, as mentioned before, CePd is a *full ferromagnetic* compound. The Ce(Pd, Ni) system undergoes an F-to-IV transformation, with T_C (= 6.5 K at $x = 0$) passing through a maximum value as Pd is substituted by Ni, but when Pd is substituted by Rh, T_C decreases continuously [12] despite the fact that the same F-to-IV transformation is induced (see figure 3). In this case the same 'matrix' compound, CePd, confronts two different behaviours which have the same low g as the starting value. From such experimental evidence, it becomes clear that the Doniach model does not properly assess the parameters that determine the behaviour of these systems.

2. Comparison between volume and electronic concentration effects

The g parameter cannot be experimentally controlled or quantified in any direct manner. In fact, the *driving* experimental parameters are the external pressure and 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 in the electronic concentration (ΔZ). In that case one has to ask whether ΔV and ΔZ are the alternative empirical parameters for defining g , and whether they are equivalent for describing the phase diagram of figure 1 and the experimental results shown

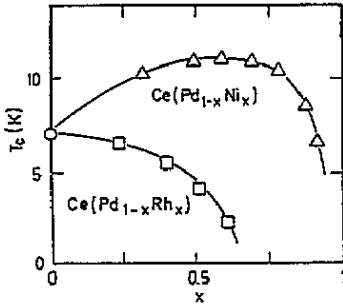


Figure 3. Ordering temperature as a function of Pd substitution by Ni or Rh.

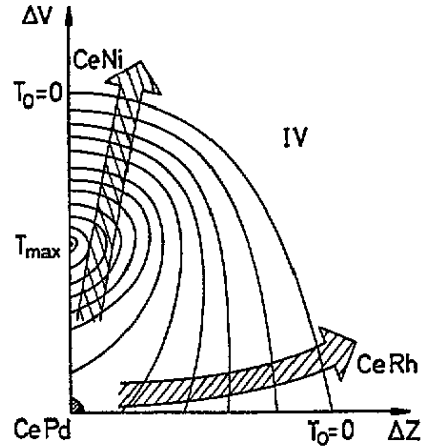


Figure 4. Schematic comparison of the respective ΔV and ΔZ effects on the magnetic to non-magnetic transformation of Ce(Pd, Ni) and Ce(Pd, Rh). The full curves indicate points of equal ordering temperature. T_{\max} indicates the maximum value of T_0 .

in figure 3. Experimentally, it is not possible to change only one of these two parameters without inducing minor variations in the other. However, there are cases where one of those variations is truly dominant. For example, by applying external pressure the main effect is a change in volume (ΔV), without a significant effect on the electronic composition ($\Delta Z \approx 0$).

In the case of the Ce(Pd, M) family, the ΔV and ΔZ effects are induced by alloying Pd with Ni and Rh respectively. In the case of Pd and Ni, they have different atomic volumes but a similar electronic structure (they belong to the same column in the periodic table), while Pd and Rh have equal atomic volumes but a different number of electrons in the 4d open shell. As well as the difference in the $T_0(x)$ dependence, the thermal, transport, structural and spectroscopic properties of these systems also have different dependences on x [12]. This experimental evidence indicates that ΔV and ΔZ produce different effects on the Ce GS evolution, which are represented in an unified diagram in figure 4 concerning the T_0 evolution with the two driving forces.

Once the difference between the volume and the electronic concentration effects has been recognized in one case, the question arises whether such a difference is in fact a general rule or not. At present, the only experimental example which allows us to compare the Ce magnetic transformation when it is driven by the mentioned parameters, starting from the same magnetic compound, is Ce(Pd, M), with M = Ni and Rh. To our knowledge other possible cases, like Ce(Ni, Cu)₅ with M = Co, Cu and Pt or Ce(Pt, M)₂, with M = Ni and Ir, have not been studied. There are, however, some sets of binary and ternary Ce compounds where one of the driving forces is dominant when the Ce ligand is alloyed, and therefore their $T_0(x)$ evolution can be compared with that of the reference Ce(Pd, M) system.

2.1. Generalization to other systems

In order to obtain a systematic comparison among different sets of compounds, some restrictions have to be applied to avoid eventual ambiguities in the conclusions. They

are the following. (i) In order to avoid spurious variations in the Ce environment no structural changes, within the substitution range, should occur. (ii) The analysed compounds should present a single lattice position for Ce and its partners, to avoid ambiguities in the environmental conditions. (iii) The Ce magnetic moment in the magnetically ordered compounds has to be localized. Conditions (i) and (ii) are self-explanatory, while (iii) requires comment. There are some Ce compounds which show band (or itinerant) magnetism (BM), like CePb₃; in such a case the magnetic order does not have an RKKY character originating in localized magnetic moments, and the magnetic structure is very unstable under alloying effects [13].

Table 1. Correlation between the occurrence (or not) of a maximum in $T_0(x)$ and the dominant effect: volume (ΔV) or electronic concentration (ΔZ). x_{\max} is the concentration at the maximum value of T_0 , and x_0 the concentration at which $T_0 \rightarrow 0$, for a generic compound $\text{Ce}(\text{X}_{1-x}\text{Y}_x)_j$. The pressure (P) is given in GPa. * denotes that there is a discontinuity in the lattice parameter at $x = 0.1$, without change of structure. NK means not known.

Compound	Dominant effect	x_{\max} (P_{\max})	x_0 (P_0)	Ref.
Alloying				
Ce(Pd, Ni)	ΔV	0.6	0.95	16
Ce(Pt, Ni)	ΔV	0.5	0.95	17
Ce(Pd, Rh)	ΔZ	—	0.7	8
Ce(In, Sn) ₃	ΔZ	—	0.15	18
Ce(Tl, Sn) ₃	ΔZ	—	0.8	10
Ce(Ge, Si) ₂	ΔV	0.5	0.7	19
Ce(Pt, Ir) ₂	ΔZ	—	NK	20
Ce(Cu, Al) ₅	ΔZ	—	0.4	21
Ce(Pd, Ni)Sn	ΔV	0.25	0.8	22
Ce(Pt, Ni)Sn	ΔZ	—	0.8	23
CeIn(Ag, Cu) ₂	ΔV	0.75	>1	24
CeRh ₂ (Ge, Si) ₂	ΔV	0.88	>1	25
Ce(Rh, Co) ₂ Si ₂	ΔV^*	—	0.12	13
Ce(Rh, Ru) ₂ Si ₂	ΔZ	—	0.4	26
Ce(Os, Ru) ₃ B ₂	ΔV	0.1	>1	27
Ce(Pd, Rh)In	ΔZ	—	0.0	28
Pressure				
CeAg	ΔV	0.7	3.7	7
CePt	ΔV	3.0	NK	29
CeP	ΔV	3.0	5.5	30
CeAs	ΔV	4.7	>8.0	30
CeAg ₂ Si ₂	ΔV	1.5	NK	31

In table 1 we list a number of binary and ternary Ce systems undergoing the magnetic to non-magnetic transformation, mainly driven by one of the two ΔV or ΔZ effects. One sees that they are correlated with the presence or absence of a maximum in $T_0(x)$. As before, ΔV is obtained by substituting elements of the same column in the periodic table (expected to be nearly isoelectronic) and ΔZ by elements having similar size. To allow for a systematic comparison we have adopted the following convention: in a generic compound $\text{Ce}(\text{X}_{1-x}\text{Y}_x)_j$, x increases when the larger atom X is substituted by the smaller atom Y, independently of the criteria used in the literature for displaying the experimental data. In

that sense the increase of x indicates a structural pressure. With respect to the compounds studied under applied pressure, all of them show a maximum in $T_0 = f(P)$, see also table 1.

The information extracted from an analysis of the more than twenty families of Ce compounds listed in table 1 tells us that the occurrence of a maximum in $T_0(x)$ is directly correlated with the reduction of the Ce–Ce spacing. Such a conclusion is in agreement with the nature of the RKKY indirect exchange via the conduction electrons. Again, it can be argued that the systems in which $T_0(x)$ continuously decreases (ΔZ effect) may be placed in the $g_{\max} < g(x) < g_0$ region. In such a case the magnetic side (i.e. the $x = 0$ compound) should show some evidence of a mixed state, which is not the case for CeGe₂ and CeCu₅ or the already discussed CePd and CeTi₃ [2]. As mentioned before, CePd is the $x = 0$ limit for the systems that either show a maximum in $T_0(x)$ (like Ce(Pd, Ni)) or show no maximum (like Ce(Pd, Rh)).

The Ce(Rh, Co)₂Si₂ system seems to be an exception to the conclusion extracted from table 1. However, analysing in detail its $T_0(x)$ dependence, one sees that in the x region, where $T_0(x)$ decreases continuously there is no change in the volume cell ($\Delta V = 0$). The ΔV effect reported in table 1 occurs in fact at $x > x_0$ [14]. Another illustrative case concerning the $T_0(x)$ dependence is the Ce(Pb, Sn)₃ system. It was not included in table 1 because of the BM character of the $x = 0$ compound CePb₃ [13] (remember restriction (iii)). Effectively, $T_0(x)$ decreases very rapidly with the Pb substitution by Sn. Also the Néel temperature of CePb₃ itself decreases with pressure [15], in contrast to the local moment magnets CeAg and CePt. A similar local-moment to itinerant (or BM) magnetism transformation was observed in Ce(Cu, Ni)₂Ge₂, in coexistence with heavy-fermion behaviour [32].

3. Conclusions

The conclusion of this comparison is that the variations of volume or electronic concentration are not equivalent as *driving forces* for inducing a magnetic to non-magnetic transformation in Ce compounds. The occurrence of a maximum in $T_0(x)$ or $T_0(P)$ is not intrinsic to the crossover from a full magnetic to a mixed state, but is rather due to the reduction of the Ce–Ce spacing before the hybridization mechanism turns on. Therefore, the magnetic character of a compound has to be checked taking into account the entropy of the ordered phase, before placing it in the $g < g_{\max}$ or $g > g_{\max}$ region. In table 1 we have listed only those systems in which one of the driving forces is dominant, but there is an equivalent number of systems where both parameters are changed simultaneously. An analysis of the characteristic concentrations at which the magnetic transformation occurs will be the subject of a forthcoming work.

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