Atypical thermodynamic behavior of Ce compounds in the vicinity of zero temperature Critical Points

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A systematic analysis of thermodynamic properties performed on Ce-base exemplary compounds allows to identify different types of behaviors as the system approaches the quantum critical region. They are recognized in the respective magnetic phase boundaries \( T_{N,C}(x) \) as a change from the classical negative curvature to a linear composition \( (x) \) dependence, the occurrence of a critical point or the evanescence at finite temperature under pressure at finite temperature. In the first case, an anomalous reduction of the entropy \( S_m \) respect to the \( S_m = R \ln 2 \) value (expected for the usual Ce-magnetic doublet ground state) is observed around \( x_{cr} \), and analyzed taking profit of detailed studies performed on \( CeIn_{3-x}Sn_x \) alloys. As expected from Maxwell relations, the volume variation \( V_0(x) \) at \( T \to 0 \) also shows a non-monotonous behavior around \( x_{cr} \).

Different regimes in the entropy variation of the ordered phase \( (S_{MO}) \) are recognized. Only in the former case \( S_{MO} \to 0 \) continuously as \( T_{N,C} \to 0 \), whereas in the second \( S_{MO}(x,B) \) remains constant till a first order transition occurs. In the third case, the degrees of freedom of the MO phase are progressively transferred to the heavy fermion component as indicated by the decreasing \( \Delta C_m(T_N) \) jump which vanishes at finite temperature.

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I. INTRODUCTION

Magnetic phase transitions can be experimentally driven by external control parameters such as chemical composition, pressure or magnetic field. Their application allows to trace the evolution of fluctuations related to a second order transition as its associated thermal energy decreases. In the limit of zero temperature, thermal fluctuations become intrinsically frozen and a phase transition may only have a quantum character. In fact, a quantum critical point (QCP) is defined \( \| \) as the \( T = 0 \) limit for a second order transition driven by one of the mentioned non-thermal control parameters. Despite of its unattainable nature, a \( T = 0 \) QCP presents a sort of 'halo' of related quantum fluctuations whose physical effects are observed at finite temperature \( \| \| \). The phenomenology arising from those low lying energy excitations is known as that of a 'non-Fermi-liquid' (NFL) \( \| \| \| \), in contrast to the canonical Fermi-liquid observed in non-magnetic regimes. One of the most relevant feature of NFL systems is the increasing density of low energy excitations reflected as a divergency of thermal parameters like specific heat divided temperature \( (C_m/T) \) when \( T \to 0 \). Other physical parameters, like magnetic susceptibility, thermal expansion and electrical resistivity also show unusual behaviors \( \| \).

In this work, we focus on the thermodynamical implications the peculiar behavior of \( C_m/T \) and the related entropy \( (S_m) \) at low temperature. The phase boundaries taken into account are driven by the current control parameters: chemical potential, pressure and magnetic field. In the former case, the chemical potential is tuned by the variation of the composition of Ce-ligands. The related experimental evidences are analyzed in Section II and discussed in Section III. These results are compared in Section IV with the phenomenology observed in other types of phase diagrams including pressure driven systems.

II. CHARACTERISTIC PROPERTIES OF CE-LIGAND ALLOYED SYSTEMS.

Three exemplary Ce binary compounds are taken as referents for the present analysis after their deeply investigated low temperature properties. In all of them the ordering temperatures \( (T_{N,C}) \) were driven within an extended range by changing the composition of Ce-ligands \( (x) \). This procedure allows to preserve the lattice of Ce magnetic atoms without changes in the local symmetry and minimizing any modification of the magnetic interactions. Their respective magnetic behaviors are antiferromagnetic (AF): \( CeIn_{3-x}Sn_x \) \( \| \| \| \) and \( CePd_3Ge_{2-x}Si_x \) \( \| \| \), and ferromagnetic (FM): \( CePd_{1-x}Rh_x \) \( \| \).

A typical magnetic phase boundary related to a second order transition shows a negative curvature as a function of applied control parameters. Such a phase boundary extrapolates to a critical value \( x^* \) as the transition temperature \( T_{N,C} \) \( 0 \), see e.g. the case of \( CeIn_{3-x}Sn_x \) in Fig. \( \| \). In the mentioned exemplary compounds, however, a
change of curvature around 2K occurs \[^{[8]}\] as shown in Fig. 1. At that concentration the system enters into a pre-critical region between \(x^* < x < x_{cr}\). That change of regime is also observed in other Ce-ligand concentration dependent systems but, to our knowledge, not in pressure or magnetic field driven systems.

The observed change of regime can be explained by taking into account the competition between the decreasing energy of the thermal fluctuations (which extrapolates to \(x^*\)) and the temperature independent energy of the quantum fluctuations. Despite of the fact that quantum fluctuations are related to \(T \rightarrow 0\) phenomena, these experimental evidences indicates that below \(\approx 2K\) the latter mechanism takes over and dominates the scenario driving \(T_N \propto |x - x_{cr}|\) as can be observed in Fig. 1, for two AF exemplary compounds. In the case of the FM one (see Fig. 1c) \(T_C(x)\) decreases asymptotically till it collapses to zero at a first order transition. Strictly, the alternative of a linear \(T_C(x)\) dependence in the very last concentrations before \(x_{cr}\) can be considered as discussed in Ref. \[^{[7]}\].

### A. Specific heat

Within the pre-critical region, the specific heat of the exemplary compounds show a common temperature dependence since the respective maxima \(C_{max}(T_{N,C})/T\) tends to a constant value \[^{[8]}\] as the critical concentration is approached, see Fig. 2. Hereafter, \(C_m\) indicates the magnetic contribution to the specific heat after phonon subtraction.
extracted from the respective La isotopic compounds. Such a behavior for \( x > x^* \) clearly differs from the observed within the canonical regime \((x < x^*)\) where \( C_{\text{max}}(T_{N,C})/T \) decreases with \( T_{N,C}(x) \). This behavior can be analyzed within the scope of the Ginzburg-Landau theory for a second order transition, where \( C_m/T = \alpha^2/2b \) at \( T_{N,C} \), being \( a \) and \( b \) the coefficients of the free energy expansion \( G(\psi,T) = G_0(T) + a(T)\psi^2 + b(T)\psi^4 \). This indicates that, within the pre-critical region, the \( G(\psi,T) \) dependence on the \( \alpha^2/b \) ratio is locked and consequently the entropy of the ordered phase decreases linearly according to the law of corresponding states.

Further peculiarities are observed in the tail of \( C_m(T)/T \) above \( T_{N,C} \) which shows a divergent \(-\log(T/T_0)\) dependence characteristic of NFL systems \([9]\). This behavior is illustrated in Fig. 3 for two AF compounds. To remark the universality of this logarithmic dependence, we compare in that figure the \( C_m(T)/T \) results for different concentrations of \( CeIn_{3-x}Sn_x \) within the pre-critical concentration range and different applied pressures \( (p) \) on \( CeCu_{5.8}Au_{0.2} \) which lies close to the critical point \([10]\). Since in both cases \( T_N \) decreases linearly with respective control parameters \( x \) and \( p \) their \( C_m(T)/T \) tails can be scaled by a simple shift of the temperature like \( \Delta T = T - T_N \). Notice the low temperature flattening of \( C_m/T \) which skips the \( T \to 0 \) divergence according to thermodynamic laws.

**B. Low temperature properties of \( CeIn_{3-x}Sn_x \)**

In this section we will analyze the low temperature magnetic contribution to the specific heat and entropy \( S_m(T) \) of \( CeIn_{3-x}Sn_x \), which was investigated in detail around its critical concentration \([5]\). Similarly to the analysis performed in Fig. 3 we present in Fig. 4 the \( C_m(T)/T \) dependence extended to seven concentrations \((0.41 \leq x \leq 0.80)\) versus the previously defined normalized temperature \( \Delta T = T - T_N \), now including the magnetically ordered phase into the negative range of \( \Delta T \), see the upper \( x\) axis. There, one can see the already mentioned scaling of the \( C_m(T > T_N)/T \) tails of the alloys belonging to the pre-critical region \((0.45 \leq x \leq 0.70)\). In order to remark the validity of this scaling, we also include in that figure the results obtained from the \( x = 0.41 \) and \( 0.80 \) alloys placed beyond limits of the pre-critical region. As it can be seen, their respective \( C_m/T \) dependencies clearly deviate from the scaled ones.

In Fig. 4, the vertical line at \( \Delta T = 0 \) line splits the \( C_m/T \) contribution in two parts, i) the ordered phase (MO), hereafter labeled as \( C_{MO}/T \) and ii) the tail at \( \Delta T > 0 \), hereafter identified as \( C_{NFL}/T \) because of its NFL behavior. Notably, also the \( C_{MO}/T \) contributions for the samples within the pre-critical region overlap each other in this representation. Samples \( x = 0.41 \) and
0.45 show a weak peak slightly below $T_N$, related to a first order transition appearing around $x = x^*$, but playing no role in the present study. The relevant feature is that the $C_{MO}/T$ overlap allows an extrapolation of $C_{MO}/T \rightarrow 0$ to $\Delta T \approx -4$ K which is independent of concentration. We remark that a $\Delta T < 0$ value does not correspond to a negative temperature but simply to a common extrapolation to a zero value of the $C_m/T$ contribution.

The key parameter to describe this peculiar behavior of the specific heat is its associated entropy, evaluated as $S_m = \int C_m/T \,dT$. According to the definition proposed for $\Delta T$, one may split the total entropy (c.f. measured $S_m(T)$) as $S_m = S_{MO} + S_{NFL}$, being $S_{MO}$ the contribution of the MO phase for $\Delta T \leq 0$ and $S_{NFL}$ the one from the NFL tail for $\Delta T \geq 0$. For the following analysis we take as reference the entropy variation of sample $x = 0.41$ because it contains largest $S_{MO}$ contribution among the samples included in Fig. 4. As it can be appreciated in the figure, the $S_{MO}(x = 0.41)$ contribution slightly exceeds 0.2$RLn2$ whereas $S_{NFL}$ reaches $\approx 0.6$ $RLn2$ (see inner right axis). Noteworthy, the full $RLn2$ value is only reached once the extrapolation to the $C_m/T = 0$ value at $\Delta T \approx -4$ K is included, as depicted using the lowest ‘$\Delta T + 4$’ and outer ‘$\Delta T + S_{NFL}$’ right axes in Fig. 4. Since $S_{NFL} \approx 0.6$ $RLn2$ does not change with concentration, but $S_{MO} \rightarrow 0$ as $x \rightarrow x_{cr}$ one concludes that about 40% of the $RLn2$ entropy is missed as $T_N \rightarrow 0$.

It is evident from Figs. 3 and 4 that the decrease of $S_{MO}(x \rightarrow x_{cr})$ as $\Delta T \rightarrow 0$ is not transferred to the NFL phase at $\Delta T > 0$ because $S_{NFL}$ is independent of concentration in this concentration range. The relevant conclusion of this analysis is that the degrees of freedom become exhausted at $x = x_{cr}$ whereas those belonging to the NFL phase remain unchanged on the 60% value of $RLn2$.

The loss of entropy showed by this Ce compound is not an exception because, in the cases where this type of analysis was performed, it was found that the $RLn2$ value for a doublet ground state (GS) is not reached. Particularly, the compounds showing a $C_{m}/T \propto \log(T/T_{0})$ dependence cannot not exceed $\approx 60\%$ $RLn2$ [2]. Since the mentioned $\log(T/T_{0})$ dependence corresponds to one of the possible scenarios for QCPs predicted by theory [2], it means that this lack of entropy or the consequent arising of zero point entropy ($S_0$) is intrinsic to the NFL phenomenology approaching that point. Simplistic explanations looking for a some extra entropy contribution at higher temperature fail because it would imply a discontinuous transference of entropy from the $T_N \rightarrow 0$ MO phase to temperature above 20 K according to Fig. 3 We recall that in CeIn$_3$ crystal-field excited quartet lie high enough in energy ($\approx 100$ K [11]) to not be involved in the present analysis.

This decrease of entropy at a fixed temperature around the critical concentration can neither be attributed to the Kondo temperature increase because, in such a case, the proper T scaling would have been $t(x) = T/T_K(x)$ instead of the observed $\Delta T = T - T_N$. A direct experimental evidence that $T_K$ practically does not change within that range of concentration is given by the fixed temperature of the maximum of the electrical resistivity ($T_{\text{max}}$).

In CeIn$_{3-x}$Sn$_x$ $T_{\text{max}} \approx 19$ K $\approx T_0$ within the pre-critical region, and it starts to increase only beyond $x_{cr}$ [12].

### III. DISCUSSION

#### A. Characteristic critical concentrations

A full magnetic phase diagram covering all the possible GS of Ce systems should include at least three characteristic critical concentrations were clear changes of regime occur. To our knowledge, the first attempt to encompassing such a phase diagram was performed nearly two decades ago by comparing different magnetic behaviors extracted from seventeen Ce systems driven by Ce-ligands alloying [13]. That analysis covered all possible Ce GS from local moment (magnetic) regime to the unstable valence (non-magnetic) one, and allowed to recognized two relevant concentrations: one related to the zero temperature extrapolation of the magnetic phase boundary (previously identified as $x^*$), and the other where the paramagnetic temperature starts to rise powered by the increase of the Kondo screening ($x_K$). Different types of phase diagrams were recognized depending whether $x^* < x_K$ or $x^* \geq x_K$. A third characteristic concentration was identified in Ce systems reaching the unstable valence regime at $x_{UV}$. This concentration is related to the appearance of the sixfold degenerated Fermi liquid behavior, originated in the Ce $J = 5/2$ Hund’s rule angular moment. This characteristic concentration exceeds the purpose of the present study because we are limited to the twofold GS regime.

Since at that time the usual low temperature limit for magnetic studies was around one degree Kelvin, no quantum fluctuation effects were evident enough to be taken into account. Therefore, the $0 \leq x \leq x^*$ range dominated by thermal fluctuations and showing the typical negative curvature of $T_{N,C}$ was taken as valid down to $T = 0$. The new available experimental information indicates
the outstanding effect to be discussed is the strik-

gance of the transition and its identification in the topological character of the state as represented by the coexistence of two ground states at a given temperature

1.0
0.5
0.0
0.8
1.0
0.8
0.6

FIG. 5: (Color online) a) Concentration dependence of the entropy $S_m(x)$ of CeIn$_{3-x}$Sn$_x$ measured up to 20K and the zero point entropy $S_0$ computed as the difference respect the total expected value $R \ln 2$. The arrow indicate the critical concentration. b) Comparison of the temperature dependence of $S_m$ between an alloy $x = 0.15$ belonging to the classical region and one lying on top of the critical concentration $x = 0.70$ showing a deficit of $\approx 40\%$.

that approaching $x^*$ there is a change of curvature (present in Fig.1), occurring at finite temperature $T_{NC} \approx 2$ K. At present, the $x \rightarrow x^*$ extrapolation is currently left aside because the $T_{NC} \rightarrow 0$ limit occurs at higher concentration ($x_{cr} > x^*$). Nevertheless, $x^*$ keeps its relevance because it identifies a characteristic concentration at which the decreasing thermal energy would have driven the phase boundary to $T = 0$ in the absence of quantum (i.e. non thermal) phenomena.

Apart from the mentioned modification of the $T_{NC}(x)$ curvature, the change of regime around $x^*$ is related to some interesting features occurring at that concentration. Among them, there is the formation of a new phase at $T_1 \leq T(x^*)$ like in CeIn$_{3-x}$Sn$_x$ [5] and CePd$_2$Ge$_{2-x}$Si$_x$ [6]. Moreover, if we compare these phase diagrams with those driven by applied pressure, one sees that the corresponding $p^*$ value of that control parameter is frequently at the edge of the appearance of superconductivity [12]. Notably, in that case there is no change of curvature in $T_N(p)$ because the phase boundary itself vanishes above the superconductive dome.

B. Pre-critical region and Zero point Entropy

Focusing now in the $x^* \leq x \leq x_{cr}$ region, the outstanding effect to be discussed is the strik-

FIG. 6: (Color online) Low temperature thermal variation of the unit cell volume normalized at $T = 8$ K, well above any quantum fluctuation effect. Thermal expansion data from [13] Inset, detail of the $V(x,T \rightarrow 0)$ variation taking as a reference the $x = 0.80$ sample placed above the critical concentration.

An alternative description for this phenomenon can be derived from the concept of 'Rare Regions' proposed in Ref. [1] where those regions can be conceived as a sort of magnetic clusters. This scenario may apply for magnetic moments interacting FM like in CePd$_{1-x}$Rh$_x$, however for AF systems like CeIn$_{3-x}$Sn$_x$ such a cluster formation is unlikely. If one takes into account that at $T_N \rightarrow 0$ only quantum fluctuations may allow the system to access to two minima via quantum tunnelling, a new degeneracy would arise as the quantum critical regime takes over. For a quantum phase transition, those minima would correspond to different phases which cannot be thermally connected at $T \rightarrow 0$.

In such a context, the entropy collected at finite temperature corresponds to the progressive thermal access to the excited Karmen’s level. In such a case a $S_{NFL} = R \ln(3/2)$ increase of entropy would
be expected instead of \( R \ln 2 \). Quantitatively, this value corresponds to the experimentally observed one because \( \ln(3/2) = 0.6 \ln 2 \).

C. Thermal Expansion

In order to confirm the present analysis of the anomalous evolution of the entropy approaching the critical point as due to an intrinsic effect, another thermodynamic parameter sensitive to this phenomenon has to be looked for. Such alternative is provided by the thermal expansion \( \beta(T, x) \) which is related to the entropy through the Maxwell relation \(-\partial S/\partial P = \partial V/\partial T\). Thus an anomalous \( S_0(x \to x_{cr}) \) dependence should have a replica in \( V_0(x \to x_{cr}) \) as \( T \to 0 \). In this case, the effective pressure is originated in the chemical pressure produced by alloying.

The thermal expansion variation of \( CeIn_{3-x}Sn_x \) was studied down to the mK range in the vicinity of the critical concentration \([15]\). In Fig. 8 we compare the thermal variation of the volume computed as \( V(T) = \int \beta dT \). Then, by following the Gr"uneisen criterion: \( V(T) = V_0(x) + V(x, T) \), we have normalized \( V(x, T) \) well above any quantum fluctuation effect, i.e. \( 4K \leq T \leq 8K \). In the inset of Fig. 8 the detail of the \( V(x, T \to 0) \) variation is shown, taking as reference the \( x = 0.8 \) alloy which lies beyond the critical point. Both abnormal \( S_0(x_{cr}) \) and \( V(x_{cr}) \) dependencies are compared in the general phase diagram for \( CeIn_{3-x}Sn_x \) presented in Fig. 7.

FIG. 8: (Color online) (a) Specific heat of the concentration dependent \( Ce_2Ni_{2-x}Pd_xSn \) system after Ref. [16] and (b) specific heat divided temperature of field dependent \( URu_2Si_2 \) after Ref. [17].

IV. DIFFERENT SCENARIOS FOR \( S_{MO} \to 0 \)

To fulfill the condition that a QCP occurs when a second order transition is driven to \( T = 0 \) by a non-thermal control parameter \( B \) it is required that the entropy condensed into the ordered phase decreases monotonously to zero, i.e. \( S_{MO} \to 0 \). This condition is in agreement with the previously mentioned constant value of \( C_{max}(T_{N,C} \leq 2K)/T \), which implies that \( C_{max}(x \to x_{cr}) \to 0 \) due to the continuous decrease of the MO degrees of freedom. Such is the behavior observed in the Ce systems presented in Section II (c.f. Fig. 2) and other celloid alloyed compounds.

According to thermodynamics, if the condition that \( S_{MO} \to 0 \) as \( T_{N} \to 0 \) is not fulfilled, the magnetic phase boundary shall end at a finite temperature critical point due to entropy accumulation when \( T_N \) decreases. Due to that entropic bottleneck a first order transition should occur to drive
In contrast to the behavior discussed in Section II, the former is a recently studied compound driven by Ce-ligands alloying, whereas the latter is the well known U compound showing hidden magnetic order. Its phase boundary is driven to zero by applying very high magnetic field \( B \). It is worth to note that the \( C_m(x\alpha B)/T \) variation of the maxima are described by practically the same function: 6.5 and 7.2/\( T \) respectively, as indicated in Fig. 8. In contrast to the behavior discussed in Section II, here is the \( C_m(T_N) \) maximum that remains constant (instead of \( C_m/T \)) till the first order transition occurs (at \( B \approx 33 \) T in URu\(_2\)Si\(_2\)). Its first order character is recognized from the value of the \( C_m(T_N) \) maximum clearly exceeding the \( \propto 1/T \) function.

These coincidences also occur in the entropy gain up to \( T_N \) which shows the same value \( S_{MO}(T_N) \approx 1.3 \) J/Ce at. K, (notice that Ce\(_2\)Ni\(_{1-x}\)Pd\(_x\)Sn contains two Ce atoms per formula unit). The fact that control parameters of different nature produce practically identical effects is a fingerprint for the universality of this behavior. In Fig. 9 we compare this \( S_{MO} \) value with the corresponding one obtained for Ce\(_3\)In\(_{3-x}\)Sn\(_x\), which decreases monotonously to zero as \( T_N \to 0 \). As expected, the \( S_{MO}(T_N) \approx 1.3 \) J/Ce at. K value exceeds the \( x \) dependent of the first group before they reach the critical point (see Fig. 9).

A third group of magnetic Ce-base systems, mostly driven by applied pressure, behave differently. The relevance of their phase diagrams arises from the frequent appearance of a superconductive phase [14], which is currently related to the AF phase boundary itself. Nevertheless the thermodynamic analysis of those phase boundaries, mainly constructed from transport properties, reveals that such a putative extrapolation is quite arbitrary. Technical difficulties for specific heat measurements at high pressure are well known, however some exemplary compounds like: CePd\(_2\)Si\(_2\) [15], CePd\(_2\)Ge\(_2\) [16], CePd\(_2\)Al\(_2\)Ga [17] and CeIn\(_3\) [21] provide relevant information to recognize their distinct behavior respect to those described in Fig. 9. The common feature of these compounds is the progressive transference of the magnetic degrees of freedom to the non magnetic heavy fermion component in the region where \( T_N(p) \) decreases. Since
AC-specific heat techniques used in the study of CePd$_2$Si$_2$ and CePd$_2$Ge$_2$ does not allow to access to absolute values of $C_m(T)$ or $S_m(T)$, we have used as quantitative reference specific heat measurements performed on CePd$_2$Al$_2$Ga [20] and CeIn$_3$ [21] measured by standard heat pulse. Particularly, in Fig. 10 we present the results obtained for the latter compound. The comparison with the other compounds is done using the relative variation of the $C_m(T_N)$ jump driven by pressure as depicted in Fig. 11. The relevant conclusion from that figure is that in all these compounds, the transition vanishes at finite temperature [22], clearly above from the appearance of superconductivity. It should be mentioned that the competition between magnetism and superconductivity observed in the family of CeThIn$_3$ compounds [23] cannot be included in this group and merits its own analysis.

As mentioned before, the distinction between different types of magnetic phase diagrams in Ce systems driven by alloying Ce-ligands is known since nearly two decades [13] and it was related to abnormal maxima of the physical properties like $\rho_0(x)$ resistivity and $\gamma(x)$ coefficient around the critical concentrations [24]. Latter on, significant experimental and theoretical progress was done increasing the knowledge of the microscopical mechanisms governing quantum critical phenomena [21]. However, those models were currently applied to a few specific systems and to our knowledge, any wide systematic comparison was performed on thermodynamic properties of Ce-base compounds. From the rich spectrum of experimental results available at present we can better correlate thermodynamic behaviors in these exotic conditions, which confirm the validity of the conclusions extracted time ago from higher temperature ($T < 1$) K properties concerning the existence of different types of magnetic phase diagrams.

V. CONCLUSIONS

In this study we have analyzed and compared the low temperature thermodynamic behavior of a number of Ce-magnetic systems showing that three types of phase diagrams can be clearly distinguished. Depending on the behavior of the $T_{N,C}$ phase boundaries, the phase diagrams can be classified as follows: i) those where the phase transition is continuously driven to zero, ii) those ending in a critical point at finite temperature, and iii) those whose phase boundaries vanish at finite temperature because their MO degrees of freedom are progressively transferred to a non magnetic component.

In the first case the possibility to reach a QCP is supported by the continuous decrease of the $S_{MO}$ entropy, which extrapolates to zero as $T_{N,C} \rightarrow 0$. Despite of its monotonous decrease, the phase boundary driven by alloying Ce-ligands shows a change of curvature at $x = x^*$. This behavior is attributed to a change of regime from a classical to the pre-critical one since beyond that concentration quantum fluctuations seem to dominate the scenario. Strikingly, such a change occurs at similar thermal energy $E_{th}/k_B \approx 2$ K in all studied systems, and below that temperature a tendency to saturation of the $C_m(T_{N,C})/T$ maxima values arises as a distinctive characteristic.

Contrary to current suppositions, the reduction of $S_{MO}$ as $T_{N,C} \rightarrow 0$ is not transferred to the paramagnetic phase as it was quantitatively demonstrated by the exemplary system CeIn$_3-x$Sn$_x$. A detailed analysis allows to evaluate an anomalous reduction of about 40% of the entropy respect to reference value $R \ln 2$ expected for a doublet GS. This missed entropy can be regarded as a zero point entropy. In the critical region, the total entropy gain up to about 20 K coincides with the $R \ln(3/2)$ value which would correspond to a modification of the degeneracy the ground state once the system enters the quantum regime and quantum tunneling plays a relevant role. The discussion about the validity of this and alternative explanations remains open.

These characteristics of the group with $S_{MO} \rightarrow 0$ monotonously are in contrast with those of the second type of phase diagrams. There, is the $C_m(T_N)$ maxima values which are found to be constant (instead of $C_m/T$ like in the first group). In this case the entropy accumulation as $T_N$ decreases makes the phase boundary to end at a finite temperature critical point. There, a first order transition drops $S_{MO}$ to 0. This scenario was detected in a system driven by Ce-ligand composition and confirmed by a well known $U$ compound driven by magnetic field. Notably both systems coincide in their $S_{MO}$ values.

The third type of behavior is clearly identified from the systems whose phase boundaries are driven by pressure. In this case, specific heat results indicate that the phase boundary itself vanishes in a progressive transference of degrees of freedom to the non-magnetic component, occurring at $T \geq 2$ K. Despite of the formation of a superconductive phase their magnetic phase boundaries do not reach that transition because it occurs below the 2 K threshold. This type of behavior cannot be excluded in Ce-ligand alloyed system thought there the occurrence of superconductivity is unlikely.
To our knowledge, most of these different experimental observations are no explained by current models focused into the physics of QCP. This is probably due to the difficulty of a quantitative treatment of thermodynamic parameters like entropy or the specific heat jump.

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