Searching for a Quantum Critical Point in Rh doped ferromagnetic Ce$_{2.15}$Pd$_{1.95}$In$_{0.9}$

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Abstract.
Low temperature magnetic and thermal ($C_m$) properties of the ferromagnetic (FM) alloys Ce$_{2.15}$(Pd$_{1-x}$Rh$_x$)$_{1.95}$In$_{0.9}$ were investigated in order to explore the possibility for tuning towards a quantum critical point (QCP) by doping Pd with Rh. As expected, the magnetic transition decreases from $T = 4.1$ K at $x = 0$ with increasing Rh concentration. However, the phase boundary splits into two transitions, the upper being antiferromagnetic (AF) whereas the lower FM. The AF phase boundary extrapolates to $T_N = 0$ for $x_{cr} \approx 0.65$ whereas the first order FM transition vanishes at $x \approx 0.3$. The quantum critical character of the $T_N \rightarrow 0$ point is inferred from the divergent $T$ dependence of the tail of $C_m/T$ observed in the $x = 0.5$ and 0.55 alloys, and the tendency to saturation of the maximum of $C_m(T_N)/T$ currently observed in exemplary Ce compounds when $T_N \rightarrow 0$. Beyond the critical concentration the unit cell volume deviates from the Vegard's law in coincidence with a strong increase of the Kondo temperature.

1. Introduction
The Ce$_{2+\delta}$Pd$_{2+\nu}$In$_{1-\nu}$ family of alloys shows an extended range of solid solution [1] with a peculiar magnetic behavior since the Ce-rich branch ($t > 0 > u$) behaves ferromagnetic (FM) whereas the Pd-rich ($t > 0 > u$) is antiferromagnetic (AF). Such a difference of magnetic structure under a slight variation of the alloy composition indicates that the energies of both phases are very similar. Another evidence for the competition between magnetic structures in this type of compounds is given by Ce$_2$Pd$_2$Sn [2], which shows a competition between ferro- and antiferromagnetic phases with a finite temperature critical point tuned by 25% Ni doping. Consequently this family of alloys are appropriate materials for testing the stability of exotic order parameters.

For this work, we have exploited the FM character of the Ce$_{2.15}$Pd$_{1.95}$In$_{0.9}$ composition to search for a quantum critical point (QCP) [3] by tuning the chemical potential through the doping of the Pd lattice with Rh, like in the previously studied pseudo-binary compound CePd$_{1-x}$Rh$_x$ [4]. For such a purpose, we have investigated the low temperature properties through magnetic ($M$) and specific heat ($C_P$) measurements performed on the Rh doped Ce$_{2.15}$(Pd$_{1-x}$Rh$_x$)$_{1.95}$In$_{0.9}$.

2. Experimental and results
This alloyed system forms continuously all along the complete Pd/Rh concentration range with the Mo$_2$B$_2$Fe type crystalline structure. The samples were prepared using a standard arc melting
procedure under an argon atmosphere, and remelted several times to ensure good homogeneity. The range of concentration investigated covers up to 50% of the total Rh by Pd substitution and sample characterization by EPMA and X-ray diffraction indicates that a small percentage of Ce(Pd\(_{1-x}\)Rh\(_x\)) with \(x\) composition slightly higher than the bulk is present.

As reported in Ref. [1] the Ce-plane, at \(z = 0.5\), contains Ce atoms placed in the crystallographic site 4\(h\) whereas Ce atoms exceeding stoichiometric concentration (i.e. \(u = 0.15\)) replace In atoms at the 2\(a\) site at the \(z = 0\) and 1 planes. Concerning structural properties, one observes that the volume of the unit cell decreases with Rh content following Vegard’s law up to \(x = 0.3\). The main structural variation as a function of concentration is observed along the c-axis.

The low temperature behavior was investigated through thermal and magnetic parameters. Concerning specific heat measurements, in Fig. 1 we present the thermal dependence of the magnetic contribution divided by temperature (\(C_m/T\)), after phonon subtraction extracted from the non-magnetic La isotypic reference compound.

As it can be seen in Fig. 1, the magnetic transition in the parent compound (\(x = 0\)) shows the characteristic \(C_m/T\) jump of second order character. However, a slight broadening at the maximum of \(C_m/T\) can be observed. This broadening was formerly interpreted as an intrinsic experimental effect [1]. The present results indicate that the sample at \(x = 0\) is actually close to a bi-critical point at \(T_{cr} = 4.1\) K since the phase boundary splits into two transitions by Rh doping. Similar feature was observed in the intensively studied CeRu\(_2\)(Ge\(_{1-x}\)Si\(_x\))\(_2\) system [5]. Also in Fig. 1 a Rh concentration dependent satellite anomaly (\(T_S(x)\)) is observed. The intrinsic character of this satellite transition is discussed below.

Magnetic \(M(T)\) measurements on the \(x = 0\) sample do not improve the identification of the bi-critical point because the FM signal largely exceeds the underlying AF cusp. The presence of this bi-critical point is not surprising if we consider the mentioned study of Ce\(_{2+\epsilon}\)Pd\(_{2+\epsilon}\)In\(_{1-\epsilon}\) solid solutions [6]. From that study, one concludes that \(T_{cr} = 4.1\) K, lies in the extrapolated values of \(T_N(u)\) from the Pd-rich AF samples (i.e. \(Pd \geq 2 + u\)) to the Ce-rich FM-branch.

Figure 1. (Color on line) Thermal and concentration dependence of the magnetic contribution to specific heat divided temperature. \(T_C\) and \(T_N\) represent respective FM and AF transitions whereas \(T_S\) identifies a concentration dependent satellite transition discussed in the text.

Figure 2. (Color on line) Comparison between thermal derivative of \(M^2(T)\) (left axis) with \(C_m(T)\) (right axis) showing the split between FM and AF transitions. The original \(M(T)\) dependence is also included (right axis). Inset: hysteresis of \(\partial M^2/\partial T\) between heating and cooling procedures.
(i.e. $Pd \geq 2 - u$). The same coincidence is observed for the paramagnetic temperature $\theta_P(u)$ extrapolated to $Pd = 1.95$ from the $Pd \geq 2$ side.

In the following we will analyze the evolution of the low temperature properties under further increase of Rh content in Ce$_{2.15}$(Pd$_{1-x}$Rh$_x$)$_{1.95}$In$_{0.9}$. The splitting between $T_N(x)$ and $T_C(x)$ becomes more pronounced in the thermal and magnetic properties of sample $x = 0.1$. That feature is observed as an incipient structure in the cusp of $C_m/T$ shown in Fig. 1 and Fig. 2. A further evidence for the splitting of both phase boundaries is obtained from $M(T)$ measurements. Taking into account that from thermodynamic properties the internal magnetic energy $U_m$ of a FM phase is related to the spontaneous magnetization, i.e. $U_m \propto M^2$, its temperature derivative $\partial M^2/\partial T$ is proportional to $C_m(T)$ [7]. In Fig. 2 we compare both parameters (left axis for $\partial M^2/\partial T$ and right axis for $C_m(T)$) showing that the mentioned structure at the transition is better defined by a $\partial M^2/\partial T$ versus $T$ dependence. The same features are observed in the $x = 0.2$ sample since the transitions increase their thermal difference ($T_N = 3.3$ K and $T_C = 2.5$ K) as observed in Fig. 1 from $C_m/T$ results. The first order character of the (lower) $T_C$ transition is evidenced by an hysteresis in $\partial M^2/\partial T$ at the lower transition which shows a shift between heating or cooling procedures as depicted in the inset of Fig. 2. The first order character of the lower transition is in agreement with the fact that the AF order parameter developing from $T_N$ suddenly changes to an FM structure at $T_C$.

Also from Fig. 1, a change of the nature of both transitions can be appreciated for $x \geq 0.3$. While $T_C(x)$ tends to vanish becoming a weak shoulder at $x = 0.3$, the $C_m(T_N)$ jump transforms into a cusp at that concentration and then into a broad maximum for $x \geq 0.4$ centered at $T_{max} = 1.8$ K ($x = 0.4$), 0.9 K ($x = 0.5$) and 0.5 K ($x = 0.55$) respectively. Those maxima are followed at higher temperature by a large tail denouncing non-Fermi-liquid behavior [3]. Coincidentally, the value of the $C_m/T$ maxima decrease, extrapolating to $\approx 1.4$ J/molK$^2$ for $T_{max} \to 0$ (see Fig. 1) as currently observed in the proximity of a QCP [8]. Particularly, sample $x = 0.55$ follows a modified power law divergence $C_m/T \propto 1/(T^{1.25} + 1)$ [9] once the $T_S$ anomaly contribution is subtracted.

**Figure 3.** (Color on line) Magnetic phase diagram showing $T_N(x)$ and $T_C(x)$ phase boundaries decrease. Hollow circle in $T_C(x=0.3)$ corresponds to the kink in $C_m(T)/T$ of Fig. 1. Negative $x$ values correspond to Ag doping and hollow symbol at Ag($x = -0.03$) to the bi-critical point.

Concerning the satellite transition at $T_S(x)$, it can be mapped out to the $T_C$ transition of...
the pseudo-binary compound CePd$_{1-x}$Rh$_x$ [4] at slightly higher (≈10%) Rh concentration. The relevant features observed in this anomaly are the following: i) the height of the $C_m(T_S)$ contribution and its associated entropy corresponds to about 7% of a CePd$_{1-x}$Rh$_x$ phase; ii) in samples with $x \geq 0.4$, $C_m(x,T = T_S)$ nicely coincide once represented as a function of a normalized temperature $t = T/T_S$. These characteristics do not coincide with random contributions expected from spurious phases. Preliminary magnetic measurements indicate that: iii) the $T_S$ anomaly is suppressed by the application of a moderate magnetic field ($B \approx 0.1$ T). Such a rapid suppression is in contrast with the magnetic behavior of pure CePd$_{1-x}$Rh$_x$ because that compound shows a robust FM phase [4]. Coincidentally, iv) the FM signal observed around $M(T_S)$ is significantly weaker that the expected from the binary compound. All these features raise the question whether the origin of the $T_S$ anomaly is due to a spurious CePd$_{1-x}$Rh$_x$ phase or to the intrinsic excess of Ce atoms placed at the ‘2a’ crystalline sites [1], with an atomic environment mimicking that of CePd$_{1-x}$Rh$_x$.

3. Magnetic Phase Diagrams

In Fig. 3 we present the phase diagram showing that the upper ($T_N$) and the lower ($T_C$) transitions converge into a bi-critical point at $x \to 0$. Both boundaries are well defined for $x \leq 0.2$, but they broaden and smear respectively for $x \geq 0.3$. Since Rh doping effect is expected to introduce holes into the conduction band, in order to confirm the existence of that critical point we have tested the possibility to move on the other direction, i.e. introducing more electrons into the band. For such a purpose we investigated the Ag doped alloy Ce$_{2.15}$(Pd$_{0.90}$Ag$_{0.10}$)$_{1.95}$In$_{0.9}$, whose preliminary thermal and magnetic properties indicate a clear FM behavior with the consequent disappearance on the AF phase at the bi-critical point, estimated at $Ag \approx 0.03$ and $T \approx 4K$ as indicated in Fig. 3. The FM character of the $T_C(x)$ phase boundary is proved by $M(T)$ measurements on respective samples. Fig. 4 presents the concentration dependence of the satellite $T_S(x)$ anomaly with its extrapolation to zero at $x \approx 0.75$, and the Kondo temperature $T_K(x)$ evaluated using the Desgranges-Schotte criterion [10]. According to this criterion, $T_K$ can be computed as the temperature at which the entropy reaches the value $S(T_K) = 2/3RLn2$. It is worth noting that the rapid increase of $T_K(x)$ coincides with the extrapolation of $T_N(x)$ to the quantum critical point and the deviation of $V(x)$ from the Vegard’s law. On the contrary, the degrees of freedom involved in the $T_S(x)$ anomaly seems not to be affected by Rh increase at least up to $x = 0.55$, see Fig. 1.

Further studies at higher Rh concentration are in progress to better determine $T_S(x)$ at lower temperature and its dependence on magnetic field in elucidate the origin of that anomaly. Simultaneously, other Ce$_{2.15}$(Pd$_{1-x}$Ag$_x$)$_{1.95}$In$_{0.9}$ alloys are being investigated to better tune the electronic concentration on the bi-critical point.

References

[1] Giovannini M., Michor H., Bauer E., Hilscher G., Rogl P., Bonelli T., Fauth F., Fischer P., Herrmannsdorfer T., Keller L., Sikora W., Saccone A., Ferro R., 2000, Phys. Rev. B 61 4044.
[2] Sereni J.G., Schmerber G., Gomez Berioso M., Chevalier B., Kappler J. P., 2012, Phys. Rev. B 85 134404.
[3] Loehneysen H. v., Rosch A., Vojta M., Wölfle P., 2007, Rev. Mod. Phys. 79 1015.
[4] Sereni J.G., Westerkamp T., Gegenward P., Geibel C., 2007, Phys. Rev. B 75 024432.
[5] Haen P., Biaud H., T. Fukuhara T., 1999, Physica B 259-261 85.
[6] Sereni J.G., Giovannini M., Gomez Berioso M., Saccone A., 2011, Phys. Rev. B 83 064491.
[7] See for example: Belov K.P., in Magnetic Transitions, Consultants Bureau Enterprises Inc., N.Y., 1961.
[8] J.G. Sereni, arXiv 1201.1724v1 cond-matter 8 Feb. 2012.
[9] Sereni J.G., 2007, J. Low Temp. Phys. 147 179.
[10] Desgranges H.-U. and Schotte K.D., 1982, Physics Letters 91A 240.