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Non-magnetic anomaly at 1K arising in Ferromagnetic $Ce_{2.15}(Pd_{1-x}Ag_x)_{1.95}In_{0.9}$

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Abstract

Magnetic and thermal properties of Ferromagnetic (FM) $Ce_{2.15}(Pd_{1-x}Ag_x)_{1.95}In_{0.9}$ alloys were studied in order to determine the Quantum Critical Point (QCP) at $T_C \rightarrow 0$. The increase of band electrons produced by Pd/Ag substitution depresses $T_C(x)$ from 4.1 K down to $T_C(x = 0.5)$=1.1 K, with a QCP extrapolated to $x_{QCP} \geq 0.5$. Magnetic susceptibility from $T > 30$ K indicates an effective moment slightly decreasing from μ_{eff}=2.56μ_B to 2.4μ_B at x=0.5. These values and the paramagnetic temperature $\theta_P \approx$ -10 K exclude significant Kondo screening effects. The $T_C(x)$ reduction is accompanied by a weakening of the FM magnetization and the emergence of a specific heat $C_m(T)$ anomaly at $T^* \approx 1$ K, without signs of magnetism detected from AC-susceptibility. The magnetic entropy collected around 4 K (i.e. the T_C of the $x = 0$ sample) practically does not change with Ag concentration: $S_m(4K) \approx 0.8$ Rln2, suggesting a progressive transfer of FM degrees of freedom to the non-magnetic (NM) component. No antecedent was found concerning any NM anomaly emerging from a FM system at such temperature. The origin of this anomaly is attributed to an *entropy bottleneck* originated in the nearly divergent power law dependence for $T > T^*$.

Keywords: Ferromagnetism, Non Fermi liquids, Quantum Criticality, Magnetic Frustration

1 Introduction

The R_2T_2X family of compounds (with R = Rare earth, T = transition metal and X = semi metal) were actively investigated during the last decade because of their peculiar magnetic properties at low temperatures (see e.g. [1]). The strongly anisotropic Mo_2B_2Fe type crystalline structure [2], with alternated magnetic and non-magnetic atomic layers, favors geometrical frustration effects originated in the triangular coordination of the R-magnetic atoms.

The extended range of solid solution of the $Ce_{2\pm u}Pd_{2\mp y}In_{1-z}$ system [3] has allowed to determine that the Ferro (FM) or Antiferromagnetic (AFM) behavior depends on the *electron-hole* relative concentration in the T-X layer [4]. In fact, the Ce-rich (i.e. electron rich) branch behaves FM, whereas the Pd-rich (i.e. hole rich) behaves AFM. In this crystalline structure

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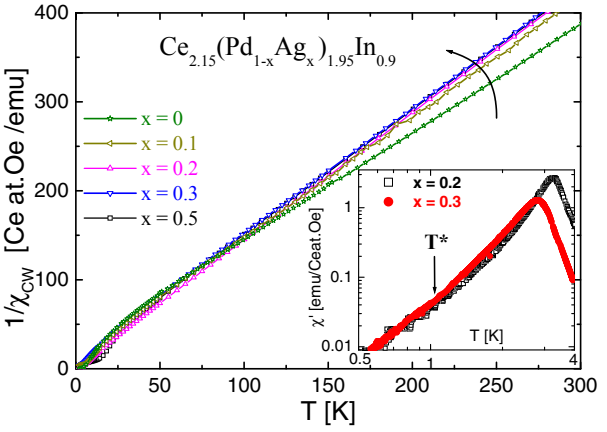

Figure 1: (Color online) Inverse of the Curie-Weiss contribution of magnetic susceptibility, after the Pauli-like contribution subtraction, measured up to room temperature with a field of 0.5 Tesla. The arrow indicates the increase of Ag concentration. Inset: Monotonous decrease of the inductive component of AC-susceptibility (χ') for samples $x = 0.2$ and 0.3 on the FM phase ($T < T_C$) in a double logarithmic representation. T* indicates the temperature of the specific heat anomaly growing with Ag content, see the text.

the triangular coordination of next magnetic neighbors (*nmn*) fulfils the condition for magnetic frustration within Ce planes [5], provided there are AFM interactions between Ce-*nmn* within the plane.

Exploiting the fact that a FM ground state can be driven by tuning the electron-hole concentration, the $Ce_{2.15}Pd_{1.95}In_{0.9}$ composition was chosen as a starting point to approach a FM quantum critical regime by doping Pd lattice with Ag in the $Ce_{2.15}(Pd_{1-x}Ag_x)_{1.95}In_{0.9}$ family of alloys. The $x = 0$ starting point lies in the vicinity of a magnetic critical point as it was determined in a previous investigation performed with Rh doping. In fact this study has shown the presence of two magnetic transitions converging to a critical point at the vicinity of $x = 0$ [6].

2 Experimental results

2.1 Sample preparation and Characterization

The samples were prepared using a standard arc melting procedure under an argon atmosphere, and they were remelted several times to ensure good homogeneity. The $Ce_{2.15}(Pd_{1-x}Ag_x)_{1.95}In_{0.9}$ alloys form continuously up to the limit of solubility at $x = 0.5$ within the Mo_2B_2Fe-type structure. The volume of the unit cell increases with Ag content following a Vegard's law up to $x = 0.5$, with the 'c/a' ratio remaining nearly constant.

2.2 Magnetic Properties

High temperature ($T > 30$ K) magnetic susceptibility results are properly described by a $\chi = \chi_{cw} + \chi_p$ dependence, where the first term corresponds to the temperature dependent Curie-

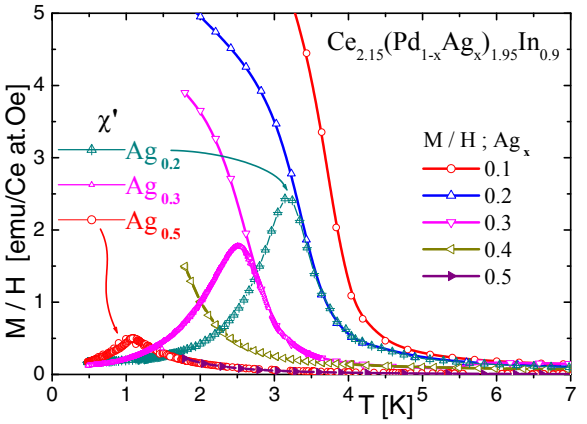

Figure 2: (Color online) Low temperature dependence of the magnetization measured with $H = 0.1$ Tesla showing the FM character of the system. The inductive component of the AC-susceptibility (χ') of some representative samples are scaled to M/H units of respective concentrations using a unique scaling factor. The χ' maxima mark the $T_C(x)$ temperatures that show a progressive decrease of with Ag content.

Weiss contribution $\chi_{cw} = \frac{Cc}{T+\theta}$ and the second to a Pauli-like contribution. This χ_p contribution is observed along the full concentration range with a value of $\chi_p = (2 \pm 0.5)10^{-4}$ emu/molCeOe. From the inverse of χ_{cw} (see Fig. 1) one extracts the Curie constant (Cc) which indicates the full development of a Ce^{3+} magnetic moment (i.e. $\mu_{eff} = 2.56\mu_B$ per Ce atom) for the pure Pd alloy. This value slightly decreases down to $\approx 2.4\mu_B$ at $x = 0.5$. The paramagnetic temperature θ_P practically does not change with concentration, remaining around $\theta_P \approx -10$ K. This negative value is evaluated as an extrapolation of $1/\chi_{cw}$ from $T > 30$ K down to $1/\chi_{cw} = 0$. At this temperature range the crystal electric field states contribute significantly. Below $T \approx 30$ K, a moderate downward curvature makes $1/\chi_{cw}$ to extrapolate to $T > 0$ revealing the FM character of the ground state.

Since $\chi_{cw}(T)$ measurements are limited down to $T = 1.8$ K, we have extended the study of the magnetic properties performing AC-susceptibility (χ') measurements down to 0.5 K on some representative samples. In the inset of Fig. 1, the $\chi'(T < 4\,K)$ results from samples $x = 0.2$ and 0.3 are presented in a double logarithmic representation that covers more than two decades of magnetic signal intensity.

In Fig. 2, the low temperature dependence of the magnetization $M(T)$, measured at $H = 0.1$ Tesla, is presented as a M/H ratio. The upturn at $T \leq 4$ K reveals the FM character of the ground state (GS). Notably, the measured magnetization decreases hand in hand with $T_C(x)$ decrease. The inductive component χ' of the measured samples is also included in this figure in order to compare them with M/H measurements. One can observe the coincident decrease of the χ' signal with $T_C(x)$, the latter identified by the maximum of $\chi'(T)$ and the maximum slope of $\partial M/\partial T$. The $\chi'(T)$ results from sample $x = 0.5$ are also included in Fig. 2 to obtain the $T_C(x = 0.5) = 1$ K value and to confirm the continuous vanishing of the FM signal.

Magnetization $M(H)$ curves at $T = 1.8$ K (not shown) of samples $x = 0.1$ and 0.2 reach 90% of its saturation value $M_{sat} = 1.1\mu_B$/Ce at. at $H \approx 0.5$ Tesla, showing a small hysteresis loop, typical for FM materials. Above that concentration ($x \geq 0.3$), the initial $M(H)$ slope weakens

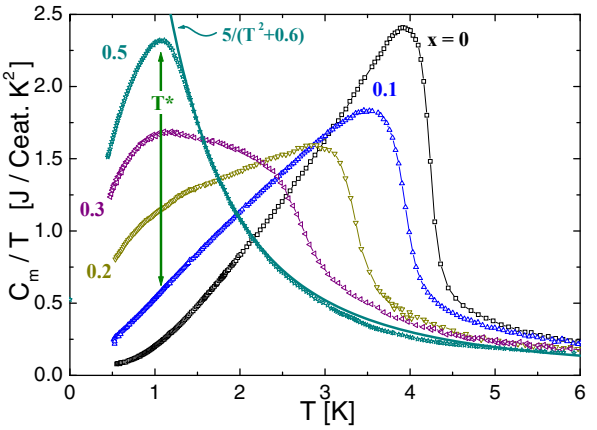

Figure 3: (Color online) Specific heat of $Ce_{2.15}(Pd_{1-x}Ag_x)_{1.95}In_{0.9}$ alloys. The continuous curve is the fit of C_m/T for $T > T^*$ in sample $x = 0.5$. Green arrow indicates the emerging anomaly at fixed temperature $T = T^*$

and transforms into a continuous curvature. In spite of that, the $x = 0.5$ alloy still shows a remanent loop of hysteresis from the vanishing FM component between $-0.2 < H < 0.2$ Tesla and $-0.15 < M < 0.15\mu_B$/Ce at. This small contribution has to be compared with the total magnetization reached at $H = 5$ Tesla: $0.9\mu_B$/Ce at.

2.3 Specific heat

The $T_C(x)$ transition is recognized in specific heat (C_m) measurements by a clear jump ΔC_m which, for the mother compound $Ce_{2.15}Pd_{1.95}In_{0.9}$, reaches the value of $\Delta C_m \approx 10$ J/Ceat.K (see Fig. 3). This value is close to the value predicted for a doublet GS [7]. At very low temperature, a $C_m(T)$ curvature can be fitted with an exponential function indicating the presence of a gap in the magnon spectrum typically occurring in strongly anisotropic systems. The magnetic contribution to the specific heat C_m is obtained after subtracting the phonon contribution extracted from a La_2Pd_2In compound.

The $\Delta C_m/T$ jump progressively decreases and broadens as $T_C(x)$ decreases. Unexpectedly, another anomaly emerges around $T^* \approx 1$ K, overcoming the FM ΔC_m jump around $x = 0.3$, but without changing its position in temperature with Ag content. This anomaly seems to be fully developed for the $x = 0.5$ alloy. It cannot be associated neither to spin glass (C_{sg}) nor to Schottky (C_{sh}) anomalies because those specific heat anomalies have an associated magnetic signal and because they do not describe the observed C_m/T thermal dependence on both sides of the maximum properly. In fact, below the respective maxima, spin glasses show a $C_{sg}/T = const.$ behavior [8] and $C_{sh} \propto \exp(1/T)$ [9], compared with the $C_m/T \propto T$ of sample $x = 0.5$. Above the maximum both specific heat anomalies decay as $C_p/T \propto 1/T^3$, which is different from the temperature dependence observed. In the following section we discuss a tentative description of the $C_m(T)/T$ tail at $T > T^*$ using a modified power law $C_m(T)/T$ dependence together with the thermodynamical implications of such a thermal dependence. Notably, the total entropy gain evaluated as $S_m(T) = \int C_m(T)/T\, dT$ up to $T = 7$ K practically does not change with Ag content, and reaches $\approx 90\%$ of Rln 2 per Ce atom at T=10 K.

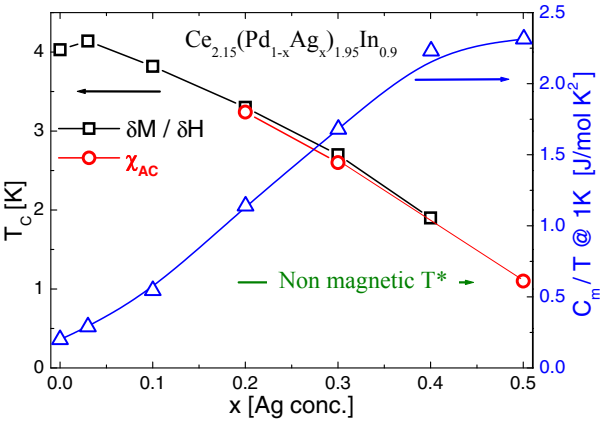

Figure 4: (Color online) Left axis: Concentration dependence of $T_C(x)$ extracted from the maximum slope of $M(T)$ for $x \leq 0.4$ alloys (black squares) and from the maximum of χ' for $x \geq 0.2$ (red circles). Right axis: C_m/T value at $T = T^*$. The Non magnetic T^* arrow indicates the temperature of the maximum of the Non magnetic anomaly at $T \approx 1\,\mathrm{K}$.

3 Discussion

Despite the fact that high temperature susceptibility measurements reveals a robust magnetic moment in Ce ions only weakly dependent on Ag concentration, $T_C(x)$ decreases hand in hand with the intensity of the FM signal. This evolution cannot be explained by usual Kondo screening of Ce magnetic moments because $-\theta_P(x) \propto T_K$ slightly depends on concentration. The increase of Ce-*nmn* spacing, driven by the expansion of the lattice parameters with Ag content, can be only partially responsible for the weakening of the RKKY interaction because it increases about 1.4% between x=0 and 0.5. Similar expansion occurs between Ce planes reflected in the increase of the 'c' axis.

The outstanding message from the $\chi'(T)$ dependence measured on samples $x = 0.2$ and 0.3, presented in the inset of Fig. 1, is the decrease of the magnetic response below T_C without any detected magnetic contribution around $T^* \approx 1\,\mathrm{K}$. The double logarithmic representation, covering more than two decades of signal variation, shows a monotonous behavior that excludes other contributions. Notice that in the alloy with $x = 0.3$ the T^* anomaly already contains a similar amount of degrees of freedom like the decreasing FM component as it can be appreciated from C_m/T measurements in Fig. 3. In Fig. 2 these two $\chi'(T)$ curves and the one from $x = 0.5$ are scaled to respective χ_{cw} values above 1.8 K using a unique scaling factor between the induced AC-voltage and the magnetic units. From this comparison one can appreciate how the maximum of the $\chi'(T)$ signal at $T = T_C$ decreases together with $T_C(x)$, extrapolating the critical concentration x_{cr} slightly beyond 0.5.

Additionally to the transference of degrees of freedom from FM component to a non-magnetic component observed in the $C_m(T, x)/T$ dependence, presented in Fig. 3, a more quantitative indication for such transference can be appreciated in Fig. 4 where the value of $C_m(x)/T$ at $T = T^*$ is depicted. From the figure it can be seen that there is a clear increase of C_m/T^* (right axis) as the FM component vanishes proportionally to T_C decrease (left axis). The same analysis can be done in terms of the entropy accumulated within the anomaly. However, at intermediate concentrations, the subtraction of each component from the total C_m/T

value becomes difficult.

The unexpected absence of magnetic signal from the T^* anomaly is the outstanding feature of this system. To our knowledge there is no antecedent reported in the literature for a *non-magnetic* anomaly at such a low temperature, at least for Ce compounds. Although some degree of magnetic disorder can be expected in the Pd/Ag plane due to the different atomic size of the atoms, this effect usually drives the magnetic system into a concentration dependent spin glass type behavior, not observed in this $C_m(T)$ anomaly. Furthermore, there is no evidence that magnetic disorder weakens a FM interaction between neighbors. For comparison, we observe that under magnetic field this transference of degrees of freedom is reversed respect to the Ag concentration effect, weakening the $C_m(T^*)$ anomaly but without detecting a change in its temperature position. Since the non-magnetic degrees of freedom are related to magnetically frustrated moments, magnetic field shall reduce frustration because it favors FM alignment.

The relevant questions arising about this system are: the origin, its non magnetic nature and the low characteristic temperature $T^* = 1\,\mathrm{K}$. The origin of this anomaly may be attributed to frustration effects because a change of sign in the RKKY magnetic interaction can be expected. Since this interaction is mediated by conduction electrons, the change from 'd'-hole Pd to 's'-electron Ag ligands modifies the polarization of the exchange interaction. Then, if an AF interaction sets on, in the Mo_2B_2Fe type structure the triangular configuration between Ce-*nmn* may lead to magnetic frustration in the vicinity of Ag atoms. This scenario may explain the lack of magnetic signal from the arising T^* anomaly. The same situation occurs for the mirror Ce-triangle respect to the Ag atom position, placed on the neighboring Ce-plane. This simultaneous propagation of the AF character explains why the FM component practically smears out already with 50% of Ag concentration. On the other hand, the random fluctuations of magnetically frustrated moments results in a non-magnetic response of the system.

The low value of T^* and the fact that it does not change with Ag concentration can be related to $T \to 0$ thermodynamic constraints. The strong increase of C_m/T at $T > T^*$ cannot be sustained down to $T = 0$ because it would required an available amount of entropy exceeding the $S_m(T) = \int C_m/T dT = R \ln 2$ limit provided by a doublet ground state. To dodge this sort of *entropy bottleneck* [10], the system is driven into an alternative temperature dependence to allow to reach $S_m = 0$ for $T \to 0$, fulfilling the $S_m \leq R \ln 2$ condition. In order to visualize the excess of entropy required by an hypothetical system whose $C_m/T(T)$ would keep growing below T^* like it does at $T > T^*$, we have included in Fig. 3 a fit performed on the $C_m/T(T > T^*)$ range as a guide to the eye. Among alternative functions, we use an heuristic function $C_m/T = D/(T^Q + E)$ proposed in Ref. [11] which was already applied to compare the thermal dependence of some heavy fermion compounds. Particularly, the entropy associated to this fit nearly doubles the $R \ln 2$ entropy limit.

In summary, we present a FM Ce-system whose $T_C(x) \to 0$, with the associated degrees of freedom decreasing hand in hand with the ordering temperature. Such a FM transition extrapolates to a $T_C = 0$ critical point slightly beyond $x = 0.5$. In this system the magnetic degrees of freedom are progressively transferred to a *non-magnetic* component that emerges as an anomaly centered at $T^* \approx 1\,\mathrm{K}$. The lack of magnetic signal from this component is attributed to an AF-frustration character driven by Ce-neighboring Ag atoms, with electron-like character, that modify the RKKY interaction sign. The constant value of $T^* \approx 1\,\mathrm{K}$ is attributed to an *entropy bottleneck* produced by the strong increase of magnetic excitations density (C_m/T) which would exceed the available degrees of freedom. This situation compels $S_m(T)$ to search for a thermodynamic trajectory that allows to reach $S_m = 0$ as $T \to 0$. The microscopic nature of its ground state remains an open question that requires μSR spectroscopy or neutron scattering investigations.

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