Emerging frustration effects in ferromagnetic Ce$_2$(Pd$_{1-x}$Ag$_x$)$_2$In alloys

J.G. Sereni 1, M. Giovannini 2,3, M. Gómez Berisso 1, F. Gastaldo 2
1 Low Temperature Div. CAB - CNEA, Conicet, 8400 Bariloche, Argentina
2 Dip. di Chimica e Chimica Industriale, Università di Genova, I-16146 Genova, Italy and
3 CNR-SPIN Corso Perrone 16152 Genova, Italy
(Dated: November 18, 2021)

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 $T_C \to 0$. The increase of hand 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 $\mu_{eff} = 2.56 \mu_B$ to $2.4 \mu_B$ at $x = 0$. These values and the paramagnetic temperature $\theta_P = -10$ 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 $T > T^*$.

I. 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$_2$B$_2$Fe 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$_{2\pm\delta}$Pd$_{2\pm\delta}$In$_{1\pm\delta}$ system [3] has allowed to determine that Ferro (FM) or Antiferromagnetic (AFM) behaviors depend on the relative concentration of electron-holes 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 the triangular coordination of next magnetic neighbors (nnn) fulfills the condition for magnetic frustration within Ce planes [5], provided there are AFM interactions between Ce-nnn 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$_{1-x}$Ag$_x$In$_{1.95}$ composition was chosen as a starting point to approach a FM quantum critical regime by doping Pd lattice with Ag in Ce$_{2.15}$(Pd$_{1-x}$Ag$_x$)$_{1.95}$In$_{0.9}$ alloys. The starting concentration $x = 0$ lies in the vicinity of a magnetic critical point, determined in a previous investigation performed with Rh doping by the presence of two magnetic transitions converging to a critical point at the vicinity of $x = 0$ [6].

II. EXPERIMENTAL RESULTS

A. 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$_2$B$_2$Fe-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.

**B. 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-Weiss contribution $\chi_{cw} = \frac{C_C}{T + \theta_p}$ and the second to a Pauli-like contribution. This $\chi_p$ contribution is observed along the full concentration range with a value of $\chi_p = (2 \pm 0.5) \times 10^{-4}$ emu/molCeOe. From the inverse of $\chi_{cw}$ (see Fig. 1) one extracts the Curie constant (C) 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 $\theta_p$ 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 ($\chi'$) 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 $\chi'$ 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 $\chi'$ 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 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.

C. Specific heat

The $T_C(x)$ transition is recognized in specific heat ($C_m$) measurements by a clear jump $\Delta C_m$ which, for the mother compound Ce$_{2.15}$Pd$_{1.95}$In$_{0.9}$, reaches the value of $\Delta C_m \approx 10$ J/Ce at. K (see Fig. 2). 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$_2$Pd$_2$In 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, overcom-
ing the FM $\Delta C_m$ 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 $C_{sg}/T = \text{const.}$ 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.

III. 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-$nnn$ 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 $T^* \approx 1$ K. The double logarithmic representation, covering more than two decades of signal variation, shows a monotous 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 $\chi_{cw}$ 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, pre-
sented in Fig. 4 a more quantitative indication for such transference can be appreciated in Fig. 3 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 $T^* = 1$ 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. 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$_2$B$_2$Fe 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 $S_m(T) = \int C_m/TdT = R \ln 2$ limit provided by a doublet ground state. To dodge this sort of entropy bottleneck, 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 $C_m(T)$ would keep growing below $T^*$ like it does at $T > T^*$, we have included in Fig. 4 a fit performed on the $C_m(T > T^*)$ 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. [10] 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 $T^* \approx 1$ 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 $T^* \approx 1$ 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 $\mu$SR spectroscopy or neutron scattering investigations.

[1] T. Muramatsu, T. Kanemasa, T. Kagayama, K. Shimizu, Y. Aoki, H. Sato, M. Giovannini, P. Bonville, V. Zlatic, I. Aviani, R. Khasanov, C. Rusu, A. Amato, K. Mydeen, M. Nicklas, H. Michor, E. Bauer, Phys. Rev. B 18 (2011) 180404(R).
[2] F. Fourgeot, P. Gravereau, B. Chevalier, L. Fourns, J. Etourneau; J. Alloys and Comp. 238 102 (1996).
[3] M. Giovannini, H. Michor, E. Bauer, G. Hilscher,
P. Rogl, T. Bonelli, F. Fauth, P. Fischer, T. Hermannsdorfer, L. Keller, W. Sikora, A. Saccone, R. Ferro; Phys. Rev. B 61 4044 (2000).
[4] J.G. Sereni, M. Giovannini, M. Gómez Berisso, A. Saccone, Phys. Rev. B 83 064419 (2011).
[5] A.P. Ramirez; Annu. Rev. Mater. Sci. 24 453 (1994).
[6] J.G. Sereni, M. Giovannini, M. Gómez Berisso, A. Saccone, J. of Phys.: Conf. Series 391 012062 (2012).

[7] See for example: P.H. Meijer, J.H. Colwell, B.P. Shah, Am. Jour. Phys., 41 (1973) 332.
[8] J.A. Mydosh in Spin Glasses: an experimental introduction. Taylor & Francis, London, 1993.
[9] A. Tari, in The Specific Heat of Matter at low temperatures, Imperial College Press, London, Great Britain, 2003.
[10] J.G. Sereni, J. Low Temp. Phys. 179 126 (2015).
[11] J.G. Sereni, J. Low Temp. Phys. 147 179 (2007).