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Field suppression of the modulated phase of Ce_2Pd_2Sn

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ABSTRACT

Low temperature magnetic (M) and thermal (C_P) properties of the intermetallic compound Ce_2Pd_2Sn have been investigated at zero and different magnetic fields. Two transitions were recognized at $T_C = 2.1\,K$ and $T_M = 4.8\,K$, with latter nearly coinciding with the extrapolated Curie–Weiss temperature $\theta_P = 4.5\,K$. The Curie factor evaluated from $T \geq T_M$, is $\approx 2\mu_B$. The positive value of θ_P, the triangular coordination of the magnetic (Ce) atoms and the weak effect of applied magnetic field, reveal that T_M cannot be considered as a canonic antiferromagnetic transition like claimed in the literature. $M(T)$ measurements under moderate magnetic fields ($0 \leq B \leq 2.5\,kOe$) show $T_C(B)$ increasing while $T_M(B)$ is practically not affected. Both transition merge in a critical point at $T_{cr} = (4.3 \pm 0.3)\,K$ for $B_{cr} = (2.1 \pm 0.3)\,kOe$, where the intermediate phase is suppressed. At $T_C = 2.2\,K$, the cusp of a first order transition is observed in $C_P(T)$. According to the proposed ferromagnetic ground state, it is followed by a $C_P(T) \propto T^{3/2} \exp(-E_g/T)$ dependence, with a gap of anisotropy $E_g \approx 7\,K$.

1. Introduction

We have recently presented preliminary studies of new $Ce_2Pd_2Sn_{1+x}$ samples [1], extending the specific heat measurements into its ferromagnetic phase down to 0.5 K. These measurements have confirmed the presence of two transitions at $T_M = 4.8\,K$ and $T_C = 2.2\,K$, the latter slightly lower the one previously reported in the literature [2]. From neutron diffraction studies [3], the magnetic structure of the intermediate phase ($T_M > T > T_C$) was recognized as incommensurated and described by modulated Ce-$4f^1$ magnetic moments.

To our knowledge, there is no systematic determination of magnetic phase diagrams for Ce_2Pd_2X compounds performed yet. This is not a minor point since in recent years a big effort was done searching for new phases associated to critical points, especially at very low temperature (see, e.g. Refs. [5,6]). Furthermore, the scarce ferromagnetic examples among Ce intermetallic compounds and the twin magnetic behavior of Ce_2T_2Sn with respect to CeT ones (T = Ni, Cu, Pd, Rh, Pt [7]) place these stannides compounds as good candidates for detailed investigations related to critical phenomena [8].

That similarity arises from the structural disposition of Ce–T atoms in the tetragonal Mo_2FeB_2-type structure [9]. This crystalline structure is strongly anisotropic and can be described as successive T + Sn (at $z = 0$) Ce (at $z = \frac{1}{2}$) layers. Trigonal and tetragonal prisms, centered around and T and Ce atoms, respectively, dispose Ce atoms in non-centro-symmetric positions along the c-direction. Such a triangular coordination of Ce magnetic atoms introduces some doubts about the possibility of a canonical antiferromagnetic structure due to frustration effects. This is the reason why we identify the upper transition as T_M instead of T_N as proposed originally in the literature [2,3].

These type of compounds show a broad range of miscibility as $Ce_2Pd_{2+x}Sn_{1-x}$ [2,4] with the magnetic properties strongly dependent on composition, we have chosen for this study a sample with stoichiometric nominal composition, i.e. Ce_2Pd_2Sn, with actual composition $Ce_{2.005}Pd_{1.998}Sn_{0.997}$ after SEM/EDX analysis. This is a sort of reference starting point since, using small variations in relative composition as control parameter, it is possible to drive magnetic transitions within a scenario of phases with competing energy values.

2. Results and discussion

The magnetic moment extracted from high temperature magnetization measurements is $\approx 2.6\mu_B$/Ce, which is very close to the expected value of $2.54\mu_B$ for the $J = \frac{5}{2}$ total angular moment. The low temperature thermal dependence of the magnetization $M(T)$ is shown in Fig. 1 for different applied fields ($1 < B < 2.2\,kOe$). For the lowest applied field ($B = 1\,kOe$) ferromagnetic correlations become dominant already at $T \approx 3.5\,K$ in agreement with the

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previous measurements at much lower applied field ($B = 50\,\mathrm{kOe}$ [1]). By increasing magnetic field, $M(T)$ at the lowest measured temperature ($T = 2\,\mathrm{K}$) also tends to the saturation value $M_S = 1.1\mu_B/\mathrm{Ce}$ previously established from $M(B)$ measurements at $T = 1.8\,\mathrm{K}$. As expected for a ferromagnetic system, the transition broadens with increasing field and tends to overlap the upper transition (T_M) at $B = 2.2\,\mathrm{KOe}$. The latter, defined as a the maximum of $M(T)$, is practically not affected by the applied field up to $B = 10\,\mathrm{kOe}$.

In Fig. 2 we show the inverse of $M/B(T)$ measured with $B = 1\,\mathrm{KOe}$. There, one can see that the Curie–Weiss temperature θ_P extrapolated from $T \leq 20\,\mathrm{K}$ is positive: $\theta_P = 4.5\,\mathrm{K}$. This is a further indication that the transition at T_M cannot be considered as a canonic antiferromagnetic one despite of the maximum observed at $M(T_M)$. The effective magnetic moment at low temperature is computed as $\mu_{eff} = \sqrt{C_c} \approx 2\mu_B$, where $C_c = M/B$ is the Curie constant extracted from the $T_M < T < 20\,\mathrm{K}$ range. This unusually large value of the magnetic moment for Ce compounds is in agreement with the observed by neutron diffraction techniques [3]. It confirms the well localized $4f^1$ state of Ce and the extremely low value of the Kondo temperature in this compound [1].

Within the intermediate phase ($T_C < T < T_M$), previously studied $M(B)$ dependence [1] showed signs of meta-magnetic transitions. This feature was investigated more in detail up to $B = 3\,\mathrm{kOe}$ and the results shown in Fig. 3. There one can see that increasing temperature, the initial linear $M(B)$ dependence turns up at higher magnetic field. Coincidentally, the hysteresis loops decrease from a coercive field $\approx 30\,\mathrm{Oe}$ at $T = 2\,\mathrm{K}$. $M(B)$ measurements also allow to define the $T_C(B)$ dependence by tracing the field dependence of the maximum of the $M(B)$ derivative isotherms (not shown). With increasing temperature, a clear maximum of this derivative occurs at higher field but with decreasing intensity till to practically vanishing at $T \approx 4.5\,\mathrm{K}$. This indicates that $T_C(B)$ approaches a critical point around that temperature.

Starting from the lowest measured temperature ($T = 0.5\,\mathrm{K}$), the thermal dependence of the magnetic contribution to specific heat (C_m) shows the typical cusp of a first order transition at $T_C = 2.2\,\mathrm{K}$ (see Fig. 4). $C_m(T)$ is determined by subtracting the phonon contribution extracted form the isotypic compound La_2T_2Sn [1] to the measured values as $C_m(T) = C_{meas}(T) - C_{La}(T)$. The first order character of T_C is confirmed by preliminary measurements of

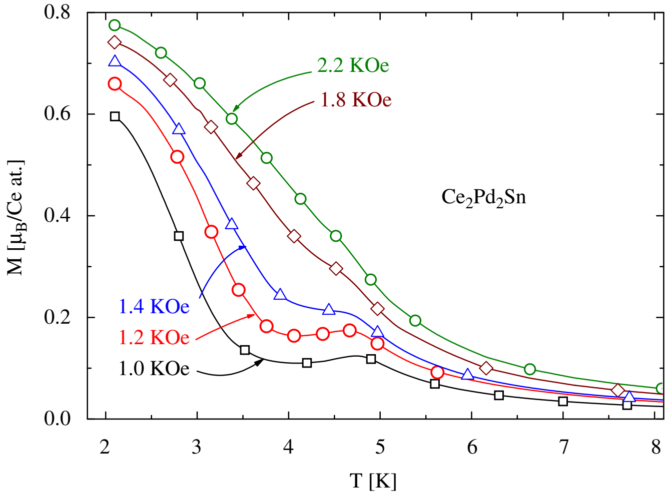

Fig. 1. Temperature dependence of the magnetization, normalized by the magnetic field: M/B, at different applied fields up to 2.2 kOe.

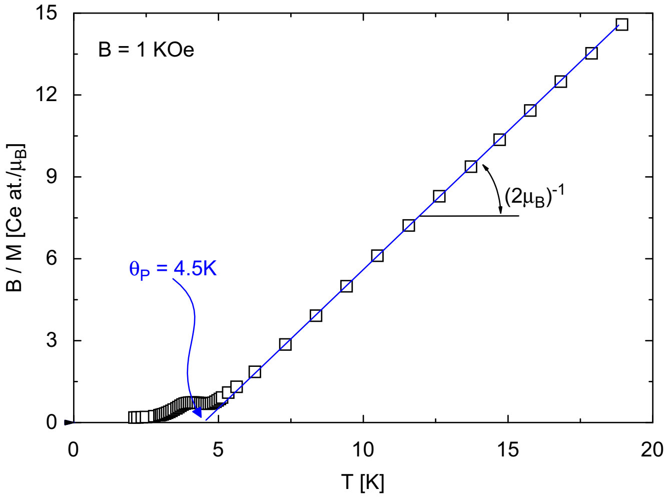

Fig. 2. Inverse susceptibility (as B/M) at low temperature to extrapolate θ_P and to extract the effective magnetic moment. Notice the $\theta_P > 0$ value.

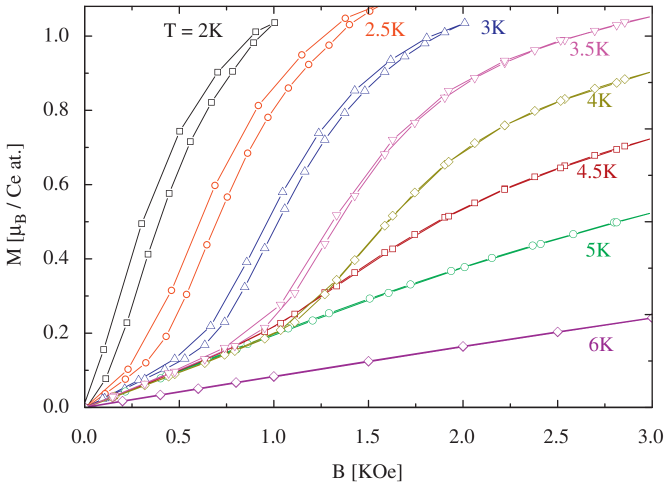

Fig. 3. Field dependence of the magnetization to show the evolution of the meta-magnetic transformation as a function of temperature.

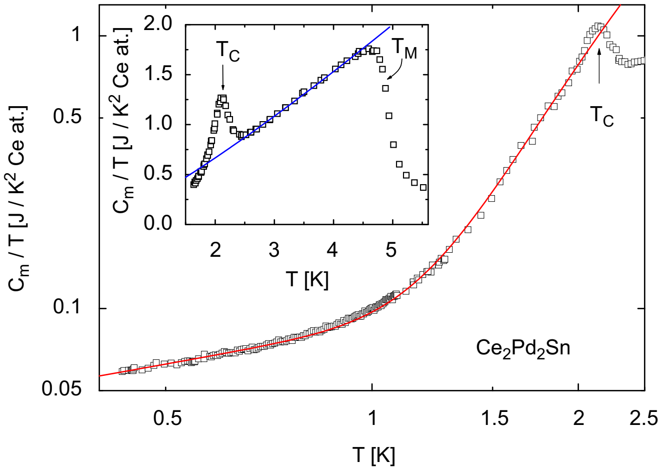

Fig. 4. Low temperature ($T \leq T_C$) C_m/T variation in the ferromagnetic phase, in log–log representation. Inset: linear C_m/T vs. T of the intermediate phase. Continuous curves are the fits described in the text.

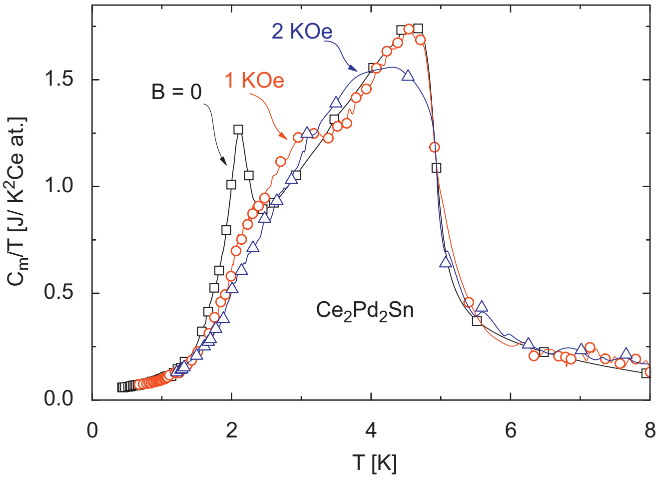

Fig. 5. Effect of applied magnetic field on specific heat in a C_m/T vs. T representation.

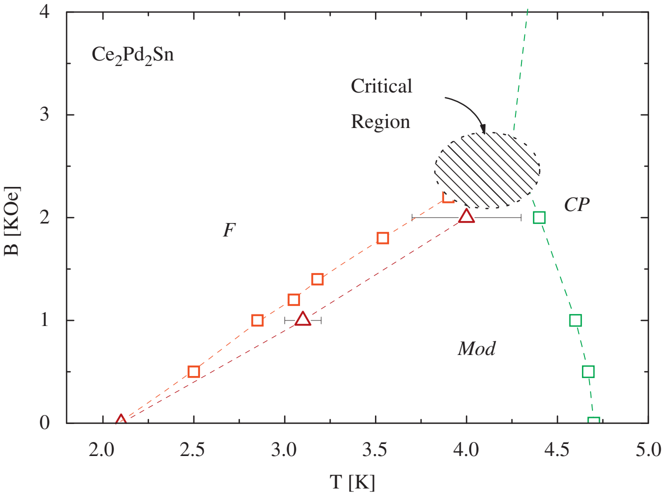

Fig. 6. Magnetic phase diagram determined by the maximum slope of $\partial M/\partial T|_{max}$ (□) and specific heat (△). *F*: ferromagnetic; *Mod*: modulated and C_P: correlated paramagnetic phases.

electrical resistivity and ac-susceptibility (not shown) where a thermal hysteresis is clearly observed between cooling and heating precesses around T_C. In the ferromagnetic phase ($T < T_C$), C_m is well described by a $C_m = \gamma + T^{3/2} \times [B_1 + B_2 \exp(-E_g/T)]$ thermal dependence [10,11]. The term $\gamma = 6\,\mathrm{mJ/K^2 Ce\,at.}$ indicates that the linear contribution to C_m is only due to free electrons with irrelevant effects of hybridization between 4f orbitals and conduction band. The two terms ($B_1 = 0.08\,\mathrm{J/K^{2.5} Ce\,at.}$ and $B_2 = 20\,\mathrm{J/K^{2.5} Ce\,at.}$) in the $T^{3/2}$ coefficient reveal a strong magnetic anisotropy in the system, with a gap ($E_g \approx 7\,\mathrm{K}$) in one direction of the magnon spectrum. Nevertheless, the $C_m \propto T^{3/2}$ dependence corresponds to a three-dimensional ferromagnetic dispersion relation [12].

Between T_C and T_M, $C_m(T)$ is fitted by a $0.29 \times T^{2.2}\,\mathrm{J/KCe\,at.}$ thermal dependence, as shown in the inset of Fig. 4. Such a dependence does not coincide with that of a canonical antiferromagnet ($\propto T^3$) but resembles one of a strongly anisotropic ferromagnet [13]. The specific heat jump $\Delta C_m \approx 8\,\mathrm{J/KCe\,at.}$ at $T = T_M$ has the characteristic of a second order transition, with a tail above T_M. Such a tail in the paramagnetic state arises from significant magnetic correlations which can be considered as precursors of the transition, characteristic of strongly anisotropic systems.

The $4f^1$ character of Ce ions in this compound and the concomitant low Kondo temperature are confirmed by the entropy gain $\Delta S_m(T)$ at the upper transition where $\Delta S_m(T_M) \approx 0.8 RLn2$ per Ce atom. This is a unusually large fraction of the total expected value $RLn2$ per Ce atom with a doublet ground state at $T \approx 4.8\,\mathrm{K}$. The remanent 20% of entropy is collected in the tail of C_m/T above T_M. This indicates the presence of a significant amount of magnetic excitations, precursors of the transition. This paramagnetic region can be identified correlated-paramagnetic below $T \approx 20\,\mathrm{K}$. The Kondo temperature T_K can be evaluated applying the Desgranges–Schotte model [14]: $\Delta S_m(T_K) \approx \frac{2}{3} RLn2$ is $T_K \approx 3\,\mathrm{K}$. To our knowledge, this is the lowest value reported for T_K in Ce-base compounds.

Included in Fig. 5 are $C_m(T)$ measurements performed under magnetic field of $B = 1$ and 2 KOe. One can see that the external field strongly affects the ferromagnetic transition and shifts T_C up to $\approx T_M$ with $B \geq 2\,\mathrm{kOe}$. The shoulder observed at $T = 2.2\,\mathrm{K}$ in the $B = 1$ KOe curve is attributed to the polycrystal character of the sample since a fraction of crystals can be oriented in the hard direction respect to the field. This effect is progressively suppressed at higher field and also explains the rounded onset of the meta-magnetic transformation presented in Fig. 3. Contrary to T_C, T_M is practically not affected by magnetic field and the maximum at $C_m(T_M)$ slightly decreases in intensity. This is a further evidence for a non-canonic antiferromagnetic character of the intermediate phase.

Field effects on this compound are resumed in the magnetic phase diagram presented in Fig. 6. The field driven transformation between the modulated (*Mod*) and ferromagnetic (*F*) phases, traced by $\partial M(T)/\partial T|_{max}$, agree with the $C_m(T_C, B)$ anomalies. On the contrary, T_M slightly decreases with applied field. Both boundaries join T_M in a critical region at $T_{cr} = (4.3 \pm 0.2)\,\mathrm{K}$ and $B_{cr} = (2.1 \pm 0.2)\,\mathrm{kOe}$, around a critical point. Further detailed $M(B)$ measurements are in progress to investigate that critical region and the behavior of $T_C(B)$ and $T_M(B)$ as they approach the critical point.

3. Conclusions

From low temperature ($T < 1\,\mathrm{K}$) measurements we conclude that Ce_2Pd_2Sn belongs to the group of scarce ferromagnetic Ce-base inter-metallics, with an exceptionally low Kondo temperature and practically no 4f-*band* hybridization effects. However, before to reach such an ordered ground state the system undergoes a transition to a modulated (probably meta-stable) phase which is suppressed applying a relatively low magnetic field. The positive value of $\theta_P = 4.5\,\mathrm{K}$ and the nearly field independent T_M transition suggest a non-trivial nature of this intermediate phase. This is in concordance with eventual frustration effects arising from the triangular coordination of Ce magnetic atoms. Nevertheless, the detailed description of the magnetic structure of this intermediate phase remains an open question which merits further investigations. T_C is a first order transition due to the discontinuity in the variation of the magnetic propagation vector at the temperature where it jumps into a commensurate magnetic structure from the incommensurate one.

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