Specific-heat study of the Ce$_{1-x}$Y$_x$PdAl system

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Abstract

We report on specific-heat measurements of the heavy-fermion compounds Ce$_{1-x}$Y$_x$PdAl
($0 \leqslant x \leqslant 1$) between 0.35 and 300 K and in magnetic fields up to 14 T. Ce$_{1-x}$Y$_x$PdAl
compounds crystallize in the hexagonal ZrNiAl-type structure and CePdAl orders
antiferromagnetically below $T_N = 2.8$ K. The specific heat measured in external magnetic fields
is also consistent with the antiferromagnetic order and the phase transition to the ferromagnetic
state in fields around 4 T. The temperature dependence of the magnetic specific heat in CePdAl
indicates magnetic correlations far above T_N. Substitution of nonmagnetic Y for magnetic Ce
ions reduces T_N rapidly and the antiferromagnetic order vanishes around $x = 0.2$. The
Sommerfeld coefficient γ of the electronic specific heat is temperature dependent and increases
strongly at low temperatures for all Ce concentrations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Rare-earth intermetallic compounds containing Ce are known to exhibit often unusual magnetic properties at low temperatures. CePdAl crystallizes in the hexagonal ZrNiAl-type structure (space group $P\bar{6}2m$) [1] and orders antiferromagnetically below $T_N = 2.7$ K [2, 3]. The enhanced γ-value (>200 mJ mol^{-1} K^{-2}), the low value of the magnetic entropy released at T_N ($\cong 0.4R \ln 2$) and the temperature dependence of electric resistivity [2, 3] are evidence of a pronounced Kondo effect. Based on the observed pressure dependence of the specific-heat anomaly [4], CePdAl seems to be located close to the maximum of T_N in Doniach's magnetic phase diagram. The long-range magnetic order below $T_N = 2.7$ K is characterized by an incommensurate propagation vector $k = (1/2, 0, \tau)$ with $\tau \cong 0.35$, and a longitudinal sine-wave modulated spin arrangement oriented along the hexagonal c-direction [5]. One-third of the Ce magnetic moments are strongly frustrated in a close relation to the kagome-like triangular arrangement of Ce atoms within the basal planes. Neutron diffraction reveals that the frustrated moments do not order down to 180 mK at least [6]. The single crystal magnetization measurements [7] reveal a strong magnetocrystalline anisotropy with the c-axis as

the easy axis, in agreement with the diffraction data. Recently, the dilution effects in Ce$_{1-x}$Y$_x$PdAl [8] and Ce$_{1-x}$La$_x$PdAl [9] have been studied. The substitution of Ce ions by nonmagnetic ions leads to a gradual suppression of magnetic order, the reduction of T_N being stronger for the Y substitution. The long-range magnetic order also disappears when Pd is substituted by Ni or Rh [10, 11].

In this paper we present a detailed analysis of the specific heat of CePdAl and Ce$_{1-x}$Y$_x$PdAl compounds. Compared to previous studies, we have performed measurements in a much broader temperature range of 0.35–300 K and extend the study of the diluted system to higher Y concentrations. A further aim of this work is to investigate the effect of applied magnetic field on the specific heat, which is surprisingly missing up to now.

2. Experimental details

Polycrystalline samples of Ce$_{1-x}$Y$_x$PdAl with $x = (0; 0.02; 0.04; 0.06; 0.08; 0.1; 0.15; 0.2; 0.3; 0.5; 0.8)$ were prepared by arc-melting stoichiometric mixtures of pure elements (4N for Ce and Y, 3N5 for Pd and 5N for Al) in a mono-arc furnace under the protection of an argon atmosphere. The
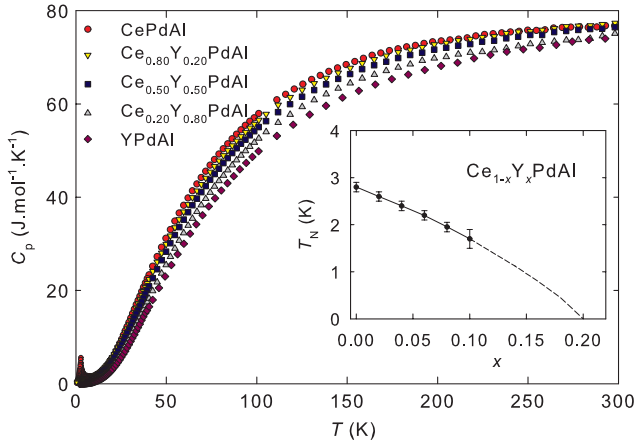
Figure 1. The specific heat of the $Ce_{1-x}Y_xPdAl$ compounds in the whole measured temperature range. Only selected representative concentrations are shown. The concentration dependence of the Néel temperature is plotted in the inset; the dashed line here is an extrapolation only.

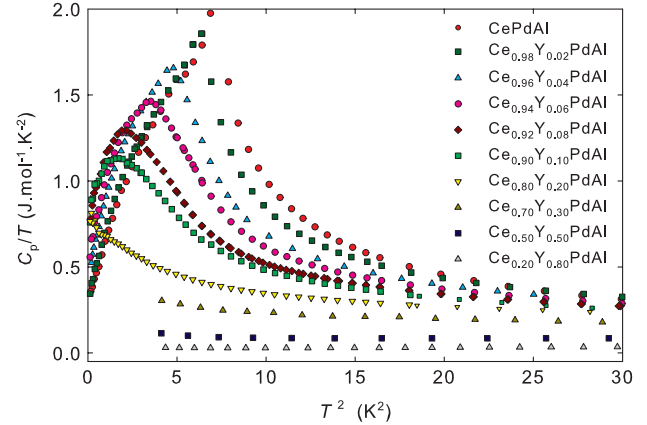**Figure 2.** Low-temperature specific heat of the $Ce_{1-x}Y_xPdAl$ compounds.

samples were turned and re-melted several times to achieve better homogeneity. The x-ray diffraction experiments on the powdered as-cast samples at room temperature showed all the samples to be single phase with a hexagonal ZrNiAl-type structure. Since an annealing process from 700 to 900 °C causes a chemical decomposition, as-cast samples were used in this study.

The specific heat was measured by the relaxation method using a Quantum Design PPMS system in the temperature range between 0.35 and 300 K and in magnetic field up to 14 T. Small samples with a mass of about 2 mg were measured at low temperatures below 10 K and in magnetic fields, whereas larger samples (∼20 mg) were used for measurements between 2 and 300 K to achieve reasonable precision at higher temperatures where the heat capacity of the sample holder increases considerably.

3. Results and discussion

The specific heat of the $Ce_{1-x}Y_xPdAl$ compounds is represented in figure 1 and the low-temperature detail in figure 2. The measured specific heat of pure CePdAl is in accordance with data presented in [2] and [3]. We observe a well pronounced anomaly with a maximum at 2.7 K. The shape of this anomaly is typical for a second-order phase transition. The idealization of the specific-heat jump under the constraint of entropy conservation yields the ordering temperature $T_N = (2.8 \pm 0.1)$ K, in agreement with previous experiments. The anomaly shifts to lower temperatures with increasing Y content and the corresponding concentration dependence of T_N is plotted in the inset of figure 1. The accuracy of the T_N determination somewhat decreases with Y content as the anomaly becomes broader. The magnetic order vanishes for compounds with ≃20% of Y.

The measured $Ce_{0.8}Y_{0.2}PdAl$ data still show a relatively strong increase of C_p/T with decreasing temperature which is qualitatively similar to the rise of specific heat observed

for $T > T_N$ in compounds with lower Y concentration. We cannot thus exclude that $Ce_{0.8}Y_{0.2}PdAl$ orders magnetically with T_N below 0.4 K. On the other hand, such an upturn of C_p/T at low temperatures is often observed in diluted systems for compounds on the verge of long-range magnetism [12]. Similar behavior was also observed for compounds from the Ce(Pd, Rh)Al series that do not show long-range magnetic order. The low-temperature data were described there by a power-law behavior $C_p/T \sim T^{-n}$ with n between 0.2 and 1.2 depending on the Pd–Rh concentration [11]. The $Ce_{0.8}Y_{0.2}PdAl$ data below ≈ 6 K can also be well described by such a power-law with n around 0.5.

In general, the specific heat of the studied materials can be expressed as a sum of the electronic, lattice and magnetic contributions:

$$C_p = C_{el} + C_{latt} + C_{mag}. \qquad (1)$$

The electronic specific heat is expressed as $C_{el} = \gamma T$, where γ is the Sommerfeld coefficient that is proportional to the density of states at the Fermi level. The magnetic contribution generally depends on the type of magnetic excitation. In the paramagnetic region, it is often called the Schottky contribution C_{Sch} and depends only on the energy splittings of the ground state multiplet in the crystal field. The contribution of lattice vibrations, C_{latt}, dominates the specific heat at high temperatures and its correct subtraction is essential for evaluation of the remaining contributions. The phonon spectrum of (Ce, Y)PdAl compounds consists of three acoustic and six optic branches. The corresponding specific heat can be described within the Debye and Einstein model.

Simultaneous fitting of all parameters of all three contributions is not credible because of a large number of correlated parameters. Nevertheless, certain quantitative estimations can be easily done for the γ value at 300 K. The lattice contribution is rather flat at temperatures close to 300 K and we can assume similar values for all Y concentrations. This assumption is corroborated by the fact that the specific heat of YPdAl and LuPdAl show only a small difference at 300 K [13]. The Schottky contribution can also be considered small and only weakly concentration dependent at 300 K. The
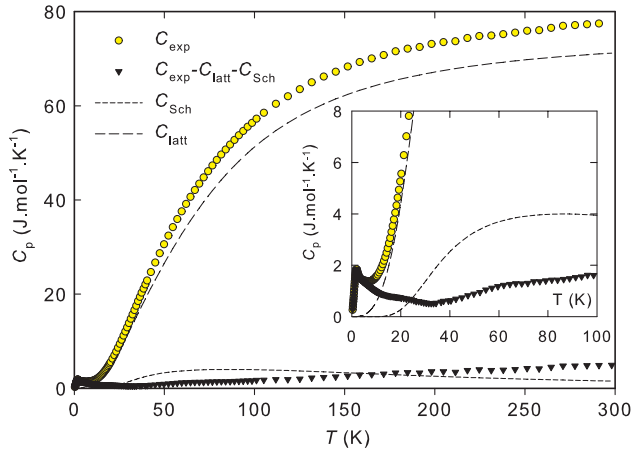
Figure 3. All contributions to the specific heat for $Ce_{0.9}Y_{0.1}PdAl$. The lattice contribution was calculated using $\theta_D = 150$ K, $\theta_{E1} = 159$ K and $\theta_{E2} = 311$ K (see text for details). The Schottky contribution was obtained using $\Delta_1 = 169$ K and $\Delta_2 = 409$ K [7].

Figure 4. The temperature dependence of the Sommerfeld coefficient of the electronic specific heat as determined from the specific heat data (see text for details). The values per (Ce, Y)PdAl formula unit are presented. The γ-values for individual concentrations remain almost unchanged above 40 K. Note the logarithmic scale.

difference between the measured specific heat of CePdAl and YPdAl ($\gamma_{YPdAl} = 5.9$ mJ mol^{-1} K^{-2} [13]) at 300 K (see figure 1) is thus predominantly due to the electronic specific heat. The measured values indicate that the γ coefficient at 300 K is 15 ± 5 mJ mol^{-1} K^{-2} for CePdAl and the Ce rich compounds. This value is much lower than the enhanced low-temperature γ value (>200 mJ mol^{-1} K^{-2}) reported previously [2, 3] and also observed in our data. It follows that there should be a strong increase of the γ coefficient with decreasing temperature. This qualitative conclusion is quite indisputable considering also uncertainties in the lattice or Schottky contributions. The temperature dependence of C_{el}/T at low temperatures is observed frequently in heavy-fermion systems [14] and also in systems with moderately enhanced γ coefficient including, for example, δ-Pu [15].

The temperature dependent γ-value together with the uncertainty in C_{latt} makes any quantitative evaluation of the Schottky contribution that is relatively smaller practically impossible. When analyzing the data in the paramagnetic region, we have therefore concentrated on the main feature which is the temperature development of C_{el}. The data for all $Ce_{1-x}Y_xPdAl$ compounds were treated in the following way: the lattice and Schottky contributions were estimated for all concentrations as explained below and then the electronic part was directly obtained from equation (1).

The specific heat of a nonmagnetic analog is often used to approximate the lattice contribution. In our case, C_{latt} of the Y rich compounds can be assumed to be close to that of YPdAl [13]. For the Ce based compounds, the specific heat of the La analog usually provides an ideal estimation of the phonon specific heat. LaPdAl unfortunately crystallizes in a different structure [1] and cannot be used for this purpose. Therefore we consider LuPdAl [13] as a nonmagnetic analog for CePdAl and Ce rich compounds. LuPdAl has a higher molar mass and a smaller unit cell than CePdAl. These two factors affect C_{latt} in an opposite way and we assume in the first approximation that they compensate each other.
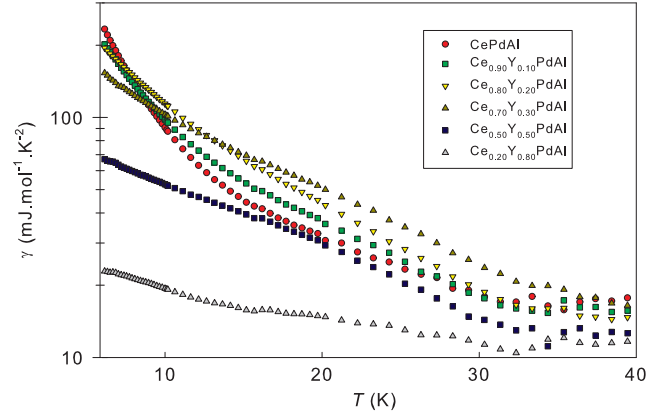
The analysis of the specific heat of YPdAl and LuPdAl [13] shows that the lattice contribution can be well described by three parameters: the Debye temperature characterizing three acoustic phonon branches ($\theta_D = 150(3)$ K for LuPdAl and 177(4) K for YPdAl) and two Einstein temperatures θ_{E1} and θ_{E2} describing two and four optic branches, respectively (see [13] for the values). We also kept the same model for the whole $Ce_{1-x}Y_xPdAl$ system. For CePdAl and the compounds with $x \leqslant 0.1$, we used the same parameters as reported for LuPdAl. For the compounds with higher Y concentration, C_{latt} was calculated using interpolated values of Debye and Einstein temperatures between those reported for YPdAl and LuPdAl [13].

The Schottky contribution was obtained using the energy level splitting (169 and 409 K) determined from magnetization measurements on CePdAl single crystal [7] and multiplied by $(1 - x)$ to reflect the Ce content. As an example, all the contributions for $Ce_{0.9}Y_{0.1}PdAl$ are plotted in figure 3. A similar picture is obtained for all other compounds. The subtraction of C_{latt} and C_{Sch} from the measured data leads to the temperature dependence of the Sommerfeld coefficient as shown in figure 4. The γ versus T dependence shows a strong increase below ~ 35 K and reaches values above 200 mJ mol^{-1} K^{-2} at 6 K for CePdAl. Above 40 K, the γ-coefficient stays almost temperature independent with a value of $\gamma_{300} \simeq 18$ mJ mol^{-1} K^{-2}, in good agreement with our preliminary estimation at 300 K. This qualitative picture holds for all other Y concentrations.

Let us now describe the specific heat of CePdAl in the magnetically ordered state. The lattice contribution is very small below 5 K. We can easily use the lattice specific heat of isostructural LuPdAl as an approximation for CePdAl without introducing any noticeable error. The remaining sum of the electronic and magnetic specific heat well below T_N is described by the following expression [16]:

$$C_{el} + C_{mag} = \gamma T + A_{mag} T^h. \qquad (2)$$

The coefficient A_{mag} is related to the spin velocity in the magnetically ordered state [17] and $h = d/\varepsilon$ with d
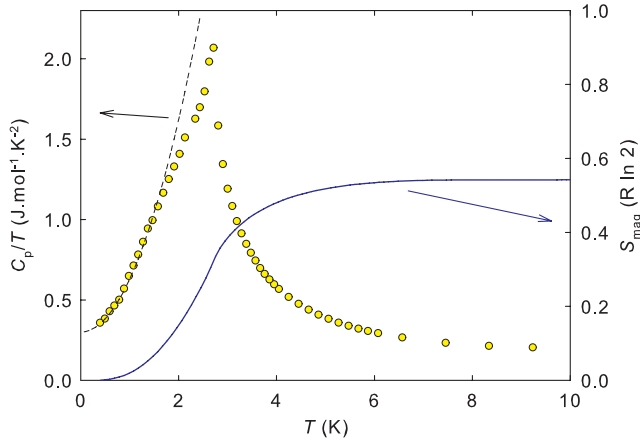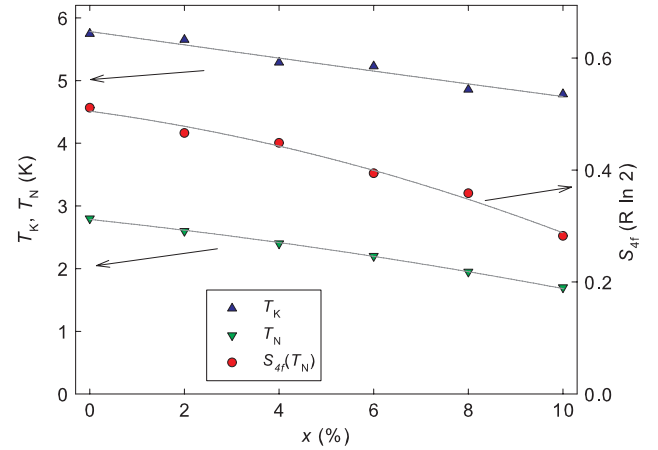
Figure 5. The specific heat and magnetic entropy of CePdAl. The dashed line represents the fit to equation (2) below 1.8 K (see the text for details).


Figure 6. Dependence of the Kondo temperature and the 4f-electron entropy (per Ce mol) at T_N on Y concentration. We also present the Néel temperature shown already in figure 1 to allow direct comparison. Dotted lines are only to guide an eye with no physical meaning.

representing the dimensionality of the magnon excitations and ε related to the type of magnetic order ($\varepsilon = 1$ for antiferromagnetic, $\varepsilon = 2$ for ferromagnetic).

The limited temperature region which can be described by expression (2) does not allow for plausible determination of the parameter h. Assuming three-dimensional antiferromagnetic order, the CePdAl data can be satisfactory described by (2) below 1.8 K (see figure 5). The fit of experimental data gives $\gamma = 300 \pm 30$ mJ mol^{-1} K^{-2}, slightly higher than the value of 250 mJ mol^{-1} K^{-2} deduced from previous specific-heat measurements [2]. Taking values of h between 3 and 2, corresponding to lower dimensionality of the antiferromagnetic order as also discussed in [18], we obtain γ-values between 250 and 300 mJ mol^{-1} K^{-2}. A similar result is achieved for Ce$_{0.98}$Y$_{0.02}$PdAl, but the analysis for higher Y concentrations is less reliable due to decreasing T_N.

Taking $\gamma = 300$ mJ mol^{-1} K^{-2} as the low-temperature limit, $\gamma = 200$ mJ mol^{-1} K^{-2} at 10 K and a linear interpolation between these values, we calculated the molar magnetic entropy at T_N as 0.35 $R \ln 2$ (see figure 5). This value is in accordance with [3], but smaller than the value of 0.55 $R \ln 2$ given in [2]. Taking into account very good agreement between our data and data determined by Schank *et al* [2], we guess that the entropy value in [2] might correspond to both C_{mag} and C_{el} which are difficult to separate. This approach with our data would lead to an entropy value at T_N of 0.51 $R \ln 2$ in accordance with [2]. The magnetic entropy continues to increase in a relatively broad temperature range above T_N up to ~6 K, indicating strong magnetic fluctuations even far above T_N. This result is consistent with the temperature dependence of the nuclear magnetic relaxation rate as observed in recent ^{27}Al NMR measurements [18]. The value of magnetic entropy at 10 K amounts to 0.54 $R \ln 2$, considerably below the value expected for a doublet ground state. The strong reduction of the magnetic entropy can be ascribed to a Kondo effect.

We have estimated T_K considering the reduction of the magnetic entropy at T_N with respect to the value of $R \ln 2$. We used a simple two-level model as in [19]. The results depend on how we calculate the magnetic entropy. Calculating

the entropy per Ce mol, S_{4f}, from $C_{4f} = C_{mag} + C_{el}$ (as in [19]) leads to Kondo temperatures between 5 and 6 K. With increasing Y concentration T_K slightly decreases as can be seen from figure 6. Calculating T_K only from C_{mag} we get somewhat higher Kondo temperature values (7 K for CePdAl) with the same concentration trend.

The influence of applied magnetic field on the specific heat is presented in figure 7. Here we should bear in mind that CePdAl is a strongly anisotropic system and we present measurements on polycrystalline samples. The observed effect thus represents only an average over all field directions with respect to the crystal structure. The magnetization [20, 7] and neutron diffraction [21] single crystal measurements reveal several metamagnetic transitions between 3 and 4 T for field applied along the *c*-axis. Although the exact origin of these metamagnetic transitions remains unknown, it was speculated that they are connected to the onset of the appearance of the magnetic moment on the frustrated third of the Ce sites and subsequent appearance of a ferromagnetic component on the remaining Ce sites [20, 21]. On the other hand, the magnetic field applied perpendicular to the *c*-axis does not break the antiferromagnetic order and the corresponding magnetization curve shows no transitions up to 7.5 T [7]. Our data for pure CePdAl (see figure 7) are generally in agreement with these observations. The anomaly around T_N first shifts gradually to lower temperatures as expected for the antiferromagnetic order. The specific heat above 3 K remains almost unchanged in fields up to 4 T. Further increase of the magnetic field above 4 T leads to a considerable increase of C_p/T at temperatures above 3 K. The magnetic entropy is thus shifted to higher temperatures, indicating ferromagnetic ordering in CePdAl above 4 T, in agreement with the magnetization and neutron diffraction data. The unchanged antiferromagnetic order for grains oriented perpendicular to the magnetic field is reflected by a persisting anomaly around $T_N = 2.7$ K. This anomaly is clearly observed even in the field of 14 T. Another observation concerns the low-temperature limit of the electronic specific
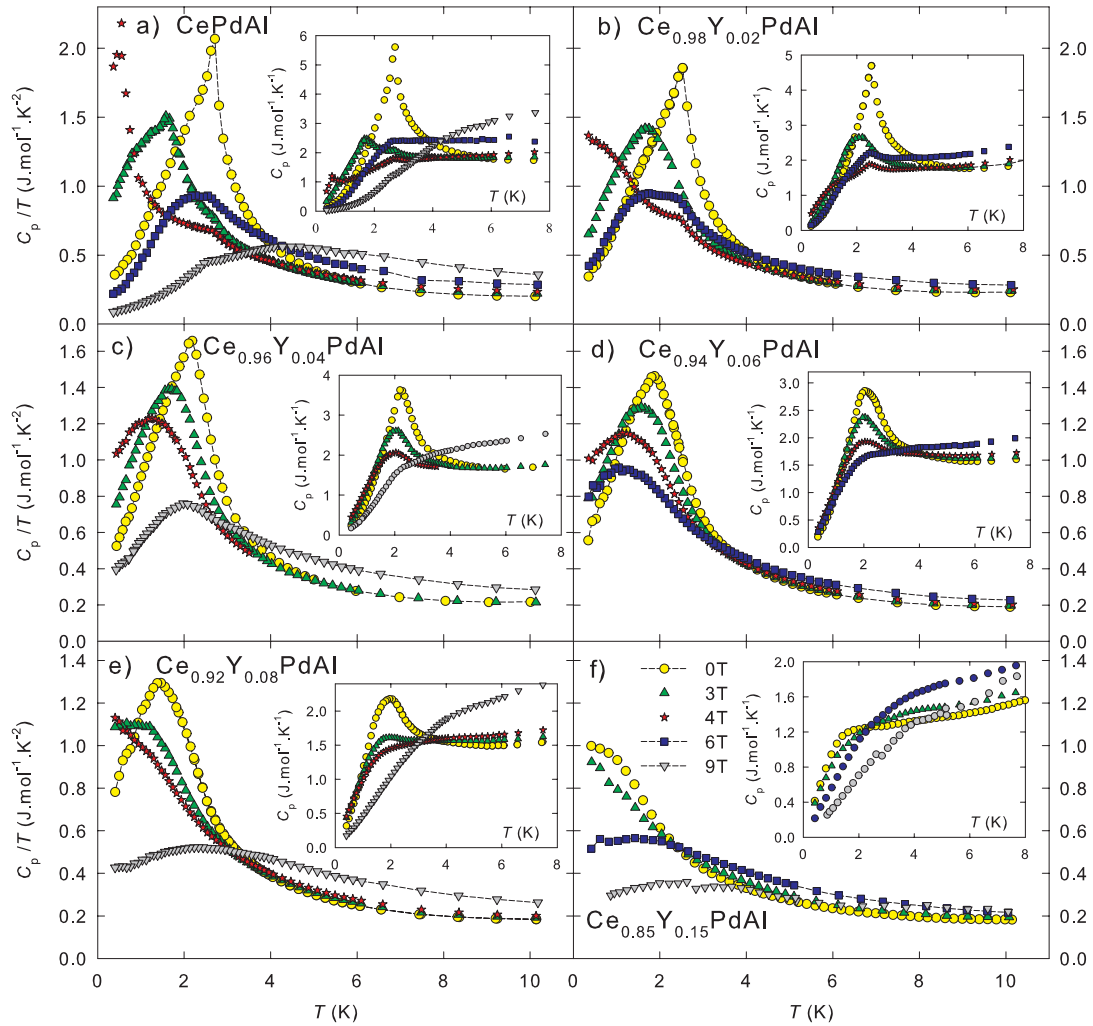
Figure 7. The specific heat of the $Ce_{1-x}Y_xPdAl$ compounds measured in external magnetic fields displayed as C_p/T versus T. The legend presented in part (f) holds for all samples. Insets in each part show the C_p versus T plot.

heat which is reduced in magnetic fields above 4 T, leading to $\gamma \simeq 50$ mJ mol^{-1} K^{-2} in 14 T. The decrease of the γ-value in the field-induced ferromagnetic state, where the frustration of one-third of the Ce moments is lifted [21], corroborates the suggestion that the third of Ce moments that are frustrated (paramagnetic) are in a heavy-fermion state [18].

The compound with 2% Y (figure 7(b)) shows behavior similar to CePdAl. With further increasing the Y content between 4 and 8%, the anomaly around T_N becomes broader in zero field. The application of a magnetic field leads to a shift of the anomaly to lower temperatures as for pure CePdAl, but the anomaly that persisted at 2.7 K disappears for Y concentrations above 6%. We can speculate that the absence of this latter anomaly is an indication of reducing the strong magnetocrystalline anisotropy in CePdAl. Neutron diffraction study of (Ce, Y)PdAl compounds is desirable to show how the magnetic structure of CePdAl is influenced by Y substitution.

4. Conclusions

We can conclude that our data confirm the antiferromagnetic order in CePdAl below $T_N = 2.8$ K and are consistent with the metamagnetic phase transition to the ferromagnetic state in applied fields above 4 T. The temperature dependence of the magnetic contribution shows that antiferromagnetic correlations develop from temperatures far above T_N. The ordering temperature decreases rapidly with increasing Y concentration and the magnetic order vanishes around $x = 0.2$. Also the Kondo temperature decreases with Y concentration. The γ-coefficient of the electronic specific heat shows a temperature dependence with a strong increase at low temperatures for all Ce concentrations. The low-temperature limit of the γ-value in CePdAl is close to 300 mJ mol^{-1} K^{-2} whereas the high-temperature value, that is constant above ~ 50 K, amounts to only 18 mJ mol^{-1} K^{-2}. The latter value is only weakly concentration dependent.

Acknowledgments

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