Low-temperature magnetic and thermal properties of CePdSb

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Low-temperature ac and dc magnetic susceptibility, high-field magnetization, and specific-heat measurements have been carried out on CePdSb. The magnetic measurements confirm the ferromagnetic transition at $T_C = 17$ K as previously reported. However, no anomaly in the specific heat is observed at that temperature, but only the onset of the magnetic contribution, $C_M(T)$. The maximum of $C_M(T)$ is observed at $T_{max} = 9.7$ K. The lack of a $C_M(T)$ jump at T_C is discussed in terms of the comparison of the exchange integrals between first- and second-nearest magnetic neighbors. Depending on their relative values, the magnetic structure can behave as low dimensional or incommensurate. The entropy of the magnetic phase ($R\ln 2$) and the low density of states ($\gamma = 11$ mJ/molK^2) excludes a Kondo-lattice character for this compound.

I. INTRODUCTION

Based on the background given by the variety of physical phenomena shown by the Ce and U binary compounds, the study of their respective ternary intermetallics has greatly developed during recent years. Among the most intensively studied families, equiatomic compounds of the type CeTX (where T is a transition metal and X a p element) show a variety of physical properties, such as magnetic order, heavy-fermion or mixed-valent behavior, and in some cases a gap formation in the density of states at low temperatures.[1,2]

Within the CePdX family of compounds, those with X = In and Sn are antiferromagnets (AF), with their respective Néel temperatures at $T_N = 1.7$ K and 7 K,[2] while that with X = Sb is ferromagnetic (F), with a Curie temperature of $T_C = 17$ K.[3] The same X-element dependence is found in the UPdX family,[4] not only in the type of magnetic order but also in the relatively high ordering temperature of the X = Sb compound. These magnetic properties of the U compounds are discussed in Ref. 4 in terms of the U-U separation with respect to the Hill limit[5] and the magnetic interactions as due to superexchange rather than a Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism.

The CeTX compounds crystallize in different structure types,[6] the most representative being ϵ-TiNiSi, ZrNiAl, and $CaIn_2$. In the $CaIn_2$-type structure the T and X atoms are statistically distributed in the f (Wyckoff notation) crystallographic position.[7] Such a random distribution of the T and X elements may contribute to the exceptionally large electrical resistivity shown by CePdSb (Ref. 3) and UPdX (X = Sn and Sb).[4] On the other hand, the gap in the density of states formed at low temperatures in the crystallographically ordered CeNiSn and CeRhSb compounds[8,9] is not observed in those with the $CaIn_2$ structure.

From its magnetic and transport properties, CePdSb was reported to be a possible ferromagnetic Kondo-lattice system.[3] The coexistence of ferromagnetism and Kondo behavior (i.e., large density of states) is an unexpected feature,[10] which merits direct confirmation by a low-temperature specific-heat measurement. We have therefore studied the low-temperature thermal and magnetic properties of the CePdSb compound in order to better understand the nature of its F ground state (GS).

II. EXPERIMENTAL DETAILS

Three samples of the ternary CePdSb compound were prepared by arc-melting stoichiometric amounts of the constituents (Ce 4N, Pd 4N, and Sb 6N pure) in an Ar atmosphere. The melting procedure was repeated to ensure the homogeneity of the samples. The weight losses during the arc-melting were lower than 1% of the total mass (of about 2 g). X-ray analysis, using Cu and Co $K\alpha$ radiation, shows a single phase corresponding to the hexagonal $CaIn_2$-type structure, with lattice parameters according to the literature.[7]

The specific-heat $C_P(T)$ measurements were performed in a ^{3}He-semiadiabatic calorimeter using the standard heat-pulse method. The ac magnetic susceptibility $\chi'_{ac}(T)$ was measured in the same cryostat to allow a direct comparison of the characteristic temperatures of the system. The inductive, $\chi'(T)$, and the dissipative, $\chi''(T)$, components of the ac susceptibility were detected by means of a mutual inductance bridge. The amplitude of the excitation field was 10 μT at the fixed frequency of 128 Hz. The frequency dependence of the ac susceptibility was analyzed with a two-phase lock-in amplifier. The magnetization $M(T)$ was measured in a standard

superconducting quantum interference device (SQUID) magnetometer, operating under fields up to $B = 5$ T, from 1.7 K to room temperature.

III. EXPERIMENTAL RESULTS

The temperature dependence of χ_{ac} for CePdSb indicates the onset of magnetic fluctuations at around 20 K, followed by a strong increase of $\chi'(T)$ with its maximum slope at 17.2 K. An abrupt increase of the dissipative component $\chi''(T)$ is observed at that temperature where the T_C is expected (see Fig. 1). The maximum values of χ' and χ'' are observed at 14 K and 15 K, respectively, more than 1 K below the maximum of $\chi_{ac}(T)$ reported in Ref. 3. A further $\chi_{ac}(T)$ measurement performed at a higher frequency (1 kHz) shifts that maximum to a higher temperature. Such a frequency dependence of these maxima suggests a nonsimple dynamics of the interacting magnetic moments. At lower temperatures $\chi'(T)$ and $\chi''(T)$ show another very broad maximum centered at 6 K, which is slightly affected by a change of frequency (0, 10, 128, and 1000 Hz).

The $M(T)$ dependence at low dc field ($B = 0.5$ mT) is similar to the $\chi_{ac}(T)$ dependence; the maximum of $-\partial M(T)/\partial T$ coincides with T_C and the maximum of $M(T)$ is found at 12 K (see Fig. 1). The broad maximum at 6 K is also observed under this low field. Although this anomaly seems not to vary with frequency, it is completely smeared out by a dc field of 5 mT. Also in Fig. 1, we show the temperature dependence of the inverse of the dc susceptibility, $\chi_{dc}^{-1}(T)$, for $T < 50$ K, which coincides with that reported in Ref. 3. From the 20 K $< T <$ 30 K range we extract a Curie-Weiss temperature of $\Theta_P = 17$ K and a Curie constant of $C_C = 0.37$ emu K/mol (below 20 K the magnetic fluctuations turn on and above 30 K the crystal-field-excited levels start to contribute). This value of Θ_P coincides with T_C, but differs from the one reported in Ref. 3 because it is extracted from the low-temperature region and therefore is referred to the Ce-doublet crystal-field GS. The magnetization curves were measured up to 2 T between 2 K and 22 K, as shown in Fig. 2. No hysteresis was observed after field cycling between $B = \pm 2$ T. The saturation magnetic moment μ_s, obtained from extrapolation to $1/B \to 0$ in a M vs $1/B$ plot, is $\mu_s \approx 0.95\mu_B$. Such a value can be compared with the moment extracted from C_C in the paramagnetic region ($\mu_{eff} = 1.7\mu_B$) through the $\mu_s = 3^{-1/2}\mu_{eff}$ relationship.[11] From the analysis of the crystal-field parameters we obtain the result that the experimental C_C and μ_s correspond to those expected from an isolated $|\pm 1/2\rangle$ doublet GS, with an effective spin 1/2 and a strongly anisotropic Landé factor: $g_{\parallel} = 6/7$ and $g_{\perp} = 18/7$, parallel and perpendicular to the hexagonal **c** axis, respectively. The calculated values are $C_C = 0.43$ emu K/mol and $\mu_s = 1.04\mu_B$, in good agreement with the experimental results. A further analysis of the paramagnetic-ferromagnetic transition at T_C can be done by means of Arrott plots. Using the general expression[12] $H/M = (T - T_C)/T_1 + (M/M_1)^2$, where T_1 and M_1 are constants, we find parallel lines in the M^2 vs H/M plot. The zero of the first term is found at 17 K, which confirms the onset of magnetic ordering at T_C.

The measured specific heat $C_P(T)$ is shown in Fig. 3. Although the magnetic fluctuations contribute to $C_P(T)$ from around 20 K, there are no traces of a phase transition at 17 K, but a continuous increase of the magnetic contribution, $C_M(T)$, as the temperature is reduced. The maximum contribution of $C_M(T)$ occurs at around 9.7 K, hereafter T_{max}, far below the reported value $T_C = 17$ K. Because of this unexpected result concerning the large difference between T_C and T_{max}, the $C_P(T)$ of a second CePdSb sample was measured, obtaining the same result. In order to better analyze the magnetic contribution we have subtracted the electronic, γT, and the phonon, $C_{ph}(T)$, contributions to the total specific heat. The Sommerfeld coefficient, $\gamma = 11$ mJ/mol K^2, was obtained from the lowest temperature range, which is quite small for a Ce compound[13] but

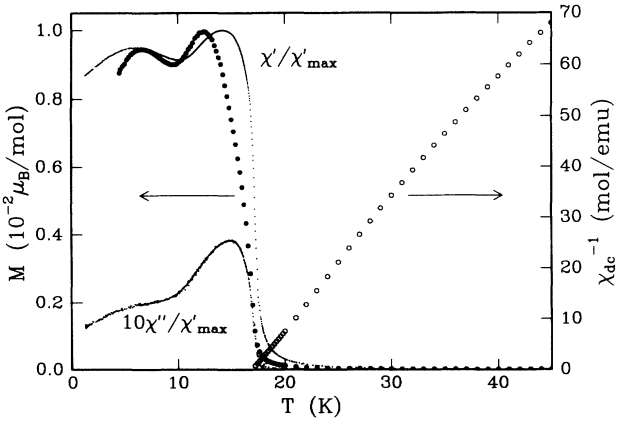

FIG. 1. Magnetization $M(T)$ (•) as a function of temperature measured under a field of $B = 0.5$ mT. Inverse of the dc susceptibility, χ_{dc}^{-1} (○), as a function of temperature in the $T > T_C = 17$ K range. Inductive, $\chi'(T)$, and dissipative, $\chi''(T)$, components of the ac susceptibility normalized to the maximum of $\chi'_{ac}(T)$ (in arbitrary units) between 1.2 K and 25 K.

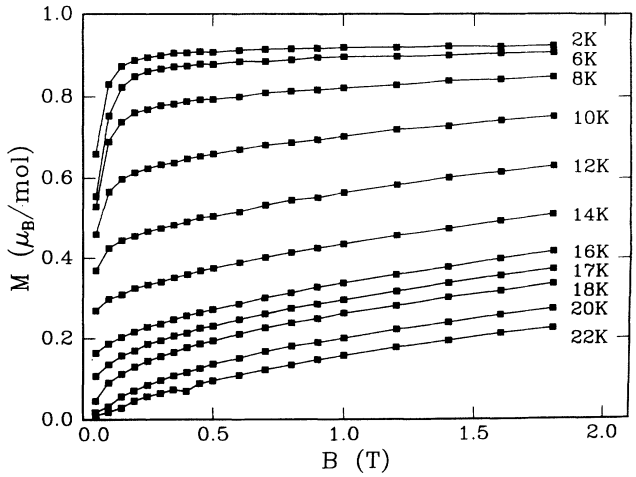

FIG. 2. Magnetization $M(T)$ as a function of field in the $B < 2$ T range and for temperatures between 2 K and 22 K.

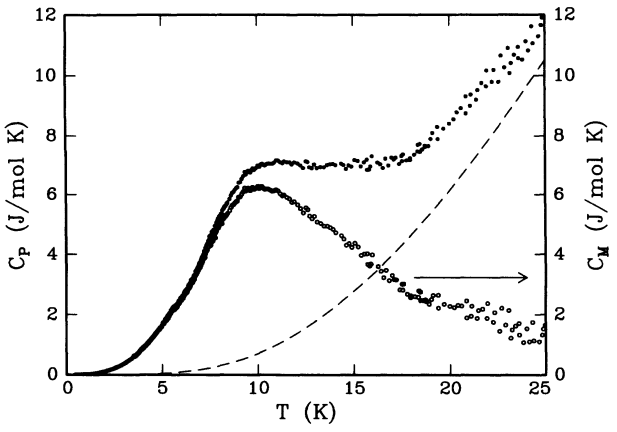

FIG. 3. Measured specific heat $C_P(T)$ of CePdSb (•) and the phonon contribution $C_{\rm ph}(T)$, from the reference compound LaAgGe (broken line) as a function of temperature. The magnetic contribution (○) is obtained from $C_M(T) = C_P(T) - \gamma T - C_{\rm ph}$(LaAgGe), where the maximum is observed at 9.7 K (see text).

comparable to that of LaPdSb: $\gamma = 4.2$ mJ/molK^2.[14] Unfortunately, the specific heat of the natural isotypic reference compound LaPdSb strongly deviates from the expected $\gamma T + \beta T^3$ behavior above 4.5 K,[14] making it unsuitable as a reference compound. We found that LaAgGe is an alternative reference system, which also forms in a $CaIn_2$ structure, has a similar molecular weight, a low-temperature phonon contribution close to that of LaPdSb, and a γ of practically zero.[15] The magnetic specific heat of CePdSb was therefore obtained as $C_M(T) = C_P(T) - \gamma T - C_{\rm ph}$(LaAgGe) (see also Fig. 3). This procedure is supported by the fact that the magnetic entropy gain, evaluated as $\Delta S = \int C_M/T\, dT$, is about $1.2R$ln2 at 25 K (see Fig. 4). This value is very close to

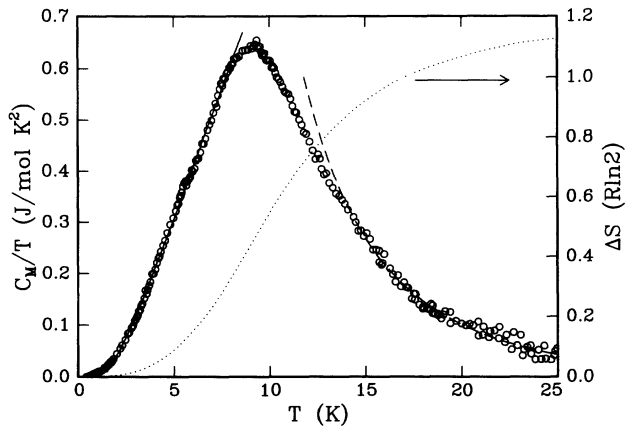

FIG. 4. Magnetic specific heat $C_M(T)$ (○) of CePdSb as a function of temperature in a C_M/T vs T plot. The continuous line is the function $G_M(T)$ fitted to the experimental data for $T < 8$ K (see text), and dashed line shows the T^{-2} dependence for $T \geq 14$ K. The entropy gain $\Delta S(T)$ is plotted as a function of temperature (dotted line), where the expected value Rln2 is reached at 17 K.

that expected for a Ce Kramers-doublet GS.

The most significant features of the $C_M(T)$ dependence are: (i) The temperature of the maximum of C_M (at $T_{\rm max} = 9.7$ K) does not coincide either with those of $\chi_{\rm ac}(T)$ and $M(T)$ or with those of their respective maximum derivatives. (ii) The entropy gain ΔS at $T_{\rm max}$ is $(1/2)R$ln2, while the expected Rln2 value is reached at 17 K (see also Fig. 4) and the increase of the internal magnetic energy ΔU up to $T_{\rm max}$ is about 1/3 of the value at 20 K. (iii) For $T \geq 14$ K, $C_M(T)$ follows a T^{-2} dependence, shown in Fig. 4 as $C_M/T \sim T^{-3}$. (iv) For $T < 8$ K, $C_M(T)$ can be described by the expression for a strongly anisotropic magnetic system with a gap δ in the magnon dispersion:[16] $G_M(T) = AT^n \exp(-\delta/T)$, where $n = 3$ for AF or $n = 3/2$ for F interactions, the fitting values being $A = 0.23$ J/molK, $n = 1.7$, and $\delta = 4.5$ K, as shown in Fig. 4. Finally, (v) a weak anomaly is observed at 6 K, coinciding with that of the low-field magnetic measurements.

IV. DISCUSSION

The absence of a specific-heat jump at T_C related to a second-order phase transition, and the difference in temperature between the $C_M(T)$ and the $M(T)$ maxima, are the most striking features of the low-temperature properties of CePdSb. Both indicate that the order parameter does not develop as expected for an isotropic system. We will explore two possibilities, one related to a strong magnetocrystalline anisotropy (or eventually low dimensionality) and the other to the incommensurability of the magnetic order parameter.

The first possibility is supported by some characteristics of the $CaIn_2$-type structure. In this compound, the Ce-Ce spacing in the **c** direction (3.95 Å) is much smaller than in the **a** direction (4.60 Å). Simultaneously, the Ce-ligand bonds (within the [1,1,$\bar{2}$,0] planes) favor the formation of a zigzag chain in the **c** direction. Within this picture the intrachain magnetic interactions J_1 are expected to be larger than the interchain ones J_2. However the random distribution of Pd and Sb in the f crystallographic sites should inhibit the development of long-range magnetic interactions.

Although most of the Ce magnetic properties in intermetallic compounds can be described as due to the conduction-electron-mediated RKKY interaction, the Ce pnictides magnetic behavior appears to be dominated by the superexchange mechanism. The prototype is precisely CeSb, which shows one of the higher ordering temperatures for Ce compounds at $T_N = 16$ K.[17] Noteworthy is the fact that, in this compound, the magnetic interactions within the Ce-Sb planes are F, regardless of the AF character of the interplane interaction.[18] The covalent character of the Ce-Sb bonds is also responsible for the large values of its electrical resistivity.[19]

We will analyze now some characteristics of low-dimensional systems which should be expected in a magnetic chain for $T \geq T_{\rm max}$.[20] They are: (i) an onset of magnetic fluctuations at $T \geq 2T_{\rm max}$ with a T^{-2} dependence of $C_M(T)$ in that region of temperature, (ii)

the maximum of $\chi(T)$ observed at a higher temperature than that of $C_M(T)$, and (iii) the low values of the $\Delta S(T_{max})/\Delta S(\infty)$ and $\Delta U(T_{max})/\Delta U(\infty)$ ratios (1/2 and 1/3, respectively). Besides the low dimensionality of the magnetic fluctuations, the long-range order may also be inhibited by the random distribution of the Ce ligands.

Although these characteristics are observed in CePdSb, some other features are not in agreement with those of a low-dimensional system. For example, the $C_M(T_{max})$ value does not fit into any of the model calculations for low-dimensional systems with spin 1/2,[20] and the low-temperature $C_M(T)$ dependence ($T < 8$ K) is well described by the expression for a three-dimensional (3D) strongly anisotropic ferromagnetic system with a finite gap in the magnon dispersion. Such a behavior below 8 K might be an indication that the 3D interactions turn on between 14 K and 8 K. A $M(T)$ curve measured under a field of 0.4 T shows a linear increase just between those temperatures, supporting the dimensional crossover. Therefore, within the low-dimensionality description the magnetic evolution of this system for decreasing temperature can be summarized as follows: the onset of ferromagnetic fluctuations is observed at around 20 K; they become cooperative at 17 K, but with a low-dimensional character and probably aligned within the plane defined by the zigzag Ce-Sb chains. Between 14 K and 8 K the interchain magnetic interactions become important and the system starts to behave as 3D with a strong anisotropic character. Finally, at low temperatures a gap is observed in the anisotropic magnon dispersion for low-energy magnetic excitations.

The second possibility (incommensurate magnetic order) is suggested by the similarities between the specific-heat and magnetization temperature dependences of CePdSb and $GdCu_5$. The latter compound shows a phase transition from paramagnetic to incommensurate AF recognized by neutron diffraction studies.[21] Although $GdCu_5$ was identified as an AF (with $T_N = 26$ K), its triangular magnetic structure results from competition of the exchange integrals between first ($J_1 < 0$) and second ($0 < J_2 < |J_1|$) -nearest magnetic neighbors.[21] This magnetic ordering results in a significant increase of $\chi(T \to T_N)$, but without any anomaly in the specific heat at that temperature.[22] As in the case of CePdSb, the maximum of $C_M(T)$ is observed far below T_N, although the magnetic fluctuations start to contribute for $T > T_N$. The very-low-temperature $C_M(T)$ dependence of $GdCu_5$ differs from that of CePdSb, but this is expected from the eightfold-degenerate Gd ground state. Both $C_M(T)$ curves practically scale for $T \leq T_N$ when they are normalized to the value of $C_M(T)$ at the ordering temperature calculated from mean-field theory. The competition between the AF and F magnetic exchange integrals does not allow one to consider CePdSb as a classical ferromagnet, as is confirmed by the absence of remanent magnetization. In this interpretation of the CePdSb and $GdCu_5$ magnetic behavior, the reason for the absence of a discontinuity of $C_M(T)$ at the ordering temperature remains unclear.

The present experimental evidence is not sufficient for a clear choice between these two possibilities as the origin of the striking CePdSb behavior. However, both have a common characteristic because they are based on the competition between two exchange interactions: J_1 and J_2.

With respect to the weak anomaly observed at 6 K, we can say that it is present in both measured samples but with different intensity and it is completely smeared out under an applied field of 5 mT. Such an anomaly was also observed in the CeSb compound with a very similar shape.[17] Anyway, from its magnetic behavior and the small contribution to the magnetic entropy, a spurious contribution cannot be excluded, as, for example, from surface oxidation.

Concerning the Kondo-lattice character proposed for this compound,[3] the $\Delta S(T) = R\ln 2$ value observed at 17 K and the value of $\mu_s \sim 1\mu_B$ (for $T \to 0$) are indications of a "full magnetic" and local character of the Ce $4f$ state. This fact is confirmed by the low value of the γ coefficient, which also indicates that there is no transference of degrees of freedom from the magnetic component to Kondo-like states. The low value of γ and the minimum Ce-Ce spacing of 3.95 Å fill two empirical conditions for the occurrence of ferromagnetism. As shown in Ref. 10, ferromagnetism in Ce and U compounds is observed only in those systems with γ below a threshold value of $\gamma_m = 3.5$ mJ/cm^{3}K^2, which corresponds to 50 mJ/molK^2 for CePdSb. Coincidentally the minimum Ce-Ce spacing, d, in this compound also falls within the range (3.7 Å$< d < 4.1$ Å) where the Ce ferromagnets are found.[10,13]

V. CONCLUSIONS

We have shown that the ferromagnetic behavior of CePdSb cannot be described within a simple isotropic picture. The temperature dependence of the magnetic contribution to the specific heat and the comparison of its maximum with that of the magnetic susceptibility can be explained by competition between two exchange interactions (intrachain J_1 and interchain J_2). If $J_1 > J_2 > 0$, the system behaves as having a magnetic structure of low dimensionality within a certain range of temperature, below which the magnetic correlations become 3D but with a strong anisotropic character. If $J_1 < 0$, but $|J_1| > J_2 > 0$, the magnetic order parameter can develop incommensurately with the lattice. Both interpretations describe quite well different features of the experimental results and therefore neutron diffraction studies are required on this compound in order to achieve an accurate microscopic picture of this system. The entropy of the magnetic transformation ($R\ln 2$) and the low density of electronic states ($\gamma = 11$ mJ/molK^2) exclude the possibility of a Kondo-lattice behavior for this compound, in agreement with the universal phenomenology of Ce ferromagnets.

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