Antiferromagnetic spin wave in Ce_2PdGe_6

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(Received 15 July 2003; revised manuscript received 18 December 2003; published 1 April 2004)

The ternary compound Ce_2PdGe_6 exhibits antiferromagnetic ordering below the temperature 11.4 ± 0.2 K, as revealed in the electrical-resistivity, static magnetic susceptibility, and low-temperature specific-heat data. The entropy associated with the magnetic structure of Ce_2PdGe_6 was found to be close to the theoretical value of $2R\ln 2$, which would be expected for a doublet ground state of Ce^{+3} ions in the compound Ce_2PdGe_6. The magnetic contribution to the heat capacity of Ce_2PdGe_6 below Néel temperature T_N was found to depend on the cube of temperature, which furnishes perhaps the most direct experimental testimony of the whole spin-wave theory for an antiferromagnetic material.

DOI: 10.1103/PhysRevB.69.132401 PACS number(s): 75.30.Ds, 75.30.−m, 75.50.Ee

Research on the issue of the spin wave in magnetic materials has been of much interest to both theorists and experimentalists for the past fifty years.[1–15] Though there are plenty of magnetic-resonance experiments or inelastic-neutron-scattering experiments to confirm the spin-wave theory, the resonance frequencies or spin wave excitations involve only the properties of very special symmetric states. Various temperature dependences have been predicted by theorists for the magnetic contribution to the heat capacity C_M below the ordering temperature. Ferromagnetic and antiferromagnetic spin wave materials were noticeably different, being proportional to $T^{3/2}$ and T^3, respectively.[15] Therefore, the specific-heat measurements provide perhaps the most direct experimental confirmation of the whole spin-wave theory. The T^3 formula for an antiferromagnetic involves the same form of temperature dependence as that for the specific heat arising from the lattice vibrations. Corrections for the effect of anisotropy or crystal electrical field will always injure the rigor of the T^3 law. Some examples are the heat capacity of β cerium[14] or heavy fermion compound $CePd_2Si_2$ (Ref. 16), etc. Recently, we have found that the magnetic contribution to the heat capacity of the compound Ce_2CuGe_6 involves a considerably larger proportionality constant than the ordinary Debije lattice term, and the T^3 behavior was capable of experimental detection in the temperature range from 0.5 K to 0.98 T_N.[17] As determined from dc susceptibility and heat capacity measurements, this compound undergoes an antiferromagnetic transition at 14.7 ± 0.2 K. In this paper, we report a new candidate of antiferromagnetic spin wave compound Ce_2PdGe_6 which exhibits a Néel temperature T_N of 11.4 ± 0.2 K. In addition to experiments on Ce_2PdGe_6, dc electrical resistivity and low-temperature heat capacity measurements on the isostructural La_2PdGe_6 have been made in order to estimate the phonon contribution to the resistivity and heat capacity of Ce_2PdGe_6.

The ternary R_2PdGe_6 (R=Ce,La) compounds crystallize in an orthorhombic Ce_2CuGe_6-type structure with space group A_{mm2} (Ref. 18). Polycrystalline samples investigated for this work were synthesized by arc melting together with stoichiometric amounts of the constituent elements in a Zr-gettered arc furnace on a water-cooled Cu hearth under purified argon of about one atmosphere. Rare-earth elements with a purity of 99.9%, Pd with 99.95% purity, and Ge with 99.999% purity were used. Due to sufficiently low vapor pressures of these elements at the melting temperature of the ternary compound, weight losses during several melting and turning cycles were about 0.08%. The arc-melted sample was then sealed under argon in a quartz tube, and annealed for 12 days at 600 °C. This heat treatment was followed by a water quench to room temperature. Powder x-ray diffraction patterns with CuK_α radiation indicated that each sample was single phase, with no additional reflections. As determined by the method of least squares fit, the refined lattice parameters **a**=0.4169(8) nm, **b**=0.4085(5) nm, **c**=2.2081(5) nm for Ce_2PdGe_6 and **a**=0.4209(2) nm, **b**=0.4104(6) nm, **c**=2.2208(7) nm for La_2PdGe_6 were then obtained.

dc electrical resistivity measurements were made between 2.0 and 300 K using a standard four-probe technique in a system fully automated for temperature stability and data acquisition.[19] Fine platinum wires (~2 mm diameter) were spot welded to the samples with small rectangular parallelpipeds of approximate dimensions $1\times1\times5$ mm^3, and served as the voltage and current leads. Data were taken with the current applied in both directions to eliminate possible thermal effects. All data presented are for the warming curves. Figure 1 displays the temperature dependence of the resistivity of Ce_2PdGe_6, La_2PdGe_6, and the magnetic resistivity ρ_m of Ce_2PdGe_6. The magnetic resistivity was estimated by subtracting the resistivity of isostructural La_2PdGe_6 from that of Ce_2PdGe_6. Figure 1 shows a clear single kink in the resistivity curve of Ce_2PdGe_6 at 11.5 K. The significance of this kink is corresponding to the magnetic ordering of the compound and will be confirmed later by the susceptibility and heat capacity measurements. The shoulder appeared in the resistivity curve of Ce_2PdGe_6 at about 120 K is a typical feature for the Kondo effects on the compounds with the crystal-field splitting. However, no evident peak and phenomeon of the coherence between Kondo states at Ce sites

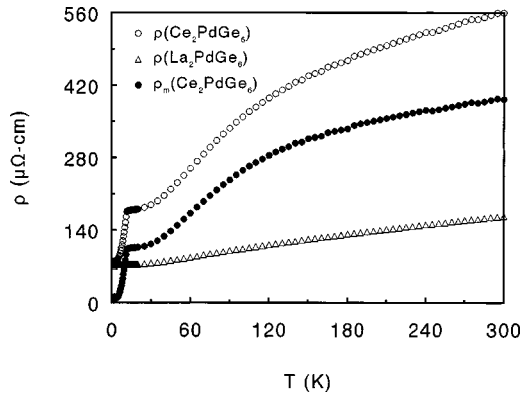

FIG. 1. Resistivity vs temperature of Ce_2PdGe_6, La_2PdGe_6, and the difference between these two compounds from 2.0 to 300 K.

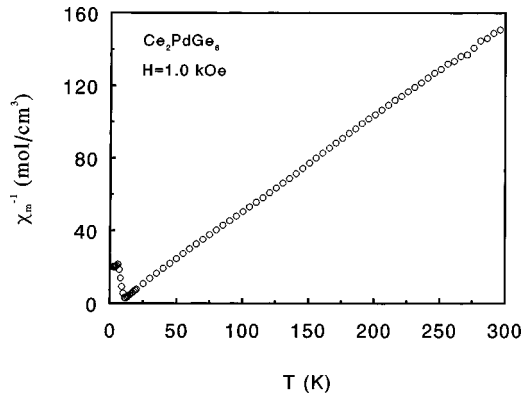

FIG. 3. Inverse molar magnetic susceptibility χ_m^{-1} vs temperature of Ce_2PdGe_6 between 2.0 and 300 K.

were observed in the magnetic resistivity curve of Ce_2PdGe_6, as shown in Fig. 1. It is suggested that the Kondo effects in the Ce_2PdGe_6 system should be not so large.

The static magnetic susceptibility of the sample was measured in a field of 1.0 kOe between 2.0 and 300 K with a commercial superconducting quantum interference device magnetometer.[19] Figure 2 depicts the molar magnetic susceptibility χ_m versus temperature T for the Ce_2PdGe_6 compound. A very sharp transition from nonmagnetic to magnetic ordering is seen at 11.4 K (peak value) from the inset of Fig. 2. The high-temperature ($>$150 K) susceptibility data, as shown in Fig. 3, can be fitted to a linear Curie-Weiss law with an effective moment of $(2.7\pm0.1)\ \mu_B$/Ce atom, a value close to the free Ce^{+3} ion value to preclude intermediate valence, and a paramagnetic Curie temperature (Θ_P) -6 K, a value in good agreement with the literature.[20] Since a large negative Curie temperature is often found in dense Kondo Ce compounds, it is thought that the Ce_2PdGe_6 compound is not a typical dense Kondo system.

The low-temperature specific-heat measurements were made using a thermal-relaxation microcalorimeter. The sample, which has two flat sides after polishing, was wiped with ~50 microgram N grease for good thermal contact and was attached to a sapphire holder on which a Ru-sapphire thin-film thermometer and a nickel-chromium heater were evaporated. The addenda was then semiadiabatically isolated from the bath by four gold-copper alloy wires for the thermal relaxation use and electrical connections. By recording the time constant τ of the temperature relaxation after switching off the heating power, the specific heat of the specimen can then be measured via $C=\kappa\tau$, where κ is the thermal conductance of the link wires. The background of the addenda and grease was properly subtracted in each separate measurement. The relative precision and the absolute accuracy of the apparatus were checked by measuring the specific heat of copper standard. An over-all precision and accuracy within ~3 and ~4% was confirmed, respectively. As indicated in Fig. 4, the specific heat vs T data curve for the sample Ce_2PdGe_6 shows a sharp Landa type of antiferromagnetic ordering peak centering at 11.20 K and a peak value approaching 29.44 J/mol formula K. The agreement of transition temperatures measured by dc susceptibility and heat capacity techniques are clear evidence of antiferromagnetism in Ce_2PdGe_6. Since there are two Ce atoms in the formula unit, we note here that the total jump in the heat capacity is about 14.72 J/mol Ce K, which is close to the value 15 J/mol Ce K as expected on the basis of mean-field theory. Valuable information can be obtained from the entropy associated with the magnetic ordering. The significance of the entropy

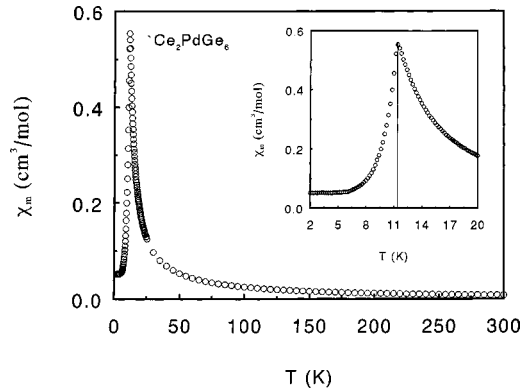

FIG. 2. Molar magnetic susceptibility χ_m vs temperature T for Ce_2PdGe_6 between 2.0 and 300 K. Inset: χ_m vs T between 2.0 and 20 K.

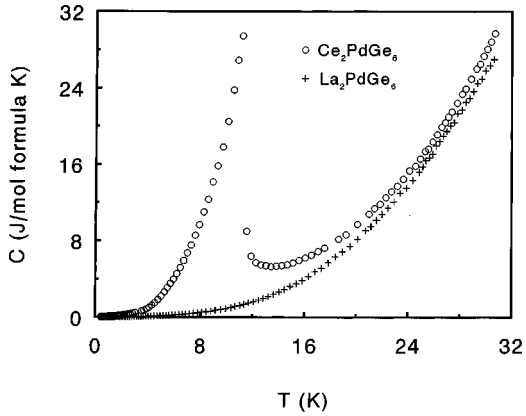

FIG. 4. Heat capacity of Ce_2PdGe_6 and La_2PdGe_6 compounds between 0.45 and 30 K.

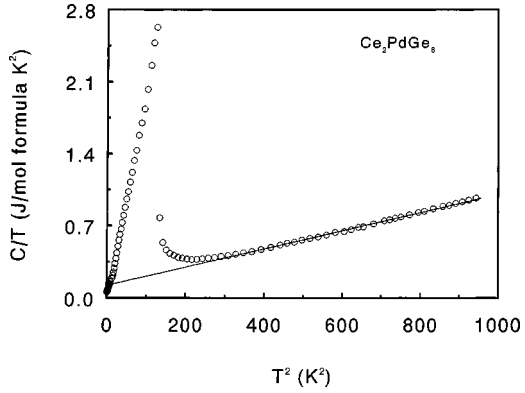

FIG. 5. Specific heat divided by temperature C/T vs T^2 of Ce_2PdGe_6 between 0.45 and 30 K. The value of γ was obtained by extrapolating the specific heat in this plot of C/T vs T^2 down to 0 K.

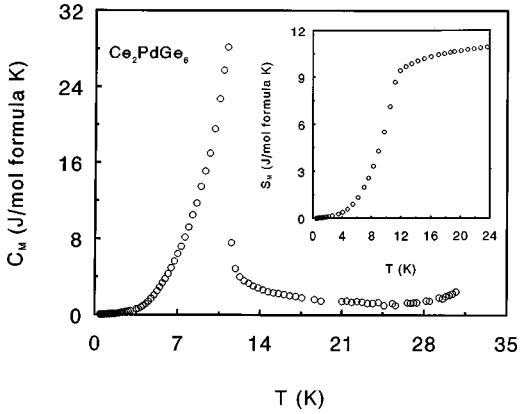

FIG. 6. Magnetic specific heat C_M vs T of Ce_2PdGe_6 between 0.45 and 30 K. Inset shows the temperature dependence of magnetic entropy for the alloy Ce_2PdGe_6.

calculations stems from a result of statistical mechanics which says the entropy associated with a system of total angular momentum J, or $2J+1$ energy levels, is given by $\Delta S = R\ln(2J+1)$, where R is the gas constant. For an alloy, the magnetic entropy becomes $cR\ln(2J+1)$, where c is the cerium concentration in atomic fraction. A determination of the electronic and lattice specific-heat contributions is complicated by the existence of the antiferromagnetic ordering peak. The specific-heat data as C/T against T^2 for Ce_2PdGe_6 are plotted in Fig. 5. It is seen that the heat capacity $C(T)$ of Ce_2PdGe_6, in the paramagnetic state at temperatures above 20 K, can be fitted to the expression $C_n = \gamma T + \beta T^3$ by a least squares analysis, which yields the value $\gamma = 110 \pm 5$ mJ/mol K^2 and $\beta = 0.88 \pm 0.01$ mJ/mol K^4, the latter value corresponding to the Debye temperature $\Theta_D = 270 \pm 5$ K. Though the compound Ce_2PdGe_6 has a rather large electronic specific heat in the paramagnetic state just above the phase transition, this γ value is drastically reduced below the phase transition to about 28 mJ/mol formula K^2 or 14 mJ/mol Ce atom K^2, as may be evaluated from our experimental data below 0.45 K. This value thus is similar to those found in normal metals or transition-metal compounds. The specific heat contributed from lattice phonons of Ce_2PdGe_6 can also be assumed to be the same as that of the isostructural nonmagnetic compound La_2PdGe_6. The temperature dependence of specific heat for La_2PdGe_6 is shown in Fig. 4. It is found that the β value for La_2PdGe_6 is very close to that of Ce_2PdGe_6. Subtracting the specific heat of La_2PdGe_6 from Ce_2PdGe_6 gives the magnetic and Schottky contributions. Because the exchange interaction may dominate the crystal-field interaction in the compound Ce_2PdGe_6, no clear Schottky anomaly induced by crystal field is seen below 28 K in the difference data curve. In Fig. 6, we have plotted the magnetic part of the heat capacity of the compound Ce_2PdGe_6 as a function of temperature. The shape of this peak with its rather long high-temperature tail, which extends to $\sim 2T_N$, is similar to that found samarium[21] and β-cerium[14] metals. From the inset of Fig. 6, the magnetic heat capacity below 22 K has a measured magnetic entropy S_M to within 1% of the theoretical value of $2R\ln 2$, which would be expected for a doublet ground state. We must point out here that the measured magnetic entropy at T_N reaches 90% of the theoretical value of $2R\ln 2$. The small reduction of the magnetic entropy below T_N is probably due to the weak Kondo effects in the compound Ce_2PdGe_6. For the magnetic contribution to the heat capacity C_M, miscellaneous temperature dependences have been proposed by theorists. Magnetic anisotropy introduces an energy gap E_g/k_B and gives rise to equations of the form

$$C_M(T) = f(T)\exp(-E_g/k_BT),$$

where $f(T)$ is a complicated function and is dependent on the nature of the spin-wave spectrum.[22–24] Some other more complicated empirical fitting functions such as

$$C_M = \gamma T + g(T)\exp(-E_g/k_BT)$$

also have been used.[16,25] Attempts to fit these data for Ce_2PdGe_6 to the empirical equations, using a least-squares computer fit, fail completely. However, an analysis of the low-temperature portion below T_N of the magnetic heat capacity of Ce_2PdGe_6 does indeed show a T^3 law (see Fig. 7) probably due to the considerable larger proportionality constants than the ordinary lattice and Schottky terms. From Fig. 7, the data between 0.45 K ($T^3 = 0.091$ K^3) and 11.2 K (T^3

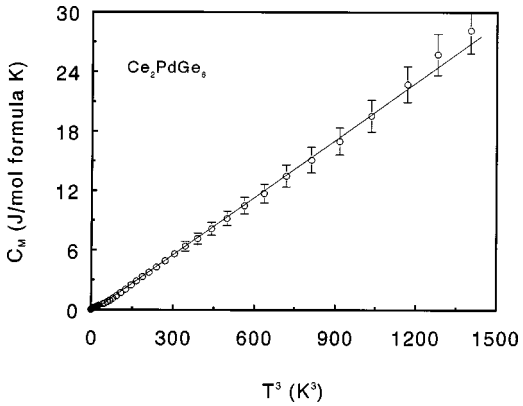

FIG. 7. Magnetic specific heat vs the temperature cubed for the compound Ce_2PdGe_6 below T_N.

$=1405\,\mathrm{K}^3$) gives a slope of 19.2 ± 0.2 mJ/mol formula K, which is much larger than the value (6.9 ± 0.1) of β cerium found by Koskimaki and Gschneidner[14] and the value (8.2 ± 0.1) of Ce_2CuGe_6 found by Tseng[17] *et al.* This suggests that in the whole temperature range below T_N the magnetic contribution of Ce_2PdGe_6 obeys the simple spin-wave theory.

The observation of T^3 behavior of the magnetic capacity below T_N for Ce_2PdGe_6 is a direct experimental testimony of the whole spin-wave theory predicted by Van Kranendonk and Van Vlecks.[15] To our knowledge, this is the first time that the magnetic heat capacity of a Ce-based compound was found to have T^3 behavior in the whole temperature range below T_N. As evidenced from the magnetic entropy associated with the magneic ordering, the orthorhombic crystal field may result in a ground-state doublet for the Ce^{3+} ions in the compound Ce_2PdGe_6. Crystal-field studies are not as common for the rare-earth salts in which the exchange interaction dominates the crystal-field interaction in the metals. Our experiments have testified the results that the Schottky contribution to the heat capacity occurs probably at higher temperatures and does not spoil the T^3 temperature dependence of magnetic heat capacity in Ce_2PdGe_6 at low temperatures below T_N.

Research at Chung Cheng University was supported by National Science Council of Republic of China under Contract No. NSC92-2112-M194-010.

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