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Antiferromagnetic Spin Wave in Ce_2CuGe_6

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Electrical-resistivity, static magnetic susceptibility, and low-temperature specific-heat data reveal that the bulk phase transition at 14.7±0.2 K in Ce_2CuGe_6 is to an antiferromagnetic state. Analysis of the temperature dependent magnetic resistivity, magnetic susceptibility and magnetic heat capacity data suggests a Kramer's doublet ground state of Ce^{+3} ions in the compound Ce_2CuGe_6. Since the estimated Kondo temperature (T_K)∼1 K is much lower than the Néel temperature (T_N=14.7 K), the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction dominates the crystal-field interaction in the antiferromagnetic interaction. The magnetic heat capacity below 0.98 T_N exhibits a T^3 behavior, which is a direct experimental confirmation and provides good evidence for antiferromagnetic spin wave according to the theory of Van Kranendonk and Van Vleck. [DOI: 10.1143/JJAP.43.L66]

KEYWORDS: antiferromagnetic spin wave, theory of Van Kranendonk and Van Vleck, Ce_2CuGe_6

The spin-wave theory has been discussed for almost half a century.[1)] Until now, the literature of spin-wave theory either by a quantum-mechanical or a semiclassical approach is still considerable[2–8)] though about fifty references are included in the review paper of ref. 1. There are, of course, plenty of magnetic resonance experiments or inelastic neutron scattering experiments to confirm the spin-wave theory.[9–11)] However, the resonance frequencies or spin wave excitations involve only the properties of very special symmetric states. Since the predicted specific heats for ferromagnetic and antiferromagnetic spin wave materials are strinkingly different, being proportional to $T^{3/2}$ and T^3, respectively, the specific-heat measurements furnish 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. And corrections for the effect of anisotropy or crystal electrical field will always spoil the rigor of the T^3 law, *e.g.*, the heat capacity of β-cerium[12)] or heavy fermion compound $CePd_2Si_2$[13)] 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. As determined from dc susceptibility and heat capacity measurements, this compound undergoes an antiferromagnetic transition at 14.7±0.2 K. In addition to experiments on Ce_2CuGe_6, electrical resistivity and low-temperature heat capacity measurements on the isostructural La_2CuGe_6 have been made in order to estimate the phonon contribution to the resistity and heat capacity of Ce_2CuGe_6.

The ternary R_2CuGe_6 (R=Ce,La) compounds crystallize in an orthorhombic Ce_2CuGe_6-type structure with space group A_{mm2} (refs. 14 and 15). 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%, Cu with 99.999% purity and Ge with 99.999% purity were purchased from Alfa Aesar, Gredmann and CERAC, respectively. 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 0.05%. The arc-melted sample was then sealed under argon in a quartz tube, and annealed for 40 h at 800°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 $a = 0.4066(5)$ nm, $b = 0.4206(7)$ nm, $c = 2.1554(1)$ nm for Ce_2CuGe_6 and $a = 0.4086(5)$ nm, $b = 0.4249(1)$ nm, $c = 2.1752(2)$ nm for La_2CuGe_6 were then obtained.

Precision 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.[16)] Fine platinum wires (∼2 mil 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_2CuGe_6, La_2CuGe_6, and the magnetic resistivity ρ_m of Ce_2CuGe_6. The magnetic

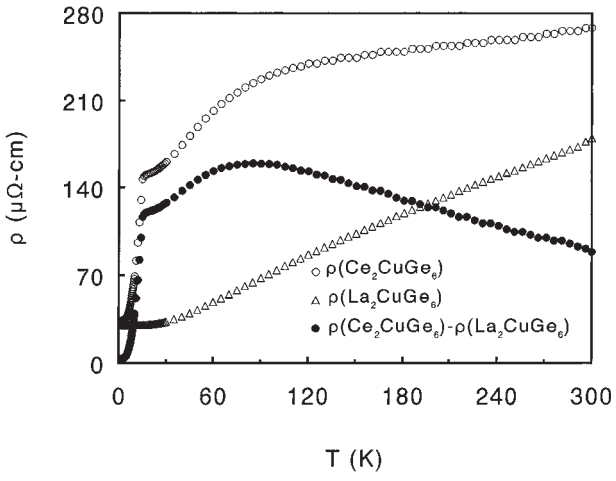

Fig. 1. Resistivity vs temperature of Ce_2CuGe_6, La_2CuGe_6 and the difference between these two compounds from 2.0 to 300 K.

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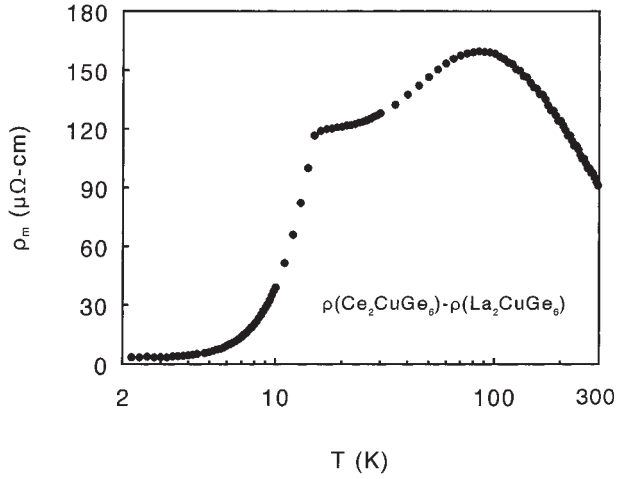

Fig. 2. Magnetic resistivity ρ_m vs ln(T) of Ce_2CuGe_6 between 2.0 and 300 K.

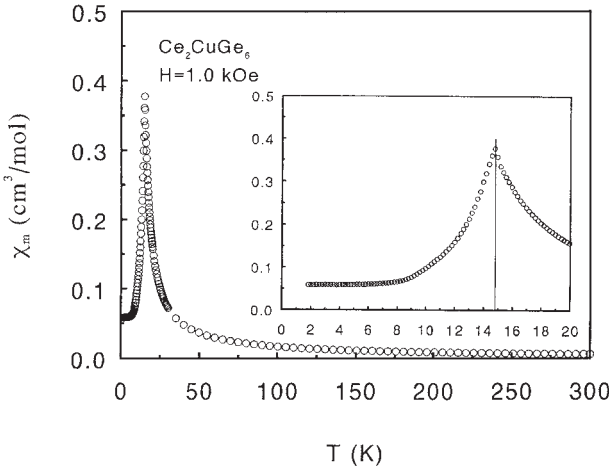

Fig. 3. Molar magnetic susceptibility χ_m vs temperature T for Ce_2CuGe_6 between 1.80 and 300 K.

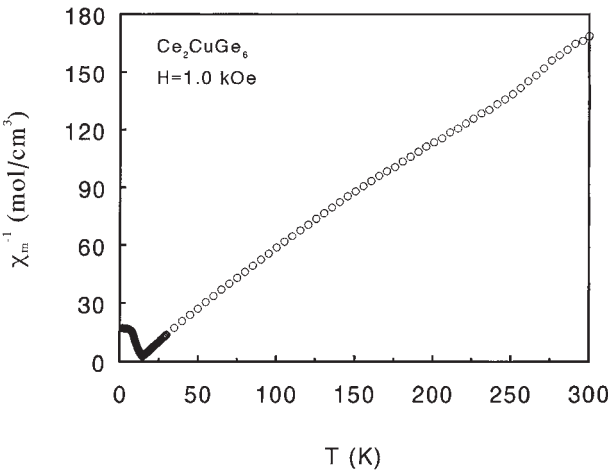

Fig. 4. Inverse molar magnetic susceptibility χ_m^{-1} vs temperature of Ce_2CuGe_6 between 1.80 and 300 K.

resistivity was estimated by subtracting the resistivity of isostructural La_2CuGe_6 from that of Ce_2CuGe_6. A single kink in the resistivity curve of Ce_2CuGe_6 is clearly evident around 15 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 most prominent feature of the magnetic resistivity curve is the presence of a broad peak around 85 K. Typically, the broad peak in the magnetic resistivity curve at about 100 K is a feature for the Kondo effect on the compound with the crystal-field splitting. The data for ρ_m are plotted as a function of ln(T) in Fig.2. A ln(T) dependence is seen in the high-temperature region, which is one of the characteristic features of dense Kondo systems. According to the theory of Cornut and Coqblin,[17] the broad bump around $T = 100$ K is associated with the combined effect of of the crystalline field on the 4f-spin and the Kondo scattering. The peak at lower temperature is thought to be due to the Kondo scattering. The disappearance of Kondo peak in the magnetic resistivity curve shown in Fig. 2 implies that the Kondo temperature should be less than 2.0 K for the compound Ce_2CuGe_6. This expection can be certified by the magnetic susceptibility measurements as follows.

The static magnetic susceptibility of the sample was measured in a field of 1.0 kOe between 1.80 and 300 K with a commercial superconducting quantum interference device (SQUID) magnetometer.[16] Figure 3 depicts the molar magnetic susceptibility χ_m versus temperature T for the Ce_2CuGe_6 compound. A very sharp transition from non-magnetic to magnetic ordering is seen at 14.7 K (peak value) from the inset of Fig. 3. The high-temperature (>70 K) susceptibility data, as shown in Fig. 4, can be fitted to a linear Curie-Weiss law with an effective moment of (2.66±0.05) μ_B/Ce-atom, a value close to the free Ce^{+3} ion value to preclude intermediate valence, and a paramagnetic Curie temperature (Θ_P) −2 K. Since the estimated Kondo temperature, (T_K) $\sim |\Theta_P/2| = 1$ K, is much lower than Néel temperature (T_N), the Kondo interaction is thought to be subordinate over the antiferromagnetic interaction as will be observed in the heat capacity measurements.

The specific heat of a piece (∼ 2 mg) cut from the sample was measured in the range of 0.5–33 K with a He^3 relaxation calorimeter using the heat pulse technique[18] in the earth's magnetic field. The sample was attached to a sapphire chip, which has two separated silicon films deposited on it to serve as heater and thermometer. The calibration of the thermometer was done against a calibrated germanium thermometer. For each point of the specific-heat measurements, a small heat power was introduced to the chip and the thermal relaxation was measured and analyzed to obtain the specific heat of the sample. As indicated in Fig. 5, the specific heat vs T data curve for the sample Ce_2CuGe_6 shows a sharp Landa-type of antiferromagnetic ordering peak centering at 14.57 K and a peak value approaching 30.06 J/mol·K. The agreement of transition temperatures measured by dc susceptibility and heat capacity techniques are clear evidence of antiferromagnetism in Ce_2CuGe_6. Valuable information can be obtained from the entropy associated with the magnetic ordering. The significance of the entropy 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. To determine the electronic and lattice specific-heat

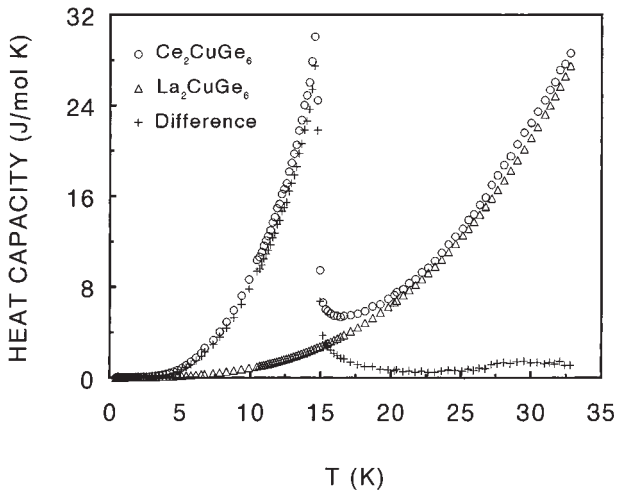

Fig. 5. Heat capacity of Ce_2CuGe_6, La_2CuGe_6, and the difference between these two compounds from 0.5 to 33 K.

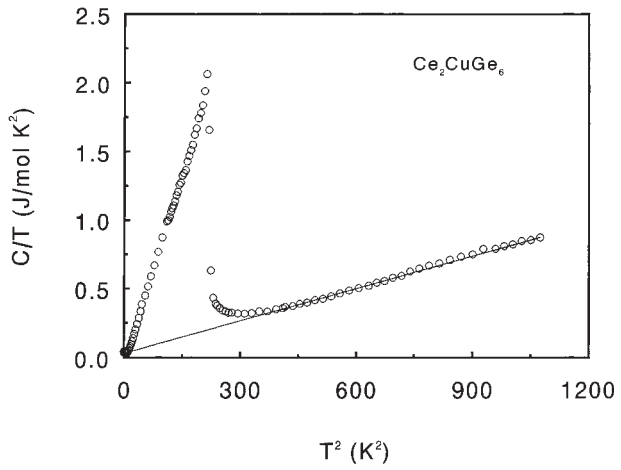

Fig. 6. Specific heat divided by temperature C/T vs T^2 of Ce_2CuGe_6 between 0.5 and 33 K. The value of γ was obtained by extrapolating the specific heat in this plot of C/T vs T^2 down to 0 K.

contributions, the specific-heat data as C/T against T^2 for Ce_2CuGe_6 are plotted in Fig. 6. It is seen that the heat capacity $C(T)$ of Ce_2CuGe_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 $\gamma = 12.2 \pm 0.2\,\mathrm{mJ/mol \cdot K^2}$ and $\beta = 0.80 \pm 0.01\,\mathrm{mJ/mol \cdot K^4}$, the latter value corresponding to the Debye temperature $\Theta_D = 280 \pm 5$ K. The specific heat contributed from lattice phonons of Ce_2CuGe_6 can also be assumed to be the same as that of the isostructural nonmagnetic compound La_2CuGe_6. The temperature dependence of specific heat for La_2CuGe_6 is shown in Fig. 5. It is found that the β value ($0.77 \pm 0.01\,\mathrm{mJ/mol \cdot K^4}$) for La_2CuGe_6 is very close to that of Ce_2CuGe_6. Subtracting the specific heat of La_2CuGe_6 from Ce_2CuGe_6 gives the magnetic and Schottky contributions. Because the exchange interaction dominates the crystal field interaction in the compound Ce_2CuGe_6, the Schottky anomaly induced by crystal field appears to be a small bump around 28 K in the difference data curve as shown in Fig. 5. Neglecting the small Schottky contributions below 25 K, the magnetic heat capacity which results has a measured magnetic entropy to within 10% of the theoretical

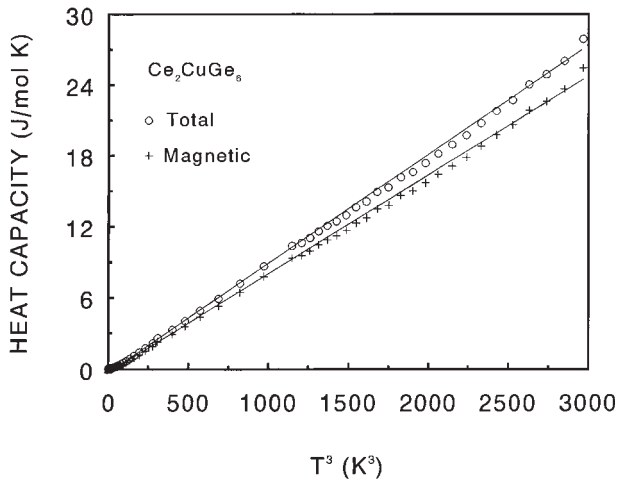

Fig. 7. Total and magnetic heat capacity vs the temperature cubed for the compound Ce_2CuGe_6 below T_N.

value of $2R\ln 2$ which would be expected for a doublet ground state. From Kramer's rule, it is expected that the crystal-field spilting of the $^2F_{5/2}$ ground-state level of the Ce^{+3} ion in the compound Ce_2CuGe_6 results in a ground-state doublet. An analysis of the low-temperature portion ($<T_N$) of the total and magnetic heat capacity of Ce_2CuGe_6 do indeed show a T^3 law up to $0.98\,T_N$ (see Fig. 7) probably due to the cosiderable larger proportionality constants than the ordinary lattice and Schottky terms. From Fig. 7, the data between 0.5 K ($T^3 = 0.125\,\mathrm{K^3}$) and 14.4 K ($T^3 = 2986\,\mathrm{K^3}$) gives a slope of $8.9 \pm 0.1\,\mathrm{mJ/mol \cdot K^4}$ and $8.2 \pm 0.1\,\mathrm{mJ/mol \cdot K^4}$ before and after subtracting the heat capacity of La_2CuGe_6 from that of Ce_2CuGe_6, respectively. This suggests that in this temperature range the magnetic contribution of Ce_2CuGe_6 follows simple spin-wave theory.

From the present study, the observation of T^3 behavior of the magnetic capacity below $0.98\,T_N$ for Ce_2CuGe_6 is a direct experimental confirmation of the whole spin-wave theory predicted by Van Kranendonk and Van Vlecks.[1] Apparently, 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 this large temperature range (0.5 K to 14.4 K). As evidenced from the magnetic resistivity data and the entropy associated with the magneic ordering, the orthorhombic crystal field may result in a ground-state doublet with an excited quartet or two excited doublets for the Ce^{3+} ions in the compound Ce_2CuGe_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 does not injure the T^3 behavior of magnetic heat capacity in Ce_2CuGe_6.

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