Low-temperature properties of the heavy-fermion antiferromagnet Ce₅CuSb₃

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The results of low-temperature magnetic susceptibility, magnetization, specific heat, electrical resistivity, magnetoresistivity, and thermoelectric power measurements on Ce₅CuSb₃ are reported. The compound crystallizes in the orthorhombic Sm₅Ge₄-type structure and shows the signatures of an antiferromagnetic ordering below T_N =3.7 K. The relatively large electronic specific heat coefficient allows to classify Ce₅CuSb₃ as a moderately heavy-fermion antiferromagnetic material. The reduction in the magnetic entropy at T_N indicates the presence of dense Kondo effect, which is supposed to be the mechanism responsible for the development of the heavy-fermion state. Within the framework of the S=1/2 resonant and two-level models, the Kondo temperature ~7(1) K has been estimated. Ce₅CuSb₃ shows large values of both Kadowaki-Woods relation and Wilson ratio, implying a considerable influence of intersite magnetic interactions.

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I. INTRODUCTION

Many cerium, ytterbium, or uranium based intermetallic compounds are known to exhibit unusual physical properties at low temperatures, for instance, intermediate valence and heavy-fermion. Basically, these properties have been explained on the basis of the Doniach lattice model, which assumes an interplay between the Ruderman-Kittel-Kasuya-Yosida (RKKY) and Kondo interactions.¹ The former interaction allows the formation of a long-range magnetic order, while the latter destroys magnetism by quenching the magnetic moments of localized *f*-electrons. Since, in the system there is only single exchange coupling parameter J, which determines strengths of both the RKKY and Kondo interactions, there appears to be a balance of these interactions in some compounds. In this concept, the ground state of the system is nonmagnetic or magnetic, but in the latter case, the system with reduced magnetic moments lies in the so-called magnetic instability regime. This situation goes with a large mass enhancement coupled with the appearance of the Kondo resonance in the electronic density of states at the Fermi energy. In consequence, the magnetic ordering temperature falls to temperature as low as possible and the heavy fermion state is formed.

Recently, we have reported the low-temperature properties for Ce₅CuSn₃.² The observed behavior is consistent with the heavy-fermion characteristics.³ Since there are two different Ce sublattices in the unit cell, this compound could become an interesting candidate for studying the competition of the RKKY and Kondo interactions in the presence of different exchange coupling parameters. In this paper, we report results of magnetic susceptibility, magnetization, specific heat, electrical resistivity, magnetoresistivity, and thermoelectric power measurements for other members of the stoichiometric 513 family of compounds, namely, Ce₅CuSb₃. We show that the investigated compound crystallizes in the orthorhombic Sm_5Ge_4 -type structure (space group *Pnma*) and orders antiferromagnetically below 3.7 K. This order is a cooperative phenomenon accompanied by a large magnetoresistance at temperature just above T_N . Ce₅CuSb₃ with the Sommerfeld coefficient of 170 mJ/mol-CeK^2 appears to be a medium heavy-fermion antiferromagnet.

II. EXPERIMENT

Polycrystalline Ce₅CuSb₃ samples were prepared by arcmelting appropriate amounts of the high-purity elements (Ce: 99.9%, Cu: 99.99%, and Sb: 99.999%) in a Ti-gettered argon atmosphere. X-ray diffraction studies at room temperature showed that the samples are single phase. All observed reflections were indexed with an orthorhombic structure of the space group *Pnma*. Lattice parameters calculated from the least-squares fitting are: a=74.72(1), b=152.58(2), and c=77.84(1)nm, Thus, in contrast to Ce₅CuSb₃ crystallizing in the hexagonal Ga₄Ti₅-type,⁴ the investigated compound comes out to adopt the orthorhombic Sm₅Ge₄-type structure.⁵ In the unit cell of Ce₅CuSb₃, the cerium atoms are expected to occupy as many as three inequivalent positions: 4c, 8d, and 8d. The antimony atoms are distributed at the positions 4c and 8d, and copper atoms at the 4c.

Dc-magnetic susceptibility, $\chi(T) = M/B$, was measured by means of a Superconducting quantum interference device (Quantum Design, MPMS-5) magnetometer in fields up to 5.5 T and in the temperature range 1.7–400 K. Specific heat, Cp(T), measurements were performed in the temperature range 2–100 K, utilizing a quasiadiabatic method. Electrical resistivity, $\rho(T)$ was measured using a four-probe dctechnique in the temperature range 1.5–300 K. The samples were rectangular with typical dimensions 0.5 mm × 0.5 mm × 5 mm. Transverse magnetoresistance measurement was performed in a fixed magnetic field of 5 on zero-field cooled sample. Isothermal magnetoresistance data were also recorded in fields up to 14 T at several selected temperatures below 50 K. Thermoelectric power was measured in the temperature range 2–300 K.

III. RESULTS

The magnetic susceptibility data of Ce_5CuSb_3 measured at a field of 0.5 T are displayed in Fig. 1. Above 100 K the



FIG. 1. Temperature dependence of the inverse mole susceptibility of Ce_5CuSb_3 . The solid line is a fit to the experimental data. Inset shows the low-temperature susceptibility of the compound.

susceptibility can be well described by the Curie-Weiss law: $\chi(T) = C/(T - \Theta_p)$. The fit to the data in the temperature range 100–400 K yields an paramagnetic temperature Curie Θ_p =7 K and an effective magnetic moment μ_{eff} /Ce-atom =2.2 μ_B . Thus, μ_{eff} is somewhat lower than the full moment expected for a free Ce³⁺-ion (2.54 μ_B). The positive sign of Θ_p points out the presence of ferromagnetic interactions between magnetic cerium ions. In the inset of Fig. 1 we show the low-temperature part of the susceptibility of Ce₅CuSb₃. We observe a maximum in the susceptibility at 3.7 K, which could be assigned to an antiferromagnetic ordering. Since, there are ferromagnetic interactions, any antiferromagnetic structure of this compound is expected to be complex. This may be associated with the three inequivalent positions of the cerium atoms in the unit cell.

We have measured magnetization at several temperatures. The typical magnetization curves below and above T_N are illustrated in Fig. 2. As expected for an antiferromagnetic compound, the magnetization of Ce₅CuSb₃ in the antiferromagnetic state exhibits a metamagnetic transition clearly seen as broad peak in the derivative dM/dH curve at approximately 4 T. However, no hysteresis effect could be observed in the data collected during increasing and subsequent



FIG. 2. Magnetization of Ce_5CuSb_3 measured at 2 and 35 K as a function of magnetic fields. The inset shows the derivative dM/dH.



FIG. 3. Temperature dependence of the specific heat derived by temperature, C_p/T . The inset shows C_p/T as a function of T^2 . The dashed and solid lines are fits to the experimental data.

decreasing field strength. We notice that the initial magnetization shows a jump, which suggests the presence of a ferromagnetic contribution. At 2 K and 5.5 T, *M* reaches a value of 0.65 μ_B , which is comparable to the full moment of a Γ_7 doublet (0.7 μ_B), but much less than the theoretical saturation moment gJ=2.143 μ_B for the Ce⁺³ ions. The magnetization at 35 K linearly varies with the strength of the applied field and it is characteristic of the behavior of compounds in the paramagnetic state.

In Fig. 3 we show the specific heat of Ce₅CuSb₃ in the form of C_p/T versus *T*. For the purpose of data analysis, we assume the specific heat to be additive, i.e., in the paramagnetic region, it consists of two distinct contributions, the lattice specific heat $C_{\rm ph}$ and the electronic specific heat $C_{\rm el}$. Assuming further that $C_{\rm el}$ is the linear function of temperature and $C_{\rm ph}$ follows the Debye function $C_{\rm ph}(T) = 9R(T/\Theta_{\rm D})^3 \int_0^{\Theta_D/T} x^4 \exp(x) / [\exp(x) - 1]^2 dx$, we may fit the experimental data for the high-temperature range 30–100 K. This fitting procedure gives $\Theta_{\rm D}^{\rm HT} = 183$ K and $\gamma^{\rm HT} = 83$ mJ/K²mol at. Ce The fitting results are shown as solid line in Fig. 3.

For the temperatures between 13–23 K we recognize that C_p/T is linear with T^2 (see inset of Fig. 3). This corresponds to a dependence

$$C_p = \gamma^{\rm LT} T + \beta T^3 \tag{1}$$

with $\gamma^{LT}=144 \text{ mJ/K}^2\text{mol}$ Ce and $\beta=0.41 \text{ mJ/K}^4$ mol Ce. Using the standard formula: $\beta=(12/5)rR(\pi^4/\Theta_D^3)$ we find the low-temperature Debye temperature $\Theta_D^{LT}=203 \text{ K}$, close to that deduced from the data in the temperature range 30-100 K. The results of the fit are illustrated in Fig. 3 as a dashed line. It should be pointed out that the simple T^3 law for the lattice contribution is expected for temperatures much smaller than the Debye temperature. In Ce₅CuSb₃ it happens below 23 K, equivalent to approximately $\Theta_D^{LT}/9$ and therefore, the estimated value Θ_D of Ce₅CuSb₃ lies in the range 183-203 K is rather consistent.

From the analysis of the specific heat data in the paramagnetic state, we find an enhancement in the electronic coefficient of the specific heat. By extrapolating the specific heat data between 1.7-3 K to T=0, we obtain an even larger value of Sommerfeld coefficient $\gamma(0)=170$ mJ/K² mol Ce. These relatively large electronic specific heat coefficients allow to classify Ce₅CuSb₃ to a class of moderate heavyfermion compounds. At this stage we suppose that the development of a strongly correlated electrons state, leading to the heavy-fermion behavior in Ce₅CuSb₃, is due to dense Kondo effect.

To examine the nature of the heavy-fermion behavior in Ce_5CuSb_3 , it is useful to calculate the Wilson ratio⁶

$$R_W = \frac{\pi^2 k_B^2}{g_J^2 \mu_{\rm eff}^2 J(J+1)} \frac{\chi(0)}{\gamma(0)}.$$
 (2)

Taking $\gamma(0) = 170 \text{ mJ/K}^2 \text{ mol Ce and } \chi(0) = 0.93 \text{ cm}^3 \text{ mol Ce for } T \rightarrow 0$, we estimated for Ce₅CuSb₃ $R_W = 1.84$. A relatively large value of R_W implies that magnetic correlations are strongly enhanced in this compound.

Clearly seen in Fig. 3, the specific heat of the compound is governed by a λ -type anomaly around 3.8 K. This maximum confirms the magnetic phase transition in Ce₅CuSb₃. However, the jump $\Delta C_{mag} \approx 4 \text{ J/K}$ mol Ce due to magnetic ordering is much reduced compared to the expected value of 12.48 J/K mol for a magnetic system with spin S=1/2. This behavior is consistent with the interpretation in the framework of the dense Kondo effect.

In a single impurity Kondo system, the Kondo temperature T_K may be estimated from a $T_K=0.68R/\gamma$ relation.^{7,8} In the case of magnetic Kondo lattice, the available data^{9,10} show that the magnetic specific heat is well described by an S=1/2 resonant level model, which was already developed by Schotte and Schotte using a mean-field approximation.¹¹ Within the framework of the model, Blanco *et al.* have calculated the relation between the magnetic specific heat and the ratio of the Kondo and ordering temperature¹²

$$\Delta C_{\rm mag} = \frac{6k_B}{\psi^{\prime\prime\prime}(\frac{1}{2}+\zeta)} \Big[\psi^{\prime}(\frac{1}{2}+\zeta) + \zeta\psi^{\prime\prime}(\frac{1}{2}+\zeta)\Big]^2, \quad (3)$$

where $\zeta = T_K / T_C 2\pi$ and ψ , ψ'' , and ψ''' are the first, second, and third derivatives of the digamma function, respectively. Applying the above expression to magnetic specific heat C_{mag} , which has been estimated by subtracting the electronic and lattice contributions from the total specific heat, we obtain $T_K = 6.8$ K for Ce₅CuSb₃.

From the C_{mag} data we may calculate the magnetic entropy, $S_{\text{mag}} = \int_0^{10} C_{\text{mag}}/T \, dT$. The magnetic entropy at T_N reaches to value of 40% of *Rln2*, corresponding to a doublet ground state. We ascribe this considerable reduction of S_{mag} to the dense Kondo effect. According to a two-level model proposed by Yashima *et al.*¹³ the reduction of the magnetic entropy at T_N is related to T_K , with a relation

$$\Delta S = R \ln[1 + \exp(-T_K/T_N)] + \frac{T_K}{T_N} \frac{\exp(-T_K/T_N)}{1 + \exp(-T_K/T_N)}.$$
 (4)

From the calculation we find T_K =8.8 K, not much differs from the value T_K estimated using the S=1/2 resonant level model.

Figure 4 shows the temperature dependence of electrical resistivity of Ce₅CuSb₃. Clearly, the electrical resistivity of



FIG. 4. Temperature dependence of the electrical resistivity measured at 0 and 5 T. The solid line is a fit to the experimental data. The inset shows the temperature derivative of the resistivity at low temperatures.

the compound shows a metallic behavior and the overall behavior remembers that of CeAl₂, an archetypal dense Kondo antiferromagnet.¹⁴ At low temperatures, the onset of the magnetic ordering is signified by a distinct drop in the resistivity. The transition temperature can be identified as a maximum in the derivative $d\rho(T)/dT$, equal to 3.7 K. This value is in concordance with the position of maximum observed in the temperature dependence of the susceptibility and the specific heat. In the ordered state, the resistivity nicely follows a quadratic temperature dependence, $\rho(T) = \rho_0 + A * T^2$ with ρ_0 =19.8 $\mu\Omega$ cm and A=1.35 $\mu\Omega$ cm K⁻². The observed T^2 dependence of the resistivity indicates that the Fermi liquid state appears in the material at low temperatures. For many U- and Ce-based heavy fermion compounds it has been shown that the ratio A/γ^2 takes a universal value of $1*10^{-5} \mu\Omega \text{ cm} (\text{mol K/mJ})^2$.¹⁵ Using the values A $\gamma = 170 \text{ mJ/K}^2 \text{ mol},$ A/γ^2 and we calculate =4.7 * 10⁻⁵ $\mu\Omega$ cm (mol K/mJ)². This value is somewhat larger than the universal value and signifies a significant influence of the magnetic interactions. In Ce₅CuSb₃, the intense drop in the resistivity, resulting in an enlargement of the value of the coefficient A may be attributable to combined effects of the loss of spin-disorder, electron-magnon interactions, and the development of coherence in the Fermiliquid state. However, referring to ordinary antiferromagnets, the prefactor A is on the order of $10^{-3} \ \mu\Omega \ cm/K^{2}$,¹⁶ we may derive that the electron-electron scattering in the coherent state is the dominant mechanism.

At high temperatures, the resistivity shows a downward curvature, deviating from quasi-linear phonon trend. To explain this behavior one should take into account apart from the spin-disorder and lattice resistivity, other contributions giving a rise to the total resistivity, like those originating from interband *s*-*d* interactions,¹⁷ Kondo effect,¹⁸ and crystalline electric field (CEF). Considering the thermoelectric power data (see below) we found an important role of the interplay between the Kondo and CEF effects on the electronic transport properties. However, to confirm this mechanism one must compare first the resistivity data to the those of a reference compound, which are not yet available.



FIG. 5. (a) Temperature dependence of the magnetoresistance of Ce_5CuSb_3 at 5 T. (b) The magnetoresistance measured at several temperatures as a function of magnetic fields.

In Fig. 4 we compare the low-temperature resistivity measured in a magnetic field of 5 T to those at the zero field. The application of the field reduces somewhat T_N from 3.7 to 3.1 K, as one can deduce from the resistivity derivative curves, shown in the inset of Fig. 4. This feature confirms the fact that the ground state of Ce₅CuSb₃ is certainly antiferromagnetic. We observe that the residual resistivity is practically the same in these two measurements. A large reduction in the resistivity is observed around 5 K, just above the magnetic phase transition. This unusual behavior can be clearly seen in the $\Delta \rho / \rho(T)$ curve shown in Fig. 5(a). The magneto resistance (MR) $\Delta \rho / \rho(T)$ is defined as $\Delta \rho / \rho = \rho(T, B)$ $-\rho(T,0)/\rho(T,0)$. Noticeably, MR reaches a huge value of -35% at 5 K and 14 T [Fig. 5(b)]. The negative MR at temperatures above T_N is regarded as due to the suppression of the Kondo effect, or/and precursor effects associated with short-range magnetic interactions.

The thermoelectric power for Ce₅CuSb₃ is displayed in Fig. 6 as a function of temperature. *S* is negative at room temperature amounting $-1.5 \mu V/K$. With decreasing temperature its absolute value increases and changes the sign at about 230 K. The most remarkable feature here is that *S* has



FIG. 6. Temperature dependence of the thermoelectric power of Ce_5CuSb_3 .

a maximum around 105 K with a value of 2.1 μ V/K and a peak at approximately 8 K. The origin of the later maximum is not much clearer. We may state that the phonon-drag mechanism can be excluded, because such a maximum normally occurs in the temperature range $0.1-0.3 * \Theta_{\rm D}$,¹⁹ and for Ce₅CuSb₃ $\Theta_D \sim 190$ K. Instead, we may suppose that this maximum is related to the change in the electronic structure. This is most plausible, since at this temperature the compound closes to the magnetic phase transition. Other possible origins of this maximum is due to the development of a coherent state, as often observed for many Kondo lattice and/or heavy-fermion systems.²⁰ In these compounds, the position of thermopower maximum at low temperatures is intimately related to T_K . For Kondo lattice compounds, a two-peak structure of S(T)-curve has usually been observed.²⁰ The origin of the high temperature maximum in S(T)-curve is a result of the competition between incoherent Kondo scattering and CEF effect.^{20,21,22} Theoretically, studies based on the Coglin-Schrieffer model have predicted that the thermoelectric power should go through a maximum at a temperature of order $\Delta/6-\Delta/3$, where Δ is an energy separation between the ground state and the first exited CEF level.^{20,21} We would like to note that the absolute S values for Ce₅CuSb₃ are rather small comparing to those of intermediate valence compounds (CePd₃ Ref. 23, CeNiIn Ref. 24) and heavy-fermion semiconductors (CeNiSn Ref. 25, U₂Ru₂Sn Ref. 26) but they are similar in magnitude with those of Kondo compounds, for instance of CePdSn²⁷, Ce₂NiGe₃,²⁸ and $\operatorname{CeT}_{x}(A1, Ga)_{4-x}$.²⁹ According to the authors of the latter references, tiny contribution of Kondo effect to the total thermoelectric power is due to a weak Kondo interaction in the compounds, manifesting themselves by small Kondo temperatures.

IV. SUMMARY

We have measured the magnetization, electrical resistivity, magnetoresistance, and thermoelectric power of Ce₅CuSb₃, and showed the this compound crystallizes in the orthorhombic Sm₅Ge₄-type structure and orders antiferromagnetically below 3.7 K. As referring to the magnetic susceptibility data and crystal structure, we suggest, however, a complexity of magnetic structure. The electronic specific heat coefficient is estimated to be 170 mJ/K² mol Ce. In joining with a large prefactor A of the quadratic term of the resistivity, Ce₅CuSb₃ can be classified to a class of moderate heavy fermion compounds. In comparison to other heavy fermion systems, the investigated compound shows larger values of both the Kadowaki-Woods and Wilson ratios, implying enhanced magnetic interactions. The Kondo temperature T_K has been estimated to be about twice as large than T_N . The magnetoresistance shows large values at temperatures above T_N , reaching -35% at 5 K and 14 T. A two-peak structure is observed in the thermoelectric power. Lowtemperature peak at 8 K is ascribed to the change in the electronic structure, while the high-temperature peak at 105 K to the interplay of the Kondo and CEF effects.

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- ³F. Steglich and S. Sullow, in *Encyclopedia of Materials: Science and Technology* (Elsevier Science, New York, 2001), p. 3746.
- ⁴ W. Rieger, E. Parthé, Monatsch. Chem. **99**, 291 (1968); K. Schubert, H. G. Meissner, M. Poetzschke, W. Rossteutscher, and E. Stolz, Naturwissenschaften **49**, 57 (1962).
- ⁵P. Villars, *Pearson's Handbook of Crystallographic data for Intermetallic Phases* (American Society for Metals, Materials Park, OH, 1997), p. 2886.
- ⁶K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975).
- ⁷L. N. Oliveira and J. W. Wilkins, Phys. Rev. Lett. **47**, 1553 (1981).
- ⁸N. Andrei, K. Furuya, and J. H. Lowenstein, Rev. Mod. Phys. **55**, 331 (1983).
- ⁹C. D. Bredl, F. Steglich, and K. D. Schotte, Z. Phys. B **29**, 327 (1978).
- ¹⁰M. J. Besmus, A. Brahta, N. Hamdaoui, and A. Meyer, J. Magn. Magn. Mater. **104–107**, 1385 (1992).
- ¹¹K. D. Schotte and U. Schotte, Phys. Lett. **55**, 38 (1975).
- ¹²J. A. Blanco, M. de Podesta, J. I. Espeso, J. C. Gomez Sal, C. Lester, K. A. McEwen, N. Patrikios, and J. Rodriguez Fernandez, Phys. Rev. B **49**, 15126 (1994).
- ¹³H. Yashima, H. Mori, N. Sato, and T. Satoh, J. Magn. Magn. Mater. **31–34**, 411 (1983).
- ¹⁴H. J. van Daal and K. H. J. Buschow, Phys. Status Solidi A 3, 853 (1970).
- ¹⁵K. Kadowaki and S. B. Woods, Solid State Commun. **58**, 507 (1986).
- ¹⁶I. A. Campbell and A. Fert, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1982), Vol. 3,

p. 747.

- ¹⁷N. F. Mott, Philos. Mag. **26**, 1249 (1972).
- ¹⁸J. Kondo, Prog. Theor. Phys. **32**, 37 (1964).
- ¹⁹F. J. Blatt, P. A. Schroeder, and C. L. Foiles, in *Thermoelectric Power of Metals* (Plenum Press, NewYork, 1976).
- ²⁰ V. Zlatić, B. Horvatic, I. Milat, B. Coqblin, G. Czycholl, and C. Grenzebach, Phys. Rev. B **68**, 104432 (2003) and references therein.
- ²¹A. K. Bhattacharjee and B. Coqblin, Phys. Rev. B 13, 3441 (1976).
- ²²S. Maekawa, S. Kashiba, M. Tachiki, and S. Takahashi, J. Phys. Soc. Jpn. 55, 3194 (1986).
- ²³D. Jaccard and J. Sierro, in *Valence Instabilities*, edited by P. Wachter and H. Boppart (North-Holland, Amsterdam 1982), p. 409.
- ²⁴ H. Fujii, T. Inouse, Y. Andoh, T. Takabatake, K. Satoh, Y. Maeno, T. Fujita, J. Sakurai, and Y. Yamaguchi, Phys. Rev. B **39**, 6840 (1989).
- ²⁵T. Takabatake, F. Teshima, H. Fujii, S. Nishigori, T. Suzuki, T. Fujita, Y. Yamaguchi, J. Sakurai, and D. Jaccard, Phys. Rev. B 41, 9607 (1990).
- ²⁶ V. H. Tran, S. Paschen, A. Rabis, N. Senthilkumaran, M. Baenitz, F. Steglich, P. de V. du Plessis, and A. M. Strydom, Phys. Rev. B 67, 075111 (2003).
- ²⁷D. T. Adroja, B. D. Padalia, S. N. Bhatia, and S. K. Malik, Phys. Rev. B **45**, 477 (1992).
- ²⁸D. Huo, J. Sakurai, T. Kuwai, Y. Isikawa, and Q. Lu, Phys. Rev. B **64**, 224405 (2001).
- ²⁹ E. Bauer, N. Pillmayr, E. Gratz, G. Hilscher, D. Gignoux, and D. Schmitt, Z. Phys. B: Condens. Matter **67**, 205 (1987); H. Flandorfer, P. Rogl, E. Bauer, H. Michor, R. Hatzl, E. Gratz, and C. Godart, J. Phys.: Condens. Matter **8**, 2365 (1996).

²V. H. Tran, J. Alloys Compd. (to be published).