CeCuSb₂ and CeNiSb: new exotic Kondo systems

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Abstract

Interesting physical properties are encountered for the ternary cerium antimonides; CeCuSb$_2$, which exhibits a great magnetoresistance at low temperature, and CeNiSb, which is a new ferromagnetic Kondo system.

1. Introduction

Ternary phase diagrams for systems comprising rare earths (RE), transition metals (M) and (sp)-type metals or non-metallic elements (X element) have been thoroughly described for few years, with particular focus on ternary silicides, germanides and stannides [1, 2]. Numerous papers were devoted to cerium compounds, the valency state of which is strongly dependent on composition [3, 4].

As the X element passes from the fourth to the fifth column of the Periodic Table, the initial covalent character of the bonds becomes more ionic. Together with the addition of one electron, this may change the Fermi level, the valency state and the magnetic properties of cerium. It is, for instance, interesting to see what happens when Sb is substituted for Sn in the CeNiSn compound, which presents a hybridization gap at low temperatures [5].

We describe in this paper the crystallographic and magnetic properties of a few antimonides in the ternary systems Ce–Ni–Sn and Ce–Cu–Sb, with emphasis on CeCuSb$_2$ and CeNiSb which exhibit interesting magnetic properties.

2. Preparation and crystallographic properties

Polycrystalline samples were prepared in an arc furnace, with subsequent annealing at about 600 °C. As the samples oxidize rather rapidly, they were kept under argon until use. Due to the high vapour pressure of Sb, samples often contain bubbles, hence the absolute value of the resistivity could not be precisely determined.

The crystallographic structures were investigated by X-ray diffraction using a Nicolet diffractometer.

Among the ternary compounds, the 1:2:2 phase CeNi$_2$Sb$_2$ has already been described [6]; it crystallizes with the CaBe$_2$Ge$_2$ structure (space group $P4/nmm$). The homologous compound CeCu$_2$Sb$_2$ was prepared starting with the stoichiometric composition. X-ray diffraction shows the occurrence of a main tetragonal phase with lattice parameters $a = 4.371$ (2) Å, $c = 10.235$ (4) Å, with a small amount of pure Cu. Thus some Cu deficiency exists in the compound, which may have composition CeCu$_{2-x}$Sb$_2$, although we cannot at present ascertain the exact composition of the sample. Pöttgen *et al.* [7] have studied the crystallographic structure of similar compounds with uranium and thorium, and found these compounds had a defect CaBe$_2$Ge$_2$-type structure, with a strong deviation from the ideal composition: the Cu or Ni content was found to range from 1.30 to 1.80. This composition will be noted as CeCu$_{1.2}$Sb$_2$.

During the course of investigating the ternary Ce–Cu–Sb diagram, we also prepared as a pure phase the 1:1:2 compound CeCuSb$_2$. This new compound also crystallizes with space group $P4/nmm$, being isomorphous with HfCuSi$_2$ type. Note that this structure may be derived from the ThCr$_2$Si$_2$ structure (space group $I4/mmm$) by elimination of one Cr atom, which changes the space group to $P4/nmm$ [8]. The cell parameters were obtained as $a = 4.342(2)$ Å, $c = 10.233$ (2) Å, and the atomic positions were refined as follows:

2 Ce in 2c: 1/4, 1/4, z, with $z = 0.749$ (1)
2 Sb in 2c: $z = 0.152(1)$
2 Sb in 2b: 3/4, 1/4, 1/2
2 Cu in 2a: 3/4, 1/4, 0.

Thus the structure is the same as that of $CeCu_{-2}Sb_2$, except for the absence of one Cu atom; the lattice parameters are also very close. It seems that a continuous phase exists between compositions $CeCuSb_2$ and $CeCu_xSb_2$, where x is about 1.6 or 1.7.

Let us note that an isomorphous phase also occurs for $CeNiSb_2$. Studies on this compound are not complete at present.

The compound CeNiSb has the same composition as the well known CeNiSn compound, which exhibits a hybridization gap at low temperature [5]. The crystallographic structure has been solved by Pecharski et al. [9]; it is hexagonal AlB_2-type (space group $P6/mmm$), with $a = 4.384$ (2) Å, $c = 4.110(2)$ Å.

3. Magnetic properties and resistivity

3.1. CeCuSb₂-CeCu₋₂Sb₂

The magnetic properties were studied from 1.5 to 300 K, in fields up to 7 T. The reciprocal susceptibility for $CeCuSb_2$ follows a Curie–Weiss law between 20 and 150 K, with an effective moment $\mu_{eff} = 2.57$ μ_B which is nearly that of Ce^{+3}, and a Curie–Weiss temperature $\theta_p = -11$ K (Fig. 1, Table 1). At higher temperatures, the reciprocal susceptibility bends down, a feature which has been previously observed in some 1:2:2 stannides and antimonides [6], and which may be due either to impurities or to some superposed

constant paramagnetism. The susceptibility reaches a maximum at 6 K, which is attributed to antiferromagnetic ordering. Below this temperature, magnetization curves remain linear with field up to 7 T.

Solid solutions where Ce is replaced by La have been studied. No significant modifications of the paramagnetic moment and of the Curie–Weiss temperature are observed (Table 1), whereas the Néel temperature decreases rapidly. It is evident, as shown by the reduction of susceptibility compared with diluted systems, that antiferromagnetic correlations occur in $CeCuSb_2$ below 20 K. The magnetic properties are summarized in Table 1.

$CeCu_{-2}Sb_2$ has a Curie–Weiss temperature of -7 K, and a Néel temperature of about 3 K. This ordering temperature is hardly visible in susceptibility curves, but more visible in the temperature derivative of resistivity. Thus, a substantial reduction of ordering temperature occurs when adding Cu in the structure.

The resistivity of $CeCuSb_2$ shows a maximum R_{max} at 7 K and a minimum R_{min} at 70 K (Fig. 2), as for concentrated Kondo systems. The resistivity drop below 7 K seems to coincide with the onset of antiferromagnetic ordering. A peculiar feature is the huge increase of resistivity from 70 to 7 K, with $R_{max}/R_{min} \approx 1.45$, which is well above the corresponding ratio found in other related Kondo-type stannides or antimonides, for instance, $CeCu_2Sb_2$.
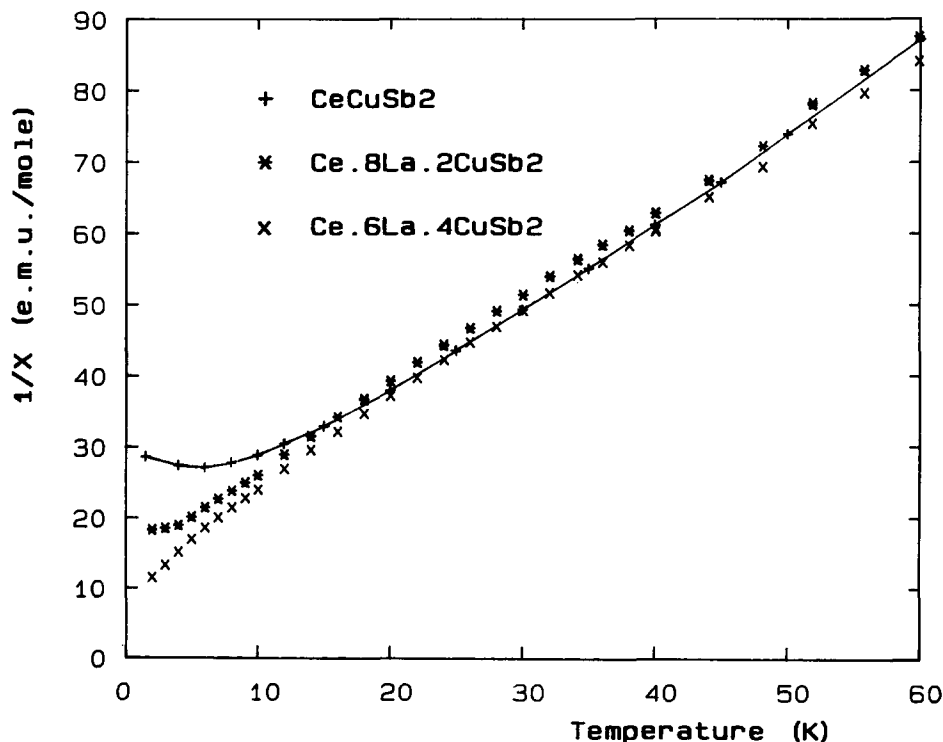

Fig. 1. Reciprocal susceptibility of $CeCuSb_2$ and diluted solid solutions (e.m.units per mole of Ce).

TABLE 1. Summary of crystallographic and magnetic properties. The effective moment μ_{eff} and Curie–Weiss temperature θ_p are obtained from fits below 150 K

Compound	a (Å)	c (Å)	μ_{eff} (μ_B)	θ_p (K)	T_c, T_N (K)
CeCuSb₂	4.342	10.233	2.57 (3)	−11 (2)	7
Ce₀.₈La₀.₂CuSb₂			2.59 (3)	−12 (2)	4
Ce₀.₆La₀.₄CuSb₂			2.59 (3)	−11 (2)	<2
CeCu₂Sb₂	4.371	10.235	2.60 (3)	−7 (2)	3
CeNi₂Sb₂	4.402	9.92	2.60 (4)	−28 (4)	2.5
CeNiSb₂	4.409	9.749	2.45 (5)	+6 (2)	7
CeNiSb	4.384	4.110	2.70 (5)	−15 (3)	7

The resistivity of LaCuSb₂ is that of a classical metallic system. The uncertainty on the geometrical factor and the presence of bubbles in the samples prevent a direct comparison with the Ce compound. Finally, the solid solution La₀.₄Ce₀.₆CuSb₂ exhibits a strong increase of resistivity at low temperature similar to that of the pure compound, with a maximum at 9 K.

The magnetoresistance of CeCuSb₂ has been investigated up to 5 T: a huge drop of resistivity is observed under the magnetic field (Fig. 3), which nearly washes out the Kondo-like anomaly.

As shown in Fig. 2 for comparison, the resistivity of CeCu₂Sb₂ compound also shows a Kondo-like behaviour, with a maximum at 17 K and a minimum at about 140 K, but the resistivity anomalies are much less pro-

nounced than for the previous compound, and of the same order of magnitude as other 1:2:2 stannides and antimonides [6]. It only shows a small negative magnetoresistance $(dR/R \approx -3 \times 10^{-3}$ under 5 T at 10 K).

3.2. CeNi₂Sb₂–CeNiSb₂

The CeNi₂Sb₂ compound has been described previously [6]. It is probable that the composition is also not stoichiometric, and that some Ni deficiency is present. It has a Curie–Weiss temperature θ_p of −28 K and a Néel temperature of 2.5 K. The magnetic properties and resistivity behaviour are close to those of the corresponding stannide CeNi₂Sn₂.

Preliminary studies of the compound CeNiSb₂ show that θ_p is positive (6 K); the compound orders at about 7 K. Below this point, a small spontaneous magnetization appears (about 0.15 μ_B), and a multistep magnetization process occurs, giving magnetization of 0.65 μ_B in 7 T at 1.5 K. As for Cu compounds, lowering the transition metal content increases the ordering temperature, possibly due to the increase in the density of states in the conduction band.

3.3. CeNiSb

The susceptibility of CeNiSb follows a Curie–Weiss law above 35 K, with an effective moment of 2.70(5) μ_B and a Curie–Weiss temperature of −15 K. However, the susceptibility deviates from this law at lower temperatures, and diverges near $T_c = 7$ K, where sponta-
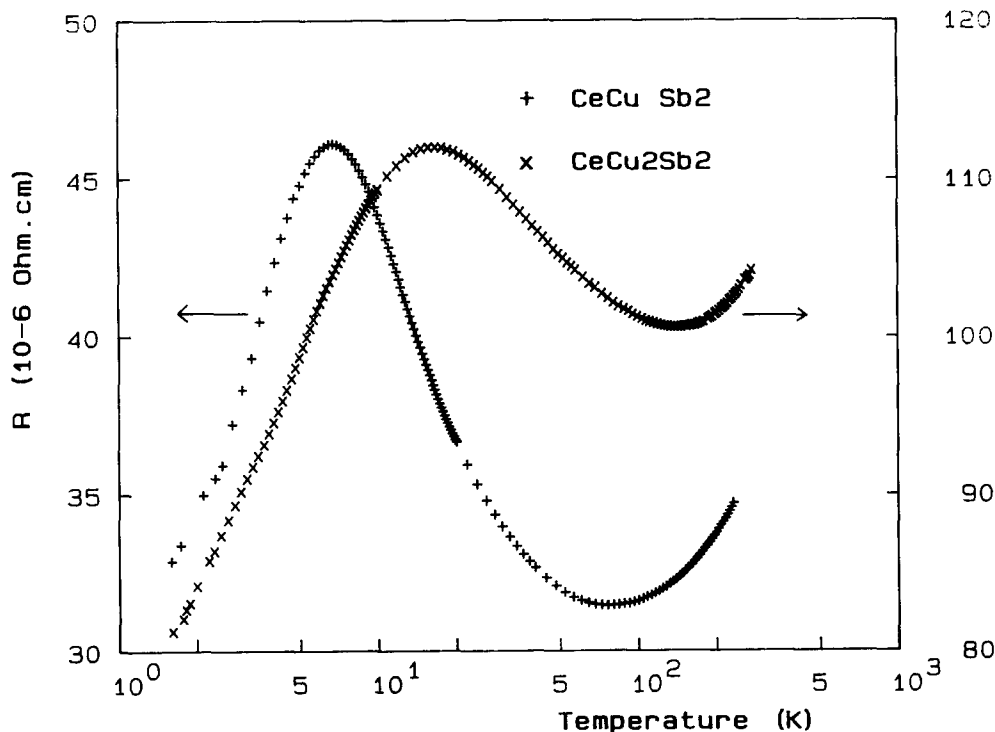

Fig. 2. Resistivity of CeCuSb₂ (left-hand scale) and CeCu₂Sb₂ (right-hand scale).
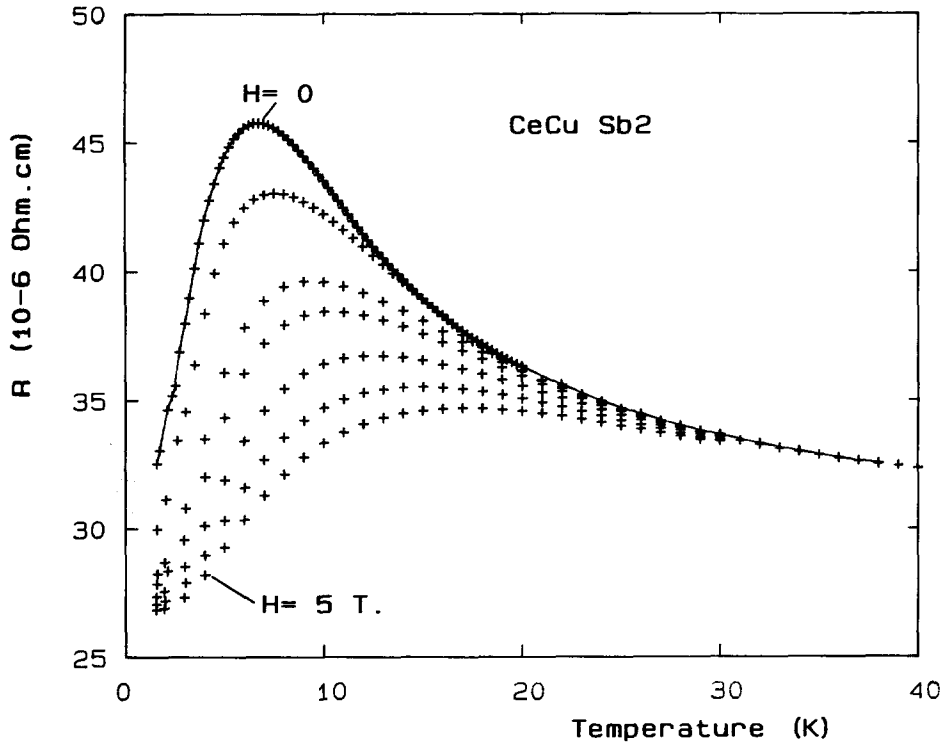
Fig. 3. Resistivity of CeCuSb₂ under increasing magnetic fields. From up to down, the field is 0, 1, 1.5, 2, 3, 4, 5 T.
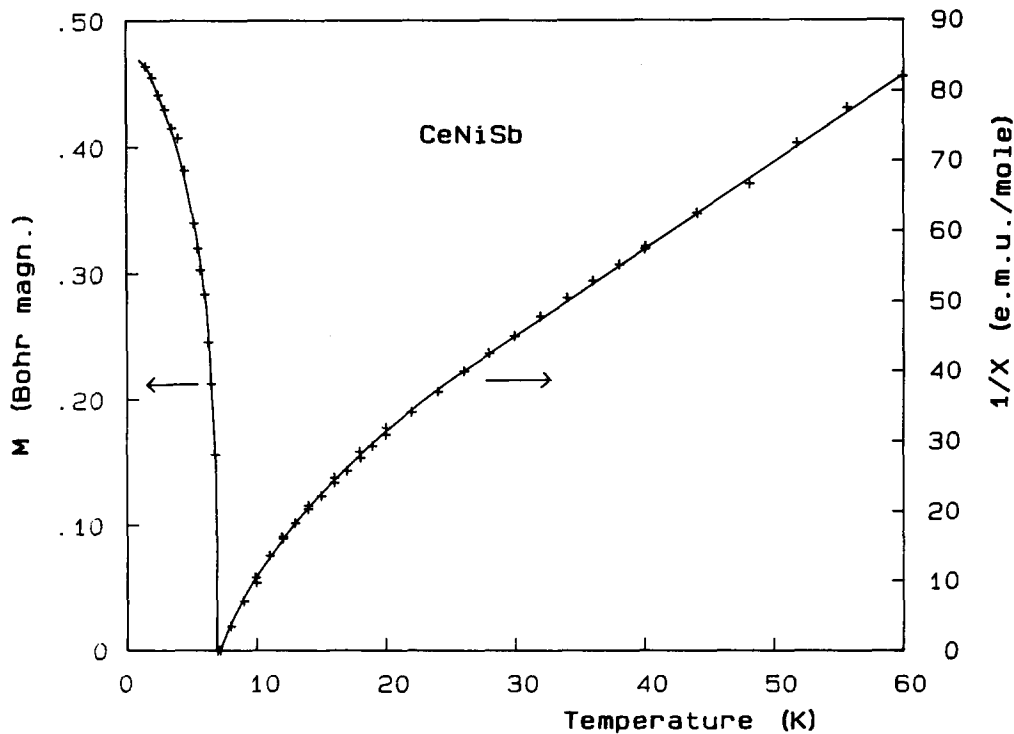

Fig. 4. Spontaneous magnetization and reciprocal susceptibility of CeNiSb.

neous magnetization appears. As the superposed susceptibility is large in the ordered state, Arrott plots (M^2 vs. H/M) were used to obtain the spontaneous moment vs. temperature (Fig. 4). The ferromagnetic moment reaches 0.48 μ_B at 1.5 K. A plot of $M^2(T)$ vs.

T^2 is nearly linear through the whole ordered range, a law which is often observed in weak ferromagnets.

The resistivity exhibits a maximum at about 60 K and a minimum around 200 K (Fig. 5). A kink in the curve occurs at 7 K, which confirms the value of the
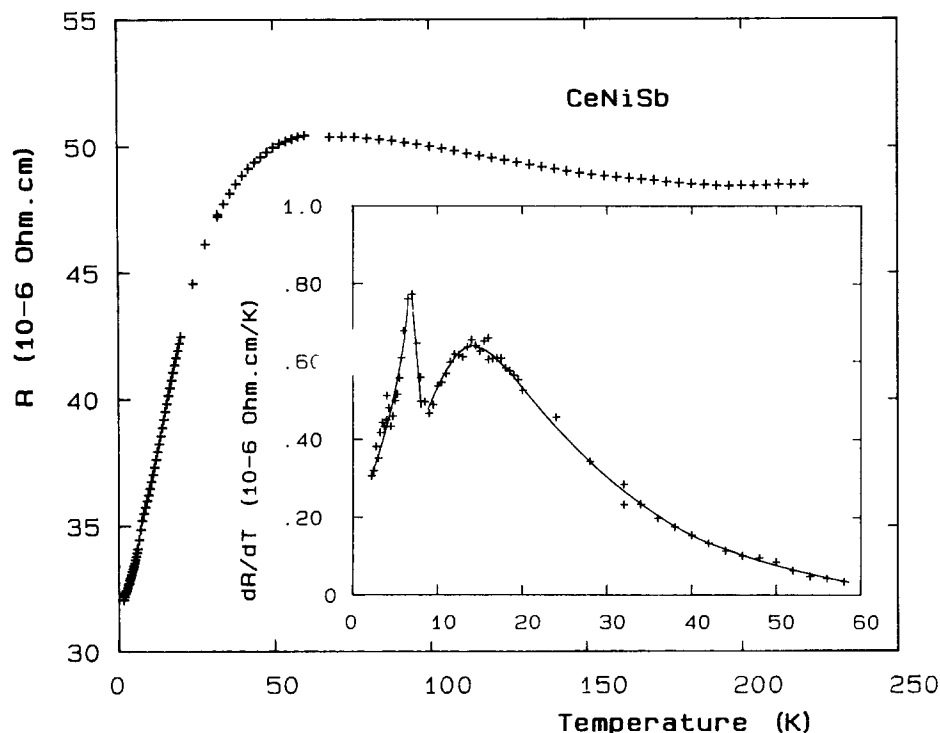
Fig. 5. Resistivity of CeNiSb and its temperature derivative.

Curie temperature. The maximum slope of resistivity vs. temperature is reached near 15 K (insert of Fig. 5).

Finally the magnetoresistance at low temperature is negative. The initial slope is vanishing in the paramagnetic range, and negative in the ferromagnetic state. Nevertheless, the magnitude of the magnetoresistance under 4 T keeps nearly the same value $(dR/R \approx -3 \times 10^{-2})$ in the ordered range.

4. Discussion

The compound $CeCuSb_2$ exhibits a rather large peak of resistivity and "great" magnetoresistance at low temperatures. A strong decrease of resistivity is observed below 7 K, which may be related to antiferromagnetic order or to the coherence of the lattice. The fact that the same behaviour is encountered in the diluted $Ce_{0.6}La_{0.4}CuSb_2$ solution means that coherence of the lattice is not the main reason for the low temperature decrease of resistivity.

The characteristic temperatures of the resistivity minimum and maximum are half those encountered for the isomorphous $CeCu_{2}Sb_2$ compound, which suggests a corresponding reduction in the characteristic energies (crystal field splittings, Kondo temperature) when reducing the Cu content. However, the shape of the anomaly, plotted as function of T in a logarithmic scale in Fig. 2, is not the same, being much narrower and

higher for $CeCuSb_2$. This may point to some significant differences in the band structure, crystal field or intersite correlations. The onset of antiferromagnetic correlations above the Néel point was also noticeable from the variation of susceptibility.

The magnetoresistance could be fitted very well between 1.5 and 8 K by the law:

$$R(H,T) = R(O,T) - DR_{max}(T)^* \; \text{arctg} \; (H/H_c(T))$$

Trying to fit it by laws with a hyperbolic tangent variation gave much worse fits. Above 10 K, the magnetoresistance has a classical H^2 behaviour in low fields, followed by a straight variation in larger fields. The change in initial behaviour from quadratic to linear with field means that the compound is magnetically ordered at low temperatures, and rules out the occurrence of a non-magnetic (heavy fermion) ground state.

Let us analyse the variation of magnetoresistance up to 8 K. The extrapolated saturation magnetoresistance DR_{max} increases with temperature up to 7 K, and stays more or less constant above. This is expected for a classical spin-disorder resistivity term, as the magnetic resistivity in zero field should vary more or less as $(M(0)^2 - M(T)^2$ up to the ordering point. It also appears from the fits that the characteristic field H_c is proportional to T, so that the argument in the arctangent may be written as $(\mu H/kT)$; hence we obtain a moment $\mu = 0.40 \; \mu_B$. The meaning of such a moment is not

evident, nor is the form of the variation itself, as the magnetization remains linear with field up to 7 T.

The large increase in resistivity and high value of the magnetoresistance may be related to the tendency to form, as for CeNiSn, a hybridization gap at low temperatures which is destroyed by the onset of magnetic order or application of an external field. Alternatively, antiferromagnetic correlations may give rise to magnetic gaps in the Fermi surface, which increase the resistivity down to the Néel point where the onset of long range order suppresses most of the spin fluctuations.

CeNiSb is a new ferromagnetic Kondo system. Despite having a different crystal structure, a comparison with CeNiSn is useful. Adding one more electron turns the system to being metallic and ferromagnetic. It is well known from Ruderman-Kittel-Kasuya-Yosida (RKKY) theory that when increasing the number of conduction electrons starting from zero, the first stable structure is the ferromagnetic one, as the susceptibility of the conduction band has a maximum for the wavevector $q = 0$. The ferromagnetic structure of CeNiSb is in line with that prediction.

The strong drop of resistivity below 60 K may be related to crystal field effects and/or to the coherence of the lattice. Study of solid solutions where Ce is diluted by La should help to solve this problem. If coherence is responsible for this drop, destroying coherence by dilution will restore the one-impurity Kondo behaviour and weaken the resistivity drop. Conversely, the same decrease of resistivity will be maintained if crystal field degeneracy is the origin. The temperature derivative of the resistivity is drawn in the insert of Fig. 5. Its shows a lambda-type anomaly at the ordering point, and a maximum at about 15 K which may be interpreted as a Schottky-like anomaly if it arises from the thermal population of crystal field levels. The paramagnetic susceptibility itself shows a strong crystal field influence below 35 K.

A puzzling effect is the large superposed susceptibility in the ordered range, which prevents ascertaining the nature of the crystal field ground state. The spontaneous magnetization of 0.48 μ_B is small. The lack of saturation may be due to a strong (uniaxial) magnetocrystalline anisotropy, which reduces the mean magnetization measured on a polycrystalline sample, to the presence of low lying crystal field excited levels, or to a noticeable

reduction of the magnetization through Kondo coupling. We may also ask whether or not the compound is truly ferromagnetic. Measurements of the anisotropy of susceptibility and magnetization on single crystals may allow determination of the crystal field level scheme. Pressure experiments will also be undertaken, in order to follow the decrease of magnetization and Curie point with increasing hybridization.

For ternary silicides and germanides, the Ce–Ni compounds generally show a larger hybridization than the corresponding Ce–Cu compounds. Most CeM₂Si₂ compounds are heavy fermion systems, and often do not order magnetically. Conversely, for antimonides, the hybridization seems slightly smaller; ordering is observed for Ni as well as Cu compounds. This trend may perhaps be ascribed to a change in ionicity of the bonding, which would stabilize the trivalent state of cerium.

Acknowledgments

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