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New phases RCu_5Sn with the $CeCu_6$ structure type

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Abstract

A series of RCu_5Sn compounds, where R = La-Sm, has been synthesized. X-ray powder diffraction shows that the crystal structure of these compounds belongs to the $CeCu_6$ structure type, but without a complete solid solution between RCu_6 and RCu_5Sn. The magnetic susceptibility and resistivity have been measured for $CeCu_5Sn$ and $PrCu_5Sn$. The $CeCu_5Sn$ compound orders antiferromagnetically at 10 K, $PrCu_5Sn$ has probably a non-ordered ground state.

Keywords: Crystal structure; Powder method; Magnetic susceptibility; Electrical resistivity; Thermopower

1. Introduction

In the R–Ni–Sn (R = rare earth) nickel-rich systems, compounds exist with formula close to RNi_5Sn [1]. The crystal structure of RNi_5Sn stoichiometric compounds, where R = La–Nd, belongs to $CeNi_5Sn$ structure type (SG: $P6_3/mmc$) [2], while the compounds with formula $RNi_{5-x}Sn_{1+x}$ formed by heavy rare earths crystallize in the $CeCu_{4.38}In_{1.62}$ structure type (SG: Pnnm) [3].

During a study of the ternary diagram Ce–Cu–Sn, we found that the alloy with composition $Ce_{15}Cu_{70}Sn_{15}$ contains an unknown phase, with a X-Ray pattern different from those of Ce–Cu and Ce–Sn binary phases. In the Pr–Cu–Sn system we also obtained a compound with the $PrCu_5Sn$ approximate composition [4], the crystal structure of which has not been yet determined. Analogous compounds are formed with La, Nd and Sm. Riani et al. [5] also report on the $CeCu_5Sn$ compound without determination of the structure. In the present paper we report on the crystal structure determination of this phase and on the magnetic and electrical properties of Ce and Pr compounds.

2. Experimental

The synthesis of the samples was carried out in an electric arc furnace by melting the rare earth (99.8% R), electrolytic copper (99.99% Cu) and tin (99.999% Sn). Then the obtained alloys were annealed at 500°C for 720 h in vacuum sealed quartz ampoules. X-Ray powder patterns were obtained using a DRON-2.0 diffractometer with Fe$K\alpha$-radiation and the crystal lattice parameters were determined for the whole series of investigated compounds. For more detailed structural investigation, the cerium phase was chosen. In this case the X-Ray measurements were also performed using the automatic powder diffractometer HCG-4A with Co$K\alpha$-radiation. Diffraction data were collected in the 2θ range 12–130° with 2θ steps of 0.02° and step times 9–30 s.

The magnetic susceptibility was measured in the temperature range 1.5–300 K under an applied field 0.3 Tesla by the extraction method. The electrical

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resistivity was measured by the classical ac current four probes method between 1.5 K and room temperature, and the thermopower was determined between 90 and 360 K by the direct comparison of a copper–sample–copper chain to a standard thermocouple.

3. Results and discussion

The detailed investigation of the crystal structure has been carried out on an alloy of the $Ce_{15}Cu_{70}Sn_{15}$ composition. At first we could not suppose that the structure belonged to the $CeCu_6$ type [6], because the positions of diffraction peaks were considerably displaced relatively to those of $CeCu_6$ and thus we tried to solve this structure ab-initio. The structure determination has been done by building a three-dimensional distribution of the interatomic function to find a trial model. The position of diffraction maxima and their integrated intensity for individual and overlapping reflections have been determined, the obtained data were used to perform the analytical indexing and the refinement of lattice parameters. The second step consisted in the refinement of the trial model by Rietveld method using a controlled calculation of usual and differential Fourier synthesis of the electron density. The parameters were atom coordinates, temperature parameters and occupation sites coefficients.

The value of the agreement factor R was 0.122. The distribution of atoms in the $CeCu_5Sn$ structure corresponds to that in the $CeCu_6$ compound, only the sites of Cu1 atoms are occupied by Sn atoms, and the Cu4 site by a statistical mixture of Cu and Sn atoms (Table 1). It is the reason why the real formula of the investigated compound is given in the form $CeCu_{4.81}Sn_{1.19}$. It can be speculated that at the $CeCu_5Sn$ composition the Cu3 site is only occupied by Cu atoms and the $CeCu_5Sn$ structure can be considered as a superstructure of the $CeCu_6$ type.

The interatomic distances of $CeCu_{4.81}Sn_{1.19}$ do not show considerable deviation from the sums of atomic radii of the components, except for Cu1–Cu4 shortened distances.

Table 1
Atomic parameters for $CeCu_{4.81}Sn_{1.19}$. Coordinates, site positions and temperature parameters B (SG: Pnma)

Atom	Site	x/a	y/a	z/c	B	N^a
Ce	4(*c*)	0.254(1)	0.25	0.442(1)	1.7(2)	4
Sn	4(*c*)	0.142(1)	0.25	0.136(1)	0.7(2)	4
Cu1	4(*c*)	0.324(2)	0.25	0.737(2)	2.3(6)	4
Cu2	4(*c*)	0.069(2)	0.25	0.905(2)	2.0(5)	4
Cu3[b]	4(*c*)	0.420(2)	0.25	0.982(1)	1.1(4)	4
Cu4	8(*d*)	0.431(1)	0.004(2)	0.189(1)	0.8(2)	8

[a] Occupation.
[b] 0.81(4)Cu + 0.19(4)Sn.

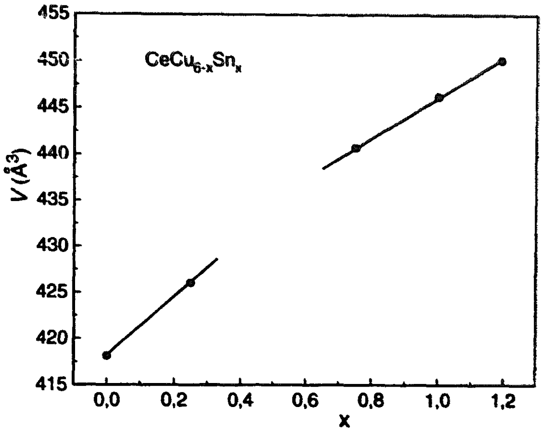

Fig. 1. Unit cell volume of $CeCu_{6-x}Sn_x$ alloys.

Up to now, it can be assumed that $CeCu_{4.81}Sn_{1.19}$ is a solid solution on the basis of $CeCu_6$ compound. $CeCu_{6-x}Sn_x$ alloys ($x = 0.25$, 0.50, 0.75, 1.00) have been prepared in addition. The X-Ray analysis showed that alloys with $x = 0.25$, 0.75 and 1.00 are homogeneous. The substitution of Cu atoms by Sn atoms leads to an increase of the volume of unit cell (Fig. 1). But a splitting or at least a broadening of reflections can be seen on the powder pattern of the $RCu_{5.5}Sn_{0.5}$ alloy, showing the existence of two phases. It was difficult to separate the lines because the lattice parameters of the two phases are too close. We think that a continuity of the solid solution between $CeCu_6$ and $CeCu_5Sn$ exists at high temperatures, but with an uncertain gap below 500°C.

Isotypic compounds with RCu_5Sn composition were also synthesized with La, Pr, Nd, Sm, their lattice parameters are given in Table 2 and the volume of the unit cells on the Fig. 2. The RCu_6 compounds exist in all R–Cu binary systems (R = La–Sm), however, the study of the Pr–Cu–Sn system has shown that below 670 K there is again no complete solid solution between $PrCu_6$ and $PrCu_5Sn$ [4]. The second solid solution including RCu_5Sn may receive the general formula $RCu_{5\pm x}Sn_{1\mp x}$.

$CeCu_6$-type compounds do not form in the R–Ni binary systems, however, the $CeNi_5Sn$ structure is built by $CeCu_6$ structure type fragments (the others parts are fragments of hypothetical RNi_7 structure)

Table 2
Unit cell parameters and its volume for RCu_5Sn

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)
$LaCu_5Sn$	8.402(4)	5.089(6)	10.691(6)	457.1
$CeCu_{4.81}Sn_{1.19}$	8.3418(9)	5.0668(5)	10.651(1)	450.2
$CeCu_5Sn$	8.317(1)	5.066(3)	10.591(2)	446.2
$PrCu_5Sn$	8.341(1)	5.071(1)	10.645(2)	450.3
$NdCu_5Sn$	8.288(5)	5.070(6)	10.571(8)	444.2
$SmCu_5Sn$	8.261(1)	4.990(1)	10.534(1)	434.2

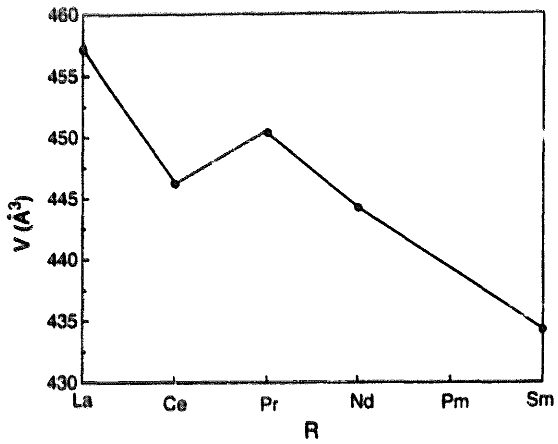

Fig. 2. Unit cell volume of RCu$_5$Sn compounds.

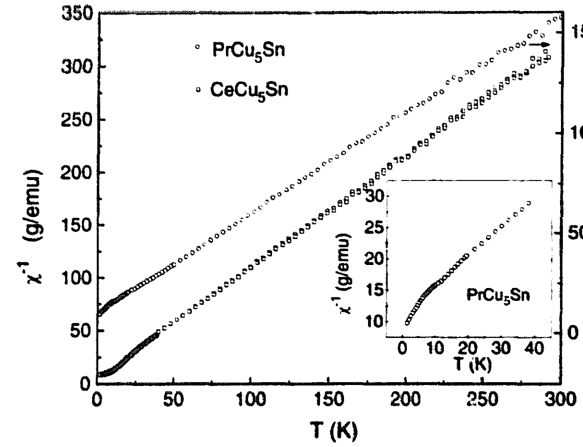

Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility for CeCu$_5$Sn and PrCu$_5$Sn.

[2]. The heavy rare earths form RNi$_5$Sn compounds of CeCu$_{4.38}$In$_{1.62}$ structure type which is practically a superstructure of CeCu$_6$ type with a double a parameter. The formation of the RNi$_5$Sn and RCu$_5$Sn compounds can be considered as a capacity of tin to stabilize the CeCu$_6$ type structure.

Some physical properties have been measured for the compositions CeCu$_5$Sn and PrCu$_5$Sn. The magnetic susceptibility of these compounds follows the Curie–Weiss law in the temperature ranges 30–300 K and 15–300 K, respectively (Fig. 3). The effective magnetic moments (μ_{eff}) and paramagnetic Curie points (θ_p) are equal to 2.60 μ_B and -4.6 K for CeCu$_5$Sn, 3.78 μ_B and -20.8 K for PrCu$_5$Sn. There is a kink on the $\chi^{-1}(T)$ curve of CeCu$_5$Sn near 30 K which corresponds to crystal field effects, and the curve flattens below 10 K, which may correspond to the Néel temperature T_N. The reciprocal susceptibility for Pr shows no sign of magnetic ordering down to 1.5 K, possibly due to a non-magnetic ground state; the slight downwards curvature below 10 K is attributed to some impurities which have still a magnetic moment.

The electrical resistivity (ρ) of CeCu$_5$Sn has a rather high magnitude. As the temperature decreases, ρ diminishes but it is nearly constant for temperatures between 12 and 20 K (Fig. 4). Below 12 K the resistivity strongly and suddenly decreases corresponding to AF order. The $\rho(T)$ dependence is similar to that for heavy fermion compounds, but no minimum appears contrary to the case of CeCu$_6$. We suppose that this is due to larger magnetic correlations and a much weaker Ce hybridization than in CeCu$_6$, resulting also in a rather high antiferromagnetic ordering temperature.

The PrCu$_5$Sn resistivity does not change strongly below 10 K. Thus, the magnetic transition is well seen on the $\chi^{-1}(T)$ and $\rho(T)$ curves of CeCu$_5$Sn, whereas it is not revealed for PrCu$_5$Sn. This confirms the absence of magnetic order in this last case, probably due to a singlet crystal field ground state.

Thermopower measurements were carried out on CeCu$_{6-x}$Sn$_x$ alloys. The magnitude of thermopower shows a dramatic decrease for $x = 0.25$ with respect to CeCu$_6$ (Fig. 5). Adding more Sn does not change the thermopower considerably.

Previous data show a strong decrease of the Kondo type interaction and heavy fermion character when replacing the Cu atoms in CeCu$_6$ by the bigger Sn atoms, and a transition from an unordered magnetic ground state to an ordered one. A similar occurrence was observed and well studied in CeCu$_{6-x}$Au$_x$ solutions for instance [7]. It was explained by a diminution of the hybridization between 4f-electrons of Ce and conduction electrons and by a simultaneous change of the antiferromagnetic interatomic interactions, as the decrease in hybridization stabilizes magnetic moments which begin to interact by RKKY mechanism [7]. In the case of Sn, the electron concentration plays a complementary role because one Sn atom, replacing

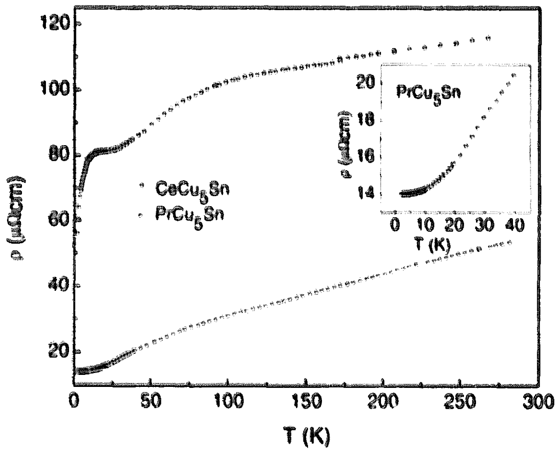

Fig. 4. Temperature dependence of the electrical resistivity for CeCu$_5$Sn and PrCu$_5$Sn.

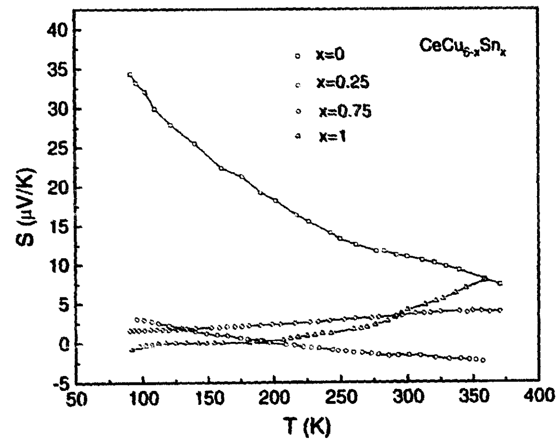

Fig. 5. Temperature dependence of the thermopower for the $CeCu_{6-x}Sn_x$ alloys.

one Cu atom, brings on three electrons more than Au atom. This may explain why Ce is magnetic in $CeCu_5Sn$, despite a lattice volume of the compound smaller than expected from those of other trivalent rare earths. It would be interesting to follow the Kondo and the Néel temperature in the series of solutions as a function of Sn content.

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