Magnetic and Transport Properties
of $R_3Cu_3Sb_4$ Compounds
(R = La, Ce, Pr, Nd, and Sm)

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Magnetic susceptibility, electrical resistivity, and thermopower of the series of the $R_3Cu_3Sb_4$ compounds (R = La−Sm) were measured over the temperature ranges 1.9–300 K (susceptibility and resistivity) and 80–370 K (thermopower). Below 25 K, resistivity of these compounds grows exponentially with decreasing temperature. For some compounds, R = Ce, Sm, a maximum on temperature dependence of resistivity is observed. $Ce_3Cu_3Sb_4$ compound undergoes a magnetic transition at 12 K.

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1. Introduction

Rare-earth metals may form with copper and antimony a series of $R_3Cu_3Sb_4$ type compounds, where R = Y, La–Sm, Gd–Er [1]. The crystal structure of these compounds is of the $Y_3Au_3Sb_4$ type ($I\bar{4}3d$ space group, $a = 0.9818$ nm). This type of structure may be derived from Pu_2C_3 type, where Sb atoms are arranged in the Pu atoms' positions (16(c)) and in the place of carbon atoms (24(d)), whereas Y and Au atoms are located in the positions 12(a) and 12(b), respectively [2]. In [3]

the magnetic and transport properties of $R_3Cu_3Sb_4$ (R = La, Ce, Gd, and Er) were reported. There was evaluated the thermoelectric potential of these ternaries.

In this paper, we present the results of resistivity measurements over the temperature range 1.9–300 K and thermopower measurements over the temperature range 80–370 K for some compounds of the $R_3Cu_3Sb_4$ series with light rare-earth elements (R = La, Ce, Pr, Nd, and Sm), which are interesting p-type thermoelectrics. We also present the results of magnetic properties investigation for Ce, Pr, and Nd compounds.

2. Experimental

The samples of $R_3Cu_3Sb_4$ compounds were obtained by melting the rare-earths (99.9% R), electrolytic copper (99.99% Cu) and antimony (99.999% Sb) in an electric arc furnace. Then, the ingots were annealed at 870 K for 700 hours in vacuum-sealed vitreous silica ampoules. The phase analysis of the samples was done on X-ray powder diffractometer DRON-2.0 with Fe K_α radiation.

Measurements of the resistivity, ρ, were carried out by a four probe method using an ac Resistance Bridge (AVS-46). The differential thermopower, S, was measured with respect to copper by a potentiometric technique. The samples used for transport measurements were cut in the form of bars with dimensions of about $1 \times 1 \times 4$ mm^3. The dc magnetic susceptibility was measured using a SQUID magnetometer (Quantum Design MPMS-5) over the temperature range from 4.5 to 300 K and in the magnetic field of 3 or 5 kOe.

3. Results and discussion

From the X-ray phase analysis we found that the prepared compounds had the $Y_3Au_3Sb_4$ type structure and no traces of any impurity phases were observed. The lattice parameter, a, diminishes continuously from 0.9817 nm for the La compound to 0.9600 nm for the Sm compound.

The resistivity of the samples is by 1 or 2 orders higher than typical ρ values for metals and alloys (Fig. 1). Above 100 K, the $\rho(T)$ plots are nearly linear for all samples, whereas at low temperatures the character of $\rho(T)$ strongly depends on the compound composition. At low temperature, for $La_3Cu_3Sb_4$, $Pr_3Cu_3Sb_4$, and $Nd_3Cu_3Sb_4$, the ρ value increases with the decrease in T, reaching its maximum value at 1.9 K. Among these three compounds, most significant changes in $\rho(T)$ are observed for the Nd compound. It is worth mentioning that over the temperature range $\approx 78–300$ K, where temperature ranges of the present studies of the Nd compound and the measurements reported in [1] overlap, a good agreement between the results of both studies is observed. For $Sm_3Cu_3Sb_4$ the ρ value increases at low temperature down to 4.3 K and then, it is nearly steady down to 1.9 K with a small anomaly at 3 K (inset in Fig. 1). In the $\rho(T)$ dependence
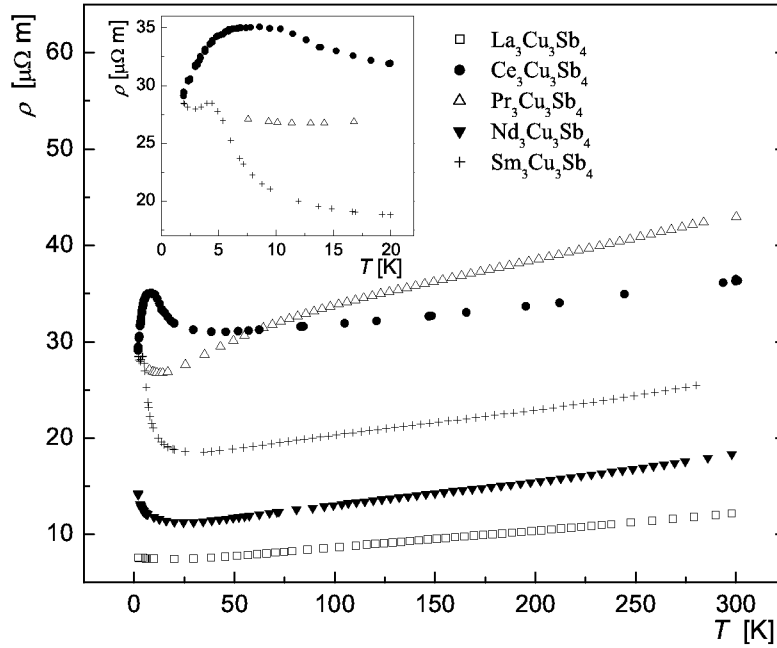
Fig. 1. Temperature dependences of resistivity for $R_3Cu_3Sb_4$ compounds.

for $Ce_3Cu_3Sb_4$, one can observe a broad minimum in the vicinity of 50 K and then, at lower temperatures, a relatively broad maximum between 5 and 10 K. The present results obtained for La, Pr, and Ce compounds differ from results of previous studies [3–7]. For example, in [5], a maximum on the temperature dependence of ρ was found at $\approx$ 200 K for the $La_3Cu_3Sb_4$ sample and at 140 K for the $Pr_3Cu_3Sb_4$ sample. The ρ values reported in [5] for the La sample are from 3 to 4 times larger, whereas the values for the Pr sample are approximately 2 or 3 times smaller than these measured for our samples. For $Ce_3Cu_3Sb_4$, which is the best-studied representative of the considered group of compounds, a maximum on $\rho(T)$ dependence and exponential decrease in resistivity with rising temperature was observed in all previous studies [3–7]. The maximum was observed at 3.3 K [3], at 12 K [5], and at 17 K [6]. Taking into account that samples prepared using the arc-melting technique show small deviations of their real composition from the theoretical stoichiometry, and that these deviations, even if not detectable by powder X-ray analysis, influence significantly transport properties of the material, all the discrepancies enumerated above can be attributed to inhomogeneities and nonstoichiometry of the samples obtained in different technological processes. For example, samples investigated in [4] and [5] showed slight tetragonal distortion of the crystal lattice, caused by Sb vacancies, whereas neutron studies [8] of the samples investigated in [6] revealed traces of the CeSb phase.
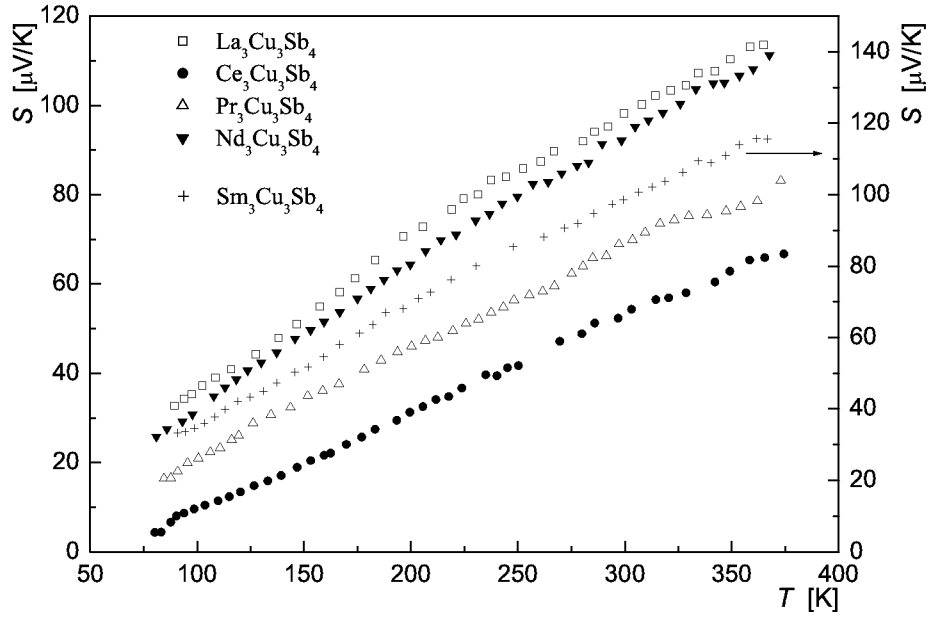
Fig. 2. Temperature dependences of differential thermopower for $R_3Cu_3Sb_4$ compounds.

The temperature dependences of the differential thermopower, S, of the studied samples are given in Fig. 2. For compounds with higher S values ($La_3Cu_3Sb_4$, $Nd_3Cu_3Sb_4$, and $Sm_3Cu_3Sb_4$) the temperature dependence of thermopower consists of two nearly linear parts, whereas for $Pr_3Cu_3Sb_4$ and $Ce_3Cu_3Sb_4$, the whole $S(T)$ dependence may be treated as linear. The evaluation of the thermoelectric power factor S^2/ρ for these compounds gives the following values at 300 K: $La_3Cu_3Sb_4$ — 7.9; $Ce_3Cu_3Sb_4$ — 0.8; $Pr_3Cu_3Sb_4$ — 1.1; $Nd_3Cu_3Sb_4$ — 4.8; and $Sm_3Cu_3Sb_4$ — 3.9 μW K^{-2} cm^{-1}. Technological differences, mentioned above, have a significant impact not only on resistivity but also on thermopower. In comparison with the present measurements, about 2 times smaller S values were measured for $La_3Cu_3Sb_4$ in [3], whereas for $Ce_3Cu_3Sb_4$ compound, greater values were found in [3] and smaller values were found in [7].

Above 50 K, the magnetic susceptibility of $R_3Cu_3Sb_4$ (R = Ce, Pr, and Nd) compounds follows the Curie law (for R = Ce) or the Curie–Weiss law with Θ_p equal to –8.3 K for R = Pr and –21.5 K for R = Nd (Fig. 3). In accordance with all previous studies [3–9], the effective magnetic moments determined from the $\chi^{-1}(T)$ plots are close to the theoretical $g_J\sqrt{J(J+1)}$ values for free R^{3+} ions, thus, no intermediate valence effects are present in this group of compounds and all R ions are in the stable 3+ state. The negative paramagnetic Curie temperature Θ_p indicates possible antiferromagnetic interactions between rare-earth ions for Pr and Nd compounds. For $Ce_3Cu_3Sb_4$, below 50 K, the $\chi^{-1}(T)$ dependence deviates
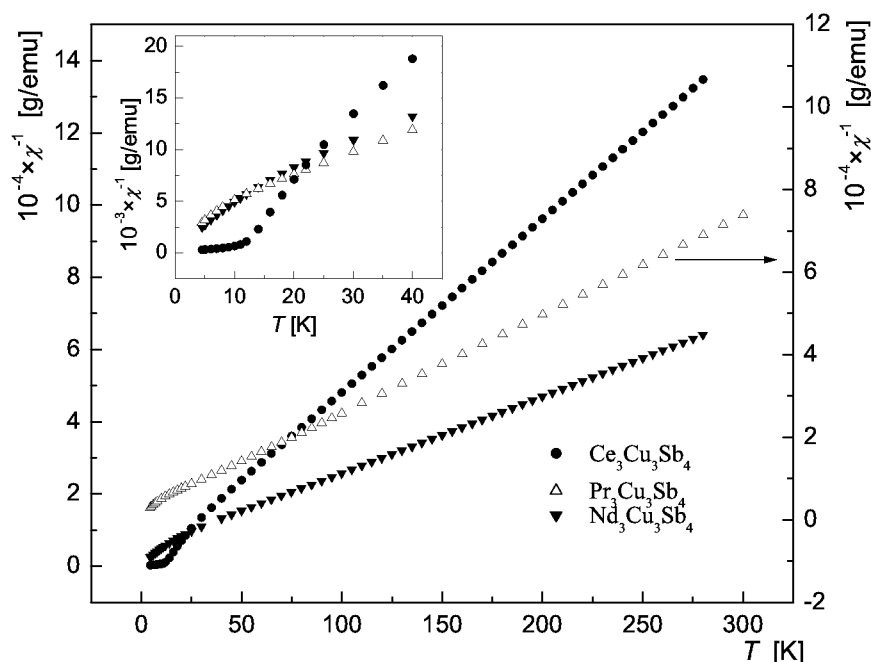
Fig. 3. Temperature dependences of magnetic susceptibility for $Ce_3Cu_3Sb_4$, $Pr_3Cu_3Sb_4$, and $Nd_3Cu_3Sb_4$ compounds.

distinctly from linearity to lower values and, at about 12 K, a transition to ferro- or ferrimagnetic ordering is observed. The specific heat studies [9] confirmed the presence of such transition and the neutron diffraction measurements [8] clearly showed that $Ce_3Cu_3Sb_4$ is a canted antiferromagnet below 12 K. The magnetic susceptibility of $La_3Cu_3Sb_4$ at 300 K in magnetic fields up to 10 kOe is small and negative ($\chi = -5.1 \times 10^{-8}$ emu/g).

At low temperature, $\rho(T)$ of $Nd_3Cu_3Sb_4$ and $Sm_3Cu_3Sb_4$ decreases exponentially with increasing temperature in 1.9–10 K and 4–20 K temperature ranges, respectively. This can be interpreted either as resistivity of heavy doped narrow-gap semiconductors, in which the energy gap is nearly filled by impurity states [1], or as a mobility effect connected with the existence of trapped magnetic polarons. The latter interpretation was proposed for Ce compound in Ref. [6]. The high positive thermopower, characterizing these materials, supports the idea that they show impurity-related p-type conductivity. In the case of intrinsic semiconductors, the two opposite currents of n- and p-type carriers would lead to small S values.

The semiconducting properties were observed in both M'M''X (where M', M'' are transition metals, and X = Sn, Sb) [10, 11] and RNiSb (R = Y, Gd–Lu) [12] ternary compounds. They have a crystal structure of the MgAgAs type ($F\bar{4}3m$ space group) and the chemical composition close to the composition of the investigated materials. Qualitatively, one can interpret the appearance of the semicon-

ducting properties of the M'M''X compounds as the result of peculiarities in their crystal structure and the appropriate concentration of valence electrons that is equal to 8 electrons/formula unit (f.u.), i.e. 32 electrons/crystal unit cell. Usually, one assumes that the nickel $3d$-level is filled and atoms of this element do not supply any band electrons, whereas other metals which have additional outer electrons on higher levels, give these electrons to the conduction band and increase the free-carriers concentration. On the other hand, atoms that have less than 10 electrons on the $3d$-shell fill this level with free electrons and thus, decrease the free-carriers concentration. For example, in TiNiSn compound we have $4 + 0 + 4 = 8$ free electrons/f.u., and in RNiSb we have $3 + 0 + 5 = 8$ free electrons/f.u. as well. It seems that the concentration of 8 electrons/f.u. is particularly convenient energetically because any deviation of the electron concentration from this value causes instability in the crystal structure and in the chemical composition. For this reason, the RCuSb compounds are not formed because their electron concentration would be equal to $3 + 1 + 5 = 9$ electrons/f.u. If we remove one R atom and one Cu atom from a hypothetical $R_4Cu_4Sb_4$ composition (4 MgAgAs unit cells), the energetically convenient $R_3Cu_3Sb_4$ composition with 32 electrons/f.u. will be formed. Simultaneously, the crystal structure will change to a more closely packed structure of the $Y_3Au_3Sb_4$ type. One unit cell of this final structure contains four formula units of the $R_3Cu_3Sb_4$ composition.

The contribution of Cu to the magnetic susceptibility seems to be negligible in the $R_3Cu_3Sb_4$ compounds, because the values of the effective magnetic moment per Ce, Pr, or Nd ion, determined in the present work, are close to the theoretical values for free R^{3+} ions. The paramagnetic Curie temperatures Θ_p of the investigated compounds seem to be proportional to the de Gennes factor, $G = (g_J - 1)^2 J(J + 1)$, thus, one can assume that the exchange interactions in these compounds are of the Ruderman–Kittel–Kasuya–Yoshida (RKKY) type, like in $RNi_{5-x}Sn_{1+x}$ compounds [13].

Taking into account that above ≈ 50 K the resistivity of all studied compounds grows linearly with increasing temperature, like in metallic materials, one can conclude that no metal–semiconductor transition appears in all studied $R_3Cu_3Sb_4$ compounds. The most probable origin of the exponential increase in resistivity at low temperature, observed in all studied $R_3Cu_3Sb_4$ samples, is the decrease in mobility of carriers caused by formation of small bound polarons, i.e. the mechanism proposed in Ref. [6], on the basis of wide neutron, magnetization, Hall effect, resistivity, and optical absorption investigation, to account for the temperature dependence of resistivity of the $Ce_3Cu_3Sb_4$ system.

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