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Magnetic phase diagram of $Tb_{3-x}Ho_xCu_4Sn_4$ system

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ABSTRACT

Magnetic phase diagram of $Tb_{3-x}Ho_xCu_4Sn_4$ was determined on the basis of magnetic and heat capacity data. X-ray diffraction data proved that these compounds crystallize in the orthorhombic $Gd_3Cu_4Ge_4$-type structure. The compounds are antiferromagnets at low temperatures and the reciprocal magnetic susceptibility obeys the Curie–Weiss law. The paramagnetic Curie temperatures are negative and their absolute values decrease with increasing Ho content. An anomalous concentration dependence of the Néel temperature is observed.

1. Introduction

The $R_3T_4X_4$ intermetallics (R is a rare earth element, T is a transition metal and X=Si, Ge and Sn) form a very interesting group of compounds. They crystallize in the orthorhombic $Gd_3Cu_4Ge_4$-type crystal structure (space group *I4/mmm*, No. 77) [1]. The unit cell consists of two formula units and the rare earth atoms occupy two non-equivalent Wyckoff positions: 2*d* and 4*e*. Magnetic and neutron diffraction data indicate very complex magnetic properties for different compositions [2,3]. For $Tb_3Cu_4Sn_4$ the Tb magnetic moments in both sublattices order below the Néel temperature equal to 17.5 K. The magnetic order is described by the propagation vector $\boldsymbol{k}=(0, 0, 1/2+\delta)$ with the magnetic moments in the *a*–*c* plane [4]. For $Ho_3Cu_4Sn_4$ two magnetic phase transitions take place: at 3.3 and 7.6 K, which is connected with ordering of Ho magnetic moments at the 4*e* and 2*d* sites, respectively. The Ho magnetic moments localized at the 2*d* sites are parallel to the *b*-axis while those at the 4*e* sites to the *a*-axis [5,6]. Our preliminary results concerning investigations of magnetic properties of the $Tb_{3-x}Ho_xCu_4Sn_4$ series of compounds were presented at ICM'09 in Karlsruhe [6].

In this work we report the results of X-ray diffraction, magnetometric and heat capacity measurements for polycrystalline $Tb_{3-x}Ho_xCu_4Sn_4$ samples (x=0, 0.5, 1.0, 1.25, 1.5, 2.0 and 2.5). On the basis of these data the magnetic phase diagram of this system was determined.

2. Experimental details

Polycrystalline samples of $Tb_{3-x}Ho_xCu_4Sn_4$ (x=0, 0.5, 1.0, 1.25, 1.5, 2.0 and 2.5) were obtained by arc melting of stoichiometric amounts of constituent elements (Tb and Ho of 99.9% purity, Cu and Sn of 99.99% purity) under high-purity argon atmosphere. Subsequently, the samples were annealed in evacuated quartz tubes at 800 °C for 1 week. The products were checked by X-ray powder diffraction at room temperature using a Panalytical X'PERT Pro diffractometer with CuK_α radiation. The dc magnetic measurements were carried out using a commercial MPMS SQUID magnetometer in the magnetic fields up to 50 kOe in the temperature range 2–300 K. The heat capacity was investigated by the relaxation method using a Quantum Design PPMS-9 platform in the temperature range 2–30 K.

3. Results

A typical X-ray diffraction pattern for $TbHo_2Cu_4Sn_4$ is shown in Fig. 1. Similar patterns were collected for the other compounds. The X-ray diffraction data were analyzed using the Fullprof program [7] assuming that all samples have the orthorhombic crystal structure of the $Gd_3Cu_4Ge_4$-type. The lattice parameters *a*, *b* and *c* and the unit cell volume *V* decrease with increasing

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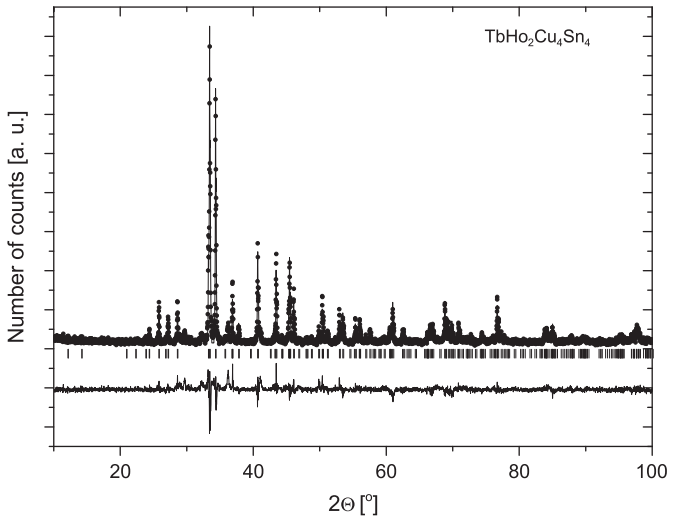

Fig. 1. X-ray diffraction pattern of $TbHo_2Cu_4Sn_4$. The solid circles mark the experimental data, the solid line is the best Rietveld-type refinement to the experimental data, the vertical ticks indicate the positions of the Bragg peaks and the solid line in the bottom of the figure shows the difference between the experiment and the refinement.

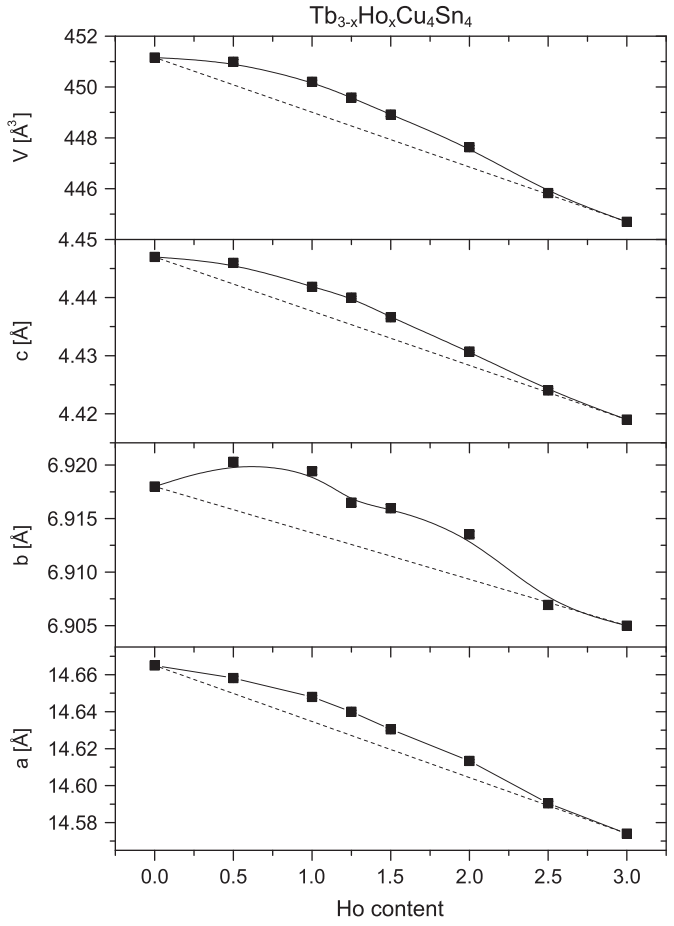

Fig. 2. Composition dependence of the lattice parameters *a*, *b* and *c* and the unit cell volume *V* for $Tb_{3-x}Ho_xCu_4Sn_4$ compounds ($0 \le x \le 3$). The solid squares mark the experimental values and the dashed lines mark the appropriate Vegard's law dependences; data for $x=3$ are from Ref. [5].

holmium content (Fig. 2) as the radius of the Tb^{3+} ion (0.923 Å) is larger than that of Ho^{3+} (0.894 Å). The Vegard law is not fulfilled, which suggests a preferential distribution of Ho ions in the unit cell. Because of the very small difference between the X-ray scattering lengths of Tb^{3+} and Ho^{3+} it is impossible to determine the distribution of the Ho^{3+} ions between 2*d* and 4*e* sublattices on the basis of our measurements.

The results of the magnetic measurements are presented in Fig. 3 and summarized in Table 1. In a wide temperature range the reciprocal magnetic susceptibility of the studied intermetallics obeys the Curie–Weiss law $\chi(T) = C/(T-\theta_p)$ with negative values of the paramagnetic Curie temperature θ_p and effective magnetic moments μ_{eff} close to the free R^{3+} ion values (Table 1). The negative values of θ_p indicate that the antiferromagnetic interactions are dominant. The absolute value of θ_p decreases with increasing Ho content (Table 1), which means that this substitution leads to weakening of the magnetic interactions along the studied series of compounds. At low temperatures a clear maximum is observed (see the upper inset in Fig. 3) at a temperature increasing with increasing Ho content: 3.8 K ($x=1.5$), 5.8 K ($x=2.0$) and 7.1 K ($x=2.5$ K). For the sample with $x=0.5$ a small anomaly at 15.9 K and an increase in the magnetic susceptibility at low temperatures is observed. Similar temperature dependence of the magnetic susceptibility were observed in $Tb_3Cu_4Sn_4$ (see Fig. 2 in [4]). For $x=1.0$ and 1.25 no anomalies in the temperature dependence of magnetic susceptibility was detected; however for those samples as well as for $x=1.5$ the temperature dependence of the reciprocal magnetic susceptibility indicates a deviation from the Curie–Weiss law below 12.5 K, 11.9 K and 10.5 K, respectively. The specific heat data (Fig. 4) confirm that these temperatures are the critical temperatures (T_N) of the magnetic ordering in these compounds. The magnetization curves measured at 2 K in the magnetic fields up to 50 kOe (the lower inset in Fig. 3) show that a metamagnetic phase transition is observed while increasing magnetic field. The magnetic measurements carried out at $T=2$ K and $H=50$ kOe lead to the magnetic moment values smaller than the average rare earth magnetic moments calculated for the appropriate nominal compositions on the basis of the free R^{3+} ion values (see Table 1)

Fig. 4 shows the heat capacity measured in zero magnetic field in the temperature range 2–30 K. For all studied compounds an anomaly about the Néel temperature is visible. The character of this anomaly changes with increasing holmium content *x*. For *x* equal to 0.0, 0.5 and 2.5 there is the λ-type anomaly; for $x=1.0$, 1.25 and 1.5 the anomaly is very small while for $x=2.0$ it is similar to the one found in spin-glass materials. The experimental value (see Table 1) of the jump in the heat capacity observed at

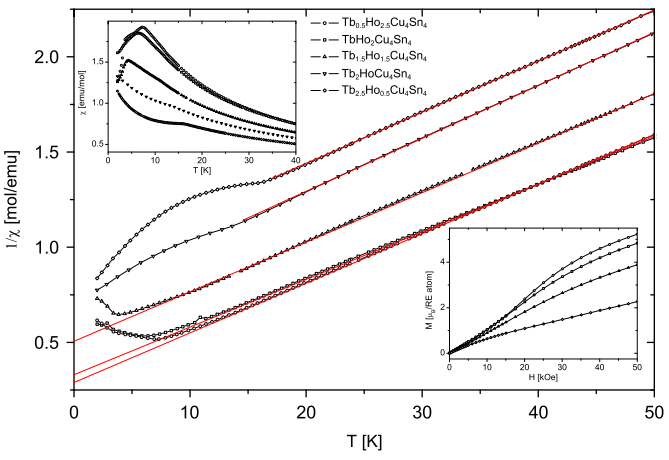

Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility of $Tb_{3-x}Ho_xCu_4Sn_4$. The solid lines represent the Curie–Weiss law. The upper inset shows the low temperature magnetic susceptibility measured in the magnetic field of 10 kOe. The lower inset displays the field dependent magnetization measured at 2 K.