Magnetic properties of \( \text{Tb}_{3-x}\text{Ho}_x\text{Cu}_4\text{Sn}_4 \)

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\textbf{Abstract.} X-ray diffraction, dc magnetization and magnetic susceptibility measurements were performed on polycrystalline \( \text{Tb}_{3-x}\text{Ho}_x\text{Cu}_4\text{Sn}_4 \) \( (x = 0-3) \) intermetallics. The X-ray data indicate that all the compounds crystallize in the orthorhombic crystal structure of the \( \text{Gd}_3\text{Cu}_4\text{Sn}_4 \)-type and are antiferromagnets at low temperatures. Their reciprocal magnetic susceptibility obeys the Curie-Weiss law above the appropriate Néel temperatures with negative values of the paramagnetic Curie temperature, which is linear function of the de Gennes factor. Anomalous concentration dependence of the Néel temperature is observed.

\textbf{1. Introduction}

\( \text{R}_3\text{T}_4\text{X}_4 \) where \( R \) is a rare earth element, \( T \) is a transition metal and \( X = \text{Si, Ge, Sn} \) form a very interesting group of compounds. They crystallize in the orthorhombic \( \text{Gd}_3\text{Cu}_4\text{Ge}_4 \)-type crystal structure (space group \( \text{I4}_1 \text{mmm} \)) [1]. The unit cell consists of two formula units and the rare earth atoms occupy two non-equivalent positions: 2d and 4e. Magnetic and neutron diffraction data indicate very complex magnetic properties at low temperatures [2]. For \( \text{Tb}_3\text{Cu}_4\text{Sn}_4 \) the magnetic structure below the Néel temperature is described by the propagation vector \( \mathbf{k} = (0, 0, \frac{1}{2}+\delta) \) [3]. In \( \text{Tb}_3\text{Cu}_4\text{Sn}_4 \) the Tb moments located at both sites are parallel to the \( a \)-axis [3]. For \( \text{Ho}_3\text{Cu}_4\text{Sn}_4 \) the magnetic phase transitions take place at 3.3 and 7.6 K. The Ho moments 2d site are oriented parallel to the \( b \)-axis whereas those of the ions at the 4e sites are oriented along \( a \)-axis [3,4]. To explain this intriguing phenomena new samples of \( \text{Tb}_{3-x}\text{Ho}_x\text{Cu}_4\text{Sn}_4 \) \( (x = 0.5, 1.0, 1.5, 2.0 \text{ and } 2.5) \) were synthesized and investigated for the magnetic properties. In this work, results of X-ray and magnetic measurements are presented.

\textbf{2. Experimental details}

Polycrystalline samples of \( \text{Tb}_{3-x}\text{Ho}_x\text{Cu}_4\text{Sn}_4 \) \( (x = 0.5, 1.0, 1.5, 2.0 \text{ and } 2.5) \) were obtained by arc melting of stoichiometric amounts of the constituent elements (Tb and Ho of 99.9 \% purity, Cu and Sn of 99.99 \% purity) under high-purity argon atmosphere. Subsequently, samples were annealed in an evacuated quartz tube at 800 °C for one week. The quality of the products was checked by X-ray powder diffraction at room temperature using a Philips PW – 3710 X’PERT diffractometer with CuK\( _\alpha \) radiation. The dc magnetic measurements were performed using a commercial MPMS SQUID magnetometer.
3. Results

The X-ray patterns were analyzed using the Fullprof program [5] indicating that all the samples have the orthorhombic crystal structure of the Gd$_3$Cu$_4$Ge$_4$-type. The composition dependence of the lattice parameters $a$, $b$ and $c$ and the unit cell volume $V$ at room temperature decreases with increasing holmium content as the radius of the Tb$^{3+}$ ion (0.923 Å) is larger than of Ho$^{3+}$ (0.894 Å). The small difference between X-ray scattering lengths of Tb$^{3+}$ and Ho$^{3+}$ ions make impossible to determine the distribution of the doped Ho$^{3+}$ ions between 2d and 4e sublattice.

The results of the magnetic measurements at low temperatures are presented in figure 1 and summarized in table 1. The characteristic maximum for antiferro – para phase transition is observed (see inset in figure 1). For $x = 0$, 0.5 and 1.0 values of $T_N$ are decreased. For $x$ between 1.5 – 3.0 the values of $T_N$ increase from 3.9 K for $x = 1.5$ up to 7.6 K for $x = 3.0$. For $x = 2.5$ below $T_N$ at $T_1 = 4.0$ K the additional phase transition is observed. Above the Néel temperature the reciprocal magnetic susceptibility obeys the Curie-Weiss law with negative values of the paramagnetic Curie temperature $\theta_p$ and an effective magnetic moment $\mu_{\text{eff}}$ close to the free R$^{3+}$ ion values. The absolute values of $\theta_p$ decrease while $\mu_{\text{eff}}$ increase with increasing $x$.

Table 1. Magnetic properties of Tb$_{3-x}$Ho$_x$Cu$_4$Sn$_4$ compounds

| Comp $x$ | $T_N$(K) | $T_1$(K) | $\theta_p$(K) | $\mu_{\text{eff}}$(\mu$_{\text{B}}$) | $H_{\text{cr}}$(kOe) | Ref. |
|----------|----------|----------|---------------|-------------------------------|-----------------|-----|
| 0        | 16.0     | -34.0    | 9.5           | 9.72                          | -               | [2] |
| 0.5      | 15.0     | -27.0    | 9.87          | 9.96                          | 10              | this work |
| 1.0      | 12.5     | -24.3    | 10.02         | 10.02                         | -               | this work |
| 1.5      | 3.9      | -19.4    | 10.06         | 10.16                         | 14              | this work |
| 2.0      | 6.8      | -12.8    | 10.24         | 10.31                         | 17              | this work |
| 2.5      | 7.1      | 4.0      | -11.2         | 10.05                         | 20              | this work |
| 3.0      | 7.6      | 3.3      | -8.4          | 10.1                          | 20              | [2] |

$T_N$: Néel temperature; $T_1$: temperature of an additional transition; $\theta_p$: paramagnetic Curie temperature; $\mu_{\text{eff}}$: effective magnetic moment in paramagnetic state; $H_{\text{cr}}$: critical field, at which metamagnetic transition occurs;

The magnetization curves at 2 K in the magnetic fields up to 50 kOe are shown in inset of figure 1. For all samples magnetization increases with increasing magnetic field. Except for $x = 1$, a metamagnetic phase transition is observed. The values of the rare earth moments at $T = 2$ K and $H = 50$ kOe are smaller than the free R$^{3+}$ ion values.

4. Summary and conclusions

The results presented in this work show that the Tb$_{3-x}$Ho$_x$Cu$_4$Sn$_4$ compounds exist for all concentrations and show the orthorhombic Gd$_3$Cu$_4$Sn$_4$-type of crystal structure.
In these compounds large R – R interatomic distances (about 4 Å) and the metallic character of electrical conductivity [6] indicate that the observed magnetic ordering results from exchange interactions described by the RKKY model. In this model the magnetic ordering temperatures in a rare earth series, described within the framework of the Weiss molecular field theory, are given by the formula [7]:

\[ T_N = \frac{2}{3} I (g_J - 1)^2 J(J+1) \]

where \( I \) is the exchange interaction parameter and \((g_J - 1)^2 J(J+1)\) is the de Gennes factor (dG). The paramagnetic Curie temperature may be expressed by

\[ \Theta_p = \frac{3\pi z^2 m^* J_f^2}{4 k_B^2 E_F} (g_J - 1)^2 J(J+1) \]

where \( z \) – average conduction electron to atom ratio, \( m^* \) - effective mass, \( E_F \) – Fermi level energy, \( J_f \) – the effective interaction between the conduction electrons and local moments \( k_B \) – Boltzmann constant.

The ordering temperatures \( T_N \) and paramagnetic Curie temperatures \( \Theta_p \) are a linear function of dG. Figure 2 shows the Néel temperatures \( T_N \) and the paramagnetic Curie temperature \( \Theta_p \) plotted against the dG factor. Only for \( \Theta_p \) a linear dependence is observed. These results suggest:

− the negative values of \( \Theta_p \) indicate that the antiferromagnetic interactions are dominant, which is in good agreement with the magnetic structure observed in \( \text{Tb}_3\text{Cu}_4\text{Sn}_4 \) and \( \text{Ho}_3\text{Cu}_4\text{Sn}_4 \) [3,4],

\[ T_N = \frac{2}{3} I (g_J - 1)^2 J(J+1) \]

\[ \Theta_p = \frac{3\pi z^2 m^* J_f^2}{4 k_B^2 E_F} (g_J - 1)^2 J(J+1) \]
the values of $\theta_p$ decrease with increasing the Ho content $x$ which is in good agreement with the values of dG factor equal to 10.5 for Tb$_3$Cu$_4$Sn$_4$ and 4.5 for Ho$_3$Cu$_4$Sn$_4$.

- The significantly deviation of $T_N$ from linearity is probably connected with the complex character of the interactions in the mixed compounds and the influence of the crystal electric field on the ordering temperatures in these compounds.

- The values of the effective magnetic moments in paramagnetic state are close to the free $R^{3+}$ ion values indicating directly that the magnetic moments are localized on the rare earth atoms. The magnetic moment values at 50 kOe and 2 K are lower than those for free $R^{3+}$ ion values (see figure 1). In all the cases the magnetization curves are not saturated. The difference between observed and calculated values of the magnetic moments $\Delta \mu_s$ are large for Tb$_3$Cu$_4$Sn$_4$ and decrease with increasing Ho content. These suggest a change in the anisotropy and or complex magnetic ordering with the change of the composition.

![Figure 2](image.png)

**Figure 2.** Néel temperatures $T_N$ and paramagnetic Curie temperatures $\theta_p$ of Tb$_{3-x}$Ho$_x$Cu$_4$Sn$_4$ compounds vs. composition $x$.

For more detailed studies of the magnetic properties of these compounds neutron diffraction experiments are planned.

References

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Figures

Figure 1. Temperature dependence of reciprocal magnetic susceptibility of Tb$_{3-x}$Ho$_x$Cu$_4$Sn$_4$. The upper inset shows the low temperature magnetic susceptibility measured in magnetic field 10 Oe. The lower inset displays the field – dependent magnetization measured at 2 K.

Figure 2. Néel temperatures T$_N$ and paramagnetic Curie temperatures $\theta_p$ of Tb$_{3-x}$Ho$_x$Cu$_4$Sn$_4$ compounds vs. composition x.