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Structural studies and magnetism of Dy₆Ni₀.₄₃Sn₀.₅ stannide

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Intermetallic compound Dy₆Ni₀.₄₃Sn₀.₅ was prepared by arc melting and annealing at 873 K. It was characterized by X-ray powder diffraction, differential thermal analysis, and electron probe microanalysis. The crystal structure of low temperature Dy₆Ni₀.₄₃Sn₀.₅ phase belongs to the orthorhombic HoCo₀.₃Ga structure type (space group Immm, a = 0.93116(1) nm, b = 0.94993(1) nm, c = 0.98947(1) nm). Crystal structure refinements showed the deviation from the ideal b:2:1 stoichiometry corresponding to the formula Dy₆Ni₀.₄₀Sn₀.₅. It exhibits a sequence of magnetic phase transitions; antiferromagnetic ordering sets in at 60 K, while further order-order magnetic phase transitions take place at lower temperatures.

Keywords: Intermetallics; Crystal structure; Magnetic properties; Heat capacity.

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Introduction

The search of new intermetallics with useful magnetic properties has brought lot of attention to compounds containing rare earths (R), d-metals (M), and p-elements (X) such as Si, Ga, Ge, Sn, In, Pb. In the R-rich region of the R-M-X ternary systems (M = Co, Ni; X = Ga, In, Sn, Pb) two series of isotypic compounds R₁₂MₓX (cubic Sm₁₂NiₓIn-type) and RₓMₓX (orthorhombic HoCo₀.₃Ga-type) were identified and studied previously [1-8]. Both types of crystal structures are characterized by the antiprismatic-trigonal coordination of the smaller atoms (Co, Ni) and by significant shortening of interatomic distances between rare earths and d-elements and between M atoms. The relationship between Sm₁₂NiₓIn and HoCo₀.₃Ga structure types is described in Ref. [8]. In the HoCo₀.₃Ga structure, the rare earth atoms form metal bonded framework yielding several types of high coordination polyhedra encapsulating the atoms of the transition metals and X elements [4]. Depending on the ratio of the size of the atoms M and X, the tendency for disorder in particular crystallographic sites is observed in these structures. For example, the compounds TbₓCo₀.₃₃Sn₀.₆₅ [9], HoₓCo₀.₁₅₁In₀.₈₅ [6], ErₓCo₀.₁₉₁In₀.₈₁ [10], and RₓMₓPb₁₋ₓ (M = Co, Ni) [8] are characterized by statistical mixture of M and X atoms in the 2a site, while in the original HoCo₀.₃Ga structure type it is occupied exclusively by Ga atoms. In Dy₆Co₀.₅Sn₀.₅, the Co atoms occupy three crystallographic sites, and only 2c position is occupied by the Sn atoms [11]. Study of isotypic compounds with bismuth [12] showed that unlike the HoCo₀.₃Ga prototype, the 2a position is occupied by Co atoms and authors propose the formula RₓCoₓBi (equal to RₓCo₀.₅Bi₀.₅) which reflects the occupancy of crystallographic positions in the structure.

Taking into account that the complex magnetic behavior arises from the connection of d- and p-electrons in rare-earth intermetallics with transition elements, the properties of stannides R₁₂NiₓSn and RₓMₓSn were explored. A study of magnetic properties revealed that the R₁₂NiₓSn intermetallics exhibit ferromagnetic ordering for Gd and Tb compounds with Tₘ = 85 K and 95 K, respectively [1]. The temperature dependencies of the magnetic susceptibility measured earlier in the range 78-293 K for RₓNiₓSn compounds (R = Tb, Dy, Er, and Tm) showed that they obey the Curie-Weiss law with effective magnetic moments close to free R³⁺ ion values [5, 7].

The isotypic stannide Er₂NiSn has been investigated as potential material for the lower temperature stage of Gifford-McMahon cryocooler [13]. Refs. [14,15]
suggested, based on specific-heat data and magnetic measurements of \( \text{Er}_6\text{Ni}_3\text{Sn} \) giving estimates of isothermal entropy change and magnetocaloric effect, that this compound can serve as material for cryogenic devices. Neutron diffraction study of \( \text{Er}_6\text{Ni}_3\text{Sn} \) showed a complex non-collinear commensurate antiferromagnetic structure [16], in which the magnetic moment values of Er atoms are significantly reduced.

The present work aims to determine structure characteristics and magnetic properties of \( \text{Dy}_6\text{Ni}_{2.4}\text{Sn}_{0.5} \). In addition, magnetic behaviour of the binary \( \text{Dy}_3\text{Sn}_3 \) is presented.

I. Experimental details

Polycrystalline samples for investigation were prepared by direct arc melting of the constituent metals (dysprosium, purity 99.9 wt. %; nickel, purity 99.99 wt. %; tin, purity 99.999 wt. %) under purified argon atmosphere (Ti as a getter) in a water-cooled copper crucible. Weight losses of the initial batch did not exceed 1 wt. %. Two pieces of the alloys were annealed separately in the evacuated quartz ampoules at \( T = 873 \) K and \( T = 1073 \) K for 720 hours and then quenched in cold water. The synthesized and annealed samples are stable under ambient conditions. The chemical composition of the prepared samples was examined by Scanning Electron Microscopy using JEOL-840A scanning microscope.

X-ray powder diffraction data were collected using STOE STADI P powder diffractometer (Cu \( K\alpha_1 \) radiation, angular range for data collection \( 6.000 \leq 2\theta \leq 110.625/0.015 \)). FullProf Suite program package [17] was used for the determination of the crystal structure parameters.

Differential thermal analysis (DTA) was used to check the temperature range of the stability of the compound (LINSEIS STA PT 1600 device, argon atmosphere). Sample was heated up to 1173 K, at a rate of 10 K/min. The weight losses during heating (TG) were less than 0.2%.

The magnetic susceptibility was measured in external magnetic fields up to 9 T in the temperature range from 2 K to 300 K using a Quantum Design PPMS extraction magnetometer. The grains of the sample were fixed in random orientation preventing rotation of individual grains under the influence of a magnetic field. The specific heat measurements were performed on a bulk sample in the same temperature range using a Quantum Design PPMS microcalorimetry setup.

The magnetic behavior of the \( \text{Dy}_3\text{Sn}_3 \) compound was measured using an extraction method in the magnetic fields up to 10 T in the temperature range 2 K to 300 K.

II. Results and discussion

2.1. Formation of compounds and crystal structure refinement

Taking into account the literature data and general stoichiometry 6:2:1 for the \( \text{R}_6\text{Ni}_3\text{Sn} \) series, a polycrystalline sample with nominal composition \( \text{Dy}_6\text{Ni}_{2.2}\text{Sn}_{1.1} \) was prepared. X-ray phase analysis of the sample showed the presence of the main phase \( \text{Dy}_6\text{Ni}_3\text{Sn} \) with the \( \text{Ho}_6\text{Co}_2\text{Ga} \) structure type and a small amount of additional binary phase \( \text{Dy}_5\text{Sn}_3 \) (Mn\text{Si}_3 \) structure type, \( a = 0.88863 \) (1), \( c = 0.64873 \) (1) nm). According to the electron probe microanalysis (EPMA) data, the determined composition of the main phase is \( \text{Dy}_6\text{Ni}_{2.7}\text{Sn}_{0.6} \), meaning lower Sn concentration in comparison with the ideal 6:2:1 stoichiometry. As the next step, we prepared a new sample with the nominal composition \( \text{Dy}_6\text{Ni}_{2.5}\text{Sn}_0 \). In order to synthesize a single-phase sample we used two different temperatures of annealing, namely 873 and 1073 K. The phase analysis of the sample annealed at 873 K proved the existence of orthorhombic phase with the \( \text{Ho}_6\text{Co}_2\text{Ga} \) structure type, while a phase with the cubic \( \text{Sn}_3\text{Ni}_3\text{In} \) structure type was identified in the sample annealed at 1073 K. To confirm a polymorphic transition we have studied the sample by the differential thermal analysis. The DTA curve measured in the heating and cooling regimes is shown in Fig. 1. Two thermal peaks are more visible on the cooling curve at 1098.5 K and 1015.3 K, respectively, which can be associated with the formation of the cubic phase and next polymorphic transition to the orthorhombic one. Thus, we can say that orthorhombic phase is stable up to \( \approx 1015 \) K.

Fig. 1. DTA plot for \( \text{Dy}_6\text{Ni}_{2.5}\text{Sn}_0 \) sample.

Analysis of X-ray powder diffraction pattern of the \( \text{Dy}_6\text{Ni}_{2.3}\text{Sn}_0 \) sample annealed at \( T = 870 \) K showed the presence of a single phase with orthorhombic \( \text{Ho}_6\text{Co}_2\text{Ga} \) type (space group \( \text{Immm} \), \( a = 0.93116 \) (1) nm, \( b = 0.94993 \) (1) nm, \( c = 0.98947 \) (4) nm). Refined atomic coordinates and displacement parameters for \( \text{Ho}_6\text{Co}_2\text{Ga} \) type phase are listed in Table 1. The refinement of the site occupancies showed that in this structure Ni atoms fully occupy the 4j position and both 4g and 2a positions for Ni atoms are occupied partially (Table 1). Thus, the chemical formula should be written as \( \text{Dy}_6\text{Ni}_{2.3}\text{Sn}_{0.5} \), what is in a good agreement with EPMA data (\( \text{Dy}_{0.66}\text{Ni}_{2.67}\text{Sn}_{0.71} \)). Obtained stoichiometry is close to the previously studied \( \text{Th}_6\text{Co}_{2.35}\text{Sn}_{0.65} \) [9] and \( \text{Rh}_2\text{M}_{2+}\text{Ph(In)}_{1.4} \) (\( M = \text{Co, Ni} \)) [6,8,10] compounds, which are characterized by a lower concentration of the \( p \)-element compared to the ordered \( \text{Ho}_6\text{Co}_2\text{Ga} \) type phase.

Crystal chemical analysis of the stannide \( \text{Dy}_6\text{Ni}_{2.4}\text{Sn}_{0.5} \) showed that this structure can be presented as a framework of Dy atoms forming prismatic and icosahedral polyhedra filled with the smaller Ni and Sn atoms (Fig. 2) The analysis of the interatomic distances in the \( \text{Dy}_6\text{Ni}_{2.4}\text{Sn}_{0.5} \) structure showed a significant variations
of the sum of the corresponding atomic radii 
\( r(Dy) = 0.177 \text{ nm}, \ r(Ni) = 0.125 \text{ nm} \): for shorter Dy-Ni distances Dy1-Ni1 = 0.2849 nm; Dy2-Ni2 = 0.2840 nm; 
Dy3-Ni2 = 0.2821 nm and Ni1-Ni1 distance 0.2440 nm. The shortening in interatomic distances in Dy6Ni23.5Sn0.5 is similar to the shortening in the prototype Ho6Co2Ga [4] 
and in other isotypic intermetallics with Sn or Pb [8, 9].

It should be pointed out that the crystal structure of 
Dy6Ni23.5Sn0.5 can be derived from the WAl12 structure type by an insertion of Ni and Sn atoms into binary WAl12 [7]. Both compounds are characterized by 3D-framework structure built by Dy and Al atoms, respectively (Fig. 3).

The analysis of the structures Ho6Co2Ga [4] and the isotypic R6M23X13 intermetallics \( (M = Co, \ Ni \ and \ X = Ga, 
In, \ Sn, \ Pb, \ and \ Bi) \) [5-12] illustrated the role of the size of the X element in structural disorder. The Ho6Co2Ga structure is completely ordered, small Ga atoms occupy two crystallographic sites 2\(c\) and 2\(a\) fully. Crystal structures of the related compounds with larger X atoms show that the crystallographic position 2\(a\), occupied only by Ga atoms in Ho6Co2Ga-type, is strongly susceptible to accommodate statistical mixtures with \( d \)-metals, what results in a deviation from the ideal stoichiometry 6:2:1. This fact was observed for the compounds Tb6Co23.5Sn0.65, Ho6Co23.5Ir0.85, Er6Co23.9In0.81, R6M23Pb(Bi)1.4 [6, 8-12], and finally for Dy6Ni23.5Sn0.5.

**2.2. Magnetic and heat capacity measurements**

For the Dy6Ni23.5Sn11 sample we performed magnetic susceptibility measurements in magnetic field of 0.05 T, 2 T, and 4 T in the temperature range 2-300 K. The field dependence of magnetization was measured in magnetic fields up to 9 T for temperatures \( T = 2, 20, \) and 40 K. Fig. 4 shows that the high temperature Curie-Weiss behavior extends down only to 60-70 K and below this temperature the values of \( \chi(T) \) become field dependent. In the paramagnetic state the temperature dependence of the inverse magnetic susceptibility \( \chi^{-1}(T) \) is well described by the Curie-Weiss law with the value of effective moment 10.60 \( \mu_B/Dy \), i.e. close to the value for free ion Dy\(^{3+}\)(10.65 \( \mu_B \)) (Fig. 5). The paramagnetic Curie temperature \( \theta_p \approx 26 \) K is lower than the transition temperature but still positive, which indicates predominant ferromagnetic interactions. Temperature behavior of the magnetic susceptibility exhibits a kink, pointing to an antiferromagnetic ordering below about

**Table 1.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>( x/a )</th>
<th>( y/b )</th>
<th>( z/c )</th>
<th>( *B_{iso} \times 10^2 \text{ (nm}^2) )</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy1</td>
<td>8(a)</td>
<td>0.2924(2)</td>
<td>0.1821(2)</td>
<td>0</td>
<td>1.17(8)</td>
<td>1</td>
</tr>
<tr>
<td>Dy2</td>
<td>8(m)</td>
<td>0.3030(2)</td>
<td>0</td>
<td>0.3233(1)</td>
<td>0.49(8)</td>
<td>1</td>
</tr>
<tr>
<td>Dy3</td>
<td>8(j)</td>
<td>0</td>
<td>0.1903(2)</td>
<td>0.2146(2)</td>
<td>0.84(8)</td>
<td>1</td>
</tr>
<tr>
<td>Ni1</td>
<td>4(j)</td>
<td>1/2</td>
<td>0</td>
<td>0.1233(6)</td>
<td>1.72(2)</td>
<td>1</td>
</tr>
<tr>
<td>Ni2</td>
<td>4(g)</td>
<td>0</td>
<td>0.3633(7)</td>
<td>0</td>
<td>1.57(6)</td>
<td>0.95(1)</td>
</tr>
<tr>
<td>Ni3</td>
<td>2(a)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.62(1)</td>
<td>0.96(1)</td>
</tr>
<tr>
<td>Sn</td>
<td>2(c)</td>
<td>1/2</td>
<td>1/2</td>
<td>0</td>
<td>0.88(1)</td>
<td>1</td>
</tr>
</tbody>
</table>

**Fig. 2.** Atomic columns in Dy6Ni23.5Sn0.5 structure formed by Dy atoms. The smaller Ni and Sn atoms are inside prismatic and icosahedral voids.

**Fig. 3.** Model of Dy6Ni23.5Sn0.5 (a) and WAl12 (b) structures.
60 K (see Fig. 4). However, $\chi(T)$ still increases below this temperature (at least in low magnetic fields) and another kink is visible at $T = 27$ K, which may suggest presence of a magnetic phase transition of the order-disorder type. A smaller anomaly is seen particularly for the 2 T data can be distinguished at 19 K. The $\chi(T)$ measurement in very low magnetic field (0.05 T) reveals a small ferromagnetic component developing below $T = 60$ K. As the size of the increment in the inset of Fig. 4 is $\approx 6 \times 10^{-5}$ m$^3$/mol f.u., i.e. $< 0.5 \mu_B$/f.u., it means less than 0.1 $\mu_B$/Dy. Hence we most likely encounter a defected antiferromagnetic structure with incomplete cancelation of sublattices, related most likely to the statistical occupancy of several crystallographic sites. Although the magnetism has been related to Dy only and no Ni moments are anticipated, the defected Dy environment brings randomness into the RKKY interaction, yielding certain features of magnetic glass, as magnetic history phenomena in antiferromagnet. This suggestion is corroborated by the fact that there is residual magnetization of 2 $\mu_B$/f.u. when returning to zero field from a high field state in $\mu_0 H = 9$ T at $T = 2$ K (see Fig. 6).

![Temperature dependence of the magnetic susceptibility $\chi(T)$ of Dy$_6$Ni$_{2.43}$Sn$_{0.5}$ in various magnetic fields. Detail of low-field data are shown in the inset.](image)

![Complementary information can be obtained from the temperature dependence of specific heat at constant pressure, $C_p(T)$. It exhibits a clear phase transition at $T = 62$ K, which remains practically unchanged in magnetic field of 2 T (Fig. 7).](image)

![As a small amount of Dy$_6$Sn$_3$ in the sample has been indicated, a question is whether some of the anomalies observed can be associated with such spurious phase. Therefore we prepared Dy$_5$Sn$_5$ sample, annealed at $T = 873$ K, and its magnetic behavior determined. According to X-ray analysis, Dy$_5$Sn$_5$ crystallizes in the Mn$_5$Sb$_3$ structure type (space group $P6_3/mmc$) with refined lattice parameters $a = 0.88633(1)$, $c = 0.64873(1)$ nm. The maximum in the temperature dependence of specific heat at constant pressure, $C_p(T)$, for Dy$_5$Sn$_5$ is close to Dy$_6$Sn$_3$.](image)
Considerable anomalies concerning the magnetic ordering of impurity phase Dy$_5$Sn$_3$ were not observed in the temperature dependence of magnetic susceptibility of Dy$_6$Ni$_{2.43}$Sn$_{0.5}$. Taking into account this result we can rule out contribution of impurity phase Dy$_5$Sn$_3$ in the magnetism of the Dy$_6$Ni$_{2.43}$Sn$_{0.5}$ stannide.

Conclusions

Structure refinements of the Dy$_6$Ni$_{2.43}$Sn$_{0.5}$ compound confirmed that this compound belongs to the orthorhombic Ho$_6$Co$_2$Ga structure type but contrary to the prototype Ho$_6$Co$_2$Ga compound a significant deviation from the 6:2:1 stoichiometry has been observed. This deviation is caused by the exclusive presence of Ni atoms at the 2$a$ site and a partial occupation of the 4$g$ and 2$a$ sites by Ni atoms. The phase situation is, however, affected by annealing.

The results of the magnetic and heat capacity measurements indicated a magnetic transition at 60 K connected with antiferromagnetic ordering. Further order-order phase transitions have been observed at lower temperatures. The calculated effective magnetic moments in paramagnetic state is close to the value for free ion Dy$^{3+}$, indicating a main role of rare earth in the magnetism of Dy$_6$Ni$_{2.43}$Sn$_{0.5}$. Statistical occupation of several Ni sites yields a glassy behavior and magnetic history phenomena.

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Structural studies and magnetism of Dy$_2$Ni$_{1.3}$Sn$_{0.5}$ stannide


[8] L.D. Gulay, M. Wolczyk, *Crystal structure of R$_6$Co$_{2+x}$Pb$_{1.3}$ (R = Y, Gd, Tb, Dy, Ho, Er, Tm, Lu) and R$_2$Ni$_{2+x}$Pb$_{1.3}$ (R = Tb, Dy, Ho, Er, Tm, Lu) compounds*, J. Alloys Compd., 315, 164 (2001); https://doi.org/10.1016/S0925-8838(00)01281-0.


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Структурні дослідження і магнетизм станіду Dy$_2$Ni$_{1.3}$Sn$_{0.5}$

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Інтерметалід Dy$_2$Ni$_{1.3}$Sn$_{0.5}$ отриманий методом електродугового плавлення і гомогенізації відпалювання за температури 873 К.Структура досліджена методами рентгенівської дифрактометрії, диференціального термічного аналізу і енергодисперсійної спектроскопії.Кристалічна структура низькотемпературної фази Dy$_2$Ni$_{1.3}$Sn$_{0.5}$ належить до орторомбічного структурного типу Ho$_6$Co$_2$Ga (просторова група Immm, a = 0.93116(1) нм, b = 0.94993(1) нм, c = 0.98947(1) нм).Структурні розрахунки засвідчили відхилення від ідеальної стехіометрії 6:2:1, що відповідає формулі Dy$_2$Ni$_{1.3}$Sn$_{0.5}$. Для сполук встановлено послідовність магнітних фазових переходів; антиферомагнітне впорядкування виникає при 60 К, подальші магнітні фазові переходи порядок-порядок відбуваються за нижчих температур.

Ключові слова: Інтерметалід, Кристалічна структура, Магнітні властивості, Питома теплоємність.