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Structural Chemistry and Magnetic Properties of $R_2Ni_{2-x}In$ (R = Gd–Er, $x = 0.22$ or 0.3) Compounds

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X-ray diffraction and magnetic measurements of $R_2Ni_{2-x}In$ (R = Ho, Dy, $x = 0.3$ and R = Gd, Tb, Er, $x = 0.22$) compounds are reported. The compounds crystallize in the tetragonal Mo_2FeB_2-type crystal structure (space group *P4/mbm*). Magnetic measurements reveal antiferromagnetic order with the Néel temperatures T_N equal to 26.4 K (Gd), 20.2 K (Tb), 8.3 K (Dy), 7.1 K (Ho), and 6.3 K (Er). For R = Gd, Tb and Er an additional phase transition below T_N is observed at 13.5, 13.1, and 5.0 K, respectively.

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1. Introduction

Intermetallic compounds of the R–T–In systems (R = rare earth metal; T = transition metal) are an object of intensive investigations of the crystal structure and the physical properties [1]. One of the leading places among them hold the compounds with the Mo_2FeB_2-type structure (space group *P4/mbm*, tP10, $Z = 2$) [2, 3], which is a ternary derivative of the binary U_3Si_2-type [4]. The concerned ternary indides were first reported with the composition R_2T_2In for T = Cu (R = Y, La–Lu) and T = Ni (R = La–Nd). Other rare earth metals form the isostructural compounds at $R_2Ni_{2-x}In$ composition (R = Y, Sm–Lu, $x = 0.22$) [5] whereas at the stoichiometric composition they form compounds with the Mn_2AlB_2-type structure (space group *Cmmm*, oC10, $Z = 2$) [6], related to the Mo_2FeB_2-type. Similar behavior has been observed for R_2Ni_2Cd compounds but in this case the Mo_2FeB_2- and Mn_2AlB_2-type modifications are connected with temperature polymorphism [7]. Both structure types can be considered as layer structures in which layers of R atoms ($z = 1/2$) alternate with layers of T and In atoms ($z = 0$) along the direction of the shorter cell parameter. The structures form homological series of compounds characterized by AlB_2 and CsCl related fragments and described by the general formula $R_{m+n}T_{2n}X_m$ ($n = 2$, $m = 2$) [1]. Defects in atomic occupation and variable composition of the Mo_2FeB_2 type compounds were confirmed by precise single crystal investigations of $Tm_2Ni_{1.896}In$ [8], $R_{2+x}Pd_{1.8}In_{1-x}$ (R = Tb, Dy, Ho, Er) [9] and $Ce_2Pd_{2+x}In_{1-x}$ [10].

Series of the Mo_2FeB_2 type compounds revealed also in numerous ternary systems with noble metals in particular palladium [11], gold [12, 13], platinum [14] and rhodium [15]. The electrical and magnetic properties of the compounds are summarized in Refs. [1, 3]. Investigations of these materials have been devoted to the $4f$-magnetism of the rare-earth atoms. Magnetic measurements revealed antiferromagnetic or ferromagnetic ordering at low temperatures [3]. Temperature dependence of magnetic susceptibility and electrical resistivity of Ce_2Ni_2In indicate the intermediate valence behavior [16, 17]. Till now magnetic properties were determined only for some tetragonal R_2Ni_2In and $R_2Ni_{2-x}In$ compounds. Magnetic and specific heat measurements carried out for Nd_2Ni_2In indicate antiferromagnetic order with the first-order magnetic phase transition at $T_N = 8$ K [18].

In this paper we report on the results of X-ray diffraction and magnetic measurements of the $R_2Ni_{2-x}In$ series of compounds for R = Gd, Tb, Er ($x = 0.22$) and Dy, Ho ($x = 0.3$). From this data the crystal structure parameters at room temperature and bulk magnetic properties versus temperature (in the temperature range between 1.9 and 300 K) and external magnetic field (up to 90 kOe) are determined.

2. Experimental details

The samples of $R_2Ni_{2-x}In$ (R = Ho, Dy, $x = 0.3$ and R = Gd, Tb, Er, $x = 0.22$), each of the total weight of 1 g, were obtained by the standard melting procedure: the appropriate for the nominal compositions amounts of the elements were arc-melted under pure argon on a water cooled copper hearth with a tungsten electrode and titanium serving as a getter. To ensure good homogeneity the samples were turned over and melted several times and then annealed at 870 K for 1 month. Ingots of rare earth metals of the purity not lower than 99.85 wt%, nickel 99.92 wt% and indium 99.99 wt% were used as the starting elements.

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The X-ray powder diffraction patterns were recorded at room temperature using a PANalytical X'Pert PRO MPD diffractometer (Cu K_α radiation, the Bragg–Brentano geometry; Institute of Physics, Jagiellonian University, Kraków, Poland). The scans were collected within the 2θ region 10–130° (step scan; step size 0.03°; counting time per step 17 s) and analyzed by the Rietveld-type line profile refinement method using the program Fullprof [19].

The DC magnetic measurements were carried out using a vibrating sample magnetometer option of the Quantum Design PPMS platform (Institute of Physics, Jagiellonian University, Kraków, Poland). For all compounds three types of DC measurements were performed. Firstly, at low temperatures and in low magnetic field of 50 Oe (to determine the temperatures of the magnetic phase transitions). Secondly, in the field of 1 kOe in the temperature range from 1.9 to 300 K (to get the value of the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_{p}). Finally, the magnetization curve was measured up to 90 kOe at 1.9 K (to determine the value of the magnetic moment in ordered state).

For all compounds the temperature dependence of the AC magnetic susceptibility $\chi_{\text{ac}} = \chi' - \text{i}\chi''$, where χ' is the real and χ'' the imaginary component, was measured at several chosen frequencies between 10 Hz and 10 kHz in the temperature range 2–40 K.

3. Results

A typical X-ray diffraction pattern for $Ho_2Ni_{1.7}In$ is shown in Fig. 1. Similar patterns were obtained for the other investigated compounds. They confirm that the investigated $R_2Ni_{2-x}In$ compounds crystallize in the tetragonal Mo_2FeB_2-type structure. The rare-earth elements occupy the Wyckoff position 4h, nickel atoms 4g and indium atoms 2a. The crystal structure parameters of $Gd_2Ni_{1.78}In$ [5] were taken as starting values for the structure refinement. Occupation of the 4g site was fixed at the refinements. The determined lattice parameters and the positional atom parameters are listed in Table I. They are in good agreement with the data published previously [5].

TABLE I

Crystal structure refinements of $R_2Ni_{2-x}In$ (R = Gd, Tb, Er, $x = 0.22$ and R = Ho, Dy, $x = 0.3$) compounds.

	Gd	Tb	Dy	Ho	Er
M [g/mol]	533.79	537.13	544.29	549.15	553.81
a [Å]	7.4132(3)	7.3859(3)	7.3674(3)	7.3496(2)	7.3308(1)
c [Å]	3.7127(2)	3.6675(2)	3.6444(2)	3.6251(1)	3.6069(1)
4 R at 4h (x, $1/2+x$, $1/2$)	0.1769(2)	0.1757(2)	0.1759(2)	0.1749(1)	0.1744(1)
3.56 Ni at 4g (x, $1/2+x$, 0)	0.3798(5)	0.3779(4)	0.3833(4)	0.3798(3)	0.3786(3)
2 In at 2a (0,0,0)					
R_{Bragg} [%]	5.7	5.5	5.1	3.4	4.1
R_F [%]	3.5	3.4	3.6	2.8	3.0

TABLE II

Magnetic properties of $R_2Ni_{2-x}In$ (R = Gd, Tb, Er, $x = 0.22$ and R = Ho, Dy, $x = 0.3$) compounds: the Néel (T_N), the paramagnetic Curie temperature (θ_{p}), the effective magnetic moment (μ_{eff}), the magnetic moment in the ordered state (μ) at $T = 1.9$ K and $H = 90$ kOe and the critical magnetic field (H_{cr}).

R	T_N [K]	T_t [K]	θ_{p} [K]	μ_{eff} [μ_B]		μ [μ_B]		H_{cr} [kOe]
				exp.	theor.	exp.	theor.	
Gd	26.4	13.5	0.45	8.15	7.94	4.3	7.0	25.6
Tb	20.2	13.1	−9.7	10.08	9.72	5.8	9.0	38.5
Dy	8.3	–	3.2	10.91	10.65	8.8	10.0	16
Ho	7. 1	–	−7.2	10.97	10.61	6.5	10.0	15
Er	6.3	5.0	−0.2	9.71	9.58	6.4	9.0	9

The temperature dependence of the real component of the AC magnetic susceptibility χ' (Fig. 2) and the DC susceptibility at 50 Oe (Fig. 3) show maxima typical for antiferromagnetic–paramagnetic phase transition at 26.4 K (Gd), 20.2 K (Tb), 8.3 K (Dy), 7.1 K (Ho) and 6.3 K (Er). For the R = Gd-, Tb-, and Er-compounds

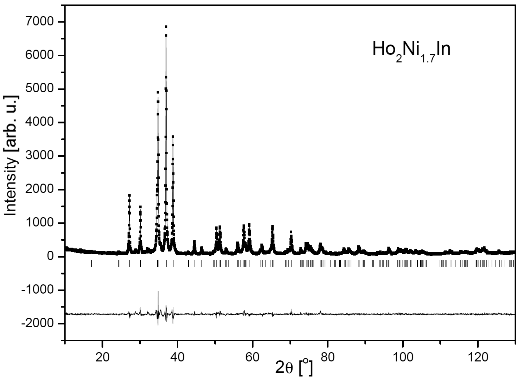

Fig. 1. X-ray diffraction pattern of $Ho_2Ni_{1.7}In$: the observed (dots), the calculated (solid line) and the difference pattern (in the bottom of the figure), the vertical bars show the positions of the Bragg reflections.

an additional anomaly below T_N is observed at T_t equal to 13.5 K, 13.1, and 5.0 K, respectively. At T_N the imaginary component of the AC magnetic susceptibility χ'' exhibits a small drop for R = Ho and a small maximum for R = Gd and Dy, while for R = Er only an anomaly at T_t is observed. These data suggest not a simple collinear antiferromagnetism but complex magnetic structures.

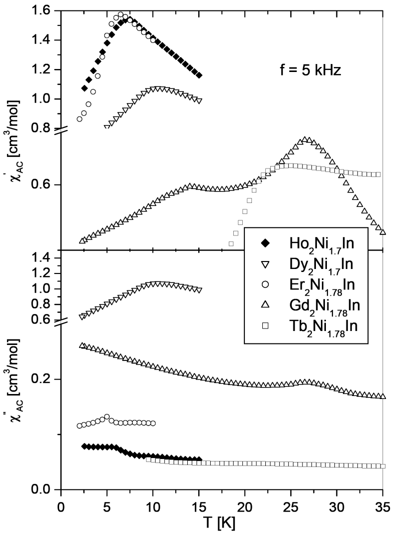

Fig. 2. Temperature dependence of the real (χ') and imaginary (χ'') component of the AC magnetic susceptibility of R_2Ni_xIn (R = Gd, Tb, Er, $x = 0.22$ and Ho, Dy, $x = 0.3$).

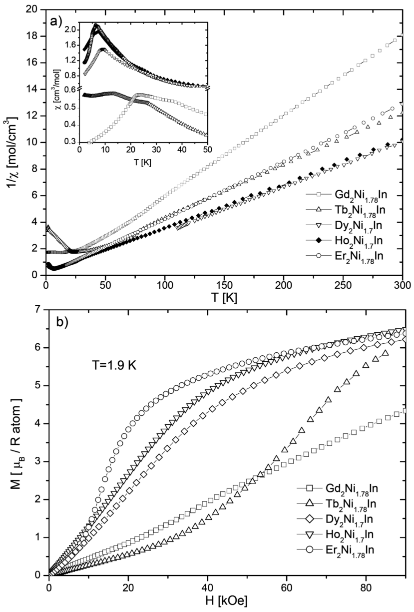

Fig. 3. Magnetic data for $R_2Ni_{2-x}In$ (R = Gd, Tb, Er, $x = 0.22$ and Ho, Dy, $x = 0.3$): (a) temperature dependence of the reciprocal magnetic susceptibility measured at 1 kOe, the inset shows the low temperature plot of the DC magnetic susceptibility versus temperature at 50 Oe, (b) magnetic field dependence of magnetization at 1.9 K.

In the paramagnetic phase the reciprocal magnetic susceptibility obeys the Curie–Weiss law (Fig. 3a) with negative values of the paramagnetic Curie temperature θ_p for R = Tb, Ho and Er and positive ones for R = Gd and Dy. The effective magnetic moments are close to the free R^{3+} ion values for all the compounds. In Fig. 3b the isothermal magnetization at $T = 1.9$ K is plotted versus magnetic field up to 90 kOe. The curves for R = Gd, Tb and Er exhibit metamagnetic character. The critical field values, corresponding to the metamagnetic transition, were found from the field dependence of $\partial M/\partial H$. The values of the magnetic moments at $T = 1.9$ K and 90 kOe are smaller than the appropriate free R^{3+} ion values. Results of the magnetic measurements are summarized in Table II.

4. Discussion and summary

The presented data confirm that the $R_2Ni_{2-x}In$ (R = Ho, Dy, $x = 0.3$ and R = Gd, Tb, Er, $x = 0.22$) compounds crystallize in the tetragonal Mo_2FeB_2-type crystal structure and order antiferromagnetically at low temperatures. In this structure the rare-earth atoms occupy the 4h sites in the a–b planes ($z = 1/2$) separated by Ni–In planes ($z = 0$). The lattice parameters a and c as well as the c/a ratio (the value close to 0.5) decrease with increasing atomic number of the rare-earth element.

The large interatomic R–R distance suggests that the interaction between the rare-earth moments is of the Ruderman–Kittel–Kasuya–Yosida (RKKY) type. In such a case the Néel temperature is expected to be a function of the de Gennes factor $(g_J-1)^2J(J+1)$, where g_J is the Landé splitting factor and J is the total angular momentum of the corresponding magnetic ion. The obtained results show that for $R_2Ni_{2-x}In$ (Fig. 4) the de Gennes scaling is not fulfilled, which indicates an influence of the crystal electric field. The values of the

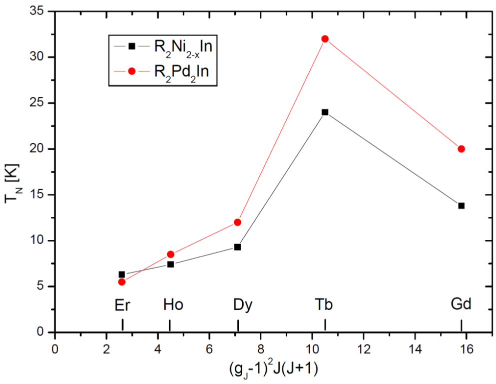

Fig. 4. Plots of the ordering temperatures versus the de Gennes factor $(g_J-1)^2J(J+1)$ for the $R_2Ni_{2-x}In$ and the isostructural R_2Pd_2In (R = Gd–Er) series of compounds; the data for R_2Pd_2In after Ref. [6].

magnetic moments in the ordered state (at $T = 1.9$ K and 90 kOe) are smaller than the free R^{3+} ion values (Table II) which might be connected with the influence of the crystal electric field. In the isostructural family of antiferromagnetic R_2Pd_2In compounds [12] as well as in the ferromagnetic R_2Cu_2In ones [20] the critical temperatures of the magnetic ordering do not obey this relation, too.

In the studied ternary indides $R_2Ni_{2-x}In$ the values of the effective magnetic moment μ_{eff} are close to the free R^{3+} ion values (Table II) suggesting that the magnetic moment is localized on the rare earth atoms only and the Ni atoms do not carry any magnetic moment. This result coincides with the results of *ab initio* electronic structure calculations for the isostructural U_2Ni_2X compounds [21–23] showing that the Ni 3*d* band is located about 3.5 eV below the Fermi level and does not participate in formation of the localized magnetic moment. The comparison of the magnetic data collected for $R_2Ni_{2-x}In$ and R_2Pd_2In for R = Gd–Er (see Fig. 4) confirms this conclusion.

Temperature dependence of the real and imaginary component of the AC magnetic susceptibility indicates changes in the magnetic order with temperature. To explain this point neutron diffraction measurements are planned.

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