Magnetic properties of the RCuIn (R = Ce, Nd, Gd, Tb, Dy, Ho, Er) and R_2CuIn_3 (R = Ce, Gd, Tb, Dy) compounds

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X-ray diffraction and magnetic measurements of RCuIn (R = Ce, Nd, Gd, Tb, Dy, Ho, Er) and R_2CuIn_3 (R = Ce, Gd, Tb, Dy) are reported. The RCuIn compounds crystallize in the hexagonal ZrNiAl-type structure. Two types of hexagonal structure were found in the R_2CuIn_3 series of compounds: the AlB_2 type for R = Ce and the $CaIn_2$ type for R = Gd, Tb, Dy. DC magnetic susceptibility measurements show that all the compounds, except those with R = Ce, order antiferromagnetically with T_N ranging from 3.1 K (R = Er) to 21 K (R = Gd) in the RCuIn series and from 25.6 K (R = Dy) to 40 K for (R = Tb) in the R_2CuIn_3 series. Neutron diffraction measurements were carried out for TbCuIn. At 1.5 K the Tb magnetic moments lie in the basal plane and form a noncollinear magnetic structure described by the propagation vector k = (½, ½, 0.2217(9)). The frustration effect characteristic of a triangular lattice is observed.

**Rare earth alloys and compounds / Intermetallics / Magnetically ordered materials /
Magnetic measurements / Neutron diffraction**

Introduction

The R-Cu-In systems (R is a rare earth element) have been thoroughly investigated. Isothermal sections of the phase diagrams and crystallographic data for series of ternary compounds are collected in the review article [1]. According to the information therein, from 4 up to 10 intermetallic compounds are formed in each system and the Ce-Cu-In system contains the highest number of compounds.

Intermetallic phases containing 33.3 at.% R are the subject of the present work. Compounds of the RCuIn stoichiometry are known for all rare earths except Eu and Yb. They crystallize in the hexagonal ZrNiAl structure type (space group *P*-62*m*), where the R, Cu and In atoms occupy the positions of Zr (the 3*g* site: x_R, 0, ½), Ni (the 1*b*: 0, 0, ½ and 2*c*: ⅓, ⅔, 0 sites) and Al (the 3*f*: x_{In}, 0, 0 site), respectively. For Er, Tm and Lu the compounds form limited homogeneity ranges as a result of In substitution for Ni [1,2]. Compounds of the R_2CuIn_3 (or $RCu_{0.5}In_{1.5}$) stoichiometry are known for all rare earths except Yb and Lu. All these compounds have solubility regions along the

isoconcentration line of the rare earth element [1]. The crystal structure of $CeCu_{0.5}In_{1.5}$ has been solved as an example of a representative of the AlB_2-type structure. The R atoms occupy the positions of the Al atoms, while the positions of the B atoms are occupied by a statistical mixture of Cu and In atoms ($Cu_{0.5}In_{1.5}$) [3].

Magnetic properties in the RCuIn series have been investigated only for R = Ce, Gd and Tb. It was reported that CeCuIn is a paramagnet down to 4.2 K [4], GdCuIn orders antiferromagnetically below T_N = 20 K [5], while the magnetic susceptibility of TbCuIn shows two maxima (at 16 and 84 K) in the temperature dependence [6].

Neutron diffraction data for TbCuIn collected in the temperature range 1.5 K and 50 K confirm a hexagonal crystal structure at 50 K. At 1.5 K the Tb magnetic moments form a noncollinear magnetic structure described by the propagation vector k = (½, ½, 0.2288(3)) [6].

Magnetic measurements carried out for R_2CuIn_3 showed that the compounds with R = Nd, Tb, Dy, Ho and Er order antiferromagnetically with the Néel temperature T_N ranging from 8 K (R = Ho) to 30 K

(R = Tb) [7]. According to neutron diffraction measurements the Tb magnetic moments, which equal 6.8 μ_B at T = 3.8 K, form a collinear antiferromagnetic structure described by the propagation vector $\mathbf{k}$ = (0, ½, 0). The Tb magnetic moments are parallel to the *c*-axis [8,9].

This paper presents magnetic data collected for two series of rare earth compounds: RCuIn (R = Ce, Nd, Gd-Er) and R_2CuIn_3 (R = Ce, Gd, Tb, Dy). For TbCuIn neutron diffraction was carried out to determine the magnetic structure.

Experimental

Polycrystalline samples were prepared by arc melting of high-purity raw metals (rare earths with a purity not worse than 99.8 wt.% main component, electrolytic copper with the purity 99.92 wt.% Cu and indium with the purity 99.99 wt.% In) in titanium-gettered argon atmosphere (p = 50 kPa). The chemical composition of the alloys was checked by measuring the weight losses, which did not exceed 1 wt.%. The total mass of each ingot was about 1.5 g. All the ingots were annealed at 870 K for 700 h in evacuated silica tubes and then quenched in cold water.

X-ray powder diffraction patterns were collected at room temperature using CuK$_\alpha$ radiation (Philips X'PERT diffractometer; Institute of Physics of the Jagiellonian University). Neutron diffraction measurements of TbCuIn were carried out in the temperature range 1.5÷50 K with the incident neutron wavelength 2.44 Å (E6 diffractometer at the Berlin Neutron Scattering Center). The diffraction data were analyzed using the Rietveld-type program Fullprof [10]. DC magnetic measurements were carried out in the temperature range 2÷300K in magnetic fields up to 50 kOe (MPMS SQUID magnetometer; Institute of Physics of the Jagiellonian University).

Results

The X-ray analysis confirms that all the obtained RCuIn alloys are single phase with ZrNiAl-type structures. A typical X-ray diffraction pattern is shown in Fig. 1. Crystallographic data calculated by

full-profile analysis [10] of the X-ray diffraction patterns are collected in Table 1 and agree well with published data [1].
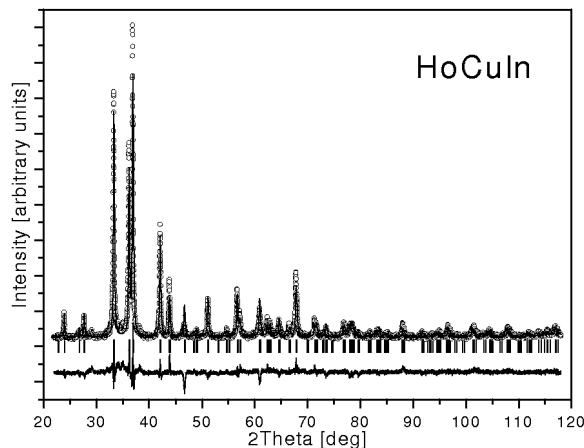

Fig. 1 X-ray powder diffraction pattern of HoCuIn.

The crystal structure parameters of TbCuIn determined from the neutron diffraction data collected at 50 K (paramagnetic region) are as follows: a = 7.404(3) Å, c = 3.946(2) Å, x_R = 0.5923(1) and x_{In} = 0.2397(1). For the R_2CuIn_3 compounds the solubility regions are known but only alloys with R = Ce, Gd, Tb and Dy were successfully prepared for the investigations. The X-ray analysis of the samples confirms that they are single phase and the diffraction patterns can be indexed using a hexagonal AlB_2- or $CaIn_2$-type structure model. Values of the refined cell parameters are listed in Table 2 and are in good agreement with published ones [1].

Results of the magnetic measurements are presented in Figs. 2 and 3. In both series of compounds investigated here the Ce compounds are paramagnets down to 2 K. All the other compounds are antiferromagnets with the Néel temperature between 21 K (R = Gd) and 3.1 K (R = Er) for RCuIn, and 40 K (R = Gd) and 25.6 K (R = Dy) for R_2CuIn_3. The anomaly at 89 K observed for GdCuIn is connected with a Gd_2Cu_2In impurity, which is a ferromagnet [11]. Except for GdCuIn, the reciprocal magnetic susceptibility obeys the Curie-Weiss law above the Néel temperature, the values of the

Table 1 Crystallographic data for RCuIn compounds (X-ray diffraction at room temperature).

Compound	Cell parameters (Å)		Atom coordinates		Reliability factors (%)	
	a	c	x_R	x_{In}	R_{Bragg}	R_F
CeCuIn	7.4915(18)	4.2452(15)	0.5832(12)	0.2486(15)	14.7	11.0
NdCuIn	7.4715(9)	4.1668(6)	0.5874(9)	0.2462(12)	9.7	8.0
GdCuIn	7.4701(15)	3.9925(9)	0.5897(21)	0.2528(21)	13.0	9.8
TbCuIn	7.4586(9)	3.9633(6)	0.5881(12)	0.2524(12)	15.0	12.8
DyCuIn	7.4486(15)	3.9297(12)	0.5914(15)	0.2464(18)	13.5	11.3
HoCuIn	7.4332(9)	3.8911(6)	0.5911(9)	0.2506(9)	12.0	8.2
ErCuIn	7.4247(6)	3.8637(6)	0.5912(9)	0.2524(12)	11.9	11.9

paramagnetic Curie temperature are negative and the effective magnetic moments are close to the free R^{3+} ion values. At $T = 2$ K and the magnetic field H = 50 kOe the values of the magnetic moments are smaller than the free R^{3+} ion values. The results of the magnetic measurements are listed in Table 3.

Table 2 Cell parameters of the R_2CuIn_3 compounds (X-ray diffraction at room temperature).

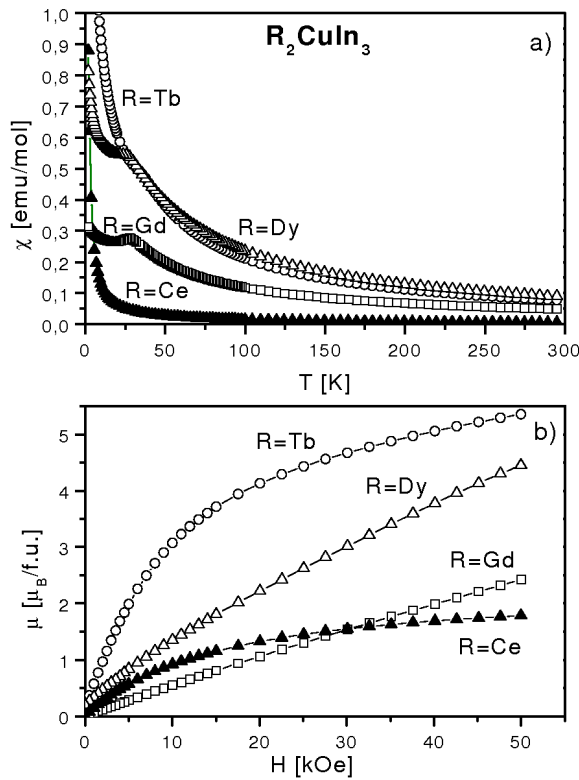| Compound	Structure type	Cell parameters (Å)	
		a	*c*
Ce_2CuIn_3	AlB_2	4.819(2)	3.874(1)
Gd_2CuIn_3	$CaIn_2$	4.7409(9)	7.3857(9)
Tb_2CuIn_3	$CaIn_2$	4.7358(6)	7.3209(6)
Dy_2CuIn_3	$CaIn_2$	4.7177(9)	7.2976(9)

Fig. 2 (a) Temperature dependence of the magnetic susceptibility and (b) magnetization curve at 2 K for RCuIn (R = Ce, Nd, Gd, Tb, Dy, Ho, Er) compounds.

Analysis of the neutron diffraction pattern of TbCuIn collected at 1.5 K confirms a noncollinear magnetic structure described by the propagation vector $\mathbf{k} = (½, ½, 0.2217(9))$ and magnetic moments in the basal plane. The temperature dependence of the magnetic peak intensities gives a Néel temperature equal 14.5 K. In the ZrNiAl-type structure the Tb magnetic moments are located at the following positions: μ_1 at $(x_R, 0, ½)$, μ_2 at $(\bar{x}_R, \bar{x}_R, ½)$ and μ_3 at $(0, x_R, ½)$. The best fit of the magnetic part of the

neutron diffraction pattern was obtained for the magnetic structure described below:

– the magnetic moment μ_1 equal 4.9(2) μ_B and slightly tilted from the *a*-axis direction,
– μ_2 equal 4.9(2) μ_B and perpendicular to the *a*-axis,
– μ_3 equal 5.5(2) μ_B and parallel to the *b*-axis.

The basal plane projection of the magnetic structure of TbCuIn is shown in Fig. 4. The magnetic structure determined here is consistent with the one presented in [6].
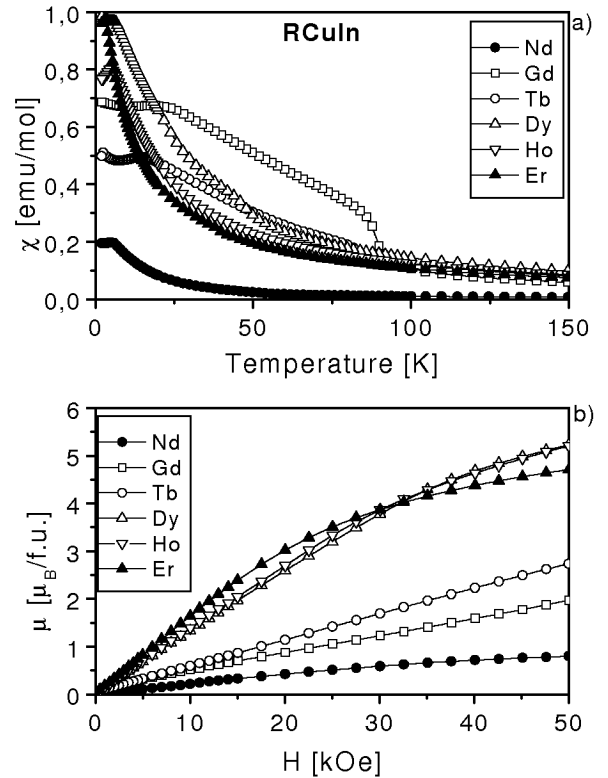

Fig. 3 (a) Temperature dependence of the magnetic susceptibility and (b) magnetization curve at 2 K for R_2CuIn_3 (R = Ce, Gd, Tb, Dy) compounds.

Discussion and conclusions

The results presented in this work confirm that the RCuIn compounds crystallize in hexagonal crystal structures of the ZrNiAl type and the R_2CuIn_3 compounds have hexagonal structures of the $CaIn_2$ (R = Gd, Tb and Dy) or AlB_2 type (R = Ce). The investigated compounds (except R = Ce) are antiferromagnets at low temperatures. The data for the RCuIn series are, in majority, the first results published concerning the magnetic properties of these compounds. The data for R_2CuIn_3 are in good agreement with the data reported in [7]. Contrary to the R_2Cu_2In compounds [11], in the RCuIn and R_2CuIn_3 compounds the magnetic moments order antiferromagnetically.

Table 3 Magnetic properties of the RCuIn and R_2CuIn_3 series of compounds.

R	RCuIn				R_2CuIn_3				R^{3+}	
	T_N (K)	Θ_p (K)	μ_{eff} (μ_B)	μ (μ_B)	T_N (K)	Θ_p (K)	μ_{eff} (μ_B)	μ (μ_B)	μ_{eff} (μ_B)	μ (μ_B)
Ce	P[a]	-15.0	2.40	0.7	P[a]	-8.6	2.52	1.8	2.54	2.14
Nd	4.9	-7.2	2.96	0.8					3.58	3.2
Gd	21.0	6.8	8.27	2.0	27.4	-31.9	7.93	2.4	7.94	7.0
Tb	14.5	-5.4	9.44	2.7	40.0	-12.3	9.77	5.4	9.72	9.0
Dy	6.2	-6.6	10.52	5.2	25.6	-20.5	10.65	4.4	10.65	10.0
Ho	5.0	-10.0	10.51	5.2					10.61	10.0
Er	3.1	-12.3	9.93	4.7					9.58	9.0

[a] paramagnetic down to 2 K

In the compounds investigated in this work the magnetic moments are localized on the rare earth atoms. The interatomic distances between these atoms are long, which suggests that the interaction between the magnetic moments is of the RKKY type. In this model the Néel temperatures T_N should follow the de Gennes factor $(g–1)^2 J(J+1)$. According to the de Gennes scaling, T_N should reach its maximum for Gd compounds. The dependence of the T_N value on the de Gennes factor for both investigated systems is plotted in Fig. 5 (data for R_2CuIn_3 (R = Er, Ho) from [7] are included). It is seen that the de Gennes scaling (marked by a dashed line in Fig. 5) is fulfilled for the RCuIn compounds, while for the R_2CuIn_3 compounds the maximum of the Néel temperature is shifted from Gd to Tb, which may result from crystalline electric field (CEF) effects [12]. The smaller values of the Tb magnetic moments in the ordered state in comparison to the paramagnetic one could also be explained as the result of the CEF. The influence of the CEF is manifested in the different directions of the Tb magnetic moments: in the basal plane for TbCuIn, but along the *c*-axis for Tb_2CuIn_3 and for the isostructural Tb_2AgIn_3 [13]. The values of the Néel temperatures are higher for the R_2CuIn_3 compounds, which suggests that the CEF effect strengthens the RKKY interaction.
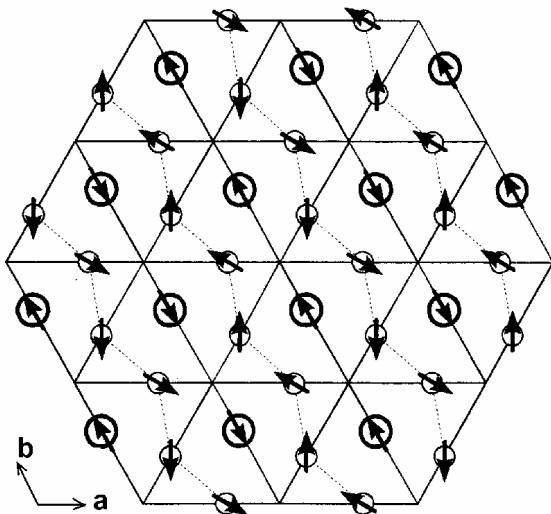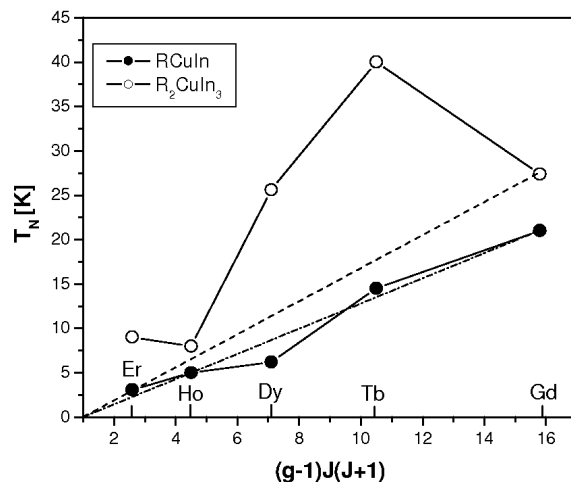

Fig. 5 Néel temperature vs. the de Gennes factor $(g–1)^2 J(J+1)$ for RCuIn and R_2CuIn_3 compounds.

In both TbCuIn and Tb_2CuIn_3 the frustration effect characteristic of a triangular lattice is observed. In TbCuIn the Tb moments build a noncollinear structure typical for a triangular lattice. In this structure neighbouring rare earth magnetic moments form an angle of 120º with each other (see Fig. 4). In Tb_2CuIn_3 a simple collinear magnetic structure with an orthorhombic unit cell (a, $\sqrt{3}\,a$, c) is developed. This magnetic ordering is in good agreement with the Ising-like model for a two-dimensional hexagonal lattice with a strong anisotropy (that forces the magnetic moment to align parallel to the *c*-axis), taking into account the exchange integrals between the first (J_1) and the second (J_2) nearest neighbours.

Based on these predictions Doukouré et al. [14] obtained the magnetic phase diagram. The magnetic structure of Tb_2CuIn_3 corresponds to the $J_1 < 0$ and $J_2 < 0$ or $J_1 > 0$ and $J_2 \geq –J_1$ set of exchange integrals.

Acknowledgements

Fig. 4 Basal plane projection of the magnetic structure of TbCuIn.

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