



Alina Gil
Akademia im. Jana Długosza w Częstochowie

THE INFLUENCE OF T- AND X- ELEMENTS ON MAGNETIC PROPERTIES OF RT_xX_2 COMPOUNDS

Summary

The RT_xX_2 ($x \leq 1$) type metallic compounds where R is a rare-earth element, T is a d-electron element and X is a p-electron element ($X = \text{Si, Ge, Sn}$) crystallize in different orthorhombic crystal structures but most of them crystallize in orthorhombic CeNiSi_2 – type (space group Cmcm). The silicides form stoichiometric compounds while the majority of germanides and stannides non stoichiometric ones.

The systems exhibit complex magnetic behaviour. The heavy rare-earth compounds ($R = \text{Tb, Dy, Ho, Er}$) are antiferromagnets at low temperatures. The magnetic moment is localized only on the rare-earth atoms. Their magnetism arises from the interaction of the magnetic moments localized on the rare-earth ions.

This work is a summary of long-term research of magnetic properties of these compounds. The obtained results were compared in purpose to determine the influence of other elements (T, X) on the magnetic ordering in the rare-earth sublattices.

Keywords: intermetallic compounds, crystal structure, magnetic ordering, localized magnetic moment

Introduction

The study of RT_xX_2 ($x \leq 1$) intermetallic compounds (R is a rare-earth, T is a d-electron metal and X is a p-electron metalloid (X = Si, Ge, Sn) lasted for many years due to their intriguing physical properties, which have both fundamental and practical significance.

The RT_xX_2 compounds crystallize in different orthorhombic crystal structures [1]:

- CeNiSi₂-type (space group Cmc₂m);
- TbFeSi₂-type, which is very similar to the CeNiSi₂, but R, T and Si atoms are located in alternating layers;
- YIrGe₂-type (space group Immm);
- LuNiSn₂-type (space group Pnma);
- TiMnSi₂ or ZrCrSi₂-type (space group Pbam);
- NdRuSi₂-monoclinic type, which is described as a distorted variant of the CeNiSi₂-type (space group P2₁/m).

The silicides crystallize in the stoichiometric structures ($x=1$), while germanides and stannides form mainly defected structures RT_xX_2 ($x < 1$) with defects in d-electron metal sublattice.

Majority of these compounds crystallize in the orthorhombic CeNiSi₂-type structure [2] and discussion in this work relates to these compounds.

Crystal structure

The CeNiSi₂ crystal structure is shown in Fig. 1. The atoms: Ce(R), Ni(T), Si1(X1) and Si2(X2) occupy the 4(c) positions: $(0, y, \frac{1}{4})$; $(0, -y, \frac{3}{4})$; $(\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4})$; $(\frac{1}{2}, \frac{1}{2}-y, \frac{3}{4})$ with different values of the y parameter: $y(\text{Ce}) = 0.1070 \text{ \AA}$, $y(\text{Ni}) = 0.3158 \text{ \AA}$, $y(\text{Si1}) = 0.4566 \text{ \AA}$ and $y(\text{Si2}) = 0.7492 \text{ \AA}$.

Characteristic feature of this structure is the coordination polyhedron of the transition metal atoms, which are located inside the slightly deformed square pyramid with X1 atoms at the corners. The base of this pyramid is formed by X2 atoms and the top corner is occupied by X1 atom. The pyramids share common corners of X2 and form two-dimensional layers perpendicular to the *b*-axis. The layers are interconnected by X1 – X1 bonds. R atoms occupy large holes in the framework having four X1, four T and four X2 atoms below.

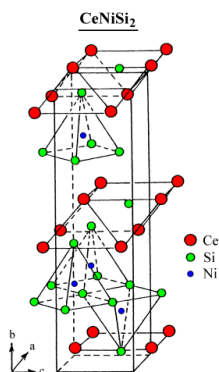


Fig. 1. Crystal structure of CeNiSi_2

Magnetic structures

The magnetic measurements indicate that all compounds with heavy rare-earth metals ($R=\text{Tb} - \text{Er}$) order antiferromagnetically at low temperatures. Above the Néel temperatures the effective magnetic moments are close to the free R^{3+} ion values ($g\sqrt{J(J+1)}$).

The crystal structure has a distinct layer character. Rare-earth atoms occupy the layers perpendicular to the b-axis and they are divided by layers of another atoms (T, X).

It is well established now that in these compounds the magnetic moment is localized only on the rare-earth atoms. Only for compounds with $T = \text{Mn}$, a localized magnetic moment on Mn has been observed.

In all series of compounds the $R^{3+} - R^{3+}$ distances are large ($d_{R-R} \approx 4 \text{ \AA}$), suggesting that direct magnetic interactions are highly improbable. The stability of the observed magnetic ordering schemes may be considered as being due to interactions via conduction electrons described by the RKKY model [3, 4, 5]. The RKKY interactions are long-range and this should lead in general, to modulated magnetic structures.

The observed decrease in the rare-earth magnetic moments values as compared with the free ion values may result from crystalline electric field effect (CEF) [6, 7].

In the case of discussed series one can observe a wide variety of magnetic structures (see Table 1).

Table 1. Magnetic structures of RT_xX_2 compounds.

RT_xX_2	T_N [K]	MST	$\mathbf{k}=(k_x, k_y, k_z)$	μ [μ_B]	MMD	Ref.
TbCoSi ₂	16	AF (Fig.2a)	$\mathbf{k}=(0,0,0)$ + spiral $\mathbf{k}=(1/2, 1/2, 1/2)$	9.16	c	[9]
TbNiSi ₂	36.7	AF (Fig.2b)	$\mathbf{k}=(0,0,0)$	8.7	c	[10, 11]
TbMn _{0.33} Ge ₂	28	AF	$\mathbf{k}=(0,0,0)$ + sin. mod. $\mathbf{k}=(0.68, 0.07, 0.17)$	8.2	c a	[12]
TbNiGe ₂	37	AF	$\mathbf{k}=(0,0,0)$	8.8	c	[13]
TbNi _{0.4} Ge ₂	16	AF	$\mathbf{k}=(0,0,0)$	5.6	c	[14]
TbNi _{0.6} Ge ₂	31	AF	$\mathbf{k}=(0,0,0)$ + sin. mod. $\mathbf{k}=(0.24, 0, 0.29)$	8.88	c	[15]
TbNi _{0.8} Ge ₂	38	AF	$\mathbf{k}=(0,0,0)$ + sin. mod. $\mathbf{k}=(0, 0.46, 0)$	8.72	c	[15]
TbCr _{0.3} Ge ₂	18.2	AF (Fig.4a,b)	$\mathbf{k}=(1/2, 0, 0)$ + $\mathbf{k}=(1/4, 0, 1/4)$	7.60 4.52	c (a-c)	[26]
TbCu _{0.4} Ge ₂	39	AF	$\mathbf{k}=(0,0,0)$	8.82	c	[14]
TbFe _{0.15} Sn ₂	18.4	AF	$\mathbf{k}=(0,0,1/2)$	8.1	(b-c)	[27]
TbCo _{0.25} Sn ₂	18.8	AF	$\mathbf{k}=(0,0,1/2)$	7.14	(a-c)	[16]
TbNi _{0.26} Sn ₂	17.4	AF (Fig.3a)	$\mathbf{k}=(0,0,1/2)$	8.05	(a-c)	[17]
DyCoSi ₂	10	AF	$\mathbf{k}=(0,0,0)$	5.74	(a-c)	[9]
DyNiSi ₂	24	AF	$\mathbf{k}=(0,1,0)$ + $\mathbf{k}=(0,0,6,0)$	7.5	c	[18]
DyMn _{0.32} Ge ₂	30	AF				[19]
DyFe _{0.15} Sn ₂	6.9	AF	$\mathbf{k}=(0,0,1/2)$	5.5	(b-c)	[27]
DyCo _{0.26} Sn ₂	7	AF				[16]
DyNi _{0.22} Sn ₂	8	AF	$\mathbf{k}=(0.36, 0, 0.34)$	9.2	(b-c)	[20]
DyCr _{0.3} Ge ₂	11.8	AF	$\mathbf{k}=(1/2, 0, 0)$ + $\mathbf{k}=(1/2, 1/2, 0)$	4.46, 7.18	(a-c)	[26]
HoCoSi ₂	6.3	AF	$\mathbf{k}=(0,0,0)$	6.72	a	[9]
HoNiSi ₂	10	AF	$\mathbf{k}=(0,0,0)$	8.13	c	[21]
HoMn _{0.33} Ge ₂	7	AF	$\mathbf{k}=(0,0,0)$	7.3	c	[19]
HoNi _{0.64} Ge ₂	11	AF	$\mathbf{k}=(0,0,0)$	6.7	c	[13]

HoCu _{0.33} Ge ₂	10.5	AF	k=(0,0,0)	8.18	c	[22]
HoFe _{0.14} Sn ₂	5.9	AF	k=(1/2,1/2,0)	6.6	(b-c)	[27]
HoCo _{0.23} Sn ₂	5.6	AF	k=(1/2,1/2,0)	6.79	(a-c)	[16]
HoNi _{0.16} Sn ₂	6.6	AF (Fig.3b)	k=(1/2,1/2,0)	7.46	(a-c)	[17]
HoCr _{0.3} Ge ₂	5.6	AF (Fig.4c)	k=(1/2,1/2,0)	6.99	c	[26]
ErCoSi ₂	2.6	AF	k=(0.47,0,1/2)	4.63	(a-c)	[23]
ErNiSi ₂	3.4	AF	k=(1/2,0,0) + k=(0.13,0.02,0.23)	7.6	b	[24]
ErMn _{0.27} Ge ₂	3.4	AF	k=(0,0,0)			[19]
ErNi _{0.65} Ge ₂	2.5	AF	k=(0,0,0)	2.8	a	[13]
ErCu _{0.25} Ge ₂	4.5	AF	k=(0,0,0)	7.89	a	[22]
ErCr _{0.3} Ge ₂	3.5	AF (Fig.4d)	k=(0,0,0.42)	8.32	a	[26]
ErFe _{0.11} Sn ₂	5.5	AF	k=(0,0,0)	7.3	a	[27]
ErCo _{0.24} Sn ₂	4.7	AF	k=(0,0,0)	6.15	a	[25]
ErNi _{0.15} Sn ₂	4	AF (Fig.3c)	k=(0,0,1/2)	9.16	a	[25]

T_N – Néel temperature

MST – magnetic structure type

MMD – magnetic moment direction

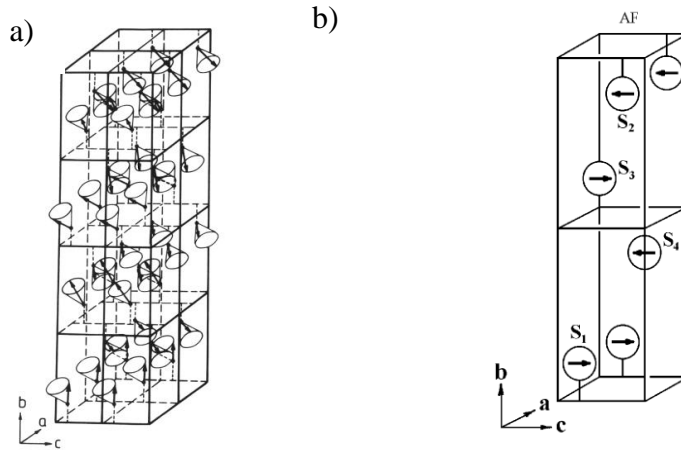


Fig. 2. a) Spiral structure of TbCoSi_2 , $k=(1/2, 1/2, 1/2)$; b) collinear antiferromagnetic structure of TbNiSi_2

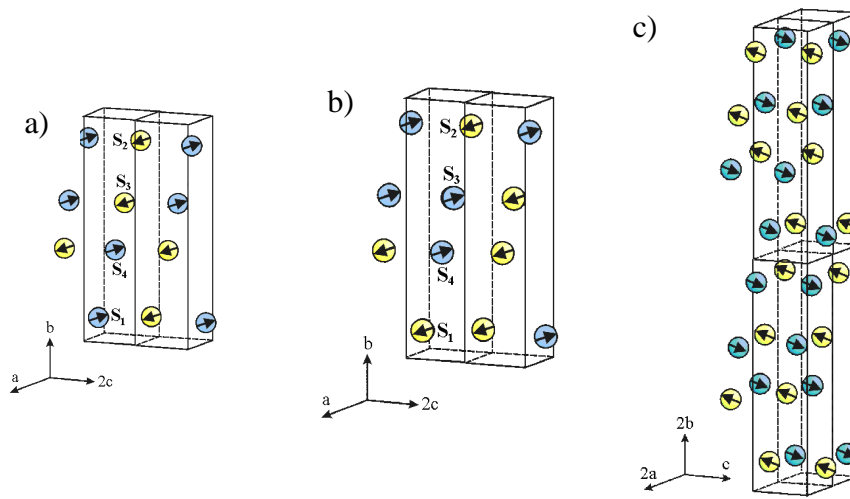


Fig. 3. Sine modulated structures of: a) $\text{TbNi}_{0.26}\text{Sn}_2$, $k=(0, 0.1, 1/2)$; b) $\text{HoNi}_{0.16}\text{Sn}_2$, $k=(1/2, 1/2, 0)$; c) $\text{ErNi}_{0.15}\text{Sn}_2$

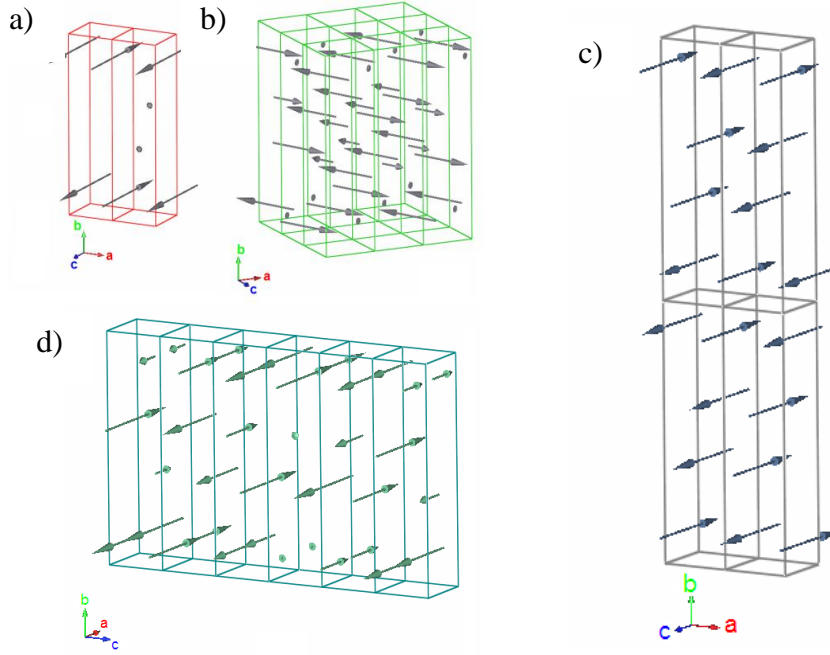


Fig. 4. Magnetic structure of $\text{TbCr}_{0.3}\text{Ge}_2$: a) propagation vector $k=(\frac{1}{2}, 0, 0)$, b) propagation vector $k=(\frac{1}{4}, 0, \frac{1}{4})$; c) $\text{HoCr}_{0.3}\text{Ge}_2$ (propagation vector $k=(\frac{1}{2}, \frac{1}{2}, 0)$); d) $\text{ErCr}_{0.3}\text{Ge}_2$ (propagation vector $k=(0, 0, 0.4187)$).

The determined magnetic structures of the investigated stannides are different than those reported for the isostructural stoichiometric RTX_2 silicides and germanides. They have simple antiferromagnetic structures with the magnetic unit cell being the same as the crystallographic one. In the silicides and germanides the magnetic moments point along the c -axis. In the stannides the rare-earth magnetic moments form an angle with the c -axis. These results indicate that the change of the X element (p-electron element) from Si/Ge to Sn influences the magnetic interactions and leads to a change in the direction of the magnetic moments.

The orientation of the magnetic moment is determined by the sign of B_2^0 parameter [8]. When the magnetic moment is parallel to the c -axis B_2^0 is negative. The positive value of B_2^0 stabilizes the other magnetic moment direction.

The crystal field parameters B_n^m can be written as:

$$B_n^m = A_n^m \langle r^n \rangle \theta_n$$

where A_n^m is the crystal field coefficient which characterizes the surrounding charge distribution, $\langle r^n \rangle$ is the mean value of the n-th power of the 4f radius and θ_n is the appropriate Stevens factor [6].

The observed change in orientation of the rare-earth magnetic moments between Tb-, Dy-, Ho- and Er- compounds is due to change of the Stevens factor α_J sign from negative for Ho to positive for Er.

Discussion

It is very difficult to determine the general rules for the influence of other elements (T, X) on the magnetic ordering in presented compounds but some important reasons are presented below.

It is well known that the magnetism of these compounds arises from the interaction of the magnetic moments localized on the rare-earth ions. There is no localized magnetic moment on d-elements. The reason for this is the change of the electronic structure of 3d transition metal shell when it becomes a component of the compound [29].

The unit cell volume of the RT_xX_2 compounds depends upon the radius of the R^{3+} ion. For stannides the unit cell volume very weakly depends on the T element because these compounds are strongly defected [4].

Pecharsky et al. [28] suggest that the $CeNiSi_2$ -type structure is closely related to the $ZrSi_2$ -type one. The $CeNiSi_2$ -type structure is formed by introduction of Ni atoms into the $ZrSi_2$ -type structure. For $x \geq 0.5$, the nonstoichiometric RT_xX_2 compounds are considered those with defected $CeNiSi_2$ structure, while for $x < 0.5$ – the doped $ZrSi_2$ structure. Both structures have the tetragonal prisms (TP) $[R_4Ge_4T_{1-x}]$ for Lu→La series. An analysis of germanium compounds let to determine one more interesting property: the number of defects in TP $[R_4Ge_4T_{1-x}]$ decreases when going from Fe through Co to Ni. This is not caused by the geometrical factor, because the sizes of the element T are almost identical, so it suggests that the change in the number of d-electrons may be significant. Similar situation is observed in tin compounds.

The determined magnetic structures of the investigated stannides are different than those reported for the isostructural stoichiometric RTX_2 silicides and germanides. These results indicate that the change of the X element (p-electron element) from Si/Ge to Sn influences the magnetic interactions and leads to a change in the direction of the magnetic moments.

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Alina Gil
Akademia im. Jana Długosza w Częstochowie

WPLYW PIERWIASTKÓW T, X NA WŁASNOŚCI MAGNETYCZNE ZWIĄZKÓW RT_xX_2

Streszczenie

Związki międzymetaliczne typu RT_xX_2 ($x \leq 1$), gdzie R – ziemia rzadka, T – metal d-elektronowy, X – metaloid (X= Si, Ge, Sn) krystalizują w różnych typach rombowych struktur, lecz większość z nich posiada strukturę rombową typu $CeNiSi_2$ (grupa przestrzenna Cmcn). Związki z krzemem tworzą układy stechiometryczne, natomiast większość związków z germanem i cyną – niestechiometryczne. W omawianych związkach obserwuje się różnorodność struktur magnetycznych. Związki z ciężkimi ziemiami rzadkimi (R=Tb, Dy, Ho, Er) są antyferromagnetykami w niskich temperaturach. Moment magnetyczny jest zlokalizowany tylko na atomach ziemi rzadkiej. Poniższa praca stanowi podsumowanie wieloletnich badań własności magnetycznych tego typu związków. Uzyskane wyniki zostały porównane w celu określenia wpływu pierwiastków T i X na uporządkowanie magnetyczne obserwowane w podsięci ziemi rzadkiej.

Słowa kluczowe: związki międzymetaliczne, struktura krystaliczna, oddziaływania magnetyczne, zlokalizowany moment magnetyczny