

The Impact of d - and p -Electron Elements on Magnetic Properties of RT_xX_2 Compounds

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Studies of rare earth compounds with transition metals are one of the dominant trends in modern magnetism and cover a wide range of research both basic and applicative nature. The main aim of the study of lanthanide compounds is to find answers to questions concerning mechanisms of interaction between the magnetic moments. A systematic study of the magnetic properties of rare-earth compounds gives hope for full understanding of magnetism in these families of compounds. For many years the RT_xX_2 compounds with the crystal structure of $CeNiSi_2$ — type are in the circle of my interests. Based on my own research and the results published in the literature by other authors, the impact of d - and p -electron elements on magnetic properties of the RT_xX_2 compounds, where $x \leq 1$ and $R = Tb, Dy, Ho, Er$; $T = Ni, Co, Cu, Fe, Mn, Cr$; $X = Si, Ge, Sn$ will be analysed.

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1. Introduction

During last decades the arrangement of the magnetic moments of lots of ternary intermetallic compounds with the RT_xX_2 composition, where R — rare earth element, T — d -electron element (transition metal), X — p -electron element were determined.

The aim of this paper is to determine the influence of d - and p -electron elements on magnetic properties of the RT_xX_2 compounds with the orthorhombic $CeNiSi_2$ type crystal structure, described by the $Cmcm$ space group.

The analysis also includes the results of the study of the $RSn_{1+x}Ge_{1-x}$ ($x \approx 0.1$) compounds which also crystallize in the orthorhombic $CeNiSi_2$ structure and they are interesting due to the replacement of the d -metal with the p -electron element and the RSn_2 compounds with orthorhombic $Cmcm$ -type structure and the study of electronic properties performed for RT_xX_2 compounds.

2. Crystal structure

Compounds of the RT_xX_2 composition, where $1 \geq x > 0$, generally crystallize in orthorhombic $CeNiSi_2$ type crystal structure ($Cmcm$ space group) described by Bodak, Gladyshevsky [1] or its derivative. The $CeNiSi_2$ crystal structure is of a layered type. Layers of the same atoms are arranged along the longest axis in the following order: $R-T-X_2-T-R-X_1-X_1-R-T-X_2-T-R$. The layered nature and anisotropy of the crystal structure ($a = 4.455(2)$ Å, $b = 17.374(4)$ Å, $c = 4.266(1)$ Å) affect the magnetic properties. The problem of nonstoichiometry in this type of structure was examined in detail by M. Francois and colleagues [2].

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3. Magnetic structures

The magnetic structures of the presented compounds were determined using neutron diffraction method. The diffraction patterns were analyzed using the Fullprof [3], a Rietvel d -type program [4]. Other complementary measurements such as magnetic susceptibility, magnetization, specific heat, electrical resistance were also used to study the magnetic properties.

The magnetometric measurements of RT_xX_2 ($R = Tb-Er$) compounds showed that all of them are antiferromagnets below the respective Néel temperatures. The Table I below presents the data collected for RT_xX_2 .

TABLE I

The data collected for RT_xX_2 (where $R = Tb-Er$, $T=3d$ element, $X = Si, Ge, Sn$) compounds with $CeNiSi_2$ type crystal structure

Comp.	TMO	MMD	T_N [K]	μ_s [μ_B]	Ref.
TbCoSi ₂	AF(G+ spiral*)	$\parallel c$	16	9.16 (5.2, 7.54*)	[5]
DyCoSi ₂	AF(G)	$a - c$	10	5.74	[6]
HoCoSi ₂	AF(G)	$\parallel a$	6.3	6.72	[6]
ErCoSi ₂	AF(SM, $k=(0.467,0,0.5)$)	$a - c$	2.6	4.63	[7]
TbNiSi ₂	AF(G)	$\parallel c$	36.2	8.7	[8]
DyNiSi ₂	AF(SM, $k_1=(0,0.2,0)$, $k_2=(0,1,0)=5k_1$, $k_3=3k_1$)	along c	24, 22	7.5	[9]
HoNiSi ₂	AF(A)	$\parallel c$	10	8.13	[10]
ErNiSi ₂	AF(SM, $k_1=(0.5,0,0)$, $k_2=(0.1262,$ $0.022,0.2273)$)	along b	3.4	7.6	[11]
TbMn _{0.33} Ge ₂	AF(G+SM, $k=($ $0.6885,0.066,$ $0.1701)$ *)	$\parallel c$, along a^*	26	8.2 (6.95, 4.5*)	[12]
HoMn _{0.33} Ge ₂	AF(G)	$\parallel c$	7	7.3	[13]

TABLE I (cont.)

Comp.	TMO	MMD	T_N [K]	μ_s [μ_B]	Ref.
TbFe _{0.25} Ge ₂	AF(G+SM, $k=(0.460,0,0.305)^*$)	$\parallel c, b-c^*$	22.6, 19.8*	4.05, 7.82*	[14]
HoFe _{0.33} Ge ₂	AF ($k=(0.5,0.5,0)$)	$\parallel c$	8	5.4	[15]
ErFe _{0.33} Ge ₂	AF(C)	$\parallel a$	2.5	5.9	[16]
TbNiGe ₂	AF(G)	$\parallel c$	37	8.8	[17]
TbNi _{0.4} Ge ₂	AF(G)	$\parallel c$	16	5.6	[18]
TbNi _{0.6} Ge ₂	AF(G+SM, $k=(0.237,0,0.294)$)	$\parallel c$	31	8.88	[19]
TbNi _{0.8} Ge ₂	AF(G+SM, $k=(0,0.462,0)$)	$\parallel c$	38	8.72	[19]
HoNi _{0.64} Ge ₂	AF(G)	$\parallel c$	11	6.7	[17]
ErNi _{0.65} Ge ₂	AF(G)	$\parallel a$	2.3	2.9	[16]
HoCo _{0.4} Ge ₂	AF ($k=(0.5,0.5,0)$)	$a-c$	8	8.0	[20]
ErCo _{0.4} Ge ₂	AF(SM, $k=(0.548,0.548,0)$)	$\parallel c$	1.5	3.3	[20]
ErCo _{0.47} Ge ₂	AF(SM, $k=(0.553,0.553,0)$)	$\parallel c$	1.5	3.3	[20]
TbCu _{0.4} Ge ₂	AF(G)	$\parallel c$	39	8.82	[18]
HoCu _{0.33} Ge ₂	AF(G)	$\parallel c$	8	8.18	[21]
ErCu _{0.25} Ge ₂	AF(G)	$\parallel a$	4.5	7.89	[21]
TbCr _{0.3} Ge ₂	AF($k_1=(0.5, 0,0)$ $k_2=(0.5, 0,0.5)$)	$\parallel c, a-c$	18.5	7.6, 4.52	[22]
DyCr _{0.3} Ge ₂	AF($k_1=(0.5, 0,0)$ $k_2=(0.5, 0,0.5)$)	$a-c$	11.8	4.46, 7.18	[22]
HoCr _{0.3} Ge ₂	AF($k=(0.5,0.5,0)$)	$\parallel c$	5.8	6.99	[22]
ErCr _{0.3} Ge ₂	AF ($k=(0,0,0.4187)$)	$\parallel a$	3.4	8.32	[22]
TbNi _{0.26} Sn ₂	AF(A, $k=(0,0,0.5)$)	$a-c$	17.4	8.05	[23]
DyNi _{0.22} Sn ₂	AF(G+SM, $k=(0.361,0,0.343)$)	$b-c$	8	9.2	[24]
HoNi _{0.16} Sn ₂	AF(A, $k=(0.5,0.5,0)$)	$a-c$	6.6	7.46	[23]
ErNi _{0.15} Sn ₂	AF(C, $k=(0,0,0.5)$)	$\parallel a$	4	9.16	[25]
TbCo _{0.25} Sn ₂	AF(A, $k=(0,0,0.5)$)	$a-c$	18.8	7.14	[26]
HoCo _{0.23} Sn ₂	AF(A, $k=(0.5,0.5,0)$)	$a-c$	5.6	6.79	[26]
ErCo _{0.24} Sn ₂	AF(C)	$\parallel a$	4.5	6.15	[25]
TbFe _{0.15} Sn ₂	AF(A, $k=(0,0,0.5)$)	$b-c$	18.4	8.1	[27]
DyFe _{0.15} Sn ₂	AF($k=(0,0,0.5)$)	$b-c$	6.9	5.5	[27]
HoFe _{0.14} Sn ₂	AF($k=(0.5,0.5,0)$)	$b-c$	5.9	6.6	[27]
ErFe _{0.11} Sn ₂	AF($k=(0.5,0.5,0)$)	$\parallel a$	5.5	7.3	[27]
TbSn _{1.12} Ge _{0.88}	AF(SM, $k=(0.4257,0,0.588)$)	$b-c$	31	9.1	[28]
DySn _{1.09} Ge _{0.91}	AF($k=(0.5,0.5,0)$)	$\parallel c$	16	7.25	[29]
HoSn _{1.1} Ge _{0.9}	AF($k=(0.5,0.5,0)$)	$\parallel c$	10.7	8.6	[28]
ErSn _{1.08} Ge _{0.92}	AF($k=(0.5,0.5,0)$), SM- $k=(0.496,0.446,0)$)	$\parallel b, b-c^*$	4.8	7.76	[28]

TMO: type of magnetic ordering, MMD: magnetic moment direction, AF: antiferromagnetic structure, SM: sine-modulated structure, A,C,G: type of magnetic structures according Bertaut symbolism, A(+ - - +), C(+ + - -), G(+ - + -), T_N : Néel temperature, μ_s : magnetic moment value in ordered state.

4. Discussion

The data presented above have shown that the RT_xX_2 compounds of the CeNiSi₂-type structure with Si form stoichiometric compounds but with Ge and Sn form defected arrangements on the T sublattice, which is conditioned by the size of X element atoms and filling of the d -electron shell of the transition metal T. Among the compounds with Ge and Sn, there exist families which crystallize as stoichiometric systems, for example RNiSn₂ [30] or RTGe₂ (T = Ir, Pd, Pt) [31], but they have a different crystal structure although they are orthorhombic too, and associated with the CeNiSi₂ structure.

It turns out that in all RT_xX_2 compounds with heavy rare earth, the antiferromagnetic ordering is observed at low temperatures and lots of variants of magnetic structures ranging from simple collinear (G,A,C according to the Bertaut Symbolism [32]) to the sine-modulated structures with commensurate or incommensurate propagation vector.

In all these ternaries the magnetic ordering is the result of the competitive long-range interactions of the RKKY-type [33–35] between the rare-earth magnetic moments (distance between adjacent atoms of the rare earth is about 4 Å) additionally influenced by crystal electric field (CEF) [36] and probably also by small quadrupole–quadrupole interactions. The transition metal atoms do not have localized magnetic moments.

The electronic structure studies of the CeCo_{0.86}Ge₂ [37] compound carried out by XPS method indicate hybridization of Ce $4f$ states with transition metal $3d$ and Ge $4p$ states, and that the Co $3d$ band is below the Fermi level, which explains the absence of a localized magnetic moment on the transition metal atom. Similarly, the XPS spectra analysis conducted for NdCo_{0.82}Ge₂ and PrCo_{0.85}Ge₂ [38] showed hybridization $4f$ electrons of the rare earth with conduction band, indicating good shielding of the f -shell of these compounds.

The electronic properties of RCrGe₂ and RCr_{0.3}Ge₂ (R = Tb, Dy, Ho or Er) were also investigated theoretically applying plane-wave DFT/PBE methodology [39]. The computational investigations confirm that the rare-earth atoms are arranged in double-layer slabs and they have essential impact on the magnetic properties of investigated compounds. It was also observed that for the stoichiometric structure the important charge is located at the Cr atoms and suggest that the R atoms and Cr possess spin-unpaired electrons. It gives conclusion that in RCrGe₂ stoichiometric crystals the Ge-electrons are shifted to the Cr atoms. The creation of nonstoichiometric RCr_{0.3}Ge₂ crystals change the distances between atoms, the R atoms are closer one to the other and simultaneously are more far from the Cr atoms. Thus, for the nonstoichiometric compounds their magnetism originates from the magnetic moments of f electrons localized on the R atoms and the d electrons of Cr do not contribute to the magnetic properties of the crystals as it was for the stoichiometric structure.

The theoretical LSDA+U calculations for TbNiGe₂, performed by Gupta [40], shown no spin polarization from Ni 3*d* electronic states and reproduce the antiferromagnetic long-range ordering of the Tb magnetic moments and their values in good agreement with the previous neutron diffraction data.

The crystal electric field influence on the ordering of magnetic moments is confirmed by the following effects:

- in all series of compounds a decrease in the magnitude of magnetic moments in the ordered state compared to the free ion R³⁺ values is observed;
- determined magnetic structures for compounds with Sn are different than for those with Ge or Si. Among them there are compounds with simple antiferromagnetic structure and the magnetic moment is along the *c*-axis, but there are also compounds where the magnetic moment of the rare earth forms an angle with the *c*-axis.

These results indicate that changing the *p*-electron element X from Si to Ge and Sn influences magnetic interactions and leads to changes in the direction of the magnetic moments.

The calculations of CEF parameters of RT_xX₂ [41, 42] suggest that the preferred direction of magnetic moment occurs in the plane (010) as well as that the B_2^0 , B_2^2 and B_4^0 parameter play an important role in the CEF Hamiltonian. Changing the direction of the magnetic moments may be related to sign changes of the Stevens α_J coefficient [43, 44] from negative for R = Tb-Ho to positive for R = Er and one can see such tendency among presented compounds.

Analysis of the magnetic properties of RSn_{1+x}Ge_{1-x} compounds shows similarity to the RT_xX₂ compounds. In RSn_{1+x}Ge_{1-x} compounds (R = Dy, Ho, Er) magnetic ordering at temperature T = 1.5 K can be described by the propagation vector $\mathbf{k} = (0.5, 0.5, 0)$, as in most compounds with Ho, Ge and Sn, e.g.: HoCr_{0.33}Ge₂ [22], HoCo_{0.4}Ge₂ [20], HoSn₂ [45], HoFe_{0.14}Sn₂ [27], HoCo_{0.23}Sn₂ [26], HoNi_{0.16}Sn₂ [23] — it is the most frequently occurring type of structure. The other most frequently occurring type of structure is AF, which can be described by the wave vector $\mathbf{k} = (0, 0, 0.5)$.

The role of the T-element in interactions between the magnetic moments of the investigated compounds seems to be insignificant. The results show that it does not have a localized magnetic moment. Incorporation of additional T atoms into the crystal lattice results in increased lattice constants and thus also in increased distance between the rare earth atoms. This results in reduction of Néel temperature (compare the values for RT_xSn₂ and RSn₂ [45] compounds). Another effect is stabilization of the collinear magnetic structures. In the RT_xSn₂ compounds collinear structures are stable up to T_N, while in RSn₂ transition to non-collinear modulated structures is observed near the T_N. Such behavior is observed in many rare earth intermetallic compounds, and is associ-

ated with competition between the RKKY-type interactions and crystalline electric field [46]. A small role of *d*-electron element was also confirmed by the investigations of RSn_{1+x}Ge_{1-x} compounds which have magnetic structures similar to the RT_xSn₂ compounds.

The role of *p*-electron element is difficult to determine. For example, the AF ($\mathbf{k} = (0.5, 0.5, 0)$) type structure is observed in all compounds except HoT_xGe₂ where T = Ni, Cu. The role of individual element is more evident in the analysis of the magnetic moments direction. In the RSn₂ compounds magnetic moments for R = Tb-Ho are parallel to the *c*-axis, while for R = Er they are parallel to the *a*-axis what is in agreement with the change of the sign of Stevens α_J constant. Incorporation of *d*-electron element causes the magnetic moments lie in the *b* – *c* or *a* – *c* plane. This shows that *d*-electron elements significantly affect altering of the parameters of the crystal electric field. It is also surprising that in TbCo_xGe₂ and DyCo_xGe₂ compounds there is no magnetic ordering, whereas for compounds with Ho and Er the magnetic ordering is observed. This fact demonstrates the complexity of magnetic interactions in this family of compounds and is difficult to explain.

5. Conclusions

The results shown in this article allow to systematize macroscopic properties (like: type of arrangement, the critical temperatures of magnetic orderings) and microscopic (like: type of arrangement and values of the rare earth magnetic moments, no magnetic moment localized on the *d*-element atoms) for the RT_xX₂ compounds. Systematization of designated magnetic structures, may help to find answer to questions concerning the mechanisms of interaction between the magnetic moments and the impact of the *d*- and *p*-electron elements on stabilization determined structures.

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