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Magnetic interaction in RT_xX_2 ternary compounds

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This work is an attempt to systematize the magnetic properties of RT_xX_2 (R – rare earth, T – transition metal, X – Si, Ge, Sn) compounds crystallizing in the orthorhombic $CeNiSi_2$-type structure. All silicides crystallize in the stoichiometric structure RTX_2, while germanides and stannides form mainly defected RT_xX_2 structures ($0 < x < 1$). This family of compounds exhibits a complex magnetic behaviour. Two factors influencing stability of various magnetic structures are considered with the purpose of finding the magnetic ordering scheme: magnetic interactions of the RKKY type and crystal electric field effect.

Key words: *rare earth compounds; magnetic structure; RKKY model; crystal electric field effect*

1. Introduction

RT_xX_2-type metallic compounds, where R is a rare-earth element, T is a 3d-electron element, and X is a p-electron element (X = Si, Ge, Sn) have been intensively investigated. The majority of these compounds crystallize in the orthorhombic $CeNiSi_2$-type structure [1].

The research is partially motivated by the possibility of obtaining novel, promising magnetic materials. The atoms in these structures: Ce (R), Ni (T), Si1 (X1), and Si2 (X2) occupy the 4(*c*) positions – $(0, y, 1/4)$, $(0, -y, 3/4)$, $(1/2, 1/2 + y, 1/4)$, $(1/2, 1/2 - y, 3/4)$ with different values of the y parameter.

All silicides crystallize in the stoichiometric structure, while germanides and stannides form mainly defected RT_xX_2 structures ($0 < x \leq 1$) with vacancies in the transition metal sublattice [2]. The stability of the crystal structure is determined by the radius of the X atoms (Si, Ge, Sn) and the degree in which the 3d band of the T element is filled up [3].

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2. Magnetic properties

Magnetic properties of RT_xX_2 compounds were studied by means of magnetic susceptibility and neutron diffraction measurements. All the magnetic data for RT_xX_2 compounds can be found in Refs. [4–37]. The measurements indicate that the majority of these compounds order antiferromagnetically at low temperatures. Above their Néel temperatures, their effective magnetic moments are close to free R^{3+} ion values $g(J(J + 1))^{1/2}$. Only for compounds with T = Mn, the magnetic moment localized on Mn is observed.

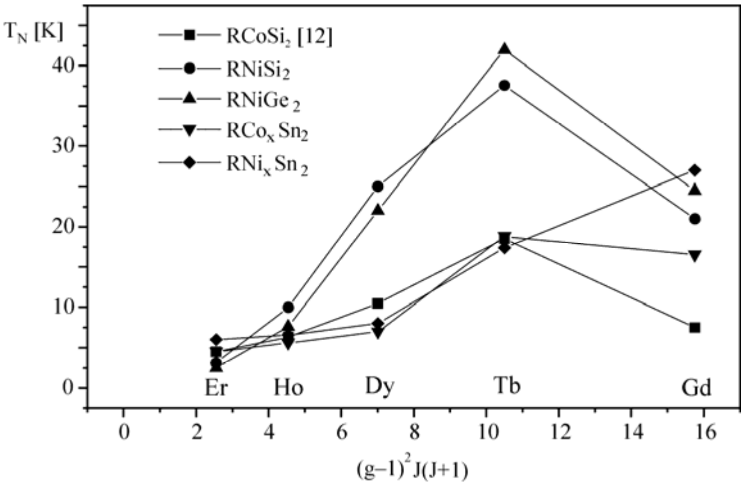

Fig. 1. Observed Néel temperatures in some RT_xX_2 intermetallics versus the de Gennes function $(g - 1)^2J(J + 1)$

Crystal structure of the compounds under investigation has a distinct layer character. Rare-earth atoms occupy layers perpendicular to the *b*-axis and are separated by layers of other atoms. In the majority of the compounds, the magnetic moments located on the same planes are coupled ferromagnetically, while the coupling between moments on adjacent planes is antiferromagnetic. The R^{3+}–R^{3+} distances are large (in $TbNiSi_2$ $d_{R-R} = 4.012$ Å, in $TbNiGe_2$ $d_{R-R} = 4.086$ Å, and in $TbNiSn_2$ $d_{R-R} = 4.021$ Å), 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 as described by the RKKY model [38–40]. RKKY interactions are long-range, which should in general lead to modulated magnetic structures. In the case of the studied series, one can observe a wide variety of orderings: collinear and non-collinear.

In this mechanism, the ordering temperature T_N should be proportional to the de Gennes factor [41]: $G = (g - 1)^2J(J + 1)$, where g is the Landé factor and J the total angular momentum of the considered rare-earth ion, which is highest for Gd-containing compounds. For the majority of systems, the maximum appears at R = Tb

(Fig. 1). The $T_{c,N}$ shift may result from the crystalline electric field effect (CEF). Thus, CEF terms should be added to the exchange Hamiltonian. The rare-earth ions are in the 4(*c*) sites of low *mm* symmetry. Neither experimental nor calculated data concerning CEF parameters for RTX_2 are available.

A comparison of structural and magnetic properties for the stoichiometric $TbNiGe_2$ compound and non-stoichiometric $TbNi_xGe_2$ compounds indicates that the lattice parameter *b* decreases from 16.681 Å to 16.142 Å with decreasing concentration *x* of Ni, and the ordering temperature T_N also decreases linearly from 42 K to 16 K. The antiferromagnetic structures are similar, whereas the magnetic moments are different. Increasing the number of defects in the Ni sublattice decreases the distances between the Tb planes, which should lead to an increase in the Néel temperature, but this is not observed.

According to RKKY theory, the exchange integral $J(R_{ij})$ between *i*-th and *j*-th magnetic ions is proportional to the conduction electron density of states at the Fermi surface for one spin direction $N(E_F)$ and to the oscillating function $F(x)$ of the distance R_{ij} and Fermi vector $\mathbf{k}_F$: $J(R_{ij}) \sim N(E_F)F(x)$, where $F(x) = (x\cos x - \sin x)x^{-4}$, and $x = 2k_FR_{ij}$. The function $F(x)$ depends on the Fermi vector, which is connected to the concentration of conduction electrons. XPS measurements of intermetallic compounds RNiX [42] have shown that the 3d band of Ni is close to the Fermi level. A change in the Ni concentration leads to a reduction of the number of states at the Fermi level and influences the strength of ordering.

One can also describe the magnetic ordering in RTX_2 compounds by five exchange integrals: J_1 and J_2 within the same (010) plane, which are strongly ferromagnetic, and J_3–J_5 describing the coupling between planes (Fig. 2).

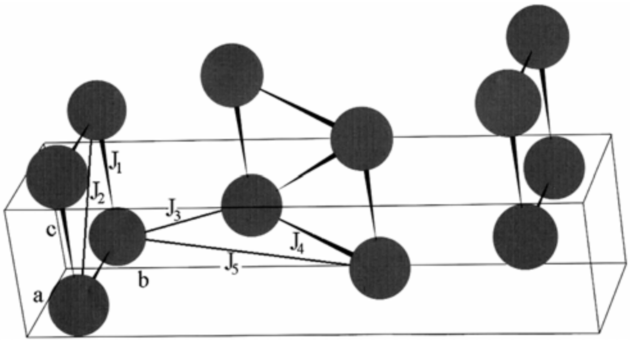

Fig. 2. Exchange integrals describing the ordering between magnetic ions in the crystal structure of $CeNiSi_2$

In the G-type antiferromagnetic structure [43], most often observed in RTX_2 compounds with the $CeNiSi_2$-type crystal structure, the exchange integral J_5 is positive, while J_3 and J_4 are negative. In the A-type antiferromagnetic structure, observed in $HoNiSi_2$, J_3 is positive while J_4 and J_5 are negative; in the C–type structure observed in $CeCu_{0.86}Ge_2$, J_4 is positive while J_3 and J_5 are negative.

In compounds with a complex magnetic structure, where the magnetic cell is either commensurate or incommensurate with the crystal structure, the magnetic ordering is compatible with one of the above-mentioned models. The appearance of complex magnetic structures suggests that long-range magnetic ordering, probably realized by conduction electrons, plays a dominant role in forming the magnetic ordering.

Ferromagnetic ordering is observed in the compounds with Pr and Nd. The majority of compounds with Si and Ge order antiferromagnetically, and the magnetic structure is of the G (+ – + –) type but compounds with Sn are antiferromagnetics of the A (+ – – +) or C (+ + – –) type.

The ordering described by the J_3 exchange integral is realized through the layer with T and X elements, and J_4 is realized through p-electron atoms, but J_5 is described by long-range ordering probably realized by conduction electrons. J_5 is negative for compounds with Sn (A, C structure types), while for compounds with Si and Ge it is positive. The unit cell volume for Sn compounds is larger than for Si, Ge compounds and suggests the differences in interatomic distances. According to RKKY theory, the exchange integral oscillates with the distance R_{ij} and Fermi vector $\mathbf{k}_F$, a change in the sign of the integral is therefore possible.

Another feature, which mainly determines the magnetic properties of rare-earth compounds, is the interaction of 4f electrons with the electric charges of the surrounding ions [44], as described by the Hamiltonian:

$$H_{CF} = \sum_{n=0}^{n'} \sum_{m=-n}^{+n} B_n^m O_n^m \left(J\right)$$

where B_n^m are the crystal field parameters and $O_n^m \left(J\right)$ represent polynomials of the the angular momentum operators J_z, J^2, J_+, and J_-. Crystal electric field effects are responsible for the observed decrease of the rare-earth magnetic moments as compared to the free ion values gJ.

The rare-earth site in RTX_2 compounds has the point symmetry *mm*. In such a symmetry, the CEF Hamiltonian can be written as:

$$H_{CF} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4$$

The B_n^m parameters were determined for RTX_2 compounds using the so-called point-charge model [45]. Computations were performed for the nearest neighbours. The results of calculations are shown in the table (the sixth-order parameters were omitted, because they are very small).

The results of calculations suggest that the fact that the preferred alignment of the magnetic moment is in the (010) plane, as well as B_2^0, B_2^2, and B_4^0, play an important role in the CEF Hamiltonian.

In most of the studied compounds with the $CeNiSi_2$-type crystal structure, the orientation of magnetic moments agrees with the positive sign of the B_2^0 parameter (along the *c*-axis) but for the compounds with Er, a negative sign of the parameter B_2^0 suggests that the *b*-axis is the preferred direction, but this is not obeyed.

Table 1. Crystal electric field parameters for $RNiSi_2$ compounds calculated using the so-called point-charge model.

R	B_2^0 [meV]	B_2^2 [meV]	B_4^0 [meV]	B_4^2 [meV]	B_4^4 [meV]
Ce	2.741	9.445	6.979	–0.229	–0.257
Pr	0.907	3.126	–0.656	0.022	0.024
Nd	0.256	0.882	–0.222	0.007	0.008
Tb	0.307	1.058	0.055	–0.002	–0.002
Dy	0.184	0.634	–0.025	0.001	0.001
Ho	0.061	0.209	–0.012	0.0004	0.0004
Er	–0.067	–0.231	0.014	–0.0005	–0.0005

3. Conclusions

The discussed compounds crystallize in an orthorhombic crystal structure of the $CeNiSi_2$ type. They exhibit complex magnetic behaviour. It is well established that in these compounds (except those with T = Mn) the magnetic moment is localized only on rare-earth atoms. Their magnetism arises from the interaction of the magnetic moments localized on rare-earth ions.

Large interatomic R–R distances (about 4 Å) suggest that the stability of the observed magnetic ordering scheme is due to interactions via conduction electrons (RKKY model).

The Néel and Curie temperatures determined for the presented families only in part follow the de Gennes scaling. This effect suggests that the main interaction leading to magnetic ordering in these systems is not purely of the RKKY-type but is modified by the crystalline electric field effect which can significantly influence the Néel temperature. CEF effects are also responsible for the observed decrease in rare-earth magnetic moments as compared to free ion values.

The conclusion may thus be drawn that the CEF plays a significant role in stabilizing magnetic ordering schemes, so that determining the CEF parameters is of great importance in understanding the nature of the magnetic properties of intermetallic compounds.

The magnetic structures of the investigated stannides are different than those reported for isostructural stoichiometric RTX_2 silicides and germanides, which have simple antiferromagnetic structures with a magnetic unit cell being the same as the crystallographic one. The sequence of magnetic moments corresponds to the G-mode (+ – + –). In the silicides and germanides, the magnetic moments are aligned along the *c*-axis. In the stannides investigated in this work, the rare-earth magnetic moments form an angle with the *c*-axis. These results indicate that changing the X element (p-electron element) from Si, Ge to Sn influences magnetic interactions and leads to a change in the direction of the magnetic moments.

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