CRYSTALLINE ELECTRIC FIELD PARAMETERS FOR RTX₂ COMPOUNDS

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Abstract: The RTₓX₂ (x≤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 = Si, Ge, Sn) crystallize in different orthorhombic crystal structures. The systems exhibit complex magnetic behaviour. Their magnetism arises from the long range interaction of the magnetic moments localized on the rare-earth ions, described by RKKY model. The 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 magnitude of the Néel temperature and decrease the rare-earth magnetic moments as compared with the free ion values. The determination of the CEF parameters is important for understanding the nature of magnetic properties of intermetallic compounds. The \( B'_n \) parameters were calculated for RTX₂ compounds using the so-called point-charge model. The quadrupole splitting observed in the Mössbauer spectra of GdTxSn₂ compounds (T = Fe, Co, Ni, Cu) allow to determined the experimental values of \( B'_2 \) parameters for RTX₂ compounds.

1. Introduction
The RTₓX₂ compounds (x ≤ 1) where R is a rare-earth, T is a d-electron metal and X (T = Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir, Pt) is a p-electron metalloid (X = Si, Ge, Sn) crystallize in different orthorhombic crystal structures [1]:
- CeNiSi₂–type (space group Cmcm);
- TbFeSi₂–type, which is very similar to the CeNiSi₂, but R, T and Si atoms are located in alternating layers;
- YIrGe₂–type (space group I4mm);
- 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).

All silicides crystallize in the stoichiometric structure (x=1), while germanides and stannides form mainly defected structures RTₓX₂ (x<1) with defects in d-electron metal sublattice. Majority of these compounds crystallize in the orthorhombic CeNiSi₂–type structure [2]. The RTGe₂ (R = Gd-Er, T = Ir, Pd, Pt) crystallize in YIrGe₂–type structure [3]. The rare earth atoms are distributed over two distinct sublattices: 4(i) and 4(h) sites with different atomic coordination. The rare-earth atom in 4(i) site has similar atom coordination as in the CeNiSi₂ type structure.
During the last few years the $\text{RT}_x\text{X}_2$ type intermetallic compounds have been a subject of intensive studies because of their intriguing physical properties, which have both fundamental and practical significance.

2. Magnetic properties

Intermetallic compounds, described in this paper, contain two kinds of elements: f-electron (lanthanide) and d-electron transition element which exhibits different properties due to localized behavior of “magnetic electrons”. The electronic configuration of rare earth metals is $4f^n5d^16s^2$; the 4f electrons are well localized and they are responsible for magnetic properties of these compounds. The 5d and 6s electrons are delocalized and give rise to the conduction band.

Magnetic measurements of $\text{RT}_x\text{X}_2$ compounds indicate that majority of compounds order antiferromagnetically at low temperatures. Above the Néel temperatures, the effective magnetic moments are close to the free $\text{R}^{3+}$ ion values:

$$\mu_{\text{eff}} = g_J\mu_B\sqrt{J(J+1)}$$

where $g_J$ is the Landé factor and $J$ – the total angular momentum of the rare-earth ion.

Only for compounds with $T = \text{Mn}$, a localized magnetic moment on Mn has been observed.

The crystal structure has a distinct layer character. Rare-earth atoms occupy the layers perpendicular to the b-axis, and they are separated by layers of other atoms. In majority of compounds, the magnetic moments located in the same planes are coupled ferromagnetically, while the coupling between two moments in adjacent planes is antiferromagnetic.

Magnetic data for the $\text{RT}_x\text{X}_2$ ternary compounds are summarized in Ref. [4].

In the $\text{RTGe}_2$ compounds the 4(h) sublattice orders magnetically at the temperature lower than the ordering temperature within the 4(i) sublattice. It indicates that coupling between magnetic moments within the 4(h) sublattice is weaker than in the 4(i) one, and that there is an additional contribution to the exchange fields on the 4(h) sites, arising from the 4(i) sublattice.

In all series of compounds, the $\text{R}^{3+}$--$\text{R}^{3+}$ distances are large (about 4 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 described by the RKKY model [5–7]. In this mechanism, the ordering temperature should be proportional to the de Gennes factor [8]:

$$G = (g_J - 1)^2 J(J+1),$$

and the highest ordering temperature should be found in the Gd-containing compounds. Contrary to the latter expectation, in majority of presented systems, the $T_N(G)$ dependence is peaked around the value of $G$ corresponding to terbium (Fig. 1). The $T_{CN}$ shifting may result from the crystalline electric field effect CEF. This is why the CEF terms should be added to the exchange Hamiltonian. The rare earth ions are in the 4(c) site of the low symmetry mm.

![Figure 1](image-url). Observed Néel temperatures in some $\text{RT}_x\text{X}_2$ intermetallics vs de Gennes function
3. Crystal electric field effect

The interaction of the CEF with the moments of rare-earth atom electrons is given by the Hamiltonian [9]:

\[ H_{CF} = \sum_{n=0}^{n'} \sum_{m=-n}^{n} B_n^m O_n^m(J) \tag{3} \]

where \( n' \) takes a maximum value of \( n \) appropriate to the rare-earth atom considered, \( B_n^m \) are the crystal field intensity parameters and \( O_n^m(J) \) represent polynomials of the angular momentum operators \( J_+ \), \( J_- \), \( J_z \) and \( J^2 \).

The rare-earth site in the RTX2 compounds has the point symmetry \( mm \). In such symmetry the CEF Hamiltonian can be written as follows:

\[ H_{CF} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6 \tag{4} \]

When \( B_2^0 \) is the leading term in the crystal field Hamiltonian, then its sign gives information about the single ion magnetic anisotropy. For a positive value of the \( B_2^0 \) parameter the basal plane (\( \perp z \)) is preferred for the magnetic moment direction while for a negative value an ordering along \( z \)-axis is anticipated [10].

The neutron diffraction data collected in Ref. [4] indicate that the rare-earth magnetic moments in RTX2 compounds prefer the orientation in the basal plane (010). In majority of RTX2 compounds with \( R = \text{Pr}, \text{Nd}, \text{Tb}, \text{Ho} \), the rare-earth moments are parallel to the \( c \)-axis and for \( R = \text{Er} \) the magnetic moment is parallel to the \( a \)-axis.

The \( B_n^m \) parameters were determined for RTX2 compounds using the so-called point-charge model [11] taking \( b \)-axis as \( z \)-axis and \( c, a \)-axes as \( x, y \)-axes respectively. In this approximation the electrostatic potentials of the most important neighbours are summed. The parameters \( B_n^m \) can be written as:

\[ B_n^m = \langle \theta_n^m \rangle \langle r^n \rangle K_n^m A_n^m \tag{5} \]

Values for \( \langle \theta_n^m \rangle \langle r^n \rangle \) have been collected by Franse and Radwański [12]. The \( K_n^m \) are constants and the coefficients \( A_n^m \) are known as the CEF coefficients.

The computations were made for the nearest neighbours (see Fig. 2). The \( B_2^0 \), \( B_2^2 \) and \( B_4^0 \) parameters are given by the formulas:

\[ B_2^0 = -\alpha_f \langle r^2 \rangle \frac{\pi e^2}{20} \sum_i Z_i \left( 3 \cos^2 \theta - 1 \right) \]
\[ B_2^2 = -\alpha_f \langle r^2 \rangle \frac{\pi e^2}{10} \sum_i Z_i \left( 2 \cos^2 \phi - 1 \right) \]
\[ B_4^0 = -\beta_f \langle r^4 \rangle \frac{4 \pi e^2}{9} \sum_i Z_i \left( 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \right) \]

where \( Z_i \) is the charge of the ion, which is located in the \((R_i, \theta_i, \phi_i)\) position.
The nearest neighbours of a rare atom in the RTX2 compounds (CeNiSi₂ – type crystal structure)

The results of calculations of $B_n^m$ are shown in Table 1 (the sixth-order parameters were omitted because they are very small).

The calculations suggest that the preferred direction of magnetic moment occurs in the plane (010) as well as that the $B_2^0$ and $B_2^2$ and $B_4^2$ parameter play an important role in the CEF Hamiltonian.

**Table 1.** Crystalline electric field parameters for RNiSn₂ compounds calculated using the so-called point-charge model

| R      | $B_2^0$ [meV] | $B_2^0$* [meV] | $B_2^2$ [meV] | $B_2^0$ [meV] | $B_2^2$ [meV] |
|--------|---------------|----------------|---------------|---------------|---------------|
| Ce     | 2.5547        | -2.5041        | 8.6024        | -0.1908       | -0.2368       |
| Pr     | 0.8456        | -0.8550        | 2.8474        | 0.0179        | 0.0222        |
| Nd     | 0.2386        | -0.2397        | 0.8035        | 0.0061        | 0.0075        |
| Tb     | 0.2862        | -0.2780        | 0.9637        | -0.0015       | -0.0019       |
| Dy     | 0.1715        | -0.1681        | 0.5774        | 0.0007        | 0.0009        |
| Ho     | 0.0566        | -0.0561        | 0.1906        | 0.0003        | 0.0004        |
| Er     | -0.0624       | 0.0613         | -0.2103       | -0.0004       | -0.0005       |

* the $B_2^0$ parameters determined using the magnitude of quadrupole splitting $\Delta E_Q$

In the most of studied compounds with the CeNiSi₂ – type crystal structure the orientation of magnetic moments agree with the positive sign of the $B_2^0$ parameter (along the c-axis) but for the compounds with Er the negative sign of $B_2^0$ parameter suggests the b-axis as the preferable direction.

It has been also found that a decrease in the number of defects in the Ni sublattice leads to an increase of the $B_2^0$ parameter and to a reduction of the $B_2^2$ parameter [4].

The samples of gadolinium stannides GdTₓSn₂ (T = Fe, Co, Ni and Cu) have been studied by $^{119}$Sn and $^{155}$Gd Mössbauer spectroscopy [13].

Since the trivalent gadolinium ions are in the ground electronic states with spherical distribution of 4f electronic charge, only the lattice term contributes to the magnitude of $V_{zz}$ in the rare earth site. Hence, the determination of the sign and magnitude of $\Delta E_Q = eV_{zz}Q$ at the Gd site together with the asymmetry parameter $\eta$ allow to estimate the quadrupolar terms $B_2^0$ and $B_2^2$ in Stevens expansion of the crystal field Hamiltonian, as they are related by two simple formulas:

$$B_2^0[K] = -\alpha_J \cdot \left\langle r^2 \right\rangle_{4f} \cdot 90.2 \cdot \Delta E_Q(^{155}Gd), \quad B_2^2 = \eta B_2^0. \quad (7)$$

Here, $\alpha_J$ is the appropriate Stevens factor; the mean squared radius of the 4f wave function $\left\langle r^2 \right\rangle_{4f}$ is expressed in atomic units and $\Delta E_Q$ in mm/s.
Görlich et al. [13] determined $\Delta E_0 = -0.32$ mm/s for GdNi$_{0.32}$Sn$_2$ compound and I determine the $B_2^0$ parameters for RNixSn$_2$ compounds which are shown in Table 1 ($B_2^0$*).

The differences in $B_2^0$ signs are not clear and more detailed analysis must be done.

The CEF effect is also visible in RTGe$_2$ (R = Pd, Pt, Ir) compounds. Rare earth atoms occupy the $4(i)$ and $4(h)$ sites with the same point group $mm$ but different atomic coordination (see Fig. 3). This results in different $B_{2m}$ parameters (Table 2) and different magnetic moment directions in particular sublattices.

![Figure 3. The nearest neighbours of a rare atom in the RPtGe$_2$ compounds: a) Tb in $4(i)$ sublattice, b) Tb in $4(h)$ sublattice](image)

| Table 2. Crystalline electric field parameters for RPtGe$_2$ (R = Tb–Er) compounds |
|---|---|---|---|---|---|---|
| R  | Sublattice | $B_2^0$ [meV] | $B_4^2$ [meV] | $B_2^0$ [meV] | $B_4^2$ [meV] | $B_4^4$ [meV] |
| Tb | $(4i)$ | 3.906 | 1.040 | 0.084 | -0.002 | -0.0008 |
|   | $(4h)$ | -0.692 | 3.634 | 0.078 | -0.005 | -0.003 |
| Dy | $(4i)$ | 2.340 | 0.623 | -0.039 | 0.001 | 0.0004 |
|   | $(4h)$ | -0.415 | 2.177 | -0.036 | 0.002 | 0.001 |
| Ho | $(4i)$ | 0.772 | 0.206 | -0.018 | 0.0005 | 0.0002 |
|   | $(4h)$ | -0.137 | 0.719 | -0.016 | 0.001 | 0.0006 |
| Er | $(4i)$ | -0.852 | -0.227 | 0.022 | -0.0006 | -0.0002 |
|   | $(4h)$ | 0.151 | -0.793 | 0.020 | -0.001 | -0.0008 |

4. Summary

The discussed RTX$_2$ compounds crystallize in the orthorhombic crystal structures of the CeNiSi$_2$ and YIrGe$_2$ types. The silicides form stoichiometric compounds while germanides and stannides show mainly non stoichiometric structures.

Their magnetism arises from the interaction of the magnetic moments localized on the rare-earth ions. The large interatomic R-R distances (about 4 Å) and the appearance of complex magnetic structures suggest that long-range magnetic ordering, realized probably by conduction electrons (RKKY model) play a dominant role in forming the magnetic ordering.

The observed decrease in the magnitude of the Néel temperature and rare-earth magnetic moments as compared with the free ion values suggests that the main interaction is not purely of the RKKY-type but is modified by the crystalline electric field effect.

The calculations of CEF parameters suggest that the preferred direction of magnetic moment occurs in the plane (010) as well as that the $B_2^0$ and $B_4^2$ parameter play an important role in the CEF Hamiltonian. In the most of studied compounds the orientations of magnetic moments agree with the positive sign of the $B_2^0$ parameter (along the c-axis).
A conclusion may thus be drawn that more information about experimentally obtained CEF parameters for this family of compounds is important.

5. References

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