

# SINGLE-ION RARE EARTH ANISOTROPY IN $\text{ThMn}_{12}$ -TYPE COMPOUNDS\*

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(Received October 1, 1993)

The single-ion rare earth anisotropy was investigated in  $\text{ThMn}_{12}$ -type compounds. For this purpose the crystal electric field parameter values were studied. In these compounds, described by formula  $\text{RFe}_{12-x}\text{T}_x$ , R = rare earth, T = Ti, V, Cr, Mo, W and Si, the T atoms have strong crystallographic site preference changing the local crystal electric field potential which "sees" the rare earth ion. The crystal electric field potentials  $A_2^0$  were calculated considering this site preference. The summations were performed taking into account the nearest neighborhood of the rare earth ion according to the recent results of band structure calculations. The charges of the surrounding Fe and T atoms were established applying the chemical bond model proposed by Pauling. The absolute value of  $A_2^0$  decreases when the content of vanadium increases in 8(i) position, which is in agreement with experimental data. Localization of Si atoms in 8(j) and 8(f) causes a decrease in  $A_2^0$ . The  $^{155}\text{Gd}$  Mössbauer spectroscopy data confirm this fact. Miedema's "macroscopic" atom model of cohesion in alloys was applied for interpretation of the role of T atoms in the isomer shift and volume effects.

PACS numbers: 75.30.Gw, 75.50.Gg

## 1. Introduction

Recent band structure calculations [1-4] showed that in the rare earth-transition metal intermetallic compounds the asphericity of the valence electron charge density of the rare earth atoms itself forms the dominant contribution to the lowest order crystal field parameter  $A_2^0$ ; the lattice contribution has also its influence. The above results are in contradiction with frequently used point charge calculations (PCC), where the charges outside the central atom produce dominant electric field gradient at the rare earth site. Sometimes, however a satisfactory description of

\*This paper was presented at the European Conference "Physics of Magnetism 93", Poznań (Poland), 1993.

crystal field effects can be obtained using point charges [5–7]. PCC can be applied when the difference of the electronegativities of the surrounding ions and rare earth ion is large (large charge transfer) and the distance between them is small (large area of contact). The above conditions are fulfilled in  $RFe_{11}Ti$  nitrides [8, 9] when rare earth atoms and surrounding nitrogen atoms are taken into account.

## 2. Pauling's chemical bond model

Taking into account the coordination of R ion at site 2(a) (see Fig. 1) the crystal electric field parameters  $A_2^0$  were calculated regarding the site preference of T atoms. The summations were performed considering only the nearest neighborhood of the rare earth atom. According to the band structure calculations of  $A_2^0$

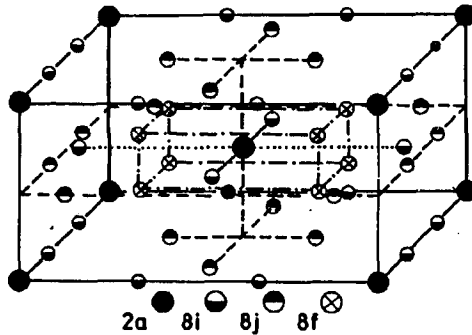


Fig. 1. The unit cell of the  $ThMn_{12}$  structure.

parameters in various rare earth–transition metal compounds [1, 2, 4], the nearest neighborhood in the vicinity of R atoms has the most important role in describing electric field gradient which “sees” the rare earth ion.

In the chemical bond model proposed by Pauling [10] the number of electrons,  $n$ , in chemical bond in metals is given by

$$n = 10^{(D(1) - D(n))/0.6}, \quad (1)$$

where  $D(1)$  is the single bonding distance and  $D(n)$  is the actual distance between the two atoms considered. The amount of ionic character of bond between atoms A and B with electronegativities  $X_A$  and  $X_B$  is given by

$$N_{\text{ionic}} = 1 - \exp[-(X_A - X_B)^2/4]. \quad (2)$$

Thus the number of electron transferred from atom A to atom B (assuming  $X_A < X_B$ ) is simply

$$n_e = nN_{\text{ionic}}. \quad (3)$$

TABLE I  
The values of single bond metallic radii  $D(1)$  and electronegativities  $X$  taken from [10].

Compound	$X$	$D(1)$ [Å]
Gd	1.2	1.623
Fe	1.8	1.165
Ti	1.5	1.324
V	1.6	1.224
Cr	1.6	1.186
Si	1.8	1.173

TABLE II  
The lattice parameters of several  $\text{GdFe}_{12-x}\text{T}_x$  compounds and corresponding distances  $D(n)$  between R ion and atoms in the nearest 8(i), 8(j) and 8(f) positions.

Compound	$a$ [Å]	$c$ [Å]	$D(n)$ [Å]		
			R-i	R-j	R-f
$\text{GdFe}_{10}\text{Si}_2$	8.460	4.797	3.055	3.062	3.223
$\text{GdFe}_{10}\text{V}_2$	8.517	4.774	3.076	3.061	3.239
$\text{GdFe}_{10}\text{Cr}_2$	8.507	4.769	3.072	3.058	3.235

TABLE III  
Calculated transferred charges from Gd ion to atoms in 8(i), 8(j) and 8(f) positions for  $\text{GdFe}_{10}\text{V}_2$  and  $\text{GdFe}_{10}\text{Si}_2$ .

$\text{GdFe}_{10}\text{V}_2$	8(i)	8(j)	8(f)
Fe	0.029	0.030	0.015
V	0.016	-	-
$\text{GdFe}_{10}\text{Si}_2$			
Fe	0.031	0.030	0.015
Si	-	0.031	0.017

In Table I there are collected (after Pauling) quantities needed in calculations; the values of single bond metallic radii and appropriate electronegativities.

In Table II the lattice parameters  $a$  and  $c$  are collected and corresponding distances between rare earth ion and atoms in the nearest 8(i), 8(j) and 8(f) positions. The lattice constants of  $\text{GdFe}_{10}\text{V}_2$  were taken from [11] and of  $\text{GdFe}_{10}\text{Cr}_2$  and  $\text{GdFe}_{10}\text{Si}_2$  from [12] and [13], respectively.

Applying Eqs. (1)–(3), the charge transfers were calculated from R ion to T (Fe) ions in 8(i), 8(j) and 8(f) positions. Results are listed in Table III. The charge transfers from R ion to T (Fe) atoms, as expected in metals, are quite small (see Table III). The spin-polarized calculations (LMTO method) of electronic structure of  $\text{YFe}_{10}\text{V}_2$  and  $\text{YFe}_{10}\text{Cr}_2$  [14] gave also small values of transferred charges, for  $\text{YFe}_{10}\text{V}_2$  there were 0.37, 0.0175, 0.1,  $-0.24$ ,  $-0.04$  for Y, Fe in 8(f), V in 8(i), Fe in 8(j), respectively. A large positive value of  $A_2^0$  calculated by authors (using PCC method), which is in complete disagreement with experimental value, is probably caused by incorrect sign of charges in positions 8(f) and 8(i). Gadolinium is less electronegative than vanadium or iron, from this point of view charges in 8(f) and 8(i) should have a negative sign.

For the calculation of  $A_2^0$  parameter the charge of R ion is also needed. From band structure calculations it follows that a charge of the Wigner–Seitz cell of Gd ion is approximately  $0e$  when performed for  $\text{ThCr}_2\text{Si}_2$ -type compounds [2]. For  $\text{GdCo}_5$  [4] the Gd charge changes from  $-0.32e$  to  $+0.21e$  depending on the Wigner–Seitz radii. We assumed a value of  $+0.3e$  for Gd charge. The distance from reference R ion to its nearest R neighbors is in the range of  $4.5$ – $12 \text{ \AA}$ . It appears that the screening of the charge causes the adopting of so small Gd charge instead of  $+3$  which was frequently used.

For calculating  $A_2^0$  a well-known formula was used [15]:

$$A_2^0 = \frac{1}{4}(-e^2) \sum_{j=1}^k \frac{q_j}{R_j^3} (3 \cos^2 \theta - 1). \quad (4)$$

$e$  stands for electron charge,  $R_j$  and  $\theta$  are the polar coordinates of the charge  $q_j$ . In case of  $\text{T} = \text{V}$  a charge in 8(i) position has been varied according to the relation

$$q_j^{8(i)} = \alpha q_V^{8(i)} + (1 - \alpha) q_{\text{Fe}}^{8(i)} \quad (5)$$

Charges of 8(j) and 8(f) for  $\text{T} = \text{Si}$  were calculated similarly.

The experimental values of  $A_2^0$  obtained from  $^{155}\text{Gd}$  Mössbauer spectroscopy [16] are  $-140 \text{ K}/a_0^2$  and  $-120 \text{ K}/a_0^2$  for  $\text{GdFe}_{10}\text{V}_2$  and  $\text{GdFe}_{10}\text{Si}_2$ , respectively. The calculated values of  $A_2^0$  have to be regarded with caution (inaccuracy of PCC calculations), however agreement with experimental values is satisfactory. The dependence of  $A_2^0$  crystal field parameter on V and Si content in the nearest neighborhood of the R ion is displayed in Fig. 2.

When the vanadium content at 8(i) site increases, the value of  $A_2^0$  increases of about  $20 \text{ K}/a_0^2$ . The change of  $A_2^0$  is not so sensitive on Si content (a decrease of about  $2 \text{ K}/a_0^2$  when changing Si content in 8(f) position, and about  $1 \text{ K}/a_0^2$  for 8(j) position). The role of coordination symmetry of rare earth ion is seen here. The variation of V content has a remarkable influence on the spin reorientation temperatures,  $T_{\text{SR}}$  [17]. The planar anisotropy of Tb in  $\text{TbFe}_{12-x}\text{V}_x$  decreases with increasing vanadium content and turns into axial for  $x$  about 2. The above calculations confirm this fact (see Fig. 2). The rare earth anisotropy in high temperatures can be estimated by [16]:

$$K^{\text{Re}} \sim -\alpha_J (J - 1) \langle r^2 \rangle A_2^0.$$

The second order Stevens factor  $\alpha_J < 0$  for Dy ion [15], when  $A_2^0$  having negative sign increases, the rare earth anisotropy decreases.  $J$  is the total angular

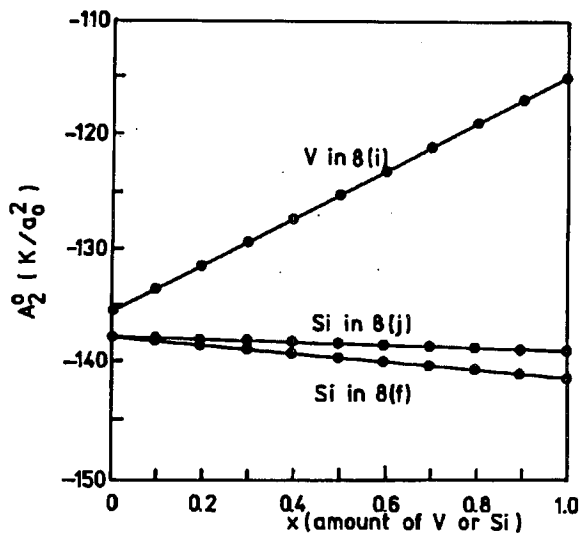


Fig. 2. Calculated crystal field parameter  $A_2^0$  dependence on T-atom content in 8(i), 8(j) and 8(f) crystallographic positions for  $\text{GdFe}_{12-x}\text{T}_x$ , T = V, Si.

momentum of the rare earth ion and  $\langle r^2 \rangle$  is the radial integral for the 4f electrons [18].

On the other hand, in  $\text{ErFe}_{12-x}\text{V}_x$  the values of  $T_{\text{SR}}$  increase when increasing vanadium content. It seems that higher order crystal field term has their influence here [19].

### 3. Miedema's model of cohesion in alloys

The influence of the T atoms and their crystallographic site preference on the anisotropy of R ion in  $\text{RFe}_{12-x}\text{T}_x$  compounds can be understood within Miedema's "macroscopic atom" model for cohesion in alloys [20]. The difference of the electron density at the contact surface between different metals  $\Delta n_{\text{ws}}$  gives a positive contribution to the enthalpy of formation, charge transfer (described in terms of electronegativity difference  $\Delta\varphi^*$ ) corresponds to a negative, ionic contribution to the heat of formation [20]:

$$\Delta H = -P(\Delta\varphi^*)^2 + Q(\Delta n_{\text{ws}}^{1/3})^2. \quad (7)$$

The proportionality constants  $P$  and  $Q$  do not much depend on the type of metal system considered. The values of  $\varphi^*$  and  $n_{\text{ws}}$  have been given for all metallic elements [20–22]. Some needed values are collected in Table IV. A large value of  $n_{\text{ws}}$  for transition metals (Fe, V, Cr) which are located in 8(i) position comparing to the  $n_{\text{ws}}$  of the R ion produce a large discontinuity of the charge in the plane perpendicular to the  $c$ -axis and containing R atom. This discontinuity enhances the anisotropy and  $|A_2^0|$  parameter. Substituting Fe (larger  $n_{\text{ws}}$ ) by V (smaller  $n_{\text{ws}}$ ) the  $|A_2^0|$  value (see Fig. 1) decreases as a cause of decreasing charge discontinuity

TABLE IV  
Miedema's electronegativity  $\varphi^*$  and the density of electrons at the boundary of the Wigner-Seitz cell,  $n_{ws}$ . Units of  $n_{ws}$  are arbitrary, one density unit equals to  $4 \times 10^{22}$  el./cm<sup>3</sup> [21, 22].

Element	$\varphi^*$ [V]	$n_{ws}$ [a.u.]
R	~3.1	~1.0
Fe	4.93	5.55
V	4.25	4.41
Cr	4.65	5.18
Si	4.70	3.37

in vicinity of the rare earth ion. On the other hand, Si atoms form two tetragonal prisms (made of 8(j) and 8(f) positions) centered by R ion (see Fig. 1). The location of Si atoms and smaller difference between  $n_{ws}^R$  and  $n_{ws}^{Si}$  parameters causes smaller value of  $|A_2^0|$ . The sensitivity of  $|A_2^0|$  on change of silicon content is also smaller (see Fig. 2).

The heat of mixing between R and V, Ti, Cr is positive and between R and Si negative [23]. According to Eq. (7) for Si atoms the negative contribution coming from  $\Delta\varphi^*$  charge transfer will dominate. The anisotropic contribution to  $A_2^0$  has partly different origin depending on T. For metallic system the charge transfer  $\Delta z$  is equal [21]:  $\Delta z = \Delta\varphi^*/M$  where  $M$  is a semi-empirical constant for solid alloys; it is equal to 1 V approximately [22]. Thus, using the values of electronegativities from Table IV we obtain charge transfer  $1.6e$  from R to Si and  $1.15e$  from R to V.

Value of isomer shift, IS, also reflects a change of local environment of the rare earth ion. The maximum of the isomer shift for A atoms surrounded by B neighbors is linearly dependent on  $\Delta\varphi^*$  and  $\Delta n_{ws}$  [22]. From <sup>155</sup>Gd Mössbauer spectroscopy [16] the isomer shift is for GdFe<sub>10</sub>Si<sub>2</sub> IS = 0.30 mm/s and for GdFe<sub>10</sub>V<sub>2</sub> and GdFe<sub>10</sub>Mo<sub>2</sub> IS = 0.22 mm/s.

The charge transfer from a metal with a low electron density to a metal with higher electron density produces a net volume contraction. It is manifested in a decrease in the atomic cell volume when T = Si comparing to unit cell when T = V or Cr. In the intermetallic compounds when A atom is surrounded by B atoms this volume contraction is proportional [22, 24]:

$$\Delta V_{AB} \propto \Delta\varphi^* (1/n_{ws}^B - 1/n_{ws}^A). \quad (8)$$

Applying the above formula we have  $\Delta V_{RSi} \propto 1.125$  and  $\Delta V_{RV} \propto 0.889$ . From this estimation is seen that contraction for T = Si is larger than for T = V stabilizing atoms, which agrees with X-ray data (see Table I). The atomic cell flattens out when Si is replaced by V, the local environment of the R ion changes and it is in turn manifested by an increase in  $|A_2^0|$  crystal field parameter.

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