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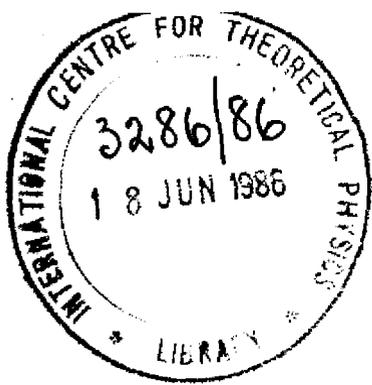CRYSTAL-FIELDS AT RARE-EARTH SITES IN $R_2Fe_{14}B$ COMPOUNDS

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CRYSTAL-FIELDS AT RARE-EARTH SITES IN $R_2Fe_{14}B$ COMPOUNDS *

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ABSTRACT

Crystal-field effects are expected to be important in $R_2Fe_{14}B$ compounds. Within a model-independent approach, it is proved that four distinct rare-earth sites exist with respect to the crystalline electric fields, namely, R(4f; z = 0), R(4f; z = 0.5 c), R(4g; z = 0), and R(4g; z = 0.5 c), and relationships are established between the corresponding crystal-fields coefficients. Further, generalized Stevens parametrizations of the crystal field coefficients are derived at three levels of approximation for the interatomic forces inside the crystal. A crystal lattice dressing effect upon the radial electronic integrals is found to occur, the magnitude of which depends on the deviation of the interatomic forces from Coulombian. Finally, computation of crystal-field coefficients in $Nd_2Fe_{14}B$ leads to results which raise questions about the validity of the simple Coulomb point-charge model.

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1. Introduction

The knowledge of the crystal fields at the rare-earth (R) sites is the first step towards the derivation of a single-ion anisotropy model for rare-earth permanent magnets. The present investigation reports crystal-field calculations for the structure $Nd_2Fe_{14}B$, which has been found to be responsible for the spectacular magnetic properties of the Nd-Fe-B magnets communicated in 1983 [1 - 3].

Previous crystal-field studies demonstrated, on one hand, the prevalence of the second-order terms in the crystal-field Hamiltonian [4] and, on the other hand, the existence of four unequivalent rare-earth positions with respect to the crystal fields [5]. The present study benefitted from both the theoretical results and the accumulation of valuable experimental data providing increased reliability to the input parameters in a theoretical crystal-field calculation.

In section 2, starting from the experimental result that $R_2Fe_{14}B$ compounds exist along all the rare-earth series, both model independent results and a generalized Stevens parametrization of the crystal-fields at R sites are derived. The method of performing the lattice sums that occur in the crystal-field coefficients is described in section 3. Numerical results and their interpretation are discussed in section 4. The paper ends with concluding remarks in section 5.

2. Generalized Stevens parametrization of the
crystal-field Hamiltonian in $R_2Fe_{14}B$ compounds

2.1. Crystal-field Hamiltonians at rare-earth sites

Subsequent to the identification of the crystal structure of the $Nd_2Fe_{14}B$ phase [6 - 8], stoichiometric compounds of $R_2Fe_{14}B$

structure have been found to occur for R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, and also for R = Y and Th and it has been established experimentally [9 - 13] that the magnetic properties (Curie temperature, magnetization, anisotropy) vary significantly with R along the $R_2Fe_{14}B$ series (a comprehensive review of the literature published up to May 1985 is given in [14]). Thus, a crystal-field study pertinent to all the $R_2Fe_{14}B$ compounds would be desirable.

Structural data by various techniques [6 - 10, 13 - 15] show that all the $R_2Fe_{14}B$ compounds crystallize in a tetragonal structure characterized by the space group $P4_2/mnm$ [16], with the elementary cell consisting of four formula units. The locations of the various kinds of atoms within the elementary cell of $Nd_2Fe_{14}B$ have been experimentally determined by several techniques [6 - 8, 15], with a remarkable degree of agreement between the reported results. In what follows, the notations and the data reported by Herbst et al. [6, 15] will be used. For the other $R_2Fe_{14}B$ compounds, lattice constants only have been published so far ([9, 10, 13], see also [14]) and this is insufficient for explicit crystal-field coefficient calculations.

The local symmetry at the two crystallographically unequivalent R sites (4f and 4g respectively) consists of two mutually orthogonal mirror planes [16]. The lattice is not invariant with respect to the space inversion around R sites. As a consequence, the crystal-field Hamiltonians for the R sites correspond to the Laue group mmm [17]. With the standard choice of the coordinate axes (x along [100], y along [010], and z along [001] – the tetragonal c - axis), we can therefore write

$$\hat{H}_{cf}(s) = \sum_{p=1}^{3} \sum_{m=0}^{p} B_{2m}^{2p}(s)\, Z_{2m}^{(2p)} \,, \tag{1}$$

where B_{2m}^{2p} are crystal-field coefficients while, up to numerical factors, $Z_{2m}^{(2p)}$ are irreducible tensor operators as defined by Wybourne [18]. They are related to the spherical harmonics by the equations

$$Z_{2m}^{(2p)} = \begin{cases} 2^{-\frac{1}{2}}\,(Y_{2p}^{-2m} + Y_{2p}^{2m}) & \text{if } m > 0\,, \\[2mm] (2^{\frac{1}{2}}i)^{-1}\,(Y_{2p}^{-2m} - Y_{2p}^{2m}) & \text{if } m < 0\,,\quad i = \sqrt{-1}\,, \\[2mm] Y_{2p}^{0} & \text{if } m = 0\,. \end{cases} \tag{2}$$

In equation (1), the argument s stands for one of the distinct R crystal-field sites within the $R_2Fe_{14}B$ lattice [5],

$$s \in \{(4\,f;\ z = 0),\ (4\,f;\ z = 0.5\ c),$$
$$(4\,g;\ z = 0),\ (4\,g;\ z = 0.5\ c)\} \,. \tag{3}$$

The lattice configurations around each term of the (4f) and (4g) pairs are related to each other by a rotation of $\pi/2$ radians around the c - axis. Then for arguments s running over the set (3), the following relationships hold for the crystal-field coefficients of Eq. (1),

$$B_{4m}^{2p}(R;\ z = 0.5\ c) = B_{4m}^{2p}(R;\ z = 0),\ m = 0,\ 1;\ R = 4f,\ 4g, \tag{4a}$$

$$B_{4m+2}^{2p}(R;\ z = 0.5\ c) = -\,B_{4m+2}^{2p}(R;\ z = 0),\ m = 0,\ 1;$$
$$R = 4f,\ 4g. \tag{4b}$$

In a change of the quantization axis away from the tetragonal c - axis, operators $Z_{2m}^{(2p)}$ of negative projections ($m < 0$) are involved. The corresponding crystal-field coefficients then satisfy

$$B_{4m+2}^{2p}(R;\ z = 0.5\ c) = B_{4m+2}^{2p}(R;\ z = 0),\ m = -1,\ -2;$$
$$R = 4f,\ 4g, \tag{4c}$$

$$B_{4m}^{2p}(R; z = 0.5 \, c) = - B_{4m}^{2p}(R; z = 0), \quad m = -1, \quad R = 4f, \, 4g. \quad (4d)$$

2.2. Generalized Stevens parametrization of the crystal-field Hamiltonian for the Laue group mmm

Eqs. (4) show that the knowledge of the crystal-field coefficients at the crystallographic R - sites (4f; z = 0) and (4g; z = 0) is necessary and sufficient to get full information on the crystal-field effects in $R_2Fe_{14}B$ compounds.

Generalized Stevens parametrizations for these coefficients can be obtained using an argument along the lines of references [19, 20]. Let the atomic sites around the reference R ion be labelled by j, $j \in \mathbb{N}^+$. Suppose that the j - th ion carries an effective charge Q_j $|e|$ and that the spatial part of its interaction with the reference R ion is described by a (possibly non-central) effective potential $v(\underset{\sim}{R}_j)$, where $\underset{\sim}{R}_j$ is the position vector of the j - th ion. The validity of the superposition of the effects coming from the different j - sites is supposed to hold [21]. Then we have the result

$$B_{2m}^{2p} = A_{2p,2m}^o \widetilde{\langle r^{2p} \rangle}_{2m}, \quad p = 1, 2, 3; \, 0 \leq m \leq p, \quad (5)$$

where the argument s of Eq. (1) has been omitted for simplicity. Here,

$$\widetilde{\langle r^{2p} \rangle}_{2m} = \langle r^{2p} \rangle + \sum_{t=1}^{\infty} \langle r^{2p+2t} \rangle A_{2p,2m}^{2t}/A_{2p,2m}^o, \quad (6)$$

where $A_{2p,2m}^{2t}$ are lattice sums given by

$$A_{2p,2m}^{2t} = - \frac{|e|^2}{4\pi \epsilon_o} \frac{4\pi}{4p+1} \left[2^{2(p+t)} \, (1/2)_{2p} \, (2p+3/2)_t \, t! \right]^{-1}$$

$$\times \sum_j Q_j \, \Delta_j^t \, \hat{Z}_{2m}^{(2p)}(v(\underset{\sim}{R}_j)), \quad p = 1, 2, 3; \, 0 \leq m \leq p; \, t \in \mathbb{N}. \quad (7)$$

In this equation, the factor $|e|^2/(4\pi \epsilon_o)$ shows that the result is expressed in SI units, while $(a)_k$ is the Pochhammer symbol,

$$(a)_o = 1, \quad (a)_k = a \, (a+1) \, \ldots \, (a+k-1), \quad k \in \mathbb{N}^+.$$

Further, Δ_j stands for the Laplacian with respect to the (X_j, Y_j, Z_j) coordinates, while the operator $\hat{Z}_{2m}^{(2p)}$ is obtained formally from Eq. (2) expressing the spherical harmonics as linear combinations of direction cosines (K_j, L_j, M_j) of the position vector $\underset{\sim}{R}_j$ and then performing the replacements

$$K_j^2 \rightarrow \partial^2/\partial X_j^2, \quad L_j^2 \rightarrow \partial^2/\partial Y_j^2, \quad M_j^2 \rightarrow \partial^2/\partial Z_j^2, \quad 1 \rightarrow \Delta_j,$$

such that $\hat{Z}_{2m}^{(2p)}$ be a $2p$ - th degree homogeneous polynomial with respect to the derivatives $\partial/\partial X_j$, $\partial/\partial Y_j$, and $\partial/\partial Z_j$ (detailed expressions of some $\hat{Z}_{2m}^{(2p)}$ operators can be found, under alternative notation, in [19]).

In Eq. (6), $\langle r^{2p} \rangle$, $p \in \mathbb{N}^+$, are free rare-earth ion radial matrix elements of 4 f electrons. For $p = 1, 2, 3$, these have been computed by Freeman and Desclaux [22] for practically all di- and trivalent ions in the rare-earth series. Eqs. (5) and (6) show that, for ions imbedded in crystal lattices, these radial matrix elements are "dressed" by the crystal-field interaction, the magnitude of this effect being determined by that of the deviation of the interatomic interactions from the purely Coulombian one (see Eqs. (10) and (11) below). Consideration of realistic ion-ion interactions shows that the effect is important. Its occurrence offers coherent explanation to the systematic discrepancies between experimental and theoretic $\langle r^n \rangle$ values [23].

If one admits that the ion-ion forces in $R_2Fe_{14}B$ compounds are central (i.e., $v(R_{\sim j}) = v(|R_{\sim j}|)$), then the contributions $\Delta_j^t \hat{z}_{2m}^{(2p)}(v(R_{\sim j}))$ to the lattice sums (7) factorize into angular and radial ionic contributions [20] and we get

$$A_{2p,2m}^{2t} = -\frac{|e|^2}{4\pi\varepsilon_o}\frac{4\pi}{4p+1}\left[2^{2(p+t)}\,(1/2)_{2p}\,(2p+3/2)_t\,t!\right]^{-1}$$

$$\times \sum_j Q_j\, z_{2m}^{(2p)}(K_j, L_j, M_j)\, F_{2p,2t}(R_j)\,, \tag{8}$$

where $z_{2m}^{(2p)}(K_j, L_j, M_j)$ are now numbers defined by equation (2), while the radial factors $F_{2p,2t}(R_j)$ are given respectively by

$$F_{2,0} = v^{(2)} - v^{(1)}/R_j\,, \tag{9a}$$

$$F_{4,0} = v^{(4)} - 6\,v^{(3)}/R_j + 15\,v^{(2)}/R_j^2 - 15\,v^{(1)}/R_j^3\,, \tag{9b}$$

$$F_{6,0} = v^{(6)} - 15\,v^{(5)}/R_j + 105\,v^{(4)}/R_j^2 - 420\,v^{(3)}/R_j^3$$

$$+ 945\,v^{(2)}/R_j^4 - 945\,v^{(1)}/R_j^5\,, \tag{9c}$$

$$F_{2p,t} = F_{2p,t-1}^{(2)} + 2\,F_{2p,t-1}^{(1)}/R_j - 2p\,(2p+1)\,F_{2p,t-1}/R_j^2\,,$$

$$t \in \mathbb{N}^+\,. \tag{9d}$$

In these equations, the arguments R_j of the functions $F_{2p,t}$ and v have been omitted for simplicity. Moreover, upper Arabic numerals in parentheses denote derivatives with respect to R_j.

A third (and crudest) level of approximation to the crystal-field coefficients (1) is the standard point charge approximation, within which the ion-ion interactions inside the crystal are supposed to be Coulombian. Then the quantities $F_{2p,t}(R_j)$, $t \geq 1$,

given by Eq. (9d) vanish idertically and the Stevens parametrization (5) reduces to the usual one,

$$B_{2m}^{2p} = A_{2p,2m}^o \langle r^{2p} \rangle\,, \tag{10}$$

with free-ion values for the radial electron integrals and expressions of the crystal-field coefficients given by

$$A_{2p,2m}^o = -\frac{|e|^2}{4\pi\varepsilon_o}\frac{4\pi}{4p+1}\sum_j (Q_j/R_j^{2p+1})\, z_{2m}^{(2p)}(K_j, L_j, M_j)\,. \tag{11}$$

3. Computation of crystal-field lattice sums in $Nd_2Fe_{14}B$

All the lattice sums (7), (8), or (11) are essentially of the form

$$\mathcal{F}(s) = \sum_{j \in LC(s)} Q_j\, T(j)\,, \tag{12}$$

where $LC(s)$ is short for lattice configuration around the rare-earth site s, with s taking values from the set (3), and $T(j)$ includes numerical coefficients, angular and distance dependent factors describing the ion-ion interaction.

To use consistently the mmm symmetry invariants, virtual neighbours are added, the coordinates of which are obtained from the actual particle coordinates with respect to the R site s by space inversion. An extended lattice configuration around the site s (ELC(s)) is obtained which has the same associated Bravais lattice (BL), but an elementary cell characterized by an extended basis structure (EBS) which depends, of course, on the chosen R site s. Then the lattice sum over ELC(s) in (12) can be split into a two-stage summation,

$$\mathcal{F}(s) = \frac{1}{2} \sum_{k \in BL} \sum_{j \in EBS(s,k)} Q_j \, T(k; j) \, . \tag{13}$$

The factor 1/2 has been introduced to compensate for the factor two increase of the number of lattice points around the centre of the elementary cell. Since the centre of the elementary cell itself is not doubled by virtual neighbour addition, it is to be counted twice in Eq. (13) at Bravais lattice vectors $R_k \neq 0$ in order to get results identical with those of Eq. (12). Here and in following, the notation EBS(s, k) means that the elementary cell is centred at the Bravais lattice vector R_k , $k \in \mathbb{N}$.

Further, the $Nd_2Fe_{14}B$ structure consists [6 - 8, 15] of a superposition of nine sublattices,

$$Nd(4f), \; Nd(4g), \; Fe(16k_1), \; Fe(16k_2),$$
$$Fe(8j_1), \; Fe(8j_2), \; Fe(4e), \; Fe(4c), \; B(4g) \, . \tag{14}$$

If the label 1 is introduced which runs over these nine values, then Eq. (13) can be written in the equivalent form

$$\mathcal{F}(s) = \sum_l Q_l \, S_l(s) \, , \tag{15}$$

where

$$S_l(s) = \frac{1}{2} \sum_{k \in BL} \sum_{j_1 \in EBS(s,k)} T(k; j_1) \, . \tag{16}$$

To compute the lattice sums for the entire set of crystal-field coefficients entering Eq. (1) and to get physically meaningful results irrespective of the spatial decay of the lattice summands $T(k; j_1)$, the BL of the crystal is replaced by finite subsets which define successive sequences such that the obtained finite volumes $\{\mathcal{V}_n | n \in \mathbb{N}\}$ are related by a similarity transform to the shape of the elementary cell of the $R_2Fe_{14}B$ structure. Sequences

$\{S_{1,n}(s) \mid n \in \mathbb{N}\}$ are obtained which converge towards $S_1(s)$, equation (16), as $n \to \infty$. The criterion of convergence for the computation is

$$\left| [S_{1,n+1}(s) - S_{1,n}(s)]/S_{1,n+1}(s) \right| < \eta \, , \quad i \geqslant 1 \, , \tag{17}$$

where η is the relative accuracy required at the output of the crystal-field calculations.

Since every sublattice remains invariant under the symmetry operations of the mmm crystallographic point group, representation domains V_n can be defined for every finite volume $\mathcal{V}_n$, such that every V_n contains crystallographically unequivalent lattice points only. Then the finite sums $S_{1,n}(s)$ in (17) are given by

$$S_{1,n}(s) = \sum_{k \in V_n} \sum_{j_1 \in EBS(s,k)} \nu(k; j_1) \, T(k; j_1) \, , \tag{18}$$

where $\nu(k; j_1)$ are weight factors which equal the number of actual lattice points that are crystallographically equivalent to j_1 .

Special care is to be taken for the lattice points located exactly at the surface of V_n . Their contributions to the lattice sums (18) have then to be shared between the volumes V_n and V_{n+1} by appropriate splitting of the weighting factors $\nu(k; j_1)$.

4. Numerical results and discussion

In the present section, numerical results are reported for the crystal-field coefficients at Nd places in $Nd_2Fe_{14}B$. The data, summarized in Table I, have been obtained within the standard Coulomb point charge approximation (10) - (11), which served as the starting hypothesis for the crystal-field calculations in

references [4] and [5] as well.

The developed computer code (written in ANS FORTRAN) has been checked to be free of errors (the main test being fulfilment of the model independent relationships (4a) and (4b)), reliable (by way of comparison of the outputs provided by the terminating criterion (17) with $i = 1$ at different accuracies η), and portable (it has been found to work accurately, in single precision, both on an IBM 370/135 and a Gould 32/97 computer). The data given in Table I have been obtained on the latter computer, with three figure accuracy at output ($\eta = .5 \times 10^{-3}$ in (17)).

The input structural data have been those of reference [6], while values for Nd^{3+} radial electron integrals have been taken from [22]. Since shielding effects are not essential for the following discussion, they have been omitted.

Important and difficult to assess are the values of the sublattice ionic charges Q_l in equation (15). In [5], the charges

$$Q_l = 3.0, \; l = 1, 2, \quad \text{and} \quad Q_l = 0, \; l = 3, 4, \ldots, 9 \; , \qquad (19a)$$

have been assumed, while in [4], the set

$$Q_l = 3.0, \; l = 1, 2, 9, \quad \text{and} \quad Q_l = -9/14, \; l = 3, 4, \ldots, 8, (19b)$$

has been considered. For the sake of comparison, the latter set of electric charges has been introduced into our programme and the values given in the first two columns of Table I have been obtained. Within the Stevens' equivalent operator approach followed in [4], certain normalization factors have been absorbed into the definition of the crystal-field coefficients ([24], Table VI). Taking them into account, agreement with reference [4] has been obtained as it concerns both the signs of the final results and the dominance of the second order terms. As it concerns the figures obtained for the

second order terms, however, a disagreement going from six to twenty percent has been found to occur. In our opinion, this originates mainly in the conditional convergence of the second order lattice sums (11) for Coulomb interactions.

While of certain significance, this disagreement, however, is not an essential point against the validity of the Coulomb point-charge crystal-field calculations performed in references [4] and [5]. Rather, the point charge sets (19) are questionable. In fact, both of them are in contradiction with the $Nd_2Fe_{14}B$ local moment data [10, 15, 25 - 27] and with the property of the moments of undergoing parallel alignment [15], as well as with theoretical band-model calculations [28]. Indeed, while the sets (19) imply partial or total Fe^{2+} d – band filling with conduction electrons, the local moment data suggest that the deviations of the low-temperature Nd^{3+} and Fe^{2+} magnetic moments from the free ion values are to be attributed to d – f electron band hybridization effects only. As a consequence, the ionic charges in $Nd_2Fe_{14}B$ should be close to the valence values. Taking into account the uniform negative free s – electron polarization effect [25], it results that a set of effective ionic charges consistent with the moment data is provided by

$$Q_l = 2.7, \; l = 1, 2, 9, \quad \text{and} \quad Q_l = 1.8, \; l = 3, 4, \ldots, 8 \; . \quad (20)$$

(The main difference from the sets (19) comes therefore from the ionic charges attributed to the six Fe sublattices.)

The use of this set of ionic charges resulted in the values reported in the last two columns of Table I. Now the crystal-field coefficients B_0^2 become large and negative, whereas the B_2^2 coefficients become positive at R sites in the plane $z = 0$ while negative at R sites in the plane $z = 0.5$ c . The expected consequence of such a result is the theoretical prediction of an easy plane of

magnetization in $Nd_2Fe_{14}B$, at variance with the experiment. The importance of such a consequence could hardly be underestimated. In our opinion, this shows that the simple Coulomb point-charge approximation (10) - (11) is too crude to/crystal-field predictions yield consistent both with the magnetic moment data and with the existence of an easy anisotropy axis. Therefore, a deeper crystal-field analysis, at the level of the parametrization (5), (6), (8), should be done to take proper account of these effects.

5. Concluding remarks

Model independent results established in section 2.1 show that there are four unequivalent crystal-field contributions to a single ion anisotropy model in $R_2Fe_{14}B$ compounds. These four contributions arise for the rare-earth sites specified in equation (3), with corresponding crystal-field coefficients related to each other by equations (4a) - (4d).

The Stevens parametrization of the crystal-field coefficients has been investigated in section 2.2 at three levels of restrictive assumptions on the spatial dependence of the interatomic forces inside the crystal. Under the most general assumption that the are interatomic forces/both distance and direction dependent, the parametrization (5) holds, with crystal lattice sums given by Eq. (7). If one admits that the interatomic forces are central, then the characteristic splitting of the crystal-field lattice sums into angular and radial contributions, Eq. (8), occurs. In both cases, the radial electronic integrals are renormalized from the free ion values used in the usual frame of the crystal-field theory to values (6) which express the "dressing-effect" of the crystal lattice. Comparison with the approximation of purely Coulombian forces shows that the dressing effect is a measure of the deviation

of the actual interatomic forces from purely Coulombian. This result gives a reasonable explanation for the systematic discrepancies between the theoretical free ion values and the experimental crystal-field values of the radial electronic integrals.

Under the hypothesis of purely Coulombian interatomic forces in $Nd_2Fe_{14}B$, crystal-field coefficients have been computed. It has been found that the model cannot simultaneously accomodate with the magnetic moment data and with the existence of an easy anisotropy axis for $Nd_2Fe_{14}B$. As a consequence, a non-contradictory crystal-field investigation should either make use of the hypothesis of non-Coulombian interatomic forces (a two-parameter Born-force model would be a reasonable candidate for such an investigation, see, e. g., [20]), or be model independent, as has been done for $SmCo_5$ magnets by Buschow et al. [29]. While the implementation of such ideas is not straightforward, we believe it should be essential to get a faithful representation about the origin of the easy anisotropy axis in $Nd_2Fe_{14}B$ and of its property of showing reorientation at low temperatures.

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Table I. Crystal-field coefficients at Nd sites in $Nd_2Fe_{14}B$ [*]

Term	Charge set (19b)		Charge set (20)	
	R(4f; z = 0)	R(4g; z = 0)	R(4f; z = 0)	R(4g; z = 0)
B_0^2	4330.	4873.	− 2608.	− 2833.
B_2^2	− 6077.	5314.	839.1	3268.
B_0^4	− 57.40	− 66.94	8.811	− 4.300
B_2^4	109.0	− 178.3	85.80	− 128.1
B_4^4	225.3	− 348.4	11.54	− 252.0
B_0^6	2.644	3.808	− .9050	− .3064
B_2^6	− 9.927	21.32	− 6.803	14.81
B_4^6	− 16.62	23.56	12.36	27.74
B_6^6	39.88	68.32	23.25	37.46

[*] Data, in K, obtained from equations (10) − (11), with three figure accuracy