CHAPTER THREE

THEORY OF CRYSTAL-FIELD EFFECTS IN 3d-4f INTERMETALLIC COMPOUNDS

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Contents

Foreword 149
1. Formal Description of the Crystal Field on Rare Earths 150
   1.1 The single-ion approximation 150
   1.2 Equivalent operator techniques for various subspaces: 4fN configuration, LS term, J multiplet, Kramers doublet 155
   1.3 Local symmetry and the exact form of $\hat{H}_{\text{CF}}$ 161
2. The Single-Ion Anisotropy Model for 3d-4f Intermetallic Compounds 166
   2.1 Macroscopic description of magnetic anisotropy 166
   2.2 The notion of an exchange-dominated RE system 170
   2.3 The single-ion model for 3d-4f intermetalics 176
   2.4 The high-temperature approximation 177
   2.5 The linear-in-CF approximation: main relations 183
   2.6 Properties of generalised Brillouin functions 188
   2.7 The linear-in-CF approximation (continued) 193
   2.8 The low-temperature approximation 199
   2.9 $J$-mixing made simple 203
3. Spin Reorientation Transitions 210
   3.1 General remarks 210
   3.2 SRTs in uniaxial magnets 214
   3.3 Spontaneous SRTs in cubic magnets 222
4. Conclusion 228
References 229

FOREWORD

Magnetic properties of 3d-4f intermetallic compounds have been reviewed on numerous occasions in recent times (Kirchmayr and Burzo, 1990; Franse

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This Chapter is to review the progress in theory in the post-Callens era, filling the gap in the literature between the anisotropy and the CF. We aim at reasserting the statement that magnetocrystalline anisotropy is the most important manifestation of the CF.

1. **Formal Description of the Crystal Field on Rare Earths**

   This section has an introductory character. We shall discuss the physical foundations of the approach that enables quantitative treatment of CF effects in RE-based hard magnetic materials—the single-ion approximation—and introduce the basics of the mathematical apparatus required for that treatment. Admittedly, this section contains mostly standard material, extensively covered in a number of monographs published in the 1960–70s (Griffiths, 1961; Ballhausen, 1962; Hutchings, 1964; Wybourne, 1965; Dieke, 1968; Abragam and Bleaney, 1970; Al’tshuler and Kozyrev, 1974). Hence the brief style of our exposition. Like in the rest of the Chapter, the approximate nature of the approach is emphasised and the bounds of its validity are set out.

   1.1 The single-ion approximation

   The main experimental fact underlying the single-ion approach to 3d-4f intermetallics rich in 3d elements is the approximate non-interaction of the RE magnetic moments therein. Of course, the single-ion model as such is not restricted to
intermetallic compounds (see e.g. Kolmakova et al., 1996), but it is in the 3d–4f intermetallics that it takes a particularly simple form. We shall therefore limit ourselves to this special case. The non-interaction of RE moments should be understood as relative weakness of the RE–RE exchange interaction in such compounds. That is, if we consider a crystal consisting of atoms of 3d and 4f elements, as shown schematically in Fig. 3.1, the 4f shell of each RE atom (hatched) interacts directly (or rather, via the 5d states) only with the 3d electrons of the transition element, but not with the 4f shells of neighbouring RE atoms. It is unimportant at this stage to specify if the 3d electrons are regarded as localised, belonging to individual atoms, or as itinerant electrons (dashed lines in Fig. 3.1).

The weakness of the 4f–4f interaction should not be mistaken for its non-existence or indetectability. Thus, the compound GdNi₅, where nickel is nonmagnetic, orders ferromagnetically at $T_C = 32$ K (Gignoux et al., 1976) entirely due to the Gd–Gd exchange. The truth, however, is that in typical hard magnetic materials the 4f–4f exchange coexists with much stronger 3d–3d and 3d–4f interactions and that the former one is negligible in comparison with the latter two.

This statement has been recently put to a direct test. The influence of the exchange on the 4f shell of Gd in GdCo₅ was probed by two different techniques: (i) by applying a very strong magnetic field that breaks the antiparallel orientation of the Gd and Co sublattices (Kuz’min et al., 2004) and (ii) by inelastic neutron scattering on the exchange-split 4f states (Loewenhaupt et al., 1994). In the first case only the 3d–4f exchange is relevant, while in the second situation the 3d–4f and the 4f–4f interactions produce a combined effect on the 4f shell. Now, the intensity of the exchange interaction determined from these two kinds of experiment turned out to be the same within the estimated uncertainty bounds. This is a direct proof of the weakness of the Gd–Gd exchange in GdCo₅. In the other compounds of the RECo₅ series the 4f–4f interaction can be neglected with even more reason, since its intensity decreases in proportion to the square of the total 4f spin.

Another corner-stone of the single-ion approach is the weakness of the 3d–4f interaction in comparison with the 3d–3d one. Hence, on the one hand, the 3d–4f exchange is all-important for the 4f subsystem. On the other hand, its action back on the 3d electrons, which are under the dominant influence of the intra-sublattice 3d–3d exchange, is relatively insignificant. Once again, it does not mean...
that the 3d electrons are completely unaware of the state of magnetisation of the 4f subsystem. The presence of a magnetic RE may result in a noticeable shift of the Curie point in an intermetallic compound with a magnetic RE as compared to its counterpart with Y or Lu. Insignificance in this instance means that the effect of the 3d-4f exchange on the 3d sublattice can be reduced to a renormalisation of the $T_C$, without changing the dependence of the 3d sublattice magnetisation $M_{3d}$ on reduced temperature, $T/T_C$. The explicit form of $M_{3d}(T/T_C)$ is given by Eq. (2.43) below.

Thus, a peculiar hierarchy of exchange interactions takes place in 3d-4f hard magnetic materials, which can be schematically expressed as $(3d-3d) \gg (3d-4f) \gg (4f-4f) \approx 0$. This fact enables us to regard the 3d subsystem as something external with respect to the RE, as something given, which orders magnetically largely due to its internal forces. Then, from the viewpoint of the 4f electrons the 3d-4f exchange can be presented as the action of an exchange field produced by the ordered 3d subsystem. Therefore, the 4f subsystem can be regarded as a conjunction of non-interacting RE atoms (ions) immersed in several fields: the 3d-4f exchange field, applied magnetic field and the CF. The latter is not literally an electric field in the crystal, so we shall avoid terming it “crystal electric field” as misleading. Rather, CF is a combination of anisotropic time-even interactions involving the 4f electrons, presented as a fictitious electrostatic potential seen by the 4f shell.

The so formulated single-ion approximation is an enormous simplification: all itinerant electron states have been eliminated and the attention has been concentrated on the 4f shell of one RE atom, which to a good approximation can be considered localised. This explains the origin of the term “single-ion”, widely applied to non-ionic solids. Of course, there are no charged ions in metals. Just the magnetic behaviour of RE’s in metallic systems is determined by the properties of the ground configuration $4f^N$, which in most solids is the same as in trivalent RE ions.

Quantitatively this behaviour can be described by means of the following Hamiltonian:

$$\hat{H}_{4f} = \hat{H}_{\text{Coulomb}} + \hat{H}_{s-o} + 2\mu_B B_{\text{ex}} \cdot \hat{S} + \mu_B B \cdot (\hat{L} + 2\hat{S}) - e \sum_{i=1}^N V_{\text{CF}}(r_i). \tag{1.1}$$

Here the first two terms describe the isotropic (Coulomb and spin-orbit) interactions within the 4f shell; the third term presents the 3d-4f interaction by means of the exchange field $B_{\text{ex}}$, acting on the 4f spin, $\hat{S} = \sum_{i=1}^N \hat{s}_i$; the fourth one describes the (Zeeman) effect of the applied magnetic field $B$. The last term in Eq. (1.1) contains the CF potential $V_{\text{CF}}$. Formally similar to an ordinary electrostatic potential, $V_{\text{CF}}(r)$ is a function of coordinates in real space, which can be expanded over a suitably chosen basis. It is convenient to use for the purpose spherical coordinates and to choose the so-called irreducible tensor operators (functions) $C_n^m(\theta, \phi)$ as the angular basis functions (Wybourne, 1965):

$$V_{\text{CF}}(r, \theta, \phi) = \sum_{n=2,4,6} \sum_{m=-n}^n V_{nm}(r)C_n^m(\theta, \phi). \tag{1.2}$$
Following a long-standing tradition, one may assume in addition that this anisotropic potential is created by electric charges situated entirely outside the region where the 4f shell is located. Then, within that region, $V_{\text{CF}}(\mathbf{r})$ must satisfy the Laplace equation. The radial functions $V_{nm}(r)$ would then turn into simple power laws,

$$V_{nm}(r) = A_{nm} r^n,$$  \hfill (1.3)

where the coefficients are known as CF parameters. The approximation (1.3) is neither physically justifiable nor really useful. However, it causes no formal difficulties, as long as configuration mixing is neglected. Within the 4f configuration the radial functions reduce to their expectation values and Eq. (1.2) is equivalent to

$$\hat{\mathcal{H}}_{\text{CF}} = \sum_{i=1}^{N} \sum_{n=2,4,6} \sum_{m=-n}^{n} B_{nm} C^{(n)}(\theta_i, \phi_i).$$  \hfill (1.4)

The quantities $B_{nm} = -e\langle V_{nm}(r) \rangle_{4f} = -eA_{nm} \langle r^n \rangle_{4f}$ are also called CF parameters. Generally speaking, $A_{nm}$ (as well as $B_{nm}$) are complex numbers such that $A^*_{nm} = (-1)^m A_{n-m}$. Indeed, the potential $V_{\text{CF}}$ must be a real quantity and $C^{(n)}(\theta, \phi)$ are complex-valued functions satisfying the condition $\left[ C^{(n)}(\theta, \phi) \right]^* = (-1)^n C^{(n)}(\theta, \phi)$ (Varshalovich et al., 1988). Terms with odd $n$’s have been omitted from the expansion (1.2), because for $n$ odd all matrix elements of $C^{(n)}(\theta, \phi)$ between any two 4f orbitals are nil\(^1\) for parity reasons. Likewise, we have left out all terms with $n > 6$, not complying with the triangle condition, $n \leq 2l$. Finally, the isotropic $n = m = 0$ term has been omitted as well; its only effect is shifting all energy levels by the same amount, $NB_{00}$.

For each $n$, the variable $m$ may take $2n + 1$ values, therefore the expansion (1.2) may contain maximum 27 terms. Thus, there are 5 basis functions with $n = 2$:

$$C^{(2)}_0(\theta, \phi) = \frac{1}{2}(3 \cos^2 \theta - 1),$$

$$C^{(2)}_{\pm 1}(\theta, \phi) = \mp \left( \frac{3}{2} \right)^{\frac{1}{2}} \cos \theta \sin \theta e^{\pm i\phi},$$

$$C^{(2)}_{\pm 2}(\theta, \phi) = \left( \frac{3}{8} \right)^{\frac{3}{2}} \sin^2 \theta e^{\pm 2i\phi},$$

et cetera. Note that all $C^{(n)}_0(\theta, \phi)$ possess cylindrical symmetry, in fact they are just the $n$\textsuperscript{th}-order Legendre polynomials of $\cos \theta$: $C^{(n)}_0(\theta, \phi) = P_n(\cos \theta)$. Another simple particular case is $C^{(n)}_{\pm n}(\theta, \phi) = (\mp 1)^n [(2n - 1)!!/(2n)!!]^{1/2} \sin^n \theta e^{\pm in\phi}$.

The choice of $C^{(n)}_m(\theta, \phi)$ for the basis is by no means unique—any complete set of functions can be used instead. For example, the spherical harmonics $Y_{nm}(\theta, \phi)$.

\(^1\) This is not to say that $A_{nm}$ must generally be nil for $n$ odd. They genuinely vanish only when the RE occupies a crystallographic site with a centre of inversion. But even when they are nonzero, these $A_{nm}$ have no effect on the eigenvalues or eigenvectors of $\hat{\mathcal{H}}_{4f}$, as long as configuration interaction is neglected.
There is a simple connection between the two sets (Edmonds, 1957):

\[ Y_{nm}(\theta, \phi) = \left( \frac{2n + 1}{4\pi} \right)^{\frac{1}{2}} C_{n}^{(n)}(\theta, \phi). \]  

(1.6)

So the five functions \( Y_{2m}(\theta, \phi) \) are obtained just by adding a prefactor \((5/4\pi)^{1/2}\) to Eqs. (1.5). Extensive collections of explicit expressions for the spherical harmonics were compiled by Varshalovich et al. (1988; all \( Y_{nm} \) with \( n \leq 5 \)) and by Görller-Walrand and Binnemans (1996; \( n \leq 7 \)).

An alternative basis set, favoured particularly by experimentalists, is the one that uses the so-called Stevens normalisation (a term introduced by Newman and Ng, 1989). It is obtained by replacing the complex-valued functions \( C_{n}^{(n)}(\theta, \phi) \) by their real combinations, \( \propto C_{n}^{(n)}(\theta, \phi) \pm C_{-n}^{(n)}(\theta, \phi) \), and omitting all cumbersome numerical prefactors. The result is simple-looking trigonometric expressions. Thus, one gets instead of Eq. (1.5) the following 5 real functions:

\begin{align*}
O_{0}^{0} &= 3 \cos^{2} \theta - 1, \\
O_{1}^{1} &= \cos \theta \sin \theta \cos \phi, \\
O_{2}^{1} &= \cos \theta \sin \theta \sin \phi, \\
O_{2}^{2} &= \sin^{2} \theta \cos 2\phi, \\
O_{2}^{2} &= \sin^{2} \theta \sin 2\phi.
\end{align*}

(1.7)

Also worth of mention are Racah’s unitary operators \( U_{m}^{(n)} \) (Racah, 1942). The connection to \( C_{m}^{(n)}(\theta, \phi) \) is provided by a factor which depends on \( n \) and also on the orbital quantum number \( l \):

\[ U_{m}^{(n)} \doteq (-1)^{n/2} \frac{[(n/2)!]^2(l - n/2)!}{n!(2l + 1)(l + n/2)!} \left[ \frac{(2l + n + 1)!}{(2l - n)!} \right]^{\frac{1}{2}} C_{m}^{(n)}(\theta, \phi), \quad n \text{ even.} \]

(1.8)

Within the 4f shell (\( l = 3 \)) the corresponding relations are:

\begin{align*}
U_{m}^{(2)} &\doteq -\left( \frac{15}{28} \right)^{\frac{1}{2}} C_{m}^{(2)}(\theta, \phi), \\
U_{m}^{(4)} &\doteq \left( \frac{11}{14} \right)^{\frac{1}{2}} C_{m}^{(4)}(\theta, \phi), \\
U_{m}^{(6)} &\doteq -\left( \frac{429}{700} \right)^{\frac{1}{2}} C_{m}^{(6)}(\theta, \phi).
\end{align*}

(1.9)

It should be emphasised that the introduced various sets of basis functions for expanding \( V_{CF}(r) \) differ only in normalisation. From the standpoint of the physical approximations involved, all the above bases are absolutely equivalent and, if used properly, must yield identical results. One should just be consistent with notation and not allow indiscriminate use of CF parameters related to distinct normalisations. To avoid confusion, it is advisable to write out expressions of type (1.2) explicitly or at least to include references to such explicit expressions.

The choice of a specific basis set is merely a matter of convenience. For example, Wybourne’s irreducible tensor operators \( C_{m}^{(n)}(\theta, \phi) \) transform most simply
under rotations of the coordinate axes and are therefore particularly suited for serious theoretical work on magnetic anisotropy. The spherical harmonics $Y_{nm}(\theta, \phi)$ are normalised to unity on a sphere, hence they are a natural choice for the angular part of atomic wave functions (Condon and Shortley, 1935), being somewhat less convenient for expanding the CF potential. The 'simple-looking' basis functions in the Stevens normalisation are useful only for very simple calculations in high-symmetry cases. In particular, they are suitable for work in Cartesian coordinates (Hutchings, 1964), which is seldom done nowadays. Finally, Racah’s operators $U^{(n)}_m$ possess the important property of having unitary reduced matrix elements within any atomic shell (hence their name). The significance of this can be learned e.g. from the book of Wybourne (1965). In this Chapter we shall not deal with problems necessitating the use of $U^{(n)}_m$ or $Y_{nm}$. So we shall use mostly the irreducible tensor operators $C^{(n)}_m$ (in various representations) and less often the operators $O^m_n$ normalised according to Stevens.

1.2 Equivalent operator techniques for various subspaces: $4f^N$ configuration, LS term, $J$ multiplet, Kramers doublet

Introducing equivalent operators in this section, we shall make a clear distinction between the following two aspects of the method: (i) reduction of the dimensionality of the space of available states at different stages of the method and the underlying physical approximations; (ii) the (formally exact) algebraic techniques facilitating the calculation of the matrix elements of $\hat{V}_{\text{CF}}$ within those reduced subspaces. The need and the possibility of the approximate treatment of $\hat{H}_{4f}$ (1.1) are due to the fact that its individual terms describe interactions of grossly disparate intensities. On the other hand, to describe thermodynamic properties in a limited temperature interval, we only require a few low-lying eigenstates of $\hat{H}_{4f}$ (to about $kT$ above the ground state), while the total number of states in a $4f^N$ configuration can be a few thousand. From the point of view of physics, everything is determined by the intensity relations between the individual terms entering in $\hat{H}_{4f}$. Several distinct situations are possible, these are considered in subsections 1.2.1–1.2.5. Subsection 1.2.6 will then be devoted to the algebraic aspect of the method.

1.2.1 No restrictions

\[ E_{\text{Coulomb}} \sim E_{\text{s-o}} \sim E_{\text{ex}} \sim E_{\text{Zeeman}} \sim E_{\text{CF}}. \]  

This is a trivial case included here for the sake of completeness. No new approximations are possible (apart from the already mentioned neglect of the configuration interaction). $\hat{H}_{4f}$ has to be diagonalised within the full $4f^N$ configuration.

1.2.2 The Russel–Saunders approximation

\[ E_{\text{Coulomb}} \gg E_{\text{s-o}} \gg E_{\text{ex}} \gg E_{\text{Zeeman}} \sim E_{\text{CF}}. \]  

The energies in the symbolic relations (1.10)–(1.15) are of the order of the overall splitting of the relevant manifold by the respective terms in Eq. (1.1). For example, $E_{\text{s-o}}\gg E_{\text{ex}}$ can be understood as $|\lambda| (2L + 1) \gg 4\mu_B B_{\text{ex}}$ or even as $|\lambda| \gg \mu_B B_{\text{ex}}$. 

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The dominant Coulomb interaction is isotropic both in the coordinate and in the spin spaces. Its eigenstates are \((2L + 1)(2S + 1)\)-fold degenerate \(LS\) terms, i.e. sets of states with given total orbital moment and total spin quantum numbers. The construction of the \(|LM_L⟩|SM_S⟩\) wave functions from one-electron orbitals \(|lm⟩\), is in principle a purely algebraic problem having an exact solution. The explicit expressions, however, may be extremely cumbersome and will not be required herein. They have been described in full detail elsewhere (Sobel’man, 1972).

The approximation here consists in restricting the space of states to those of the ground \(LS\) term [subject to the usual Hund’s rules: \(S = \frac{1}{2}(2l + 1 - |2l + 1 - N|)\) and \(L = S(2l + 1 - 2S)\)]. Within that space \(\hat{H}_{\text{Coulomb}}\) reduces to a constant which will be omitted. The remaining four terms of Eq. (1.1) are projected on the ground term in the first approximation (i.e. their matrix elements on the \(|LM_L⟩|SM_S⟩\) states are computed) and diagonalised.

Validity of the Russell–Saunders approximation is determined by the strong inequality \(E_{\text{Coulomb}} \gg E_{\text{s-o}} \gg \max(E_{\text{ex}}, E_{\text{Zeeman}}, E_{\text{CF}})\). Since it involves only intra-atomic interactions it has been investigated in a rather exhaustive manner. Though generally inaccurate for the RE’s, the Russell–Saunders approximation holds surprisingly well for their ground \(LS\) terms, which are all more than 96% pure (Dieke, 1968). This suffices for our purpose in this Chapter. In what follows we shall regard the Russell–Saunders approximation as valid in all cases.

### 1.2.3 The single-multiplet approximation (within the Russell–Saunders coupling scheme)

\[
E_{\text{Coulomb}} \gg E_{\text{s-o}} \gg E_{\text{ex}} \sim E_{\text{Zeeman}} \sim E_{\text{CF}}.
\]  

(1.12)

This is a particular case of the previous one. The added approximation here is the one expressed by the inequality \(E_{\text{s-o}} \gg \max(E_{\text{ex}}, E_{\text{Zeeman}}, E_{\text{CF}})\). It is generally not a very good approximation, particularly for the light RE’s and most notoriously for samarium. On the other hand, this approximation is vital for the analytical tractability of many important problems. Its validity is hard to estimate a priori, since it depends on the characteristics of the solid, in particular on the relation between \(E_{\text{ex}}\) and \(E_{\text{CF}}\). We shall dedicate a special section (2.9) to the question of validity of the single-\(J\) approximation in exchange-dominated systems (tentatively defined by \(E_{\text{ex}} \gg E_{\text{CF}}\); see Section 2.2 for more a detailed definition).

Technically the approximation is straightforward: \(\hat{H}_{\text{Coulomb}} + \hat{H}_{\text{s-o}}\) reduces to a constant and is omitted; \(\hat{H}_{\text{ex}} + \hat{H}_{\text{Zeeman}} + \hat{H}_{\text{CF}}\) is projected on the ground \(J\) manifold comprising the \(2J + 1\) states of type \(|LSJM⟩\), where \(J = L \pm S\) (3rd Hund’s rule). These are constructed from the states of the ground \(LS\) term according to the following simple relation (Condon and Shortley, 1935):

\[
|LSJM⟩ = \sum_{M', M''} C_{LM'M''}^{JM} |LM'M'⟩|SM''⟩,
\]

(1.13)

where \(C_{LM'M''}^{JM}\) are the so-called Clebsch–Gordan coefficients (CGC)—exactly known functions of the quantum numbers \(J, M, L, M', S, M''\). The CGC have been extensively tabulated (Varshalovich et al., 1988; Rotenberg et al., 1959). More
information about the CGC can be found in Chapter 8 of Varshalovich et al. (1988), including explicit expressions for $C_{LM}^{M'}M''$ in the practically important particular case of a ground multiplet obeying the 3rd Hund’s rule, $J = L \pm S$.

1.2.4 CF-dominated RE systems

$$E_{\text{Coulomb}} \gg E_{\text{s-o}} \gg E_{\text{CF}} \gg E_{\text{ex}} \sim E_{\text{Zeeman}}.$$  (1.14)

A special case of the situation considered in the previous subsection. It has little relevance to hard magnetic materials and is included here just for completeness. The subspace of accessible states is shaped by the CF, so it depends essentially on the symmetry of the crystallographic site occupied by the RE and also on the value of $J$.

The analysis is particularly simple at low temperatures, where the magnetic behaviour is determined by the ground CF level. This may typically be either a singlet ($J$ is an integer) or a Kramers doublet ($J$ semi-integral). Within the ground CF level $\hat{H}_{\text{CF}}$ as well as $\hat{H}_{\text{Coulomb}} + \hat{H}_{\text{s-o}}$ reduce to irrelevant constants and can be omitted. Of course, the CF still governs the properties dependent on the wave functions of the ground state, e.g. the effective $g$-factor of a doublet.

Often a pair of closely situated singlets make an accidental doublet, or a quasi-doublet. The presence of the CF is then manifest in the zero-field splitting of such a quasi-doublet, as well as determining the $g$-factor.

1.2.5 Exchange-dominated RE systems

$$E_{\text{Coulomb}} \gg E_{\text{s-o}} \gg E_{\text{ex}} \gg E_{\text{CF}} \sim E_{\text{Zeeman}}.$$  (1.15)

This special case is most closely relevant to RE-based hard magnetic materials, it will be investigated in greater detail in subsequent sections. Either part of the double inequality $E_{\text{s-o}} \gg E_{\text{ex}} \gg E_{\text{CF}}$ may fail under certain circumstances, which imposes substantial limitations on the applicability of this approximation. These will be considered separately for each half of the inequality (Sections 2.2 and 2.9).

1.2.6 Chains of equivalent operator representations

In the previous sections we have analysed several possible intensity relations between the individual interactions within $\hat{H}_{4f}$. In each case the quantitative description consisted in projecting some of the terms of Eq. (1.1) onto one of a hierarchically organised chain of subspaces within the $4f^{N}$ configuration: $LS$ term, $J$ multiplet, Kramers doublet... Thus, the problem in each case reduces to computing the matrix elements of $V_{\text{CF}}$ within one of those subspaces. The equivalent operator technique makes this task easier. Let us consider the following chain of equivalence

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$^{3}$ The rather straightforward handling of the remaining terms of Eq. (1.1) has been described in many standard texts on quantum mechanics (e.g. Van Vleck, 1932; Condon and Shortley, 1935; Schiff, 1949). We shall make use of these well-known results according as we need them.
relations:
\[
\sum_{i=1}^{N} r_i^2 C_m^{(2)}(\theta_i, \phi_i) \equiv \langle r^2 \rangle_4 \sum_{i=1}^{N} C_m^{(2)}(\theta_i, \phi_i) \equiv \alpha_l \langle r^2 \rangle \sum_{i=1}^{N} C_m^{(2)}(\hat{l}_i)
\]
\[
= \alpha_L \langle r^2 \rangle \sum_{i=1}^{N} C_m^{(2)}(\hat{L}) \equiv \alpha \langle r^2 \rangle \sum_{i=1}^{N} C_m^{(2)}(\hat{J}) \equiv (\pm) \text{ const.}
\]
(1.16)

Here \( C_m^{(2)}(\hat{J}) \) denotes the following operator expressions\(^4\):

\[
C_0^{(2)}(\hat{J}) = \frac{1}{2} \left[ 3 \hat{J}_z^2 - J(J + 1) \right],
\]

\[
C_{\pm 1}^{(2)}(\hat{J}) = \pm \left( \frac{3}{8} \right)^{1/2} \left[ \hat{J}_z (\hat{J}_x \pm i \hat{J}_y) + (\hat{J}_x \pm i \hat{J}_y) \hat{J}_z \right],
\]

\[
C_{\pm 2}^{(2)}(\hat{J}) = \left( \frac{3}{8} \right)^{1/2} (\hat{J}_x \pm i \hat{J}_y)^2
\]
while \( C_m^{(2)}(\hat{l}) \) and \( C_m^{(2)}(\hat{L}) \) are the same expressions, but with \( \hat{l} \) or \( \hat{L} \) substituted for \( \hat{J} \). Each operator in the chain (1.16) is defined in a distinct space of states, e.g. \( C_m^{(2)}(\hat{L}) \) operate within an LS term. Each subsequent space is a subspace of the previous one. Any matrix element of an operator standing on the right of the equivalence sign ‘\( = \)’ between any two states belonging to the space where that operator is defined equal the corresponding matrix element of the operator on the left-hand side of ‘\( = \)’. The opposite is not necessarily true. For example,

\[
\langle LSJ M' | \alpha_l C_m^{(2)}(\hat{L}) | LSJM \rangle = \langle LSJ M' | \alpha J C_m^{(2)}(\hat{J}) | LSJM \rangle. \quad (1.18)
\]

However, if \( J \neq J' \), then

\[
\langle LSJ M' | \alpha_l C_m^{(2)}(\hat{L}) | LSJM \rangle \neq 0 = \langle LSJ M' | \alpha J C_m^{(2)}(\hat{J}) | LSJM \rangle. \quad (1.19)
\]

That is, the matrix elements of the two operators coincide only within a subspace where both of them are defined. Hence the use of a special sign of equivalence in Eq. (1.16) instead of the usual equality sign.

The reason for having so many different representations for the CF is merely convenience—each one is ideally suited for computing matrix elements within the corresponding space of states. The choice of that space is not arbitrary; it constitutes an approximation and is dictated by the physical situation under study, examples

\(^4\) These can be obtained from Eqs. (1.5) using the following simple rules:

(i) convert \( r^n C_n^m(\theta, \phi) \) to Cartesian coordinates, replacing \( r^2 \) with \( x^2 + y^2 + z^2 \);

(ii) symmetrise each monomial, e.g. \( xy = \frac{1}{2}(xy + yx) \);

(iii) substitute \( \hat{J}_x, \hat{J}_y, \hat{J}_z \) for \( x, y, z \), respectively.

The most complete list of explicit expressions for \( C_m^{(n)}(\hat{J}) \), with \( 0 \leq n \leq 8 \), was compiled by Lindgård and Danielsen (1974).
being given in the preceding sections. For example, the $J$-representation is particularly convenient for a $J$ multiplet, the matrix elements of the second-order operators (1.17) are then given by

$$\langle LSJM'|C_0^{(2)}(\hat{J})|LSJM \rangle = \frac{1}{2}[3M^2 - J(J + 1)]\delta_{M',M},$$

$$\langle LSJM'|C_{\pm 1}^{(2)}(\hat{J})|LSJM \rangle = \mp(M' + M)\left[\frac{3}{8}(J \pm M')(J \mp M)\right]^{\frac{1}{2}}\delta_{M',M \pm 1},$$

(1.20)

$$\langle LSJM'|C_{\pm 2}^{(2)}(\hat{J})|LSJM \rangle = \left[\frac{3}{8}(J \pm M')(J - 1 \pm M')(J \mp M)(J - 1 \mp M)\right]^{\frac{1}{2}}\delta_{M',M \pm 2}.$$

Similar explicit expressions can be also written for the matrix elements of the higher-order operators $C_m^{(4)}(\hat{J})$ and $C_m^{(6)}(\hat{J})$.

The equivalence coefficients in Eq. (1.16), $\alpha_l, \alpha_L, \alpha_J$, are known rational numbers. In general, $\alpha_l$ is given by

$$\alpha_l = \frac{-2}{(2l - 1)(2l + 3)}$$

(1.21)

that is, $\alpha_l = -2/45$ for all RE's.

A general explicit expression for $\alpha_L$ is quite complicated, but for a ground term obeying Hund's rules, $S = \frac{1}{2}(2l + 1 - |2l + 1 - N|)$, $L = S(2l + 1 - 2S)$, it simplifies to (Bleaney and Stevens, 1953):

$$\alpha_L = \pm\alpha_l \frac{2l + 1 - 4S}{2l - 1}$$

(1.22)

where the upper sign is required for a shell less than half full, and the lower sign for a shell more than half full.

Expressions for the Stevens coefficients $\alpha_J$ are generally extremely cumbersome (Wybourne, 1965). Of interest to us here are only those for the ground multiplets of the RE's, $J = L \pm S$. These are given by

$$\alpha_J = \alpha_L \times \begin{cases} (L + 1)(2L + 3), & \text{if } J = L - S \text{ (light RE)} \\ (J + 1)(2J + 3), & \text{if } J = L - S - 1 \\ L(2L - 1), & \text{if } J = L + S - 1 \\ J(J - 1), & \text{if } J = L + S \text{ (heavy RE).} \end{cases}$$

(1.23)

The values computed using Eq. (1.23) are collected in Table 3.1.

Chains of equivalence relations similar to (1.16) can be also written for higher-order operators $C_n^{(4)}$ and $C_n^{(6)}$, the coefficients therein being $\beta_{l,L,J}$ ($n = 4$) and $\gamma_{l,L,J}$ ($n = 6$). By analogy with the second-order case, $\beta_l$ and $\gamma_l$ are given by general expressions similar to Eq. (1.21); for all RE's $\beta_l = 2/495$ and $\gamma_l = -4/3861$. Formulae similar to (1.22) exist for $\beta_L$ and $\gamma_L$ in the case of a Hund's ground term (Bleaney and Stevens, 1953). The fourth- and sixth-order Stevens factors, $\beta_J$ and
\[ \langle LSJM'|C_m^{(n)}(\mathbf{J})|LSJM \rangle = \frac{1}{2^n} \sqrt{\frac{(2J+n+1)!}{(2J+1)(2J-n)!}} C_{J\text{M}n}^{M'M'} \]  

The matrix elements of \( C_m^{(n)}(\hat{L}) \) between the states \(|LM_L\rangle\) or those of \( C_m^{(n)}(\hat{J}) \) between \(|lm\rangle\) are obtained from Eq. (1.24) through the obvious substitution of \( L \) or \( l \) for \( J \) etc.

A less obvious fact with rather far-reaching consequences is that the matrix element of \( C_m^{(n)} \) in any representation between \(|LSJM\rangle\) is proportional to the same CGC \( C_{J\text{M}n}^{M'M'} \), the proportionality factor being independent of the ‘projection’ quantum numbers \( m, M, M' \). This statement is known as the Wigner–Eckart theorem (Edmonds, 1957; Varshalovich et al., 1988). It is the foundation-stone of the method of equivalent operators, since it directly follows that in order to compute such matrix elements, one only needs (apart from the standard CGC) a set of coefficients for \( n = 2, 4, 6 \), that is \( \alpha, \beta \) and \( \gamma \).

Choosing one or another representation for \( C_m^{(n)} \) is thus a matter of convenience. On the contrary, the choice of a correct set of basis states for \( \mathcal{H}_{4f} \) is very important,
it involves approximations and should be based upon intensity relations of type (1.10)–(1.15).

Likewise, it is a matter of convention whether to use $C_n^m$ or $U_n^m$. The Wigner–Eckart theorem is valid for all of them. The chains of equivalences for $Y_{nm}$ and $U_n^m$ look exactly the same as those for $C_n^m$, including the values of the coefficients $\alpha, \beta$ and $\gamma$. Moreover, the same equivalences hold for the operators $O_n^m$ normalised according to Stevens, which do not obey the Wigner–Eckart theorem. Indeed, there is a fairly straightforward connection between Eqs. (1.5) and (1.7):

\[
O_n^0 = 2C_n^{(2)} , \quad O_n^1 = \left( \frac{1}{6} \right)^{\frac{1}{2}} (C_n^{(2)} - C_n^{(2)}) , \quad \text{etc.}
\]  

These relations are valid in any representation: coordinate, $l$, $L$ or $J$. Hence equations of type (1.16) hold for $O_n^m$ as well. It was in fact for $O_n^m$ that the principle of equivalence was first stated (Stevens, 1952).

Combining Eqs. (1.25) with the Wigner–Eckart theorem (1.24), one can express matrix elements of $O_n^m$ in terms of linear combinations of CGC. These expressions are less convenient for analytical work and are seldom used because the coefficients therein depend not just on $n$, but also on $m$ (a high price to pay for the apparent simplicity of the Stevens normalisation). More common are direct tabulations of the matrix elements of $O_n^m$ (Stevens, 1952; Hutchings, 1964; Abragam and Bleaney, 1970; Al'tshuler and Kozyrev, 1974).

1.3 Local symmetry and the exact form of $\hat{H}_{\text{CF}}$

Towards the conclusion of this introductory section, let us take a closer look at what exactly determines the number of relevant terms in the expansion of the CF potential (1.2). As long as configuration mixing is neglected, this number cannot exceed 27, but is usually far less than that—just 2 in the highest-symmetry case (cubic point groups $T_d$, $O$ or $O_h$):\footnote{For compactness we use the Stevens normalisation for the CF operators, since we do not intend calculating their matrix elements in this subsection. In this context the operators $O_n^m$ should not be hastily identified with their $J$-representation, i.e. with $O_n^m(J)$. The symmetry considerations determining the form of $\hat{H}_{\text{CF}}$ are quite independent of the chosen representation. Therefore, depending on the situation, $O_n^m$ in Eqs. (1.26)–(1.32) may be understood as $\sum_{\mathbf{r}=1}^{N} O_n^m(\theta, \phi)$ or as $O_n^m(L)$ etc. The loosely defined CF parameters are denoted with lower-case letters, to avoid confusion with properly specified CF parameters.}

\[
\hat{H}_{\text{CF}} = b_4 (O_4^0 + 5O_4^1) + b_6 (O_6^0 - 21O_6^1).
\]  

(1.26)

Not seldom one comes across an erroneous assertion of Eq. (1.26) being characteristic of the ‘cubic symmetry’ in general (Lea et al., 1962, to give just one example). In reality however, if the local symmetry of the RE site is described by either one of the cubic point groups $T$ or $T_h$ (cf. Table 3.2), $\hat{H}_{\text{CF}}$ must contain an extra sixth-order term:

\[
\hat{H}_{\text{CF}} = b_4 (O_4^0 + 5O_4^1) + b_6 (O_6^0 - 21O_6^1) + b'_6 (O_6^2 - O_6^6).
\]  

(1.27)

This expression is clearly distinct from Eq. (1.26), so the need to take this matter further should raise no doubts. (Many of such misstatements originate from the
old CF theory, aimed exclusively at d-ions and therefore limited to fourth-order terms.)

Now, with full rigour one can say that the form of $\hat{H}_{CF}$ is uniquely determined by the point group describing the local symmetry of the crystallographic site occupied by the RE. The traditional combinations of point groups called syngonies, or crystal systems (cubic, tetragonal etc., Table 3.2) provide no valid basis for judgement in this question.\textsuperscript{6}

The form of $\hat{H}_{CF}$ also depends on the orientation of the coordinate system in relation to the crystallographic directions. In the above example (1.26) all three coordinate axes were set parallel to 4-fold symmetry axes. A rotation through $\pm \pi/4$ around $z$ would correspond to a simultaneous change of sign of the coefficients of $O_4^4$ and $O_6^4$ in Eq. (1.26). Setting the $z$ axis along a 2- or a 3-fold crystal axis would lead to Eqs. (6.14) or (6.15) of Hutchings (1964). Note that the number of independent CF parameters (in this case, two) is independent of the choice of the

\textsuperscript{6} Sometimes the name of a crystal system is used as a synonym for the most symmetric (holohedral) point group of that crystal system (listed last under each of the headings in Table 3.2). Such liberty with the terms should be avoided, as it only causes confusion.
coordinate system. In the examples that follow the \( z \) axis will always be set along a
high-symmetry crystal direction.

Local symmetry is the symmetry of the whole crystal seen from the standpoint
of the RE. (If RE atoms occupy several non-equivalent sites in a crystal, there are
generally as many distinct symmetries.) It should not be confounded with the ‘type
of coordination’, or the shape of the polyhedron made by the nearest neighbours of
the RE. Figure 3.2 illustrates this point in two dimensions: the nearest neighbours
of the central atom form a perfect square, described by the point group \( D_{4h} \). The
true local symmetry is however lower, \( C_{4h} \). The corresponding expressions for \( \hat{H}_{CF} \)
are distinct, cf. Eqs. (1.31) and (1.32) below.

On the other hand, the local symmetry of the RE site should be distinguished
from the crystallographic class, or the point group describing the crystal as a
whole, regardless of the viewpoint. Thus, the famous permanent magnet materials
RE\(_2\)Fe\(_{14}\)B (space group \( P4_2/mnm—D_{14h} \)) belong to the tetragonal crystallographic
class \( D_{4h} \). The RE atoms occupy sites of two kinds, \( 4f \) and \( 4g \), the symmetry
of both being described by the orthorhombic point group \( C_{2v} \). A definitive re-
ference in this matter is the International Tables for Crystallography (Hahn, 1983).
For the space group \( P4_2/mnm \) one reads there, on page 459 of volume A, that
the \( 4f(\mathbf{xz}0) \) and the \( 4g(\mathbf{xx}0) \) sites both have the symmetry of \( m.2m \), that is \( mm2 \),
or \( C_{2v} \). When comparing atomic positions described in the original literature and
in the International Tables, one should be aware of the possible multiple choices of
the origin and axes orientations.

Having determined the local point group, we are ready to formulate the main
principle governing the form of \( \hat{H}_{CF} \). It sounds surprisingly simple: \( \hat{H}_{CF} \) may only
contain terms invariant under all symmetry operations of the local group. Alterna-
tively, in terms of the theory of representations: only the terms which belong to
the identity, or totally symmetric irreducible representation of the local point group
may enter in \( \hat{H}_{CF} \).

Let us demonstrate this principle for the point group \( C_4 (m) \). It is convenient to
rewrite Eqs. (1.7) in Cartesian coordinates:
\[ O_2^0 = \frac{3z^2}{r^2} - 1, \]
\[ O_2^1 = \frac{xz}{r^2}, \quad \Omega_2^1 = \frac{yz}{r^2}, \]
\[ O_2^2 = \frac{x^2 - y^2}{r^2}, \quad \Omega_2^2 = \frac{2xy}{r^2}. \] (1.28)

The group \( C_s \) contains a single non-trivial symmetry element—a mirror plane perpendicular to the \( z \) axis. Being invariant in this case is equivalent to being even in \( z \). The allowed second-order terms thus are \( O_2^0, O_2^1 \) and \( \Omega_2^1 \). This analysis is extended in a natural way to higher-order operators. The result is that all \( O_n^m \) and \( \Omega_n^m \) with both \( n \) and \( m \) even enter in \( \hat{H}_{CF} \) (those with \( n > 6 \) do not affect the \( 4f \) shell and need not be included). A convenient collection of explicit expressions for \( O_n^m \) and \( \Omega_n^m \) can be found in Appendix V of Al’tshuler and Kozyrev (1974). Alternatively, one may use the extensive list of tesseral harmonics, \( Z_{nm} \propto O_n^m \) and \( Z_{nm} \propto \Omega_n^m \), compiled by Görller-Walrand and Binnemans (1996, Appendix 2).

The orthorhombic point group \( D_{2h} (mmm) \) contains three mutually perpendicular mirror planes, as well as combinations thereof. The invariant terms are those even in all three coordinates, i.e. \( O_2^2 \) and \( \Omega_2^2 \) from Eqs. (1.28), and generally \( O_n^m \) with \( n \) and \( m \) even.

One need not perform this analysis every time anew. Exhaustive results for all 32 point groups have been obtained and tabulated (Bradley and Cracknell, 1972; Altmann and Herzig, 1994; Görller-Walrand and Binnemans, 1996). For example, for the simplest hexagonal point group \( C_6 \) one finds on page 64 of Bradley and Cracknell (1972) the following table:

<table>
<thead>
<tr>
<th>( 6 ) (( C_6 ))</th>
<th>( m \mod 6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>0</td>
</tr>
<tr>
<td>( B )</td>
<td>3</td>
</tr>
<tr>
<td>( 1^E_1 )</td>
<td>4</td>
</tr>
<tr>
<td>( 2^E_1 )</td>
<td>2</td>
</tr>
<tr>
<td>( 1^E_2 )</td>
<td>1</td>
</tr>
<tr>
<td>( 2^E_2 )</td>
<td>5</td>
</tr>
</tbody>
</table>

The relevant information is in the first line, corresponding to the totally symmetric irreducible representation \( A \). It reads: allowed are all spherical harmonics \( Y_{nm} \) (or \( C_m^{(n)} \), or \( U_m^{(n)} \)) with \( n \) arbitrary and \( m = 0 \mod 6 \), i.e. 0, \( \pm 6, \pm 12 \) etc. (note that those with \( n \) odd are not forbidden, cf. footnote 1). Turning to the Stevens convention and limiting ourselves to \( n = 2, 4, 6 \), we arrive at

\[ \hat{H}_{CF} = b_{20} O_2^0 + b_{40} O_4^0 + b_{60} O_6^0 + b_{66} \Omega_6^6 \] (1.29)

where all the coefficients are real numbers. Equation (1.29) is related to the coordinate system whose \( z \) axis is parallel to the 6-fold crystal axis [001] and whose \( \chi \) axis is set along an elementary translation vector in the basal plane [100]. The last term in (1.29) can be eliminated by rotating the coordinate system around the
Theory of Crystal-Field Effects in 3d-4f Intermetallic Compounds

z axis through an (unknown a priori) angle $\phi_0$, such that $\tan 6\phi_0 = b'_{66}/b_{66}$. Equation (1.29) is also valid for the hexagonal point groups $C_{3h}$ and $C_{6h}$.

Let us consider another hexagonal group, $D_6$. The corresponding table is on page 65 of Bradley and Cracknell (1972). The top part of it looks as follows:

<table>
<thead>
<tr>
<th>$622$ ($D_6$)</th>
<th>$l$</th>
<th>$m \mod (+6)$</th>
<th>$\phi$-dep</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>0</td>
<td>0</td>
<td>c</td>
</tr>
<tr>
<td>$A_2$</td>
<td>7</td>
<td>6</td>
<td>s</td>
</tr>
</tbody>
</table>

Once again, what we need is in the first line of the table (the second line, though related to the identity representation $A_1$, contains information on odd harmonics of order seven or higher). According to the convention adopted by Bradley and Cracknell (1972), $l$ in the header is an abbreviation of $l \mod (+2)$. Thus, we read: allowed are the harmonics with $l$, in our notation $n = 0 \mod (+2)$ and $m = 0 \mod (+6)$. The last column further specifies: when $m \neq 0$, only symmetric combinations of type $(Y_{nm} + Y_{n-m}) \propto \cos m\phi$ are admissible, i.e. $O^m_n$ as opposed to $\Omega^m_n$. One therefore has

$$\hat{\mathcal{H}}_{\text{CF}} = b_{20} O^0_2 + b_{40} O^0_4 + b_{60} O^0_6 + b_{66} O^6_6. (1.30)$$

The same expression is obtained for the hexagonal groups $C_{6v}, D_{3h}$ and $D_{6h}$.

A further example—tetragonal point groups $C_4, S_4$ and $C_{4h}$:

$$\hat{\mathcal{H}}_{\text{CF}} = b_{20} O^0_2 + b_{40} O^0_4 + b_{44} O^4_4 + b_{44} \Omega^4_4 + b_{60} O^0_6 + b_{64} O^4_6 + b_{64} \Omega^4_6. (1.31)$$

Note that no rotation in the basal plane can reduce this expression to Eq. (1.32), i.e. eliminate $b_{44}$ and $b_{64}$ simultaneously. (This was only possible in the old CF theory, aimed mainly at spectroscopic properties of d-ions, hence the misconception of the ‘united tetragonal symmetry’.)

The expression for the remaining tetragonal groups ($D_4, C_{4v}, D_{2d}, D_{4h}$) is as follows:

$$\hat{\mathcal{H}}_{\text{CF}} = b_{20} O^0_2 + b_{40} O^0_4 + b_{44} O^4_4 + b_{60} O^0_6 + b_{64} O^4_6. (1.32)$$

Summarising this subsection, the precise form of the CF Hamiltonian cannot be inferred from vague general categories like cubic (hexagonal, tetragonal etc.) symmetry. Rather, it is uniquely determined by the local point group of the crystallographic site occupied by the RE and can be inquired about in widely available tables (Bradley and Cracknell, 1972; Altmann and Herzig, 1994). Finally, one can consult the nearly complete list (missing are the cubic groups $T$, $T_h$ and $O$) of explicit expressions for $\hat{\mathcal{H}}_{\text{CF}}$ in terms of $C_m^{(n)}$ (Görller-Walrand and Binnemans, 1996, Appendix 3).
2. **THE SINGLE-ION ANISOTROPY MODEL FOR 3d-4f INTERMETALLIC COMPOUNDS**

2.1 Macroscopic description of magnetic anisotropy

Let us consider a macroscopic system held at temperature $T$ in an applied magnetic field $\mathbf{B}$. These *external* parameters may vary only quasi-statically, so that at all times the system remains at thermal equilibrium. The standard thermodynamic description of such a system is afforded by specifying its free energy $F(T, \mathbf{B}, \ldots)$, which is a *characteristic function* of $T$, $\mathbf{B}$ and perhaps further external parameters. The equations of state are then obtained by taking partial derivatives of the free energy with respect to its variables:

\[
S(T, \mathbf{B}, \ldots) = -\left(\frac{\partial F}{\partial T}\right)_B, \tag{2.1}
\]

\[
M(T, \mathbf{B}, \ldots) = -\left(\frac{\partial F}{\partial B}\right)_T. \tag{2.2}
\]

Here $S, M, \ldots$ are the system’s *internal* parameters: entropy, magnetisation, etc. External and internal parameters make pairs of conjugate thermodynamic variables: $T$–$S$, $\mathbf{B}$–$M$, etc. In this Chapter we shall deal mainly with the magnetic equation of state (2.2). This is not to say that the caloric equation of state (2.1) is less important. The entropy plays a central role in magneto-thermal properties, such as specific heat and magnetocaloric effect (Tishin and Spichkin, 2003).

Alternatively to using the equilibrium free energy $F(T, \mathbf{B})$ one can take as a starting point the non-equilibrium with respect to magnetisation thermodynamic potential $\Phi(T, \mathbf{B}, M)$. Unlike the usual equilibrium potentials, $\Phi$ depends on both conjugate variables, $\mathbf{B}$ and $M$, and the corresponding equation of state is obtained by minimising it with respect to the internal parameter $M$:

\[
\left(\frac{\partial \Phi}{\partial M}\right)_{T, \mathbf{B}} = 0 \tag{2.3}
\]

and $(\partial^2 \Phi/\partial M^2)_{T, \mathbf{B}} > 0$. The so minimised thermodynamic potential is the equilibrium free energy, $\min_M \Phi(T, \mathbf{B}, M) = F(T, \mathbf{B})$.

Both approaches are of course equivalent, as long as they lead to the same magnetic equation of state, either in the form of Eq. (2.2) or of Eq. (2.3). The free energy is the preferred route when the system’s partition function $Z(T, \mathbf{B})$ can be computed; then $F$ is given by the well-known relation of the statistical mechanics, $F = -kT \ln Z$.

In turn, $\Phi$ is advantageous in phenomenological theories since its dependence on $M$ and $\mathbf{B}$ can be inferred from the rather general considerations of symmetry. For example, a ferromagnet near its Curie point is described by (Landau and Lifshitz, 1958):

\[
\Phi(T, \mathbf{B}, M) = \Phi_0 + \frac{1}{2} aM^2 + \frac{1}{4} bM^4 + \cdots - \mathbf{B} \cdot \mathbf{M} \tag{2.4}
\]
where the quantities $\Phi_0, a, b, \ldots$ depend on temperature and other external parameters, e.g. pressure, but not on magnetic field or magnetisation. The only assumptions used in the construction of the expansion (2.4) are the time-evenness of $\Phi$ and the smallness of $M$. It is however sufficient to obtain a number of useful predictions regarding the thermodynamic behaviour of ferromagnets near the Curie point.

Up to this point we have not paid much attention to the fact that both $B$ and $M$ are vectors, which means that in effect one has to deal with three pairs of conjugate magnetic variables. The system under consideration was tacitly assumed isotropic (therefore at equilibrium $M || B$), so setting one of the coordinate axes along $B$ reduced the description to a single pair of scalar variables.

Now we turn to the anisotropic case, which is both more general and more interesting, since it demonstrates to full extent the advantages of the symmetry approach based on the use of the non-equilibrium thermodynamic potential $\Phi(T, B, M)$. The coefficients in the Landau expansion (2.4) now become tensor quantities. For example, $\frac{1}{2}a M^2$ is replaced with $\frac{1}{4} \sum a_{\alpha\beta} M_\alpha M_\beta$, where $a_{\alpha\beta}$ is a tensor of rank two, the sum being taken over $\alpha, \beta = x, y, z$. Many of the components of $a_{\alpha\beta}, b_{\alpha\beta\gamma\delta}$ etc. may be equal to each other or vanish for symmetry reasons. More strictly, this depends on the point group describing the symmetry of the crystal as a whole (since we are dealing with macroscopic properties), also known as the crystallographic class. Thus, for any point group of the cubic crystal system (see Table 3.2) the expansion (2.4) takes the following form:

$$\Phi(T, B, M) = \Phi_0 + \frac{1}{2} a M^2 + \frac{1}{4} b M^4 + b'(M_x^2 M_y^2 + M_y^2 M_z^2 + M_z^2 M_x^2)$$

$$+ \cdots - B \cdot M.$$  

In this case the anisotropy makes its first appearance in the terms of fourth order. However, in lower-symmetry crystals it affects second-order terms as well.

In certain classes of phenomena the magnitude of the magnetisation vector varies little, while its direction may change significantly. In such a situation it is convenient to use as internal thermodynamic parameter the direction of $M$, rather than its Cartesian components. Direction cosines or spherical angles can be used for the purpose. A specific example is the behaviour of a ferromagnet well below the Curie point in a weak to moderate magnetic field. The energy associated with a noticeable change of $|M|$ is of the order of $T_C \sim 10^3$ K per atom ($\sim 10^3$ K for ferromagnets less suitable for applications). The anisotropy energy is usually much smaller, reaching $\sim 10^1$ K per atom in YCo$_5$—one of the most strongly anisotropic 3d magnets (Alameda et al., 1981). The RE contribution to the anisotropy energy may exceed 100 K per RE atom at low temperature (Radwański, 1986), which upon averaging over all atoms in an iron- or cobalt-rich compound would yield $\sim 2 \times 10^1$ K per atom. This is significantly less than the 3d–3d exchange energy. At any rate, it should be kept in mind that the formalism of magnetic anisotropy is an approximate one and that its validity is limited by the requirement that $|M|$ should be essentially constant. It does not apply near $T_C$, in very strong magnetic fields or when $|M|$ is itself strongly anisotropic. The latter restriction concerns e.g. YCo$_5$, where $|M|$ changes by as much as 4% upon reorientation (Alameda et al., 1981). In general, the
approach might fail in RE compounds at low temperatures. From now on we limit ourselves to such phenomena where $|M(T, B)| = M_s(T)$, i.e. the magnitude of the magnetisation is practically independent of applied field and equals the spontaneous magnetisation. The anisotropic version of Landau’s expansion then becomes

$$
\Phi = \Phi_0 + \frac{1}{2} M_s^2(T) \sum_{\alpha, \beta} a_{\alpha\beta} n_{\alpha} n_{\beta} + \frac{1}{4} M_s^4(T) \sum_{\alpha, \beta, \gamma, \delta} b_{\alpha\beta\gamma\delta} n_{\alpha} n_{\beta} n_{\gamma} n_{\delta} + \cdots - M_s(T) n \cdot B
$$

(2.6)

where $n \equiv M/|M|$ is a unit vector in the direction of the magnetisation. The fact that only quadratic and quartic terms have been written out explicitly does not imply rapid convergence of the expansion (2.6) or that its truncation after the quartic term is legitimised in any way. The situation here is radically different from that in a ferromagnet near $T_C$—the subject of Landau’s theory of second-order phase transitions (Landau and Lifshitz, 1958). The truncation of Eq. (2.4) was based on the obvious fact that $M_s \to 0$ as $T \to T_C$. Conversely, $M_s$ is not at all small in Eq. (2.6). It is to be assumed that the series (2.6) diverges, unless proven otherwise. Equation (2.6) is too general to be useful. Let us rewrite it for some commonly encountered special cases. The key point here is the invariance of each term of the expansion under all symmetry operations of the crystallographic class. Thus, for the cubic classes $T_d$, $O$ and $O_h$ Eq. (2.6) becomes

$$
\Phi = \Phi_0' + E_a - M_s(T) n \cdot B
$$

(2.7)

where

$$
\Phi_0' = \Phi_0 + \frac{1}{2} a M_s^2(T) + \frac{1}{4} b M_s^4(T) + \cdots
$$

and

$$
E_a = K_1 (n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2) + K_2 n_x^2 n_y^2 n_z^2 + \cdots
$$

(2.8)

The quantity $E_a$—the anisotropic part of the thermodynamic potential in the absence of magnetic field—is known as anisotropy energy, while $K_1$, $K_2$ etc. are called anisotropy constants. The latter may depend on temperature and other external parameters, but not on magnetic field. The dependence of $\Phi$ on $B$ is limited to the last, Zeeman term of Eq. (2.7). Equation (2.8) was first obtained by Gans and Czerlinsky (1932).

For the cubic crystallographic classes $T$ and $T_h$ the anisotropy energy contains an extra sixth-order term in addition to that in Eq. (2.8):

$$
K_3 [n_x^2 n_y^2 (n_z^2 - n_x^2) + n_y^2 n_z^2 (n_x^2 - n_y^2) + n_z^2 n_x^2 (n_y^2 - n_z^2)].
$$

(2.9)

This term is invariant under the rotations around the 3-fold axes (equivalent to cyclic permutations within the triplet $n_x^2, n_y^2, n_z^2$), but is not invariant with respect to rotations through $90^o$ about the 4-fold axes (pair permutations of the type $n_x^2 \leftrightarrow n_y^2$). Therefore, it is allowed in the lower-symmetry cubic groups $T$ and $T_h$, containing 3-fold axes only, and forbidden in the higher-symmetry cubic groups $T_d$,.*
Theory of Crystal-Field Effects in 3d-4f Intermetallic Compounds

169

$O_h$, which include 4-fold axes as well. A direct parallel can be drawn here to Eqs. (1.26), (1.27) describing the CF for the same point groups.

For non-cubic point groups it is customary to describe the direction of $M$ by means of the conventional spherical angles $\theta$ and $\phi$. The polar axis is conveniently set along a high-symmetry crystallographic direction, whose choice presents no difficulty except for the triclinic groups $C_{1}$ and $C_{i}$. The anisotropy energy, $E_a(\theta, \phi)$, is then expanded over a suitably chosen basis, e.g. over the irreducible tensor operators:

$$E_a = \sum_{n=2}^{\infty} \sum_{m=-n}^{n} \kappa_{nm} C_{m}^{(n)}(\theta, \phi). \quad (2.10)$$

Note that there is no generally valid reason to truncate this expansion after any finite number of terms.

An added advantage of presenting $E_a$ as Eq. (2.10) is the possibility to exploit the formal analogy with the CF potential (1.2). A particular point group dictates the same form of both $E_a(\theta, \phi)$ and $V_{CF}(r, \theta, \phi)$. Therefore, the expressions obtained in Section 1.3 for specific point groups can be simply taken over. Alternatively, one can consult the tables recommended therein (Bradley and Cracknell, 1972; Altmann and Herzig, 1994; Görller-Walrand and Binnemans, 1996).

Thus, by analogy with Eq. (1.30), we write for the hexagonal crystallographic classes $D_{6h}$, $C_{6h}$, $D_{3h}$ and $D_{6h}$:

$$E_a = \kappa_{20} P_{2}(\cos \theta) + \kappa_{40} P_{4}(\cos \theta) + \kappa_{60} P_{6}(\cos \theta) \quad (2.11)$$

It will be remembered that $C_{0}^{(n)}(\theta, \phi) \equiv P_{n}(\cos \theta)$, $P_{n}(x)$ being the Legendre polynomials.

Another conventional form of this expression is due to Mason (1954):

$$E_a = K_{1} \sin^{2} \theta + K_{2} \sin^{4} \theta + K_{3} \sin^{6} \theta + K_{4} \sin^{4} \theta \cos 6\phi + \cdots \quad (2.12)$$

The fairly straightforward relations between the anisotropy constants $K_i$ and $\kappa_{nm}$ can be found e.g. in Appendix B to the review of Franse and Radwański (1993) in Volume 7 of this Handbook.

The corresponding expression for the hexagonal classes $C_{6h}$, $C_{3h}$ and $C_{6h}$ contains an extra sixth-order term, $K_4'' \sin^6 \theta \sin 6\phi \propto \Omega_6^6$ in Eq. (1.29).

Finally, the anisotropy energy of tetragonal crystals is given by

$$E_a = K_{1} \sin^{2} \theta + K_{2} \sin^{4} \theta + K_{2}' \sin^{4} \theta \cos 4\phi + K_{2}'' \sin^{4} \theta \sin 4\phi \quad + K_3 \sin^{6} \theta + K_1' \sin^{6} \theta \cos 4\phi + K_1'' \sin^{6} \theta \sin 4\phi + \cdots \quad (2.13)$$

where the constants $K_1''$ and $K_1''$ are nonzero if the crystallographic class is $C_{4}$, $S_{4}$ or $C_{4h}$, but must vanish if it is $D_{4}$, $C_{4v}$, $D_{2d}$ or $D_{4h}$.

---

7 This does not mean that the local symmetry of the RE site and the symmetry of the crystal as a whole are necessarily described by the same point group. When these point groups are distinct, so are the expressions for $E_a$ and $V_{CF}$ (cf. the example of RE$_2$Fe$_{14}$B in Section 1.3).
Recapitulating, magnetic anisotropy energy $E_a$ is that part of the non-equilibrium with respect to $\mathbf{M}$ thermodynamic potential $\Phi(T, B, M)_{|\mathbf{B}=0}$ which depends on the direction of $\mathbf{M}$ in a situation when $|\mathbf{M}|$ is known not to depend on applied magnetic field $\mathbf{B}$. The dependence $E_a(M/|\mathbf{M}|)$ is usually presented as a series in powers of the direction cosines of $\mathbf{M}$, whose form is dictated by the point group describing the symmetry of the crystal as a whole—the crystallographic class. As regards the convergence of the series, the formal theory is unable to make any positive prediction in this respect. Such predictions, leading to truncated expansions, can only be obtained in specific microscopic models, when the coefficients (anisotropy constants) prove proportional to growing powers of a small parameter. In the absence of a valid model, no custom or convention can justify the use of expressions truncated after the terms of 2nd, 4th or 6th order.

Throughout this subsection we have been dealing with standard thermodynamic potentials, fit to describe macroscopic systems, containing very large numbers of atoms. The introduced concepts of ‘anisotropy energy’ and ‘anisotropy constant’ are inapplicable to nanoscopic systems, just as does not apply to them the notion of temperature.

2.2 The notion of an exchange-dominated RE system

Let us consider a RE–transition metal compound satisfying the validity conditions for the single-multiplet approximation. We assume for simplicity that the applied magnetic field is nil. Following Section 1.2.3, the properties of the RE subsystem in this compound are described by a single-ion Hamiltonian, $\hat{\mathcal{H}}_{ex} + \hat{\mathcal{H}}_{CF}$, projected on the ground $\mathcal{J}$ multiplet:

$$\hat{\mathcal{H}}_{4f} = 2(g\mathcal{J} - 1)\mu_B \mathbf{B}_{ex} \cdot \hat{\mathbf{J}} + \sum_{n=2,4,6} \sum_{m=-n}^{n} B_{nm} C(n) (\hat{\mathbf{J}}).$$

(2.14)

Here $\mathbf{B}_{ex}$ is the exchange field on the RE produced by the ordered 3d sublattice, $B_{nm}$ are CF parameters incorporating the Stevens factors. Despite all simplifications, the Hamiltonian (2.14) is still very complicated, since it contains in the general case a large number of free parameters. Our consideration in this section will therefore be limited to a special case of the so-called exchange-dominated RE system. On the one hand, this will greatly simplify the calculations. On the other hand, the approximation, if not taken too far, is likely to apply to real hard magnetic materials.

It is clear from the outset that the CF can be regarded neither as infinitesimally small, nor as negligible in comparison with the 3d-4f exchange. A strong CF is indispensable to a good permanent magnet performance. At the same time, many of these materials feature low-temperature RE magnetic moments close to the free-ion value $g\mathcal{J} \mathcal{J}$, as if the strong CF were not there at all. So, how exactly weak should the CF be to account for this behaviour?

To answer this question, let us first consider a fictitious ‘training’ RE whose ground multiplet has $\mathcal{J} = 1$. This is the simplest system displaying non-vanishing CF effects. (Being time-even, the CF does not split the simpler $\mathcal{J} = 1/2$ multiplets). When $\mathcal{J} = 1$, the triangle rule dictates that only second-order CF terms are
relevant. Our hypothetical system is supposed to be a permanent magnet material, i.e. a uniaxial crystal in which the magnetisation of the 3d sublattice is parallel to the high-symmetry axis \(z\) (consequently, \(\mathbf{B}_{\text{ex}}\) is antiparallel to \(z\)). We assume in addition that the local symmetry of the RE site is uniaxial as well, i.e. that it is described by a point group belonging to either of the three syngonies: tetragonal, trigonal or hexagonal. Then a single CF term is allowed—that in \(C_2^{(2)}\) —and Eq. (2.14) turns into

\[
\hat{\mathcal{H}}_{4f} = 2(1 - g_J) \mu_B B_{\text{ex}} \hat{J}_z + B_{20} \left( \frac{3}{2} \hat{J}_z^2 - 1 \right). \tag{2.15}
\]

The matrix of this Hamiltonian is obviously diagonal in the \(|JM\rangle\) basis, the three eigenvalues being obtainable through the substitution of \(M = 0, \pm 1\) for \(\hat{J}_z\) in Eq. (2.15). Of interest to us here is the energy level pattern, rather than the eigenvalues as such. So we set the ground state energy to zero and normalise the overall multiplet splitting to unity. The so defined level pattern (Fig. 3.3) is fully determined by a single dimensionless parameter—the CF-to-exchange ratio,

\[
\eta = \frac{B_{20}}{\Delta_{\text{ex}}} \tag{2.16}
\]

where

\[
\Delta_{\text{ex}} = 2|g_J - 1| \mu_B B_{\text{ex}} \tag{2.17}
\]

is the exchange splitting between two adjacent levels of the multiplet.

The converse is generally not true—knowing the pattern does not enable one to establish the value of \(\eta\) even for such a simple system (unless the levels are unambiguously labelled). For example, an equidistant spectrum could correspond to either \(\eta = 0\) or \(2\) or \(-2\), the three situations being physically quite distinct.

One finds by inspecting Fig. 3.3 that from the standpoint of the level sequence the entire \(\eta\) axis is split into three domains separated by the points \(\eta = \pm \frac{2}{3}\), where two levels cross over.

\[ \text{Figure 3.3} \quad \text{Normalised energy level pattern of a didactic RE with } J = 1. \text{ The curved portions of the middle level are hyperbolae described by } E = \frac{2}{(1 - \frac{3}{2} \eta)}, \eta < -\frac{2}{3}, \text{ and } E = 1 - \frac{2}{(1 + \frac{3}{2} \eta)}, \eta > \frac{2}{3}. \text{ The hatched interval around the origin is the location of broadly exchange-dominated systems.} \]
We now define that a $J = 1$ RE system is exchange-dominated in the strict sense if its locus in Fig. 3.3 lies near the origin, that is if $|\eta|$ is much less than the size of the central segment, $|\eta| \ll \frac{2}{3}$. The same system will be called exchange-dominated in the broad sense if its $\eta$ lies somewhere within the central domain, $|\eta| \ll \frac{2}{3}$, but not too close to its boundaries. (The latter clause is to exclude the nearly degenerate case, $|\eta| = \frac{2}{3} - \varepsilon$, $0 \leq \varepsilon \ll \frac{2}{3}$.) The domain corresponding to broadly exchange-dominated systems is shown in Fig. 3.3 by hatching. Everywhere within the hatched area (in fact, also everywhere left of it) the low-temperature magnetic moment is constant and equals $g_J \mu_B$, or rather $g_J \mu_B \cdot \text{sign}(1 - g_J)$.

Before attempting a generalisation of these definitions for arbitrary $J$, let us consider one more particular case. This time it is a ‘nearly real’ RE with $J = 5/2$ in a hexagonal CF. Were it not for the extremely strong $J$-mixing that makes the single-multiplet approximation fail, this example would be fully relevant to e.g. SmCo$_5$. Our goal however is not so much to develop an accurate quantitative approach to Sm-based magnets, as to demonstrate the concept of exchange-dominated RE systems on something more realistic than the above example of plain $J = 1$.

Thus, within the single-multiplet approximation, the Hamiltonian of a RE with $J = 5/2$ in an exchange field $B_{\text{ex}}$ antiparallel to $z$ and in a hexagonal CF has the following form:

$$
\hat{H}_{4f} = 2(1 - g_J)\mu_B B_{\text{ex}} \hat{J}_z + B_{20} \left( \frac{3}{2} \hat{J}_z^2 - \frac{35}{8} \right) + B_{40} \left( \frac{35}{8} \hat{J}_z^4 - \frac{475}{16} \hat{J}_z^2 + \frac{2835}{128} \right). 
$$

The eigenvalues $E_M$ are obtained by substitution of $M = \pm 1/2, \pm 3/2, \pm 5/2$ for $\hat{J}_z$:

$$
E_{\pm 1/2} = \pm \frac{1}{2} \Delta_{\text{ex}} - 4B_{20} + 15B_{40},
$$
$$
E_{\pm 3/2} = \pm \frac{3}{2} \Delta_{\text{ex}} - B_{20} - \frac{45}{2}B_{40},
$$
$$
E_{\pm 5/2} = \pm \frac{5}{2} \Delta_{\text{ex}} + 5B_{20} + \frac{15}{2}B_{40},
$$

(2.19)

where $\Delta_{\text{ex}}$ is the exchange splitting (2.17) and it has been assumed for definiteness that, like in Sm$^{3+}$, $g_J < 1$. The energy level pattern is determined by two dimensionless parameters: $\eta$, defined according to Eq. (2.16), and $\xi$, given by

$$
\xi = \frac{B_{40}}{\Delta_{\text{ex}}}. 
$$

(2.20)

The latter describes the strength of the 4th-order CF in relation to the 3d-4f exchange. The $\eta \xi$ plane can be divided into 53 domains, each one of them characterised by a certain sequence of the energy levels (Fig. 3.4). Of primary interest to us is the central domain, which contains the origin. There, the level sequence (i.e. the dependence of $E_M$ on $M$) is monotonic, just as it would be without any CF.
Figure 3.4 Character of the splitting of the ground sextet of a RE with $J = 5/2$, depending on the domains delimited by the oblique lines the eigenvalue sequence $E_M$, arranged in ascending order, defines a permutation of the six values of the quantum number $M$ characteristic of that domain. Level cross-over takes place at the domain boundaries. The domains within each one of the three sectors separated by the bold lines have the same ground state: $M = -5/2$ (west), $-3/2$ (north), $-1/2$ (south-east). The hatched area near the origin marks the location of broadly exchange-dominated systems. The dark diamond corresponds to SmCo$_5$.

At the domain boundaries the levels cross over. Let us demonstrate this for the levels with $M = -5/2$ and $-3/2$ assuming, by analogy with Sm$^{3+}$, that $g_J < 1$. Then, in the absence of CF, the level with $M = -5/2$ is the ground state and the one with $M = -3/2$ is the first excited state. The cross-over condition is obtained by equating the last two of the equations (2.19), in which the lower signs must be taken. Upon division by $\Delta_{ex}$

$$6\eta + 30\xi = 1.$$  

(2.21)

This equation corresponds to a straight line in the $\eta\xi$ plane, namely, to that which makes the north-east border of the central domain in Fig. 3.4. Taking the other three combinations of upper/lower signs in the last two Eqs. (2.19) yields three more equations similar to (2.21), but with different right-hand sides. The four equations describe the set of four negatively sloping parallel lines in Fig. 3.4. Two further sets of four parallel lines are obtained in a similar fashion from the cross-over conditions $E_{\pm 1/2} = E_{\pm 3/2}$ and $E_{\pm 1/2} = E_{\pm 5/2}$. The four lines delimiting the central parallelogram correspond to the crossings of the adjacent levels of the monotonic spectrum, i.e. those with $\Delta M = \pm 1$. There are five pairs of adjacent levels in a sextet, however no line is generated by the equation $E_{1/2} = E_{-1/2}$.

Likewise, the conditions $E_{3/2} = E_{-3/2}$ and $E_{5/2} = E_{-5/2}$ produce no extra lines in the $\eta\xi$ plane. The physical reason of this is the time-even character of the CF, on which grounds the latter does not affect the splitting of pairs of Kramers-conjugate states. These are split by the exchange interaction alone, the level sequence within each pair depending on the sign of the difference $1 - g_J$. In the case of Sm$^{3+}$,
\( g_J = 5/7 < 1 \), the levels with negative \( M \) lie always below their positive counterparts.\(^8\) Consequently, only these three levels, \( M = -1/2, -3/2, -5/2 \), can claim the privilege of becoming ground state. On this principle, the entire \( \eta \xi \) plane can be divided into three sectors. These are separated by the bold lines in Fig. 3.4. We shall concentrate primarily on the west sector (containing the central parallelogram), where the ground state is \( M = -5/2 \). The north sector corresponds to \( M = -3/2 \) being the ground state, while in the south-east sector it is \( M = -1/2 \).

A strictly exchange-dominated \( J = 5/2 \) system can now be readily defined as such a system whose locus in the \( \eta \xi \) diagram is close to the origin, the proximity being understood relative to the dimensions of the central domain. This definition is equivalent to a pair of strong inequalities \(|\eta| \ll 1/6, |\xi| \ll 1/30\).

\( J = 5/2 \) system is exchange-dominated in the broad sense if its locus lies inside the central parallelogram of Fig. 3.4, excluding the regions close to its boundaries, as shown by the hatching. The hatched area belongs to the west sector of the drawing, where the low-temperature magnetic moment is \( g_J J = g_J 5/2 \).

The reason for the duplicate definition is that typical RE-based hard magnetic materials are broadly exchange-dominated systems, without being such in the strict sense. For example, the dark diamond, corresponding to the archetypal permanent magnet material SmCo\(_5\), is situated half way between the origin and the boundary of the central domain of Fig. 3.4.\(^9\)

The above definitions can now be easily generalised for an arbitrary \( J > 5/2 \). In addition to the parameters \( \eta \) and \( \xi \), defined by Eqs. (2.16), (2.20), a third parameter \( \zeta \) needs to be introduced, to describe the relative intensity of the (axial) sixth-order CF:

\[
\zeta = \frac{B_{60}}{\Delta_{\text{ex}}}.
\]

The \( \eta \xi \zeta \) parameter space is divided by a number of planes into many domains, according to the order of the eigenvalues \( E_M \). Within the central domain (containing the origin) the eigenvalue sequence is monotonic: the ground state has the maximum (or negative maximum) possible \( M \), the \( M \) of the first excited level differs from the latter by 1, etc. The eigenvalue sequences in the other domains correspond to permutations of the monotonic one.

The boundaries of the central polyhedron are obtained from cross-over conditions for the levels with \( \Delta M = \pm 1 \). The respective gaps can be presented as \( \Delta_{\text{ex}} + \Delta_i \), where \( \Delta_{\text{ex}} \) is the exchange contribution (2.17), common for all pairs of adjacent levels, \( \Delta_i \) are the CF contributions (numbered from bottom to top, Kuz’min, 1995):

\[
\Delta_1 = -\frac{3}{2}(2J - 1)B_{20} - \frac{5}{4}(2J - 1)(2J - 2)(2J - 3)B_{40} - \frac{21}{32}(2J - 1)(2J - 2)(2J - 3)(2J - 4)(2J - 5)B_{60},
\]

\( \Delta_i \) are the CF contributions (numbered from bottom to top, Kuz’min, 1995).

\(^8\) According to the adopted convention, the positive \( \zeta \) direction is parallel to \( M_{3d} \) and antiparallel to \( B_{\text{ex}} \).

\(^9\) The following values were used: \( B_{\text{ex}} = 295 \) T, \( B_{20} = -2 \) meV, \( B_{40} = 0 \) (Kuz’min et al., 2002).
\[ \Delta_2 = \frac{3}{2} (2J - 3) B_{20} - \frac{5}{4} (2J - 10)(2J - 2)(2J - 3) B_{30} \]
\[ - \frac{21}{32} (2J - 21)(2J - 2)(2J - 3)(2J - 4)(2J - 5) B_{60}, \]
eq.

Equating \( \Delta_{ex} + \Delta_i \) to zero, one obtains upon dividing by \( \Delta_{ex} \) the equations of the boundaries of the central domain, e.g.

\[ \frac{3}{2} (2J - 1) \eta + \frac{5}{4} (2J - 1)(2J - 2)(2J - 3) \xi \]
\[ + \frac{21}{32} (2J - 1)(2J - 2)(2J - 3)(2J - 4)(2J - 5) \zeta = 1 \]
and so on. In the special case of \( J = 5/2 \) Eq. (2.24) turns, as expected, into Eq. (2.21).

A RE system with an axial CF corresponds to a point in the \( \eta \xi \zeta \) space. One can demand that this point be close to the origin, the proximity being related to the dimensions of the central polyhedron. The same condition can be expressed as a strong inequality,

\[ |\Delta_i| \ll \Delta_{ex}. \] (2.25)

A system satisfying (2.25) will be called exchange-dominated in the strict sense.

Alternatively, the locus must lie inside the central polyhedron, not too close to its boundaries:

\[ |\Delta_i| < \Delta_{ex}(1 - \delta), \quad 0 < \delta \ll 1. \] (2.26)

This is a broadly exchange-dominated RE system. Clearly, any strictly exchange-dominated system is also broadly exchange-dominated. The converse is not true. In order to ensure the free-ion value of the low-temperature magnetic moment, \( g_J J \mu_B \), it suffices for an axially-symmetric RE system to be broadly exchange-dominated.

All the above-said can be applied to real materials—which do not possess the axial symmetry—provided that \( B_{nm} \) with \( m \neq 0 \) are not too large as compared to \( B_{n0} \) (which appears to be fulfilled in most cases). Then, to first order in \( B_{nm}/\Delta_{ex} \), the presence of non-axial CF terms has no effect on the low-temperature magnetic moment of the R.E.\(^{10}\)

Summarising, we have formulated two different concepts of an exchange-dominated RE system. When the first of them applies, it is strictly justified to use the first-order perturbation theory in \( B_{nm}/\Delta_{ex} \) (see subsection 2.5\(^{11}\)). Most real R.E.-based magnets, however, fit the second (broad) but not the first definition. For

\(^{10}\) Indeed, reduction of the ground-state magnetic moment is a time-even effect. The corresponding expression, \( \mu_{\text{CF}}/\mu_{\text{free-ion}} = 1 - \text{const}_1 (B_{nm}/\Delta_{ex}) - \text{const}_2 (B_{nm}/\Delta_{ex})^2 - \ldots \), may not contain odd powers of \( \Delta_{ex} \propto B_{ex} \), therefore \( \text{const}_1 = 0 \).

\(^{11}\) This does not include Sm-based magnets, on account of the failure of the single-multiplet approximation. Luckily, the magnetic moment of Sm in intermetallics is so small—even its sign varies from compound to compound (Givord et al., 1980)—that it can be safely neglected altogether.
such materials the equations of subsection 2.5 are still qualitatively correct, despite some lack of rigorous foundation. These equations are strictly inapplicable when neither of the above two definitions is satisfied.

2.3 The single-ion model for 3d-4f intermetallics

Our goal in this subsection is to formulate a general recipe for computing the RE contribution to the magnetic anisotropy energy $E_a$ proceeding from the parameters entering in the single-ion RE Hamiltonian $\hat{H}_{4f}$. The latter will be treated in the single-multiplet approximation, the only exception being Section 2.9, dedicated specifically to $J$-mixing. As stated in Section 1.1, the single-ion approach to describing the properties of the RE subsystem in 3d-4f intermetallics relies on the peculiar hierarchy of exchange interactions in these compounds. Thanks to it, the 3d subsystem can be regarded as something external, whose action on the RE is described by means of an exchange field $B_{ex}$. This enables one to treat the RE subsystem as an ensemble of non-interacting 'ions', each one of which is described by the following Hamiltonian:

$$\hat{H}_{4f} = 2(g_J - 1)\mu_B B_{ex} \cdot \hat{J} + g_J \mu_B B \cdot \hat{J} + \sum_{n,m} B_{nm} C_m^{(n)} (\hat{J}).$$  (2.27)

As pointed out in Section 2.2, $B_{ex}$ is antiparallel to the 3d magnetisation $M_{3d}$. If $\hat{H}_{4f}$ is related to the crystallographic coordinate axes, the dependence on the orientation of $M_{3d}$ enters into the first term of Eq. (2.27). The angles $\theta$ and $\phi$ defining the orientation of $M_{3d}$ are external thermodynamic parameters in relation to the RE subsystem. The latter is described by the usual equilibrium canonical distribution,

$$F_{4f}(\theta, \phi) = -kT \ln Z_{4f}(\theta, \phi)$$  (2.28)

where the RE partition function is

$$Z_{4f}(\theta, \phi) = \text{tr} \exp \left( -\frac{\hat{H}_{4f}}{kT} \right).$$  (2.29)

With respect to the 3d subsystem (and therefore to the combined 3d-4f system) $\theta$ and $\phi$ are internal parameters, i.e. the former is described by means of a non-equilibrium thermodynamic potential $\Phi_{3d}(\theta, \phi)$. The equilibrium values of $\theta$ and $\phi$ are determined through minimisation of the combined thermodynamic potential,

$$\min_{\theta,\phi} \left[ \Phi_{3d}(\theta, \phi) + F_{4f}(\theta, \phi) \right].$$  (2.30)

At this stage we do not specify the form of $\Phi_{3d}(\theta, \phi)$. Suffice it to say that, like Eq. (2.27), $\Phi_{3d}$ contains anisotropy energy and a Zeeman term.

Despite the fact that it only takes a few equations (2.27)–(2.30) to formulate the single-ion model, it proves impossible to obtain a general explicit expression for $F_{4f}(\theta, \phi)$. The main difficulty is taking the trace of the matrix exponential in Eq. (2.29). One exception is the special case of $J = 1$, when such an expression does exist (Kuz’min, 1995). This was used to demonstrate that $F_{4f}(\theta, \phi)$ cannot in
general be presented as a truncated expansion of type (2.8)–(2.13). Such a presentation requires that the anisotropy constants $K_i$ or $\kappa_{nm}$ contain incrementing powers of a small parameter, which is only true in some special cases when additional approximations can be made. If valid, the same approximations enable one to evaluate the anisotropy constants.

It is interesting to note that validity of the very same approximations allows to settle the often raised question about the effect of non-collinearity of the 3d and 4f sublattices. The point is that the above-defined angles $\theta$ and $\phi$ determine the orientation of just the 3d sublattice magnetisation $M_{3d}$. As regards the RE moment $\mu_R$, its orientation is described by the angles $\theta_R$ and $\phi_R$, which are generally speaking distinct from $\theta$ and $\phi$. The RE magnetisation is an internal thermodynamic parameter, so it does not figure explicitly in the above algorithm (2.8)–(2.13). For any given $\theta$ and $\phi$, the angles $\theta_R = \arccos(\mu_R^z / |\mu_R|)$ and $\phi_R = \arctan(\mu_R^y / \mu_R^x)$ can be found from the relation

$$\mu_R = -\frac{\partial F_{4f}}{\partial B} = -g_J \mu_B (\hat{j}) = -\frac{g_J \mu_B}{Z_{4f}(\theta, \phi)} \text{tr} \exp\left(-\frac{\hat{H}_{4f}}{kT}\right).$$

(2.31)

The problem posed by the non-collinearity is that the angles obtained through the minimisation of the total thermodynamic potential of the system (2.30) do not correspond to the orientation of the system’s total magnetisation. This difficulty will be shown to disappear as soon as there is a valid reason to truncate the series for $E_a$.

To summarise, there are two possibilities. Either, one of the above-mentioned approximations is valid and then one can (i) truncate the expansion for $E_a$, (ii) obtain explicit expressions for the anisotropy constants entering in the truncated expansion, and (iii) neglect the non-collinearity of the 3d and 4f sublattices. Or, there is no such a valid approximation; then the standard description by means of anisotropy constants is impossible, as none of the above three preconditions can be secured. Of course, the general equations (2.27)–(2.31) are then still valid and can be used to compute $M(B)$ (not the anisotropy constants) numerically.

Consequently, we shall no longer dwell on the sterile general formalism, but rather proceed to the most important special cases.

### 2.4 The high-temperature approximation

Let us recast Eqs. (2.28), (2.29) in a different form,

$$F_{4f}(\theta, \phi) = -\frac{J \Delta_{\text{ex}}}{x} \ln \left[ \text{tr} \exp\left(-x \frac{\hat{H}_{4f}}{J \Delta_{\text{ex}}}ight) \right]$$

(2.32)

where $x$ is a quantity equivalent to Langevin’s magneto-thermal ratio,

$$x = \frac{J \Delta_{\text{ex}}}{kT}$$

(2.33)

and $\Delta_{\text{ex}}$ is the exchange splitting (2.17).
Assuming that $x$ is a small parameter, we can expand $F_{4t}$ in powers of $x$ in the spirit of Kramers–Opechowski:

$$F_{4t}(\theta, \phi) = -\frac{J \Delta_{ex} \ln(2J + 1)}{x} \frac{\text{tr}\hat{H}_{4t}^2}{2J(2J + 1)\Delta_{ex}} x - \frac{\text{tr}\hat{H}_{4t}^3}{6J^2(2J + 1)\Delta_{ex}^2} x^2 + \cdots$$  \hspace{1cm} (2.34)

It has been taken into account that $\text{tr}\hat{H}_{4t} = 0$.

The first term in (2.34) is obviously isotropic, i.e. it does not depend on either $\theta$ or $\phi$. Let us demonstrate that the second term is isotropic, too. To this end it is convenient to rewrite the Hamiltonian (2.27) as follows:

$$\hat{H}_{4t} = C(n) \theta \cdot \hat{J} + \hat{H}_{CF}.$$  \hspace{1cm} (2.35)

Here $n = M_{3d}/|M_{3d}|$ is a unit vector in the direction of the 3d magnetisation, $M_{3d} = B_{ex}$, and it has been assumed that $B \ll B_{ex}$ in order to ensure that $\mu_R$ remains essentially independent of $B$. We shall make use of a helpful orthogonality relation for the operators $C_m^{(n)}(\hat{J})$ (Kuz’min, 1995), which readily follows from the well-known orthogonality of the CGC:

$$\text{tr}[C_m^{(n)}(\hat{J})C_{-m'}^{(n)}(\hat{J})] = (-1)^m \frac{2^{-2n}}{2n + 1} \frac{(2J + n + 1)!(2J - n)!}{(2J + 1)!} \delta_{nn} \delta_{mm'}.$$  \hspace{1cm} (2.36)

where the trace is taken over the states of any $J$ multiplet, such that $2J \geq n$.

Directing the $z$ axis along $n$ and noting that $\hat{J}_z \equiv C_0^{(1)}(\hat{J})$, we write

$$\text{tr}\hat{H}_{4t}^2 = \Delta_{ex}^2 \text{tr}(\hat{J}_z^2) + 2\text{sign}(1 - g_J) \Delta_{ex} \text{tr}[\hat{H}_{CF} C_0^{(1)}(\hat{J})] + \text{tr}\hat{H}_{CF}^2.$$  \hspace{1cm} (2.37)

The first term is just $\frac{1}{2} J(J + 1)(2J + 1)\Delta_{ex}^2$. The second term vanishes by virtue of the orthogonality relation (2.36), as $\hat{H}_{CF}$ contains only $C_m^{(n)}(\hat{J})$ with $n$ even. Finally, the third term of Eq. (2.37) can be considered in the crystallographic coordinates, then its independence of the orientation of $M_{3d}$ or $B_{ex}$ becomes obvious.

Going back to Eq. (2.34), the first non-vanishing contribution to the anisotropy energy comes from the term in $x^2$, which contains $\text{tr}\hat{H}_{4t}^3$. We thus proceed to its evaluation. We shall use the presentation of $\hat{H}_{4t}$ as a binomial (2.35), just as we did when computing $\text{tr}\hat{H}_{4t}^2$.

The invariance of the free energy with respect to time inversion means that all terms odd in $\hat{J}$ must vanish, while $\text{tr}\hat{H}_{CF}^3$ obviously does not depend on the orientation of $M_{3d}$. The only source of anisotropy in $\text{tr}\hat{H}_{4t}^3$ is the mixed product $3\Delta_{ex}^2 \text{tr}[n \cdot \hat{J}^2 \hat{H}_{CF}]$.

Let us write out this expression in the crystallographic coordinates, limiting ourselves to tetragonal, trigonal and hexagonal point groups as most relevant to permanent magnets:

$$3\Delta_{ex}^2 \text{tr}(\hat{J}_x \sin \theta \cos \phi + \hat{J}_y \sin \theta \sin \phi + \hat{J}_z \cos \theta)^2 \times [B_{20} C_0^{(2)}(\hat{J}) + 4^{th}\text{- and } 6^{th}\text{-order terms}].$$  \hspace{1cm} (2.38)
Note that the square of the parenthesis in this equation contains products of the Cartesian components of the total angular momentum, which are linear combinations of $C^{(m)}(\hat{J})$ with $n = 2$ and 0, $C^{(0)}_0 \equiv 1$:

\[
\hat{J}^2_x = \frac{1}{3} J(J + 1) - \frac{1}{3} C^{(2)}_0(\hat{J}) + \left(\frac{1}{6}\right)^{\frac{1}{2}} \left[ C^{(2)}_2(\hat{J}) + C^{(2)}_{-2}(\hat{J}) \right]
\]

\[
\hat{J}^2_y = \frac{1}{3} J(J + 1) - \frac{1}{3} C^{(2)}_0(\hat{J}) - \left(\frac{1}{6}\right)^{\frac{1}{2}} \left[ C^{(2)}_2(\hat{J}) + C^{(2)}_{-2}(\hat{J}) \right]
\]

\[
\hat{J}^2_z = \frac{1}{3} J(J + 1) + \frac{2}{3} C^{(2)}_0(\hat{J})
\]

(2.39)

This is just a transformation inverse to Eqs. (1.17). There is no need to write out the mixed products, $\hat{J}_x \hat{J}_y$ etc., since they do not contain $C^{(2)}_0(\hat{J})$. Due to the orthogonality relation (2.36), only the terms in $C^{(2)}_0(\hat{J})$ survive in Eq. (2.38). Since $C^{(2)}_0(\hat{J})$ enters into $\hat{J}^2_x$ and $\hat{J}^2_y$ with the same coefficient $-\frac{1}{3}$, the terms in $\sin^2 \theta \cos^2 \phi$ and in $\sin^2 \theta \sin^2 \phi$ will enter in the final expression for $F_{4f}(\theta, \phi)$ also with the same factor. Therefore, in this approximation $F_{4f}$ does not depend on the azimuthal angle $\phi$.

Carrying out the calculations, we present the RE free energy as follows:

\[
F_{4f}(\theta, \phi) = F_0 + E_a,
\]

where $F_0$ is the isotropic part and $E_a$ is the anisotropy energy,

\[
E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \cdots
\]

(2.40)

\[
K_1 = -\frac{(J + 1)(2J - 1)(2J + 3)}{40J}B_{20}x^2 + O(x^3).
\]

(2.41)

Thus, the leading term of the high-temperature expansion of the first anisotropy constant is proportional to the second-order CF parameter $B_{20}$ and to $x^2$. Its independence of the higher-order CF parameters arises from the orthogonality relation (2.36).

Quite similarly one arrives at the conclusion that $K_2 \equiv \text{const.} \times B_{40}x^4 + O(x^5)$ (Kuz’min, 1995). In general, the high-temperature series for an anisotropy constant multiplying $\sin^n \theta$ begins with a term in $x^n$, whose coefficient is a linear combination of $n^\text{th}$-order CF parameters $B_{nm}$. This fact ensures the convergence of the expansion (2.40) at small $x$ (high $T$).

\[\text{In most high-symmetry cases these combinations contain a single CF parameter. For example, for the anisotropy constants in Eq. (2.13) one gets} \ K_4 \propto x^2 B_{20}, \ K_2 \propto x^4 B_{40}, \ K_2' \propto x_4 \Re B_{44}, \ K_2'' \propto x^4 \Im B_{44}, \ K_3 \propto x^6 B_{60}, \ K_3' \propto x^8 \Re B_{64}, \ K_3'' \propto x^8 \Im B_{64}.\]
Thus, to terms in $x^2$, the anisotropy energy is simply $K_1 \sin^2 \theta$, where

$$K_1 = \frac{1}{10} J(J + 1)(2J - 1)(2J + 3)(g_J - 1)^2 B_{20} \left( \frac{\mu_0 B_{ex}}{kT} \right)^2. \quad (2.42)$$

Note the very special role of the second-order CF parameter $B_{20}$. It and it alone can guarantee the persistence of the anisotropy (and therefore of the coercivity) of a permanent magnet material to high temperature, which is of vital importance for most industrial applications.

Even more important is to have a large exchange field $B_{ex}$, since $K_1$ is proportional to $B_{ex}^2$. The value of $B_{ex}$ depends on temperature. To minimize its reduction at elevated temperatures, one should not just seek to increase the $T_C$, but also to reduce the parameter $s$ describing the shape of the dependence $M_{3d}(T)$ (Kuz’min, 2005),

$$B_{ex} \propto M_{3d} \propto \left[ 1 - s \left( \frac{T}{T_C} \right)^{\frac{3}{2}} - (1 - s) \left( \frac{T}{T_C} \right)^{\frac{5}{2}} \right]^\frac{1}{2}. \quad (2.43)$$

So far in this Section it has been assumed for simplicity that the local symmetry of the RE site and the symmetry of the crystal as a whole are described by point groups allowing just one second-order CF parameter $B_{20}$ and accordingly, a single second-order anisotropy term, $K_1 \sin^2 \theta$. However, we have already (Section 1.3) seen an example of permanent magnet materials, RE$_2$Fe$_{14}$B, whose crystallographic class is tetragonal, $D_{4h}$, while the local symmetry is orthorhombic, $C_{2v}$. The latter admits an extra second-order CF parameter $B_{22}$ (purely real in Wybourne’s notation). Consequently, an extra term in $\sin^2 \theta$ should appear in Eq. (2.40), that describing the anisotropy in the basal plane, $K'_1 \sin^2 \theta \cos 2\phi$, with $K'_1 = \text{const.} \times B_{22} x^2 + O(x^3)$. It turns out upon a closer look at the structure (Fig. 3.5) that four equivalent RE sites split into two pairs with different orientations of the local symmetry axes. (Recall that the simplest form of the CF—with two second-order CF parameters—refers
to the local axes). Before the macroscopic anisotropy energy can be obtained by summing up the single-ion contributions, these have to be related to the same coordinates. The simplest way to do it is to rotate the local axes of one-half of the RE sites (e.g. of those situated at \( z = 1/2 \), see Fig. 3.5) through \( 90^\circ \) about \([001]\). Such a rotation is equivalent to a change of sign of \( B_{22} \) for those sites, while their \( B_{20} \) remains unchanged. As the summation over all RE sites is performed, the terms \( \propto B_{22} \cos 2\phi \), incompatible with the crystallographic class, simply cancel out. Thus, the presence of a nonzero \( B_{22} \) has no bearing on Eqs. (2.40)–(2.42) or on the exceptional role of \( B_{20} \). This applies to most permanent magnet materials, insofar as they belong to one of the medium-symmetry crystal systems: tetragonal, trigonal or hexagonal.

To conclude the discussion of RE\(_2\)Fe\(_{14}\)B, we note that there are two non-equivalent RE sites, 4f and 4g. For simplicity, only the former are shown in Fig. 3.5. The 4g sites are situated on the vacant diagonals and possess similar symmetry properties, to the extent that the above-mentioned cancellation of the terms in \( B_{22} \) takes place for both kinds of RE sites independently. The final expression for \( K_1 \) should be a sum of two terms identical to (2.42) but with different \( B_{20} \) and \( B_{ex} \). There is, however, direct experimental evidence that in Gd\(_2\)Fe\(_{14}\)B the exchange fields on the two Gd sites are equal to within a few percent (Loewenhaupt et al., 1996). This fact enables us to still use the simple expression (2.42) for the RE\(_2\)Fe\(_{14}\)B compounds, provided that \( B_{20} \) is understood as \( \frac{1}{2}(B_{20}^{4f} + B_{20}^{4g}) \). The averaging here is justified by the fact that \( B_{ex}^{4f} = B_{ex}^{4g} \) and does not require that \( B_{20}^{4f} \approx B_{20}^{4g} \). A recent X-ray diffraction experiment has revealed that \( B_{20}^{4f} \) and \( B_{20}^{4g} \) are essentially different (Haskel et al., 2005).

In order to set the lower bound to the domain of validity of the high-temperature approximation, the expansion in powers of \( x \) should be continued. It was established (Kuz’min, 1995) that the main contribution to \( K_1 \) beyond \( x^2 \) comes from the term \( \propto B_{20} x^4 \) (even though nonzero contributions from other CF parameters may be present as well—not necessarily linear). In this approximation

\[
K_1 = -\frac{(J + 1)(2J - 1)(2J + 3)}{40J} B_{20} x^2 (1 - d_J x^2) \quad (2.44)
\]

where

\[
d_J = \frac{8J^2 + 8J + 5}{84J^2} \quad (2.45)
\]

The quantity \( d_J \) is practically independent of \( J \), varying between 0.11 for \( J = 8 \) and 0.14 for \( J = 5/2 \) (Kuz’min, 1995, Table I). For estimations one can take the fractional error of the high-temperature approximation to be just \( 0.12x^2 \) for all RE’s. This translates to 7\% at \( T = 300 \) K for Tm\(_2\)Fe\(_{14}\)B. Though it may not always be sufficient for accurate calculations in the room-temperature range, the simplicity of Eq. (2.42) makes it nevertheless useful for analysing the behaviour of permanent magnet materials at \( T > 300 \) K.
In the same approximation, to $T^{-2}$, Eq. (2.31) yields for the RE magnetic moment (Boutron, 1973):

\begin{align}
\mu_{R,x,y} &= B'_x C \frac{C}{T} \left[ 1 + \frac{1}{20} (2J - 1)(2J + 3) \frac{B_{20}}{kT} + \cdots \right] \\
\mu_{R,z} &= B'_z C \frac{C}{T} \left[ 1 - \frac{1}{10} (2J - 1)(2J + 3) \frac{B_{20}}{kT} + \cdots \right]
\end{align}

where $B' = 2(1 - g_J^2)B_{ex} + B$ is the effective magnetic field on the RE, $C = J(J + 1)g_J^2 \mu_B^2 / 3k$ is the Curie constant. Within the same accuracy, the susceptibility can be recast in the Curie–Weiss form,

\begin{align}
\chi_{||,\perp} &= \frac{C}{T - \theta_{||,\perp}}
\end{align}

where

\begin{align}
k\theta_|| &= \frac{1}{10} (2J - 1)(2J + 3) B_{20} \\
k\theta_\perp &= -\frac{1}{20} (2J - 1)(2J + 3) B_{20}.
\end{align}

Note the validity of the Elliott formula (Elliott, 1965):

\begin{align}
k(\theta_|| - \theta_\perp) &= \frac{3}{20} (2J - 1)(2J + 3) B_{20}.
\end{align}

The first anisotropy constant $K_1$ can be presented as

\begin{align}
K_1 &= \frac{\chi_{||} - \chi_{\perp}}{2} (B')^2
\end{align}

which in the considered approximation is equivalent to the earlier obtained result (2.42), provided that $B \ll B_{ex}$. In other words, the RE subsystem behaves in this approximation as an anisotropic paramagnet in an effective magnetic field. For this reason at high $T$ the susceptibility anisotropy, $\chi_{||} - \chi_{\perp}$, just like $K_1$, depends on a single CF parameter $B_{20}$.

To finalise this section, let us consider the effect of non-collinearity of the sublattices and the possibility to allow for it by introducing two sets of orientation angles and anisotropy constants, one for each sublattice. (Up no now we had to do with a single set of angles, $\theta$ and $\phi$, corresponding to the orientation of $M_{3d}$, while the respective anisotropy constants were mere sums, $K_{3d} + K_{4d}$).

Examination of Eqs. (2.46), (2.47) reveals two sources of non-collinearity: (i) possible violation of the condition $B \ll B_{ex}$ while $B || B_{ex}$, and (ii) the terms in $B_{20}$ in square brackets—a purely CF effect. As a result, $M_{3d} || B_{ex} || B' || \mu_R$. We exclude from the outset the possibility that the strong inequality $B \ll B_{ex}$ may fail—the concept of anisotropy constants formulated in Section 2.1 requires that $|\mu_R|$ be independent of $B$. Our consideration in this section will therefore be limited to the CF-induced non-collinearity (ii).

13 A situation when $B \sim B_{ex}$ is neither unattainable experimentally (see e.g. Kostyuchenko et al., 2003) nor intractable theoretically—the formalism of Section 2.3 still applies.
Let us rewrite the square bracket of Eq. (2.47) as follows,

\[ 1 - \frac{(2J - 1)(2J + 3)}{10J} \eta x \]  

(2.53)

where \( \eta \) is defined by Eq. (2.16). Assume that the system under consideration is at least broadly exchange-dominated. Then its parameter \( \eta \) must not exceed the \( \eta \)-axis intercept of the plane (2.24) delimiting the central polyhedron,

\[ |\eta| < \frac{2}{3(2J - 1)} \]  

(2.54)

In a strictly exchange-dominated case this should become a strong inequality, cf. (2.25). By virtue of (2.54), the square bracket of Eq. (2.47) can be recast as

\[ 1 + ax \]  

(2.55)

where \( |a| < (2J + 3)/15J \approx 0.2 \). It will be recalled that the high-temperature approximation is valid when the quantity \( d_j x^2 \approx 0.12x^2 \) in Eq. (2.44) is small as compared with unity. Fulfilment of this condition for a hard magnetic material guarantees the smallness of the anisotropic terms in \( B_{20} \) in Eqs. (2.46), (2.47). Hence the approximate collinearity of \( \mu_{\text{ex}} \) and \( B' \approx B_{\text{ex}} \parallel M_3 \), which becomes exact in the limit \( x \to 0, B/B_{\text{ex}} \to 0 \).

One should take into account that permanent magnet materials are mostly light RE-iron or cobalt intermetallics rich in the 3d element, so that the RE contributes only a small part of the total magnetisation. Therefore, the apparent CF-induced non-collinearity, that is the deviation of \( M_3 \) (its orientation defined by \( \theta, \phi \)) from \( M_3 + M_{4f} \), will be even less significant than suggested by the estimate (2.55).

Conversely, the non-collinearity can play a very important role in heavy RE-based ferrimagnets, especially when \( |M_{4f}| \approx |M_3| \). We shall not consider such systems any further since they were described in detail in Volume 9 of this Handbook (Zvezdin, 1995).

Let us go back to the more important for applications class of phenomena when the material is an iron- or cobalt-rich light RE-based intermetallic compound and the applied magnetic field does not exceed what can be expected from a permanent-magnet assembly, \( \sim 2 \) T. In such a situation the high-temperature approximation (2.42) applies at and above room temperature. Its validity justifies the truncation of the expansion (2.40). Furthermore, it guarantees the smallness of the non-collinearity effects, so that the system behaves essentially as a single-sublattice magnet.

Validity of the high-temperature approximation has also interesting consequences for spin reorientation transitions (SRT) in these materials. This question, however, will be deferred until Section 3, devoted specially to the SRT.

2.5 The linear-in-CF approximation: main relations

In the preceding subsection we deduced a truncated quasi-single-sublattice expression for the anisotropy energy, \( E_a = K_1 \sin^2 \theta \), and obtained an explicit formula for the RE contribution to \( K_1 \). All this was achieved thanks to the presence of the
small parameter $x = J \Delta_{ex}/kT$. No specific restrictions had to be imposed on the CF, as long as it remained not much stronger than the 3d-4f exchange, $|\Delta_i| \lesssim \Delta_{ex}$. (Otherwise the high-temperature expansion should be in powers of $\Delta_i/kT$ rather than $x$.)

Let us now consider a special case when it is additionally known that the CF on the RE is weak as compared with the 3d-4f exchange. The definition of a strictly exchange-dominated RE system (2.25) can be rewritten as follows:

$$|B_{nm}| \ll (2J)^{1-n} \Delta_{ex}. \quad (2.56)$$

This condition applies, rigorously speaking, only to $B_{n0}$. The extension to all CF parameters is based upon a probably not unreasonable assumption that off-diagonal CF parameters cannot be much greater than their diagonal counterparts: $|B_{nm}| \leq |B_{n0}|, \ m \neq 0$. Anyhow, the smallness of the CF, justifying its treatment as a perturbation with respect to the exchange, is the principal starting point of this subsection.

Our second assumption concerns the strength of applied magnetic field $\mathbf{B}$. Namely, we assume that $\mathbf{B}$ always remains much weaker than the 3d-4f exchange field $\mathbf{B}_{ex}$, to make sure that the magnitude of the RE magnetic moment does not depend on $\mathbf{B}$. This is a necessary condition for the use of the formalism of anisotropy constants (Section 2.1).

Thus, in zeroth approximation only the first term of the RE Hamiltonian (2.14) or (2.27) is taken into consideration. The result is an equidistant energy spectrum,

$$E_M = \text{sign}(1 - g_J) \Delta_{ex} M, \quad M = -J, -J + 1, \ldots, J, \quad (2.57)$$

leading to the well-known partition function (Smart, 1966),

$$Z_J(x) = \frac{\sinh\left(\frac{2J+1}{2J} x\right)}{\sinh\left(\frac{1}{2J} x\right)}. \quad (2.58)$$

Note that here, unlike in the preceding subsection, the Langevin ratio $x$ (2.33) is not necessarily small.

The RE magnetic moment in this approximation is given by

$$\mu_R = -g_J \mu_B \langle \hat{J}_z \rangle = \text{sign}(1 - g_J) g_J \mu_B J B_J(x). \quad (2.59)$$

The $z$ axis here is directed along the 3d magnetisation vector $\mathbf{M}_{3d}$, so that $\mathbf{B}_{ex}$ points in the negative $z$ direction. There is of course no anisotropy or non-collinearity in the zeroth approximation.

Allowance for a nonzero applied magnetic field will to first approximation add a Zeeman term $-\mathbf{\mu}_R \cdot \mathbf{B}$ to the zeroth-order RE free energy, $F_{4f} = -kT \ln Z_J(x)$, whereas allowance for the CF will produce the anisotropy energy $E_a$. Thus, $F_{4f}$ will acquire the structure of Eq. (2.7). Our primary objective in this subsection is to compute the first-order, or linear in $B_{nm}$ contribution to $E_a$. Note that the absence of non-collinearity effects in this approximation is a natural feature of the perturbation theory. The truncation of the expansion of $E_a$ after the terms in $\sin^6 \theta$ will occur automatically due to the presence of the small parameter.
The first-order anisotropy correction to $F_{\text{CF}}$ is merely a thermal average of the perturbation $\hat{H}_{\text{CF}}$ taken over the eigenstates of the unperturbed Hamiltonian:

$$E_a = \langle \hat{H}_{\text{CF}} \rangle = \sum_{n=2,4,6} B'_{n0} \langle C_0^{(n)}(\hat{J}) \rangle.$$  \hfill (2.60)

This expression contains only $C_m^{(n)}(\hat{J})$ with $m = 0$, diagonal in the $JM$ representation. We wish to emphasize that these operators are defined in the coordinate system with $z \parallel M_3$, the latter not necessarily parallel to any of the high-symmetry crystal directions. To mark this fact, the CF parameters in Eq. (2.60) are primed. They are related to the ‘usual’ non-primed CF parameters (defined with respect to the crystallographic axes) by means of the following linear transformation:

$$B'_{n0} = \sum_{m=-n}^{n} B_{nm} C_m^{(n)}(\theta, \phi).$$  \hfill (2.61)

The rotation angles $\theta$ and $\phi$ are just the angles determining the orientation of $M_3$ in relation to the crystallographic axes.

To find the average values in Eq. (2.60), we note that $C_0^{(n)}(\hat{J})$ are operator polynomials in $\hat{J}_z$, of order $n$ and of the corresponding parity, cf. the explicit expressions (Lindgård and Danielsen, 1974). The averages of powers of $\hat{J}_z$ can be computed with the aid of the following identity (Kazakov and Andreeva, 1970):

$$\langle \hat{J}_z^n \rangle = \frac{1}{Z_J(x)} \sum M^n \exp \left[ -\text{sign}(1-g_J) \frac{xM}{J} \right]$$

$$= \frac{[-J\text{sign}(1-g_J)]^n}{Z_J(x)} \frac{d^n Z_J}{dx^n}. \hfill (2.62)$$

Apparently, for any given $J$ and $n$, the quantity $\langle \hat{J}_z^n \rangle$ is up to a sign determined by the Langevin ratio $x$ alone. Therefore, the averages of $C_0^{(n)}(\hat{J})$ can be conveniently presented as functions of $x$, the so-called generalised Brillouin functions (GBF) $B_J^{(n)}(x)$:

$$\langle C_0^{(n)}(\hat{J}) \rangle = [-\text{sign}(1-g_J)]^n J^n B_J^{(n)}(x). \hfill (2.63)$$

Naturally, the sign only matters for $n$ odd, whereas relevant to magnetic anisotropy are $n = 2, 4, 6$. One could in principle omit the cumbersome square bracket from Eq. (2.63), as it was done by Kuz’min (1992). However, we prefer to keep the sign multiplier, since we intend on using GBF with odd $n$ later on in this section. In fact, Eq. (2.59) above is nothing else but a special case of Eq. (2.63) with $n = 1$.

By virtue of Eqs. (2.61), (2.63), the anisotropy energy (2.60) takes the standard form (2.10), with the anisotropy constants given by

$$\kappa_{nm} = B_{nm} J^n B_J^{(n)}(x) \hfill (2.64)$$

where $n = 2, 4, 6$. All higher-order anisotropy constants vanish in this approximation.
Equation (2.64) is the main result of the linear (in $B_{nm}$) theory of magnetocrystalline anisotropy. Its convenience is the one-to-one correspondence between the quantities $\kappa_{nm}$ and $B_{nm}$. The temperature dependence of each $\kappa_{nm}$ is given by a single GBF. Expressions for the more conventional anisotropy constants $K_i$ are readily obtainable hence. For example, those entering in Eq. (2.12), relevant to the hexagonal point groups $D_6$, $C_{6v}$, $D_{3h}$ and $D_{6h}$, are given by:

$$
K_1 = -\frac{3}{2} B_{20} J^2 B_J^{(2)}(x) - 5 B_{40} J^4 B_J^{(4)}(x) - \frac{21}{2} B_{60} J^6 B_J^{(6)}(x) \\
K_2 = \frac{35}{8} B_{40} J^4 B_J^{(4)}(x) + \frac{189}{8} B_{60} J^6 B_J^{(6)}(x) \\
K_3 = -\frac{231}{16} B_{60} J^6 B_J^{(6)}(x) \\
K' = \frac{\sqrt{231}}{16} B_{66} J^6 B_J^{(6)}(x).
$$

(2.65)

The CF parameters in these relations are normalised according to Wybourne (1965). The conversion to the Stevens convention is straightforward, an example was given by Kuz’min et al. (1996). The only ‘advantage’ of the Stevens notation is that the coefficients in Eqs. (2.65) become integers. Note the division of the anisotropy constants and CF parameters in two groups: axial $K_i \propto$ linear combinations of $B_{n0}$, and basal-plane anisotropy constants $K'_i \propto B_{nm}$ with $m \neq 0$. The temperature dependence in all cases is described by three GBF, $B(n)J(x)$, $n = 2, 4, 6$.

We wish to point out that while all anisotropy constants of order higher than six are strictly nil in the considered approximation, there is no grounds whatsoever for assuming hierarchical intensity relations of type $|K_1| \gg |K_2| \gg |K_3|$ among those which are nonzero. Such a situation may be realised at high temperature, $x \ll 1$, where $B_J^{(n)}(x) \propto x^n$ and therefore $B_J^{(2)}(x) \gg B_J^{(4)}(x) \gg B_J^{(6)}(x)$. When it does happen, it is only because $x$ is small, irrespective of the strength of the CF in relation to the 3d-4f exchange (see the preceding subsection). At low temperatures (large $x$) all GBF are $\sim 1$ and consequently all nonzero anisotropy constants are of the same order of magnitude, cf. the coefficients of $B_{60}$ in Eqs. (2.65). Neglecting $K_3$ (or $K_3$ and $K_2$) in this situation is a serious mistake.

It has been tacitly assumed that the local symmetry of the RE site and the crystallographic class are described by the same point group. Another possibility is that the local symmetry is lower than the crystallographic class, then some extra CF parameters may be allowed. The contributions from the latter must however cancel out upon summation over all RE atoms, just like it happened to $B_{22}$ in RE$_2$Fe$_{14}$B in the previous subsection. In the linear approximation such ‘latent’ CF parameters do not affect the macroscopic magnetic anisotropy at all.

Let us now turn to computing first-order CF corrections to the RE magnetic moment (2.59). We should in principle repeat the calculation of the RE free energy with a nonzero applied magnetic field $B$ and differentiate the former with
Theory of Crystal-Field Effects in 3d-4f Intermetallic Compounds

respect to the latter. It is easier, however, to exploit the formal similarity of \(B\) and \(B_{ex}\) and to differentiate the already obtained expression for \(F_{4f}\) with respect to \(\Delta_{ex}\):

\[
\mu_R = -g_J \mu_B \langle \hat{J}_z \rangle = -\text{sign}(1 - g_J) g_J \mu_B \frac{\partial F_{4f}}{\partial \Delta_{ex}} \tag{2.66}
\]

where

\[
F_{4f} = -kT \ln Z_J(x) + \sum_{n=2,4,6} B'_{n0} B'_{nJ}(x) \tag{2.67}
\]

and \(x\) is related to \(\Delta_{ex}\) through Eq. (2.33). The first term in Eq. (2.67) is the isotropic part of the free energy while the sum represents the \(E_a\). The angles \(\theta\) and \(\phi\) are supposed to be constant and determine the easy magnetization direction with respect to the crystallographic axes. (Typically in permanent-magnet materials \(\theta = 0\), in which case the primes of the CF parameters in Eq. (2.67) may be omitted.) Carrying out the differentiation in Eq. (2.66), we arrive at

\[
\mu_R = \text{sign}(1 - g_J) g_J \mu_B J_B(x) \left[ 1 - \sum_{n=2,4,6} \frac{B'_{n0}}{\Delta_{ex}} D_j^{(n)}(x) \right] \tag{2.68}
\]

where

\[
D_j^{(n)}(x) = J^{-1} x \frac{dB_{j}^{(n)}(x)}{dx}
= J^{-1} x \left[ \frac{n + 1}{2n + 1} B_j^{(n+1)}(x) - B_j^{(n)}(x) \right. \\
\left. + \frac{n}{2n + 1} \frac{(2J + n + 1)(2J - n + 1)}{4J^2} B_j^{(n+1)}(x) \right] \tag{2.69}
\]

The structure of Eq. (2.68) is rather obvious: the prefactor of the square bracket is the free-ion value (2.59), while the sum inside the square bracket is the CF correction, \(\propto B'_{n0}/\Delta_{ex}\). The derivative has been taken with the aid of Eq. (2.78), proved in the next subsection.

Looking back at the main relations for \(E_a\) and \(\mu_R\) obtained in the linear-in-CF approximation, we note the central role played by the GBF, defined by means of Eq. (2.63). In the case of \(E_a\) these are just three functions, with \(n = 2, 4, 6\), whereas the expression for the magnetic moment also contains GBF with \(n\) odd. To understand the obtained results, we need to know some general properties of the GBF. These will be formulated—and in most cases also proved—in the next subsection. The discussion of the linear approximation will then be resumed in Section 2.7.
2.6 Properties of generalised Brillouin functions

2.6.1 Some elementary properties

2.6.1.1 Special values of $n$

The following relations are obtainable directly from the definition (2.63), taking into account that $C^{(0)}_0 \equiv 1$, $C^{(1)}_0 = \hat{J}_z$:

$$B^{(0)}_j(x) \equiv 1$$

$$B^{(1)}_j(x) = B_j(x) = \frac{2J + 1}{2J} \coth \left( \frac{2J + 1}{2J} x \right) - \frac{1}{2J} \coth \left( \frac{1}{2J} x \right).$$

Thus, a GBF of order one is the usual Brillouin function. Hence the term ‘generalised’ Brillouin functions.

2.6.1.2 Triangle inequality

The GBF equal identically zero, unless $n \leq 2J$. Indeed, by virtue of the definition (2.63) and the Wigner–Eckart theorem (1.24),

$$B^{(n)}_j(x) \propto \sum_{M=-J}^J e^{-xM/J} C^{JM}_{JMn0}.$$\

The CGC on the right vanish if the triangle inequality within the triplet $(J, J, n)$ is not satisfied (Varshalovich et al., 1988).

2.6.1.3 Parity

GBF of odd/even order $n$ are, respectively, odd/even functions of $x$:

$$B^{(n)}_j(-x) = (-1)^n B^{(n)}_j(x).$$

This follows from Eq. (2.72) and the known parity property of the CGC (Varshalovich et al., 1988):

$$C^{J-M}_{J-Mn0} = (-1)^n C^{JM}_{JMn0}.$$\

2.6.1.4 Monotonicity

For any $x > 0$, $0 < n \leq 2J$,

$$\frac{dB^{(n)}_j(x)}{dx} > 0.$$\

The proof for arbitrary $n$ is rather complicated and is not reproduced here. For $n = 1$ it follows from the fact that the square bracket in Eq. (2.80) is the dispersion of $\hat{J}_z$, a positive-definite quantity.

2.6.1.5 The limit $x \to 0$ ($T \to \infty$)

$$B^{(n)}_j(0) = \begin{cases} 1, & \text{if } n = 0 \\ 0, & \text{if } n > 0. \end{cases}$$

Taking the average in Eq. (2.63) is straightforward in this limit, since all Boltzmann’s exponentials equal unity and therefore $B^{(n)}_j(0) \propto (2J + 1)^{-1} \text{tr} C^{(n)}_0(\hat{J})$. 

Thus, a GBF of order one is the usual Brillouin function. Hence the term ‘generalised’ Brillouin functions.
2.6.1.6 Asymptotic behaviour at low temperatures \((x \gg J)\)

\[
B_j^{(n)}(x) \approx \frac{1}{(2J)^n} \frac{(2J)!}{(2J - n)!} \left[ 1 - \frac{n(n + 1)}{2J} \exp\left(-\frac{x}{J}\right) + \cdots \right]. \tag{2.76}
\]

The prefactor is obtained in the limit \(T = 0\) by averaging over the ground state \((M = J)\) using Eq. (1.24) and the explicit expression for the CGC \(C_{Jn}^{JJ}\) (Varshalovich et al., 1988). Allowing for the (exponentially small) population of the first excited level yields the correction term of Eq. (2.76). The special case of \(n = 1\) describes the magnetic moment:

\[
\mu_{\text{R}} \propto B_J(x) \approx 1 - J^{-1} e^{-x/J}. 
\]

Hence follows the approximate relation:

\[
B_j^{(n)}(x) \propto (\mu_{\text{R}})^{n(n+1)/2} \tag{2.77}
\]

known as Zener’s \(n(n + 1)/2\) power law (Zener, 1954; Callen and Callen, 1966; Goodings and Southern, 1971).

2.6.2 Differential relations and properties thence deduced

2.6.2.1 First derivative

The first derivative of a GBF is given by

\[
\frac{dB_j^{(n)}(x)}{dx} = \frac{n + 1}{2n + 1} B_j^{(n+1)}(x) - B_j(x) B_j^{(n)}(x) + \frac{n}{2n + 1} \frac{(2J + n + 1)(2J - n + 1)}{4J^2} B_j^{(n-1)}(x). \tag{2.78}
\]

To prove this relation, differentiate the identity (2.62) with respect to \(x\) one more time (the discrete parameters \(J\) and \(n = k\) being fixed):

\[
\frac{d(J_z^k)}{dx} = \frac{-\text{sign}(1 - g_J)}{J} \text{cov}(J_z, J_z^k) = \frac{-\text{sign}(1 - g_J)}{J} \left[ \{J_z^{k+1}\} - \{J_z^k\} \right]. \tag{2.79}
\]

Multiplying this relation by an appropriate coefficient and summing up over \(k\) of the same parity so as to assemble the expression for \(C_0^{(n)}(\hat{J})\), one arrives at

\[
\frac{d(C_0^{(n)}(\hat{J}))}{dx} = -\frac{\text{sign}(1 - g_J)}{J} \left[ \{\hat{J}_z C_0^{(n)}(\hat{J})\} - \{\hat{J}_z\} C_0^{(n)}(\hat{J}) \right] \tag{2.80}
\]

or, on foot of the definition (2.63),

\[
\frac{dB_j^{(n)}(x)}{dx} = \frac{-\text{sign}(1 - g_J)}{J} \left[ \{\hat{J}_z C_0^{(n)}(\hat{J})\} - B_J(x) B_j^{(n)}(x) \right]. \tag{2.81}
\]

Transforming the first term by means of the identity

\[
\hat{J}_z C_0^{(n)}(\hat{J}) = \frac{n + 1}{2n + 1} C_0^{(n+1)}(\hat{J}) + \frac{n}{2n + 1} \frac{(2J + n + 1)(2J - n + 1)}{4} C_0^{(n-1)}(\hat{J}) \tag{2.82}
\]

one finally obtains Eq. (2.78).
It remains to prove Eq. (2.82). It is apparently an expansion of the product $C(1)_0 C(n)_0$ in irreducible tensor operators of appropriate parity. The triangle rule admits only terms in $C(n\pm 1)_0$. The prefactor of the term in $C(n+1)_0$ is readily obtained by equating the coefficients of $\hat{J}_{z}^{2n+1}$ on both sides of Eq. (2.82). Note that the factor of $\hat{J}_{z}^{n}$ in $C(n)_0 (\hat{J})$ is the same as that of the leading term of the corresponding Legendre polynomial, i.e. $2^n(2n)!/(n!)^2$. Thus, we get

$$\hat{J}_{z} C(n)_0 (\hat{J}) = \frac{n + 1}{2n + 1} C(n+1)_0 (\hat{J}) + f(n, J) C(n-1)_0 (\hat{J}). \quad (2.83)$$

The remaining unknown factor $f(n, J)$ is evaluated by substituting Eq. (2.83) into (2.81) and letting $x$ go to infinity, whereas $B(n)_J (x) \to (2J)^{n}(2J)!/(2J-n)!$ and $dB(n)_J (x)/dx \to 0$, cf. Eq. (2.76). This completes the proof of Eq. (2.82) and consequently of Eq. (2.78).

2.6.2.2 Power series expansion At small $x$ (high temperatures) the GBF can be presented as follows:

$$B(n)_J (x) = \frac{1}{(2n+1)!!(2J)^{2n} (2J+1)(2J-n)!} \left[ x^n - n \frac{J(J+1) + \frac{1}{8}(n+3)}{3J^2(2n+3)} x^{n+2} + O(x^{n+4}) \right]. \quad (2.84)$$

The leading coefficient of this expansion is readily obtained by applying the differential relation (2.78) $k$ times, in order to compute the $k$th derivative of the GBF. Note that only the lowest-order GBF needs to be followed. Thus we write:

$$\frac{dB(n)_J (x)}{dx} = \frac{n}{2n+1} \frac{(2J+n+1)(2J-n+1)}{(2J)^2} B(n-1)_J (x) + \text{higher-order GBF}$$

$$\frac{d^2 B(n)_J (x)}{dx^2} = \frac{n(n-1)}{(2n+1)(2n-1)} \frac{(2J+n+1)(2J+n)(2J-n+1)(2J-n+2)}{(2J)^4} B(n-2)_J (x)$$

$$+ \text{higher-order GBF}$$

$$\frac{d^k B(n)_J (x)}{dx^k} = \frac{n!(n-k)!}{(2n+1)!!/(2n-2k+1)!!} \left[ x^{n-k} - \frac{(2J+n+1)(2J-n+k)}{(2J)^{2k}(2J+1+n-k)(2J-n)!} B(n-k)_J (x) + \text{higher-order GBF} \right]$$
By virtue of Eq. (2.75), one gets at $x = 0$:

$$
\left. \frac{d^k B_j^{(n)}(x)}{dx^k} \right|_{x=0} = \begin{cases} 
0, & \text{if } k < n \\
\frac{n!}{(2n+1)!} \frac{(2J+n+1)!}{(2J+1)(2J-n)!}, & \text{if } k = n.
\end{cases}
$$ (2.85)

Hence follows the leading coefficient of the expansion (2.84).

The coefficient of the term in $x^{n+2}$ is derived along the same lines, but this requires more cumbersome algebra and will not be reproduced here.

2.6.2.3 Explicit expressions

Equation (2.78) can be recast as a recurrence formula

$$
B_j^{(n+1)}(x) = \frac{2n+1}{n+1} \left[ \frac{dB_j^{(n)}(x)}{dx} + B_j(x)B_j^{(n)}(x) \right]
- \frac{n}{n+1} \left( \frac{(2J+n+1)(2J-n+1)}{4J^2} \right) B_j^{(n-1)}(x).
$$ (2.86)

Starting from the already known GBF of zeroth and first orders (2.70), (2.71) and working up, one can obtain in explicit form the GBF of an arbitrarily high order. Note the cancellation of the terms in $\coth^2 \left[ x/2J \right]$ arising from the derivative and from the product of two GBF in the square bracket of Eq. (2.86). As a consequence, GBF of any order $n > 1$ are linear in $\coth \left[ x/2J \right]$.

Conversely, the highest power of $\coth \left[ x/2J \right]$ increments by one each time Eq. (2.86) is used. Therefore, the GBF can be presented as follows (Kuz'min, 1992):

$$
B_j^{(n)}(x) = P_n(\xi, \eta) - Q_n(\xi, \eta) \coth \left( \frac{2J+1}{2J} x \right)
$$

$$
\xi = \frac{1}{2J} \coth \frac{x}{2J}, \quad \eta = \frac{1}{2J}.
$$ (2.87)

The polynomials $P_n$ and $Q_n$ obey the following recurrence relations:

$$
P_{n+1} = \frac{2n+1}{n+1} \left[ \left( \eta^2 - \xi^2 \right) \frac{\partial P_n}{\partial \xi} - \left( 1 + \eta \right) Q_n - \xi P_n \right]
- \frac{n}{n+1} \left[ 1 + 2\eta + (1-\eta^2)\eta^2 \right] P_{n-1}
$$

$$
Q_{n+1} = \frac{2n+1}{n+1} \left[ \left( \eta^2 - \xi^2 \right) \frac{\partial Q_n}{\partial \xi} - \left( 1 + \eta \right) P_n - \xi Q_n \right]
- \frac{n}{n+1} \left[ 1 + 2\eta + (1-\eta^2)\eta^2 \right] Q_{n-1}.
$$ (2.88)

Table 3.3 contains explicit expressions for $P_n(\xi, \eta)$ and $Q_n(\xi, \eta)$ with $n \leq 7$ obtained by means of Eqs. (2.88). Note that for $n$ odd these functions differ in sign from the analogous expressions of Magnani et al. (2003).\textsuperscript{14} The convention adopted herein ensures that the plots of all GBF at $x > 0$ lie entirely in the first quadrant.

\textsuperscript{14} We also note a misprint in their $A_5(\xi, \eta)$: the inner-most parenthesis $(-22 + 3\eta)$ should be multiplied by $-\eta$ rather than by $+\eta$. 

\textsuperscript{14} We also note a misprint in their $A_5(\xi, \eta)$: the inner-most parenthesis $(-22 + 3\eta)$ should be multiplied by $-\eta$ rather than by $+\eta$. 

The explicit expressions for the GBF were first obtained by Brillouin (1927, \( n = 1 \)), Yoshida (1951, \( n = 2 \)), Kazakov and Andreeva (1970, \( n = 4, 6 \)), Kuz’min (2002, \( n = 3 \)), Magnani et al. (2003, \( n = 5, 7 \)).

**2.6.2.4 The quasi-classical limit, \( J \to \infty \)** In the limit of very large \( J \) the GBF turn into the so-called reduced modified Bessel functions:

\[
\lim_{J \to \infty} B_J^{(n)}(x) = \hat{I}_{n+\frac{1}{2}}(x). \tag{2.89}
\]

The latter were introduced to the theory of magnetic anisotropy by Keffer (1955) and are defined as follows:

\[
\hat{I}_{n+\frac{1}{2}}(x) = I_{n+\frac{1}{2}}(x)/I_{\frac{1}{2}}(x) \tag{2.90}
\]

where \( I_n(x) \) are modified spherical Bessel functions of the first kind (Abramowitz and Stegun, 1972, Chapter 10).

To prove (2.89), note that by definition \( \hat{I}_{\frac{1}{2}}(x) \equiv 1 = B_J^{(0)}(x) \), while

\[
\hat{I}_{3/2}(x) = \coth x - 1/x = L(x) = \lim_{J \to \infty} B_J(x) \tag{2.91}
\]
that is the well-known Langevin function. Finally, the recurrence formula (2.86) goes over to

\[ \hat{I}_{n+3/2}(x) = \frac{2n+1}{n+1} \left( \frac{d\hat{I}_{n+1/2}(x)}{dx} + \hat{I}_{3/2}(x)\hat{I}_{n+1/2}(x) \right) - \frac{n}{n+1} \hat{I}_{n-1/2}(x) \]  

whose validity can be easily verified using the recurrence relation for the modified spherical Bessel functions, Eq. (10.2.19) of Abramowitz and Stegun (1972). Thus, by induction, for any \( n > 0 \) the function \( \hat{I}_{n+3/2}(x) \) obtained by means of Eq. (2.92) is the quasi-classical limit of the GBF \( B_{j}^{(n+1)}(x) \), q.e.d.

### 2.6.3 Selected properties of the functions \( D_{j}^{(n)}(x) \)

Most of these readily follow from the definition of \( D_{j}^{(n)}(x) \), Eq. (2.69), and the corresponding properties of the GBF. For example, the parity:

\[ D_{j}^{(n)}(-x) = (-1)^{n-1} D_{j}^{(n)}(x). \]  

It follows from the monotonicity of the GBF that

\[ D_{j}^{(n)}(x) > 0, \quad \text{if} \ x > 0, \ n > 0. \]  

The asymptotic behaviour at large \( x (x \gg J) \) is described by

\[ D_{j}^{(n)}(x) \approx \frac{n(n+1)}{2^{n+1}J^{3}} \frac{(2J)!}{(2J-n)!} x e^{-x/J}. \]  

Note that \( D_{j}^{(n)}(x) \to 0 \) as \( x \to \infty \).

Alternatively, for \( x \) small, one has

\[ D_{j}^{(n)}(x) = \frac{3n}{(2n+1)!!2^{2n}J^{n}} \frac{(2J+n+1)!}{(J+1)(2J+1)(2J-n)!} x^{n+1} + O(x^{n+1}). \]  

Obviously, \( D_{j}^{(n)}(0) = 0 \) for all \( n > 1 \).

Vanishing at both ends of the semi-infinite interval \( 0 < x < \infty \), positive and continuous everywhere within, the functions \( D_{j}^{(n)}(x) \), \( n > 1 \), must have at least one maximum at a certain point \( x_{\text{max}} > 0 \). In fact, there is exactly one maximum on the positive semi-axis, see Fig. 3.6. For larger \( n \) the maxima are situated farther to the right, their height scaling roughly as \( J^{n}/n \).

### 2.7 The linear-in-CF approximation (continued)

Let us now return to the discussion of the main results of the linear theory, Eqs. (2.64), (2.65), (2.68). We shall rely on our newly acquired knowledge of the properties of the GBF. It is convenient to plot the GBF \( B_{j}^{(n)}(x) \), \( n = 2, 4, 6 \), against inverse Langevin’s ratio \( 1/x \), which is approximately proportional to absolute temperature \( T \), Fig. 3.7. A feature that immediately draws attention in this graph is the presence of plateaus in the low-temperature region. On account of the exponentially rapid approach to saturation characteristic of the GBF, cf. Eq. (2.76), the plateaus in Fig. 3.7 have fairly sharply defined widths \( \sim 1/5J \).
Figure 3.6  Graphs of the functions $D_j^{(n)}(x)$ (rescaled) with $J = 6$ and $n = 2, 4, 6$ (a); rescaled positions (b) and rescaled heights (c) of the maxima of the functions $D_j^{(n)}(x)$, plotted vs $J$. 
Figure 3.7 Generalised Brillouin functions for $J = 8$, plotted against $1/x$.

The plateaus disappear completely in the limit $J \to \infty$, as the GBF go over to the reduced Bessel functions (2.89), employed in the quasi-classical theory of magnetic anisotropy (Keffer, 1955; Callen and Callen, 1966). The awkward fact that this constitutes a violation of the third law of thermodynamics was circumvented in the classical theory by putting to the fore the dependence of the anisotropy constants on magnetisation, rather than on temperature. This maneuvering has become obsolete after the introduction of the GBF.

Let us reiterate: below a certain point all anisotropy constants become independent of temperature, or saturated. One of the consequences of this is that spontaneous spin reorientation transitions (SRT) can take place only above a certain temperature. Quantitatively this temperature is determined by the exchange field on the RE. For example, for HoFe$_2$, where the relation between $x$ and $T$ is given by $x \approx 750/T$ (Kuz’min, 2001), the functions $B^{(n)}(x)$ are saturated below $1/x \approx 0.02$ (Fig. 3.7), or $T \approx 15$ K.

The height of a low-temperature plateau is determined by the numerical factor in front of the square bracket in Eq. (2.76); it tends to unity only when $J \to \infty$. For example, $B_j^{(2)}(\infty) = 1 - 1/2J$. Accordingly, the low-temperature values of the anisotropy constants are given by (Goodings and Southern, 1971):

$$\kappa_{nm}|_{T=0} = \frac{(2J)!}{2^n(2J-n)!} B_{nm}. \quad (2.97)$$

Here $B_{nm}$ are the CF parameters normalised according to Wybourne. They include the Stevens factors, therefore, their magnitudes decrease as $n$ increases. As against that, the coefficients of $B_{nm}$ in Eq. (2.97) grow with $n$. As a result, at low temperatures the anisotropy constants $\kappa_{2m}$, $\kappa_{4m}$ and $\kappa_{6m}$ are of the same order of magnitude. Similarly, there is no reason to presume that either $K_3$ or $K_2$ in Eq. (2.12) could be neglected at low temperatures. (Terms of order higher than six in $\sin \theta$ do vanish though.)
The situation is quite different in the high-temperature case. According to Eqs. (2.65), (2.84), $K_i$ fall off with temperature as $T^{-2i}$. Therefore, at around room temperature and above it one can neglect $B_{J}^{(4)}(x)$ and $B_{J}^{(6)}(x)$. In this approximation $K_2$ and $K_3$ vanish, while $K_1$ is given by

$$K_1 = -\frac{3}{2} B_{20} J^2 B_{J}^{(2)}(x).$$

(2.98)

The quality of this approximation can be judged by the linearity of the magnetisation curves along the hard direction. Thus, the room-temperature magnetisation curves of RE$_2$Fe$_{14}$B with the heaviest RE are practically linear (Yamada et al., 1988). However, in the case of Nd$_2$Fe$_{14}$B one can still see some residual curvature at $T = 290$ K, which disappears at higher temperatures. In such a situation it may be sensible to leave $K_1$ and $K_2$ and to neglect $K_3$.

From the fact that the GBF with $n > 0$ vanish at $x = 0$ and grow at any $x > 0$ it follows that these GBF are positive within the physically meaningful interval of values of $x$, $0 < x < \infty$. Therefore, the signs of the anisotropy constants $\kappa_{nm}$ entering in Eq. (2.10) are determined by the signs of the respective CF parameters $B_{nm}$ (these in turn depending on the signs of the Stevens factors) and cannot change as temperature varies. The same is true in relation to the anisotropy constants $\tilde{K}_3$ and $K'_3$, cf. Eqs. (2.65). The latter quantity determines the orientation of the easy magnetisation direction in the basal plane for most hexagonal crystals (point groups $D_6$, $C_{6v}$, $D_{3h}$ and $D_{6h}$).

Equations (2.65) predict for the dependence $K_2(T)$ three possible shapes. These are sketched in Fig. 3.8. Apparently, $K_2$ can change sign no more than once. We
shall come back to this argument in Section 3, in connection with the SRT in TbCo$_5$.

As regards $K_1$, it can in principle change sign twice, and even more times when the 3d contribution is taken into account.

Let us now consider the connection between the linear theory and the high-temperature expansion of Section 2.4. That these two approximations are closely related should not come as a surprise—we have already noted that the leading term in the high-temperature expansion of anisotropy constants is always linear in CF. For example, for the axial anisotropy constants one can write in general (Kuz’m’in, 1995):

$$K_i = \text{const} \times B_{2i,0} x^{2i} + O(x^{2i+1}).$$  \hspace{1cm} (2.99)$$

The coefficient of $x^{2i+1}$ and of the subsequent terms may be non-linear in CF parameters. (In fact, terms even in $x$ must be odd in $B_{nm}$ and even in $B_{nm}$).

The first term of Eq. (2.99) may be regarded as the leading term of an expansion of $K_i$ in powers of several variables: $x$, $B_{20}$, $B_{40}$ etc. (or $x$ and the dimensionless quantities introduced in Section 2.2: $\eta$, $\xi$ etc.). The same series can be obtained in a different way: first $K_i$ is expanded in powers of $B_{nm}$, then the coefficients of the obtained expansion (first of all, those of the terms linear in $B_{nm}$) are further expanded in powers of $x$. In other words, Eqs. (2.65) of the linear theory are expanded in a series of powers of $x$ using Eq. (2.84):

$$K_{n/2} = \frac{(-1)^n/2}{2^{2n}n!(2n + 1)J^n (2J + 1)(2J - n)!} B_{n0} x^n + O(x^{n+2})$$

$$n = 2, 4, 6. \hspace{1cm} (2.100)$$

Comparing this with the general expansion (2.99), one immediately gets an expression for the unknown constant therein. Equation (2.44) is not but a special case of (2.100) with $n = 2$, where the expansion is taken to the next, quartic in $x$ term. Omitted from the approximate relation (2.44) are the term in $x^3$ (whose coefficient is a homogeneous quadratic form in $B_{nm}$) and parts of the term in $x^4$, namely, one which is linear in $B_{40}$ and the other one cubic in $B_{nm}$. The omitted contributions were evaluated for TbCo$_5$ and found small (Kuz’m’in, 1995).

Thus, the linear theory becomes asymptotically exact at high temperatures ($x$ small) because the leading terms of both expansions, (2.99) and (2.100) coincide. In other words, non-linear terms die out more rapidly with temperature. For typical permanent magnet materials the linear in $B_{nm}$ contribution is also dominant at moderately high temperatures, where terms in $x^4$ are no longer negligible, the term in $B_{20}x^4$ prevailing over the one in $B_{40}x^4$. Hence Eq. (2.44). One concludes that the high-temperature version of the linear theory (2.98) should be more accurate than Eq. (2.41) for exchange-dominated systems at intermediate temperatures, because the former includes—albeit approximately—the higher-order terms: in $x^4$, $x^6$ etc.

An added advantage of Eq. (2.98) is its sensible behaviour in the limit of very low temperatures, where it is generally speaking invalid. Thanks to the presence of an unexpanded GBF, Eq. (2.98) inoffensively tends to a finite limit as $x \rightarrow \infty$, whereas (2.41) diverges.
As against that, Eq. (2.41) has the advantage of being very simple and is ideally suited for discussing the high-temperature behaviour of permanent magnets. It can also be easily solved for \( x \).

Before closing the subsection, let us touch upon the question of the influence of CF on the RE magnetic moment, described by Eq. (2.68). According to the above-stated properties of the functions \( D_j(x) \) and \( J_j(x) \), namely Eq. (2.95), this effect should be negligibly small at the temperature of liquid He, that is exactly where experimentalists usually try to detect it. The reason why they prefer to compare the measured RE moment with the free-ion expression (2.59) just at low temperatures is rather mundane. The Brillouin function is saturated there, so one does not need to worry about its unknown argument. Unfortunately, the saturation also kills off the sought CF effect.

This effect reaches its maximum at a finite temperature. For example, in Nd\(_2\)Fe\(_{14}\)B the six-order CF contribution to \( \mu_{\text{Nd}} \) peaks at \( T \approx 80 \) K (\( x \approx 9 \)), where it amounts to \(-2\%\) of the total Nd moment (at the same temperature).\(^{15}\) At room temperature the sixth-order effect is a factor of 20 weaker, \(-0.1\%\), and may be safely neglected. The fourth-order contribution is maximum at \( T = 120 \) K, or \( x \approx 6.2 \), where it reaches \(-1.6\%\). This reduces to about one-half of a per cent at ambient temperature, negligible in most cases. Finally, the second-order CF effect is maximum at room temperature, \( T = 290 \) K (\( x \approx 2.3 \)), where the function \( D_{\frac{3}{2}}(x) \) equals approximately 2.6. Accordingly, its relative contribution to \( \mu_{\text{Nd}} \) is \(+7.7\%\). One should bear in mind however, that less than one-seventh of the total magnetisation of Nd\(_2\)Fe\(_{14}\)B at ambient temperature comes from the Nd sublattice. When related to the total magnetisation, the second-order CF effect reduces to a mere 1%. Thus, the CF contribution to magnetisation hardly needs to be taken into account in technical calculations of permanent-magnet devices. In any case, at or above room temperature only second-order CF matters.

The influence of the CF on the magnetisation is most noticeable near SRT,\(^{16}\) where rotation of the easy magnetisation direction leads to a rapid change of the primed CF parameters (2.61) with temperature. Obviously, this effect is more pronounced in ferrimagnetic intermetallic compounds with the heavy RE and at first-order SRT. Further consideration of this phenomenon will be deferred till Section 3.

At very high temperatures (\( x \lesssim 1 \)) the influence of the CF on \( \mu_R \) decreases. The least rapidly falls off the second-order CF effect. According to Eq. (2.96), at small \( x \)

\[
D_j^{(2)}(x) \approx \frac{(2J-1)(2J+3)}{10J} x.
\]  

(2.101)

Putting this into Eq. (2.68), we arrive at Eqs. (2.46), (2.47). Note that by virtue of Eq. (2.61), \( B'_{20} = B_{20} \) when \( B'|z (\theta = 0) \), and \( B'_{20} = -\frac{1}{2}B_{20} \) when \( B'|\perp z \).

---

\(^{15}\) Our estimates are based on the CF parameters of Cadogan et al. (1988), converted to the Wybourne normalisation and averaged over the two Nd sites: \( B_{20} = -4.4 \) K, \( B_{40} = 0.092 \) K, \( B_{60} = 0.02 \) K. For simplicity, no distinction was made between primed and non-primed CF parameters below the SRT point, \( T_{SR} = 135 \) K. The exchange splitting, \( \Delta_{\text{ex}} = 168 \) K at \( T = 0 \), comes from the same source. At finite temperatures \( \Delta_{\text{ex}} \) was scaled down in proportion to the iron sublattice magnetisation. We used the scaling factors 0.987, 0.976 and 0.891 for \( T = 80, 120 \) and 290 K. These were computed using Eq. (2.43) with \( s = 0.7 \) and \( T_C = 592 \) K.

\(^{16}\) This effect is not attributable to the RE sublattice alone.
\( \theta = \pi / 2 \). This manifests once again the intimate connection between the linear-in-CF and the high-temperature approximations.

### 2.8 The low-temperature approximation

Following the introduction of the general single-ion model in Section 2.3, we have considered two closely inter-related approximations: the high-temperature one (Section 2.4) and the one linear in CF (Sections 2.5–2.7). These were ‘good’ approximations, in the sense that their validity in any particular case was easy to verify, at least a posteriori.

In this subsection we shall formulate an approximation that unfortunately lacks the same quality. It has been already said that the standard theory of magnetic anisotropy is generally inapplicable to RE-transition metal magnets at low temperatures—the expansion of the free energy in powers of \( \sin \theta \) cannot be truncated and the very description in terms of a single angle \( \theta \) is no longer meaningful on account of significant non-collinearity of the sublattices. When an analytical description of some sort at low \( T \) is possible, it should be necessarily limited to a special case, i.e. it should involve extra assumptions apart from the smallness of \( T \).

As such an additional condition, we shall now assume that the CF has a predominantly axial character, or that \( B_{nm} \) with \( m \neq 0 \) are small in comparison with \( B_{n0} \). A rigorous verification of this hypothesis would require the knowledge of all CF parameters, including those with \( m \neq 0 \), which in this approach we do not presume to have. In that sense, this is an uncontrolled approximation.

So let the CF be approximately axial and let the system under consideration be broadly exchange-dominated. This implies that the ground state is \( |JM \rangle \), with \( M = -\text{sign}(1-g_J)J \), the first excited state has \( M = -\text{sign}(1-g_J)(J-1) \), etc.

The positive \( z \) direction is, as usual, that of the 3d magnetisation vector. The latter coincides with the high-symmetry crystallographic axis \([001]\), or at the most makes with it an infinitesimal angle \( \theta \). Such a situation is characteristic of permanent magnets—otherwise the material would simply lose its hard magnetic properties, first of all the coercivity.

The reason why it makes sense to limit the consideration to the vicinity of the point \( \theta = 0 \) is explained in Fig. 3.9. At \( T = 0 \) the free energy is the ground state energy, shown as a solid line. It may not always be a smooth function of the angle \( \theta \), because the RE energy levels may cross over at some finite values of \( \theta \). Just such a case is shown in Fig. 3.9a. A more realistic example is REFe\(_{11}\)Ti (Hu et al., 1990, Fig. 8 therein). It is clear that the displayed dependence \( F(\theta) \) cannot be approximated with a smooth function like \( K_1 \sin^2 \theta \) or \( K_1 \sin^2 \theta + K_2 \sin^4 \theta \) across the entire interval from 0 to 90°. For \( \theta \) small, such a presentation—in the spirit of Landau’s theory (Landau and Lifshitz, 1958)—is still possible and even useful. Indeed, when a second-order SRT occurs (Fig. 3.9b), the main events take place near the point \( \theta = 0 \) (or perhaps near \( \theta = \pi / 2 \), in which case the small angle \( \pi / 2 - \theta \) should be regarded as the order parameter). Of course, the benefit of presenting the anisotropy energy as \( K_1 \sin^2 \theta \) in close vicinity to \( \theta = 0 \) is not limited to second-order SRT. A number of other phenomena—nucleation, transverse alternating-current susceptibility, magnetic resonance etc.—require such a presentation.
Thus, under the above assumptions, the RE Hamiltonian (2.35) falls into two parts:

$$\hat{H}_{4f} = \text{sign}(1 - g_J) \Delta_{ex} \cos \theta \hat{J}_z + \sum_{n=2,4,6} B_{n0} C_n^{(0)} (\hat{J})$$

$$+ \text{sign}(1 - g_J) \Delta_{ex} \sin \theta \hat{J}_x. \quad (2.102)$$

The first one of them is diagonal in the $JM$ representation, while the second one can be treated as a perturbation since it contains an infinitesimal quantity $\sin \theta$.

We restrict ourselves to the region of low temperatures, $kT \ll 2\Delta_{ex} + \Delta_1 + \Delta_2$, where we can neglect thermal population of all but the lowest two levels of the RE. It will be recalled that $\Delta_{ex} + \Delta_1$ is a gap separating the ground and the first excited states when $\theta = 0$. Its two parts, due to the exchange and the CF, are defined by Eqs. (2.17) and (2.23), respectively. Similarly, $\Delta_{ex} + \Delta_2$ stands for the gap between the first and the second excited levels.

Expanding the centre of gravity of the lowest two levels and the gap between them in powers of the small parameter $\sin^2 \theta$,

$$E_{\text{cg}}(\theta) = E_{\text{cg}}(0) + V \sin^2 \theta + \cdots$$

$$\Delta(\theta) = \Delta_{ex} + \Delta_1 + 2W \sin^2 \theta + \cdots$$

we get

$$K_1 = V - W \tanh \frac{\Delta_{ex} + \Delta_1}{2kT}. \quad (2.103)$$

The quantities $V$ and $W$ are evaluated using the standard second-order perturbation theory:

$$E_{\text{cg}} = E_{\text{CF}} + \frac{2J - 1}{2} \Delta_{ex} \cos \theta - \frac{2J - 1}{4} \frac{\Delta_{ex}^2 \sin^2 \theta}{\Delta_{ex} \cos \theta + \Delta_1 + \Delta_2}$$

$$\Delta(\theta) = \Delta_1 + \Delta_{ex} \cos \theta + J \frac{\Delta_{ex}^2 \sin^2 \theta}{\Delta_{ex} \cos \theta + \Delta_1 + \Delta_2} - \frac{2J - 1}{2} \frac{\Delta_{ex}^2 \sin^2 \theta}{\Delta_{ex} \cos \theta + \Delta_1 + \Delta_2}. \quad (2.104)$$
Here $E_{\text{CF}}$ is the CF contribution to $E_{\text{CF},i}$, independent of $\theta$. Corrections of order higher than 2 in perturbation theory contain only terms of order higher than 2 in $\sin \theta$ and therefore need not be considered. Presenting $\cos \theta$ as $1 - \frac{1}{2} \sin^2 \theta + \cdots$ and collecting terms in $\sin^2 \theta$ in Eqs. (2.104), we arrive at

$$V = \frac{2J - 1}{4} \frac{\Delta_{\text{ex}} \Delta_2}{\Delta_{\text{ex}} + \Delta_2} \quad (2.105)$$

$$W = V - \frac{J}{2} \frac{\Delta_{\text{ex}} \Delta_1}{\Delta_{\text{ex}} + \Delta_1}. \quad (2.106)$$

The set of Eqs. (2.103), (2.105) and (2.106) gives the coefficient $K_1$ of the Landau expansion in powers of $\sin \theta$ at low temperatures.

The interplay of the CF and the exchange interactions can be best seen at $T = 0$, as the hyperbolic tangent in Eq. (2.103) becomes unity and $K_1$ reduces to

$$K_1 = \frac{J}{2} \frac{\Delta_{\text{ex}} \Delta_1}{\Delta_{\text{ex}} + \Delta_1}. \quad (2.107)$$

Insofar as their influence on $K_1$ is concerned, the exchange and the CF act like two resistors connected in parallel—additive are the reciprocal splittings rather than the splittings themselves. In the extreme case of exchange domination, $\Delta_1/\Delta_{\text{ex}} \to 0$, Eq. (2.107) turns into

$$K_1 = \frac{J}{2} \Delta_1. \quad (2.108)$$

Here one can recognise the first one of the equations (2.65) of the linear theory, taken at $T = 0$, or $x = \infty$. Indeed,

$$K_1 = - \sum_{n=2,4,6} \frac{1}{2} n(n + 1) J^n B_j^{(n)} (\infty) B_n = - \sum_{n=2,4,6} \frac{n(n + 1)}{2^{n+1}} \frac{(2J)!}{(2J - n)!} B_n = \frac{J}{2} \Delta_1$$

where Eqs. (2.76) and (2.23) have been used.

When $\Delta_1$ is small (as compared with $\Delta_{\text{ex}}$) but finite, Eq. (2.107) can be expanded in powers of the ratio $\Delta_1/\Delta_{\text{ex}}$:

$$K_1 = \frac{J}{2} \Delta_1 \left( 1 - \frac{\Delta_1}{\Delta_{\text{ex}}} + \cdots \right). \quad (2.109)$$

Thus, an added advantage of the low-temperature approximation is that it provides a quantitative criterion of the performance of the linear theory at $T = 0$. Indeed, according to Eq. (2.109), the fractional error of the ‘linear’ equation (2.108) can be judged by the smallness of the ratio $\Delta_1/\Delta_{\text{ex}}$, or $2K_1/J \Delta_{\text{ex}}$. The latter combination contains quantities more readily accessible to experiment. (We would like to remind that $K_1$ stands here for the RE contribution to the first anisotropy constant at $T = 0$.) For example, at $T = 4.2$ K TbCo$_5$ has $K_{1\text{Tb}} = -99$ K (Ermolenko, 1980) and $B_{\text{ex}} \approx 220$ T (Ballou et al., 1989), or $\Delta_{\text{ex}} \approx 150$ K. Hence $2K_{1\text{Tb}}/6\Delta_{\text{ex}} = -0.22$, i.e. the linear approximation is accurate within 22%. This estimate, referred to $T = 0$, is the upper bound of the inaccuracy of the linear-in-CF approximation.
As stated in the previous subsection, the linear theory performs better at higher temperatures and becomes exact in the limit \( T \to \infty \).

Let us now demonstrate how the low-temperature approximation to \( K_1 \) can be used to evaluate the temperature of a second-order SRT of the type easy axis—easy cone. Such transitions are not uncommon in hard magnetic materials, \( \text{Nd}_2\text{Fe}_{14}\text{B} \) being the best-known example with \( T_{\text{SR}} = 135 \text{ K} \) (Deryagin et al., 1984; Givord et al., 1984). A necessary condition for such a transition is that \( K_1 = 0 \) at \( T = T_{\text{SR}} \), or

\[
K_{3d} + V - W \tanh \frac{\Delta_{\text{ex}} + \Delta_1}{2kT_{\text{SR}}} = 0
\]

whence

\[
kT_{\text{SR}} = \frac{\Delta_{\text{ex}} + \Delta_1}{\ln \left( 1 + 2 \frac{V + K_{3d}}{W - V - K_{3d}} \right)}.
\]

(2.110)

Taking for \( \text{Nd}_2\text{Fe}_{14}\text{B} \) the exchange and CF parameters of Cadogan et al. (1988) averaged over the two Nd sites, one finds from Eqs. (2.23) \( \Delta_1 = -74.7 \text{ K} \) and \( \Delta_2 = 178 \text{ K} \), as well as \( \Delta_{\text{ex}} = 167 \text{ K} \). Hence \( V = 172 \text{ K} \) and \( W = 476 \text{ K} \), by way of Eqs. (2.105) and (2.106). The anisotropy constant of the iron sublattice \( K_{3d} \) is taken equal to that of \( \text{Y}_2\text{Fe}_{14}\text{B} \), which at low temperatures was found to be \( 6.0 \text{ K/Y atom} \) (Givord et al., 1984). Then Eq. (2.110) yields \( T_{\text{SR}} = 117 \text{ K} \).

This compares rather well with \( T_{\text{SR}} = 122 \text{ K} \), obtained numerically by Piqué et al. (1996) using the full algorithm of the single-ion model (Section 2.3) and the same parameters as above. The discrepancy between the experimental transition point, \( T_{\text{SR}} = 135 \text{ K} \), and the calculated ones is inherent in the exchange and CF parameters of Cadogan et al. (1988) rather than being a consequence of the approximations introduced in this subsection—see the discussion by Piqué et al. (1996).

For \( \text{Ho}_2\text{Fe}_{14}\text{B} \) the situation is similar. The transition point found from Eq. (2.110), \( T_{\text{SR}} = 57 \text{ K} \) (Kuz’min, 1995), agrees well with that obtained numerically using the same parameters, \( T_{\text{SR}} = 56 \text{ K} \) (Piqué et al., 1996), both being somewhat lower than the experimental value, \( T_{\text{SR}} = 63 \pm 2 \text{ K} \) (Piqué et al., 1996).

Let us recapitulate: at low temperatures the free energy of a RE-based hard magnetic material generally cannot be presented as a truncated expansion in powers of \( \sin \theta \), Eq. (2.12) or similar. Such a presentation is however possible in a certain neighbourhood of the point \( \theta = 0 \), where Eq. (2.12) has the meaning of Landau’s expansion, its convergence ensured by the smallness of \( \sin \theta \). Then, upon some additional assumptions, a useful analytical expression (2.103) can be obtained for \( K_1 \) (and in principle also for \( K_2 \) etc.).

\[\text{Here } K_1 \text{ is of course the total anisotropy constant, including the contributions from the 3d and the 4f subsystems.}\]
2.9 J-mixing made simple\textsuperscript{18}

In this last part of Section 2 we shall finally get down to elucidating the importance of the so far neglected effect of J-mixing on the single-ion magnetic anisotropy. What most workers in the field know about J-mixing can be summarised as the following ‘Three Myths’.

1. J-mixing is a complex phenomenon, not readily amenable to quantitative treatment. Allowing for it necessitates large-scale computer calculations. Too many factors play a role, so little can be demonstrated conclusively.

2. Quantitatively, J-mixing leads to serious consequences only in samarium compounds. For the other REs this effect is not very important, if not exactly unnoticeable. Given the formidable difficulties of its description (Myth 1), it is better to neglect it. The neglect is certainly justified for the heavy REs.

3. When it comes to allowing for J-mixing, the effect can be best visualised at low temperatures. There, both the calculations are more transparent and the anomalies are sharper. When proved unimportant at low $T$, J-mixing may be neglected at any temperature.

The above three statements contain only one grain of truth: that the J-mixing is most distinctly manifest in samarium compounds (and also in those of trivalent europium, not often come across among hard magnetic materials). The rest is misconceptions. In this subsection, according as the truth will gradually unfold, we shall be coming back to the ‘Three Myths’ to point out the falsity of this or that constituent statement.

Since J-mixing in the light and the heavy REs is described by slightly different equations, we shall first consider in some detail only the former. The main results for the heavy RE case will be stated briefly towards the end of the subsection.

We begin with writing down a model Hamiltonian for a single RE ion in the absence of applied magnetic field. The Hamiltonian is defined on the ground LS term, treated in the Russell–Saunders approximation, and contains terms describing spin-orbit coupling, exchange interaction and the CF:

\[ \hat{H}_{4f} = \hat{H}_{\text{so}} + \hat{H}_{\text{ex}} + \hat{H}_{\text{CF}} = \lambda \hat{L} \cdot \hat{S} - 2\mu_B B_{ex} \hat{S}_z + \sum_{n,m} A'_{nm} C^{(n)}_m (\hat{L}). \] (2.111)

Here the $z$ axis has been chosen to be parallel to the 3d sublattice magnetisation $M_{3d}$ (therefore antiparallel to the exchange field $B_{ex}$), which does not necessarily coincide with any of the high-symmetry crystallographic directions. Accordingly, the CF parameters in Eq. (2.111) are primed, to distinguish them from the usual, non-primed CF parameters defined in the crystallographic coordinate system.

We aim at describing the lower part of the energy spectrum of the RE, involved in forming the thermodynamic properties of the solid. To this end we construct an effective Hamiltonian $\hat{\mathcal{H}}$ defined on the ground $J$ manifold of the light RE, $J = L - S$,

\[ \hat{\mathcal{H}} = \Delta_{ex} \hat{J}_z + \sum_{n,m} B'_{nm} C^{(n)}_m (\hat{J}) + \delta \hat{V}. \] (2.112)

\textsuperscript{18} This subsection follows the work of Kuz’min (2002).
Here $B'_{nm}$ are CF parameters in the $J$ representation, incorporating the Stevens factors. They are related to the quantities $A'_{nm}$ in Eq. (2.111) through known rational factors. E.g., for $n = 2$ this relation is given by Eq. (1.23): 
\[ B'_{nm}/A'_{nm} = (L + 1)(2L + 3)/(J + 1)(2J + 3). \]
Similar expressions can also be written for $n = 4$ and 6.

The effective Hamiltonian $\hat{\mathcal{H}}$ (2.112) differs from the usual single-multiplet Hamiltonian (2.14) in a very important way: it incorporates an operator $\delta \hat{V}$ containing second-order corrections bilinear in $\hat{H}_{\text{ex}}$ and $\hat{H}_{\text{CF}}$, the latter two regarded as perturbations with respect to $\hat{H}_{\text{so}}$. Although it operates within the ground multiplet, $\delta \hat{V}$ contains inter-multiplet matrix elements of $\hat{H}_{\text{ex}}$ and $\hat{H}_{\text{CF}}$.

Subsequently we intend treating the last two terms of Eq. (2.112) as perturbations with respect to the first one, limiting ourselves to first-order corrections. Therefore, all terms with $m \neq 0$ may be omitted from the sum in Eq. (2.112). As regards the operator $\delta \hat{V}$, we only need to compute its matrix elements diagonal in $M$:
\begin{equation}
\delta \hat{V}_{MM} = -\frac{2}{\Delta_{\text{so}}} \langle J + 1, M | \hat{H}_{\text{ex}} | JM \rangle \langle J + 1, M | \hat{H}_{\text{CF}} | JM \rangle
\end{equation}
where $\Delta_{\text{so}} = \lambda(J + 1)$ is the spin-orbit splitting between the centres of gravity of the ground $(J)$ and the first excited $(J + 1)$ multiplets.

The inter-multiplet matrix element of $\hat{H}_{\text{ex}} = -2\mu_{B}\hat{B}_{\text{ex}}\hat{S}_z$, required for Eq. (2.113), is given by
\begin{equation}
\langle J + 1, M | \hat{H}_{\text{ex}} | JM \rangle = -\sqrt{(L + 1)(J + 1)(2J + 1)} \frac{C_{J+1,M}^{JM}}{\Delta_{\text{ex}}}.
\end{equation}
This expression has been obtained from the well-known formula (88) of Van Vleck (1932) by setting $J = L - S$, as appropriate for the ground multiplet of a light RE, and factoring out the CGC:
\begin{equation}
C_{J+1,M}^{JM} = \sqrt{(J + 1)^2 - M^2} \sqrt{(2J + 1)(J + 1)}.
\end{equation}

One of the advantages of Eq. (2.114) is that it depends on the exchange field $B_{\text{ex}}$ through the quantity $\Delta_{\text{ex}}$, which is the exchange splitting of the ground multiplet defined by Eq. (2.17). This will enable us to reduce the effect of $J$-mixing to a renormalisation of the standard (without $J$-mixing) expression for the anisotropy constants (2.64), which depends on the characteristics of the ground multiplet only.

For the inter-multiplet matrix element of the CF one can write
\begin{equation}
\langle J + 1, M | \hat{H}_{\text{CF}} | JM \rangle = \sum_{n=2,4,6} B'_{n0} \left\{ \begin{array}{ccc} L & S & J + 1 \\ J & n & L \end{array} \right\} \frac{1}{2^n} \sqrt{\frac{(2J + n + 1)!}{(2J + 1)(2J - n)!}} C_{J+1,Mn}^{JM}.
\end{equation}
This is a generalisation of the intra-multiplet form (1.24) of the Wigner-Eckart theorem. The change from Eq. (1.24) to Eq. (2.115) consists, apart from the obvious modification of the CGC, in adding the ratio of the two 6\(j\) symbols, as follows from Eqs. (6-4) and (6-5) of Wybourne (1965). The CF parameters \(B'_{n0}\) employed in Eq. (2.115) include the Stevens factors. This is in line with our strategy of describing the \(J\)-mixing in terms of the characteristics of the ground multiplet.

As we further restrict ourselves to the Hund ground state of the light RE, Eq. (2.115) simplifies significantly, to become

\[
\langle J + 1, M | \hat{\mathcal{H}}_{\text{CF}} | JM \rangle = - \sum_{n=2,4,6} B'_{n0} \frac{1}{2^n} \sqrt{\frac{n(n+1)S(2J + n + 1)!}{(L + 1)(2J + n + 2)(2J - n + 1)!)}} C_{JM0}^{J+1,M} \cdot (2.116)
\]

Putting Eqs. (2.114) and (2.116) into Eq. (2.113) results in

\[
\delta \tilde{V}_{MM} = \frac{\Delta_{\text{ex}}}{\Delta_{\text{so}}} \sum_{n=2,4,6} B'_{n0} \frac{1}{2^{n-1}} \sqrt{\frac{n(n+1)(J+1)(2J+1)(2J+n+1)!}{(2J+3)(2J+n+2)(2J-n+1)!}}} \times C_{JM10}^{J+1,M} C_{JMn0}^{J+1,M} \cdot (2.117)
\]

Note the cancellation of explicit dependence on the quantum numbers \(L\) and \(S\). Of course, Eq. (2.117) still depends on \(L\) and \(S\) implicitly, through the relation \(J = L - S\), used in the derivation.

Replacing the product of two CGCs in Eq. (2.117) by a linear combination of two CGCs through the following identity [a particular case of Eq. (8.7.37) of Varshalovich et al. (1988)],

\[
C_{JM10}^{J+1,M} C_{JMn0}^{J+1,M} = \frac{1}{2(2J+1)(2n+1)} \sqrt{\frac{n(n+1)(2J+3)}{J+1}} \times \left[ \sqrt{(2J+n+1)(2J+n+2)} C_{JM,n-1,0}^{JM} - \sqrt{(2J-n)(2J-n+1)} C_{JM,n+1,0}^{JM} \right]
\]

and comparing the result with Eq. (1.24), one concludes that the effective Hamiltonian \(\hat{\mathcal{H}}\), or rather its part diagonal in \(M\), can be presented as follows:

\[
\hat{\mathcal{H}} = \Delta_{\text{ex}} \hat{J}_z + \sum_{n=2,4,6} B'_{n0} \left\{ C_0^{(n)}(\hat{J}) - \frac{\Delta_{\text{ex}}}{\Delta_{\text{so}}} \frac{n(n+1)}{2n+1} \right.
\]

\[
\times \left[ \frac{2J+n+1}{2} C_0^{(n-1)}(\hat{J}) - \frac{2}{2J+n+2} C_0^{(n+1)}(\hat{J}) \right]\}
\]

\[
(2.118)
\]

\(19\) To obtain Eq. (2.116) one should use the recurrence relation (9.6.5) of Varshalovich et al. (1988), with \(a = f = L = J + S\), \(b = S\), \(c = d = J\), and note that the last \(6j\) symbol therein vanishes because its three upper indices do not satisfy the triangle rule. One can then isolate the ratio of the remaining two \(6j\) symbols and substitute it into Eq. (2.115).
It is now apparent that the effect of $J$-mixing is a renormalisation of the CF, which vanishes in the limit $\Delta_{ex}/\Delta_{so} \to 0$.

The remaining steps are quite similar to what was done in Section 2.5. The sum in Eq. (2.118) is treated as a perturbation with respect to the first term, $\Delta_{ex} \tilde{J}_z$. The primed CF parameters are transformed to the crystallographic coordinates using Eq. (2.61). The thermal averages of the irreducible tensor operators are replaced by GBFs according to Eq. (2.63), recalling that $\text{sign}(1 - g_J) = 1$ for the light REs. The energy corrections of first order in $B_{nm}$ take the form of the anisotropy energy (2.10), in which

$$\kappa_{nm} = B_{nm} J^n \left\{ B_j^{(n)}(x) + \frac{\Delta_{ex} n(n + 1)}{\Delta_{so} 2n + 1} \right. \times \left. \left[ \frac{2J + n + 1}{2J} B_j^{(n-1)}(x) - \frac{2J}{2J + n + 2} B_j^{(n+1)}(x) \right] \right\} \quad (2.119)$$

with $x = J \Delta_{ex}/kT$.

Thus, the effect of $J$-mixing on the $n^{th}$-order anisotropy constant $\kappa_{nm}$ consists in renormalising its temperature dependence, which in the absence of the $J$-mixing is described by a single GBF of the same order $n$, cf. Eq. (2.64). Now Eq. (2.119) contains two extra terms, with $B_j^{(n\pm1)}(x)$. As one would expect, these corrections vanish when $\Delta_{ex}/\Delta_{so} \to 0$.

Equation (2.119) enables us to reach a definite conclusion about the sense of the effect. Let us consider the square bracket of Eq. (2.119) in the limit $T \to 0$, or $x \to \infty$. Making use of Eq. (2.76), we get

$$\left[ \frac{2J + n + 1}{2J} B_j^{(n-1)}(\infty) - \frac{2J}{2J + n + 2} B_j^{(n+1)}(\infty) \right] = B_j^{(n)}(\infty) \left( \frac{2J + n + 1}{2J - n + 1} - \frac{2J - n}{2J + n + 2} \right) > 0. \quad (2.120)$$

Obviously, the numerator of the first fraction in the parenthesis is greater than, and its denominator is less than their respective counterparts in the second fraction. It is easy to see that the square bracket of Eq. (2.119) will remain positive at any temperature, as $B_j^{(n+1)}(x)$ decays with temperature more rapidly than $B_j^{(n-1)}(x)$. Therefore, $J$-mixing always enhances the intra-multiplet anisotropy, irrespective of the sign of the latter.

It follows from Eq. (2.120) that in the classical limit, $J \to \infty$, the contribution to $\kappa_{nm}$ from the $J$-mixing in the light REs vanishes at $T = 0$—a first indication that low temperatures may not be the best choice for appreciating the size of the effect, contrary to the generally accepted view (Myth 3).

Equation (2.119) can be put to a further good use: setting to zero all GBFs of order higher than two, one arrives at a simple high-temperature version of the formalism. Let us additionally limit ourselves to tetra-, hexa- or trigonal crystals. Then the anisotropy energy is just $K_1 \sin^2 \theta$, where

$$K_1 = -\frac{3}{2} \kappa_{20} = -\frac{3}{2} B_{20} J^2 \left[ B_j^{(2)}(x) + \left( \frac{6J + 3}{5J} \right) \frac{\Delta_{ex}}{\Delta_{so}} B_j(x) \right]. \quad (2.121)$$
Figure 3.10 Quantities relevant to Eq. (2.119) for $\text{RE} = \text{Nd}$ ($J = 9/2$, $n = 2$), plotted against $1/x$: — $y = 1.6B_{9/2}(x)$, $-$ $y = \frac{54}{50}B_{9/2}^{(3)}(x)$, $\cdots$ the difference of the previous two.

Here the second term in the square brackets, representing the correction for $J$-mixing, depends on temperature through the familiar Brillouin function—a sign of simplicity yet to come (contrary to Myth 1). The correction term should be small due to the ratio $\Delta_{ex}/\Delta_{eo}$. However, at elevated temperatures it tends to zero more slowly (as $1/T$) than the first, intra-multiplet term, $B_{J}(J/\Delta_{ex}/kT) \propto 1/T^2$. Therefore, the relative importance of the $J$-mixing effect must increase with temperature. This constitutes a final departure from Myth 3.

As has been demonstrated in Section 2.4, the leading term in the rigorous high-temperature expansion for $K_1$ is linear in the CF parameter $B_{20}$. In other words, all other terms, including those nonlinear in $B_{nm}$, die out more rapidly as $T \to \infty$. Therefore, Eq. (2.121) becomes asymptotically accurate at elevated temperatures. This happens irrespective of the strength of the CF in relation to the exchange, as both become weak in comparison with the thermal energy $kT$.

In practice, Eq. (2.121) applies to 3d-4f compounds upward of room temperature. Thus, according to Fig. 3.10, in Nd-based magnets the approximation breaks down (the third-order term is no longer negligible) at $x \sim 3$. This corresponds to $T \approx 220$ K, assuming for the exchange field on Nd a value typical for hard magnetic materials, $B_{ex} = 400$ T.

The above argument is unaffected by the slow temperature variation of the exchange splitting $\Delta_{ex}$. Implicitly, we assume that, while in the high-temperature regime, the system is still not close to the Curie point (the $T_C$ of a good permanent magnet should exceed ambient temperature by a factor of at least 2).

As a measure of relative importance of the $J$-mixing in the room-temperature range one can use the ratio of the second term in the square brackets of Eq. (2.121)
to the first one,
\[ \varepsilon = \frac{6}{5} \frac{2J + 3 \Delta_{ex}}{2J - \Delta_{so}} \frac{B_J(J \Delta_{ex}/kT)}{B_J^{(2)}(J \Delta_{ex}/kT)}. \]  

(2.122)

Obviously, this quantity does not depend on the CF. In the high-temperature regime, which is primarily of interest to us, \( \varepsilon \) is also independent of the exchange field \( B_{ex} \), or \( \Delta_{ex} \). Indeed, expanding the Brillouin functions in Eq. (2.122) by means of Eq. (2.84) and keeping just the leading terms, one gets
\[ \varepsilon = \frac{12}{2J - 1} \frac{kT}{\Delta_{so}}. \]  

(2.123)

Thus, for a given RE, the fractional contribution of \( J \)-mixing to second-order anisotropy is determined by temperature alone and does not depend on characteristics of the solid, such as CF or exchange field. This conclusion is valid in the room-temperature range as well as at higher temperatures. The importance of \( J \)-mixing grows in direct proportion to absolute temperature.

Calculations similar to the above can also be carried out for the second half of the RE series, where the ground multiplets have \( J = L + S \). Omitting the details, we only state the result. The heavy-RE counterparts of the general expression (2.119), the high-temperature approximation (2.121) and the fractional contribution estimate (2.123) are, respectively, the following relations:

\[ \kappa_{nm} = B_{nm}J^n \left\{ B_J^{(n)}(x) + \frac{\Delta_{ex} n(n + 1)}{2n + 1} \left[ \frac{2J - n + 1}{2J} B_J^{(n-1)}(x) - \frac{2J}{2J - n} B_J^{(n+1)}(x) \right] \right\} \]  

(2.124)

\[ K_1 = -\frac{3}{2} B_{20}J^2 \left[ B_J^{(2)}(x) + \left( \frac{6}{5} \frac{2J - 1}{2J} \right) \frac{\Delta_{ex}}{\Delta_{so}} B_J(x) \right] \]  

(2.125)

\[ \varepsilon = \frac{12}{2J + 3 \Delta_{so}} \frac{kT}{\Delta_{so}}. \]  

(2.126)

One peculiar feature of the \( J \)-mixing in the heavy REs is that the effect is strictly nil at \( T = 0 \) [for verification put \( B_J^{(n)}(\infty) = (2J)^{-n}(2J)!/(2J - n)! \) into Eq. (2.124)]. The physical reason is that the ground state of an exchange-dominated heavy RE does not take part in the \( J \)-mixing (see Fig. 3.11) since it cannot find itself a partner with the same magnetic quantum number, \( M = J \), among the states of the first excited multiplet, whose \( M \) do not exceed \( J' = J - 1 \).

To summarise, contrary to the common perception (Myth 3), the influence of \( J \)-mixing on thermodynamic properties of RE magnets grows with temperature. In the limit \( T \to 0 \) the effect either vanishes completely (light RE with \( J \to \infty \), heavy RE with arbitrary \( J \)) or is very small. Its smallness at low temperatures is no indication that it may be neglected in the room-temperature range.

The insuperable complexity of the \( J \)-mixing has proved to be a yet another myth (Myth 1). Where it matters most—at ambient temperature and above—this effect can be accounted for by means of back-of-the-envelope calculations using Eqs. (2.123), (2.126).
Figure 3.11  Comparison of $J$-mixing in a light and a heavy RE. In both cases the mixing states have the same $M$ and different $J$. The ground state of a heavy RE is not involved in the $J$-mixing.

Table 3.4  Fractional contribution of $J$-mixing to the second-order anisotropy constant $K_1$, as given by Eq. (2.123) for the light REs (upper part of the table) and by Eq. (2.126) for the heavy REs (lower part)

<table>
<thead>
<tr>
<th>RE</th>
<th>$J$</th>
<th>$\Delta_{ao}$ (K)</th>
<th>$\varepsilon$ ($T = 300$ K)</th>
<th>$\varepsilon$ ($T = 400$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>4</td>
<td>3100</td>
<td>0.166</td>
<td>0.221</td>
</tr>
<tr>
<td>Nd</td>
<td>9/2</td>
<td>2740</td>
<td>0.164</td>
<td>0.219</td>
</tr>
<tr>
<td>Sm</td>
<td>5/2</td>
<td>1440</td>
<td>0.625</td>
<td>0.833</td>
</tr>
<tr>
<td>Tb</td>
<td>6</td>
<td>2880</td>
<td>0.083</td>
<td>0.111</td>
</tr>
<tr>
<td>Dy</td>
<td>15/2</td>
<td>4740</td>
<td>0.042</td>
<td>0.056</td>
</tr>
<tr>
<td>Ho</td>
<td>8</td>
<td>7480</td>
<td>0.025</td>
<td>0.034</td>
</tr>
</tbody>
</table>

* Taken from Elliott (1972).

Finally, the insignificance of the $J$-mixing in REs other than Sm (Myth 2) is disproved by the data presented in Table 3.4. At $T = 400$ K even terbium—a heavy RE—is subject to an 11% correction, while in Pr and Nd it is as high as 22%. In heavier REs the effect is noticeably smaller, for two reasons. Firstly, the larger denominator in the prefactor of Eq. (2.126) as compared with Eq. (2.123).
This alone makes the size of the effect in Ho a factor of 0.3 smaller than in Pr. A reduction by a further factor 0.4 comes from the larger spin-orbit splitting $\Delta_{so}$, especially high towards the end of the RE series.

Sm-based magnets should be considered separately. There, the second-order $J$-mixing correction to $K_1 \propto 1/\Delta_{so}$, is the size of the main, intra-multiplet contribution. It is therefore likely that corrections of higher orders in $1/\Delta_{so}$, neglected in Eqs. (2.119)-(2.126), are not small. The contribution of $J$-mixing to sixth-order anisotropy constants (responsible e.g. for the anisotropy in the basal plane in the hexagonal ferromagnets $\text{Sm}_2\text{Fe}_{17}$ and $\text{Sm}_2\text{Co}_{17}$) can hardly be called a correction, since the intra-multiplet effect is strictly nil. Equation (2.115) for the matrix element of $\hat{H}_{CF}$ is invalid, because the $6j$ symbol in the denominator equals zero (the numerator is also nil since $B_{60}' \propto \gamma_J = 0$). Calculations in that case should be performed using an alternative approach developed by Magnani et al. (2003) specially for the purpose. The role of the Stevens coefficient $\gamma_J$ is then played by another quantity, $\delta_6$, which is negative for Sm. When the sign of $\delta_6$ is taken into consideration, the anisotropic properties of Sm compounds—first of all the SRTs—are no longer incomprehensible.

Our review of the theoretical apparatus for the description of single-ion magnetocrystalline anisotropy has reached its close. All along we tried to illustrate the relevance of the various approximations by performing simple calculations for well-known hard magnetic materials. Our intention was to encourage experimentalists to use, where possible, the approximate equations for do-it-yourself calculations. Perhaps the best demonstration of the advantages of the single-ion model cast in analytical form is still to come. We are just turning to the phenomena where magnetic anisotropy manifests itself most vividly—spin reorientation transitions (SRT).

3. Spin Reorientation Transitions

3.1 General remarks

The third and last section of this Chapter is dedicated to the phenomenon of spin reorientation transitions (SRT). Of interest to us here are not SRTs as such—a vast subject covered in excellent reviews and monographs (Belov et al., 1976, 1979)—but only some peculiar features of the SRTs viewed from the standpoint of the single-ion anisotropy model. Our main goal is to demonstrate that the single-ion model is more than an ad hoc theory explaining already known experimental facts. Rather, it possesses a certain power of prediction. Where the underlying approximations are valid, the strength of the model is such that all experimental findings not fitting in its framework eventually prove wrong. This point will be illustrated with a number of examples.

A spin reorientation transition (SRT) is a phase transition consisting in a change of orientation of ordered magnetic moments—which can be distributed among several sublattices—with respect to crystallographic axes. Obviously, such magnetic transitions (called order-order transitions) are essentially distinct from the usual magnetic ordering of e.g. a ferromagnet at the Curie point. Even among order-order
transitions SRTs can be singled out in a separate class, on the grounds that they do not involve any change of the mutual orientation of the sublattice moments, only their orientation in relation to the crystal axes changes. Following this definition, metamagnetic transitions or field-induced transitions of ferrimagnets into a non-collinear state, are excluded from the scope of this section. Metamagnetism was reviewed by Levitin and Markosyan (1988) and by Goto et al. (2001). A chapter about the field-induced transitions in ferrimagnets appeared in Volume 9 of this Handbook (Zvezdin, 1995).

Just like phase transitions in general, SRTs can be of first or of second order. In the former case the orientation angle experiences a discontinuity at the transition point, whereas in the latter case the angle itself varies continuously, but its first derivative is discontinuous. For all that, the change of symmetry, essential in second-order SRTs, is always abrupt. Therefore, no matter if an SRT is of first or of second order—it takes place at a point, rather than within an interval. For instance, the process of spontaneous spin reorientation shown in Fig. 3.12a comprises two second-order SRTs as well as continuous rotation of the magnetisation vector in the interval between the two transition points. This rotation is of course not a phase transition. Likewise, a mere change of slope of the \( \theta(T) \) dependence (Fig. 3.12b) does not amount to an SRT. The crucial difference is that at a transition point the angle \( \theta \) takes a special high-symmetry value, 0 or \( \pi/2 \). When this is the case, the derivative of the orientation angle diverges on approach to the transition point from the lower-symmetry phase (Landau and Lifshitz, 1958). In a first-order SRT there is no restriction on the critical values of \( \theta \): in general both are distinct from 0 or \( \pi/2 \) (Fig. 3.12c), but either one of them or both may also take higher-symmetry values.

Second-order SRTs need not always come in pairs as shown in Fig. 3.12a. It is not inconceivable that the process of spin reorientation starting at the point \( T_2 \) may not reach completion before the temperature reaches 0 K. Well-known examples of single second-order SRTs are those taking place in Gd metal (Corner et al., 1962) and in Nd\(_2\)Fe\(_{14}\)B (Deryagin et al., 1984; Givord et al., 1984).

All the above applies, practically without change, also to magnetic field-induced transitions. Interestingly, an infinitesimal magnetic field applied at an angle to the easy magnetisation direction is sufficient to provoke a second-order SRT. Saturating in a finite field, characteristic of magnetisation along a hard direction, is also a second-order SRT (by contrast, under general orientation of the field the approach to saturation is asymptotic, without an SRT). Apart from such ubiquitous and trivial second-order SRTs, there are also field-induced SRTs of first order. In this case the upper critical value of the angle \( \theta \) may correspond either to low or to high symmetry (Figs. 3.13d, 3.13f); however, the lower critical value is always low-symmetry. The reason is the afore-mentioned transition to a low-symmetry phase induced by an infinitesimal magnetic field. Hereafter we shall concentrate on spontaneous SRTs. Magnetic field-induced SRTs of first order (FOMPs) were described in detail in Volume 5 of this Handbook (Asti, 1990).

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20 According to the generally accepted definition, spontaneous SRTs take place as a result of temperature change, at zero magnetic field and ambient pressure.
It is an interesting peculiarity of second-order SRTs that Landau’s theory of second-order phase transitions (Landau and Lifshitz, 1958) applies to them practically without restrictions. In this sense SRTs differ significantly from order-disorder transitions. Estimations show that the interval where Landau’s theory fails due to critical fluctuations is very narrow in the case of SRTs, $10^{-7} \ldots 10^{-4}$ K (Belov et al., 1976). Physically, this is because the fluctuations arising near an SRT have a very large correlation length.

**Figure 3.12** Temperature dependence of orientation angle $\theta$: (a) 2 second-order SRTs, (b) no SRT, (c) a first-order SRT.
Figure 3.13 Examples of magnetic field-induced SRTs: (a, b) 2 second-order SRTs, (c, d) 2 second-order SRTs and 1 first-order SRT (type II FOMP), (e, f) 1 second-order SRT and 1 first-order SRT (type I FOMP). Note the ubiquity of the trivial second-order SRT at $B \to 0$. 
3.2 SRTs in uniaxial magnets

3.2.1 Graphic representation

In this subsection we shall introduce the concept of phase diagrams and relate the diagrams of different levels within the hierarchy of approximations to the anisotropy energy.

We begin with the simplest expression,

\[ E_a = K_1 \sin^2 \theta. \]  (3.1)

According to Section 2.4, this formula is relevant to a uniaxial magnet at high temperatures \( T \gtrsim 300 \text{ K} \). Obviously, a system described by Eq. (3.1) may have just two stable states:

\[ \theta = \begin{cases} 0, & \text{if } K_1 > 0 \\ \pi/2, & \text{if } K_1 < 0. \end{cases} \]  (3.2)

These are traditionally called ‘easy axis’ and ‘easy plane’. A first-order phase transition takes place at the point \( K_1 = 0 \). This information is summarised in Fig. 3.14.

Let us now turn to a more complicated example. Consider a system whose anisotropy energy is given by

\[ E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta. \]  (3.3)

Minimisation with respect to \( \theta \) yields the following equilibrium phases (Casimir et al., 1959):

\[ \theta = \begin{cases} 0, & \text{if } K_1 > \max(0, -K_2) \\ \arcsin \sqrt{-K_1/2K_2}, & \text{if } -2K_2 < K_1 < 0 \\ \pi/2, & \text{if } K_1 < \min(-2K_2, -K_2). \end{cases} \]  (3.4)

This rather complex combination of if-statements can be visualised with the aid of a simple diagram in the \( K_1-K_2 \) plane, Fig. 3.15. Note the presence of a new phase ‘easy cone’, with intermediate values of \( \theta \) between 0 and \( \pi/2 \). The bold lines separating the domains of different phases are phase transition lines of first (dashed) or second (solid) order. For simplicity we shall not go into the difference between the existence of a phase and its stability.

Introducing a dimensionless ratio \( K_1/|K_2| \), one can display the same information in quasi-one-dimensional diagrams, Fig. 3.16. Obviously, two such graphs are needed to show the qualitatively distinct cases of \( K_2 > 0 \) and \( K_2 < 0 \), Figs. 3.16a and 3.16b, respectively.

What happens if \( K_2 = 0 \)? In other words, how can one graphically go over to the limit \( K_2 \rightarrow 0 \)? The above-considered Eq. (3.1) is not but a particular case of the more general Eq. (3.3). Therefore, there must be a way to obtain Fig. 3.14 from Figs. 3.15 and/or 3.16.

The graphic operation turning Fig. 3.16 into Fig. 3.14 is zooming out. Indeed, letting \( K_2 \) go to zero means scaling Fig. 3.16 down, reducing it. Looking at Fig. 3.16 on an ever decreasing scale, one gradually ceases to distinguish the details. On a very small scale the easy-cone domain shrinks to non-existence and the transition occurs...
Figure 3.14  Phase diagram of the simplest uniaxial magnet.

Figure 3.15  Phase diagram of a uniaxial magnet with two anisotropy constants (Casimir et al., 1959).

Figure 3.16  The information of Fig. 3.15 presented as two one-dimensional diagrams: (a) $K_2 > 0$, (b) $K_2 < 0$.

at the origin. Figures 3.16a and 3.16b are no longer different from each other, both becoming identical to Fig. 3.14.

Moving in the opposite direction, one can regard Fig. 3.16 as a refinement of Fig. 3.14. According as one zooms in, it becomes apparent that the transition occurs not quite at the origin and that the sign of $K_2$ does matter.
Let us apply these ideas to the analysis of a more complete expression for the anisotropy energy:

\[ E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta. \]  

(3.5)

This expression is relevant to exchange-dominated RE magnets\(^{21}\) at arbitrary temperature. The properties of such a system cannot be concisely formulated either as inequalities of type (3.2) or (3.4) (the latter is already too cumbersome and far too involved), nor as a phase diagram similar to Fig. 3.15 in the \(K_1K_2K_3\) parameter space—comprehensibility does not belong to the virtues of 3-dimensional drawings. We are left with the only acceptable choice—a quasi-2-dimensional diagram in reduced coordinates. (We say ‘quasi’, because one always needs two drawings to show all possible cases, cf. Figs. 3.16a and 3.16b.) Choosing the reduced variables, we follow certain guidelines. The diagrams should be easy to relate to those of the cruder approximations (3.1) and (3.3). Quantities prone to changing sign are unsuitable candidates for the denominators. For instance, Asti’s choice of \(K_2/K_1\) and \(K_3/K_1\) (Asti, 1990) is rather inconvenient: every time \(K_1(T)\) changes sign, the locus of the system goes to infinity, to reappear on the other sheet of the diagram. Clearly, \(K_1/K_3\) and \(K_2/K_3\) would be a better choice because, as stated in Section 2.7, \(K_3\) as a function of temperature is always sign-definite.

We find the variables \(K_1/|K_3|\) and \(K_2/|K_3|\) even more suitable, in accordance with the requirement that the shape of the diagram should depend possibly little on the sign of \(K_3\) and that \(|K_3|\) should act as a scaling factor when going over to the limit \(K_3 \to 0\). The phase diagram in such coordinates is displayed in Figs. 3.17a \((K_3 > 0)\) and 3.17b \((K_3 < 0)\). The notation for the phases is the same as in Figs. 3.15 and 3.16, however, now the angle \(\theta\) in the easy-cone phase is determined from the condition (Asti, 1990):

\[ \sin^2 \theta = \frac{\sqrt{K_2^2 - 3K_1K_3 - K_2}}{3K_3}. \]  

(3.6)

SRTs of five different kinds are possible: there can be a first- and a second-order SRT between every two phases out of the three present in Fig. 3.17, except the pair easy axis—easy plane, where only a first-order transition can take place. A second-order transition easy axis—easy plane is impossible in principle, because none of the two phases is more symmetric than the other (in other words, neither of the two symmetry groups is a subgroup of the other one).

The domain boundaries in Fig. 3.17 are mainly straight lines, the curved portions AO and BC being parabolic arcs. The equations describing these boundaries—the necessary conditions of the SRTs—are collected in Table 3.5. A general necessary condition of a second-order SRT is that the second derivative of the anisotropy energy with respect to the angle must vanish at the point corresponding to the higher-symmetry phase. E.g. for the transition easy axis—easy cone this condition is \(\partial^2 E_a/\partial \theta^2 \big|_{\theta=0} = 0\) or \(K_1 = 0\). In the case of first-order SRTs, a general

\(^{21}\) In real crystals the anisotropy energy may also depend on the angle \(\phi\), cf. Eqs. (2.12), (2.13). Our simplified analysis makes use of the well-known fact that in the vast majority of SRTs only the angle \(\theta\) changes, while \(\phi\) remains constant, fixed by the symmetry. For instance, in the case of the hexagonal crystallographic classes \(D_h\), \(C_{6v}\), \(D_{3h}\) and \(D_{6h}\), this means \(\phi = 0\) or \(\pi/6\), which reduces Eq. (2.12) to (3.5) with \(K_3 \to K_3 \pm K_3'\).
**Figure 3.17** Phase diagram of a uniaxial magnet with three anisotropy constants: (a) $K_3 > 0$, (b) $K_3 < 0$.

**Table 3.5** Necessary conditions of the SRTs in Fig. 3.17

<table>
<thead>
<tr>
<th>Phases involved</th>
<th>1$^{st}$-order SRT</th>
<th>2$^{nd}$-order SRT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Easy axis–easy cone</td>
<td>$K_2 = -2\sqrt{K_1K_3}$</td>
<td>$K_1 = 0$</td>
</tr>
<tr>
<td>Easy plane–easy cone</td>
<td>$K_2/K_3 = 1 - 2\sqrt{1 + K_1/K_3}$</td>
<td>$K_1 + 2K_2 + 3K_3 = 0$</td>
</tr>
<tr>
<td>Easy axis–easy plane</td>
<td>$K_1 + K_2 + K_3 = 0$</td>
<td>no SRT</td>
</tr>
</tbody>
</table>
necessary condition is that the function $E_{\theta}(\theta)$ must take equal values at the points corresponding to the two phases in question. Thus, for the first-order transition easy axis—easy cone this condition is as follows: $E_{\theta}(\theta_{\text{cone}}) = E_{\theta}(0) = 0$. Substituting Eq. (3.6) into Eq. (3.5) and equating the latter to zero yields $K_2 = -2\sqrt{K_1 K_3}$.

Finally, neglecting graphically the third anisotropy constant ($K_3 \to 0$) consists in zooming out of Fig. 3.17. Then the small details are gradually lost, the points $A$, $B$ and $C$ merge with the origin and both sheets of the phase diagram turn into Fig. 3.15. Thus, Fig. 3.15 can be regarded as a cruder, lower-resolution version of Fig. 3.17, and vice-versa Fig. 3.17 is a more precisely defined version of Fig. 3.15, taking account of the sign of $K_3$.

3.2.2 Peculiarities following from the single-ion model
In this subsection some specific predictions of the single-ion model regarding spontaneous SRTs in uniaxial magnets will be considered. Admittedly, these predictions can only be formulated as a number of separate statements, or ‘rules’, unlike in the case of cubic magnets, where a fully-fledged coherent theory can be developed (see Section 3.3 below). Nevertheless, these ‘rules’ deserve some respect. Experience shows that ignoring them may lead to easily avoidable mistakes.

In the crudest approximation, zooming out of all phase diagrams, an SRT takes place in a uniaxial magnet when its first anisotropy constant changes sign. This statement is certainly true for the room-temperature range and might be somewhat qualified for low temperatures. Staying for the moment near room temperature, there is one natural reason for $K_1$ to change sign in a 3d-4f intermetallic compound—the competition of the 3d and the 4f contributions. Indeed, since the high-temperature approximation applies to the RE, $K_1 = K_{3d} - \frac{3}{2} \alpha_J B_{20} J^2 B^{(2)}_J(x)$.

Here $\alpha_J$ is the first Stevens factor and $B_{20}$ is the leading CF parameter in the coordinate representation, Eq. (1.4). Note that the product $\alpha_J B_{20}$ in Eq. (3.7) equals the quantity $B_{20}$ in Eq. (2.98). On account of the known properties of the function $B^{(2)}_J(x)$, Section 2.6, the second term in Eq. (3.7) is sign-definite and falls off monotonically with temperature. The same is true in respect of $K_{3d}$; it is smaller in magnitude but also decreases more slowly with temperature than the RE contribution. Therefore, in order for $K_1$ to become zero near ambient temperature, the two terms in Eq. (3.7) must have opposite signs. Applied to a particular family of RE-iron or RE-cobalt compounds, where $K_{3d}$ and $B_{20}$ are both sign-definite, this means that, depending on the combination of signs of $K_{3d}$ and $B_{20}$, spontaneous SRTs will occur either in the compounds of the REs with $\alpha_J$ positive, or on the contrary, only in those where $\alpha_J$ is negative. This ‘Stevens $\alpha_J$ rule’ is followed by the vast majority of uniaxial RE-iron and RE-cobalt intermetallics (Buschow, 1988, 1991; Kirchmayr and Burzo, 1990; Li and Coey, 1991; Franse and Radwański, 1993). Exceptions do happen, however, for the obvious reason that higher-order CF terms may interfere in the anisotropy energy balance, as the high-$T$ approximation gradually breaks down below room temperature.

22 A rare exception is the compound Y$_2$Fe$_{14}$B, where $K_1(T)$ is non-monotonic (Bartashevich et al., 1990).
We wish to emphasise that the single-ion theory is not concerned with the task of evaluating \textit{ab initio} the CF parameters $B_{nm}$, nor with predicting their signs. Rather, it regards them as phenomenological parameters. It should not be confounded with the point-charge model. The well-known fact that the latter generally fails in metallic systems leaves the single-ion theory undefeated.

Let us refine our analysis and take into consideration the second anisotropy constant $K_2$ [in the case of tetragonal magnets, Eq. (2.13), this should be understood as the combination $K_2 - \sqrt{(K_2')^2 + (K_2'')^2}$]. As we still remain in the room-temperature range, we may neglect all anisotropy constants but $K_1$ and $K_2$, taking for the latter just the fourth-order CF term in Eq. (2.65):

$$K_2 = \frac{35}{8} \beta J B_{40} J^4 B^{(4)}_J(x).$$

(3.8)

Here $\beta J$ is the second Stevens factor and $B_{40}$ is the CF parameter in the coordinate representation, Eq. (1.4). The product $\beta J B_{40}$ in Eq. (3.8) is equivalent to the quantity $B_{40}$ in Eq. (2.65). In tetragonal magnets the role of $B_{40}$ in Eq. (3.8) is played by the combination $B_{40} - \left(\frac{35}{8}\right)^{1/2} \text{sign} \beta J |B_{44}|$.

The occurrence of a spontaneous spin reorientation is still subject to the ‘Stevens $\alpha J$ rule’. However, the presence of a nonzero $K_2$ brings about some variety: the reorientation may proceed as a single first-order SRT or by way of two second-order SRTs (Fig. 3.12a displays the latter possibility). Which of the two scenarios will take place is decided by the sign of $K_2$ (Horner and Varma, 1968), which is in turn determined by the sign of the second Stevens factor $\beta J$ (the 3d contribution to $K_2$ is negligible).

As an illustration, let us consider the well-studied archetypal permanent magnet materials RECo$_5$. In accordance with the ‘Stevens $\alpha J$ rule’, spontaneous SRTs are observed in all RECo$_5$ where $\alpha_J < 0$, that is with RE = Pr (Yermolenko, 1983), Nd, Tb (Lemaire, 1966), Dy (Ohkoshi et al., 1977) and Ho (Lemaire, 1966; Chuev et al., 1981a). Moreover, for RE = Pr, Nd, Dy and Ho the SRTs are distinctly of second order. This is in perfect agreement with the ‘Stevens $\beta J$ rule’, because all four above-mentioned REs have $\beta J < 0$ (Table 3.1).

In contrast, Tb has $\beta J > 0$, therefore, the SRT in TbCo$_5$ must be of first order. This definite prediction of the single-ion theory is apparently at variance with experiment, which interprets the reorientation process in TbCo$_5$ as two closely situated second-order SRTs. The situation is aggravated further by the fact that it is not just from bulk magnetic measurements (Ermolenko, 1980) that this conclusion was made. Also neutron diffraction experiments (Lemaire and Schweizer, 1967; Kelarev et al., 1980) reportedly detected in TbCo$_5$, in a narrow interval just above 400 K, the presence of an easy-cone phase with intermediate values of $\theta$ between 0 and $\pi/2$.

It should be noted that these data are open to another interpretation. Namely, that two phases—easy axis and easy plane—coexist in the vicinity of the SRT (which is of first order, as predicted by the single-ion model). The relative content of the two phases varies gradually with temperature, from the pure easy plane below $\sim 400$ K to the pure easy axis above $\sim 425$ K. This interpretation is corroborated by the peculiar shape of the temperature dependence of the angle $\theta$ observed...
in TbCo₅. It resembles the dashed curve in Fig. 3.18. Such a shape of the dependence \( \theta(T) \), described by the complementary error function, is characteristic of ‘smear-ed out’ first-order SRTs (Kuz’mín, 2000). It is clearly distinct from the arcsine-type dependence (solid line) with two sharp second-order transition points \( T_1 \) and \( T_2 \). The inhomogeneity of composition, necessary for smearing out of a first-order SRT, is present in TbCo₅, whose real stoichiometry is TbCo₅₊δ, with \( δ \approx 0.1 \).

According as the experimental arguments in favour of two second-order SRTs in TbCo₅ become less unambiguous, the single-ion theory, on the contrary, strengthens its insistence on a single first-order SRT. Beyond all doubt is the general analysis of Horner and Varma (1968) demonstrating that an SRT must be of first order if \( K_2 < 0 \) and of second order if \( K_2 > 0 \). On the other hand, the shape of the dependence \( \theta(T) \) in the other RECo₅ undergoing spontaneous spin reorientation (RE = Pr, Nd, Dy, Ho) bears close resemblance to the continuous curve of Fig. 3.18, with two square-root-type anomalies characteristic of Landau’s theory.²³

The SRTs are clearly of second order, and therefore \( K_2 > 0 \), in the aforementioned RECo₅ with \( β_J < 0 \). By virtue of Eq. (3.8), \( K_2 \) must be negative in TbCo₅, where \( β_J > 0 \).

The only (unlikely) loophole in our logic might be that \( T = 400 \) K is not high enough a temperature and that \( K_2 \) in TbCo₅, negative at the highest temperatures as it should be, becomes positive somewhere above \( T = 425 \) K due to an extraordinarily large sixth-order CF term, cf. the second one of Eqs. (2.65). This remote possibility can be ruled out completely. Indeed, as stated in Section 2.7, \( K_2 \) cannot change sign more than once. And in TbCo₅, \( K_2 < 0 \) at \( T = 4.2 \) K, as found experi-

²³ In the case of PrCo₅, where the reorientation process is incomplete, only the higher-temperature anomaly is observed, \( T_1 \) being effectively negative.
mentally by Ermolenko (1980). Therefore, $K_2$ is negative at any temperature. Thus, the single-ion theory still insists that the SRT in TbCo$_5$ must be of first order.

The true situation in TbCo$_5$ has been finally established in recent scanning differential calorimetry experiments (Tereshina et al., 2007), which revealed a nonzero latent heat of the SRT—an ultimate proof that it is of first order. The single-ion model made no mistake.

Let us formulate a yet another specific prediction of the model. When the easy direction lies in the basal plane, its orientation within the plane for a certain family of tetragonal compounds is determined by the sign of the second Stevens coefficient $\beta_J$, whereas in hexagonal compounds it follows the third Stevens factor $\gamma_J$. Moreover, in the latter case the orientation within the basal plane cannot change as temperature is lowered. In tetragonal compounds such a reorientation may take place no more than once, but in reality SRTs of this kind are extremely rare.

For definiteness, we limit ourselves to the hexagonal crystallographic classes $D_6$, $C_6v$, $D_3h$ and $D_6h$, where the anisotropy energy is presentable as Eq. (2.12) with the anisotropy constants given by Eqs. (2.65). By assumption, $\theta \equiv \pi/2$. Therefore, the equilibrium value of the angle $\phi$, either 0 or $\pi/6$, is determined by the sign of the quantity $K'_3$,

$$K'_3 = \frac{\sqrt{231}}{16} \gamma_J B_{66} J^6 B_J^{(6)}(x).$$  \hfill (3.9)

Again, we have factored out the Stevens coefficient $\gamma_J$, so that the product $\gamma_J B_{66}$ in Eq. (3.9) is equivalent to the quantity $B_{66}$ in the last one of Eqs. (2.65).

Thus, if the product $\gamma_J B_{66}$ is negative, the easy magnetisation direction within the basal plane is the $a$ axis, or [100], corresponding to $\phi = 0$. If $\gamma_J B_{66} > 0$, then the easy axis is $b$, or [120], $\phi = \pi/6$. For a given family of RE-iron or RE-cobalt compounds, all having $B_{66}$ of the same sign, the easy direction is determined by the sign of the third Stevens factor $\gamma_J$.

This ‘Stevens $\gamma_J$ rule’ can be best illustrated by our favourite example—the RECo$_5$ compounds—whose symmetry is described by the holohedral hexagonal group $D_{6h}$. Back in the 1960’s it was found from neutron diffraction on NdCo$_5$ and TbCo$_5$ (Lemaire, 1966; Lemaire and Schweizer, 1967) and also from magnetic measurements on a single crystal of HoCo$_5$ (Katsuraki and Yoshii, 1968) that the easy direction within the basal plane in all those compounds is the $a$ axis. This is not illogical, since Nd, Tb and Ho have $\gamma_J < 0$, see Table 3.1. Following the same logic, the easy direction in PrCo$_5$ and in DyCo$_5$ must be the $b$ axis, because $\gamma_J > 0$ for both Pr and Dy. Indeed, magnetisation data obtained on a PrCo$_5$ single crystal (Yermolenko, 1983) confirmed that the easy direction there rotates from the $c$ towards the $b$ axis (even though the reorientation process is not completed down to $T = 0$).

Unexpectedly, DyCo$_5$ falls out of line. A magnetisation study of a single crystal (Ohkoshi et al., 1977) concluded that the easy direction at and below room temperature is the $a$ rather than the $b$ axis. This statement was reiterated in the work of Berezin et al. (1980) and even in the neutron diffraction paper of Chuyev et al. (1981b). The single-ion model seems to have received a fatal blow and will never recover.
However, a more careful perusal of the above articles reveals a number of discrepancies. Thus, according to Ohkoshi et al. (1977), the \( a \) axis is the same as the \([110]\) direction and the \( b \) axis is \([100]\), which is rather unusual. A clue to their unconventional notation may be found in their previous paper (Ohkoshi et al., 1976), stating that in NdCo\(_5\) the easy direction below \( T = 245 \) K is the \( b \) axis, or \([100]\) (while in reality it is the \( a \) axis, or \([100]\)). Apparently, the authors use a non-standard set of Bravais vectors where two of them, lying in the basal plane, make an angle of 60°, rather than 120° as in the standard hexagonal set. Moreover, the direction of those Bravais vectors is called the \( b \) axis, while their bisector is called the \( a \) axis. In short, Ohkoshi et al. (1976, 1977) seem to have swapped the \( a \) and \( b \) axes, as compared with the standard notation. Of course, this is not but a plausible conjecture.

Furthermore, the text of the paper of Berezin et al. (1980) speaks of an easy axis \( a \) and a hard axis \( b \). However, from the experimental magnetisation curves in Fig. 1 thereof one concludes that the opposite is true. Namely, that the easy magnetisation direction is the \( b \) axis.

Finally, in their neutron diffraction experiments the unsuspecting Chuyev et al. (1981b) did not at all pose the problem of checking the orientation of the easy direction within the basal plane of DyCo\(_5\), having taken for granted that it was along the \( a \) axis.

At our instance, Skokov (2007) have recently conducted a series of purposeful tests on a single crystal of DyCo\(_5\), which have established that the easy magnetisation direction at and below room temperature lies along the crystallographic axis \( b \), i.e. \([120]\), exactly as predicted by the single-ion model, or by the ‘Stevens \( \gamma_J \) rule’.

The above examples demonstrate—quite convincingly in our view—that the single-ion theory of magnetocrystalline anisotropy has the power of prediction. To the extent that it enables an armchair theoretician to find mistakes in experimental papers. In this connection, the recent attempts to question the validity of the single-ion approach and even to supplant it with a new mechanism (Irkhin, 2002) can only arouse bewilderment. We reiterate, however: in order for the strength of the single-ion model to be fully appreciated, it has to be kept strictly apart from the task of computing the CF parameters \( ab \text{ initio} \). Certain progress has been achieved in the latter field, too (Hummler and Fähnle, 1996; Novák, 1996), based on the density functional theory rather than on the naive point-charge model.

### 3.3 Spontaneous SRTs in cubic magnets

In the crudest approximation, the anisotropy energy of any cubic crystal is given by

\[
E_a = K_1 (n_x^2n_y^2 + n_y^2n_z^2 + n_z^2n_x^2). \tag{3.10}
\]

The equilibrium phases are the 6-fold degenerate \([100]\) and 8-fold degenerate \([111]\). The former is energetically favourable at \( K_1 > 0 \), the latter at \( K_1 < 0 \). A first-order SRT takes place at the point \( K_1 = 0 \). This information is presented graphically in a one-dimensional phase diagram, Fig. 3.19.
Let us consider a more realistic expression for the anisotropy energy (2.8), valid for the cubic crystallographic classes possessing 4-fold symmetry axes,\(^{24}\) \(O\), \(T_d\) and \(O_h\):

\[
E_a = K_1 \left( n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2 \right) + K_2 n_x^2 n_y^2 n_z^2. \tag{3.11}
\]

This expression is relevant to cubic exchange-dominated 3d-4f compounds, such as e.g. Laves phases \(\text{REFe}_2\) and \(\text{RECo}_2\). In that case the omission of terms of order higher than six is a valid approximation. It is also justified to neglect the 3d contribution to the fourth- and sixth-order anisotropy constants. This contribution, originating from the relatively weak spin-orbit coupling, decreases rapidly as the order of the anisotropy constants \(n\) increases \((\propto \lambda^n)\). In practice, it can play a role only in second-order anisotropy constants, here forbidden by the symmetry. Thus, not unreasonably we expect that the linear theory of Section 2.5 should apply to the systems under consideration to full extent.

Proceeding from the CF Hamiltonian (1.26), where \(O_n^m\) are meant to be the usual Stevens operators in the \(J\) representation, and repeating the manipulations of Section 2.5, we get for the anisotropy constants the following expressions:

\[
K_1 = -40 J^4 b_4 B_4^{(4)}(x) - 168 J^6 b_6 B_6^{(6)}(x) \\
K_2 = 1848 J^6 b_6 B_6^{(6)}(x). \tag{3.12}
\]

Here \(B_j^{(4,6)}(x)\) are the fourth- and sixth-order generalised Brillouin functions (GBF, Section 2.6) and \(x\) is the magneto-thermal ratio (2.33).

Figure 3.20 displays the phase diagram of a cubic magnet described by Eq. (3.11) \((\text{Smit and Wijn, 1959})\). We observe the presence of an additional phase—the 12-fold degenerate \([110]\). In the considered approximation all the transitions are of first order.

It is convenient to present the information contained in the two-dimensional phase diagram (Fig. 3.20) as quasi-one-dimensional diagrams, Fig. 3.21. There, the role of the coordinate is played by the ratio \(K_1/|K_2|\). The need to distinguish two essentially distinct cases according to the sign of \(K_2\) brings about the two sheets of the diagram, Figs. 3.21a and 3.21b. This insignificant complication is outweighed by the advantages of Fig. 3.21. The latter is related in a rather straightforward way to Fig. 3.19, this relation being a graphic realisation of neglecting \(K_2\), or taking the limit \(K_2 \rightarrow 0\). Zooming out of Fig. 3.21, one gradually loses out of sight the details like the intermediate \([110]\) domain or the deviation of the transition point

\(^{24}\) It will be recalled that in the case of the cubic classes \(T\) and \(T_h\) an extra six-order term (2.9) must be taken into account.
Figure 3.20  Phase diagram of a cubic magnet with two anisotropy constants (Smit and Wijn, 1959). The oblique phase boundaries are $9K_1 + 4K_2 = 0$ (second quadrant) and $9K_1 + K_2 = 0$ (fourth quadrant).

Figure 3.21  A quasi-one-dimensional presentation of the phase diagram of Fig. 3.19: (a) $K_2 > 0$, (b) $K_2 < 0$.

from the origin. What eventually remains of either part of Fig. 3.21 is two semi-axes, the blank positive [100] and the hatched negative [111], that is just Fig. 3.19.

The more important advantage of Fig. 3.21 is its one-dimensionality. Thanks to it, the SRT conditions can be presented simply as taking on of certain universal values, $-4/9$, 0 and $1/9$, by the variable $K_1/|K_2|$. By means of Eqs. (3.12) these conditions can be readily expressed in terms of the dimensionless CF ratio $b_4/|b_6|$. It is still necessary to distinguish two particular cases according to the sign of $b_6$. Namely:

A. $b_6 > 0$ ($K_2 > 0$). There are two transitions:

1. [111]–[110] at $K_1/|K_2| = -4/9$. By virtue of Eqs. (3.12), this is equivalent to

$$
\frac{b_4}{|b_6|} = \frac{49}{3} \frac{J_2 B_2^{(6)}(x)}{B_2^{(4)}(x)}.
$$

(3.13)
2. [110]–[100] at $K_1/|K_2| = 0$, whence

$$ \frac{b_4}{|b_6|} = -\frac{21}{5} J^2 \frac{B_J^{(6)}(x)}{B_J^{(4)}(x)}. $$ (3.14)

B. $b_6 < 0 \ (K_2 < 0)$. One further transition is possible:

3. [111]–[100] at $K_1/|K_2| = 1/9$, which yields

$$ \frac{b_4}{|b_6|} = -\frac{14}{15} J^2 \frac{B_J^{(6)}(x)}{B_J^{(4)}(x)}. $$ (3.15)

It is time to take advantage of the one-dimensionality of the chosen representation. Having saved a dimension in Fig. 3.21, we now have the option of adding a new second dimension to our diagrams. We choose the quantity $1/x$ for this role, which will enable us to include temperature evolution of the system into the picture. The variable $1/x$ is more convenient for the purpose than $x$, because at low temperatures $1/x$ is directly proportional to $T$; in any case its dependence on $T$ is monotonic.

Now Eqs. (3.13)–(3.15) describe curves in the plane $1/x - b_4/|b_6|$, Fig. 3.22. It is interesting to note that one and the same special function is involved in all three cases—the ratio of the sixth- to the fourth-order GBF—only the prefactors differ. The advantage of the coordinates employed in Fig. 3.22 is that the phase boundaries therein are universal (apart from their dependence on the quantum number $J$, Fig. 3.22 corresponds to $J = 8$). Anyhow, the topology of the phase diagrams does not depend on $J$, while the ordinates of the points $A$, $B$ and $C$ are given by simple formulae: $\frac{10}{6} (J-2)(2J-5)$, $\frac{3}{10} (J-2)(2J-5)$ and $\frac{7}{15} (J-2)(2J-5)$, respectively. Therefore, for any other $J$ diagrams similar to Fig. 3.22 can be sketched rather straightforwardly. Accurate drawings should present no major difficulties either, since all GBF have been tabulated (Kuz’min, 1992).

Temperature evolution of a specific compound can be depicted in Fig. 3.22 by a horizontal line, because the quantity $b_4/|b_6|$ proper of the system remains constant.
as ‘temperature’ \(1/x\) varies. If this horizontal line crosses one of the curves, a spontaneous SRT takes place at the temperature \(T\) corresponding to the abscissa of the crossing-point. Thus, spontaneous SRTs follow a scenario fully determined by the ratio \(b_4/|b_6|\) and independent of the strength of the exchange interaction (as long as the system is exchange-dominated, see Section 2.2). Knowledge of the exchange field on the RE and of its temperature dependence is only needed for establishing the quantitative relation between \(x\) and \(T\). The sign of \(b_6\) is very important, since it decides to which sheet of the phase diagram, Figs. 3.22a or 3.22b, the system belongs. To determine \(\text{sign}(b_6)\), it suffices to find \(\text{sign}(K_2)\) at any temperature.

A number of more specific conclusions can be drawn.

1. No more than one spontaneous SRT can take place in any one system.
2. If the low-temperature phase is \([100]\), a spontaneous SRT is in principle impossible.
3. If the low-temperature phase is \([110]\), a spontaneous SRT will take place inevitably.
4. If the low-temperature phase is \([111]\) and \(b_4 > 0\), no spontaneous SRT is possible.
5. If the low-temperature phase is \([111]\) and \(b_4 < 0\), an SRT is inevitable, \([100]\) being the high-temperature phase.

Table 3.6 summarises the predictions of the single-ion theory and the experimental information on the easy magnetisation directions and spontaneous SRTs in the cubic Laves phases REFe\(_2\) and RECo\(_2\). Full-potential density-functional calculations (Diviš et al., 1995) yielded a positive sign for the fourth-order CF parameter in the coordinate representation (i.e. for the quantity \(b_4/\beta J\)) and a negative sign for \(b_6/\gamma J\). Accordingly, in Table 3.6, \(\text{sign}(b_4) = \text{sign}(\beta J)\) and \(\text{sign}(b_6) = -\text{sign}(\gamma J)\), cf. Table 3.1. For \(\text{RE} = \text{Sm}\) \(\gamma J\) is undefined, its role being played by the quantity \(\delta_6 < 0\) (Magnani et al., 2003). Therefore, \(b_6 > 0\) for SmFe\(_2\) and SmCo\(_2\).

Examining Table 3.6 one observes that the single-ion model agrees with experiment in all cases without exception. It should be noted that in each case the model makes a binding prediction of the high-\(T\) phase as well as predicting an optional low-\(T\) phase. In order for the low-\(T\) option to be realised, i.e. in order for the spontaneous SRT to actually happen, the ratio \(b_4/|b_6|\) must be within certain bounds, also predicted by the theory. In some exceptional cases, e.g. in ErFe\(_2\) and in ErCo\(_2\), the model can rule out the possibility of an SRT altogether. However, in general the single-ion theory is not concerned with calculating CF parameters \textit{ab initio}, therefore it cannot be held responsible for wrongly predicted SRTs in specific compounds. Allegations of failure of the single-ion model sometimes found in the literature are in fact reports of failures of various modifications of the point-charge model (confused with the single-ion one).

In those cases when the CF parameters are considered known, their non-compliance with the single-ion model is a sure sign of mistake. Thus, according to Gignoux et al. (1975, last line of Table I) \(b_4/|b_6|\) in HoCo\(_2\) is about \(-204\). However, the fact that HoCo\(_2\) undergoes a spontaneous SRT \([110]-[100]\) means that this ratio must be between 0 and \(-138.6\), cf. Fig. 3.22a. Further checks unearth an apparent inconsistency between the values \(b_6 = 2.3 \times 10^{-5}\) K and \(K_2 = 10^9\) erg/cm\(^3\).
Table 3.6  Easy directions of magnetisation in the cubic Laves phases REFe$_2$ and RECo$_2$. In each case the model makes a binding prediction of the high-temperature orientation (right-hand symbol), the predicted low-temperature phase being optional

<table>
<thead>
<tr>
<th>RE</th>
<th>Single-ion model</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sign $b_4$</td>
<td>Sign $b_6$</td>
</tr>
<tr>
<td>Pr</td>
<td>$-$1</td>
<td>$-$1</td>
</tr>
<tr>
<td>Nd</td>
<td>$-$1</td>
<td>+1</td>
</tr>
<tr>
<td>Sm</td>
<td>$+$1</td>
<td>+1</td>
</tr>
<tr>
<td>Tb</td>
<td>$+$1</td>
<td>+1</td>
</tr>
<tr>
<td>Dy</td>
<td>$-$1</td>
<td>$-$1</td>
</tr>
<tr>
<td>Ho</td>
<td>$-$1</td>
<td>+1</td>
</tr>
<tr>
<td>Er</td>
<td>$+$1</td>
<td>$-$1</td>
</tr>
<tr>
<td>Tm</td>
<td>$+$1</td>
<td>+1</td>
</tr>
<tr>
<td>Yb</td>
<td>$-$1</td>
<td>$-$1</td>
</tr>
</tbody>
</table>


reported by Gignoux et al. (1975). According to the second one of Eqs. (3.12), at $T = 0$ and $J = 8$, $K_2$ must equal 166,486,320 $b_6 = 3.8 \times 10^3$ K/f.u., or $1.15 \times 10^{10}$ erg/cm$^3$, which is an order of magnitude too high. Given that $K_2$ was determined experimentally, one is left to conclude that the reported value of $b_6$ (and most likely of $b_4$ as well) is mistaken.

There are also examples of false SRTs in the literature, later proved to be artefacts. For instance, an impossible transition [100]–[111] ‘discovered’ by Shimotomai et al. (1980) in PrFe$_2$ (a quick glance at Fig. 3.22 is sufficient to conclude that [100] cannot be the low-$T$ phase in a spontaneous SRT). Or, e.g. an incomplete transition [100]–[110] in YbFe$_2$ (Meyer et al., 1981), where the easy direction ‘slightly deviates’ from [100] above $T \approx 50$ K. Apart from the afore-mentioned fact that [110] can only be the low-$T$ phase in a spontaneous SRT and [100] can only be the high-$T$ one, the general theory (Section 3.1) states that the orientation angle always changes sharply near an SRT, even if the latter is of second order (Fig. 3.12a). It is like an airplane, which cannot take off or land ‘slightly’.

Most tortuous was the way to the truth in the case of HoFe$_2$. An early review by Taylor (1971, Table 7 thereof) gave the correct easy magnetisation direction, [100], without any SRT. This view was soon reiterated by Atzmony et al. (1972), who interpreted the Mössbauer spectrum of HoFe$_2$ at $T = 4.2$ K as being characteristic of the [100] phase. Had the authors seen the above Conclusion 2, they would have put a full stop at this point. The [100] phase has the simplest, most reliably identified Mössbauer spectrum, our Conclusion 2 is therefore quite useful.

Anyhow, this was not to be, and during the decade of the 1970’s articles of the same authors were coming out (Atzmony and Dublon, 1977 and references therein), claiming having observed an SRT in HoFe$_2$ at around 14 K. The disproval finally came in the form of a direct specific heat measurement (Germano et al.,
which found in that temperature range no anomaly characteristic of a phase transition.

To be fair to Atzmony et al., their version of the events was not impossible, but rather improbable. Between \( T = 0 \) and 14 K the ratio \( B_8^{(6)}(x)/B_8^{(4)}(x) \) in Eq. (3.14) changes by as little as a quarter of a percent [for HoFe\(_2\), \( x \approx 750 \) K/T (Kuz’min, 2001)]. In order for the SRT at about 14 K to become reality, nature would have to set the ratio \( b_4/|b_6| \) within a very narrow interval immediately above \(-138.6\). In reality, \( b_4/|b_6| \approx -184 \) (Germano et al., 1979).

The controversy around the SRT in HoFe\(_2\) is typical of the state of the theory in the 1970’s. The basics of setting and diagonalising the RE Hamiltonian were well known by then, whereas the approximations introduced in this Chapter were not. Thus, it was unknown that the sequence of phases is determined by a sole quantity—the ratio \( b_4/|b_6| \)—and does not depend on the exchange field at all. That is, out of the three disposable model parameters only one is relevant to deciding if a spontaneous SRT is to take place. The presence of irrelevant parameters in the early calculations could not bring about but confusion.

Also unsound were the attempts to ‘explain’ the complex Mössbauer spectra observed in some REFe\(_2\) by way of intermediate low-symmetry orientations of the easy magnetisation direction (Atzmony and Dariel, 1974). Such an explanation involves necessarily a large anisotropy constant of eighth order. The linear theory— whereby this and all higher-order anisotropy constants are strictly nil—is admittedly an approximation. It is, however, a well-founded approximation, so what is forbidden by it can only be small. A rather more plausible but prosaic explanation could be that the samples investigated by Atzmony and Dariel (1974) were not single-phase.

The theory developed in this subsection and expressed graphically in Fig. 3.22 is not limited to the cubic Laves phases. Without major modifications it applies e.g. to the RE\(_e\)Fe\(_{23}\) compounds. One subtlety needs to be taken into consideration, however: the local symmetry of the \( 24e \) sites occupied by the RE in RE\(_e\)Fe\(_{23}\) is not cubic, but rather tetragonal, \( C_{4v} \). Therefore, five nonzero CF parameters are allowed, cf. Eq. (1.32). Equations (3.12) are still valid, provided that linear combinations of 4th- and 6th-order CF parameters, \( \frac{1}{12}(7B_{40} + B_{44}) \) and \( \frac{1}{24}(3B_{60} - B_{64}) \), are substituted for \( b_4 \) and \( b_6 \), respectively. These combinations arise in the process of averaging over the \( 24e \) sites with differently oriented local 4-fold axes (parallel to \( [100], [010], \) and \( [001] \)). The second-order CF parameter \( B_{20} \) is averaged out completely. Figure 3.22 is then valid too, provided the ordinate is defined as \((14B_{40} + 2B_{44})/|3B_{60} - B_{64}|\).

4. Conclusion

We are about to close this Chapter about crystal-field effects in 3d-4f intermetallics. From the subject of CF on REs we moved on to magnetocrystalline anisotropy and further on to SRTs. En route we touched upon the influence of the CF on the magnetic moment of the RE. Of course, the narrow path we took does
not cover the whole area of CF-related phenomena. For example, magnetostriction can be described—similarly to anisotropy constants—by expressions involving generalised Brillouin functions (Kuz’min, 1992). However, in this Chapter we deliberately did not enter into the topic of magnetostriction. It will be exhaustively covered in an extensive monograph by Professor A. del Moral, due to appear shortly. Likewise, the route towards SRTs is not but one of many ways to proceed from the subject of magnetic anisotropy. Other possible connections include micromagnetism, ac susceptibility, coercivity, magnetic resonance etc.

This Chapter is addressed primarily to experimentalists. At the intuitive level, most of them would be well familiar with the physics of the phenomena discussed above. They might be less forthcoming when it comes to committing themselves to a quantitative estimate, for the obvious reason that a computer program able to ‘take account of everything’ is hard to come by. A message we tried to get across is that taking everything into account is not always necessary. When valid, a suitable approximation may offer the invaluable advantages of a concise analytical expression—greater transparency and simplicity of calculations.

This turned out particularly well in the case of the $J$-mixing effect, Section 2.9, where expressions suitable for back-of-the-envelope calculations (2.123, 2.126) were obtained. Another example worthy of mention is the newly developed in Section 3.3 theory of spontaneous SRTs in exchange-dominated cubic magnets. Its main statement is ultimately simple: as temperature varies, the system goes through a sequence of (at the most two) phases which is unambiguously determined by a single quantity—a ratio of fourth- and sixth-order CF parameters. As regards uniaxial magnets, there the main results can be formulated as the ‘Stevens $\alpha J$, $\beta J$ and $\gamma J$ rules’. Even though they do not constitute an accomplished theory, these rules are nonetheless binding necessary conditions, to the extent that their violation is a nearly certain sign of a mistake. It was also graphically shown how the classical phase diagram of a uniaxial magnet (Fig. 3.15) is modified when a third anisotropy constant is allowed for, establishing a simple visual relation between Figs. 3.15 and 3.17. Last but not least, the interplay of the 3d-4f exchange and the CF in the expression for the leading anisotropy constant $K_1$, was shown to take a particularly transparent form at high $T$ (2.42) and also when $T \rightarrow 0$ (2.107). Our goal was to bring all these simple findings to the notice of workers in the field of magnetic materials.

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