2

MAGNETIC STRUCTURES

The *mean-field theory* introduced in the previous section is used in this chapter as a basis for examining some of the magnetic structures assumed by the rare earth metals. The theory is presented at length in the first section. Beginning with the expression for the free energy, some general results are established for the magnetization, and applied analytically to the calculation of the susceptibility in the *high-temperature* limit. The mean-field approximation is then developed, and a numerical method for solving the resulting equations self-consistently, for magnetic structures which are commensurable with the lattice, is described. The *Landau expansion* of the free energy in terms of the *order parameters* of the magnetic system provides the starting point for a discussion of a number of the periodic magnetic structures which arise as a result of the long range of the indirect-exchange interaction. The ordering temperatures are calculated by analytical means, and the relative stability of different structures compared. In the following section, the important extension by Callen and Callen of the Zener power-law for the temperature dependence of the magnetic anisotropy is derived. The thermal expectation values $\langle O_l^m \rangle$ of the *Stevens operators* are calculated and their dependence on the magnetization determined. From the free energy, the *magnetic anisotropy* and the *magnetoelastic coefficients* are deduced. We conclude with a detailed discussion of some *magnetic structures*, using the aforementioned analytical methods, supplemented by numerical calculations, to help identify those characteristics of the magnetic interactions which lead to the stability of different moment-configurations under various conditions. This account is illustrated by various examples, with emphasis on the the diverse magnetic phases of Ho. Among other structures, we consider the *ferromagnet*, the *cone*, the *helix*, the *longitudinal wave*, the *cycloid*, and commensurable *spin slips.* The effect of a magnetic field in stabilizing *fan* and *helifan* structures, and the ordering of *thin films* and *superlattices*, are also discussed.

2.1 Mean-field theory of magnetic ordering

The simplest form of Hamiltonian which is adequate to explain the occurrence of most of the observed magnetic structures is

$$\mathcal{H} = \sum_i \mathcal{H}_{\rm cf}(i) - \frac{1}{2}\sum_{ij} \mathcal{J}(ij)\, \mathbf{J}_i \cdot \mathbf{J}_j + \mathcal{H}_{\rm Z}, \qquad (2.1.1a)$$

where the first sum is the single-ion crystal-field Hamiltonian

$$\mathcal{H}_{\rm cf}(i) = \sum_{l=2,4,6} B_l^0 O_l^0(\mathbf{J}_i) + B_6^6 O_6^6(\mathbf{J}_i), \qquad (2.1.1b)$$

the two-ion term is assumed to be isotropic, and the Zeeman term is

$$\mathcal{H}_{\rm Z} = -\sum_i \boldsymbol{\mu}_i \cdot \mathbf{H}_i. \qquad (2.1.1c)$$

The field may vary spatially, so that we must specify its value on each site, writing $\mathbf{H}_i \equiv \mathbf{H}(\mathbf{R}_i)$, and the magnetic moment on the ith ion is $\boldsymbol{\mu}_i = g\mu_B \mathbf{J}_i$.

The static-susceptibility tensor may be derived as the second derivative of the free energy, and we shall therefore begin by recapitulating a few basic thermodynamic results. The free energy is

$$F = U - TS = -\frac{1}{\beta}\ln Z, \qquad (2.1.2)$$

where U is the internal energy, S the entropy, and $\beta = (k_B T)^{-1}$. The partition function is

$$Z = {\rm Tr}\big\{e^{-\beta\mathcal{H}}\big\} = \sum_p e^{-\beta E_p}. \qquad (2.1.3)$$

Tr indicates the trace over a complete set of states, and the final summation may be performed if the eigenvalues E_p of the Hamiltonian are known. The expectation value of an operator A is

$$\langle A \rangle = \frac{1}{Z}{\rm Tr}\big\{A e^{-\beta\mathcal{H}}\big\}. \qquad (2.1.4)$$

The derivative of the free energy with respect to a variable x is

$$\frac{\partial F}{\partial x} = -\frac{1}{\beta Z}\frac{\partial Z}{\partial x} = \frac{1}{Z}{\rm Tr}\left\{\frac{\partial \mathcal{H}}{\partial x} e^{-\beta\mathcal{H}}\right\} = \Big\langle \frac{\partial \mathcal{H}}{\partial x} \Big\rangle. \qquad (2.1.5)$$

This expression is obtained by utilizing the invariance of the trace to the basis used, assuming it to be independent of x and a cyclic permutation of the operators, thus allowing a conventional differentiation of the exponential operator, as may be seen by a Taylor expansion. This result is general, but the exponential operator can only be treated in this simple way in second derivatives if $\partial\mathcal{H}/\partial x$ commutes with the Hamiltonian, which is usually not the case. However, we may be interested only in the leading-order contributions in the limit where β is small, i.e. at *high* *temperatures*. Expanding in powers of β, we may use the approximation $\exp\{-\beta\mathcal{H}\} \simeq 1 - \beta\mathcal{H} + \frac{1}{2}\beta^2\mathcal{H}^2$. In this case, we may proceed as above, and the result is

$$\begin{aligned}\frac{\partial^2 F}{\partial x \partial y} = \Big\langle \frac{\partial^2 \mathcal{H}}{\partial x \partial y} \Big\rangle + \beta \Big(\Big\langle \frac{\partial \mathcal{H}}{\partial x} \Big\rangle \Big\langle \frac{\partial \mathcal{H}}{\partial y} \Big\rangle - \Big\langle \frac{\partial \mathcal{H}}{\partial x} \frac{\partial \mathcal{H}}{\partial y} \Big\rangle \Big) \\ -\frac{\beta^2}{2} \Big\langle \Big[\frac{\partial \mathcal{H}}{\partial x}, \frac{\partial \mathcal{H}}{\partial y} \Big] \mathcal{H} \Big\rangle + \mathcal{O}(\beta^3),\end{aligned} \tag{2.1.6}$$

where the second- and higher-order terms vanish if one of the derivatives of $\mathcal{H}$ commutes with $\mathcal{H}$ itself.

In many instances, it is more convenient to consider the angular momentum rather than the magnetic moment, with a corresponding field variable $\mathbf{h}_i = g\mu_B \mathbf{H}_i$, so that the Zeeman term (2.1.1*c*) becomes

$$\mathcal{H}_\mathrm{Z} = -\sum_i \boldsymbol{\mu}_i \cdot \mathbf{H}_i = -\sum_i \mathbf{J}_i \cdot \mathbf{h}_i. \tag{2.1.7}$$

Since the exchange and anisotropy terms in $\mathcal{H}$ do not depend explicitly on the field, $\partial\mathcal{H}/\partial H_{i\alpha} = -\mu_{i\alpha}$ and, using eqn (2.1.5), we have

$$\langle \mu_{i\alpha} \rangle = -\partial F / \partial H_{i\alpha} \quad \text{or} \quad \langle J_{i\alpha} \rangle = -\partial F / \partial h_{i\alpha}. \tag{2.1.8}$$

Next, we define the non-local susceptibilities

$$\chi^{\mu}_{\alpha\beta}(ij) = \partial\langle\mu_i\rangle / \partial H_{j\beta} = -\partial^2 F / \partial H_{i\alpha} \partial H_{j\beta}, \tag{2.1.9a}$$

and similarly

$$\chi^{\mathbf{J}}_{\alpha\beta}(ij) = (g\mu_B)^{-2} \chi^{\mu}_{\alpha\beta}(ij) = -\partial^2 F / \partial h_{i\alpha} \partial h_{j\beta}, \tag{2.1.9b}$$

and the corresponding Fourier transforms, e.g.

$$\chi^{\mathbf{J}}_{\alpha\beta}(\mathbf{q}) = \frac{1}{N} \sum_{ij} \chi^{\mathbf{J}}_{\alpha\beta}(ij) e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} = \sum_j \chi^{\mathbf{J}}_{\alpha\beta}(ij) e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}. \tag{2.1.9c}$$

The final equality only applies in a uniform system. If the field is increased by an infinitesimal amount $\delta\mathbf{H}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_i)$, the individual moments are changed by

$$\delta\langle\mu_{i\alpha}\rangle = \sum_j \sum_\beta \chi^{\mu}_{\alpha\beta}(ij) \delta H_\beta(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_j}, \tag{2.1.10a}$$

according to (2.1.9). Hence the added harmonically-varying field introduces one Fourier component in the magnetization:

$$\delta M_\alpha(\mathbf{q}) = \frac{1}{V} \sum_i \delta\langle\mu_{i\alpha}\rangle e^{-i\mathbf{q}\cdot\mathbf{R}_i} = \frac{N}{V} \sum_\beta \chi^{\mu}_{\alpha\beta}(\mathbf{q}) \delta H_\beta(\mathbf{q}), \tag{2.1.10b}$$

proportional to the susceptibility at the wave-vector considered. The usual definition of the susceptibility components (per unit volume), as used in Chapter 1, is $\delta M_\alpha(\mathbf{q})/\delta H_\beta(\mathbf{q})$. The susceptibility used in (2.1.10*b*) differs from this by the factor V/N, i.e. we are here considering the susceptibility per atom instead of per unit volume. Furthermore, since we shall not make any further use of $\chi^{\mu}_{\alpha\beta}(\mathbf{q})$, we shall reserve the notation $\chi_{\alpha\beta}(\mathbf{q})$ for the $\mathbf{q}$-dependent susceptibility $\chi^{\mathbf{J}}_{\alpha\beta}(\mathbf{q})$, introduced in eqn (2.1.9*b*), throughout the rest of the book. So in terms of the susceptibility per atom, 'in units of $(g\mu_B)^2$', the above equation may be written

$$\delta\langle J_\alpha(\mathbf{q})\rangle = \frac{1}{N}\sum_i \delta\langle J_{i\alpha}\rangle e^{-i\mathbf{q}\cdot\mathbf{R}_i} = \sum_\beta \chi_{\alpha\beta}(\mathbf{q})\delta h_\beta(\mathbf{q}), \tag{2.1.10c}$$

with the upper index $\mathbf{J}$ in $\chi^{\mathbf{J}}_{\alpha\beta}(\mathbf{q})$ being suppressed from now on.

2.1.1 The high-temperature susceptibility

In order to calculate $\overline{\overline{\chi}}(\mathbf{q})$ in zero field, we shall first use the approximation (2.1.6) to the derivative of the free energy, valid at high temperatures. In this limit $\langle \mathbf{J}_i\rangle = \mathbf{0}$, and only one term in the expansion is non-zero:

$$\chi_{\alpha\beta}(ij) = \beta\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}(1-\beta\mathcal{H})\big\}\big/\mathrm{Tr}\big\{1-\beta\mathcal{H}\big\}, \tag{2.1.11}$$

to second order in β. The commutator in the third term on the right-hand side of (2.1.6) is either zero or purely imaginary (if $i = j$ and $\alpha \neq \beta$), showing immediately that the expectation value of this term must vanish in all cases. To first order in β, we obtain from (2.1.11)

$$\chi_{\alpha\beta}(ij) \simeq \beta\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}\big\}\big/\mathrm{Tr}\big\{1\big\} = \tfrac{1}{3}J(J+1)\beta\delta_{\alpha\beta}\delta_{ij}\,,$$

using the product of the eigenvectors of $J_{i\alpha}$ as the basis, and recalling that

$$\sum m^2 = \tfrac{1}{3}J(J+1)(2J+1),$$

when m runs from $-J$ to J. In order to calculate the second-order contribution, we shall utilize the general tensor properties of the Stevens operators, which satisfy the orthogonality condition:

$$\begin{aligned} &\mathrm{Tr}\big\{O_l^m(\mathbf{J}_i)O_{l'}^{m'}(\mathbf{J}_j)\big\} = \delta_{ij}\delta_{ll'}\delta_{mm'}\mathrm{Tr}\big\{[O_l^m(\mathbf{J}_i)]^2\big\} \\ \text{and}\qquad &\mathrm{Tr}\big\{O_l^m(\mathbf{J}_i)\big\} = 0, \end{aligned} \tag{2.1.12}$$

when l and l' are both non-zero. O_0^0 is just the identity operator. $J_{i\alpha}$ is a linear combination of $O_1^m(\mathbf{J}_i)$, $m = -1, 0, 1$, and (2.1.12) then implies that the trace of the Hamiltonian (2.1.1) vanishes, and hence that the denominator in (2.1.11) is $\mathrm{Tr}\{1\} = (2J+1)^N$. For the second-order term in the numerator, we find

$$\begin{aligned}\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}\mathcal{H}\big\} &= \delta_{ij}B_2^0\,\mathrm{Tr}\big\{J_{i\alpha}J_{i\beta}O_2^0(\mathbf{J}_i)\big\} - \mathcal{J}(ij)\,\mathrm{Tr}\big\{J_{i\alpha}J_{j\beta}\mathbf{J}_i\cdot\mathbf{J}_j\big\}\\ &= \delta_{ij}\delta_{\alpha\beta}B_2^0\,\mathrm{Tr}\big\{J_{i\alpha}^2[3J_{iz}^2 - J(J+1)]\big\} - \delta_{\alpha\beta}\mathcal{J}(ij)\,\mathrm{Tr}\big\{J_{i\alpha}^2J_{j\alpha}^2\big\},\end{aligned}$$

utilizing that $J_{i\alpha}J_{j\beta}$ is a linear combination of second- and lower-rank tensors for $i = j$, and a product of first-rank tensors for $i \neq j$. When $\alpha = z$ (or ζ), we may readily calculate the first trace, using

$$\sum m^4 = \tfrac{1}{15}J(J+1)(2J+1)(3J^2+3J-1).$$

The traces with $\alpha = x$ or $\alpha = y$ must be equal, and using this equality in the case $\alpha = x$, for instance, we may replace J_x^2 in the trace by $\frac{1}{2}(J_x^2 + J_y^2) \rightarrow \frac{1}{2}J(J+1) - \frac{1}{2}J_z^2$. As the constant term multiplied by $3J_z^2 - J(J+1)$ does not contribute (as $\mathrm{Tr}\{3J_z^2 - J(J+1)\} = 0$), the trace with $\alpha = x$ or y is equal to $-1/2$ times that with $\alpha = z$. Only the single-ion terms contribute to the trace when $i = j$ ($\mathcal{J}(ii)$ is assumed to be zero), and of these only the lowest-rank term B_2^0 appears, to leading order. The two-ion coupling only occurs in the trace, and hence in $\chi_{\alpha\beta}(ij)$, when $i \neq j$, and this contribution may be straightforwardly calculated. To second order in β, the off-diagonal terms are zero, whereas

$$\begin{aligned}\chi_{\alpha\alpha}(ij) = \delta_{ij}\tfrac{1}{3}J(J+1)\beta\big[1 - \tfrac{2}{5}(3\delta_{\alpha\zeta} - 1)B_2^0(J-\tfrac{1}{2})(J+\tfrac{3}{2})\beta\big]&\\ + \big[\tfrac{1}{3}J(J+1)\beta\big]^2\mathcal{J}(ij).&\end{aligned}$$

Introducing the Fourier transform of the two-ion coupling,

$$\mathcal{J}(\mathbf{q}) = \sum_j \mathcal{J}(ij)e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}, \tag{2.1.13}$$

we find that, to the order considered, the inverse of the **q**-dependent susceptibility may be written

$$1/\chi_{\alpha\alpha}(\mathbf{q}) = \frac{3k_BT}{J(J+1)} + (3\delta_{\alpha\zeta} - 1)\frac{6(J-\frac{1}{2})(J+\frac{3}{2})}{5J(J+1)}B_2^0 - \mathcal{J}(\mathbf{q}) + \mathcal{O}(1/T). \tag{2.1.14}$$

The inverse susceptibility in the high-temperature limit thus increases linearly with the temperature, with a slope inversely proportional to the square of the effective paramagnetic moment ($\propto \{J(J+1)\}^{1/2}$). The susceptibilities determined experimentally by magnetization measure-

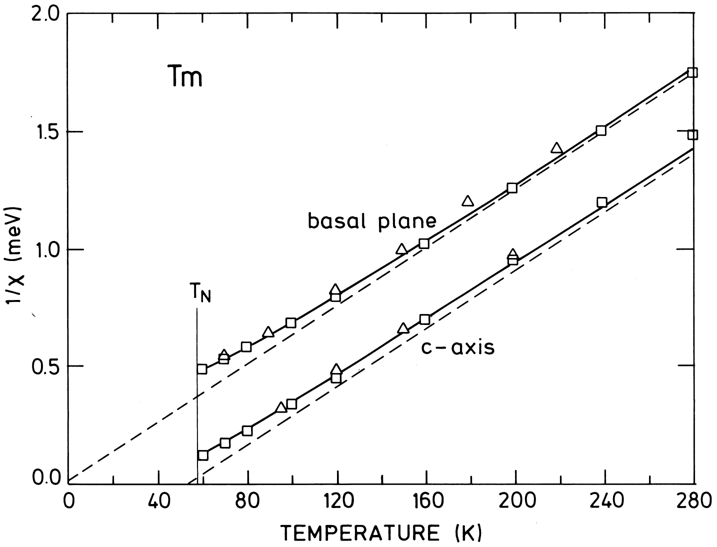

Fig. 2.1. The inverse susceptibility, in atomic units, in Tm above T_N. The full lines depict the results of a mean-field calculation and the dashed lines are extrapolations of the high-temperature limit. Experimental values are also shown. The MF theory predicts a deviation from the high-temperature expression as the ordering temperature is approached from above, because of crystal-field anisotropy effects.

ments are the bulk values at zero wave-vector. The straight lines found at high temperatures for the inverse-susceptibility components $1/\chi_{\alpha\alpha}(\mathbf{0})$ versus temperature may be extrapolated to lower values, as illustrated in Fig. 2.1. The values at which these lines cross the temperature axis are the *paramagnetic Curie temperatures* $\theta_{\|}$ and $\theta_{\perp}$, determined respectively when the field is parallel and perpendicular to the c-axis (ζ-axis). The high-temperature expansion then predicts these temperatures to be

$$k_B\theta_{\|} = \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{0}) - \tfrac{4}{5}(J-\tfrac{1}{2})(J+\tfrac{3}{2})B_2^0, \qquad (2.1.15a)$$

and

$$k_B\theta_{\perp} = \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{0}) + \tfrac{2}{5}(J-\tfrac{1}{2})(J+\tfrac{3}{2})B_2^0. \qquad (2.1.15b)$$

Hence the paramagnetic Curie temperatures are determined by the lowest-rank interactions in the Hamiltonian, i.e. those terms for which $l+l'=2$. The difference between the two temperatures depends only on B_2^0, because of the assumption that the two-ion coupling is an *isotropic*

Heisenberg exchange. The mean temperature $(\theta_{\|}+2\theta_{\perp})/3$ is determined by $\mathcal{J}(\mathbf{0})$ which, from (2.1.13), is the algebraic sum of the isotropic two-ion interactions, and this temperature may be measured directly with a polycrystalline sample. The two basal-plane components are found to be equal. This is not just due to the assumption of high temperatures, but is generally valid as long as there is no ordered moment in the basal-plane. In this case, the c-axis is a three-fold symmetry axis, or effectively a six-fold axis, due to the symmetry of the basal-plane anisotropy B_6^6 in the Hamiltonian. The susceptibility is a second-rank tensor, according to (2.1.9), and it cannot therefore vary under rotation about a three- or six-fold axis.

2.1.2 The mean-field approximation

The high-temperature expansion may be extended to higher order in β, but the calculations rapidly become more complex, so we shall instead adopt another approach, the mean-field approximation. In this method, the correlated fluctuations of the moments around their equilibrium values are neglected. In order to introduce $\langle\mathbf{J}_i\rangle$ into the Hamiltonian, we utilize the identity

$$\mathbf{J}_i\cdot\mathbf{J}_j=(\mathbf{J}_i-\langle\mathbf{J}_i\rangle)\cdot(\mathbf{J}_j-\langle\mathbf{J}_j\rangle)+\mathbf{J}_i\cdot\langle\mathbf{J}_j\rangle+\mathbf{J}_j\cdot\langle\mathbf{J}_i\rangle-\langle\mathbf{J}_i\rangle\cdot\langle\mathbf{J}_j\rangle.$$

The MF approximation then consists in neglecting the first term on the right-hand side, which is associated with two-site fluctuations, since $i\neq j$. The Hamiltonian (2.1.1) is then effectively decoupled into a sum of N independent terms for the single sites; $\mathcal{H}\simeq\sum_i\mathcal{H}_{\mathrm{MF}}(i)$, where

$$\mathcal{H}_{\mathrm{MF}}(i)=\mathcal{H}_{\mathrm{cf}}(i)-\mathbf{J}_i\cdot\mathbf{h}_i-\big(\mathbf{J}_i-\tfrac{1}{2}\langle\mathbf{J}_i\rangle\big)\cdot\sum_j\mathcal{J}(ij)\langle\mathbf{J}_j\rangle, \tag{2.1.16}$$

in the presence of an external magnetic field $\mathbf{h}_i=g\mu_B\mathbf{H}_i$. Introducing the effective field

$$\mathbf{h}_i^{\mathrm{eff}}=\mathbf{h}_i+\sum_j\mathcal{J}(ij)\langle\mathbf{J}_j\rangle, \tag{2.1.17a}$$

we may write the MF Hamiltonian

$$\mathcal{H}_{\mathrm{MF}}(i)=\mathcal{H}_{\mathrm{cf}}(i)-\mathbf{J}_i\cdot\mathbf{h}_i^{\mathrm{eff}}+\tfrac{1}{2}\langle\mathbf{J}_i\rangle\cdot(\mathbf{h}_i^{\mathrm{eff}}-\mathbf{h}_i). \tag{2.1.17b}$$

Self-consistent solutions of the MF equations may sometimes be obtained analytically, but numerical methods may be used more generally, provided that the periodicity of the magnetic structure is commensurable with that of the lattice. For an assumed distribution of $\langle\mathbf{J}_j\rangle$, the effective field and hence the MF Hamiltonian for the ith site is calculated.

Diagonalizing this Hamiltonian, we may derive the partition function Z_i, the free energy F_i, and the expectation value $\langle \mathbf{J}_i \rangle$ for this site. The last term in (2.1.17*b*) just adds a constant contribution to F_i, without affecting $\langle \mathbf{J}_i \rangle$. Performing this calculation for all the different ions, we determine the various values of $\langle \mathbf{J}_j \rangle$, and the total free energy is the sum of the F_i. The derived values of $\langle \mathbf{J}_j \rangle$ are used as the input for a new MF Hamiltonian, and this iterative procedure is repeated until self-consistency is attained. The self-consistent solution of the MF Hamiltonian may be one in which $\langle \mathbf{J}_i \rangle$ is non-zero even in zero field, thus describing the occurrence of a spontaneous ordering of the moments.

Having found the self-consistent solution for the angular momenta, we may proceed to calculate the susceptibility. The MF Hamiltonian for the ith site has been diagonalized, and we shall denote the $(2J+1)$ eigenstates by $|\, p>$, with corresponding energy eigenvalues E_p. If the effective field is changed by a small amount $\delta h_\beta^{\text{eff}}$, the Zeeman term $-J_{i\beta}\delta h_\beta^{\text{eff}}$ must be added to the Hamiltonian, and $E_p^{(1)} = E_p - <p\,|\, J_{i\beta}\,|\, p>\delta h_\beta^{\text{eff}}$, to first order in the perturbation, provided that $|\, p>$ is a set which diagonalizes the perturbation within the possibly degenerate subspaces of the zero-field Hamiltonian. The new eigenstates are

$$|\, p^{(1)}> = |\, p> - \delta h_\beta^{\text{eff}} {\sum_{p'}}' |\, p'><p'\,|\, J_{i\beta}\,|\, p> /(E_p - E_{p'}),$$

where the terms for which $E_p = E_{p'}$ vanish. Using (2.1.3) and (2.1.4), we then have, to first order in $\delta h_\beta^{\text{eff}}$,

$$\begin{aligned}\langle J_{i\alpha}^{(1)} \rangle = \sum_p <p^{(1)}\,|\, J_{i\alpha}\,|\, p^{(1)}>n_p^{(1)} &= \sum_p <p\,|\, J_{i\alpha}\,|\, p>n_p^{(1)} \\ &- \delta h_\beta^{\text{eff}} {\sum_{pp'}}' <p\,|\, J_{i\alpha}\,|\, p'><p'\,|\, J_{i\beta}\,|\, p>n_p/(E_p - E_{p'}) \\ &- \delta h_\beta^{\text{eff}} {\sum_{pp'}}' <p\,|\, J_{i\beta}\,|\, p'><p'\,|\, J_{i\alpha}\,|\, p>n_p/(E_p - E_{p'}),\end{aligned}$$

where the last two sums extend over states for which $E_p \neq E_{p'}$. The population factor of the pth level at $\delta h_\beta^{\text{eff}} = 0$ is $n_p = \exp(-\beta E_p)/Z_i$, and $n_p^{(1)}$ is the corresponding factor at the field $\delta h_\beta^{\text{eff}}$. By differentiation, we find

$$\begin{aligned}\partial n_p^{(1)}/\partial(\delta h_\beta^{\text{eff}}) &= \big\{<p\,|\, J_{i\beta}\,|\, p> - \sum_{p'} <p'\,|\, J_{i\beta}\,|\, p'>n_{p'}\big\}\beta n_p \\ &= \big\{<p\,|\, J_{i\beta}\,|\, p> - \langle J_{i\beta}\rangle\big\}\beta n_p.\end{aligned}$$

Introducing this result in the equation above, and interchanging p and

p' in the last sum, we obtain finally:

$$\chi^o_{\alpha\beta}(i) = \partial\langle J_{i\alpha}\rangle/\partial h^{\text{eff}}_\beta = \sum_{pp'}^{E_p\neq E_{p'}} \frac{<p\,|\,J_{i\alpha}\,|\,p'><p'\,|\,J_{i\beta}\,|\,p>}{E_{p'}-E_p}(n_p - n_{p'})$$
$$+\ \beta\sum_{pp'}^{E_p=E_{p'}} <p\,|\,J_{i\alpha}\,|\,p'><p'\,|\,J_{i\beta}\,|\,p>n_p - \beta\langle J_{i\alpha}\rangle\langle J_{i\beta}\rangle. \qquad (2.1.18)$$

The second summation is transformed in such a way that it is no longer necessary for $J_{i\beta}$ to be diagonal within the degenerate subspaces, as required initially. The first term in the susceptibility is the *Van Vleck* contribution, which becomes constant at zero temperature, whereas the second term, the *Curie* contribution, diverges as $1/T$ in the low-temperature limit. The susceptibility deduced above is that determining the response due to a change of the *effective* field, $\delta\langle\mathbf{J}_i\rangle = \overline{\overline{\chi}}^o(i)\delta\mathbf{h}^{\text{eff}}_i$, whereas we wish to know the response due to a small change of the *external* field. If a small harmonically-varying field $\delta\mathbf{h}_\mathbf{q}\exp(i\mathbf{q}\cdot\mathbf{R}_i)$ is applied, the effective field, according to (2.1.17*a*), is

$$\delta\mathbf{h}^{\text{eff}}_i = \delta\mathbf{h}_\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{R}_i} + \sum_j \mathcal{J}(ij)\overline{\overline{\chi}}^o(j)\delta\mathbf{h}^{\text{eff}}_j.$$

This equation may be solved by a Fourier transformation if $\overline{\overline{\chi}}^o(i) = \overline{\overline{\chi}}^o$ is site-independent, which it is so long as $\langle\mathbf{J}_i\rangle$ is independent of i, as in the high-temperature paramagnetic phase, for example, where $\langle\mathbf{J}_i\rangle = \mathbf{0}$. Neglecting any site-dependence of $\overline{\overline{\chi}}^o$, and introducing the notation $\delta\mathbf{h}^{\text{eff}}_i = \delta\mathbf{h}^{\text{eff}}_\mathbf{q}\exp(i\mathbf{q}\cdot\mathbf{r}_i)$, we get

$$\delta\mathbf{h}^{\text{eff}}_\mathbf{q} = \left\{1 - \overline{\overline{\chi}}^o\mathcal{J}(\mathbf{q})\right\}^{-1}\delta\mathbf{h}_\mathbf{q},$$

or, by the definition of the susceptibility,

$$\overline{\overline{\chi}}(\mathbf{q}) = \left\{1 - \overline{\overline{\chi}}^o\mathcal{J}(\mathbf{q})\right\}^{-1}\overline{\overline{\chi}}^o. \qquad (2.1.19a)$$

In the following, we shall assume that the external magnetic field is zero. With this restriction, $\overline{\overline{\chi}}(\mathbf{q})$ is diagonal in the $(\xi\eta\zeta)$-coordinate system, and the reciprocal susceptibility, in the MF approximation, may be written

$$1/\chi_{\alpha\alpha}(\mathbf{q}) = 1/\chi^o_{\alpha\alpha} - \mathcal{J}(\mathbf{q}). \qquad (2.1.19b)$$

In the degenerate case, (2.1.18) implies that $\chi^o_{\alpha\alpha} = \beta J(J+1)/3$. However, if $\mathcal{H}_{\text{cf}}$ is non-zero, the expression (2.1.18) for the susceptibility becomes quite complex. A drastic simplification is achieved by assuming a small value of β. In this high temperature limit, $\overline{\overline{\chi}}^o$ may be calculated by a procedure equivalent to that used in deriving (2.1.14), except that $\mathcal{J}(ij) = 0$. Hence, to second order in β, we have

$$\chi^o_{\alpha\alpha} \simeq \tfrac{1}{3}J(J+1)\beta\big[1 - \tfrac{2}{5}(3\delta_{\alpha\zeta} - 1)(J - \tfrac{1}{2})(J + \tfrac{3}{2})B^0_2\beta\big]. \qquad (2.1.20)$$

Introducing (2.1.20) in (2.1.19), we obtain the same result as previously derived in (2.1.14), demonstrating that the MF approximation is correct in the high-temperature limit. Although the thermal fluctuations increase when the temperature is raised, they also become increasingly uncorrelated. It is the latter effect which is the most pronounced, and the correction to the MF value of the free energy, proportional to the correlation energy of the two-site fluctuations $\mathcal{J}(ij)\{\langle \mathbf{J}_i \cdot \mathbf{J}_j\rangle - \langle \mathbf{J}_i\rangle \cdot \langle \mathbf{J}_j\rangle\}$, decreases with temperature at high temperatures. In the other limit of zero temperature, the correlation effects are much stronger, but the fluctuations themselves are small. We may therefore also expect the MF approximation to be accurate in this limit, and to provide a useful interpolation at intermediate temperatures.

$\overline{\overline{\chi}}^o$ increases steadily with decreasing temperature. If the crystal-field ground state is degenerate, the second sum in (2.1.18) is non-zero and $\overline{\overline{\chi}}^o$ diverges in the zero-temperature limit. Because of the Kramers degeneracy, the ground state is always at least doubly degenerate if $2J$ is odd. When J is an integer, the ground state may be a singlet, in which case $\overline{\overline{\chi}}^o$ saturates at a constant value at zero temperature. Except in this special case, it is always possible to find a temperature where $1/\chi_{\alpha\alpha}(\mathbf{q})$ is zero, corresponding to an infinite $\chi_{\alpha\alpha}(\mathbf{q})$. The largest value of the $\mathbf{q}$-dependent susceptibility is found at the wave-vector $\mathbf{Q}$ at which $\mathcal{J}(\mathbf{q})$ has its maximum. Of the three non-zero components of $\overline{\overline{\chi}}(\mathbf{Q})$, the cc-component is the largest if B^0_2 is negative. If B^0_2 is positive, on the other hand, the two equal basal-plane components are the largest. It is the maximum component of the susceptibility at $\mathbf{q} = \mathbf{Q}$ which first diverges when the system is cooled. This divergence signals that the paramagnetic ground-state becomes unstable against the formation of an ordered state in which the moments are modulated with the wave-vector $\mathbf{Q}$, and point along or perpendicular to the c-direction, depending on whether B^0_2 is respectively negative or positive. Hence, a second-order phase transition takes place at this critical temperature, called the Curie temperature, T_C, or the Néel temperature, T_N, depending on whether $\mathbf{Q} = \mathbf{0}$ or $\mathbf{Q} \neq \mathbf{0}$. Just below T_N, the ordered moment $\langle \mathbf{J}_i\rangle$ is small, and the free energy of the ith ion may be expanded in powers of this moment. In order to establish this expansion, we first consider the Hamiltonian $\mathcal{H}'(i) = \mathcal{H}_{\rm cf}(i) - \mathbf{J}_i \cdot \mathbf{h}$. The corresponding free energy may be written

$$F'_i = F_0/N - \langle \mathbf{J}_i\rangle \cdot \mathbf{h} + \sum_\alpha A_\alpha \langle J_{i\alpha}\rangle^2 + \sum_{\alpha\beta} B_{\alpha\beta}\langle J_{i\alpha}\rangle^2 \langle J_{i\beta}\rangle^2 + \cdots .$$

Except for the field term, this expansion only includes products of components in which the sum of the exponents is even, because of time-reversal symmetry. Using the equilibrium condition $\partial F_i'/\partial\langle J_{i\alpha}\rangle = 0$, and recalling that $\langle J_{i\alpha}\rangle = \chi^o_{\alpha\alpha}(\sigma = 0)h_\alpha$ to leading order, in the zero-field limit, we obtain

$$A_\alpha = \big\{2\chi^o_{\alpha\alpha}(\sigma = 0)\big\}^{-1}, \tag{2.1.21a}$$

where $\chi^o_{\alpha\alpha}(\sigma = 0)$ is the MF susceptibility (2.1.18), in the limit of zero magnetization (field). The susceptibility decreases with increasing magnetization (or field), as described by the fourth-order terms. An order-of-magnitude estimate of $B_{\alpha\beta}$ may be obtained by neglecting $\mathcal{H}_{\rm cf}(i)$. In this case, the magnetization as a function of the field is given by the Brillouin function (1.2.31):

$$\langle J_{i\alpha}\rangle = JB_J(\beta Jh_\alpha) \simeq \tfrac{1}{3}J(J+1)\beta h_\alpha\big\{1 - \tfrac{1}{15}(J^2 + J + \tfrac{1}{2})\beta^2h_\alpha^2\big\},$$

which, in combination with the equilibrium condition for the free energy, determines $B_{\alpha\alpha}$. The off-diagonal terms may be obtained straightforwardly by utilizing the condition that, when $\mathcal{H}_{\rm cf}(i)$ is neglected, the free energy should be invariant with respect to any rotation of the magnetization vector, implying that all the coefficients $B_{\alpha\beta}$ are equal, or

$$B_{\alpha\beta} \approx \frac{9}{20}\frac{J^2 + J + \frac{1}{2}}{J^3(J+1)^3}k_BT. \tag{2.1.21b}$$

The introduction of the crystal-field terms of course modifies this result, but rather little in the high-temperature limit. Under all circumstances, the effective six-fold symmetry around the c-axis implies that $B_{\alpha\beta}$ is symmetric, $B_{\xi\xi} = B_{\eta\eta} = B_{\xi\eta}$, and $B_{\xi\zeta} = B_{\eta\zeta}$, and it also eliminates the possibility that any other fourth-order terms may contribute. The expansion of the free energy of the total system, when the external field is zero, is obtained from the expansion of F_i', summed over i, by substituting the *exchange* field $\mathbf{h}_i^{\rm eff} = \sum_j \mathcal{J}(ij)\langle\mathbf{J}_j\rangle$ for $\mathbf{h}$, and adding the 'constant' $\frac{1}{2}\langle\mathbf{J}_i\rangle\cdot\mathbf{h}_i^{\rm eff}$, so that

$$F = F_0 - \frac{1}{2}\sum_{ij}\mathcal{J}(ij)\langle\mathbf{J}_i\rangle\cdot\langle\mathbf{J}_j\rangle + \sum_i\Big[\sum_\alpha A_\alpha\langle J_{i\alpha}\rangle^2 + \sum_{\alpha\beta}B_{\alpha\beta}\langle J_{i\alpha}\rangle^2\langle J_{i\beta}\rangle^2\Big] \tag{2.1.22}$$

to fourth order in the magnetization. This expansion of the free energy in terms of the *order parameter(s)* is called the *Landau expansion*.

Assuming the ordered phase to be described by a single wave-vector, we may write

$$\langle J_{i\alpha}\rangle = J\sigma_\alpha\cos(\mathbf{q}\cdot\mathbf{R}_i + \varphi_\alpha), \tag{2.1.23}$$

where $\sigma_\alpha = \sigma_\alpha(\mathbf{q})$ is the relative magnetization at the wave-vector $\mathbf{q}$. Introducing this into the free-energy expression, and utilizing the condition that $\sum_i \cos(\mathbf{q}'\cdot\mathbf{R}_i + \varphi) = 0$, if $\mathbf{q}'$ is not a reciprocal lattice vector, we find

$$\begin{aligned} f = (F - F_0)/N = \tfrac{1}{4}J^2 \sum_\alpha \{2A_\alpha - \mathcal{J}(\mathbf{q})\}\sigma_\alpha^2 \\ + \tfrac{1}{8}J^4 \sum_{\alpha\beta} B_{\alpha\beta}\{2 + \cos 2(\varphi_\alpha - \varphi_\beta)\}\sigma_\alpha^2\sigma_\beta^2, \end{aligned} \qquad (2.1.24)$$

if $4\mathbf{q}$ is different from a reciprocal lattice vector. The coefficients of the second power are thus $\propto \{2A_\alpha - \mathcal{J}(\mathbf{q})\} = 1/\chi_{\alpha\alpha}(\mathbf{q}, \sigma = 0)$, where the susceptibility is evaluated at zero magnetization. As long as all the second-order coefficients are positive, at any value of $\mathbf{q}$, the free energy is at its minimum when $\sigma_\alpha = 0$, i.e. the system is paramagnetic. The smallest of these coefficients are those at $\mathbf{q} = \mathbf{Q}$, where $\mathcal{J}(\mathbf{q})$ has its maximum. In the heavy rare earths, with the exception of Gd, $\mathbf{Q}$ is non-zero and is directed along the c-axis. Depending on the sign of B_2^0, the magnetic structures occurring in the heavy rare earths may be divided into two classes, which we will discuss in turn.

2.1.3 Transversely ordered phases

When $B_2^0 > 0$, as in Tb, Dy, and Ho, the two basal-plane components of $\overline{\overline{\chi}}(\mathbf{Q})$ both diverge at the same critical temperature T_N. Using the approximate high-temperature value (2.1.20) for the susceptibility, we find that $1/\chi_{\xi\xi}(\mathbf{Q}, \sigma = 0) = 1/\chi_{\eta\eta}(\mathbf{Q}, 0) = 2A_\xi - \mathcal{J}(\mathbf{Q})$ vanishes at the temperature determined by

$$k_B T_N \simeq \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{Q})\big[1 + \tfrac{2}{5}(J - \tfrac{1}{2})(J + \tfrac{3}{2})B_2^0/k_B T_N\big]. \qquad (2.1.25)$$

Below T_N, both σ_ξ and σ_η are generally non-zero at the wave-vector $\mathbf{Q}$, and the free energy f, given by (2.1.24) with $\sigma_\zeta = 0$, is minimized when $\sigma_\xi(\mathbf{Q}) = \sigma_\eta(\mathbf{Q}) = \sigma_\mathbf{Q}$, and

$$\sigma_\mathbf{Q} = \left(\frac{\mathcal{J}(\mathbf{Q}) - 2A_\xi}{4J^2 B_{\xi\xi}}\right)^{1/2} \quad ; \quad \varphi_\xi - \varphi_\eta = \pm\frac{\pi}{2}, \qquad (2.1.26a)$$

corresponding to the helical ordering:

$$\begin{aligned} \langle J_{i\xi}\rangle &= J\sigma_\mathbf{Q}\cos(\mathbf{Q}\cdot\mathbf{R}_i + \varphi) \\ \langle J_{i\eta}\rangle &= \pm J\sigma_\mathbf{Q}\sin(\mathbf{Q}\cdot\mathbf{R}_i + \varphi). \end{aligned} \qquad (2.1.26b)$$

The length of the angular-momentum vector is $J\sigma_\mathbf{Q}$, independent of the site considered. There are two energetically-degenerate configurations, a right- or a left-handed screw, depending on the choice of sign. From the condition $1/\chi_{\xi\xi}(\mathbf{Q},0) \propto (T - T_N)$, sufficiently close to T_N, we get the usual MF result that the order parameter $\sigma_{\mathbf{Q}} \propto (T_N - T)^{1/2}$. Although $1/\chi_{\xi\xi}(\mathbf{Q},0)$ becomes negative below T_N, the inverse of the actual susceptibility, $1/\chi_{\xi\xi}(\mathbf{Q}) = 1/\chi_{\xi\xi}(\mathbf{Q},\sigma_{\mathbf{Q}})$, does not. Analogously to the derivation of A_α in (2.1.21*a*), it may be seen that $1/\chi_{\xi\xi}(\mathbf{Q})$ is a second derivative of the free energy, i.e.

$$
\begin{aligned}
1/\chi_{\xi\xi}(\mathbf{Q}) &= \partial^2 f/\partial(J\sigma_{\mathbf{Q}})^2 \\
&\simeq 1/\chi_{\xi\xi}(\mathbf{Q},\sigma=0) + 12J^2 B_{\xi\xi}\sigma_{\mathbf{Q}}^2 = -2/\chi_{\xi\xi}(\mathbf{Q},\sigma=0).
\end{aligned}
$$

Hence, $1/\chi_{\xi\xi}(\mathbf{Q})$ is non-negative, as it must be to ensure that the system is stable, as is also the case for any other component of the susceptibility.

Because $|\langle \mathbf{J}_i\rangle|$ is constant, the *umklapp* contributions to the free energy in (2.1.24), for which $4Q$ is a multiple of the reciprocal-lattice parameter $4\pi/c$, cancel. The free energy of the helix is therefore independent of the lattice, at least to the fourth power in the magnetization. If the anisotropy terms in $\mathcal{H}_{\rm cf}$ can be neglected, the helix is the most stable configuration satisfying the condition that $|\langle \mathbf{J}_i\rangle| = J\sigma$ is constant. With this constraint, only the two-ion interaction term in the free energy (2.1.22) may vary, and this may be minimized by the method of Lagrange multipliers (Nagamiya 1967). We will begin with the weaker constraint; $\sum_i \langle \mathbf{J}_i\rangle^2 = N(J\sigma)^2$ is constant, which means that we have to minimize the energy expression

$$
\begin{aligned}
U &= -\frac{1}{2}\sum_{ij}\mathcal{J}(ij)\langle \mathbf{J}_i\rangle\cdot\langle \mathbf{J}_j\rangle + \lambda\sum_i \big(\langle \mathbf{J}_i\rangle^2 - (J\sigma)^2\big) \\
&= N\sum_{\mathbf{q}}\big\{-\tfrac{1}{2}\mathcal{J}(\mathbf{q}) + \lambda\big\}\langle \mathbf{J}(\mathbf{q})\rangle\cdot\langle \mathbf{J}(-\mathbf{q})\rangle - N\lambda(J\sigma)^2,
\end{aligned}
\tag{2.1.27a}
$$

where the introduction of $\langle \mathbf{J}_i\rangle = \sum_{\mathbf{q}}\langle \mathbf{J}(\mathbf{q})\rangle \exp(i\mathbf{q}\cdot\mathbf{R}_i)$, as in (2.1.10*c*), yields the second form. Minimizing this expression with respect to $\langle \mathbf{J}(-\mathbf{q})\rangle$, we obtain the following equation:

$$
\partial U/\partial\langle \mathbf{J}(-\mathbf{q})\rangle = N\big\{-\mathcal{J}(\mathbf{q}) + 2\lambda\big\}\langle \mathbf{J}(\mathbf{q})\rangle = 0,
$$

assuming $\mathcal{J}(-\mathbf{q}) = \mathcal{J}(\mathbf{q})$. For a given value of λ, this condition is only satisfied if either $\langle \mathbf{J}(\mathbf{q})\rangle = \mathbf{0}$, or if $\mathbf{q} = \mathbf{q}_\lambda$, where $\mathcal{J}(\mathbf{q}_\lambda) = 2\lambda$, which implies that only $\langle \mathbf{J}(\mathbf{q}_\lambda)\rangle$ may be non-zero. Introducing this condition in U, we find

$$
U = -N\lambda(J\sigma)^2 = -\tfrac{1}{2}N\mathcal{J}(\mathbf{q}_\lambda)(J\sigma)^2, \tag{2.1.27b}
$$

which is then minimized with respect to $\mathbf{q}$ when $\mathbf{q}_\lambda = \mathbf{Q}$, at which wave-vector $\mathcal{J}(\mathbf{q})$ has its maximum. Hence the two-ion energy attains its minimum when only the two Fourier components $\langle \mathbf{J}_i(\pm\mathbf{Q})\rangle$ are non-zero. The stronger constraint that $|\langle \mathbf{J}_i\rangle|$ should be constant is then met only by the helix (2.1.26). In the zero-temperature limit, this constraint derives from the fact that the moments attain their saturation value, $|\langle \mathbf{J}_i\rangle| = J$, immediately the exchange field is not identically zero, since $\chi^o_{\alpha\alpha}(\sigma = 0)$ diverges in this limit when $\mathcal{H}_{\mathrm{cf}} = 0$. At elevated temperatures, it is clear that the sum of the single-ion terms in the free energy (the A- and B-terms in (2.1.22)) is most effectively minimized if the minimum condition is the same for all the ions. When $\mathcal{H}_{\mathrm{cf}} = 0$, there are no restrictions on the plane in which the moments spiral; it may be rotated freely, without change in energy, as long as $|\mathbf{J}_i|$ is constant and all the components vary with the wave-vector $\mathbf{Q}$. This behaviour is analogous to that of the Heisenberg ferromagnet, which may be considered as a helically ordered system with $\mathbf{Q} = \mathbf{0}$. If $\mathbf{Q}$ is not perpendicular to the plane in which the moments lie, the structure is called the *tilted helix* (Elliott 1971; Sherrington 1972) and the extreme case, with $\mathbf{Q}$ in the plane of the moments, is the *cycloidal structure.* When $B^0_2 > 0$, the orientation of the plane is stabilized to be perpendicular to the c-axis, and with $\mathbf{Q}$ along this axis we obtain the true helical structure.

If $B^0_2 > 0$ is the only crystal-field parameter of importance, the regular helix is the stable structure in the whole temperature interval between zero and T_N. If the Landau expansion (2.1.22) is continued to the sixth power in the magnetization, a term appears proportional to B^6_6, distinguishing between the a- and b-directions in the basal-plane. Instead of using this expansion, we shall consider the alternative expression for the free energy, to leading order in B^6_6,

$$\begin{aligned} F &\simeq F_1 - \frac{1}{2}\sum_{ij}\mathcal{J}(ij)\langle \mathbf{J}_i\rangle\cdot\langle \mathbf{J}_j\rangle + \sum_i B^6_6\langle O^6_6(\mathbf{J}_i)\rangle \\ &= F_1 - \frac{1}{2}\sum_{ij}(J\sigma)^2\mathcal{J}(ij)\cos(\phi_i - \phi_j) + \sum_i \kappa^6_6\cos 6\phi_i, \end{aligned} \tag{2.1.28}$$

where $\mathbf{J}_i = J\sigma(\cos\phi_i, \sin\phi_i, 0)$ and F_1 is the part independent of ϕ_i. The expectation values are those obtained in the limit $B^6_6 = 0$, i.e. σ and κ^6_6 are assumed to be independent of the angle ϕ_i. The presence of the six-fold anisotropy term distorts the helix. In order to solve the equilibrium equation

$$\partial F/\partial\phi_i = (J\sigma)^2\sum_j \mathcal{J}(ij)\sin(\phi_i - \phi_j) - 6\kappa^6_6\sin 6\phi_i = 0,$$

we introduce the expansion

$$\phi_i = u_i + \gamma\sin 6u_i + \cdots \qquad ; \quad u_i = \mathbf{Q}\cdot\mathbf{R}_i, \tag{2.1.29a}$$

using the series

$$\begin{aligned}\exp[&i(u+\gamma\sin 6u)]\\ &= J_0(\gamma)e^{iu} + J_1(\gamma)\big(e^{i7u} - e^{-i5u}\big) + J_2(\gamma)\big(e^{i13u} + e^{-i11u}\big) + \cdots\\ &\simeq e^{iu} + \frac{\gamma}{2}\big(e^{i7u} - e^{-i5u}\big), \qquad (2.1.29b)\end{aligned}$$

where $J_n(x)$ are the Bessel functions. To leading order in γ, the equilibrium equation then gives

$$\gamma = \frac{12\kappa_6^6}{(J\sigma)^2\big\{2\mathcal{J}(\mathbf{Q}) - \mathcal{J}(5\mathbf{Q}) - \mathcal{J}(7\mathbf{Q})\big\}}, \qquad (2.1.30a)$$

and the free energy is reduced proportionally to γ^2:

$$F/N = F_1/N - \tfrac{1}{2}(J\sigma)^2\mathcal{J}(\mathbf{Q}) - \tfrac{1}{8}(J\sigma)^2\big\{2\mathcal{J}(\mathbf{Q}) - \mathcal{J}(5\mathbf{Q}) - \mathcal{J}(7\mathbf{Q})\big\}\gamma^2. \qquad (2.1.30b)$$

The hexagonal anisotropy introduces harmonics, of equal magnitude, in the basal-plane moments at the wave-vectors $6\mathbf{Q} \pm \mathbf{Q}$ and, in higher order, at the wave-vectors $6m\mathbf{Q} \pm \mathbf{Q}$. If κ_6^6, and thus also γ, are negative, the easy directions in the plane are the a-axes. In the special case where the angle $u_i = \pi/12$, i.e. the unperturbed ith moment is half-way between an easy and a hard direction, the largest change $\phi_i - u_i = \gamma$ occurs in the orientation of the moments, and the angle to the nearest easy direction is reduced, since u_i lies between 0 and $\pi/6$, and κ_6^6 is negative. The moments in the helix are therefore distorted so that they bunch around the easy axes.

The above calculation is not valid if Q is 0 or $2\pi/c$, when the hexagonal anisotropy may be minimized without increasing the exchange energy, as it may also if the (average) turn angle ω of the moments from one hexagonal plane to the next is a multiple of $60°$, so that $6Q$ is an integer times $4\pi/c$. The products of the fifth and seventh harmonics introduce additional umklapp contributions to the free energy if $12Q$ is a multiple of the *effective* reciprocal-lattice spacing $4\pi/c$, implying that the cases where ω is $p30°$ and $p = 1, 3, 5$ are also special. In higher order, corrections appear whenever $m12Q = p4\pi/c$, where m and p are integers and $0 \leq p \leq 6m$, i.e. at any commensurable value of Q, but the corrections decrease rapidly with m, excluding cases where m and p have common factors. In contrast to the result found above, the commensurable contributions depend on the absolute phase φ in (2.1.26b), and an adjustment of this phase will quite generally allow the system to reduce the anisotropy energy through the umklapp terms. This change in energy may compensate for the increase in the exchange energy when the ordering wave-vector $\mathbf{Q}$ is changed from its value $\mathbf{Q} = \mathbf{Q}_0$, at which

$\mathcal{J}(\mathbf{q})$ has its maximum, to a nearby commensurable value $\mathbf{Q}_c$. Hence the hexagonal anisotropy couples the helical magnetic structure to the lattice, and it may induce continuous or abrupt changes of the ordering wave-vector as a function of temperature, as discussed, for instance, by Bak (1982). In Ho, $12Q_0$ is close to $4\pi/c$, and the hexagonal anisotropy is large at low temperatures. Experimental investigations have shown that a number of commensurable values of $\mathbf{Q}$ are stabilized in this system, as we shall discuss in more detail in the last section of this chapter.

2.1.4 Longitudinally ordered phases

When B_2^0 is negative, as in Er and Tm, $\chi_{\zeta\zeta}(\mathbf{Q})$ is the component of the susceptibility which diverges at the highest temperature, and the high-temperature expansion predicts that $2A_\zeta - \mathcal{J}(\mathbf{Q})$ vanishes at a critical temperature determined by

$$k_BT_N \simeq \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{Q})\big[1-\tfrac{4}{5}(J-\tfrac{1}{2})(J+\tfrac{3}{2})B_2^0/k_BT_N\big]. \qquad (2.1.31)$$

Just below this temperature, only the component σ_ζ at the wave-vector $\mathbf{Q}$ is non-zero and, from the free energy expansion (2.1.24), $\partial f/\partial\sigma_\zeta = 0$ determines the relative magnetization as

$$\sigma_\zeta(\mathbf{Q}) = \sigma_{\mathbf{Q}} = \left(\frac{\mathcal{J}(\mathbf{Q})-2A_\zeta}{3J^2B_{\zeta\zeta}}\right)^{1/2}. \qquad (2.1.32)$$

The free energy is independent of the phase $\varphi = \varphi_\zeta$, so we set $\varphi = 0$. If we add another Fourier component with $\mathbf{q} \neq \pm\mathbf{Q}$:

$$\langle J_{i\zeta}\rangle = J\sigma_{\mathbf{Q}}\cos(\mathbf{Q}\cdot\mathbf{R}_i) + J\sigma_{\mathbf{q}}\cos(\mathbf{q}\cdot\mathbf{R}_i+\varphi') \qquad (2.1.33)$$

then, if $m\mathbf{Q} \pm n\mathbf{q}$ is different from a reciprocal lattice vector, where m and n are integers and $m+n=\pm 4$, the free energy is

$$f = \tfrac{1}{4}J^2\big[\{2A_\zeta-\mathcal{J}(\mathbf{Q})\}\sigma_{\mathbf{Q}}^2 + \{2A_\zeta-\mathcal{J}(\mathbf{q})\}\sigma_{\mathbf{q}}^2\big] + \tfrac{1}{8}J^4B_{\zeta\zeta}\big[3\sigma_{\mathbf{Q}}^4+3\sigma_{\mathbf{q}}^4$$
$$+\,12\sigma_{\mathbf{Q}}^2\sigma_{\mathbf{q}}^2 + 4\sigma_{\mathbf{Q}}^3\sigma_{\mathbf{q}}\delta_{\mathbf{q},\pm3\mathbf{Q}}\cos\varphi' + 4\sigma_{\mathbf{Q}}\sigma_{\mathbf{q}}^3\delta_{3\mathbf{q},\pm\mathbf{Q}}\cos3\varphi'\big]. \qquad (2.1.34)$$

This result shows that, if $\mathbf{q} = 3\mathbf{Q}$ or $\mathbf{q} = \frac{1}{3}\mathbf{Q}$, there is an extra fourth-order contribution to the free energy ($\mathbf{q} \to -\mathbf{q}$ represents the same structure with $\varphi' \to -\varphi'$). Of these two special cases, the one where $\mathbf{q} = 3\mathbf{Q}$ is the most interesting, because the extra term is linear in $\sigma_{3\mathbf{Q}}$. This means that the third harmonic appears simultaneously with the basic Fourier component at $\mathbf{Q}$. Minimizing the free energy given by (2.1.34), we find

$$\sigma_{3\mathbf{Q}} = \frac{J^2B_{\zeta\zeta}}{\mathcal{J}(\mathbf{Q})-\mathcal{J}(3\mathbf{Q})}\sigma_{\mathbf{Q}}^3 \quad ; \quad \varphi' = \varphi+\pi, \qquad (2.1.35a)$$

neglecting a term proportional to $\sigma_{\mathbf{Q}}^2$ in the denominator. The 3**Q**-component is thus proportional to $\sigma_{\mathbf{Q}}^3$, and hence to $(T_N - T)^{3/2}$. Denoting the wave-vector at which $\mathcal{J}(\mathbf{q})$ has its maximum by $\mathbf{Q}_0$, we conclude that the appearance of the third harmonic implies that f has its minimum at a value of $\mathbf{Q}$ slightly different from $\mathbf{Q}_0$. Minimizing the free energy with respect to $\mathbf{Q}$ along the c-axis, by requiring $\partial f/\partial Q = 0$, we obtain to leading order

$$Q = Q_0 - 3\frac{\mathcal{J}'(3\mathbf{Q}_0)}{\mathcal{J}''(\mathbf{Q}_0)}\left(\frac{\sigma_{3\mathbf{Q}}}{\sigma_{\mathbf{Q}}}\right)^2. \tag{2.1.35b}$$

$\mathcal{J}''(\mathbf{Q}_0)$ is negative, so the shift $Q - Q_0$ has the same sign as $\mathcal{J}'(3\mathbf{Q}_0)$ and is proportional to $(T_N - T)^2$. The other special case, $3\mathbf{q} = \mathbf{Q}$, reflects the possibility that, if $\mathcal{J}(\mathbf{Q}_0/3)$ is close to $\mathcal{J}(\mathbf{Q}_0)$, the system may reduce its energy by making a *first order* transition to a state where $\mathbf{Q} \simeq \mathbf{Q}_0/3$ is the fundamental wave-vector, with the third harmonic being close to $\mathbf{Q}_0$. The presence of a term in the free energy cubic in the order parameter, $\sigma_{\mathbf{Q}/3}$ in this case, implies that the transition becomes of first order, so that the order parameter changes discontinuously from zero to a finite value. The $\mathbf{Q}_0/3$-transition appears to be of no importance in real systems, so we shall return to the discussion of the other case. If the free energy is expanded to higher (even) powers in the relative magnetization, it is clear that the $(2n + 2)$-power term leads to a contribution proportional to $\sigma_{(2n+1)\mathbf{Q}}\sigma_{\mathbf{Q}}^{2n+1}$ which, in combination with the term quadratic in $\sigma_{(2n+1)\mathbf{Q}}$, implies that the ordering at the fundamental wave-vector $\mathbf{Q}$ induces a $(2n + 1)$-harmonic proportional to $\sigma_{\mathbf{Q}}^{2n+1} \propto (T_N - T)^{(2n+1)/2}$. Starting as a pure sinusoidally modulated wave at T_N, the moments approach the *square wave*

$$\langle J_{i\zeta}\rangle = \frac{4J}{\pi}\big(\cos x - \tfrac{1}{3}\cos 3x + \tfrac{1}{5}\cos 5x - \tfrac{1}{7}\cos 7x + \cdots\big)_{x=\mathbf{Q}\cdot\mathbf{R}_i+\varphi}, \tag{2.1.36a}$$

in the limit of zero temperature where $\langle J_{i\zeta}\rangle = \pm J$, neglecting strong anisotropy effects. Although the behaviour of the angular momentum is simple, the dependence of the free energy on the wave-vector is complicated. It is only when the ordering is incommensurable, i.e. mQ is different from any multiple of the length $4\pi/c$ of the reciprocal-lattice vector along the c-axis, that the energy of the square-wave structure at $T = 0$ is

$$f(0) = \langle\mathcal{H}_{\mathrm{cf}}\rangle - \frac{4J^2}{\pi^2}\big\{\mathcal{J}(\mathbf{Q}) + \tfrac{1}{9}\mathcal{J}(3\mathbf{Q}) + \tfrac{1}{25}\mathcal{J}(5\mathbf{Q}) + \cdots\big\}. \tag{2.1.36b}$$

An infinitesimal change of the ordering wave-vector from $\mathbf{Q}$, which minimizes $f(0)$, to $\mathbf{Q}_c$ may make it commensurable with the lattice, so that

$mQ_c = p(4\pi/c)$ and additional umklapp terms contribute to the free energy. Again these contributions depend on the absolute phase φ, and there will always be values of Q_c close to Q leading to a lower free energy than that obtained in the incommensurable case. In the low-temperature limit, the modulation of the c-axis moment is therefore locked to the lattice periodicity. This tendency is already apparent close to T_N. In the expansion of the free energy considered above for $m = 4$, umklapp terms modify the fourth-power coefficient, and analogous effects occur in higher powers of the magnetization. This indicates that the system may stay commensurable even near T_N although, in the close neighbourhood of T_N, the critical fluctuations neglected here may oppose this tendency. The optimal value of Q_c may change as a function of temperature, in which case the system will exhibit a number of first-order, or possibly continuous, transitions from one commensurable structure to another. Of these structures, those for which $Q_c = 3Q_c = 5Q_c = \cdots$, i.e. $Q_c = 0$ or $2\pi/c$, are particularly stable, as they only involve one wave-vector, so that $f(0) = \langle \mathcal{H}_{\rm cf} \rangle - \frac{1}{2} J^2 \mathcal{J}(\mathbf{Q}_c)$ (in this connection, we note that $1 + \frac{1}{9} + \frac{1}{25} + \cdots = \pi^2/8$). The anisotropic Ising-model with competing interactions, the so-called *ANNNI* model, is a simplified version of the above, and it shows a rich variety of different incommensurable, commensurable, and chaotic ordered structures as a function of temperature and the coupling parameters (Bak 1982).

2.1.5 Competing interactions and structures

The complex behaviour of the longitudinally ordered phase is a consequence of the competition between the single-ion part of the free energy, which favours a structure in which the magnitude of the moments varies as little as possible, particularly at low temperature, and the two-ion contributions, which prefer a single-$\mathbf{Q}$ ordering. When B_2^0 is positive, helical ordering satisfies both tendencies without conflict. This points to another alternative which the longitudinal system may choose. Although $\chi_{\zeta\zeta}(\mathbf{Q})$ decreases below T_N, the two perpendicular components continue to increase, and they may therefore diverge at a lower temperature T_N'. Assuming the expansion (2.1.24) of the free energy still to be valid at T_N', and neglecting the third and higher harmonics of $\langle J_{i\zeta} \rangle$, we may write it:

$$f = f(\sigma_{\mathbf{Q}}) + \tfrac{1}{4} J^2 \sum_{\alpha=\xi,\eta} \big[2A_\xi - \mathcal{J}(\mathbf{Q}) + B_{\xi\zeta}(J\sigma_{\mathbf{Q}})^2 \{2 + \cos 2(\varphi_\alpha - \varphi)\} \big] \sigma_\alpha^2 + \tfrac{1}{8} J^4 B_{\xi\xi} \big[3\sigma_\xi^4 + 3\sigma_\eta^4 + 2\{2 + \cos 2(\varphi_\xi - \varphi_\eta)\} \sigma_\xi^2 \sigma_\eta^2 \big]. \quad (2.1.37)$$

The effective coefficient of σ_α^2 ($\alpha = \xi$ or η) is smallest when $\varphi_\alpha = \varphi \pm \frac{\pi}{2}$, meaning that the basal-plane moments appearing just below T_N', where this coefficient vanishes, are locked to be out of phase by 90° with the c-axis component. This phase difference arises because the transverse MF susceptibility $\chi^o_{\xi\xi}$ for the single sites increases as the c-axis exchange field falls. Using the estimate (2.1.21b) for the B-tensor, and the high-temperature value for A_ξ, we find the transition temperature to be

$$\begin{aligned} k_BT'_N \simeq \tfrac{1}{3}J(J+1)\mathcal{J}(\mathbf{Q})\Big[1 + \tfrac{2}{5}(J-\tfrac{1}{2})(J+\tfrac{3}{2})B^0_2/k_BT'_N \\ - \tfrac{3}{20}\{1+\tfrac{1}{2}(J+1)^{-2}\}\sigma^2_{\mathbf{Q}}\Big]. \end{aligned} \tag{2.1.38}$$

A slightly better estimate may be obtained by calculating the MF value of the transverse susceptibility directly, in the presence of a non-zero exchange field, which just causes the replacement of $\sigma_{\mathbf{Q}}$ in (2.1.38) by $3\sigma_{\mathbf{Q}}\mathcal{J}(\mathbf{Q})/[J(J+1)k_BT'_N]$ (Miwa and Yosida 1961). However, both results are based on the high-temperature expansion, which ceases to be valid at low temperatures. In the zero-temperature limit, $\chi^o_{\xi\xi}$ of the ith site remains finite, being of the order $J/h^{\text{eff}}_{i\zeta}$. This saturation implies that the transition does not necessarily occur. If the c-axis is favoured too strongly by the anisotropy terms, the basal-plane components remain disordered at low temperatures, as is observed in Tm. When the basal-plane moments order, as in Er, eqn (2.1.38) may give a reasonable estimate of the transition temperature. As mentioned previously, the modulation of the basal-plane moments, just below T'_N, is locked at 90° out of phase with that of the c-axis component. Since this applies to both components, only a linearly-polarized moment can develop at the transition temperature, with a relative magnitude $\sigma_\perp = (\sigma^2_\xi + \sigma^2_\eta)^{1/2}$, in a specified but arbitrary direction in the plane. If the sixth-power terms are included in the free energy, B^6_6 favours either the a- or the b-directions, but there are still six equivalent but different directions of the moments in the basal plane with equal energies. To be specific, we may assume that B^6_6 is negative and that the ordered moments in the basal plane establish themselves along the ξ-axis. In this case, the moments all lie in the ξ–ζ plane in an elliptic cycloidal structure. Displaced to a common origin, the hodograph of the moments is an ellipse, with its principal axes along the ξ- and ζ-axes, as is illustrated, in connection with our discussion of Er, in Fig. 2.6 on page 120. The c-axis moments will still show a strong tendency towards squaring up with decreasing temperature, as long as they are large compared with the basal-plane moments. Because of the phase-locking between the components, the higher odd-harmonics in the modulation of the c-axis moments will also be reflected in the basal-plane.

At high temperatures, B^0_2 is the dominant anisotropy parameter, and its sign determines whether the system orders in a helically or longitudinally polarized structure, when $\mathbf{Q}_0$ is along the c-axis. If B^0_2 is still the most important axial-anisotropy parameter in the low-temperature limit, the helix is still a stable structure at $T = 0$ whereas, in the longitudinally polarized case, the tendency to minimize the variation of the lengths of the moments may result in two different paths. Either the system stays in the longitudinally polarized phase, ending up as a (commensurable) square-wave structure at $T = 0$, or it goes through a transition to an elliptic cycloidal structure. The path which is chosen depends on the magnitude of B_2^0; if the effective axial anisotropy $-B_2^0\langle O_2^0\rangle$ is sufficiently large, the ordering of the basal-plane moments is quenched. It has already been mentioned in Section 1.5 that this anisotropy depends on the magnetization, being proportional approximately to σ^3. We shall discuss this renormalization in more detail in the next section, but it is worth mentioning here that this behaviour of the effective anisotropy-parameter means that there is an intermediate range of B_2^0 for which the system makes a transition to the elliptic cycloidal structure, but leaves it again at a lower temperature, by returning to the longitudinally polarized phase when $-B_2^0\langle O_2^0\rangle$ becomes large enough. When B_4^0 and B_6^0 are included, a more realistic situation may occur, in which the low-temperature anisotropy favours an orientation of the moments making an angle θ with the c-axis, which is neither 0 or $\pi/2$ but some, temperature-dependent, intermediate value. In the case of the helix, this means that there will be a critical temperature T_N' (below T_N) where the effective axial anisotropy parameter vanishes, and below which the c-axis moments are ordered. If the ordering wave-vector for the c-axis component is the same as the helical wave-vector, the structure adopted is the tilted helix. However the two-ion coupling between the c-axis moments, $\mathcal{J}_\parallel(\mathbf{q})$ with $\mathbf{q} \parallel c$-axis, is not restricted by any symmetry argument to be equal to the coupling between the basal-plane moments, $\mathcal{J}_\perp(\mathbf{q}) = \mathcal{J}(\mathbf{q})$ with its maximum at $\mathbf{q} = \mathbf{Q}_0$. If the maximum of $\mathcal{J}_\parallel(\mathbf{q})$ lies at a $\mathbf{q} \neq \mathbf{Q}_0$, the c-component will order at this wave-vector and not at $\mathbf{Q}_0$, as the extra energy gained by the c-component by locking to the basal-plane moments is very small, being proportional to $\{B_6^6\langle O_6^6\rangle/(J\sigma)^2\mathcal{J}(\mathbf{Q})\}^2$. When B_2^0 is negative, a non-zero value of θ favours the elliptic cycloidal structure, compared to the longitudinally polarized phase. If the system is already in the cycloidal phase, it may undergo a new second-order transition, in which the plane of the ellipse starts to tilt away from the ξ–ζ plane, in close correspondence with the behaviour of the helix. Referring back to eqn (2.1.37), we observe that this transition occurs when the coefficient of σ_η^2, with $\varphi_\eta = \varphi\,(+\pi) = \varphi_\xi \pm \pi/2$, becomes zero. The phase-locking energy, comprising the terms in (2.1.37) involving φ_η, is more important in this case than in the helix, but it is nevertheless possible that the third component may order at a wave-vector different from that of the other two. If the η-component is locked at the same wave-vector as the two other components, and if the ellipse is tilted just such an amount that $\sigma_\eta = \sigma_\xi$, the structure is a helix superimposed on a modulated c-axis moment. If a transition to the tilted cycloidal structure has occurred, and the hexagonal anisotropy is small, it might be favourable for the system at a lower temperature to pass directly, via a first-order transition, to this helical structure in which the c-axis component is no longer phase-locked to the basal-plane moments.

Instead of basing our analysis on the Hamiltonian (2.1.1), we may use symmetry arguments for deriving the most general behaviour of the magnetic ordering in hcp crystals. We have already indicated that $\mathcal{J}_\parallel(\mathbf{q})$ may differ from $\mathcal{J}_\perp(\mathbf{q})$ and mentioned some of the consequences. The assumption that the c-axis is effectively a six-fold axis of the lattice leads to the strong restriction that the expansion of the free energy, (2.1.22) or (2.1.24), only involves even powers of each of the Cartesian components, when $\mathbf{q}$ is along this axis. This has the consequence, for example, that all the main transitions, at T_N or T'_N, are predicted to be of second order, excluding those involving changes of the same component, i.e. transitions between different commensurable structures. However, there are two-ion terms which reflect the fact that the c-axis is only a three-fold axis. The term of lowest rank has the form

$$\begin{aligned}\mathcal{H}_3(i \in s\text{'th plane}) = (-1)^s K_3\Big[&(J_{i\zeta} - \tfrac{1}{2}\langle J_{i\zeta}\rangle)\big\langle O_3^{-3}(\mathbf{J}_{s+1}) - O_3^{-3}(\mathbf{J}_{s-1})\big\rangle \\ &+ (O_3^{-3}(\mathbf{J}_i) - \tfrac{1}{2}\langle O_3^{-3}(\mathbf{J}_i)\rangle)\big\langle J_{s+1,\zeta} - J_{s-1,\zeta}\big\rangle\Big], \qquad (2.1.39)\end{aligned}$$

in the MF approximation, where only interactions between neighbouring planes are included. $O_3^{-3} = (J_+^3 - J_-^3)/2i$, and $\mathbf{J}_{s\pm1}$ denotes a moment in the $(s\pm1)$th plane. The contribution of this coupling to the expansion (2.1.22) of the free energy to the fourth power is found by adding $\sum_i \langle\mathcal{H}_3\rangle$ to F, using the approximation $\langle O_3^{-3}(\mathbf{J}_i)\rangle \propto \langle J_{i\eta}\rangle(3\langle J_{i\xi}\rangle^2 - \langle J_{i\eta}\rangle^2) = \langle J_\perp\rangle^3 \sin 3\phi_i$. One remarkable effect is that this coupling introduces a term linear in $\langle J_{i\zeta}\rangle$ in the helix. If the basal-plane moments are ordered with the wave-vector $\mathbf{Q}$, they induce a c-axis moment modulated with a wave-vector along the c-axis of length $2\pi/c - 3Q$, provided that $6\mathbf{Q}$ is not a reciprocal lattice vector. In the elliptic cycloidal structure, this coupling induces an ordering of the η-component at the two wave-vectors of length $2\pi/c - Q$ and $2\pi/c - 3Q$, when the ellipse is assumed to lie in the ξ–ζ plane and only the fundamental at Q is considered. Although this additional coupling may not change the nature of the transitions at T_N or T'_N, it has qualitative consequences for the magnetic structures, and it may introduce new effects associated with commensurability. For instance, the three-fold symmetrical interaction will favour the commensurable structure with $Q = \pi/2c$ (an average turn angle of 45°). In the case of a helix with this particular period, the coupling induces a modulation of the c-axis moments with the same wave-vector, $2\pi/c - 3Q = Q$, causing a tilting of the plane of the helix.

2.1.6 Multiply periodic structures

We have so far only considered order parameters which are specified by two $\mathbf{Q}$-vectors ($\pm\mathbf{Q}$), or one $\mathbf{Q}$ plus a phase. This is a consequence of the assumption that $\mathbf{Q}$ is along the c-axis. If $\mathbf{Q}$ is in the basal-plane, as in the light rare earths Pr and Nd, there are six equivalent ordering wave-vectors, $\pm\mathbf{Q}_1$, $\pm\mathbf{Q}_2$, and $\pm\mathbf{Q}_3$, where the three vectors make an angle of 120° with each other. This leads to the possibility that the ordered structure is a *multiple*-$\mathbf{Q}$ *structure*, where

$$\langle \mathbf{J}_i \rangle = \mathbf{J}_1 \cos(\mathbf{Q}_1 \cdot \mathbf{R}_i + \varphi_1) + \mathbf{J}_2 \cos(\mathbf{Q}_2 \cdot \mathbf{R}_i + \varphi_2) + \mathbf{J}_3 \cos(\mathbf{Q}_3 \cdot \mathbf{R}_i + \varphi_3) \tag{2.1.40}$$

referred to as *single-, double-,* or *triple*-$\mathbf{Q}$ ordering, depending on the number of vectors $\mathbf{J}_p$ which are non-zero. The transition at T_N will generally involve only a single real vector $\mathbf{J}_p$ for each $\mathbf{Q}_p$, as implicitly assumed in (2.1.40). We will not therefore consider multiple-$\mathbf{Q}$ cycloidal/helical structures, but restrict the discussion to configurations which correspond to the type observed in Pr or Nd. We furthermore neglect the complications due to the occurrence of different sublattices in the dhcp crystals, by assuming the lattice to be primitive hexagonal. This simplification does not affect the description of the main features of the magnetic structures. On the hexagonal sites of Pr and Nd, the ordered moments below T_N lie in the basal plane. This confinement is not primarily determined by the sign of B_2^0, but is decisively influenced by the anisotropic two-ion coupling

$$\mathcal{H}_{\rm an} = \frac{1}{2} \sum_{ij} \mathcal{K}(ij) \big[(J_{i\xi} J_{j\xi} - J_{i\eta} J_{j\eta}) \cos 2\phi_{ij} + (J_{i\xi} J_{j\eta} + J_{i\eta} J_{j\xi}) \sin 2\phi_{ij} \big], \tag{2.1.41}$$

where ϕ_{ij} is the angle between the ξ-axis and the projection of $\mathbf{R}_i - \mathbf{R}_j$ on the basal plane. This anisotropic coupling, which includes a minor contribution from the classical dipole–dipole interaction, is known from the excitation spectrum to be of the same order of magnitude as the isotropic coupling in Pr, as we shall discuss in Chapter 7, and must be of comparable importance in Nd. We define the coupling parameter $\mathcal{K}(\mathbf{q}) = \mathcal{K}_0(q) + \mathcal{K}_6(q) \cos 6\psi_q$, where ψ_q is the angle between $\mathbf{q}$ (in the basal plane) and the ξ-axis, and $\mathcal{K}_0(q) \pm \mathcal{K}_6(q)$ is the Fourier transform of $\pm\mathcal{K}(ij) \cos 2\phi_{ij}$ when $\mathbf{q}$ is respectively parallel or perpendicular to the ξ-axis. Introducing $\mathbf{J}_p = J\boldsymbol{\sigma}_p$, and assuming the moments to be perpendicular to the c-axis, we find the mean-field free energy of second order in σ_p to be

$$f_2(\sigma_p) = \tfrac{1}{4}J^2 \sum_p \big[\{2A_\xi - \mathcal{J}(\mathbf{Q}_p)\}\sigma_p^2 + \mathcal{K}(\mathbf{Q}_p)\{2(\boldsymbol{\sigma}_p\cdot\hat{\mathbf{Q}}_p)^2 - \sigma_p^2\}\big], \tag{2.1.42}$$

where $\hat{\mathbf{Q}}_p = \mathbf{Q}_p/Q_p$. In Pr and Nd, the maximum of $\mathcal{J}(\mathbf{q}) \pm \mathcal{K}(\mathbf{q})$ is found at $\mathbf{q} = \mathbf{Q}$ along the η-axis, or the other equivalent b-axes, with Q being about one fourth of the distance to the Brillouin-zone boundary, and $\mathcal{K}(\mathbf{Q})$ is negative. The transition between the paramagnetic phase and a phase described by (2.1.40), with $\mathbf{J}_p$ lying in the hexagonal plane, then occurs when the coefficient $2A_\xi - \mathcal{J}(\mathbf{Q}) + \mathcal{K}(\mathbf{Q})$ vanishes, at which temperature the corresponding factor for the c-component of the moments, $2A_\zeta - \mathcal{J}(\mathbf{Q})$, is still positive in Pr and Nd. Besides confining the moments to the hexagonal planes, $\mathcal{K}(\mathbf{Q})$ also removes the degeneracy between the two states in which $\mathbf{J}_p$ is parallel or perpendicular to $\mathbf{Q}_p$. With a negative $\mathcal{K}(\mathbf{Q})$, the anisotropic coupling favours a longitudinal ordering of the moments at T_N, with $\mathbf{J}_p$ parallel to $\mathbf{Q}_p$. Just below T_N, the magnitude of the ordered moments is determined by $f_2(\sigma_p)$, together with the fourth-order contributions. When the moments lie in the basal plane ($B = B_{\xi\xi} = B_{\eta\eta} = B_{\xi\eta}$), we obtain, from eqn (2.1.22),

$$\begin{aligned} f_4(\sigma_p) &= B\frac{1}{N}\sum_i \big(\langle\mathbf{J}_i\rangle\cdot\langle\mathbf{J}_i\rangle\big)^2 \\ &= BJ^4\Big[\tfrac{3}{8}\sum_p \sigma_p^4 + \tfrac{1}{4}\sum_{p\neq p'}\big\{\sigma_p^2\sigma_{p'}^2 + 2(\boldsymbol{\sigma}_p\cdot\boldsymbol{\sigma}_{p'})^2\big\}\Big]. \end{aligned} \tag{2.1.43}$$

Introducing the effective order parameter σ, defined by $\sigma^2 = \sum_p \sigma_p^2$, we obtain further:

$$f \simeq f_2(\sigma_p)+f_4(\sigma_p) = \tfrac{1}{4}J^2\big\{2A_\xi - \mathcal{J}(\mathbf{Q})+\mathcal{K}(\mathbf{Q})\big\}\,\sigma^2 + \tfrac{3}{8}J^4B\,\sigma^4, \tag{2.1.44}$$

assuming $\mathbf{J}_p$ parallel to $\mathbf{Q}_p$ along the three b-axes making an angle of 120° with each other ($\hat{\mathbf{Q}}_p\cdot\hat{\mathbf{Q}}_{p'} = -1/2$ when $p \neq p'$). Hence the free energy, in this approximation, is independent of whether the ordering is single-, double- or triple-$\mathbf{Q}$. Instead of utilizing (2.1.22), we may appeal to symmetry arguments, by which the fourth-order term may readily be seen to have the general form

$$f_4(\sigma_p) = u\sum_p \sigma_p^4 + \tfrac{1}{2}v\sum_{p\neq p'}\sigma_p^2\sigma_{p'}^2, \tag{2.1.45a}$$

as long as the angles between the different $\boldsymbol{\sigma}_p$ vectors remain at 120° (Bak and Lebech 1978). Introducing the parameter $w \equiv v - 2u$, we may write this:

$$f_4(\sigma_p) = u\big(\sum_p \sigma_p^2\big)^2 + \tfrac{1}{2}w\sum_{p\neq p'}\sigma_p^2\sigma_{p'}^2 = (u+\gamma w)\sigma^4, \tag{2.1.45b}$$

where $\gamma = 0$, 1/4, or 1/3 respectively, in a single-, double-, or triple-**Q** structure. If only an isotropic two-ion coupling and the crystal-field terms are included, $2u = v$ or $w = 0$, and the different multiple-**Q** structures are degenerate to the fourth power of the order parameter. This situation is not changed by the anisotropic dipole coupling $\mathcal{K}(\mathbf{q})$ introduced above (as long as $\boldsymbol{\sigma}_p$ is parallel to $\mathbf{Q}_p$). However, two-ion quadrupole couplings may remove the degeneracy. For example, the coupling $\mathcal{K}_2(ij)J_{i+}^2 J_{j-}^2$ makes a contribution proportional to

$$w \sim 3\mathcal{K}_2(\mathbf{0}) + \mathcal{K}_2(2\mathbf{Q}) - 2\mathcal{K}_2(\mathbf{Q}) - 2\mathcal{K}_2(\mathbf{Q}_1 - \mathbf{Q}_2). \tag{2.1.46}$$

Depending on the detailed **q**-dependence of this coupling, it may lead to a positive or a negative contribution to w. If w is positive, the single-**Q** structure is stable, and conversely a negative w leads to a triple-**Q** structure just below T_N. The Landau expansion for this case has been discussed by Forgan (1982), Walker and McEwen (1983) and McEwen and Walker (1986), who all take the possible contributions to w as being of magnetoelastic origin. In Pr, the dominating magnetoelastic interaction is known to be due to the γ-strain coupling, and a rough estimate (including both the uniform and modulated γ-strain) indicates that v is unaffected, whereas the reduction of u proportional to $B_{\gamma 2}^2/c_\gamma$, with the parameters of (1.5.27), is about 10%, corresponding to a *positive* contribution to w of about $0.2u$, or to an energy difference between the single- and double-**Q** structures of $\sim 0.05u\sigma^4$. If the other quadrupolar contributions are unimportant, as is indicated by the behaviour of the excitations in Pr (Houmann *et al.* 1979), we should expect the single-**Q** structure to be favoured in Pr and Nd, at least close to T_N.

If w is relatively small, the single- or triple-**Q** structures may only be stable in a narrow temperature range below T_N, because the sixth-order contributions may assume a decisive influence. A number of new effects appear in this order, but the most important stems from the possibility that the moments and the wave-vectors may rotate away from the b-directions, as first considered by Forgan (1982). The $(\boldsymbol{\sigma}_p \cdot \boldsymbol{\sigma}_{p'})^2$-term in (2.1.43) may drive such a rotation, because it favours an orthogonal configuration of the different $\boldsymbol{\sigma}_p$ vectors, since B is positive. This term does not appear in the single-**Q** structure, whereas in the triple-**Q** case, $f_4(\sigma_p)$ is reduced quadratically with θ_p, where θ_p is the angle between $\mathbf{J}_p$ and the nearest b-direction. However, the much larger quadratic increase of $f_2(\sigma_p)$, due to $\mathcal{K}(\mathbf{Q})$, will eliminate any tendency for θ_p to become non-zero. In contrast, $f_4(\sigma_p)$ depends linearly on θ_p in the double-**Q** structure, and the free energy can always be reduced by allowing the two components $\boldsymbol{\sigma}_1$ and $\boldsymbol{\sigma}_2$ (with $\boldsymbol{\sigma}_3 = \mathbf{0}$) to rotate towards each other. Defining $\mathcal{J}_6(Q)$ equivalently to $\mathcal{K}_6(Q)$, i.e. $\mathcal{J}(\mathbf{Q}) = \mathcal{J}_0(Q) + \mathcal{J}_6(Q)\cos 6\psi_Q$, and using the constraint that the change of ψ_Q for the pth component must have the same sign as θ_p, we may write the angular-dependent part of the free energy, to the fourth power of the magnetization, as

$$\begin{aligned} f(\theta,\psi) = \tfrac{1}{4}J^2\big[-\mathcal{J}_6(Q) + \mathcal{K}_6(Q)\cos 2(\theta-\psi)\big] \\ \times\{\sigma_1^2\cos(\pi+6\psi)+\sigma_2^2\cos(5\pi-6\psi)\} \\ +\tfrac{1}{4}J^2\mathcal{K}_0(Q)(\sigma_1^2+\sigma_2^2)\cos 2(\theta-\psi) + BJ^4\sigma_1^2\sigma_2^2\cos^2(2\pi/3-2\theta). \end{aligned} \tag{2.1.47a}$$

For definiteness, we have chosen the case where the angle between the ξ-axis and $\boldsymbol{\sigma}_1$ or $\boldsymbol{\sigma}_2$ is respectively $\pi/6+\theta$ and $5\pi/6-\theta$ (by symmetry $\theta=\theta_1=-\theta_2$). Analogously to θ, ψ is the angle between $\mathbf{Q}_p$ and the nearest b-axis. Introducing $\sigma^2 = 2\sigma_1^2 = 2\sigma_2^2$, and expanding $f(\theta,\psi)$ to second order in the small angles, we obtain

$$\begin{aligned} f(\theta,\psi) = f_0 - \tfrac{9}{2}(J\sigma)^2\{\mathcal{J}_6(Q)-\mathcal{K}_6(Q)\}\,\psi^2 - \tfrac{1}{2}(J\sigma)^2\mathcal{K}(\mathbf{Q})(\theta-\psi)^2 \\ - \tfrac{1}{4}(J\sigma)^4B(\sqrt{3}\theta-2\theta^2). \end{aligned} \tag{2.1.47b}$$

We note that, with the chosen sign conventions, $\mathcal{K}(\mathbf{Q}) = \mathcal{K}_0(Q)-\mathcal{K}_6(Q)$ and $\mathcal{J}_6(Q)-\mathcal{K}_6(Q)$ are both negative. The additional contribution to the free energy of the double-$\mathbf{Q}$ structure is minimized when

$$\theta = \frac{\sqrt{3}B(J\sigma)^2}{4|\mathcal{K}(\mathbf{Q})|}+\psi \quad ; \quad \psi = \frac{\sqrt{3}B(J\sigma)^2}{36|\mathcal{J}_6(Q)-\mathcal{K}_6(Q)|}, \tag{2.1.48a}$$

neglecting the small term proportional to $B\theta^2$, in which case

$$\Delta f = -\tfrac{3}{32}B^2(J\sigma)^6\bigg(-\frac{1}{\mathcal{K}(\mathbf{Q})}-\frac{1}{9}\frac{1}{\mathcal{J}_6(Q)-\mathcal{K}_6(Q)}\bigg). \tag{2.1.48b}$$

Introducing $A = A_\xi(T=T_N)$, i.e. $\mathcal{J}(\mathbf{Q})-\mathcal{K}(\mathbf{Q}) = 2A$, then for Pr we have: $\mathcal{K}(\mathbf{Q}) \simeq -0.24A$, $\mathcal{J}_6(Q)-\mathcal{K}_6(Q) \simeq -0.05A$, and $BJ^2 \simeq 0.35A$. These values may also provide a reasonable estimate in the case of Nd. Inserting them in (2.1.48), we find that $\theta \simeq 3\psi \simeq 1.0\sigma^2$, and $\Delta f \simeq -0.2BJ^4\sigma^6 \simeq -0.5u\sigma^6$. So, even though Δf is of sixth order in σ, it outweighs the small fourth-order energy difference of $w\sigma^4/4$ between the single- and the double-$\mathbf{Q}$ structure when $\sigma^2 \approx 0.1$, if $w \simeq 0.2u$ as estimated above. The temperature T_N' at which this occurs is $\sim 0.97\,T_N$, i.e. ~ 0.9 K below T_N in Nd. Hence, if w is positive and has the estimated small magnitude, the system will first undergo a second-order transition from the paramagnetic phase to a single-$\mathbf{Q}$ structure, which will only be stable as long as σ^2 is small. At T_N', slightly below T_N, the system will make a first-order transition to a double-$\mathbf{Q}$ structure, in which the moments $\mathbf{J}_1$ and $\mathbf{J}_2$ are rotated slightly towards each other and away from the symmetry axes, as also are the ordering wave-vectors $\mathbf{Q}_1$ and $\mathbf{Q}_2$. These rotations are proportional to σ^2.

The explicitly sixth-order contribution to the free energy, proportional to $(1/N)\sum_i(\langle\mathbf{J}_i\rangle\cdot\langle\mathbf{J}_i\rangle)^3$, is somewhat smaller than the estimated value of Δf, and it leads to energy differences between the different multiple-**Q** structures which are a further order of magnitude smaller. The hexagonal-anisotropy term, which also appears in this order, is minute compared to the anisotropy introduced by $\mathcal{K}(\mathbf{Q})$ in Pr and Nd, and its influence on the turn angles ψ and θ should be negligible. The only other new effect in this order is the appearance of higher harmonics. The mechanism is identical to that discussed in Section 2.1.4 for the longitudinally-polarized phase, but in addition to the occurrence of third harmonics at the wave-vectors $3\mathbf{Q}_p$, equivalently to (2.1.35a), they also appear at all possible combinations of $2\mathbf{Q}_p \pm \mathbf{Q}_{p'}$ $(p \neq p')$ in the multiple-**Q** structures. In the triple-**Q** structure, one might expect third harmonics also at $\mathbf{Q}_1 \pm \mathbf{Q}_2 \pm \mathbf{Q}_3$, but the new wave-vectors derived from this condition are either **0**, which changes the symmetry class of the system, or twice one of the fundamental wave-vectors, which are energetically unfavourable because they do not contribute to the 'squaring up'. These extra possibilities in the triple-**Q** case are not therefore realized. The appearance of the higher 'odd' harmonics is not important for the energy differences between the different multiple-**Q** structures, but they may provide an experimental method for differentiating between the various possibilities (Forgan *et al.* 1989). In a neutron-diffraction experiment, the scattering intensity at the fundamental wave-vectors in a multi-domain single-**Q** structure, with an equal distribution of the domains, is the same as that produced by a triple-**Q** structure. These structures may then be distinguished either by removing some of the domains by applying an external field, or by using scattering peaks at, for instance, $2\mathbf{Q}_1 \pm \mathbf{Q}_2$ to exclude the possibility of a single-**Q** structure.

The discussion of this section has been based exclusively on the MF approximation, which neglects the important dynamical feature that a system close to a second-order phase-transition will show strong correlated fluctuations in the components which order at the transition. A discussion of the effects of the *critical fluctuations* is beyond the scope of this book, and we refer instead to the recent introduction to the field by Collins (1989), in which references may be found to the copious literature on the subject. Although the MF approximation does not take into account the contributions to the free energy from the critical fluctuations, it gives a reasonable estimate of the transition temperatures in the rare earth metals, which can all be characterized as three-dimensional systems with long-range interactions. The fluctuations contribute to the free energy on both sides of the transition, and they only suppress the transition temperature by a few per cent in such systems. The Landau expansion considered above does not predict the right *critical* *exponents*, but it is nevertheless decisive for which *universality classes* the phase transitions belong to. The transitions which are predicted to be continuous by the MF theory, i.e. all those considered above which are not accompanied by a change of **Q** to a commensurable value, may be driven into (weak) first-order behaviour by the fluctuations. An important parameter for determining the nature of the phase transition is the product (n) of the number of components of the order parameter, and of the star of the wave-vector (Mukamel and Krinsky 1976; Bak and Mukamel 1976), the latter being two, corresponding to ±**Q**, for the periodically-ordered heavy rare earths. If $n \leq 3$, the transition is expected to remain continuous, which is in accord with the observation by Habenschuss *et al.* (1974) of a second-order transition in Er, since $n = 2$ for the transition between the paramagnetic and the longitudinally ordered phase. The transition from the paramagnet to the helix is less clear-cut, since it belongs to the class $n = 4$, and a theoretical analysis by Barak and Walker (1982) suggested that it might be discontinuous. The bulk of the experimental evidence points towards a continuous transition (Brits and du Plessis 1988) but some measurements, especially by Zochowski *et al.* (1986) on pure Dy, indicate a very weak discontinuity. In the case of the multiple-**Q** structures, the fluctuations may drive the transition to the single-**Q** structure to be discontinuous, whereas that to the triple-**Q** structure, if it is stable, should stay continuous (Bak and Lebech 1978). In Nd, for example, a single-**Q** state is formed at T_N and the transition is found to be weakly discontinuous (Zochowski and McEwen 1986). In accordance with the MF analysis above, a first-order transition leads to a double-**Q** structure less than a degree below T_N (McEwen *et al.* 1985).