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Mean and differential magnetic susceptibilities in metal complexes

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Abstract

The magnetic susceptibility is introduced as a thermodynamic quantity which requires a partial differentiation of the magnetization according to the applied field. This differential (isothermal) magnetic susceptibility differs from the frequent definition of the mean magnetic susceptibility if the behaviour the magnetic material is non-linear (generally it is at low temperature and high magnetic fields).

Keywords: Magnetism; Magnetic susceptibility; Zero-field splitting; Multiplets with magnetic angular momentum

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1. Introduction

Measurements of the temperature dependence of the magnetic susceptibility belong to important sources of information about metal complexes. After an appropriate fit of experimental data to a theoretical model, the set of magnetic parameters which characterize the microscopic properties of the metal-containing entities (complexes, dimers, clusters, ordered systems like chains, etc.) is obtained. This allows a reconstruction of the spacing of energy levels whose separation is only a few wavenumbers.

A few excellent monographs devoted to magnetic susceptibilities and molecular magnetism exist [1–12]; however, some important factors are often ignored. First, the magnetic susceptibility is a quantity introduced through the thermodynamics and thus it is a partial derivative of the magnetization. Often it is assumed that the metal complexes belonging to molecular paramagnets behave like linear magnetics and thus the magnetic susceptibility could be treated as a simple ratio of the magnetization and the applied field. With lower temperature and in a ramping field, however, this assumption becomes untrue. Therefore, there is a need for a clear differentiation between mean magnetic susceptibility (which is an approximation under certain conditions) and differential susceptibility (which is the correct thermodynamic quantity). There exist several common situations where this difference becomes evident (Curie paramagnets, zero-field splitting (ZFS) systems, systems with magnetic angular momentum, clusters, etc.) and the present publication is devoted to these problems.

Magnetochemistry customarily uses the cgs and emu units systems. A correct transcription into the SI unit system is not a trivial task and it is almost absent in the available literature. For instance, the electron spin Zeeman term needs to be written as

$$\hat{H}^{Z} = \mu_B g_e \boldsymbol{B} \cdot \boldsymbol{S}[\hbar^{-1}]$$

since the spin operator, when acting on its eigen-kets, will generate $\hbar$. On the other hand, the spin–orbit (SO) (or spin–spin) interaction term should be written as

$$\hat{H}^{so} = \lambda \boldsymbol{L} \cdot \boldsymbol{S}[\hbar^{-2}]$$

and the interaction parameter λ has a dimension of $[E]$. Magneto-chemical equations and formulae are presented strictly in SI units in this review.

2. Magnetic quantities

The external magnetic field is characterized by magnetic induction vector $\boldsymbol{B}(B_x, B_y, B_z)$ which is interrelated with the magnetic field strength vector $\boldsymbol{H}(H_x, H_y, H_z)$ through the material constant termed permeability μ, viz.

$$\boldsymbol{B} = \mu \boldsymbol{H}$$

Here we assumed a homogeneous isotropic material, but in general the permeability is a second-rank tensor $\overline{\overline{\mu}}$ having 3×3 elements. The applied magnetic field is modified by the bulk magnetic properties of the substance and thus the magnetic field inside the sample becomes

$$\boldsymbol{B} = \mu_0 \boldsymbol{H} + \boldsymbol{M}$$

where the permeability of vacuum is $\mu_0 = 4\pi \times 10^{-7}$ kg m s^{-2} A^{-2}. The vector quantity $\boldsymbol{M}$ just introduced is termed the magnetization. Physically it represents a magnetic moment of the body or sample per volume element. The moving electrons present in any substance generate microscopic magnetic moments $\boldsymbol{m}_i$. The magnetic moment vector is introduced through the intensity of the closed current I of charged particles and the corresponding surface vector $\boldsymbol{S}$ normal to the plane of the movement

$$\boldsymbol{m} = I\boldsymbol{S}$$

Hence

$$\boldsymbol{M} = \boldsymbol{m}/V = (1/V) \sum_i \boldsymbol{m}_i$$

More exactly, for an inhomogeneous material a differentiation should be applied

$$\boldsymbol{M} = \mathrm{d}\boldsymbol{m}/\mathrm{d}V$$

In vacuum the magnetization vanishes and thus it holds true that

$$\boldsymbol{B}_{\mathrm{vac}} = \mu_0 \boldsymbol{H}$$

By combining the above expressions we obtain

$$\boldsymbol{M} = \frac{\boldsymbol{B}}{\mu_0} - \boldsymbol{H} = \frac{\boldsymbol{B} - \boldsymbol{B}_{\mathrm{vac}}}{\mu_0} = \left(\frac{\mu}{\mu_0} - 1\right)\boldsymbol{H} = \bar{\chi}\boldsymbol{H}$$

Here, a mean volume magnetic susceptibility was introduced

$$\bar{\chi} = \boldsymbol{M}/\boldsymbol{H}$$

Its more general definition, valid for non-linear magnetics, is (Fig. 1)

$$\chi = \mathrm{d}\boldsymbol{M}/\mathrm{d}\boldsymbol{H}$$

This is the differential volume magnetic susceptibility.

For anisotropic materials the susceptibility is a second-rank tensor $\bar{\bar{\chi}}$. The mass susceptibility and molar susceptibility are respectively

$$\chi_\rho = \chi/\rho$$

$$\chi_{\mathrm{mol}} = \chi_\rho M_{\mathrm{r}} = \chi M_{\mathrm{r}}/\rho$$

where ρ is the density and M_{r} the molar mass.

The important relationships in magnetism are collected in Table 1. The corresponding expressions in the SI as well as the cgs and emu unit systems are compared since the latter are still more frequently used than the former. Table 2 contains units for magnetic properties [12].

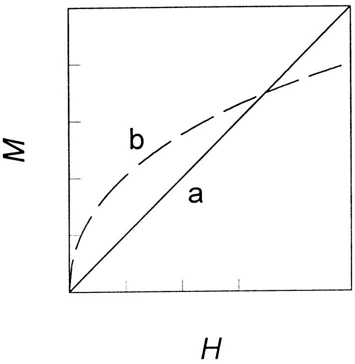


Fig. 1. Definition of the volume susceptibility: (a) linear magnetics, $\bar{\chi} = \boldsymbol{M}/\boldsymbol{H} = \mathrm{const.}$; (b) non-linear magnetics, $\chi = \mathrm{d}\boldsymbol{M}/\mathrm{d}\boldsymbol{H} = f(\boldsymbol{H})$.

Table 1
Basic relationships in magnetism

Quantity	SI units	cgs and emu units
Magnetic induction	$\boldsymbol{B}=\mu_0(\boldsymbol{H}+\boldsymbol{M})$ $\boldsymbol{B}=\mu\boldsymbol{H}$	$\boldsymbol{B}=\boldsymbol{H}+4\pi\boldsymbol{M}$ $\boldsymbol{B}=\mu\boldsymbol{H}$
Permeability	$\mu_r=\mu/\mu_0=1+\chi$	$\mu=1+4\pi\chi$
Volume magnetization	$\boldsymbol{M}=\boldsymbol{m}/V$	$\boldsymbol{M}=\boldsymbol{m}/V$
Volume susceptibility	$\chi=\mathrm{d}\boldsymbol{M}/\mathrm{d}\boldsymbol{H}$	$\chi=\mathrm{d}\boldsymbol{M}/\mathrm{d}\boldsymbol{H}$
Volume energy density	$W=(1/2)\boldsymbol{B}\cdot\boldsymbol{H}$	$W=(1/8\pi)\boldsymbol{B}\cdot\boldsymbol{H}$

The density of the magnetic field energy (volume energy density) is

$$W=\tfrac{1}{2}\boldsymbol{H}\cdot\boldsymbol{B}$$

and the magnetic energy E [J] of the sample with volume V is

$$E=\tfrac{1}{2}V\boldsymbol{H}\cdot\boldsymbol{B}$$

The magnetic induction expressed through a volume susceptibility tensor is

$$\boldsymbol{B}=\overline{\overline{\mu}}\cdot\boldsymbol{H}=\mu_0(\overline{\overline{1}}+\overline{\overline{\chi}})\cdot\boldsymbol{H}$$

or for individual components

$$B_a=\mu_0\sum_b(\delta_{ab}+\chi_{ab})H_b$$

so that the energy becomes

$$\begin{aligned}E&=\tfrac{1}{2}V\sum_a H_aB_a=\tfrac{1}{2}V\mu_0\sum_a\sum_b H_a(\delta_{ab}+\chi_{ab})H_b\\&=\tfrac{1}{2}V\mu_0(H_x^2+H_y^2+H_z^2)+\tfrac{1}{2}V\mu_0\sum_a\sum_b H_a\chi_{ab}H_b=E_0+E_2\end{aligned}$$

The term E_0 is the energy of the magnetic field inside the sample. The term E_2 represents the interaction energy of the sample with the applied field.

A common approach is to consider the energy of the system dependent upon the magnetic induction

$$E=f(\ldots,\boldsymbol{B},\ldots)$$

and in terms of a Taylor expansion it is

$$E=E_0+\sum_a(\partial E/\partial B_a)B_a+\tfrac{1}{2}\sum_a\sum_b(\partial^2E/\partial B_a\partial B_b)B_aB_b+\ldots$$

The first derivatives define the (microscopic) magnetic moment vector $\boldsymbol{\mu}(\mu_x,\mu_y,\mu_z)$

$$\mu_a=-(\partial E/\partial B_a)$$

so that the interaction energy of the permanent magnetic moment of the system

Table 2
Units for magnetic properties

Quantity	Symbol	cgs and emu units	Conversion to SI	SI units
Magnetic flux	Φ	Mx (maxwell), G cm^2	10^{-8}	Wb (weber), V s
Magnetic flux density, magnetic induction	$\boldsymbol{B}$	G (gauss)	10^{-4}	T (tesla), Wb m^{-2}
Magnetic potential differ., magnetomotive force	U, F	Gb (gilbert)	$10/4\pi$	A (ampere)
Magnetic field strength, magnetizing force	$\boldsymbol{H}$	Oe (oersted), Gb cm^{-1}	$10^3/4\pi$	A m^{-1}
Volume magnetization	$\boldsymbol{M}$	emu cm^{-3}	10^3	A m^{-1}
Mass magnetization	$\boldsymbol{\sigma}$, $\boldsymbol{M}$	emu g^{-1}	1	A $\mathrm{m}^2\,\mathrm{kg}^{-1}$
Molar magnetization	$\boldsymbol{M}_{\mathrm{mol}}$, $\boldsymbol{M}$	emu mol^{-1}	10^{-3}	A $\mathrm{m}^2\,\mathrm{mol}^{-1}$
Magnetic polarization, intensity of magnetization	$\boldsymbol{J}$, $\boldsymbol{I}$	emu cm^{-3}	$4\pi\times10^{-4}$	T, Wb m^{-2}
Magnetic moment	$\boldsymbol{m}$, $\boldsymbol{\mu}$	emu, erg G^{-1}	10^{-3}	A m^2, J T^{-1}
Magnetic dipole moment	$\boldsymbol{j}$	emu, erg G^{-1}	$4\pi\times10^{-10}$	Wb m
Volume susceptibility	χ, κ	dimensionless, emu cm^{-3}	4π	dimensionless
Mass susceptibility	χ_ρ, κ_ρ	$\mathrm{cm}^3\,\mathrm{g}^{-1}$, emu g^{-1}	$4\pi\times10^{-3}$	$\mathrm{m}^3\,\mathrm{kg}^{-1}$
Molar susceptibility	χ_{mol}, κ_{mol}	$\mathrm{cm}^3\,\mathrm{mol}^{-1}$, emu mol^{-1}	$4\pi\times10^{-6}$	$\mathrm{m}^3\,\mathrm{mol}^{-1}$
Permeability	μ	dimensionless	$4\pi\times10^{-7}$	H m^{-1}, Wb $\mathrm{A}^{-1}\,\mathrm{m}^{-1}$
Vacuum permeability	μ_0	1	$4\pi\times10^{-7}$	H m^{-1}
Relative permeability	μ_r	not defined	—	dimensionless
Volume energy density	W	erg cm^{-3}	10^{-1}	J m^{-3}
Demagnetization factor	D, N	dimensionless	$1/4\pi$	dimensionless

with the magnetic field is

$$E_1 = -\sum_a \mu_a B_a = -\boldsymbol{\mu} \cdot \boldsymbol{B}$$

The second derivatives form the reduced magnetic susceptibility tensor $\bar{\bar{\kappa}}$ with components

$$\kappa_{ab} = (\partial \mu_a / \partial B_b) = -\partial^2 E / \partial B_a \partial B_b$$

and thus the interaction energy of the system with the magnetic field becomes

$$E_2 = -\tfrac{1}{2} \sum_a \sum_b B_a \kappa_{ab} B_b = -\tfrac{1}{2} \boldsymbol{B} \cdot \bar{\bar{\kappa}} \cdot \boldsymbol{B}$$

The reduced susceptibility and volume (mass, molar) susceptibility are interrelated through

$$\chi_{ab} = (\mu_0 / V) \kappa_{ab}$$

$$(\chi_\rho)_{ab} = (\mu_0 / m) \kappa_{ab}$$

$$(\chi_{\mathrm{mol}})_{ab} = (\mu_0 / n) \kappa_{ab}$$

3. Thermodynamic relationships

3.1. State functions

The first law of thermodynamics postulates that the internal energy, which is a state function, consists of the heat Q and the work w

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}w$$

In the most common presentation the work embraces the volume work $\mathrm{d}w = -p\,\mathrm{d}V$. However, other forms of the work are possible (the surface work $\mathrm{d}w = \boldsymbol{s} \cdot \mathrm{d}\boldsymbol{\sigma}$, the mechanical work $\mathrm{d}w = \boldsymbol{F} \cdot \mathrm{d}\boldsymbol{r}$, the electric work $\mathrm{d}w = q\,\mathrm{d}U$) and the magnetic work

$$\mathrm{d}w = \mu_0 \boldsymbol{H} \cdot \mathrm{d}\boldsymbol{M}$$

is one of them. The individual constituents of the last expression have their dimensions as follows: μ_0 [J A^{-2} m^{-1}], H [A m^{-1}] and M [A m^{-1}]; then the expression has the dimension [J m^{-3}] which refers to the volume energy. It is assumed hereafter that the other energy quantities (U, E, F, G, TS, CT) possess the same dimension.

Making use of $\mathrm{d}Q = T\,\mathrm{d}S$ we arrive at the expression for the internal energy

$$\mathrm{d}U = T\,\mathrm{d}S + \mu_0 H\,\mathrm{d}M, \quad (p = \text{const.},\ V = \text{const.},\ n_i = \text{const.})$$

Table 3
Thermodynamic functions in magnetism

Function $X=X(A,B)$	Exact differential $\mathrm{d}X=\left(\frac{\partial X}{\partial A}\right)_B \mathrm{d}A+\left(\frac{\partial X}{\partial B}\right)_A \mathrm{d}B$	Relationship
Internal energy $U=U(S,M)$	$\mathrm{d}U=T\,\mathrm{d}S+\mu_0 H\,\mathrm{d}M$	$\left(\frac{\partial T}{\partial M}\right)_S=\mu_0\left(\frac{\partial H}{\partial S}\right)_M$
Enthalpy (E instead of H) $E=E(S,H)$	$\mathrm{d}E=T\,\mathrm{d}S-\mu_0 M\,\mathrm{d}H$	$\left(\frac{\partial T}{\partial H}\right)_S=-\mu_0\left(\frac{\partial M}{\partial S}\right)_H$
Helmholtz free energy $F=F(T,M)$	$\mathrm{d}F=-S\,\mathrm{d}T+\mu_0 H\,\mathrm{d}M$	$\left(\frac{\partial S}{\partial M}\right)_T=-\mu_0\left(\frac{\partial H}{\partial T}\right)_M$
Gibbs energy $G=G(T,H)$	$\mathrm{d}G=-S\,\mathrm{d}T-\mu_0 M\,\mathrm{d}H$	$\left(\frac{\partial S}{\partial H}\right)_T=\mu_0\left(\frac{\partial M}{\partial T}\right)_H$
Entropy $S=S(T,M)$	$\mathrm{d}S=\frac{C_M}{T}\mathrm{d}T+\left(\frac{\partial S}{\partial M}\right)_T \mathrm{d}M$	
$S=S(T,H)$	$\mathrm{d}S=\frac{C_H}{T}\mathrm{d}T+\left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H$	

Since the internal energy U is an exact differential, so

$$\left(\frac{\partial T}{\partial M}\right)_S=\mu_0\left(\frac{\partial H}{\partial S}\right)_M$$

The other thermodynamic functions are introduced in a similar way (Table 3) [8,9]. Of three observables (H, M, T), only two are independently variable, which is expressed by the constraint

$$\left(\frac{\partial H}{\partial T}\right)_M\left(\frac{\partial T}{\partial M}\right)_H\left(\frac{\partial M}{\partial H}\right)_T=-1$$

3.2. Heat capacities

In the classical thermodynamics dealing with the volume work two sorts of heat capacity are distinguished: C_V and C_p. The specific heat c_V [J g^{-1} K^{-1}] and the molar heat capacity C_V [J mol^{-1} K^{-1}] are interrelated through

$$C_V=c_V M_\mathrm{r}$$

where M_r is the molar mass.

The difference between C_V and C_p for solids is

$$C_p-C_V=T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p$$

Making use of the relationship among state variables $p=p(V, T)$, in the differential form

$$\mathrm{d}p=\left(\frac{\partial p}{\partial V}\right)_T \mathrm{d}V+\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}T$$

at constant pressure $\mathrm{d}p=0$; thus we get

$$\left(\frac{\partial p}{\partial T}\right)_V=-\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

Then the difference between the molar heat capacities becomes

$$C_p-C_V=-T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p^2=\frac{TV_\mathrm{m}\beta^2}{K_T}$$

where V_m is the molar volume. The isothermal compressibility measured at constant temperature is introduced through the formula

$$K_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

and the coefficient of the volumetric expansion is

$$\beta=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

For isotropic solids, β is related to the coefficient of linear thermal expansion α by

$$\beta=\frac{1}{l^3}\left(\frac{\partial l^3}{\partial T}\right)_p=\frac{3}{l}\left(\frac{\partial l}{\partial T}\right)_p=3\alpha$$

where l is the dimension of a cube of the solid. The mechanical stability of a solid requires $K_T>0$ and consequently $C_p \geqslant C_V$. Although data on linear thermal expansion are available for many solids over a broad interval of temperature, experimental values of compressibility are often known around room temperature only.

By introducing the adiabatic compressibility measured at constant entropy

$$K_S=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

one can derive an expression

$$C_p/C_V=K_T/K_S$$

In the thermodynamics dealing with the magnetic work, the following sorts of heat capacity are defined:

$$C_M = \left(\frac{\partial Q}{\partial T}\right)_M = T\left(\frac{\partial S}{\partial T}\right)_M$$

$$C_H = \left(\frac{\partial Q}{\partial T}\right)_H = T\left(\frac{\partial S}{\partial T}\right)_H$$

It is of interest to express $C_H - C_M$ and C_H/C_M in terms of observables (H, M, T). Making use of expressions for entropy

$$\mathrm{d}S = \frac{C_M}{T}\,\mathrm{d}T + \left(\frac{\partial S}{\partial M}\right)_T \mathrm{d}M = \frac{C_H}{T}\,\mathrm{d}T + \left(\frac{\partial S}{\partial H}\right)_T \mathrm{d}H$$

and taking into account the relationships listed in Table 3 we get

$$\frac{C_M}{T}\,\mathrm{d}T - \mu_0\left(\frac{\partial H}{\partial T}\right)_M \mathrm{d}M = \frac{C_H}{T}\,\mathrm{d}T + \mu_0\left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

This equation can be rewritten as

$$\frac{C_H - C_M}{T}\,\mathrm{d}T = -\mu_0\left(\frac{\partial H}{\partial T}\right)_M \mathrm{d}M - \mu_0\left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

or

$$\mathrm{d}T = -\frac{T}{C_H - C_M}\,\mu_0\left(\frac{\partial H}{\partial T}\right)_M \mathrm{d}M - \frac{T}{C_H - C_M}\,\mu_0\left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H$$

and compared with the identity

$$\mathrm{d}T = \left(\frac{\partial T}{\partial M}\right)_H \mathrm{d}M + \left(\frac{\partial T}{\partial H}\right)_M \mathrm{d}H$$

The same coefficients of dM require the validity of

$$-\frac{T}{C_H - C_M}\,\mu_0\left(\frac{\partial H}{\partial T}\right)_M = \left(\frac{\partial T}{\partial M}\right)_H$$

The boundary among observables allows us to eliminate

$$\left(\frac{\partial H}{\partial T}\right)_M = -\left(\frac{\partial M}{\partial T}\right)_H \left(\frac{\partial H}{\partial M}\right)_T$$

and finally we arrive at the formula

$$C_H - C_M = \mu_0 T\left(\frac{\partial M}{\partial T}\right)_H^2 \left(\frac{\partial H}{\partial M}\right)_T$$

The second expression for entropy can be also written in the form of

$$\mathrm{d}T=\frac{T}{C_H}\,\mathrm{d}S-\frac{T}{C_H}\,\mu_0\left(\frac{\partial M}{\partial T}\right)_H\mathrm{d}H$$

and compared with the identity

$$\mathrm{d}T=\left(\frac{\partial T}{\partial S}\right)_H\mathrm{d}S+\left(\frac{\partial T}{\partial H}\right)_S\mathrm{d}H$$

yielding the same coefficient at dH, i.e.

$$-\frac{T}{C_H}\,\mu_0\left(\frac{\partial M}{\partial T}\right)_H=\left(\frac{\partial T}{\partial H}\right)_S$$

The first expression for entropy can be rearranged as

$$\mathrm{d}T=\frac{T}{C_M}\,\mathrm{d}S+\frac{T}{C_M}\,\mu_0\left(\frac{\partial H}{\partial T}\right)_M\mathrm{d}M$$

and again compared with the identity

$$\mathrm{d}T=\left(\frac{\partial T}{\partial S}\right)_M\mathrm{d}S+\left(\frac{\partial T}{\partial M}\right)_S\mathrm{d}M$$

giving the same coefficient at dM, viz.

$$\frac{T}{C_M}\,\mu_0\left(\frac{\partial H}{\partial T}\right)_M=\left(\frac{\partial T}{\partial M}\right)_S$$

The ratio of the magnetic heat capacities stands

$$\frac{C_H}{C_M}=-\frac{\left(\frac{\partial M}{\partial T}\right)_H\left(\frac{\partial H}{\partial T}\right)_S}{\left(\frac{\partial M}{\partial T}\right)_S\left(\frac{\partial H}{\partial T}\right)_M}=-\frac{\left(\frac{\partial T}{\partial M}\right)_S\left(\frac{\partial H}{\partial T}\right)_S}{\left(\frac{\partial T}{\partial M}\right)_H\left(\frac{\partial H}{\partial T}\right)_M}=\frac{\left(\frac{\partial M}{\partial H}\right)_T}{\left(\frac{\partial M}{\partial H}\right)_S}$$

Now we introduce the isothermal susceptibility (measured at a constant temperature)

$$\chi_T=\left(\frac{\partial M}{\partial H}\right)_T$$

and the adiabatic susceptibility (measured at a constant entropy)

$$\chi_S=\left(\frac{\partial M}{\partial H}\right)_S$$

The ratio of the magnetic heat capacities is just the ratio of the magnetic susceptibilities

$$C_H/C_M=\chi_T/\chi_S$$

Important relationships among heat capacities are collected in Table 4. It is worth noting that the relations between the heat capacities and compressibilities in the classical thermodynamics have an analogy in the relations between the magnetic heat capacities and magnetic susceptibilities.

Table 4
Relationships for heat capacities

Function[a]	Heat capacity	Expression[b]
(a) Volume work		
$U(S, V)$	$C_V=\left(\frac{\partial U}{\partial T}\right)_V$	$C_V=N_{\mathrm{A}}\frac{\partial}{\partial T}\left[kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V\right]_V$
$E(S, p)$	$C_p=\left(\frac{\partial E}{\partial T}\right)_p$	$C_p=N_{\mathrm{A}}\frac{\partial}{\partial T}\left[kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V+kT\left(\frac{\partial \ln Z}{\partial \ln V}\right)_T\right]_p$
	C_p-C_V	$T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_p=-T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p^2$
	C_p/C_V	$\left(\frac{\partial V}{\partial p}\right)_T\Big/\left(\frac{\partial V}{\partial p}\right)_S=K_T/K_S$
$S(T, V)$		$\mathrm{d}S=\frac{C_V}{T}\,\mathrm{d}T+\left(\frac{\partial p}{\partial T}\right)_V\mathrm{d}V$
$S(T, p)$		$\mathrm{d}S=\frac{C_p}{T}\,\mathrm{d}T-\left(\frac{\partial V}{\partial T}\right)_p\mathrm{d}p$
(b) Magnetic work		
$U(S, M)$	$C_M=\left(\frac{\partial U}{\partial T}\right)_M$	$C_M=N_{\mathrm{A}}\frac{\partial}{\partial T}\left[kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_M\right]_M$
$E(S, H)$	$C_H=\left(\frac{\partial E}{\partial T}\right)_H$	$C_H=N_{\mathrm{A}}\frac{\partial}{\partial T}\left[kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_M+kT\left(\frac{\partial \ln Z}{\partial \ln M}\right)_T\right]_H$
	C_H-C_M	$-\mu_0 T\left(\frac{\partial H}{\partial T}\right)_M\left(\frac{\partial M}{\partial T}\right)_H=\mu_0 T\left(\frac{\partial H}{\partial M}\right)_T\left(\frac{\partial M}{\partial T}\right)_H^2$
	C_H/C_M	$\left(\frac{\partial M}{\partial H}\right)_T\Big/\left(\frac{\partial M}{\partial H}\right)_S=\chi_T/\chi_S$
$S(T, M)$		$\mathrm{d}S=\frac{C_M}{T}\,\mathrm{d}T-\mu_0\left(\frac{\partial H}{\partial T}\right)_M\mathrm{d}M$
$S(T, H)$		$\mathrm{d}S=\frac{C_H}{T}\,\mathrm{d}T+\mu_0\left(\frac{\partial M}{\partial T}\right)_H\mathrm{d}H$

[a] Enthalpy is denoted as E; H is the magnetic field strength.

[b] These expressions include results of statistical thermodynamics which will be met later.

4. Alternating fields

4.1. Alternating current (AC) susceptibility

As long as a magnetic field is switched on the magnetization needs some time to achieve a thermodynamic equilibrium. The magnetic susceptibility measured at thermal equilibrium is the isothermal susceptibility χ_T.

In an alternating field, however, the situation is different. The AC is used to generate the alternating magnetic field (Fig. 2). The time evolution of the magnetic field strength is

$$H_{AC}=H_0\cos(\omega t)$$

with H_0 the amplitude of the field, ω the angular frequency of the AC field ($\omega=2\pi\nu$).

The magnetization M_{AC} cannot follow the incident field immediately and it is shifted by a phase angle θ, so that

$$M_{AC}=M_0\cos(\omega t-\theta)$$

This formula can be rewritten using the relationship

$$\cos(\alpha-\beta)=\cos\alpha\cos\beta+\sin\alpha\sin\beta$$

Then the time evolution of the magnetization is

$$M_{AC}=M_0\cos\theta\cos(\omega t)+M_0\sin\theta\sin(\omega t)=\chi' H_0\cos(\omega t)+\chi'' H_0\sin(\omega t)$$

with

$$\chi'=(M_0/H_0)\cos\theta$$

$$\chi''=(M_0/H_0)\sin\theta$$

The quantity just introduced is the magnetic susceptibility having two components. The in-phase (real) component is χ' and it corresponds to the dispersive magnetic

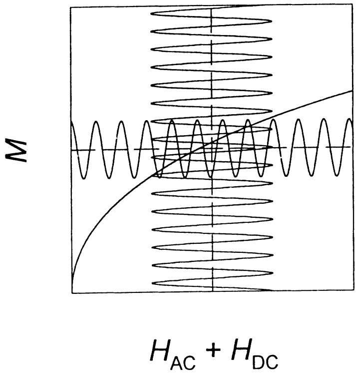


Fig. 2. AC measurement in conjunction with an applied DC field.

response; therefore it is termed the dispersion. The out-of-phase (imaginary) component is χ'' and it corresponds to the energy dissipation (i.e. the energy absorbed by the material from the applied AC field); it is termed the absorption. Normally the out-of-phase component χ'' is small and it varies around zero (being lower by orders of magnitude than χ'). It adopts significance (positive values) when the sample, owing to some processes inside the material, absorbs the magnetic energy.

Thus the magnetic susceptibility in an alternating field, the AC susceptibility, can be viewed as a complex quantity

$$\chi = \chi' + \mathrm{i}\chi''$$

The components of the AC susceptibility depend upon the frequency of the applied field. When the frequency of the field is low, the magnetization can readily follow the applied field so that the low-frequency limit corresponds to the isothermal susceptibility

$$\lim_{\omega \to 0} \chi = \left(\frac{\partial M_{\mathrm{AC}}}{\partial H} \right)_T = \chi_T$$

This is comparable with the susceptibility measured in static fields. The greater the frequency, the lower the AC susceptibility, which in the opposite limit approaches the adiabatic value

$$\lim_{\omega \to \infty} \chi = \left(\frac{\partial M_{\mathrm{AC}}}{\partial H} \right)_S = \chi_S$$

The recovery of a perturbed system to a new equilibrium is described by introducing the relaxation time τ

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \frac{M(\infty) - M(t)}{\tau}$$

where $M(\infty)$ is the equilibrium magnetization and $M(t)$ is the magnetization at time t.

An example of such a relaxation process is represented by the transfer of energy between the magnetic spin entity and the lattice vibrations (spin–lattice relaxation). The isothermal, adiabatic and AC susceptibilities are interrelated through (Fig. 3)

$$\chi_{\mathrm{AC}} = \frac{\chi_T - \chi_S}{1 + \mathrm{i}\omega\tau} + \chi_S$$

and for individual components

$$\chi'(\omega) = \frac{\chi_T - \chi_S}{1 + \omega^2\tau^2} + \chi_S$$

$$\chi''(\omega) = \frac{\omega\tau(\chi_T - \chi_S)}{1 + \omega^2\tau^2}$$

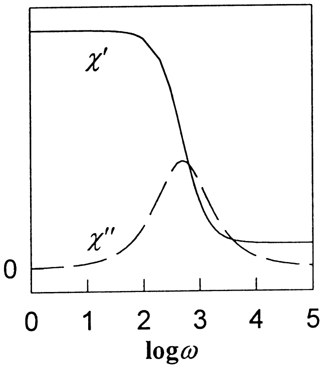


Fig. 3. Frequency dependence of the AC susceptibility.

Now for $\omega \ll \tau^{-1}$ the in-phase component becomes the isothermal susceptibility $\chi' = \chi_T$ and the out-of-phase component approaches zero. On the contrary, for $\omega \gg \tau^{-1}$ the in-phase component equals the adiabatic susceptibility $\chi' = \chi_S$, and χ'' vanishes again. Just for $\omega = \tau^{-1}$ the out-of-phase component adopts a maximum value of

$$\chi'' = (\chi_T - \chi_S)/2$$

The alternating magnetic field can be combined with an admixture of the constant field generated by a direct current (DC). The magnetic moment is induced in a sample through the application of the DC bias field, produced either by the primary coil or by a superconducting magnet.

4.2. *Harmonic susceptibilities*

If the material response in AC magnetization measurements is non-linear, the magnetization oscillations do not follow the fundamental susceptibility perfectly. The perfect sinusoidal AC field induces the non-sinusoidal oscillations of the magnetization which can be described as a sum of several sinusoidal components oscillating at the harmonics of the driving frequency [13] (Fig. 4)

$$M_{AC}(t) = H_0 \sum_n [\chi'_n \cos(n\omega t) + \chi''_n \sin(n\omega t)]$$

Here χ'_n and χ''_n define the in-phase and out-of-phase components of the harmonic susceptibilities

$$\chi_n = \chi'_n + i\chi''_n$$

for the harmonic degree $n = 1, 2, 3, \ldots$.

Full characterization of a magnetic material with non-linear response requires measurements of harmonic susceptibilities beyond the fundamental susceptibility

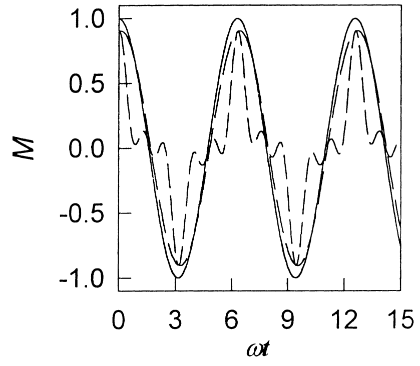


Fig. 4. AC magnetization response to harmonic susceptibilities: (a) solid, perfect first harmonics; (b) long dashed, a shift due to complex susceptibility; (c) short dashed, a warping due to third and fifth harmonics.

χ_1. These are useful, for example, in the identification of multiple phase transitions in high T_C superconductors and in the determination of magnetic phase diagrams.

5. Demagnetization correction

The magnetic field H actually acting on a sample of definite geometrical shape consists of two contributions: the applied external field H_a and the demagnetizing field H_d

$$H = H_a + H_d$$

The origin of the demagnetizing field lies in the magnetic poles on the surface of a magnetized specimen; the sample behaves like a magnet of an opposite polarization as is that of the applied field. The greater the magnetization, the greater the demagnetizing field with the opposite sign

$$H_d = -NM$$

The proportionality constant N is termed the demagnetization factor (dimensionless in SI) and it can be evaluated from the sample shape. Then the internal magnetic field becomes

$$H = H_a - NM$$

As $0 < N < 1$, the internal field is lower than the applied field: $H < H_a$.

The susceptibility which is measured experimentally refers to the external susceptibility which is characteristic of the sample

$$\chi_{ext} = dM/dH_a$$

On the contrary, the internal susceptibility, which is characteristic of the material, is

$$\chi_{\mathrm{int}} = \mathrm{d}M/\mathrm{d}H$$

These quantities are interrelated through

$$\chi_{\mathrm{int}} = \chi_{\mathrm{ext}}/(1 - N\chi_{\mathrm{ext}})$$

For AC susceptibility both χ_{ext} and χ_{int} are complex. The individual components are related

$$\chi'_{\mathrm{int}} = [\chi'_{\mathrm{ext}} - N(\chi'^2_{\mathrm{ext}} + \chi''^2_{\mathrm{ext}})]/[N^2(\chi'^2_{\mathrm{ext}} + \chi''^2_{\mathrm{ext}}) - 2N\chi'_{\mathrm{ext}} + 1]$$

$$\chi''_{\mathrm{int}} = \chi''_{\mathrm{ext}}/[N^2(\chi'^2_{\mathrm{ext}} + \chi''^2_{\mathrm{ext}}) - 2N\chi'_{\mathrm{ext}} + 1]$$

For many magnetic materials the demagnetization correction for the susceptibility is not important since $\chi \ll 1$, which implies $\chi_{\mathrm{int}} \approx \chi_{\mathrm{ext}}$. When the susceptibility is high, the demagnetization correction adopts its significance.

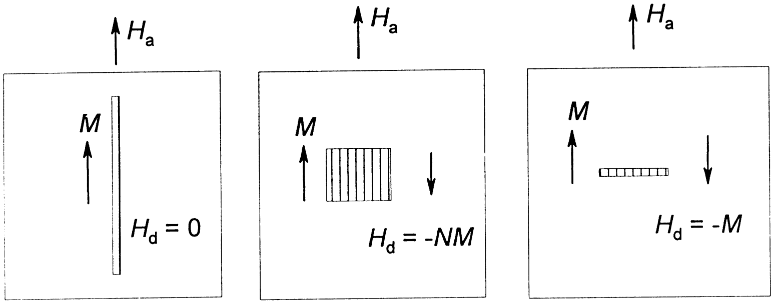
In general, the demagnetization is a second rank tensor $\bar{\bar{N}}$ entering the vector equation

$$\boldsymbol{H} = \boldsymbol{H}_{\mathrm{a}} + \boldsymbol{H}_{\mathrm{d}} = \boldsymbol{H}_{\mathrm{a}} - \bar{\bar{N}} \cdot \boldsymbol{M}$$

The demagnetization correction is applicable only to the volume susceptibility. This requires an accurate determination of the sample volume which might not be trivial. Normally the amount of sample is determined by weighing and it refers to the sample mass. The determination of the volume is less accurate and more complex for powders.

The demagnetization factors were derived for several important bodies: a spheroid, a cylinder and a thin film (Fig. 5).

(a) For ellipsoids the magnetic poles are distributed in such a way that the demagnetizing field H_{d} is uniform (also H_{a}, H and M are uniform). If $\boldsymbol{H}_{\mathrm{a}}$ is along a principal axis of the ellipsoid, N is a scalar quantity. If $\boldsymbol{H}_{\mathrm{a}}$ is not along a principal



a b c

Fig. 5. Demagnetizing field: (a) in a bar (long needle); (b) in a cylinder; (c) in a slab (thin film).

axis and $\chi \neq 0$, $\boldsymbol{M}$ is uniform but not coaxial with $\boldsymbol{H}_a$. The direction and magnitude of $\boldsymbol{M}$ depend on χ.

(b) For spheroids N does not depend on susceptibility and is a function of the aspect ratio $\gamma = l_z/l_x$ (a ratio of the polar axis l_z to the equatorial axis l_x) [14,15]

(1) for $\gamma < 1$: $N = [1 - \gamma(1-\gamma^2)^{-1/2} \cos^{-1}\gamma]/(1-\gamma^2)$
(2) for $\gamma = 1$: $N = 1/3$
(3) for $\gamma > 1$: $N = [\gamma(\gamma^2-1)^{-1/2} \cosh^{-1}\gamma - 1]/(\gamma^2-1)$.

(c) For cylinders $N = f(\chi, \gamma)$ where $\gamma = l/d$ is the ratio of the length to the diameter of the cylinder

(1) for $\chi \to 0$: M is uniform
(2) for $\chi \to \infty$: $H_d = -H_a$ are uniform
(3) for $\chi \to -1$: $(M + H_d) = -H_a$ are uniform.

The magnetometric demagnetization factor for cylinders, when the response of the full volume is detected, is defined as

$$N^{(m)} = -\langle H_d \rangle_V / \langle M \rangle_V$$

where an average over the volume of the cylinder was applied. This is a function $N^{(m)} = f(\chi, \gamma)$ so that values for $\chi \to 0$ (Table 5) are different from those for $\chi \to -1$.

Note that the sum of the transverse and longitudinal magnetometric demagnetization factors for cylinders obeys

for $\chi \to 0$: $\eta = 2N_{\perp}^{(m)} + N_{\parallel}^{(m)} = 1$

Table 5
Longitudinal magnetometric demagnetization factor for cylinders with $\chi \to 0$[a]

$\gamma = l/d$	$N^{(m)}$	$\gamma = l/d$	$N^{(m)}$	$\gamma = l/d$	$N^{(m)}$
0.0	1.000	2.0	0.181	4.0	0.0978
0.1	0.796	2.1	0.174	4.1	0.0956
0.2	0.680	2.2	0.167	4.2	0.0935
0.3	0.594	2.3	0.161	4.3	0.0914
0.4	0.528	2.4	0.155	4.4	0.0895
0.5	0.474	2.5	0.149	4.5	0.0876
0.6	0.430	2.6	0.144	4.6	0.0858
0.7	0.393	2.7	0.140	4.7	0.0841
0.8	0.361	2.8	0.135	4.8	0.0824
0.9	0.334	2.9	0.131	4.9	0.0808
1.0	0.311	3.0	0.127	5.0	0.0793
1.1	0.291	3.1	0.123	5.5	0.0723
1.2	0.273	3.2	0.120	6.0	0.0666
1.3	0.257	3.3	0.116	6.5	0.0616
1.4	0.242	3.4	0.113	7.0	0.0573
1.5	0.230	3.5	0.110	7.5	0.0536
1.6	0.218	3.6	0.107	8.0	0.0503
1.7	0.207	3.7	0.105	8.5	0.0473
1.8	0.198	3.8	0.102	9.0	0.0447
1.9	0.189	3.9	0.100	10.0	0.0403

[a] According to Ref. [16].

Table 6
Magnetometric demagnetization factors[a]

	$\chi=-1$		$\chi\to 0$	
	$N_{\parallel}^{(m)}$	$N_{\perp}^{(m)}$	$N_{\parallel}^{(m)}$	$N_{\perp}^{(m)}$
Cylinders, $\gamma=l/d$				
0	1	0	1	0
0.25	0.6764	0.2136		
0.5	0.5258	0.2928	0.474	0.263
1	0.3692	0.3669	0.311	0.344
2	0.2341	0.4237	0.181	0.409
4	0.1361	0.4596	0.0978	0.451
∞	0	0.5	0	0.5
Long needle			0	1/2
Sphere			1/3	1/3
Thin film			0	1

[a] According to Ref. [17].

for $\chi\to-1$: $\eta\geqslant 1$
as indicated in Table 6.

(d) When the applied magnetic field is perpendicular to the plane of a thin film ($\gamma\to 0$) the longitudinal demagnetization factor approaches unity. For a substance with $\chi\to-1$ (a perfectly shielding superconductor) there is

$$\lim_{\substack{\chi\to-1\\ N\to 1}}\chi_{\mathrm{ext}}=\lim_{\substack{\chi\to-1\\ N\to 1}}\chi_{\mathrm{int}}/(1+N\chi_{\mathrm{int}})=\lim_{N\to 1}[-1/(1-N)]=-\infty$$

and thus the measured external susceptibility adopts very highly negative values.

6. Overview of magnetic susceptibilities

A list of the different types of magnetic susceptibility, including some useful relationships among them, is given in Table 7. The most important message from this overview is that one should take careful note of the proper definition when speaking about magnetic susceptibility.

The popular experimental techniques involve the Faraday or Gouy balance measurements where the quantity being measured is the force acting on a body when it is in the magnetic field

$$\boldsymbol{F}=-\boldsymbol{\nabla}w$$

The work done in bringing a body of volume V with uniform magnetization $\boldsymbol{M}$ into a magnetic field is

$$\mathrm{d}w=-\mu_0 V\boldsymbol{H}\cdot\mathrm{d}\boldsymbol{M}$$

Table 7
Various types of magnetic susceptibility

Susceptibility	Relationship
Reduced	$\kappa_{ab}=-(\partial^2 E/\partial B_a\,\partial B_b)$
Volume	$\chi_{ab}=(\partial M_a/\partial H_b)=\mu_0(\partial M_a/\partial B_b)=(\mu_0/V)\kappa_{ab}$
Mass	$\chi_\rho=\chi/\rho$
Molar	$\chi_{\mathrm{mol}}=\chi_\rho M_{\mathrm{r}}=\chi M_{\mathrm{r}}/\rho$
Mean	$\bar{\chi}=M/H=\mu_0 M/B$
Isothermal	$\chi_T=(\partial M/\partial H)_T$
Adiabatic	$\chi_S=(\partial M/\partial H)_S$
AC	$\chi=\chi'-\mathrm{i}\chi''$
Dispersion	$\chi'=(M_0/H_0)\cos\theta$
Absorption	$\chi''=(M_0/H_0)\sin\theta$
Harmonic	$\chi_n=\chi_n'-\mathrm{i}\chi_n''$
External	$\chi_{\mathrm{ext}}=\mathrm{d}M/\mathrm{d}H_{\mathrm{a}}$
Internal	$\chi_{\mathrm{int}}=\mathrm{d}M/\mathrm{d}H=\chi_{\mathrm{ext}}/(1-N\chi_{\mathrm{ext}})$
Averaged	$\chi_{\mathrm{av}}=(2\chi_\perp+\chi_\parallel)/3$

For isotropic non-ferromagnetic materials with volume susceptibility χ it is

$$\mathrm{d}\boldsymbol{M}=\chi\,\mathrm{d}\boldsymbol{H}$$

and thus

$$w=-\mu_0 V\int \chi\boldsymbol{H}\cdot\mathrm{d}\boldsymbol{H}$$

For susceptibility independent of the field, $\bar{\chi}=$const., there is

$$w=-\tfrac{1}{2}\mu_0 V\bar{\chi}\boldsymbol{H}^2$$

and the force becomes expressed as

$$\boldsymbol{F}=\tfrac{1}{2}\mu_0\chi V(\boldsymbol{\nabla}H^2)$$

When the sample is allowed to move in one direction (z) only, then one gets

$$F_z=\mu_0\chi V H_z\frac{\partial H}{\partial z}=\mu_0\chi_\rho m H_z\frac{\partial H}{\partial z}$$

Evidently, the susceptibility obtained from such experiments is the “mean mass susceptibility”. This quantity, for linear magnetics, is close to the isothermal susceptibility. However, the deviations from the linear behaviour increase with

(a) increasing magnetic field,
(b) temperature lowering,
(c) sample magnetization.

Then, dealing with the mean magnetic susceptibility becomes incorrect.

As already mentioned, the induction methods, such as AC susceptibility measurements, yield the value of the “differential adiabatic susceptibility”. This can be scanned either in the single mode (giving rise to $|\chi|$) or, alternatively, in the dual mode (when the dispersion χ' and the absorption χ'' are distinguished). The adiabatic susceptibility approaches the isothermal susceptibility only when the frequency of the alternating field is small.

7. Statistical thermodynamics

7.1. Introduction to statistical treatment

Let us consider a simple model, with only two attainable energy states. A good representation could be an assembly of N similar spins, each independent of the others. We are interested in the properties of the average, in the thermodynamic limit, when $N \to \infty$. The energy of the spins in an applied magnetic field is

$$e = -\mu_e B = -(\pm\tfrac{1}{2} g\mu_B)B = \mp\tfrac{1}{2} g\mu_B B = \mp\epsilon$$

where the minus sign is valid for the n spins pointing parallel to the field direction (lower energy) and the plus sign for the $(N-n)$ spins pointing antiparallel. Then the average energy $\bar{E}$ of each spin is expressed through the total energy as follows [18]:

$$\bar{E} = \frac{E}{N} = \frac{(N-n)\epsilon - n\epsilon}{N} = (1-2p)\epsilon$$

with the fraction of spins pointing parallel to the field direction

$$p = \frac{n}{N}$$

The probability $Q(n)$ of attaining the configuration of the average energy is a product of two probabilities: the statistical probability $S(n)$ and the thermal probability $P(E)$

$$Q(n) = S(n)P(E)$$

The statistical probability contains in the numerator a binomial coefficient which counts the number of the distinct arrangements of N spins which exactly have the energy $E=(N-2n)\epsilon$, and in the denominator the total number of distinct configurations 2^N

$$S(n) = \frac{N!}{n!(N-n)!}\frac{1}{2^N}$$

An application of the Stirling formula (valid well for large N) yields

$$\ln(N!) \approx N\ln N - N + \ldots$$

and thus we get

$$\ln S(n) = N\ln N - N - [n\ln n - n + (N-n)\ln(N-n) - (N-n) + N\ln 2]$$

which can be rewritten as

$$\ln S(n) = -N[\ln 2 + p \ln p + (1-p)\ln(1-p)]$$

Because of an explicit dependence on the number of particles, the $\ln(S)$ is an extensive quantity.

The thermal probability of the system having energy E is given by the Maxwell–Boltzmann factor

$$P(E) = \exp(-\beta E) = \exp(-E/kT)$$

($\beta = 1/kT$).Such a function accommodates the following requirements:
(1) $\ln(P)$ is an extensive quantity;
(2) $\ln(P)$ is dimensionless;
(3) P and hence $\ln(P)$ favours low energies (it must be maximal in the ground state);
(4) Q should be maximized to receive the most probable values of p and $\bar{E}$.
We introduce the free energy F through the relationship

$$2^N Q = \exp(-\beta F) = \exp(-F/kT)$$

so that

$$-\frac{F}{kT} = \ln(2^N Q) = N \ln 2 + \ln Q = \ln P(E) - N[p \ln p + (1-p)\ln(1-p)]$$

$$= -\frac{E}{kT} - N[p \ln p + (1-p)\ln(1-p)]$$

Then the free energy per spin becomes

$$f = \frac{F}{N} = \frac{E}{N} + kT[p \ln p + (1-p)\ln(1-p)]$$

$$= (1-2p)\epsilon + kT[p \ln p + (1-p)\ln(1-p)]$$

The last expression contains only a single undetermined parameter p which can be determined from the requirement of Q attaining a maximum, equivalent to f being a minimum

$$0 = \frac{\mathrm{d}f}{\mathrm{d}p} = -2\epsilon + kT\left[\ln p + p\frac{1}{p} + (-1)\ln(1-p) + (1-p)\frac{1}{1-p}(-1)\right]$$

or

$$\ln\left(\frac{1-p}{p}\right) = -\frac{2\epsilon}{kT}$$

yielding the result for the thermal equilibrium value of p

$$p = \frac{1}{1 + \exp(-2\epsilon/kT)}$$

Now having the fraction of spins aligned parallel to the field direction determined, the evaluation of the thermodynamic functions is straightforward; the free energy per spin is

$$f=-kT\ln[2\cosh(\epsilon/kT)]$$

and the internal energy per spin is

$$u=\bar{E}=-\epsilon\tanh(\epsilon/kT)$$

7.2. *Partition function*

For a more complex situation the set of non-interacting particles is separated into a number of subsets, each having energy $\epsilon_i n_i$. The free energy is written as

$$F=\sum_i f_i=\sum_i [\epsilon_i p_i+kTp_i\ln p_i]$$

Such a function is to be minimized with the constraint that all fractions are summed up to the unity, i.e.

$$\sum_i p_i=1$$

The actual functional to be minimized contains the Lagrange multiplier λ in front of the constraint

$$\tilde{F}=\sum_i [\epsilon_i p_i+kTp_i\ln p_i]+\lambda\sum_i p_i=\min$$

which yields

$$0=\frac{\partial\tilde{F}}{\partial p_i}=\epsilon_i+kT\left(\ln p_i+p_i\frac{1}{p_i}\right)+\lambda$$

or

$$p_i=\left[\exp\left(-\frac{\lambda+kT}{kT}\right)\right]\exp(-\epsilon_i/kT)$$

Hence we have

$$\sum_i p_i=\left[\exp\left(-\frac{\lambda+kT}{kT}\right)\right]\sum_i\exp(-\epsilon_i/kT)=1$$

and

$$\left[\exp\left(-\frac{\lambda+kT}{kT}\right)\right]=\frac{1}{\sum_i\exp(-\epsilon_i/kT)}$$

Making use of

$$Z=\sum_i \exp(-\epsilon_i/kT)$$

for the definition of the partition function Z (for "Zustandsumme"), the individual fractions become

$$p_i=\frac{\exp(-\epsilon_i/kT)}{Z}$$

All the thermodynamic functions (U, H, S, F, G, C_p, C_V, but also M, C_H, C_M, χ_T, χ_S) can be expressed with the help of the partition function. For example, the mean energy per particle is

$$\bar{E}=\sum_i p_i\epsilon_i=\frac{\sum_i \epsilon_i \exp(-\epsilon_i/kT)}{Z}$$

and since

$$\sum_i \epsilon_i \exp(-\beta\epsilon_i)=-\sum_i \frac{\partial}{\partial\beta}\exp(-\beta\epsilon_i)=-\frac{\partial Z}{\partial\beta}$$

this results in

$$\bar{E}=-\frac{1}{Z}\frac{\partial Z}{\partial\beta}=-\frac{\partial \ln Z}{\partial\beta}$$

For N particles the internal energy becomes

$$U=N\bar{E}$$

The entropy can be expressed as

$$S=k(\ln Z+\beta\bar{E})=k\ln Z+\frac{\bar{E}}{T}$$

and the free energy as

$$F=U-TS=-NkT\ln Z$$

The valuable expressions in terms of the partition function of a canonical system are presented in Table 8.

The partition function for a molecule is formed of the partition functions for individual types of energy increments (motions), i.e. from the translational, rotational, internal rotational (free rotation, hindered rotation), vibrational, electronic and nuclear spin partition functions

$$z^{\mathrm{mol}}=z^{\mathrm{t}}z^{\mathrm{r}}z^{\mathrm{ir}}\ldots z^{\mathrm{v}}z^{\mathrm{e}}z^{\mathrm{n}}$$

These increments have been expressed for certain model cases as indicated in Table 9.

Table 8
Thermodynamic functions in terms of the canonical partition function

Function	General expression (per particle)	Standard state of a perfect gas (1 mol)[a]
$U(S, V)$	$kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_{V,N}$	
$F(T, V)$	$-kT \ln Z$	
$p=-\left(\frac{\partial F}{\partial V}\right)_{T,N}$	$kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$	RT/V
pV	$kT\left(\frac{\partial \ln Z}{\partial \ln V}\right)_{T,N}$	RT
$H(S, p)$	$kT\left(\frac{\partial \ln Z}{\partial \ln T}\right)_{V,N}+kT\left(\frac{\partial \ln Z}{\partial \ln V}\right)_{T,N}$	$H_T^\circ=H_0^\circ+RT\left(\frac{\partial \ln Z}{\partial \ln T}\right)_p$
$\left.\begin{matrix} S(U, V) \\ S(H, p)\end{matrix}\right\}$	$k \ln Z+k\left(\frac{\partial \ln Z}{\partial \ln T}\right)_{V,N}$	$S_T^\circ=R \ln\left(\frac{Z}{N_A^*}\right)+R\left(\frac{\partial \ln Z}{\partial \ln T}\right)_p$
$G(T, p)$	$-kT \ln Z+kT\left(\frac{\partial \ln Z}{\partial \ln V}\right)_{T,N}$	$G_T^\circ=H_0^\circ-RT \ln\left(\frac{Z}{N_A^*}\right)$
$C_V=\left(\frac{\partial U}{\partial T}\right)_{V,N}$	$k\left(\frac{\partial \ln Z}{\partial \ln T}\right)_{V,N}+k\left[\frac{\partial^2 \ln Z}{\partial(\ln T)^2}\right]_{V,N}$	
$C_p=\left(\frac{\partial H}{\partial T}\right)_{p,N}$		$C_p^\circ=R\left(\frac{\partial \ln Z}{\partial \ln T}\right)_p+R\left[\frac{\partial^2 \ln Z}{\partial(\ln T)^2}\right]_p$

[a] $U_0^\circ=H_0^\circ=F_0^\circ=G_0^\circ=N_A(E_0^{\mathrm{el}}+\epsilon_0^{\mathrm{vib}})$; N_A^* is the numerical value of the Avogadro constant (number of particles per mole).

For a system of N identical non-interacting particles the total partition function is
(a) distinguishable particles (like in a solid state)

$$Z=(z)^N$$

(b) non-distinguishable particles (like in a perfect gas)

$$Z=\frac{(x)^N}{N!}$$

Using the Stirling formula

$$\ln N! \approx N \ln N-N$$

the last expression can be rewritten as

$$\ln Z=N \ln z-\ln N!=N[\ln(z/N)+1]$$

All energies entering the partition function should be related to the same reference state E_0. Usually this is a state of free, independent molecules in the ground nuclear and electronic configuration with the lowest values of quantum numbers for other

Table 9
Partition functions for a molecule

Type	Typical value	Model	Expression[a]
Translational, z^{t}	$10^{25}V$	particle in a rectangular box $V=abc$	$(2\pi mkT)^{3/2}h^{-3}V$
Rotational, z^{r}	10^3	solid rotator	$8\pi^2(8\pi^3 I_{\mathrm{A}}I_{\mathrm{B}}I_{\mathrm{C}})^{1/2}(kT)^{3/2}h^{-3}/\sigma$
linear molecule	10^2		$8\pi^2 IkTh^{-2}/\sigma$
Internal rotation			
free, z^{fr}	10	symmetric rotator	$(8\pi^3 I_{\mathrm{r}}kT)^{1/2}h^{-1}/\sigma_{\mathrm{m}}$
hindered, z^{hr}	10	periodical potential	$z^{\mathrm{fr}}\int_0^{2\pi}\exp[-(1-\cos n\alpha)V_0]\,\mathrm{d}\alpha$
Vibrational, z^{v}	10	harmonic oscillator	$\prod_{i=1}^{3n-6}\frac{1}{1-\exp(-h\nu_i/kT)}$
zero-point	1		$\sum_{i=1}^{3n-6}\exp(-h\nu_i/2kT)$
anharmonic corrections, z^{a}	1	anharmonic oscillator	$\prod_i^{3n-6}\left\{1-\frac{g_i^{\mathrm{v}}(g_i^{\mathrm{v}}+1)hx_{ii}/kT}{[\exp(h\nu_i/kT)-1]^2}\right\}$
Electronic, z^{e}	1	adiabatic potential minima	$\sum_i g_i^{\mathrm{e}}\exp[-(E_i-E_0)/kT]$
Nuclear, z^{n}	1	nuclear spins	$\prod_N(2I_N+1)$

[a] Symbols used: m, mass of the molecule; I_{A}, moments of inertia; I_{r}, reduced moment of inertia; σ, symmetry number; α, angle of the hindered rotation; V_0, barrier to internal rotation; ν_i, frequencies of the fundamental vibrations; x_{ii}, anharmonicity constants; g_i^{e}, degeneracy of electronic states; E_i, energies of electronic states; E_0, reference energy level (origin); I_N, nuclear spin number.

motions. This means that E_0 includes the zero-point vibration energy $\epsilon_0^{\mathrm{vib}}$ as well. Then for a system of N molecules

$$U_0=NE_0=N(E_0^{\mathrm{el}}+\epsilon_0^{\mathrm{vib}})$$

represents the internal energy of a perfect gas.

A unimolecular reaction A⇔B in the gas phase is characterized by the equilibrium constant

$$K_p=\exp\left(-\frac{G_{T,\mathrm{B}}^{\circ}-G_{T,\mathrm{A}}^{\circ}}{RT}\right)=\left(\frac{z_{\mathrm{B}}}{z_{\mathrm{A}}}\right)\exp\left(-\frac{H_{0,\mathrm{B}}^{\circ}-H_{0,\mathrm{A}}^{\circ}}{RT}\right)$$

For the general type of a chemical reaction

$$\sum_i \nu_i A_i=0$$

(the stoichiometric coefficients ν_i are negative for reactants and positive for products) the equilibrium constant becomes expressed through

$$-RT \ln K_p = \sum_i v_i G^\circ_{T,i}$$

and since

$$G^\circ_{T,i} = H^\circ_{T,i} - RT \ln\left(\frac{z_i}{N^*_\mathrm{A}}\right)$$

this implies the validity of

$$K_p = \prod_i \left(\frac{z_i}{N^*_A}\right)^{v_i} \exp\left(-\sum_i v_i H^\circ_{T,i}/RT\right)$$

7.3. Partition function in magnetism

When the individual particles of the system have the magnetic moments μ_i, then their energies in the presence of a field B are

$$\epsilon_i = -\mu_i B$$

The thermal average of the macroscopic magnetic moment is

$$\bar{\mu} = \sum_i p_i \mu_i = \frac{\sum_i \mu_i \exp(\beta\mu_i B)}{Z}$$

and since

$$\sum_i \mu_i \exp(\beta\mu_i B) = \frac{1}{\beta} \sum_i \frac{\partial}{\partial B} \exp(\beta\mu_i B) = \frac{1}{\beta} \frac{\partial Z}{\partial B}$$

it follows that

$$\bar{\mu} = \frac{1}{\beta Z} \frac{\partial Z}{\partial B} = kT \frac{\partial \ln Z}{\partial B}$$

If N is the number of magnetic moments per unit volume, the magnetization can be expressed as

$$M = NkT \frac{\partial \ln Z}{\partial B} = -\frac{\partial F}{\partial B}$$

The magnetic susceptibility adopts the form of

$$\chi = \mu_0 \frac{\partial M}{\partial B} = -\mu_0 \frac{\partial^2 F}{\partial B^2}$$

However, the magnetic moment is a vector and the magnetic susceptibility a second-rank tensor, so that the rigorous transcription is

$$\chi_{ab} = \mu_0 \frac{\partial}{\partial B_a} \left[\frac{\sum_i (\mu_i)_b \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)} \right]$$

with

$$(\mu_i)_b = -\frac{\partial \epsilon_i}{\partial B_b}$$

Important expressions of the statistical thermodynamics in magnetism are collected in Table 10.

Table 10
Thermodynamic functions of magnetism in terms of the canonical partition function

Function[a]	General expression (per particle)
$U(S, M)$	$kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_M$
$F(T, M)$	$-kT \ln Z$
$M = -\left(\frac{\partial F}{\partial B}\right)_T$	$kT\left(\frac{\partial \ln Z}{\partial B}\right)_T$
$\mu_0 HM$	$kT\left(\frac{\partial \ln Z}{\partial \ln B}\right)_T$
$E(S, H) = U(S, M) - \mu_0 HM$	$kT\left(\frac{\partial \ln Z}{\partial \ln T}\right)_M - kT\left(\frac{\partial \ln Z}{\partial \ln B}\right)_T$
$\left.\begin{array}{l} S(U, M) = (U-F)/T \\ S(E, H) = (E-G)/T \end{array}\right\}$	$k \ln Z + k\left(\frac{\partial \ln Z}{\partial \ln T}\right)_M$
$G(T, H) = F(T, M) - \mu_0 HM$	$-kT \ln Z - kT\left(\frac{\partial \ln Z}{\partial \ln B}\right)_T$
$C_M = \left(\frac{\partial U}{\partial T}\right)_M$	$k\left(\frac{\partial \ln Z}{\partial \ln T}\right)_M + k\left[\frac{\partial^2 \ln Z}{\partial (\ln T)^2}\right]_M$
$C_H = \left(\frac{\partial E}{\partial T}\right)_H$	
$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T$	$-\mu_0\left(\frac{\partial^2 F}{\partial B^2}\right)_T$
$\chi_S = \left(\frac{\partial M}{\partial H}\right)_S$	

[a] Symbol E is used for enthalpy instead of H which is the magnetic field strength.

7.4. Density matrix

The density matrix (the thermal average density matrix operator) is introduced through

$$\rho = \frac{\exp(-\beta\hat{H})}{Z}$$

The partition function Z is the trace (sum of diagonal elements) of a matrix for which the diagonal elements are

$$A_{ii} = \exp(-\beta\epsilon_i)$$

Such a matrix would be obtained as the representation in the orthogonal eigenstates of a Hamiltonian $\hat{H}$. Thus Z is no longer an operator; it is a number serving as the normalization constant. The above density matrix is normalized

$$\mathrm{Tr}\{\rho\} = 1$$

and can be used to compute the thermal average of any observable or operator

$$\langle A\rangle_T = \mathrm{Tr}\{A\rho\} = \mathrm{Tr}\{\rho A\}$$

Thus the thermal average energy is the internal energy

$$U = \bar{E} = N_A\bar{H} = N_A\langle\hat{H}\rangle_T = N_A\mathrm{Tr}\{\hat{H}\rho\} = N_A\frac{\mathrm{Tr}\{\hat{H}\exp(-\beta\hat{H})\}}{\mathrm{Tr}\{\exp(-\beta\hat{H})\}}$$

and since it holds true that

$$Z = \exp(-\beta F) = \mathrm{Tr}\{\exp(-\beta\hat{H})\}$$

also a well-known thermodynamic identity is obeyed

$$U = \frac{\partial(\beta F)}{\partial\beta}$$

The normalized density matrix satisfies

$$-\frac{\partial\rho}{\partial\beta} = (\hat{H} - \langle\hat{H}\rangle_T)\rho$$

The molar heat capacity can be expressed through the formula

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial\beta}\frac{\partial\beta}{\partial T} = \frac{\partial U}{\partial\beta}\frac{\partial}{\partial T}\left(\frac{1}{kT}\right) = -\frac{1}{kT^2}\frac{\partial U}{\partial\beta}$$

$$= -N_Ak\beta^2\frac{\partial}{\partial\beta}\left[\frac{\mathrm{Tr}\{\hat{H}\exp(-\beta\hat{H})\}}{\mathrm{Tr}\{\exp(-\beta\hat{H})\}}\right]$$

After the derivatives are accomplished, the following form appears:

$$C_V = -R\beta^2 \frac{\partial}{\partial\beta} \frac{\sum_i \hat{H} \exp(-\beta\hat{H})}{\sum_i \exp(-\beta\hat{H})}$$

$$= -R\beta^2 \frac{\left[\sum_i (-\hat{H}^2)\exp(-\beta\hat{H})\right]\left[\sum_i \exp(-\beta\hat{H})\right] - \left[\sum_i \hat{H}\exp(-\beta\hat{H})\right]\left[\sum_i (-\hat{H})\exp(-\beta\hat{H})\right]}{\left[\sum_i \exp(-\beta\hat{H})\right]^2}$$

$$= R\beta^2 \left\{ \frac{\sum_i (\hat{H}^2)\exp(-\beta\hat{H})}{\sum_i \exp(-\beta\hat{H})} - \left[\frac{\sum_i \hat{H}\exp(-\beta\hat{H})}{\sum_i \exp(-\beta\hat{H})}\right][\ldots]^{2} \right\}$$

$$= \mathrm{R}\upbeta^2 \{\langle\hat{H}^2\rangle_T - \langle H\rangle_T^2\}$$

which can be rewritten through a statistical variance as follows

$$C_V = R\beta^2 \langle(\hat{H} - U)^2\rangle_T$$

This result can be interpreted as the heat capacity (measured at the constant volume) being a thermal fluctuation in the internal energy.

As long as the magnetic field is applied, the Hamiltonian relaxes to

$$\hat{H} = \hat{H}_0 - B\hat{M}$$

where $\hat{M}[AM^2 = \mathrm{JT}^{-1}]$ is the magnetization operator. The thermal average magnetization is

$$\bar{M} = \langle M\rangle_T = \mathrm{Tr}\{\hat{M}\rho\} = -\frac{\partial F}{\partial B}$$

The molar isothermal magnetic susceptibility is then expressed as

$$\chi_T = N_{\mathrm{A}}\mu_0 \frac{\partial}{\partial B}\langle M\rangle_T = N_{\mathrm{A}}\mu_0 \frac{\partial}{\partial B}\left[\frac{\mathrm{Tr}\{\hat{M}\exp(-\beta\hat{H})\}}{\mathrm{Tr}\{\exp(-\beta\hat{H})\}}\right]$$

An analogous procedure of the differentiation as above yields the final result

$$\chi_T = N_{\mathrm{A}}\mu_0\beta\langle(\hat{M} - \bar{M})^2\rangle_T$$

which can be interpreted as the isothermal magnetic susceptibility, in fact, being a thermal fluctuation of the magnetization.

8. Temperature dependence of magnetic susceptibility

8.1. Magnetization formula

Statistical thermodynamics yields a result that the thermal average of the (molar) magnetization can be evaluated through the formula

$$M = N_A \frac{\sum_i \mu_i \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)} = N_A \frac{\sum_i \left(-\frac{\partial \epsilon_i}{\partial B}\right) \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

where the energy levels ϵ_i somehow depend upon the magnetic field. The molar differential magnetic susceptibility is obtained as the first derivative of the magnetization

$$\tilde{\chi} = \mu_0 \frac{\partial M}{\partial B}$$

If the above functions $\epsilon_i = f(B)$ and $M = f(B)$ were simple analytic functions, the treatment would be trivial.

Having the partition function of the system determined

$$Z = \sum_i^m \exp(-\epsilon_i/kT)$$

the magnetization can be expressed as

$$M = -\frac{\partial F}{\partial B} = N_A kT \frac{\partial \ln Z}{\partial B} = N_A \frac{1}{Z} \sum_i \left(-\frac{\partial \epsilon_i}{\partial B}\right) \exp(-\epsilon_i/kT)$$

Then the differential magnetic susceptibility is

$$\tilde{\chi} = \mu_0 \frac{\partial M}{\partial B} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} \left\{ \left[\sum_i \left(\frac{\partial \epsilon_i}{\partial B}\right)^2 \exp(-\epsilon_i/kT) - (kT) \sum_i \left(\frac{\partial^2 \epsilon_i}{\partial B^2}\right) \right.\right.$$
$$\left.\left. \times \exp(-\epsilon_i/kT) \right] Z - \left[\sum_i \left(\frac{\partial \epsilon_i}{\partial B}\right) \exp(-\epsilon_i/kT) \right]^2 \right\}$$

This formula for the magnetic susceptibility is useful when the magnetic energy levels $E_i = f(B)$ are simple analytic functions of the magnetic induction from which the first and second derivatives are easy to derive.

Normally the situation is more complex and one should follow the following steps.

(1) For the system under study an appropriate Hamiltonian is to be postulated. This is not necessarily an isotropic Hamiltonian; $\hat{H}_\parallel$ (parallel) and $\hat{H}_\perp$ (perpendicular) components can be distinguished in the case of an axial symmetry, or, $\hat{H}_x$, $\hat{H}_y$ and $\hat{H}_z$ components when the symmetry is even lower.

(2) Some magnetic parameters enter the matrix elements of the Hamiltonian con-

cerned: these are magnetogyric factors (g-factors, components of the g-tensors) and the coupling constants (components of the spin–spin coupling tensors D, in the case of an isotropic exchange abbreviated as J).

(3) The energy levels are received as eigenvalues of the Hamiltonian matrix spanning the wave function space. The wave functions concerned are represented by the set of spin functions, or a set of wavefunctions for coupled angular momenta (SO at one centre; spin–spin among more centres, etc.). Thus the basis set size can vary from two spin functions for a single $s=\frac{1}{2}$ centre to several millions, e.g. $N=6^8$ for a cluster of eight Fe(III) centres.

(4) From the field dependence of the energy levels $\epsilon_i=f(B)$ the first derivatives should be obtained. In the case of a vanishing field the derivatives should be taken in the limit from the right side ($B\rightarrow0^+$) because the applied field is non-negative.

As a result of this procedure, the magnetization and, consequently, the magnetic susceptibility are complicated (mostly implicit) functions of T, B, and a set of magnetic parameters. For linear magnetics (such as molecular paramagnets) the magnetization increases linearly with the field and the susceptibility is a field independent quantity

$$\bar{\chi}=\mu_0\frac{M}{B}=\frac{M}{H}$$

8.2. High-temperature approximation

Frequently we are interested in a region of temperature in which the energy levels are small compared with the thermal energy

$$\epsilon_i \ll kT$$

The partition function expanded in powers of T then becomes [19]

$$\frac{Z}{N}=\frac{1}{N}\left[\sum_{i=1}^{N}\left(1-\frac{\epsilon_i}{kT}+\frac{\epsilon_i^2}{2(kT)^2}-\dots\right)\right]$$

$$=1-\frac{\bar{\epsilon}}{kT}+\frac{\overline{\epsilon^2}}{2(kT)^2}-\dots=1+\sum_{p=1}^{\infty}b_pT^{-p}$$

Here N is the total number of energy levels ϵ_i and the expanding coefficients are

$$b_p=(-1)^p\frac{1}{p!k^p}\frac{1}{N}\sum_{i=1}^{N}(\epsilon_i)^p=(-1)^p\frac{\overline{(\epsilon/k)^p}}{p!}$$

Then the series expansion for ln Z is

$$\ln Z=\ln N-\sum_{n=1}^{\infty}a_nT^{-n}$$

with new coefficients

$$a_n = b_n - \tfrac{1}{2}\sum_{p=1}^{n-1} b_{n-p}b_p + \tfrac{1}{3}\sum_{p=1}^{n-2}\sum_{q=1}^{n-2} b_{n-p-q}b_pb_q + \dots$$

Now the molar magnetization can be expressed as

$$M = N_A\mu_0 k \sum_{n=1}^{\infty}\left(\frac{\partial a_n}{\partial B}\right)_T T^{-(n-1)}$$

This formula is further simplified if the origin of energy is chosen in such a way so that

$$\bar{\epsilon} = \frac{1}{N}\sum_{i=1}^{N}\epsilon_i = 0$$

holds true. In this case the leading terms of the magnetization are

$$M = N_A\mu_0\left[\frac{1}{2kT}\left(\frac{\partial\overline{\epsilon^2}}{\partial B}\right)_T - \frac{1}{6(kT)^2}\left(\frac{\partial\overline{\epsilon^3}}{\partial B}\right)_T + \dots\right]$$

The advantage of this high-temperature expansion is that we need not determine the individual energy levels but can use the theorem of the invariance of the trace of a matrix. For example, to find the value of $\overline{\epsilon^2}$ we square the Hamiltonian and pick out only the diagonal terms. On summing these terms over all possible values, many of the sums cancel. For example, the ZFS Hamiltonian of the form

$$\hat{H}^S = \mu_B B(g_x l\hat{S}_x + g_y^2 m\hat{S}_y + g_z n\hat{S}_z)[\hbar^{-1}] + (D_x\hat{S}_x^2 + D_y\hat{S}_y^2 + D_z\hat{S}_z^2)[\hbar^{-2}]$$

yields the mean value of

$$\overline{\epsilon^2} = (\mu_B B)^2(g_x^2 l^2 + g_y^2 m^2 + g_z^2 n^2)\frac{S(S+1)}{3} + (D_x^2 + D_y^2 + D_z^2)\frac{S(S+1)(2S-1)(2S+3)}{30}$$

and

$$\overline{\epsilon^3} = (\mu_B B)^2(g_x^2 l^2 D_x + g_y^2 m^2 D_y + g_z^2 n^2 D_z)\frac{S(S+1)(2S-1)(2S+3)}{30}$$

8.3. Van Vleck formula

The field dependence of the energy levels of magneto-active particles (atoms, molecules, clusters) can be expressed through a Taylor expansion. This leads to the appearance of several terms: linear in B (the first order Zeeman term), quadratic in

B (the second-order Zeeman term), etc. [1]

$$\epsilon_i = \epsilon_i^{(0)} + \epsilon_i^{(1)} B + \epsilon_i^{(2)} B^2 + \ldots$$

Then the Boltzmann factors can be replaced as follows:

$$\begin{aligned}\exp(-\epsilon_i/kT) &= \exp[-(\epsilon_i^{(0)} + \epsilon_i^{(1)} B + \epsilon_i^{(2)} B^2 + \ldots)/kT] \approx \exp(-\epsilon_i^{(0)}/kT) \\ &\quad \times \exp(-\epsilon_i^{(1)} B/kT) \approx \exp(-\epsilon_i^{(0)}/kT)[1 - \epsilon_i^{(1)} B/kT]\end{aligned}$$

where only dominating contributions survive. The magnetic moment is truncated at the second term

$$\mu_i = -\frac{\partial \epsilon_i}{\partial B} = -\frac{\partial}{\partial B}[\epsilon_i^{(0)} + \epsilon_i^{(1)} B + \epsilon_i^{(2)} B^2 + \ldots] = -\epsilon_i^{(1)} - 2\epsilon_i^{(2)} B + \ldots$$

To this approximation the thermal average magnetization can be expressed as follows:

$$\begin{aligned} M &= N_A \frac{\sum_i \mu_i \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)} \\ &= N_A \frac{\sum_i [-\epsilon_i^{(1)} - 2\epsilon_i^{(2)} B] \exp(-\epsilon_i^{(0)}/kT)[1 - \epsilon_i^{(1)} B/kT]}{\sum_i \exp(-\epsilon_i^{(0)}/kT)[1 - \epsilon_i^{(1)} B/kT]} \\ &= N_A \frac{\sum_i [-\epsilon_i^{(1)} - 2\epsilon_i^{(2)} B + (\epsilon_i^{(1)})^2 B/kT + 2B^2 \epsilon_i^{(1)} \epsilon_i^{(2)}/kT] \exp(-\epsilon_i^{(0)}/kT)}{\sum_i \exp(-\epsilon_i^{(0)}/kT)[1 - \epsilon_i^{(1)} B/kT]} \end{aligned}$$

In the limit of the vanishing field we have

$$M(B \to 0) = N_A \frac{\sum_i [-\epsilon_i^{(1)}] \exp(-\epsilon_i^{(0)}/kT)}{\sum_i \exp(-\epsilon_i^{(0)}/kT)} = 0$$

and for paramagnetic substances with the zero permanent magnetic polarization this should vanish. Retaining only terms linear in B, we arrive at the approximate expression for the magnetization

$$M = N_A B \frac{\sum_i \left[\frac{(-\epsilon_i^{(1)})^2}{kT} - 2\epsilon_i^{(2)} \right] \exp(-\epsilon_i^{(0)}/kT)}{\sum_i \exp(-\epsilon_i^{(0)}/kT)}$$

This derivation is evidently valid for substances obeying a linear dependence of the magnetization upon the applied magnetic field (paramagnets) and is very important. The expression for the mean magnetic susceptibility is straightforward:

$$\bar{\chi}=\mu_0\frac{M}{B}=\mu_0 N_{\mathrm{A}}\frac{\sum_i\left[\dfrac{(-\epsilon_i^{(1)})^2}{kT}-2\epsilon_i^{(2)}\right]\exp(-\epsilon_i^{(0)}/kT)}{\sum_i \exp(-\epsilon_i^{(0)}/kT)}$$

This is the famous van Vleck formula [1].

The van Vleck formula can be improved by maintaining some more terms in the numerator as well as in the denominator in the expression for the magnetization. The Zeeman coefficients, however, should be accessible and the derivative of the magnetization provided numerically. Then the magnetic susceptibility becomes a function of the magnetic field.

8.4. Generalized van Vleck formula

The van Vleck formula presupposes knowledge of the orientation of the principal molecular susceptibilities. For molecules lacking symmetry a generalized expression has been derived [20].

The magnetization in the given direction is expressed as

$$M_a=N_{\mathrm{A}}\frac{\sum_i(\mu_a)_i\exp(-\epsilon_i/kT)}{\sum_i\exp(-\epsilon_i/kT)}=N_{\mathrm{A}}\frac{\sum_i\left(-\dfrac{\partial\epsilon_i}{\partial B_a}\right)\exp(-\epsilon_i/kT)}{\sum_i\exp(-\epsilon_i/kT)}$$

In terms of the perturbation theory the energy of a magnetic level, to the second order, is

$$\epsilon_i=\epsilon_i^0+\sum_a\langle i|\hat{\mu}_a|i\rangle B_a+\sum_a\sum_b\sum_{j\neq i}\frac{\langle i|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_b|i\rangle}{\epsilon_i^0-\epsilon_j^0}B_aB_b$$

The basis set has been chosen in such a way that all groups of the levels degenerate before the perturbations are diagonal with respect to μB. Then the first derivative becomes

$$\frac{\partial\epsilon_i}{\partial B_a}=\langle i|\hat{\mu}_a|i\rangle+\sum_b\sum_{j\neq i}\frac{\langle i|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_b|i\rangle+\langle i|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|i\rangle}{\epsilon_i^0-\epsilon_j^0}B_b$$

Following the treatment of van Vleck, much simplification is obtained for a small magnetic field when the following expression is fulfilled:

$$\exp(-\epsilon_i/kT)\approx\exp(-\epsilon_i^0/kT)\left[1-\sum_a\langle i|\hat{\mu}_a|i\rangle B_a/kT\right]$$

On substitution into the magnetization formula and maintaining only terms linear in the field we get

$$M_a = N_\mathrm{A} \frac{\sum_b B_b \sum_i \left[\langle i|\hat{\mu}_a|i\rangle\langle i|\hat{\mu}_b|i\rangle/kT + \sum_{j\neq i} \frac{\langle i|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_b|i\rangle + \langle i|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|i\rangle}{\epsilon_i^0 - \epsilon_j^0} \right] \exp(-\epsilon_i^0/kT)}{\sum_i \exp(-\epsilon_i^0/kT)}$$

It has been claimed that the residual magnetization disappears in the zero field and coefficients of higher powers of the field are negligible. The generalized van Vleck formula for the magnetic susceptibility is [20]

$$\bar{\chi}_{ab} = N_\mathrm{A}\mu_0 \frac{\sum_i \left[\langle i|\hat{\mu}_a|i\rangle\langle i|\hat{\mu}_b|i\rangle/kT + \sum_{j\neq i} \frac{\langle i|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_b|i\rangle + \langle i|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|i\rangle}{\epsilon_i^0 - \epsilon_j^0} \right] \exp(-\epsilon_i^0/kT)}{\sum_i \exp(-\epsilon_i^0/kT)}$$

This reduces to the common van Vleck formula when applied to a diagonal element of the susceptibility tensor

$$\bar{\chi}_{aa} = N_\mathrm{A}\mu_0 \frac{\sum_i \left[\langle i|\hat{\mu}_a|i\rangle^2/kT + 2\sum_{j\neq i} \frac{\langle i|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_a|i\rangle}{\epsilon_i^0 - \epsilon_j^0} \right] \exp(-\epsilon_i^0/kT)}{\sum_i \exp(-\epsilon_i^0/kT)}$$

The choice of the basis set affects the first term of the magnetic susceptibility. Let us consider two matrices, ***A*** and ***B***, with elements in a completely general basis set

$$A_{kl} = \langle k|\hat{\mu}_a|l\rangle$$

and

$$B_{kl} = \langle k|\hat{\mu}_b|l\rangle$$

There exists a unitary transformation relating the general matrix ***B*** to the diagonal form $\boldsymbol{D}_b$

$$\boldsymbol{D}_b = \boldsymbol{B}' = \boldsymbol{U}^{-1}\boldsymbol{B}\boldsymbol{U}$$

The same transformation when applied to ***A*** may not yield a diagonal matrix

$$\boldsymbol{A}' = \boldsymbol{U}^{-1}\boldsymbol{A}\boldsymbol{U}$$

The product of the matrices is

$$\boldsymbol{A}'\boldsymbol{B}'=(\boldsymbol{U}^{-1}\boldsymbol{A}\boldsymbol{U})(\boldsymbol{U}^{-1}\boldsymbol{B}\boldsymbol{U})=\boldsymbol{U}^{-1}(\boldsymbol{A}\boldsymbol{B})\boldsymbol{U}$$

Since the trace of a matrix ($\boldsymbol{C}=\boldsymbol{A}\boldsymbol{B}$) is invariant under a unitary transformation we can write

$$\sum_k \sum_l A'_{kl}B'_{lk}=\sum_k \sum_l A_{kl}B_{lk}$$

and because the matrix $\boldsymbol{B}'$ was diagonal, we get

$$\sum_i A'_{ii}B'_{ii}=\sum_k \sum_l A_{kl}B_{lk}$$

We have proven that the following relationship holds true:

$$\sum_i \langle i|\hat{\mu}_a|i\rangle\langle i|\hat{\mu}_b|i\rangle=\sum_k \sum_l \langle k|\hat{\mu}_a|l\rangle\langle l|\hat{\mu}_b|k\rangle$$

where the indices k and l run over all elements of a general basis set including situations when the energy levels are degenerate $\epsilon_l^0=\epsilon_k^0$.

8.5. Partition function formula

The molecular Hamiltonian can be split into the field independent part and the part linear in the magnetic field [21]

$$\hat{H}=\hat{H}_0+\hat{H}'=\hat{H}_0+\sum_a \hat{Z}_a B_a$$

The zero-field Hamiltonian $\hat{H}_0$ includes the SO and spin–spin interactions and eventually the crystal field operators; the first-order Zeeman term $\hat{H}'$ comprises the orbital and spin contributions. The matrix elements of the full Hamiltonian in the chosen basis set are

$$H_{\nu\lambda}=\langle \nu|\hat{H}|\lambda\rangle$$

By the diagonalization of such a matrix

$$\epsilon=\boldsymbol{C}^{+}\boldsymbol{H}\boldsymbol{C}$$

the set of eigenvalues ϵ and the corresponding eigenvectors

$$|i\rangle=\sum_\nu C_{i\nu}|\nu\rangle$$

are obtained. Using the eigenvectors, the matrix elements of the magnetic moment operator are expressed as

$$(\mu_a)_i=-\frac{\partial\epsilon_i}{\partial B_a}=-\frac{\partial\langle i|\hat{H}|i\rangle}{\partial B_a}=-\langle i|\hat{Z}_a|i\rangle=-\sum_\nu \sum_\lambda C^{+}_{i\nu}(Z_a)_{\nu\lambda}C_{\lambda i}$$

Now the application of the magnetization formula yields

$$M_a = N_A \frac{\sum_i (\mu_a)_i \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)} = -N_A \frac{\sum_i \langle i|\hat{Z}_a|i\rangle \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

$$= -N_A \frac{\sum_i \left(\sum_v \sum_\lambda C_{iv}^+ (Z_a)_{v\lambda} C_{\lambda i}\right) \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

The diagonal component of the susceptibility tensor at a temperature T is

$$\bar{\chi}_{aa} = -\frac{N_A \mu_0}{B_a} \frac{\sum_i \langle i|\hat{Z}_a|i\rangle \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

$$= -\frac{N_A \mu_0}{B_a} \frac{\sum_i \left(\sum_v \sum_\lambda C_{iv}^+ (Z_a)_{v\lambda} C_{\lambda i}\right) \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

The powder averaging is achieved using the magnetic fields [21]

$$B_x = B_y = B_z = B/\sqrt{3}$$

and

$$\bar{\chi}_{\mathrm{av}} = \tfrac{1}{3}(\bar{\chi}_{xx} + \bar{\chi}_{yy} + \bar{\chi}_{zz}) = -\frac{N_A \mu_0}{\sqrt{3} B_a} \frac{\sum_a^{x,y,z} \sum_i \langle i|\hat{Z}_a|i\rangle \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

$$= -\frac{N_A \mu_0}{\sqrt{3} B_a} \frac{\sum_a^{x,y,z} \sum_i \left(\sum_v \sum_\lambda C_{iv}^+ (Z_a)_{v\lambda} C_{\lambda i}\right) \exp(-\epsilon_i/kT)}{\sum_i \exp(-\epsilon_i/kT)}$$

8.6. Polynomial fit formula

The above treatment requires determination of the eigenvalues as well the eigenvectors of the Hamiltonian. However, evaluation of eigenvalues represents only a fraction of the time required for the determination of all eigenvectors. It might be a great advantage to develop a method where only the eigenvalues need to be calculated [22].

For a given set of trial magnetic parameters the eigenvalues ϵ_{ai} in the given direction ($a = x, y, z$) are monotonous functions of the magnetic induction B and, therefore, a Taylor expansion is possible:

$$\epsilon_{ai}=\epsilon_{ai}^{(0)}+\epsilon_{ai}^{(1)}\Delta B+\epsilon_{ai}^{(2)}\Delta B^2+\epsilon_{ai}^{(3)}\Delta B^3+\epsilon_{ai}^{(4)}\Delta B^4+\ldots$$

with

$$\epsilon_{ai}^{(n)}=\frac{1}{n!}\left(\frac{\partial^n\epsilon_{ai}}{\partial B^n}\right)=c_{ai}^{(n)}$$

being the coefficients (derivatives) to be determined.

It is easy to generate $\epsilon_{ai,m}$ values for $m=3$ to 5 (or more) discrete points of B_m around a certain reference B_0, i.e.

$$B_m=B_0\pm N\delta$$

with $N=0, 1, 2,\ldots$. Thus it holds that

$$\epsilon_{ai,m}=c_{ai}^{(n)}+c_{ai}^{(n)}(\Delta B_m)+\ldots+c_{ai}^{(n)}(\Delta B_m)^n$$

for

$$\Delta B_m=B_m-B_0$$

and $n=m-1$. In a matrix form, the row matrices are interrelated through

$$(\epsilon_{ai,1}\quad \epsilon_{ai,2}\quad \ldots\quad \epsilon_{ai,m})=(c_{ai}^{(0)}\quad c_{ai}^{(1)}\quad \ldots\quad c_{ai}^{(n)})\begin{pmatrix}1 & 1 & \ldots & 1\\ \Delta B_1 & \Delta B_2 & \ldots & \Delta B_m\\ \ldots & \ldots & \ldots & \ldots\\ \Delta B_1^n & \Delta B_2^n & \ldots & \Delta B_m^n\end{pmatrix}$$

or

$$\boldsymbol{e}=\boldsymbol{cB}$$

with the working field matrix defined as follows

$$\boldsymbol{B}=\begin{pmatrix}1 & 1 & \ldots & 1\\ \Delta B_1 & \Delta B_2 & \ldots & \Delta B_m\\ \ldots & \ldots & \ldots & \ldots\\ \Delta B_1^n & \Delta B_2^n & \ldots & \Delta B_m^n\end{pmatrix}$$

Then the row matrix $\boldsymbol{c}$ of expansion coefficients $c_{ai}^{(n)}$ is calculated provided the inverse $\boldsymbol{B}^{-1}$ exists

$$\boldsymbol{c}=\boldsymbol{eB}^{-1}$$

Assembling the rows into matrices we have

$$\begin{pmatrix} \epsilon_{a1,1} & \epsilon_{a1,2} & \cdots & \epsilon_{a1,m} \\ \epsilon_{a2,1} & \epsilon_{a2,2} & \cdots & \epsilon_{a2,m} \\ \cdots & \cdots & \cdots & \cdots \\ \epsilon_{am,1} & \epsilon_{am,2} & \cdots & \epsilon_{am,m} \end{pmatrix} = \begin{pmatrix} c_{a1}^{(0)} & c_{a1}^{(1)} & \cdots & c_{a1}^{(n)} \\ c_{a2}^{(0)} & c_{a2}^{(1)} & \cdots & c_{a2}^{(n)} \\ \cdots & \cdots & \cdots & \cdots \\ c_{am}^{(0)} & c_{am}^{(1)} & \cdots & c_{am}^{(n)} \end{pmatrix} \begin{pmatrix} 1 & 1 & \cdots & 1 \\ \Delta B_1 & \Delta B_2 & \cdots & \Delta B_m \\ \cdots & \cdots & \cdots & \cdots \\ \Delta B_1^n & \Delta B_2^n & \cdots & \Delta B_m^n \end{pmatrix}$$

or

$$\boldsymbol{E} = \boldsymbol{CB}$$

and thus in one step all coefficients in the given direction ($a = x, y, z$) are determined

$$\boldsymbol{C} = \boldsymbol{EB}^{-1}$$

Only the $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$ coefficients enter the van Vleck formula for the components of the molar paramagnetic susceptibility which relaxes to the "polynomial fit formula" of the form

$$\chi_{aa} = N_A \mu_0 \frac{\sum_i \left[\frac{(c_{ai}^{(1)})^2}{kT} - 2c_{ai}^{(2)} \right] \exp(-c_{ai}^{(0)}/kT)}{\sum_i \exp(-c_{ai}^{(0)}/kT)}$$

In order to secure a good numerical stability, B_0 and δ should not be too low; instead the matrix $\boldsymbol{B}$ tends to be singular. For instance, $H_0 = 800\ \mathrm{A\ m^{-1}}$ ($B_0 = \mu_0 H_0$) and $\delta = (B_0/10)$ represent a good choice. The stability of the van Vleck coefficients $c^{(0)}$, $c^{(1)}$ and $c^{(2)}$ can be examined by increasing the number m of the terms in the Taylor expansion from 3 to 4 or 5.

From the computational point of view, evaluation of three to five sets of eigenvalues is much faster than one diagonalization with a full set of eigenvectors. This is more effective especially when large-dimensional matrices are concerned.

For a more precise average of the powder molar susceptibility a numerical integration over the polar angles is possible

$$\chi_{av} = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} \chi(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi$$

$$= -\frac{1}{4\pi} \int_{-1}^{+1} \left[\int_0^{2\pi} \chi(\vartheta, \varphi) \, d\varphi \right] d(\cos \vartheta)$$

The (spin) Zeeman term entering the total magnetic Hamiltonian is expressed as

$$\hat{H}'(\vartheta_k, \varphi_l) = \mu_B B_m (g_x \sin \vartheta_k \cos \varphi_l \hat{S}_x + g_y \sin \vartheta_k \sin \varphi_l \hat{S}_y + g_z \cos \vartheta_k \hat{S}_z)[\hbar^{-1}]$$

and this generates the angular-dependent susceptibility $\chi(\vartheta_k, \varphi_l)$. In practice a sphere is cut into several discrete grid points, say 25 values for ϑ_k and 25 values for φ_l, at which the susceptibility is evaluated. Then the integral is substituted for the finite sum formula

$$\chi_{\mathrm{av}} = \frac{\sum_k \sum_l \chi(\vartheta_k, \varphi_l)\Delta_k(\cos\vartheta)\Delta_l(\varphi)}{\sum_k \sum_l \Delta_k(\cos\vartheta)\Delta_l(\varphi)}$$

8.7. Finite difference formula

The need for the numerical determination of the expansion coefficients has already been emphasized by König and Kremer [23]. They, however, used a finite difference formula of the form

$$\mu_{ai}(B_0) = -\left(\frac{\partial\epsilon_{ai}(B)}{\partial B}\right)B_0 \approx -\frac{\Delta\epsilon_{ai}}{\Delta B} = \frac{[\epsilon_{ai}(B_0-\delta)]-[\epsilon_{ai}(B_0+\delta)]}{2\delta}$$

where the energy levels are evaluated at the three values of the fields: $\epsilon_i(B_0-\delta)$, $\epsilon_i(B_0)$ and $\epsilon_i(B_0+\delta)$. Then the magnetization formula is applied in the form of

$$M_a = N_{\mathrm{A}} \frac{\sum_i \mu_{ai}(B_0)\exp[-\epsilon_{ai}(B_0)/kT]}{\sum_i \exp[-\epsilon_{ai}(B_0)/kT]}$$

and the mean magnetic susceptibility results as follows:

$$\bar{\chi}_{aa} = \mu_0 \frac{M_a}{B_0}$$

The finite difference formula is applicable when the curvature of the energy levels is almost constant within the interval δ. This can be provided by reducing the value of δ with increasing reference field B_0.

It will be demonstrated below that the finite difference formula is obtained from the above more general polynomial fit formula under special assumptions. Let us consider the working field matrix in the form of

$$\boldsymbol{B} = \begin{pmatrix} 1 & 1 & 1 \\ B_0-\delta & B_0 & B_0+\delta \\ (B_0-\delta)^2 & (B_0)^2 & (B_0+\delta)^2 \end{pmatrix}$$

Its inverse is

$$\boldsymbol{B}^{-1} = \frac{1}{2\delta^2}\begin{pmatrix} B_0(B_0+\delta) & -2B_0-\delta & 1 \\ -(B_0^2-\delta^2) & 4B_0 & -2 \\ B_0(B_0-\delta) & -2B_0+\delta & 1 \end{pmatrix}$$

This immediately yields the first-order expansion coefficient as

$$c_i^{(1)} = \sum_{k=1}^{3} \epsilon_k (B^{-1})_{k,2} = \frac{1}{2\delta^2} \{[\epsilon_1(B_0-\delta)](-2B_0-\delta) + [\epsilon_2(B_0)](4B_0) + [\epsilon_3(B_0+\delta)](-2B_0+\delta)\}$$

This can be written as consisting of two terms

$$c_i^{(1)} = \frac{1}{2\delta^2} \{[\epsilon_1(B_0-\delta)](-\delta) + [\epsilon_3(B_0+\delta)](+\delta)\} + \frac{1}{2\delta^2} \{[\epsilon_1(B_0-\delta)](-2B_0) + [\epsilon_2(B_0)](4B_0) + [\epsilon_3(B_0+\delta)](-2B_0)\}$$

or

$$c_i^{(1)} = -\frac{1}{2\delta} \{[\epsilon_1(B_0-\delta)] - [\epsilon_3(B_0+\delta)]\} + O(B_0/\delta^2)$$

Omitting the remainder $O(B_0/\delta^2)$, being a correction for the non-constant curvature of the energy level, we get the result

$$\mu_i = -c_i^{(1)} = \frac{1}{2\delta} \{[\epsilon_1(B_0-\delta)] - [\epsilon_3(B_0+\delta)]\}$$

which is identical with the postulate of König and Kremer.

8.8. Polynomial magnetization formula

The polynomial fit formula can be applied for a more exact evaluation of the magnetization

$$M_a(B_m) = N_A \frac{\sum_i \mu_{ai}(B_m) \exp[-\epsilon_{ai}(B_m)/kT]}{\sum_i \exp[-\epsilon_{ai}(B_m)/kT]}$$

Since the expansion coefficients appearing in each energy level are accessible

$$\epsilon_{ai,m} = c_{ai}^{(0)} + c_{ai}^{(1)}(\Delta B_m) + \ldots + c_{ai}^{(n)}(\Delta B_m)^n$$

then the microscopic magnetic moments become expressed as follows

$$\mu_{ai}(B_m) = -\frac{\partial \epsilon_{ai,m}}{\partial B_m} = -[c_{ai}^{(1)}(\Delta B_m) + 2c_{ai}^{(2)}(\Delta B_m) \ldots + nc_{ai}^{(n)}(\Delta B_m)^{n-1}]$$

This is how the limitations of the van Vleck formula can be overcome. As above, the evaluation of the mean magnetic susceptibility is

$$\bar{\chi}_{aa} = \mu_0 \frac{M_a}{B_m}$$

The evaluation of the differential susceptibility requires a mapping of the field dependence of the magnetization; hence

$$\tilde{\chi}_{aa} = \mu_0 \frac{\partial M_a(B)}{\partial B}$$

This no longer represents any conceptual problem: from the field dependence of the microscopic magnetic moments

$$\mu_{ai}(B_m) = -\frac{\partial \epsilon_{ai,m}}{\partial B_m} = -[c_{ai}^{(1)}(\Delta B_m) + 2c_{ai}^{(2)}(\Delta B_m)\ldots + nc_{ai}^{(n)}(\Delta B_m)^{n-1}]$$

the field dependent magnetization results

$$M_a(B_m) = N_{\mathrm{A}} \frac{\sum_i \mu_{ai}(B_m)\exp[-\epsilon_{ai}(B_m)/kT]}{\sum_i \exp[-\epsilon_{ai}(B_m)/kT]}$$

This can be a subject of the polynomial fit

$$M_a(B_m) = d_a^{(0)} + d_a^{(1)}(\Delta B_m) + d_a^{(2)}(\Delta B_m)^2 + \ldots$$

where the expansion coefficients $d_a^{(m)}$ can be determined analogously as outlined above. Let us consider a transformation

$$(M_{a,1} \quad M_{a,2} \quad \ldots \quad M_{a,m}) = (d_a^{(0)} \quad d_a^{(1)} \quad \ldots \quad d_a^{(n)}) \begin{pmatrix} 1 & 1 & \ldots & 1 \\ \Delta B_1 & \Delta B_2 & \ldots & \Delta B_m \\ \ldots & \ldots & \ldots & \ldots \\ \Delta B_1^n & \Delta B_2^n & \ldots & \Delta B_m^n \end{pmatrix}$$

or

$$\boldsymbol{M} = \boldsymbol{dB}$$

Then the inverse transformation is

$$\boldsymbol{d} = \boldsymbol{MB}^{-1}$$

and the differential magnetic susceptibility is simply given via the first-order expansion coefficient

$$\chi_{aa} = \mu_0 d_a^{(1)}$$

As an example, for the working field matrix

$$\boldsymbol{B}=\begin{pmatrix} 1 & 1 & 1 \\ B_0-\delta & B_0 & B_0+\delta \\ (B_0-\delta)^2 & (B_0)^2 & (B_0+\delta)^2 \end{pmatrix}$$

and its inverse

$$\boldsymbol{B}^{-1}=\frac{1}{2\delta^2}\begin{pmatrix} B_0(B_0+\delta) & -2B_0-\delta & 1 \\ -(B_0^2-\delta^2) & 4B_0 & -2 \\ B_0(B_0-\delta) & -2B_0+\delta & 1 \end{pmatrix}$$

we obtain

$$d_a^{(1)}=\sum_{k=1}^{3} M_{a,k}(B^{-1})_{k,2}=\frac{1}{2\delta^2}\{[M_{a,1}(B_0-\delta)](-2B_0-\delta)+[M_{a,2}(B_0)](4B_0) \\ +[M_{a,3}(B_0+\delta)](-2B_0+\delta)\}$$

and two terms of the differential magnetic susceptibility appear

$$\chi_{aa}=\mu_0 d_a^{(1)}=\mu_0\frac{1}{2\delta}\{-[M_{a,1}(B_0-\delta)]+[M_{a,3}(B_0+\delta)]\} \\ +\mu_0\frac{B_0}{\delta^2}\{-[M_{a,1}(B_0-\delta)]+2[M_{a,2}(B_0)]-[M_{a,3}(B_0+\delta)]\}$$

In the case of linear magnetics there is

$$M_{a,1}(B_0-\delta)=M_{a,2}(B_0)-\Delta M$$

$$M_{a,3}(B_0+\delta)=M_{a,2}(B_0)+\Delta M$$

and the above formula correctly collapses to

$$\chi_{aa}=\mu_0\frac{\Delta M}{\delta}=\bar{\chi}_{aa}$$

8.9. Brillouin function

The magnetic energy expressed as

$$E=-\boldsymbol{M}\cdot\boldsymbol{B}=-\mu_0\boldsymbol{M}\cdot\boldsymbol{H}$$

tends to align the magnetic moments parallel to the applied field. This is in competition with the thermal energy kT which favours the disorder of magnetic moments.

The projection of the magnetic moment along the quantum axis (z) can adopt only discrete values and the corresponding Zeeman Hamiltonian term is

$$\hat{H}^{Z} = -g_J \mu_B B_z \hat{J}_z [\hbar^{-1}]$$

The energy levels forming a $(2J+1)$-multiplet are expressed as follows

$$\epsilon(M_J) = -g_J \mu_B B_z \langle J, M_J | \hat{J}_z | J, M_J \rangle [\hbar^{-1}] = -g_J \mu_B B_z M_J$$

This allows one to define the partition function as a sum

$$Z = \sum_{M_J=-J}^{+J} \exp(g_J \mu_B B_z M_J / kT) = \sum_{m=-J}^{+J} \exp(-\eta m)$$

for the parameter

$$\eta = \frac{g_J \mu_B B_z}{kT}$$

This is a finite geometric series which can be exactly summed to yield

$$Z = \frac{\exp(-\eta J) - \exp[\eta(J+1)]}{1 - \exp(\eta)}$$

On multiplying the numerator and denominator by $\exp(-\eta/2)$ we get the expression

$$Z = \frac{\exp[-\eta(J+1)] - \exp[\eta(J+1)]}{\exp(-\eta/2) - \exp(\eta/2)} = \frac{\sinh[\eta(J+1/2)]}{\sinh(\eta/2)}$$

Notice some expressions for the hyperbolic functions

$$\sinh(x) = \frac{\exp(x) - \exp(-x)}{2}$$

$$\cosh(x) = \frac{\exp(x) + \exp(-x)}{2}$$

$$\coth(x) = \frac{\cosh(x)}{\sinh(x)} = \frac{\exp(x) + \exp(-x)}{\exp(x) - \exp(-x)}$$

The magnetization obeys the relation of the statistical thermodynamics according to which

$$M = -\frac{\partial F}{\partial B} = N_A kT \frac{\partial \ln Z}{\partial B} = (N_A kT) \frac{\partial \ln Z(\eta)}{\partial \eta} \frac{\partial \eta}{\partial B}$$

$$= (N_A kT) \left(\frac{g_J \mu_B}{kT} \right) \frac{\partial \ln Z(\eta)}{\partial \eta}$$

The derivative is expressed as follows

$$\frac{\partial \ln Z(\eta)}{\partial \eta}=\frac{\partial}{\partial \eta}\ln\left\{\frac{\sinh[\eta(J+1/2)]}{\sinh(\eta/2)}\right\}=\frac{\partial}{\partial \eta}\ln\{\sinh[\eta(J+1/2)]\}$$

$$-\frac{\partial}{\partial \eta}\ln[\sinh(\eta/2)]=\frac{\cosh[\eta(J+1/2)]}{\sinh[\eta(J+1/2)]}(J+1/2)-\frac{\cosh(\eta/2)}{\sinh(\eta/2)}\frac{1}{2}$$

Then the magnetization becomes

$$M=(N_A g_J \mu_0 J)\left\{\frac{J+1/2}{J}\coth[\eta(J+1/2)]-\frac{1}{2J}\coth(\eta/2)\right\}$$

or

$$M=M_0 B_J(\eta)$$

where

$$M_0=N_A g_J \mu_B J$$

is the maximum available magnetization (at the zero temperature). Here the Brillouin function has been introduced as

$$B_J(\eta)=\frac{J+1/2}{J}\coth[\eta(J+1/2)]-\frac{1}{2J}\coth(\eta/2)$$

This function is plotted in Fig. 6 for some representative values of spins.

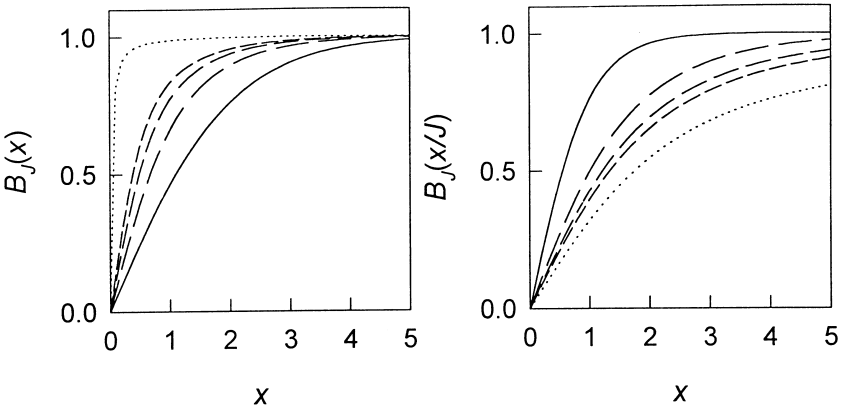


Fig. 6. Brillouin function for $J=1/2$, 3/2, 5/2, 7/2 and 50: (a) for an argument x; (b) for a reduced argument (x/J).

The Brillouin function can be met in literature also in the form

$$B'_J(x)=B_J(x/J)=\frac{J+1/2}{J}\coth\left(x\frac{J+1/2}{J}\right)-\frac{1}{2J}\coth\left(x\frac{1}{2J}\right)$$

which differs from the previous presentation in the argument being divided by J.

For a small argument (when the field B is small and T is high enough) the expansion

$$\coth(x)\approx\frac{1}{x}+\frac{x}{3}$$

can be used, which yields an approximate expression for the Brillouin function

$$B_J(\eta)\approx\eta\frac{J+1}{3}$$

Then the magnetization becomes a linear function of the applied field, hence

$$M=M_0B_J(\eta)=(N_Ag_J\mu_BJ)\left(\frac{g_J\mu_B\mu_0H}{kT}\right)\frac{J+1}{3}=\frac{C}{T}H$$

where the Curie constant is introduced as

$$C=\frac{N_A\mu_0\mu_B^2g_J^2J(J+1)}{3k}$$

This may be rewritten by introducing the effective magnetic moment

$$\mu_{\mathrm{eff}}=\mu_Bg_J\sqrt{J(J+1)}$$

as follows:

$$C=\frac{N_A\mu_0}{3k}\mu_{\mathrm{eff}}^2$$

8.10. Langevin function

In the classical model the magnetic entities carry a localized magnetic moment $\boldsymbol{m}_0$ having an arbitrary direction. The magnetic energy in an applied field is

$$E=-Bm_0\cos\theta=-\mu_0Hm_0\cos\theta$$

where θ is the angle between vectors $\boldsymbol{m}_0$ and $\boldsymbol{H}$. In the partition function the summation over a continuous change of $\cos\theta$ leads to the integral

$$Z=\int_{-1}^{+1}\exp(\mu_0m_0H\cos\theta/kT)\,\mathrm{d}\cos\theta=\int_{-1}^{+1}\exp(xu)\,\mathrm{d}u=\frac{2\sinh(x)}{x}$$

with the parameter

$$x=\frac{\mu_0 m_0 H}{kT}$$

The proportion of magnetic moments whose direction belongs to the solid angle

$$\mathrm{d}\Omega=2\pi\sin\theta\,\mathrm{d}\theta$$

is given by the Boltzmann statistics as

$$\mathrm{d}N=\frac{\exp(xu)\,\mathrm{d}u}{Z}$$

The average value of the magnetic moment $\boldsymbol{m}$ along the field is

$$m=\langle m_0\cos\theta\rangle=kT\frac{\partial\ln Z}{\partial B}$$

This yields the magnetization expressed as

$$M=M_0 L(x)$$

where the Langevin function has been introduced

$$L(x)=\coth(x)-\frac{1}{x}$$

For small values of the argument the Langevin function can be expanded to yield

$$L(x)\approx\frac{x}{3}$$

In such a case the magnetization varies linearly with the applied field

$$M=M_0\frac{x}{3}=(N_{\mathrm{A}}m_0)\left(\frac{\mu_0 m_0 H}{3kT}\right)=\frac{C_{\mathrm{cl}}}{T}H$$

where the (classical) Curie constant is

$$C_{\mathrm{cl}}=\frac{N_{\mathrm{A}}\mu_0 m_0^2}{3k}$$

The Langevin function is obtained in the classical limit to the reduced Brillouin function as

$$L(x)=\lim_{J\to\infty}B_J'(x)$$

or simply by setting a large number for J in the Brillouin function. The behaviour of the Langevin function is simulated in Fig. 6 by setting $J=50$.

9. Curie paramagnets

Let us investigate the situation of having an orbitally non-degenerate atomic term ${}^{2S+1}S$ or a molecular state ${}^{2S+1}A$ and ${}^{2S+1}B$. In the absence of thermally accessible excited states the only contribution to the spin Hamiltonian is an isotropic (spin) Zeeman term

$$\hat{H}^{Z} = \mu_{\mathrm{B}} g_{\mathrm{e}} B_z \hat{S}_z [\hbar^{-1}]$$

With the kets $|i\rangle = |S, M_S\rangle$ this produces the eigenvalues

$$\epsilon_i = \mu_{\mathrm{B}} g_{\mathrm{e}} B_z M_S$$

Then the molar magnetization is given through the Brillouin function as

$$M_z = (N_{\mathrm{A}} \mu_{\mathrm{B}} g_{\mathrm{e}} S) B_S(\eta)$$

for the argument

$$\eta = \frac{\mu_{\mathrm{B}} g_{\mathrm{e}} B_z}{kT}$$

For small arguments ($\eta \ll 1$, small fields, high temperature) an expansion of the Brillouin function is possible

$$B_S(\eta) \approx \frac{S+1}{3} \eta$$

and then the magnetization becomes a linear function of the field

$$M_z = (N_{\mathrm{A}} \mu_{\mathrm{B}} g_{\mathrm{e}} S) \frac{S+1}{3} \frac{\mu_{\mathrm{B}} g_{\mathrm{e}} \mu_0 H_z}{kT}$$

Consequently, the mean molar magnetic susceptibility obeys the Curie law

$$\bar{\chi}_{\mathrm{mol}} = \frac{M_z}{H_z} = \frac{N_{\mathrm{A}} \mu_0 \mu_{\mathrm{B}}^2}{k} \frac{S(S+1)}{3} \frac{g_{\mathrm{e}}^2}{T} = C_0 \frac{S(S+1)}{3} \frac{g_{\mathrm{e}}^2}{T}$$

with the reduced Curie constant

$$C_0 = \frac{N_{\mathrm{A}} \mu_0 \mu_{\mathrm{B}}^2}{k}$$

The behaviour of the magnetization with respect to the magnetic field is shown in Fig. 7.

The obedience of the Curie law implies that the product function

$$(\bar{\chi}_{\mathrm{mol}} T) = C$$

versus T is a straight line with zero slope.

When the linear approximation to the Brillouin function is not fulfilled the

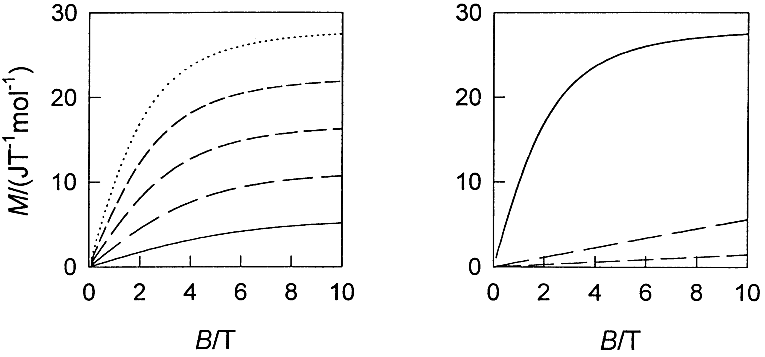


Fig. 7. Molar magnetization versus magnetic field for paramagnets: (a) individual curves correspond to $S=1/2$ (solid), 1 (long dashed), 3/2 (medium dashed), 2 (short dashed) and 5/2 (dotted) for $T=4.2$ K; (b) individual curves correspond to $T=4.2$ (solid), 77 (long dashed) and 300 K (medium dashed) for $S=5/2$.

magnetic susceptibility is no longer given by a simple ratio $\bar{\chi}=M/H$, but a derivative should be applied in order to obtain the differential susceptibility

$$\chi=\frac{\partial M}{\partial H}=\mu_0\frac{\partial M}{\partial B}$$

This is evident from Fig. 8, where the differential magnetic susceptibility is

$$\chi_{\mathrm{mol}}=C_0\frac{g^2}{T}\left((S+1/2)^2\left\{1-\left[\frac{\exp(x)+\exp(-x)}{\exp(x)-\exp(-x)}\right]^2\right\}\right.$$
$$\left.-\frac{1}{4}\left\{1-\left[\frac{\exp(y)+\exp(-y)}{\exp(y)-\exp(-y)}\right]^2\right\}\right)$$

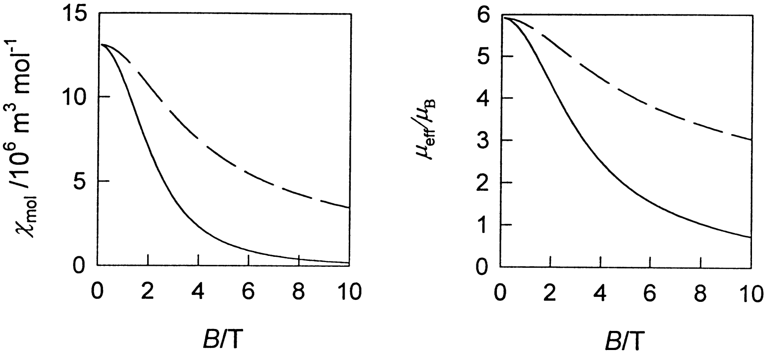


Fig. 8. Correct (solid line, based on the differential susceptibility) and approximate (dashed line, based on the mean susceptibility) functions for an $S=5/2$ paramagnet at $T=4.2$ K.

for the arguments

$$x=(S+1/2)\frac{g\mu_{\mathrm{B}}B}{kT}$$

and

$$y=\frac{1}{2}\frac{g\mu_{\mathrm{B}}B}{kT}$$

10. ZFS systems

10.1. Zero-field energy

The Hamiltonian that accounts for the spin–spin interaction in the simplest form is

$$\hat{H}^{\mathrm{zfs}}=\sum_a\sum_b D'_{ab}\hat{S}_a\hat{S}_b[\hbar^{-2}]$$

Assuming that the coordinate axes are identical with the principal axes of the D-tensor, only the diagonal elements contribute

$$\hat{H}^{\mathrm{zfs}}=\sum_a D'_{aa}\hat{S}_a^2[\hbar^{-2}]=(D'_{xx}\hat{S}_x^2+D'_{yy}\hat{S}_y^2+D'_{zz}\hat{S}_z^2)[\hbar^{-2}]$$

By introducing new parameters

$$D=\tfrac{1}{2}(-D'_{xx}-D'_{yy}+2D'_{zz})$$

$$E=\tfrac{1}{2}(D'_{xx}-D'_{yy})$$

$$K=\tfrac{1}{3}(D'_{xx}+D'_{yy}+D'_{zz})$$

the equivalent form of the $\hat{H}^{\mathrm{zfs}}$ operator is

$$\hat{H}^{\mathrm{zfs}}=\left[D(\hat{S}_z^2-\tfrac{1}{3}\hat{S}^2)+E(\hat{S}_x^2-\hat{S}_y^2)+K\hat{S}^2\right][\hbar^{-2}]$$

(a simple substitution for parameters serves as a proof). Notice, the D and E parameters remain unchanged when the same constant term is added (subtracted) to the diagonal elements of the D-tensor. The constant term $K\hat{S}^2$ can be deleted from further consideration since it uniformly shifts all the energy levels. The omission of the constant term, in fact, corresponds to subtraction of one-third of the trace of the D-tensor from the diagonal elements

$$\tilde{D}_{ab}=D'_{ab}-\tfrac{1}{3}(D'_{xx}+D'_{yy}+D'_{zz})\delta_{ab}$$

Consequently, the (diagonal) D-tensor becomes traceless

$$\tilde{D}_{xx}+\tilde{D}_{yy}+\tilde{D}_{zz}=0$$

for

$$\hat{H}^{\mathrm{zfs}}=(\tilde{D}_{xx}\hat{S}_x^2+\tilde{D}_{yy}\hat{S}_y^2+\tilde{D}_{zz}\hat{S}_z^2)[\hbar^{-2}]$$

Now the D-tensor components and the ZFS parameters are interrelated through

$$D=\tfrac{3}{2}\,\tilde{D}_{zz}=-\tfrac{3}{2}\,(\tilde{D}_{xx}+\tilde{D}_{yy})$$

$$E=\tfrac{1}{2}\,(\tilde{D}_{xx}-\tilde{D}_{yy})$$

and

$$\tilde{D}_{xx}=-\tfrac{1}{3}\,D+E$$

$$\tilde{D}_{yy}=-\tfrac{1}{3}\,D-E$$

$$\tilde{D}_{zz}=\tfrac{2}{3}\,D$$

It is customary [24] to assign the three principal values of the D-tensor in such a way that the following relations are fulfilled

$$|\tilde{D}_{zz}|\geqslant|\tilde{D}_{yy}|\geqslant|\tilde{D}_{xx}|$$

Consequently, the asymmetry parameter

$$\eta=\frac{3E}{D}=\frac{\tilde{D}_{xx}-\tilde{D}_{yy}}{\tilde{D}_{zz}}$$

is restricted to the range

$$0\leqslant\eta\leqslant1$$

Nevertheless, a different convention [25] assumes that

$$\check{D}_{xx}=-\tfrac{1}{3}\,D-E$$

$$\check{D}_{yy}=-\tfrac{1}{3}\,D+E$$

$$\check{D}_{zz}=\tfrac{2}{3}\,D$$

and introduces the new parameter

$$\lambda=\frac{E}{D}=\frac{\check{D}_{yy}-\check{D}_{xx}}{3\check{D}_{zz}}$$

restricted to

$$-\tfrac{1}{3}\leqslant\lambda\leqslant+\tfrac{1}{3}$$

With this fixation E is always positive and thus the sign of λ determines the sign of D and vice versa.

With the help of the angular momentum matrices it is easy to construct the ZFS Hamiltonian matrix for the given value of S (Table 11). In the absence of the external magnetic field the $\hat{H}^{\mathrm{zfs}}$ term is the only perturbation that influences the magnetic energy levels (except the case of $S=1/2$ for which this vanishes). Then the energy levels in the zero magnetic field are obtained by solving the secular equation

$$\det\{\langle M_S|\hat{H}^{\mathrm{zfs}}|M'_S\rangle - \delta_{M_S,M'_S}\epsilon\} = 0$$

The corresponding eigenvalues are listed in Table 11 when the analytic solution exists. The effect of the D and E parameters on energy levels is displayed in Figs. 9 and 10.

10.2. Splitting in the magnetic field

The presence of the magnetic field is covered by the following form of the Hamiltonian

$$\hat{H}^{\mathrm{mg}} = \hat{H}^{\mathrm{zfs}} + \hat{H}^{\mathrm{Z}}$$

Table 11
Matrices of the ZFS Hamiltonian

Matrix $\langle M_S\|\hat{H}^{\mathrm{zfs}}\|M'_S\rangle$	Eigenvalues
$S=1/2$ $\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$	
$S=1$ $\begin{pmatrix} (1/3)D & 0 & E \\ 0 & -(2/3)D & 0 \\ E & 0 & (1/3)D \end{pmatrix}$	$\epsilon_1 = -(2/3)D$ $\epsilon_2 = (1/3)D + E$ $\epsilon_3 = (1/3)D - E$
$S=3/2$ $\begin{pmatrix} D & 0 & \sqrt{3}E & 0 \\ 0 & -D & 0 & \sqrt{3}E \\ \sqrt{3}E & 0 & -D & 0 \\ 0 & \sqrt{3}E & 0 & D \end{pmatrix}$	$\epsilon_1 = \epsilon_2 = -\sqrt{D^2 + 3E^2}$ $\epsilon_3 = \epsilon_4 = +\sqrt{D^2 + 3E^2}$
$S=2$ $\begin{pmatrix} 2D & 0 & \sqrt{6}E & 0 & 0 \\ 0 & -D & 0 & 3E & 0 \\ \sqrt{6}E & 0 & -2D & 0 & \sqrt{6}E \\ 0 & 3E & 0 & -D & 0 \\ 0 & 0 & \sqrt{6}E & 0 & 2D \end{pmatrix}$	$\epsilon_1 = -D - 3E$ $\epsilon_2 = -D + 3E$ $\epsilon_3 = 2D$ $\epsilon_4 = -2\sqrt{D^2 + 3E^2}$ $\epsilon_5 = +2\sqrt{D^2 + 3E^2}$
$S=5/2$[a] $\begin{pmatrix} (10/3)D & 0 & \sqrt{10}E & 0 & 0 & 0 \\ 0 & -(2/3)D & 0 & \sqrt{18}E & 0 & 0 \\ \sqrt{10}E & 0 & -(8/3)D & 0 & \sqrt{18}E & 0 \\ 0 & \sqrt{18}E & 0 & -(8/3)D & 0 & \sqrt{10}E \\ 0 & 0 & \sqrt{18}E & 0 & -(2/3)D & 0 \\ 0 & 0 & 0 & \sqrt{10}E & 0 & (10/3)D \end{pmatrix}$	$\epsilon_1 = \epsilon_2 = -2D\alpha\cos[(\pi - \arccos\beta)/3]$ $\epsilon_3 = \epsilon_4 = -2D\alpha\cos[(\pi + \arccos\beta)/3]$ $\epsilon_5 = \epsilon_6 = 2D\alpha\cos[(\arccos\beta)/3]$

[a] Goniometric solution of a cubic equation for $\alpha = \sqrt{28(1 + 3E^2/D^2)/9}$ and $\beta = 80(1 - 9E^2/D^2)/(3\alpha)^3$.

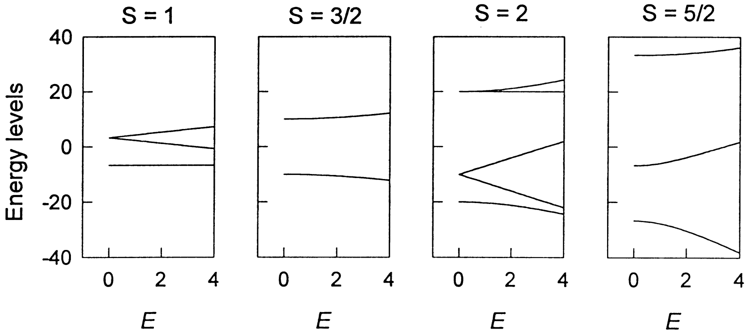


Fig. 9. Energy levels of $S=1$, 3/2, 2 and 5/2 paramagnets split in the zero field; $D=10$ (arbitrary units).

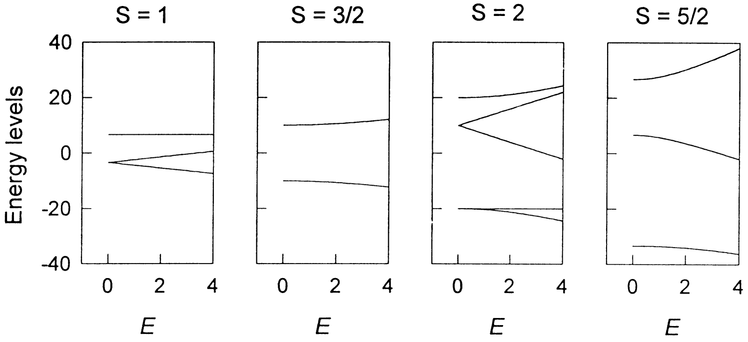


Fig. 10. Energy levels of $S=1$, 3/2, 2 and 5/2 paramagnets split in the zero field; $D=-10$ (arbitrary units).

where the (spin) Zeeman term is given as

$$\hat{H}^{Z}=\mu_{B}(g_{x}B_{x}\hat{S}_{x}+g_{y}B_{y}\hat{S}_{y}+g_{z}B_{z}\hat{S}_{z})[\hbar^{-1}]$$

Then the energy levels are obtained as eigenvalues of the secular equation

$$\det\{\langle M_{S}|\hat{H}^{\mathrm{mg}}|M_{S}'\rangle-\epsilon_{i,a}\delta_{M_{S},M_{S}'}\}=0$$

for individual Cartesian directions ($a=x, y, z$).

Let us first assume the case of $E=0$ (only axial anisotropy, no rhombic anisotropy). For the first case of $S=1$ the three secular equations in individual directions can be combined into a single equation

$$\det\begin{pmatrix}1\cdot G_{z}+D-\epsilon & (1/\sqrt{2})G_{-} & 0\\ (1/\sqrt{2})G_{+} & 0-\epsilon & (1/\sqrt{2})G_{-}\\ 0 & (1/\sqrt{2})G_{+} & -1\cdot G_{z}+D-\epsilon\end{pmatrix}=0$$

where the Zeeman parameters are

$$G_z = g_z \mu_B B l_z$$

$$G_\pm = G_x \pm \mathrm{i} G_y = \mu_B B(g_x l_x \pm \mathrm{i} g_y l_y)$$

with l_x, l_y and l_z representing the direction cosines for the vector $\boldsymbol{B}$ relative to symmetry axes.

The next case of $S = 3/2$ starts from the secular equation

$$\det\begin{pmatrix} (3/2)G_z + 2D - \epsilon & (\sqrt{3}/2)G_- & 0 & 0 \\ (\sqrt{3}/2)G_+ & (1/2)G_z + 0 - \epsilon & 1 \cdot G_- & 0 \\ 0 & 1 \cdot G_+ & -(1/2)G_z + 0 - \epsilon & (\sqrt{3}/2)G_- \\ 0 & 0 & (\sqrt{3}/2)G_+ & -(3/2)G_z + 2D - \epsilon \end{pmatrix} = 0$$

the case of $S = 2$ from the equation

$$\det\begin{pmatrix} 2G_z + 4D - \epsilon & 1 \cdot G_- & 0 & 0 & 0 \\ 1 \cdot G_+ & G_z + D - \epsilon & (\sqrt{6}/2)G_- & 0 & 0 \\ 0 & (\sqrt{6}/2)G_+ & 0 - \epsilon & (\sqrt{6}/2)G_- & 0 \\ 0 & 0 & (\sqrt{6}/2)G_+ & -G_z + D - \epsilon & 1 \cdot G_- \\ 0 & 0 & 0 & 1 \cdot G_+ & -2G_z + 4D - \epsilon \end{pmatrix} = 0$$

and finally the case of $S = 5/2$ from the equation

$$\det\begin{pmatrix} (5/2)G_z + 6D - \epsilon & (\sqrt{5}/2)G_- & 0 & 0 & 0 & 0 \\ (\sqrt{5}/2)G_+ & (3/2)G_z + 2D - \epsilon & (\sqrt{8}/2)G_- & 0 & 0 & 0 \\ 0 & (\sqrt{8}/2)G_+ & (1/2)G_z - \epsilon & (\sqrt{9}/2)G_- & 0 & 0 \\ 0 & 0 & (\sqrt{9}/2)G_+ & -(1/2)G_z - \epsilon & (\sqrt{8}/2)G_- & 0 \\ 0 & 0 & 0 & (\sqrt{8}/2)G_+ & -(3/2)G_z + 2D - \epsilon & (\sqrt{5}/2)G_- \\ 0 & 0 & 0 & 0 & (\sqrt{5}/2)G_+ & -(5/2)G_z + 6D - \epsilon \end{pmatrix} = 0$$

Table 12
Eigenvalues of the magnetic Hamiltonian matrices for $E=0$ shifted to an appropriate zero-level

	M_S	Parallel ($\|$) $G_{\|}=g_{\|}\mu_B B_{\|}$	Perpendicular ($\perp$) $G_{\perp}=g_{\perp}\mu_B B_{\perp}$	Approximate ($\perp$)[a]
$S=1$	$+1$	$D+G_{\|}$	$[D+(D^2+4G_{\perp}^2)^{1/2}]/2$	$D+G_{\perp}^2/D$
	-1	$D-G_{\|}$	D	D
	0	0	$[D-(D^2+4G_{\perp}^2)^{1/2}]/2$	$-G_{\perp}^2/D$
$S=3/2$	$+3/2$	$2D+(3/2)G_{\|}$	$D+G_{\perp}/2+[D^2+G_{\perp}^2-DG_{\perp}]^{1/2}$	$2D+(3/8)G_{\perp}^2/D$
	$-3/2$	$2D-(3/2)G_{\|}$	$D-G_{\perp}/2+[D^2+G_{\perp}^2+DG_{\perp}]^{1/2}$	$2D+(3/8)G_{\perp}^2/D$
	$+1/2$	$(1/2)G_{\|}$	$D+G_{\perp}/2-[D^2+G_{\perp}^2-DG_{\perp}]^{1/2}$	$G_{\perp}-(3/8)G_{\perp}^2/D$
	$-1/2$	$-(1/2)G_{\|}$	$D-G_{\perp}/2-[D^2+G_{\perp}^2+DG_{\perp}]^{1/2}$	$-G_{\perp}-(3/8)G_{\perp}^2/D$
$S=2$	$+2$	$4D+2G_{\|}$	—[b, d]	$4D+(1/3)G_{\perp}^2/D$
	-2	$4D-2G_{\|}$	—[b]	$4D+(1/3)G_{\perp}^2/D$
	$+1$	$D+G_{\|}$	—[b]	$D+(7/6)G_{\perp}^2/D$
	-1	$D-G_{\|}$	—[b]	$D+(7/6)G_{\perp}^2/D$
	0	0	—[b, e]	$-3G_{\perp}^2/D$
$S=5/2$	$+5/2$	$6D+(5/2)G_{\|}$	—[b]	$6D+(5/16)G_{\perp}^2/D$
	$-5/2$	$6D-(5/2)G_{\|}$	—[b]	$6D+(5/16)G_{\perp}^2/D$
	$+3/2$	$2D+(3/2)G_{\|}$	—[b]	$2D+(11/16)G_{\perp}^2/D$
	$-3/2$	$2D-(3/2)G_{\|}$	—[b]	$2D+(11/16)G_{\perp}^2/D$
	$+1/2$	$(1/2)G_{\|}$	—[b, c]	$(3/2)G_{\perp}-G_{\perp}^2/D$
	$-1/2$	$-(1/2)G_{\|}$	—[b, c]	$-(3/2)G_{\perp}-G_{\perp}^2/D$

[a] Restriction: $D\gg g_{\perp}\mu_B B_{\perp}$; $g_{\perp}^2=g_x^2=g_y^2$; $g_{\|}^2=g_z^2$.

[b] The second-order perturbation theory yields the approximate eigenvalues as $\epsilon_i^{(2)}=H_{ii}^{(0)}+H_{ii}^{(1)}+\sum_{j\neq i}[H_{ij}^2/(H_{ii}^{(0)}-H_{jj}^{(0)})]$.

[c] The first-order perturbation theory requires a diagonalization of the submatrix having degenerate diagonal elements.

[d] Exact eigenvalue is $[5D+(9D^2+4G_{\perp}^2)^{1/2}]/2$.

[e] Exact eigenvalue is $[5D-(9D^2+4G_{\perp}^2)^{1/2}]/2$.

According to Table 12, the eigenvalues of the magnetic Hamiltonian matrices are simple analytical functions for the case of $E=0$. Their dependence upon the magnetic field is presented in Figs. 11 and 12. It can be seen that the energy levels in the parallel direction vary strictly linearly with the field strength. In the perpendicular

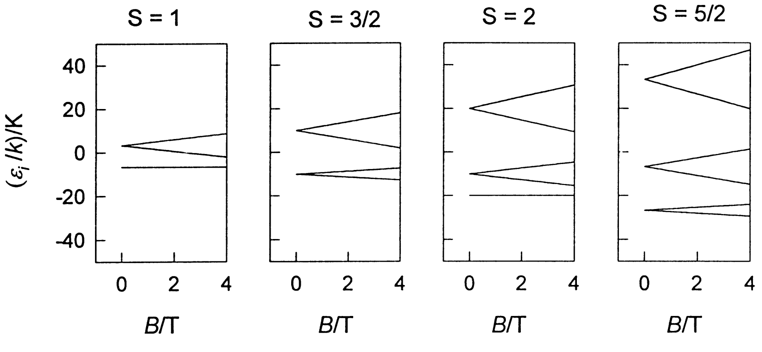


Fig. 11. The energy levels of ZFS systems ($D/k=10$ K, $E=0$) in the parallel ($\|$, z) direction.

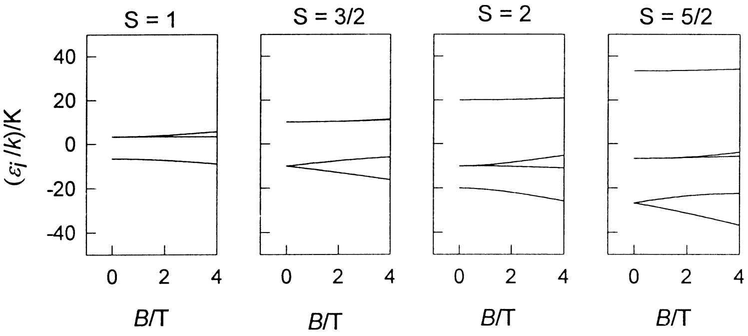


Fig. 12. The energy levels of ZFS systems ($D/k = 10$ K, $E = 0$) in the perpendicular ($\perp$, x, y) direction.

direction a quadratic dependence is well visible for lower fields; at higher fields, however, the dependence tends to be linear.

The square roots present in the analytical formulae for the eigenvalues in the perpendicular direction can be further expanded by utilizing the formula

$$\sqrt{1+x} = 1 + \tfrac{1}{2}x - \tfrac{1}{8}x^2 + \ldots$$

viz.

$$[D + (D^2 + 4G_\perp^2)^{1/2}]/2 = \frac{D}{2} + \frac{D}{2}\left[1 + \frac{4G_\perp^2}{D^2}\right]^{1/2}$$

$$\approx \frac{D}{2} + \frac{D}{2}\left[1 + \frac{1}{2}\frac{4G_\perp^2}{D^2} + \ldots\right] = D + \frac{G_\perp^2}{D} + O_3(G)$$

but

$$D + G_\perp/2 + (D^2 + G_\perp^2 - DG_\perp)^{1/2} = D + \frac{G_\perp}{2} + D\left(1 + \frac{G_\perp^2 - DG_\perp}{D^2}\right)^{1/2}$$

$$\approx D + \frac{G_\perp}{2} + D\left[1 + \frac{1}{2}\frac{G_\perp^2 - DG_\perp}{D^2} - \frac{1}{8}\left(\frac{G_\perp^2 - DG_\perp}{D^2}\right)^2 + \ldots\right] = 2D + \frac{3}{8}\frac{G_\perp^2}{D} + O_3(G)$$

We can then write approximate formulae where terms proportional to B^2 appear. Such expressions are particularly useful in applying the van Vleck equation, since the identification of the van Vleck coefficients is an easy task. However, one should be careful in this procedure since the expansion is applicable only when $x \ll 1$, which is equivalent to the restriction

$$D \gg g_\perp \mu_B B_\perp$$

Numerically this means that

$$(D/k)[\mathrm{K}] \gg 2.0 \times (9.3 \times 10^{-24}\ \mathrm{J\,T^{-1}})/(1.4 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times B[\mathrm{T}]$$

Otherwise the formulae diverge.

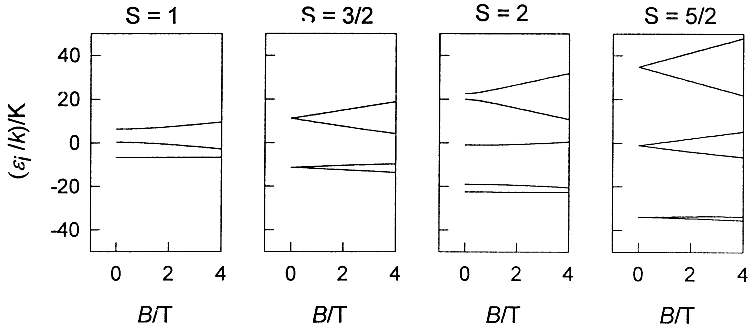


Fig. 13. Energy levels of ZFS systems ($D/k=10$ K and $E/k=3$ K) in the parallel direction.

The involvement of the E parameter is a bit more complex. The structure of the secular equation does not allow a splitting into the blocks of dimension 2 or 3 so that, in general, an analytical solution does not exist. The eigenvalues for the given set of parameters (D, E and gB) are obtained numerically. Standard diagonalization routines can be used for this purpose.

Normally it is assumed that the ZFS parameters obey the relationship

$$|D| \geqslant 3E \geqslant 0$$

Otherwise one can interchange the Cartesian axes (which cannot influence the properties of the system), but the above relationship is fulfilled [24]. The data displayed in Figs. 13 and 14 were generated for values which are close to the limiting case.

10.3. Axial magnetic anisotropy

The most frequent treatment is that the components of the magnetic susceptibility are derived for the case of $D \neq 0$ and $E=0$ by utilizing the van Vleck equation. For this purpose we need the van Vleck coefficients as they result from the approximate

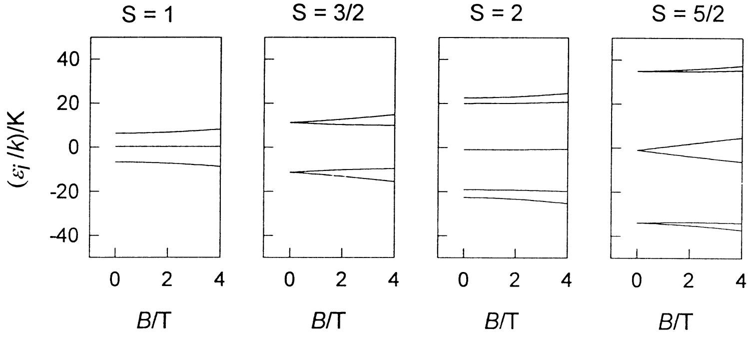


Fig. 14. Energy levels of ZFS systems ($D/k=10$ K and $E/k=3$ K) in the perpendicular direction.

Table 13
Van Vleck coefficients for ZFS systems ($E=0$)

	M_S	$\epsilon_i^{(0)}$	$\epsilon_{i,\parallel}^{(1)}/\mu_B$	$\epsilon_{i,\perp}^{(1)}/\mu_B$	$\epsilon_{i,\perp}^{(2)}/\mu_B^2$
$S=1$	$+1$	D	$+g_\parallel$	0	$+g_\perp^2/D$
	-1	D	$-g_\parallel$	0	0
	0	0	0	0	$-g_\perp^2/D$
$S=3/2$	$+3/2$	$2D$	$+(3/2)g_\parallel$	0	$+(3/8)g_\perp^2/D$
	$-3/2$	$2D$	$-(3/2)g_\parallel$	0	$+(3/8)g_\perp^2/D$
	$+1/2$	0	$+(1/2)g_\parallel$	$+g_\perp$	$-(3/8)g_\perp^2/D$
	$-1/2$	0	$-(1/2)g_\parallel$	$-g_\perp$	$-(3/8)g_\perp^2/D$
$S=2$	$+2$	$4D$	$+2g_\parallel$	0	$+(1/3)g_\perp^2/D$
	-2	$4D$	$-2g_\parallel$	0	$+(1/3)g_\perp^2/D$
	$+1$	D	$+g_\parallel$	0	$+(7/6)g_\perp^2/D$
	-1	D	$-g_\parallel$	0	$+(7/6)g_\perp^2/D$
	0	0	0	0	$-3g_\perp^2/D$
$S=5/2$	$+5/2$	$6D$	$+(5/2)g_\parallel$	0	$+(5/16)g_\perp^2/D$
	$-5/2$	$6D$	$-(5/2)g_\parallel$	0	$+(5/16)g_\perp^2/D$
	$+3/2$	$2D$	$+(3/2)g_\parallel$	0	$+(11/16)g_\perp^2/D$
	$-3/2$	$2D$	$-(3/2)g_\parallel$	0	$+(11/16)g_\perp^2/D$
	$+1/2$	0	$+(1/2)g_\parallel$	$+(3/2)g_\perp$	$-g_\perp^2/D$
	$-1/2$	0	$-(1/2)g_\parallel$	$-(3/2)g_\perp$	$-g_\perp^2/D$

expansion of magnetic energy levels. Based on Table 12, the non-zero van Vleck coefficients are arranged in Table 13; notice that

$$\epsilon_{i,\parallel}^{(2)}=0$$

holds true for the ZFS systems.

Having the van Vleck coefficients determined, their substitution into the van Vleck equation yields the analytical formulae for the parallel and perpendicular components of the magnetic susceptibility (Table 14). However, one should keep in mind the above-mentioned restriction under which the expansion of the square roots is applicable.

Using the formulae for the magnetic susceptibility, a modelling of important

Table 14
Formulae for the susceptibility components of a ZFS system ($E=0$)[a]

$S=1$	$\chi_\parallel=(C_0g_\parallel^2/T)[2\exp(-x)]/[1+2\exp(-x)]$
	$\chi_\perp=(C_0g_\perp^2/T)(2/x)[1-\exp(-x)]/[1+2\exp(-x)]$
$S=3/2$	$\chi_\parallel=(C_0g_\parallel^2/T)(1/4)[1+9\exp(-2x)]/[1+\exp(-2x)]$
	$\chi_\perp=(C_0g_\perp^2/T)\{1+(3/4x)[1-\exp(-2x)]\}/[1+\exp(-2x)]$
$S=2$	$\chi_\parallel=(C_0g_\parallel^2/T)[2\exp(-x)+8\exp(-4x)]/[1+2\exp(-x)+2\exp(-4x)]$
	$\chi_\perp=(C_0g_\perp^2/T)\{(6/x)[1-\exp(-x)]+(4/3x)[\exp(-x)-\exp(-4x)]\}/[1+2\exp(-x)+2\exp(-4x)]$
$S=5/2$	$\chi_\parallel=(C_0g_\parallel^2/4T)[1+9\exp(-2x)+25\exp(-6x)]/[1+\exp(-2x)+\exp(-6x)]$
	$\chi_\perp=(C_0g_\perp^2/4T)\{9+(8/x)[1-\exp(-2x)]+(5/2x)[\exp(-2x)-\exp(-6x)]\}/$ $[1+\exp(-2x)+\exp(-6x)]$

[a] Substitution: $x=D/kT$; restriction: $D\gg g_\perp\mu_B B_\perp$.

magneto-chemical curves, like χ_a versus T, $(\chi_a T)$ versus T, χ_{av} versus T, $(\chi_{av}T)$ versus T, and μ_{eff} versus T, is possible. Some results are presented in Fig. 15.

It can be seen that the $(\chi_{av}T)$ versus T curves are nicely linear with zero slope at higher temperature. With decreasing temperature these exhibit a drop: the greater $|D|$ is, the higher the temperature at which the turning is evident. It should be noted that the curves $(\chi_{av}T)$ versus T are rather insensitive to the sign of the D-parameter and, therefore, it is problematic (perhaps impossible) to establish the sign of the D-parameter from the powder sample data only. By measuring the oriented single crystals, however, the sign of the D-parameter is well determined.

10.4. Rhombic magnetic anisotropy

The involvement of the E-parameter is complicated by the absence of analytical formulae for the corresponding energy levels

$$\epsilon_{i,a} = f(D, E, g_a, B_a)$$

Numerical solutions of the secular equations, nevertheless, exist and thus some more complex procedures outlined in Section 3 can be applied to get the magnetic suscepti-

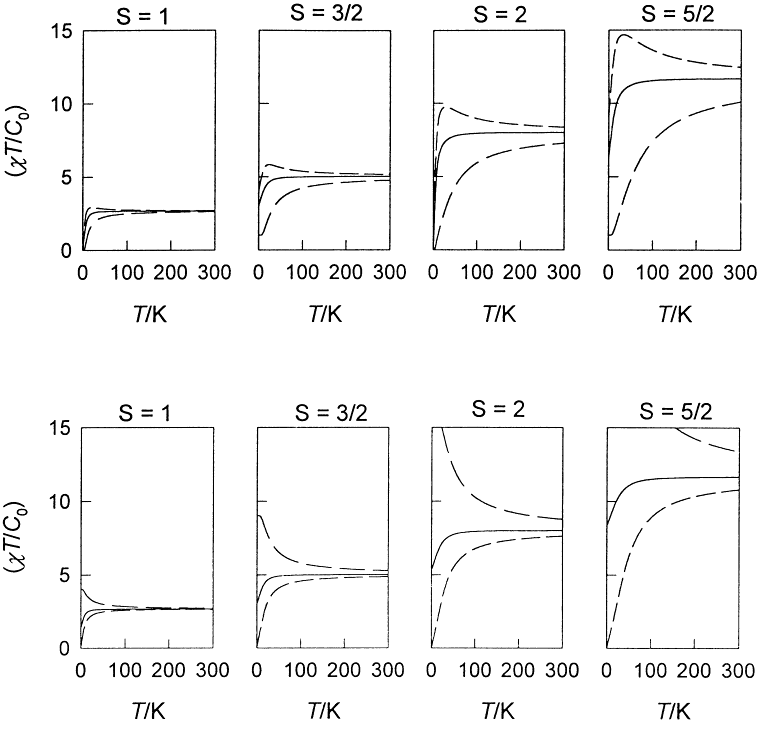


Fig. 15. Magnetic susceptibility components for ZFS systems: (a) $D/k = 20$ K; (b) $D/k = -20$ K; long dashed, $\chi_{\parallel}$; short dashed, $\chi_{\perp}$; solid, χ_{av}.

bility components

$$\chi_a = f(D, E, g_a; T)$$

A few analytical solutions for eigenvalues are listed in Table 15.

10.5. Magnetization of a ZFS system

For a low temperature and high fields the ZFS systems are no longer linear magnetics. The thermal energy kT is of the order of the magnetic energy and of the order of the ZFS energy

$$D \approx g\mu_B B \approx kT$$

and thus a more fundamental treatment is required.

Let us consider an $S=2$ system under the constraint of $E=0$. The energy levels (Table 12) can be substituted into the partition function so that

$$Z_{\parallel} \approx \sum_{i=1}^{5} \exp(-\epsilon_{i,\parallel}/kT) = \exp(0) + \exp[-(D+\gamma B)/kT] + \exp[-(D-\gamma B)/kT]$$
$$+ \exp[-(4D+2\gamma B)/kT] + \exp[-(4D-2\gamma B)/kT]$$

Table 15
Analytical expressions for exact eigenvalues of ZFS systems [24,26]

Spin	Direction	Shifted eigenvalues
$S=1$	z	$D+(E^2+G_z^2)^{1/2}$
		0
		$D-(E^2+G_z^2)^{1/2}$
	x	$D+E$
		$(D-E)/2-[(D-E)^2/4+G_x^2]^{1/2}$
		$(D-E)/2+[(D-E)^2/4+G_x^2]^{1/2}$
	y	$(D+E)/2+[(D+E)^2/4+G_y^2]^{1/2}$
		$(D+E)/2-[(D+E)^2/4+G_y^2]^{1/2}$
		$D-E$
$S=3/2$	z	$D+G_z/2+[(D+G_z)^2+3E^2]^{1/2}$
		$D-G_z/2+[(D-G_z)^2+3E^2]^{1/2}$
		$D+G_z/2-[(D+G_z)^2+3E^2]^{1/2}$
		$D-G_z/2-[(D-G_z)^2+3E^2]^{1/2}$
	x	$D+G_x/2+[(D-G_x/2)^2+3(E+G_x/2)^2]^{1/2}$
		$D-G_x/2+[(D+G_x/2)^2+3(E-G_x/2)^2]^{1/2}$
		$D+G_x/2-[(D-G_x/2)^2+3(E+G_x/2)^2]^{1/2}$
		$D-G_x/2-[(D+G_x/2)^2+3(E-G_x/2)^2]^{1/2}$
	y	$D+G_y/2+[(D-G_y/2)^2+3(E-G_y/2)^2]^{1/2}$
		$D-G_y/2+[(D+G_y/2)^2+3(E+G_y/2)^2]^{1/2}$
		$D+G_y/2-[(D-G_y/2)^2+3(E-G_y/2)^2]^{1/2}$
		$D-G_y/2-[(D+G_y/2)^2+3(E+G_y/2)^2]^{1/2}$

with

$$\gamma \equiv g_\parallel \mu_B$$

Then the molar magnetization is

$$M_\parallel = N_A kT \left(\frac{\partial \ln Z_\parallel}{\partial B} \right)_T = N_A \frac{\gamma}{Z_\parallel} \{ -\exp[-(D+\gamma B)/kT]$$

$$+\exp[-(D-\gamma B)/kT] - 2\exp[-(4D+2\gamma B)/kT]$$

$$+2\exp[-(4D-2\gamma B)/kT]\}$$

No expansions of the exponentials are permitted. The approximation

$$\bar{\chi}_\parallel = \mu_0 \frac{M_\parallel}{B} \quad \text{[false]}$$

is violated and a more laborious derivation of the differential magnetic susceptibility formula is necessary

$$\chi_\parallel = \mu_0 \frac{\partial M_\parallel}{\partial B} = N_A \mu_0 \gamma \frac{\partial}{\partial B} \frac{1}{Z_\parallel} \{\exp[(D+\gamma B)/kT] - \exp[(D-\gamma B)/kT]$$

$$+2\exp[(4D+2\gamma B)/kT] - 2\exp[(4D-2\gamma B)/kT]\}$$

yielding

$$\chi_\parallel = \frac{C_0}{T} \frac{g_\parallel^2}{Z_\parallel^2} \langle Z_\parallel \{\exp[-(D+\gamma B)/kT] + \exp[-(D-\gamma B)/kT]$$

$$+4\exp[-(4D+2\gamma B)/kT] + 4\exp[-(4D-2\gamma B)/kT]\}$$

$$-\{-\exp[-(D+\gamma B)/kT] + \exp[-(D-\gamma B)/kT]$$

$$-2\exp[-(4D+2\gamma B)/kT] + 2\exp[-(4D-2\gamma B)/kT]\}^2 \rangle$$

These formulae can be written in the form

$$M_\parallel = N_A \mu_B \frac{g_\parallel}{Z_\parallel} T_1$$

$$\chi_\parallel = \frac{C_0}{T} \frac{g_\parallel^2}{Z_\parallel^2} (Z_\parallel T_2 - T_1^2)$$

with the terms

$$T_1 = -\exp[-(D+\gamma B)/kT] + \exp[-(D-\gamma B)/kT]$$

$$-2\exp[-(4D+2\gamma B)/kT] + 2\exp[-(4D-2\gamma B)/kT]$$

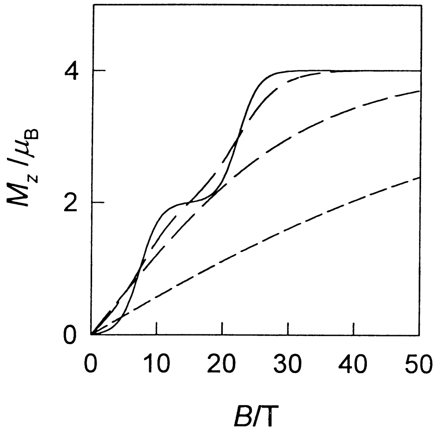


Fig. 16. Parallel magnetization per atom versus magnetic field for an $S=2$ ZFS system, $D/k=1$ K; individual curves correspond to $T=2$ (solid), 4.2, 20 and 77 K.

and

$$T_2 = \exp[-(D+\gamma B)/kT] + \exp[-(D-\gamma B)/kT] + 4\exp[-(4D+2\gamma B)/kT] + 4\exp[-(4D-2\gamma B)/kT]$$

The magnetization formula has been used to generate the curves displayed in Fig. 16. It can be seen that some abrupt steps appear in the magnetization curve. These are less pronounced, and even disappear, when the temperature is high enough. The individual steps correspond to a change of the ground state due to the magnetic perturbation: the $M_S=0$ is the ground state below the first critical field B_{c1}; above it the $M_S=-1$ becomes the ground state until the second critical field B_{c2} is reached. Above it the $M_S=-2$ adopts the role of the ground state.

Parallel magnetization and magnetic susceptibility terms for ZFS systems are given in Table 16 and plotted in Figs. 17 and 18. Formulae for an $S=3/2$ system are given in Table 17 and the magnetization data are plotted in Fig. 19.

10.6. Λ-tensor

In a rigorous treatment the magnetic parameters that describe the ZFS can be are expressed as follows:

(1) the reduced magnetic susceptibility tensor

$$-\tfrac{1}{2}\kappa_{ab}^{\text{para}} = -\sum_{K\neq 0} \frac{X_a^{0K} X_b^{K0}}{E_K - E_0}$$

(2) the differential magnetogyric-ratio tensor

$$\Delta g_{ab} = -S_a^{-1} \sum_{K\neq 0} \frac{Y_a^{0K} X_b^{K0}}{E_K - E_0} - S_b^{-1} \sum_{K\neq 0} \frac{X_a^{0K} Y_b^{K0}}{E_K - E_0}$$

Table 16
Terms of the parallel magnetization and magnetic susceptibility for ZFS systems ($E=0$)

$Z_{\parallel}$	T_1	T_2
$S=1$		
$1+\exp[-(D+\gamma B)/kT]$	$-\exp[-(D+\gamma B)/kT]$	$\exp[-(D+\gamma B)/kT]$
$+\exp[-(D-\gamma B)/kT]$	$+\exp[-(D-\gamma B)/kT]$	$+\exp[-(D-\gamma B)/kT]$
$S=3/2$		
$\exp[-(+\gamma B/2)/kT]$	$-(1/2)\exp[-(+\gamma B/2)/kT]$	$(1/4)\exp[-(+\gamma B/2)/kT]$
$+\exp[-(-\gamma B/2)/kT]$	$+(1/2)\exp[-(-\gamma B/2)/kT]$	$+(1/4)\exp[-(-\gamma B/2)/kT]$
$+\exp[-(2D+\gamma B3/2)/kT]$	$-(3/2)\exp[-(2D+\gamma B3/2)/kT]$	$+(9/4)\mathrm{e\ xp}[-(2D+\gamma B3/2)/kT]$
$+\exp[-(2D-\gamma B3/2)/kT]$	$+(3/2)\exp[-(2D-\gamma B3/2)/kT]$	$+(9/4)\exp[-(2D-\gamma B3/2)/kT]$
$S=2$		
$1+\exp[-(D+\gamma B)/kT]$	$-\exp[-(D+\gamma B)/kT]$	$\exp[-(D+\gamma B)/kT]$
$+\exp[-(D-\gamma B)/kT]$	$+\exp[-(D-\gamma B)/kT]$	$+\exp[-(D-\gamma B)/kT]$
$+\exp[-(4D+2\gamma B)/kT]$	$-2\exp[-(4D+2\gamma B)/kT]$	$+4\exp[-(4D+2\gamma B)/kT]$
$+\exp[-(4D-2\gamma B)/kT]$	$+2\exp[-(4D-2\gamma B)/kT]$	$+4\exp[-(4D-2\gamma B)/kT]$
$S=5/2$		
$\exp[-(+\gamma B/2)/kT]$	$-(1/2)\exp[-(+\gamma B/2)/kT]$	$(1/4)\exp[-(+\gamma B/2)/kT]$
$+\exp[-(-\gamma B/2)/kT]$	$+(1/2)\exp[-(-\gamma B/2)/kT]$	$+(1/4)\exp[-(-\gamma B/2)/kT]$
$+\exp[-(2D+\gamma B3/2)/kT]$	$-(3/2)\exp[-(2D+\gamma B3/2)/kT]$	$+(9/4)\exp[-(2D+\gamma B3/2)/kT]$
$+\exp[-(2D-\gamma B3/2)/kT]$	$+(3/2)\exp[-(2D-\gamma B3/2)/kT]$	$+(9/4)\exp[-(2D-\gamma B3/2)/kT]$
$+\exp[-(6D+\gamma B5/2)/kT]$	$-(5/2)\exp[-(6D+\gamma B5/2)/kT]$	$+(25/4)\exp[-(6D+\gamma B5/2)/kT]$
$+\exp[-(6D-\gamma B5/2)/kT]$	$+(5/2)\exp[-(6D-\gamma B5/2)/kT]$	$+(25/4)\exp[-(6D-\gamma B5/2)/kT]$

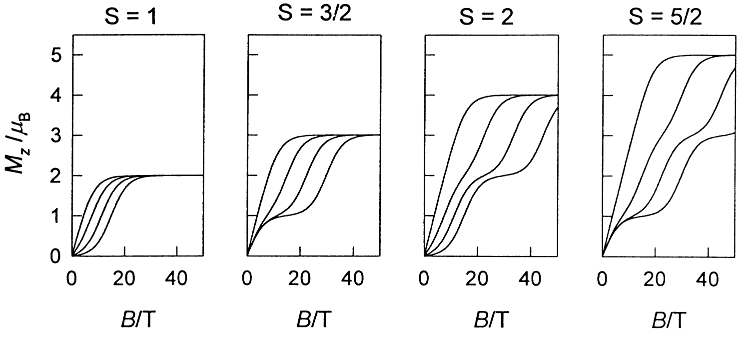


Fig. 17. Parallel magnetization per atom versus magnetic field for ZFS systems: $T=4.2$ K; $D/k=5$, 10, 15 and 20 K.

(3) the spin–spin interaction tensor

$$-\tfrac{1}{2}D_{ab}=-S_a^{-1}S_b^{-1}\sum_{K\neq 0}\frac{Y_a^{0K}Y_b^{K0}}{E_K-E_0}$$

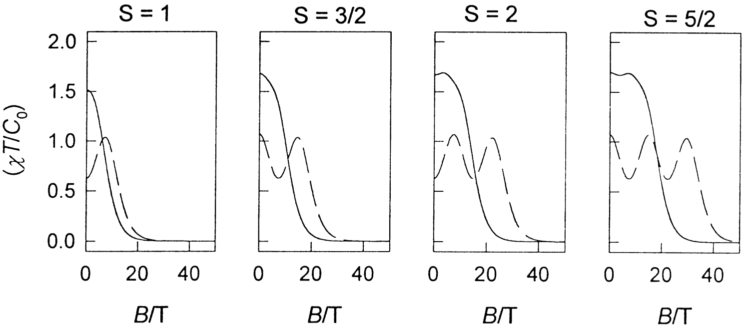


Fig. 18. Magnetic susceptibility function for ZFS systems: $T=4.2$ K; $D/k=5$ (solid) and 10 K (dashed).

with

$$X_a^{AB}=\mu_B\left\langle \Psi_A\left|\sum_{i=1}^{n}\hat{l}_{Gia}\right|\Psi_B\right\rangle[\hbar^{-1}]$$

where the position of the ith electron refers to a common gauge origin, and

$$Y_a^{AB}=\left\langle \Psi_A\left|\sum_{i=1}^{n}\xi_N(r_{Ni})\hat{l}_{Nia}\hat{s}_{ia}\right|\Psi_B\right\rangle[\hbar^{-2}]$$

where the position of the ith electron refers to the Nth nucleus and $\xi_N(r_{Ni})$ is the SO coupling constant.

Let us assume a mononuclear complex with the gauge origin coinciding with the central atom. Then one can introduce a molecular Λ-tensor as follows

$$\Lambda_{ab}^{\mathrm{mol}}=-\sum_{K\neq 0}\frac{\langle 0|\hat{L}_a|K\rangle\langle K|\hat{L}_b|0\rangle}{E_K-E_0}[\hbar^{-2}]$$

with

$$\langle A|\hat{L}_a|B\rangle=\left\langle \Psi_A\left|\sum_{i=1}^{n}\hat{l}_{Nia}\right|\Psi_B\right\rangle$$

The Λ-tensor represents the contribution of the angular momentum in the second-order perturbation theory to the magnetic parameters. For a single heavy centre with the kets restricted to a single atomic term there is

$$Y_a^{AB}=\langle\Psi_A|\lambda(\boldsymbol{L}\cdot\boldsymbol{S})_a|\Psi_B\rangle[\hbar^{-2}]$$

where a SO splitting parameter λ occurs. Then

$$S_a^{-1}Y_a^{AB}=\lambda\langle A|\hat{L}_a|B\rangle[\hbar^{-1}]$$

The above assumptions imply that the set of magnetic parameters becomes expressed

Table 17
Exact magnetization formulae for an $S=3/2$ system

$$M_z=-\frac{1}{2}\frac{N_A\mu_B g_z}{Z_z}\langle +\exp\{-[+G_z/2+\sqrt{(D+G_z)^2+3E^2}]/kT\}\{+1+[+2(D+G_z)]/\sqrt{(D+G_z)^2+3E^2}\}$$
$$+\exp\{-[-G_z/2+\sqrt{(D-G_z)^2+3E^2}]/kT\}\{-1+[-2(D-G_z)]/\sqrt{(D-G_z)^2+3E^2}\}$$
$$+\exp\{-[+G_z/2-\sqrt{(D+G_z)^2+3E^2}]/kT\}\{+1-[+2(D+G_z)]/\sqrt{(D+G_z)^2+3E^2}\}$$
$$+\exp\{-[-G_z/2-\sqrt{(D-G_z)^2+3E^2}]/kT\}\{-1-[-2(D-G_z)]/\sqrt{(D-G_z)^2+3E^2}\}\rangle$$

$$M_x=-\frac{1}{2}\frac{N_A\mu_B g_x}{Z_x}\langle$$
$$+\exp\{-[+G_x/2+\sqrt{(D-G_x/2)^2+3(E+G_x/2)^2}]/kT\}$$
$$\times\{+1+[-(D-G_x/2)+3(E+G_x/2)]/\sqrt{(D-G_x/2)^2+3(E+G_x/2)^2}\}$$
$$+\exp\{-[-G_x/2+\sqrt{(D+G_x/2)^2+3(E-G_x/2)^2}]/kT\}$$
$$\times\{-1+[+(D+G_x/2)-3(E-G_x/2)]/\sqrt{(D+G_x/2)^2+3(E-G_x/2)^2}\}$$
$$+\exp\{-[+G_x/2-\sqrt{(D-G_x/2)^2+3(E+G_x/2)^2}]/kT\}$$
$$\times\{+1-[-(D-G_x/2)+3(E+G_x/2)]/\sqrt{(D-G_x/2)^2+3(E+G_x/2)^2}\}$$
$$+\exp\{-[-G_x/2-\sqrt{(D+G_x/2)^2+3(E-G_x/2)^2}]/kT\}$$
$$\times\{-1-[+(D+G_x/2)-3(E-G_x/2)]/\sqrt{(D+G_x/2)^2+3(E-G_x/2)^2}\}\rangle$$

$$M_y=-\frac{1}{2}\frac{N_A\mu_B g_y}{Z_y}\langle$$
$$+\exp\{-[+G_y/2+\sqrt{(D-G_y/2)^2+3(E-G_y/2)^2}]/kT\}$$
$$\times\{+1+[-(D-G_y/2)-3(E-G_y/2)]/\sqrt{(D-G_y/2)^2+3(E-G_y/2)^2}\}$$
$$+\exp\{-[-G_y/2+\sqrt{(D+G_y/2)^2+3(E+G_y/2)^2}]/kT\}$$
$$\times\{-1+[+(D+G_y/2)+3(E+G_y/2)]/\sqrt{(D+G_y/2)^2+3(E+G_y/2)^2}\}$$
$$+\exp\{-[+G_y/2-\sqrt{(D-G_y/2)^2+3(E-G_y/2)^2}]/kT\}$$
$$\times\{+1-[-(D-G_y/2)-3(E-G_y/2)]/\sqrt{(D-G_y/2)^2+3(E-G_y/2)^2}\}$$
$$+\exp\{-[-G_y/2-\sqrt{(D+G_y/2)^2+3(E+G_y/2)^2}]/kT\}$$
$$\times\{-1-[+(D+G_y/2)+3(E+G_y/2)]/\sqrt{(D+G_y/2)^2+3(E+G_y/2)^2}\}\rangle$$

$$Z_z=\exp\{-[+G_z/2+\sqrt{(D+G_z)^2+3E^2}]/kT\}$$
$$+\exp\{-[-G_z/2+\sqrt{(D-G_z)^2+3E^2}]/kT\}$$
$$+\exp\{-[+G_z/2-\sqrt{(D+G_z)^2+3E^2}]/kT\}$$
$$+\exp\{-[-G_z/2-\sqrt{(D-G_z)^2+3E^2}]/kT\}$$

$$Z_x=\exp\{-[+G_x/2+\sqrt{(D-G_x/2)^2+3(E+G_x/2)^2}]/kT\}$$
$$+\exp\{-[-G_x/2+\sqrt{(D+G_x/2)^2+3(E-G_x/2)^2}]/kT\}$$
$$+\exp\{-[+G_x/2-\sqrt{(D-G_x/2)^2+3(E+G_x/2)^2}]/kT\}$$
$$+\exp\{-[-G_x/2-\sqrt{(D+G_x/2)^2+3(E-G_x/2)^2}]/kT\}$$

$$Z_y=\exp\{-[+G_y/2+\sqrt{(D-G_y/2)^2+3(E-G_y/2)^2}]/kT\}$$
$$+\exp\{-[-G_y/2+\sqrt{(D+G_y/2)^2+3(E+G_y/2)^2}]/kT\}$$
$$+\exp\{-[+G_y/2-\sqrt{(D-G_y/2)^2+3(E-G_y/2)^2}]/kT\}$$
$$+\exp\{-[-G_y/2-\sqrt{(D+G_y/2)^2+3(E+G_y/2)^2}]/kT\}$$

as follows:

$$-\tfrac{1}{2}\,\kappa_{ab}^{\text{para}}=\mu_B^2\Lambda_{ab}^{\text{at}}$$

$$\Delta g_{ab}=2\lambda\Lambda_{ab}^{\text{at}}$$

and

$$-\tfrac{1}{2}\,D_{ab}=\lambda^2\Lambda_{ab}^{\text{at}}=D'_{ab}$$

The traceless D-tensor is introduced by subtracting one-third of the trace of the D-

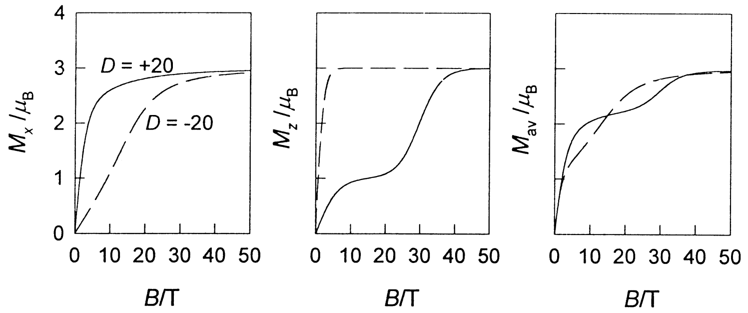


Fig. 19. Parallel, perpendicular and averaged magnetization for an $S=3/2$ ZFS system: $D/k=20$ (solid) and -20 K (dashed), $E=0$, $T=4.2$ K.

tensor; hence

$$\tilde{D}_{aa}=D'_{ab}-t\delta_{ab}$$

with

$$t=\tfrac{1}{3}\,\mathrm{Tr}(\overline{\overline{D'}})=\tfrac{1}{3}\,(D'_{xx}+D'_{yy}+D'_{zz})=\tfrac{1}{3}\,\lambda^2(\Lambda_{xx}+\Lambda_{yy}+\Lambda_{zz})$$

Then the axial ZFS parameter is expressed as

$$D=\tfrac{3}{2}\,\tilde{D}_{zz}=\lambda^2[\Lambda_{zz}-\tfrac{1}{2}\,(\Lambda_{xx}+\Lambda_{yy})]$$

and the rhombic ZFS parameter as

$$E=\tfrac{1}{2}\,(\tilde{D}_{xx}-\tilde{D}_{yy})=\tfrac{1}{2}\,\lambda^2(\Lambda_{xx}-\Lambda_{yy})$$

The g-tensor components become

$$g_{aa}=g_{\mathrm{e}}+2\lambda\Lambda_{aa}$$

and the κ-tensor components are

$$\kappa_{aa}^{\mathrm{para}}=-2\mu_{\mathrm{B}}^2\Lambda_{aa}$$

The temperature-independent paramagnetic term is

$$\chi^{\mathrm{TIP}}=\tfrac{1}{3}\,(\chi_{xx}+\chi_{yy}+\chi_{zz})=N_{\mathrm{A}}\mu_0\,\tfrac{1}{3}\,(\kappa_{xx}+\kappa_{yy}+\kappa_{zz})$$
$$=-N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2\,\tfrac{2}{3}(\Lambda_{xx}+\Lambda_{yy}+\Lambda_{zz})$$

(Note: a different sign of the Λ-tensor and different definitions of the parameters D and E can be met in the literature.)

On the basis of the above relationships one can conclude that the three principal components of the Λ-tensor can be used in expressing the complete set of magnetic parameters that describe the ZFS in mononuclear complexes, i.e. g_{xx}, g_{yy}, g_{zz}, D and E. In addition, they define the temperature-independent paramagnetic term χ^{TIP}. Therefore, it is possible to reconstruct the components of the Λ-tensor having the set of magnetic parameters determined from an appropriate fit of experimental data. However, an opposite procedure is possible: to consider the components of the Λ-tensor as the principal quantities which determine the ZFS parameters. Then one can considerΛ_{xx}, Λ_{yy}, Λ_{zz} and λ as a set of free parameters subjected to optimization. In performing such a procedure, the following optimization scheme can be followed[22].

(1) A trial set of (Λ_{xx}, Λ_{yy}, Λ_{zz}, λ) is used in evaluating the set of magnetic parameters (g_{xx}, g_{yy}, g_{zz}, D, E).

(2) The spin Hamiltonian matrices $\boldsymbol{H}_a$ are constructed from the (g_{xx}, g_{yy}, g_{zz}, D, E) set and the "working" values of B_m. Atomic units (hartree) are an appropriate system of units for this purpose.

(3) For a series of B_m values the eigenvalues $\epsilon_{ia}(B_m)$ are found by diagonalizing the spin Hamiltonian matrices. From the field dependence of energy levels:

(a) the van Vleck coefficients result, or

(b) the microscopic magnetic moments μ_{ia} are evaluated.

Consequently, the magnetic susceptibility is evaluated either via the van Vleck formula (mean magnetic susceptibility), or by differentiating the molar magnetization (differential magnetic susceptibility); see Section 8.

The (powder) averaged magnetic susceptibility is corrected for the temperature-independent paramagnetic term

$$\chi_{\mathrm{av}}^{\mathrm{Calc.}}=\tfrac{1}{3}(\chi_{xx}+\chi_{yy}+\chi_{zz})+\chi^{\mathrm{TIP}}$$

A proper error functional is constructed of calculated and experimental data (the latter corrected for an underlying diamagnetism) and subjected to the minimization.

The set of the optimized parameters (Λ_{xx}, Λ_{yy}, Λ_{zz}, λ) can be considered either as a final set or as a first appropriate estimate for the set of magnetic parameters (g_{xx}, g_{yy}, g_{zz}, D, E) and χ^{TIP}, being refined by a subsequent optimization.

11. Centres with magnetic angular momentum

11.1. Magnetic angular momentum

The spin Hamiltonian that accounts for the orbital angular momentum contribution is

$$\hat{H}^S=\mu_{\mathrm{B}}\boldsymbol{L}\cdot\boldsymbol{B}[\hbar^{-1}]+\mu_{\mathrm{B}}g_{\mathrm{e}}\boldsymbol{S}\cdot\boldsymbol{B}[\hbar^{-1}]+\lambda\boldsymbol{L}\cdot\boldsymbol{S}[\hbar^{-2}]$$

where the first term is the orbital Zeeman term, the second is the spin Zeeman term and the third is the SO coupling term.

A non-zero contribution of the orbital angular momentum, a magnetic angular momentum, requires that the matrix elements of the atomic term functions $|\Psi_i\rangle=|L, M_L, S, M_S\rangle$ are non-zero

$$\langle\Psi_i|\hat{L}_a|\Psi_j\rangle\neq 0$$

In predicting this property, group theory is applicable (Table 18). The angular momentum operator $\hat{L}_a$ ($a = x, y, z$) has the same transformation properties as the rotation operator $\hat{R}_a$ in the point group characterizing the symmetry of the molecule. It transforms as the irreducible representation Γ_a of this group. The above requirement is equivalent to the condition that the direct product of the irreducible representations Γ_i of the wave function (which is a reducible representation Γ_r) contains the irreducible representation of the angular momentum (or rotation) operator Γ_a, viz.

$$\Gamma_\mathrm{i} \otimes \Gamma_\mathrm{i} = \Gamma_\mathrm{r} = \Gamma_a + \ldots$$

The involvement of the orbital angular momentum has the following consequences:

(1) the basis set being considered covers all combinations of the orbital and spin wave functions; it results from a direct product of the orbital and spin functions;

(2) the SO coupling removes the degenerate ${}^{2S+1}\Gamma$ state. The Zeeman term may be considered as a perturbation acting on the eigenstates of $\hat{H}^\mathrm{so} = \lambda \boldsymbol{L} \cdot \boldsymbol{S} [\hbar^{-2}]$. This is because the SO splitting ranges between $\Delta E/hc = 100$ to $500\ \mathrm{cm}^{-1}$, whereas for laboratory magnetic fields $\mu_\mathrm{B} g_\mathrm{e} B/hc \approx 0.5$ to $5\ \mathrm{cm}^{-1}$;

(3) the magnetic anisotropy adopts importance and the electronic g-factor is replaced by the g-tensor;

(4) the magnetic susceptibility is a complicated function of magnetic parameters (λ, g-components) and often violates the Curie law even at relatively high temperature.

Table 18

Existence of the magnetic angular momentum (MAM) for d^n cubic complexes

d^n	Free ion term	O_h group[a]		MAM	T_d group[b]		MAM
		Config.	Term		Config.	Term	
d^1	^2D	t_{2g}^1	$^2T_{2g}$	yes	e^1	^2E	no
d^2	^3F	t_{2g}^2	$^3T_{1g}$	yes	e^2	$^3A_2$	no
d^3	^4F	t_{2g}^3	$^4A_{2g}$	no	$e^2t_2^1$	$^4T_1$	yes
		—	—	—	e^3	^2E	no
d^4	^5D	$t_{2g}^3\ e_g^1$	^5E_g	no	$e^2t_2^2$	$^5T_2$	yes
		t_{2g}^4	$^3T_{1g}$	yes	e^4	$^1A_1$	no
d^5	^6S	$t_{2g}^3\ e_g^2$	$^6A_{1g}$	no	$e^2t_2^3$	$^6A_1$	no
		t_{2g}^5	$^2T_{2g}$	yes	$e^4t_2^1$	$^2T_2$	yes
d^6	^5D	$t_{2g}^4\ e_g^2$	$^5T_{2g}$	yes	$e^3t_2^3$	^5E	no
		t_{2g}^6	$^1A_{1g}$	no	$e_4t_2^2$	$^3T_1$	yes
d^7	^4F	$t_{2g}^5\ e_g^2$	$^4T_{1g}$	yes	$e_4t_2^3$	$^4A_2$	no
		$t_{2g}^6\ e_g^1$	^2E_g	no	—	—	—
d^8	^3F	$t_{2g}^6\ e_g^2$	$^3A_{2g}$	no	$e_4t_2^4$	$^3T_1$	yes
d^9	^2D	$t_{2g}^6\ e_g^3$	^2E_g	no	$e_4t_2^5$	$^2T_2$	yes

[a] $\Gamma(\mathbf{L}) = T_{1g}$.

[b] $\Gamma(\mathbf{L}) = T_2$.

11.2. Atomic multiplets

The SO interaction in free atoms alters the atomic terms $|\Psi_i\rangle = |L, M_L, S, M_S\rangle$ into atomic multiplets denoted as $|L, S, J, M_J\rangle = |JM\rangle$. The energies of multiplets are given as follows:

$$E_0(J) = \left\langle JM \left| \sum_i \xi \boldsymbol{l}_i \cdot \boldsymbol{s}_i \right| JM \right\rangle [\hbar^{-2}] = \langle JM|\lambda \boldsymbol{L} \cdot \boldsymbol{S}|JM\rangle[\hbar^{-2}]$$

$$= \frac{\lambda}{2} \langle JM|\hat{J}^2 - \hat{L}^2 - \hat{S}^2|JM\rangle[\hbar^{-2}] = \frac{\lambda}{2} [\mathrm{J}(\mathrm{J}+1) - \mathrm{L}(\mathrm{L}+1) - \mathrm{S}(\mathrm{S}+1)]$$

where λ (in units of energy) stands for the SO splitting parameter, constant within a given term. The axis along $\hat{J}_z$ adopts a meaning of the quantization axis and thus

$$\hat{J}_z|JM\rangle = M|JM\rangle[\hbar]$$

The electronic Zeeman operator

$$\hat{H}^Z = \mu_B \boldsymbol{L} \cdot \boldsymbol{B}[\hbar^{-1}] + \mu_B g_e \boldsymbol{S} \cdot \boldsymbol{B}[\hbar^{-1}]$$

has the following diagonal matrix elements:

$$E_1(J, M) = \langle JM|\hat{H}^Z|JM\rangle$$

With the help of the "replacement theorem" these matrix elements can be replaced by those of the total angular momentum operator

$$\langle JM|\boldsymbol{L} + g_e \boldsymbol{S}|JM'\rangle = g_J \langle JM|\boldsymbol{J}|JM'\rangle$$

where g_J is a constant for a given J, independent of the projections M or M'. In determining the proportionality constant the Wigner–Eckart theorem can be used, i.e.

$$\langle LSJM|\boldsymbol{L}_z|LSJM\rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} \langle LSJ\|\boldsymbol{L}\|LSJ\rangle$$

The 3*j*-symbol is either tabulated or is easily evaluated [27]:

$$\begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} = (-1)^{J-M} \frac{M}{[J(J+1)(2J+1)]^{1/2}}$$

The reduced matrix element of a vector operator (tensor operator of the first rank) is expressed in terms of the 6*j*-symbol as follows:

$$\langle LSJ\|\boldsymbol{L}\|LSJ\rangle = (2J+1)(-1)^{L+S+J+1} \begin{Bmatrix} J & 1 & J \\ L & S & L \end{Bmatrix} \langle L\|\boldsymbol{L}\|L\rangle$$

where

$$\langle L\|\boldsymbol{L}\|L\rangle = [(2L+1)(L+1)L]^{1/2}[\hbar]$$

and

$$\begin{Bmatrix} J & 1 & J \\ L & S & L \end{Bmatrix} = (-1)^{L+S+J+1} \frac{2[J(J+1)+L(L+1)-S(S+1)]}{[(2J)(2J+1)(2J+2)(2L)(2L+1)(2L+2)]^{1/2}}$$

Then we arrive at the expression

$$\langle LSJM|\hat{L}_z|LSJM\rangle = \frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)} M[\hbar^1]$$

Now the energy in the first-order perturbation theory is

$$\begin{aligned} E_1(J, M) &= \langle JM|\hat{H}^{Z}|JM\rangle = \mu_B \boldsymbol{B}\cdot\langle JM|\boldsymbol{L}+g_e\boldsymbol{S}|JM\rangle[\hbar^{-1}] \\ &= \mu_B \boldsymbol{B}\cdot\langle JM|g_e\boldsymbol{J}-(g_e-1)\boldsymbol{L}|JM\rangle[\hbar^{-1}] \\ &\approx \mu_B \boldsymbol{B}\cdot\langle JM|2\boldsymbol{J}-\boldsymbol{L}|JM\rangle[\hbar^{-1}] \end{aligned}$$

Without loss of generality we take the field parallel to the z-axis

$$\begin{aligned} E_1(J, M) &= \mu_B B_z\langle JM|2\hat{J}_z-\hat{L}_z|JM\rangle[\hbar^{-1}] \\ &= \mu_B B_z\left[2M - \frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)} M\right] \end{aligned}$$

and a comparison with

$$E_1(J, M) = \mu_B B_z g_J\langle JM|\hat{J}_z|JM\rangle[\hbar^{-1}] = \mu_B B_z g_J M$$

finally yields the Landé factor

$$g_J = 1 + \frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}$$

which can be rewritten as

$$g_J = \frac{3}{2} + \frac{S(S+1)-L(L+1)}{2J(J+1)} = \frac{3}{2} + \frac{(S+L+1)(S-L)}{2J(J+1)}$$

For some special cases one has

	g_J
$L=0$	$=g_S=2$
$S=0$	$=g_L=1$
$J=0$	$=2+S=2+L$

It should be mentioned that the orbital and spin angular momentum vectors define the electronic magnetic momentum vector

$$\boldsymbol{\mu} = -\frac{\partial \epsilon(J, M)}{\partial B} = -\mu_{\mathrm{B}}(\boldsymbol{L} + g_{\mathrm{e}}\boldsymbol{S})[\hbar^{-1}]$$

which is not collinear with the total angular momentum vector

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$$

because of $g_{\mathrm{e}} \neq 1$. Consequently, the vector $\boldsymbol{\mu}$ exhibits a rapid precession about the direction of $\boldsymbol{J}$ and thus only a component of $\boldsymbol{\mu}$ along $\boldsymbol{J}$ is conserved.

In concluding, the diagonal matrix elements of the electron Zeeman operator are

$$\langle JM|\hat{H}_z^Z|JM\rangle = \mu_{\mathrm{B}} g_J B_z \langle JM|\hat{J}_z|JM\rangle[\hbar^{-1}] = \mu_{\mathrm{B}} g_J B_z M$$

The off-diagonal matrix elements are calculated with the help of the relationship [28,29]

$$\begin{aligned}\langle J-1, M|\hat{L}_z|JM\rangle &= \langle J-1\|\boldsymbol{L}\|J\rangle[(J+M)(J-M)]^{1/2}\\ &= -\left\{\frac{[J^2-(L-S)^2][(L+S+1)^2-J^2]}{4J^2(4J^2-1)}\right\}^{1/2}(J^2-M^2)^{1/2}[\hbar]\end{aligned}$$

and they are

$$\langle J'M|\hat{H}_z^Z|JM\rangle = \mu_{\mathrm{B}} B_z[2\langle J'M|\hat{J}_z|JM\rangle - \langle J'M|\hat{L}_z|JM\rangle][\hbar^{-1}]$$

Since the first term vanishes, the off-diagonal matrix elements are

$$\begin{aligned}\langle J'M|\hat{H}_z^Z|JM\rangle &= -\mu_{\mathrm{B}} B_z \langle J'M|\hat{L}_z|JM\rangle][\hbar^{-1}]\\ &= \mu_{\mathrm{B}} B_z\left\{\frac{[J^2-(L-S)^2][(L+S+1)^2-J^2}{4J^2(4J^2-1)}\right\}^{1/2}(J^2-M^2)^{1/2}\end{aligned}$$

for

$$J' = J-1$$

Depending on the relationships among the energy levels and the thermal energy, several limiting cases can be distinguished:
(1) wide multiplets
(2) narrow multiplets
(3) multiplets of intermediate width
(4) multiplets with orbital reduction
(5) multiplets split by the crystal field of ligands.
These are briefly characterized below (Fig. 20).

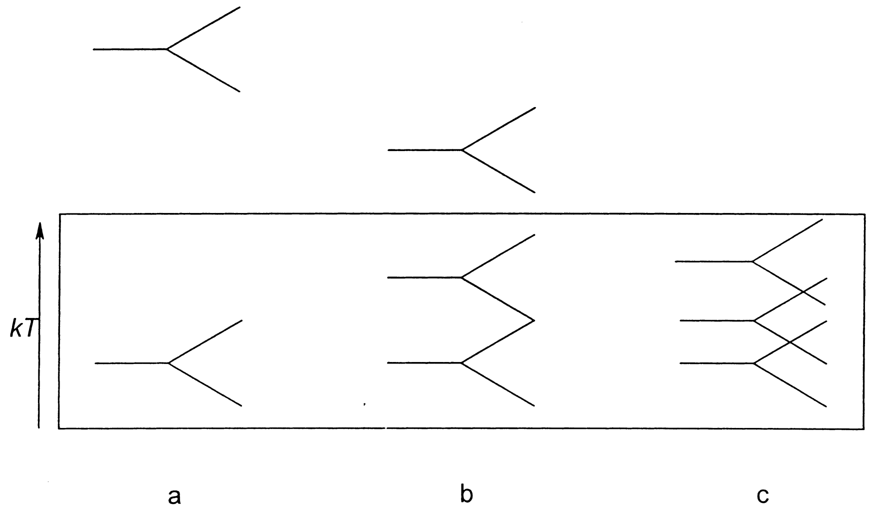


Fig. 20. A multiplet width compared with thermal energy: (a) wide multiplets; (b) multiplets of intermediate width; (c) narrow multiplets.

11.3. Wide multiplets

An excited multiplet lies far above the ground one, so that only the energy levels within the ground multiplet are thermally populated. There are $2J+1$ magnetic levels within a given multiplet of the total angular momentum quantum number J. In the magnetic field their energies are given by the electronic Zeeman term as

$$\epsilon(J, M_J)=\langle JM_J|\hat{H}_z^Z|JM_J\rangle=\mu_B g_J B_z\langle JM_J|\hat{J}_z|JM_J\rangle[\hbar^{-1}]=\mu_B g_J B_z M_J$$

Table 19
Properties of some lanthanide ions

$4f^n$	Ion	Ground state	Excited state	$\Delta E/hc$ (cm^{-1})	g_J	ξ/hc (cm^{-1})	$\chi_{mol}T/C_0$
1	Ce(III)	$^2F_{5/2}$	$^2F_{7/2}$	2200	6/7	640	2.12
2	Pr(III)	$^3H_4$	$^3H_5$	2100	4/5	800	4.26
3	Nd(III)	$^4I_{9/2}$	$^4I_{11/2}$	1900	8/11	900	4.37
4	Pm(III)	$^5I_4$	$^5I_5$	1600	3/5		2.39
5	Sm(III)	$^6H_{5/2}$	$^6H_{7/2}$	1000	2/7	1200	0.23
6	Eu(III)	$^7F_0$	$^7F_1$	300	5	1415	0
7	Gd(III)	$^8S_{7/2}$	$^6P_{7/2}$	30 000	2		21.00
8	Tb(III)	$^7F_6$	$^7F_5$	2000	3/2	1620	31.50
9	Dy(III)	$^6H_{15/2}$	$^6H_{13/2}$	—	4/3	1820	37.78
10	Ho(III)	$^5I_8$	$^5I_7$	—	5/4	2080	37.50
11	Er(III)	$^4I_{15/2}$	$^4I_{13/2}$	6500	6/5	2360	30.61
12	Tm(III)	$^3H_6$	$^3H_5$	—	7/6	2800	19.05
13	Yb(III)	$^2F_{7/2}$	$^2F_{5/2}$	10 000	8/7	2940	6.85

Following the procedure for the derivation of the magnetization expressed via the Brillouin function (Part 8.9) one gets

$$M = M_0 B_J(\eta)$$

with

$$M_0 = N_A \mu_B g_J J$$

and the argument

$$\eta = \frac{g_J \mu_B B_z}{kT}$$

For a small argument of the Brillouin function (when the field B is small and T is high enough) the magnetization becomes a linear function of the applied field

$$M \approx M_0 \frac{J+1}{3} \eta = \frac{N_A \mu_B^2 g_J^2 J(J+1)}{3kT} B$$

Consequently, the magnetic susceptibility obeys the Curie law of the form

$$\chi = \mu_0 \frac{\partial M}{\partial B} = \frac{N_A \mu_0 \mu_B^2 g_J^2 J(J+1)}{3kT}$$

The above requirements are well fulfilled for Gd(III) and Eu(II) derivatives ($4f^7$ systems, $^8S_{7/2}$ ground state); Table 19. The magnetic susceptibility is isotropic and follows the Curie law for $J = 7/2$.

11.4. Narrow multiplets

Let us consider a multiplet of J values whose width is small compared with kT. In this rather hypothetical case the probabilities of occupation of each of the states are all equal. This situation is characterized by the condition

$$E_J^{(0)}/kT \approx 0$$

which allows the omission of the Boltzmann factors in the van Vleck equation for the paramagnetic susceptibility

$$\chi_{\mathrm{mol}} = N_A \mu_0 \frac{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} \frac{(g_J \mu_B M)^2}{kT} \exp[-E_J^{(0)}/kT]}{\sum_{J=|L-S|}^{L+S} \sum_{M=-J}^{+J} \exp[-E_J^{(0)}/kT]}$$

This relaxes to the form

$$\chi_{\text{mol}} = \frac{N_{\text{A}}\mu_0\mu_{\text{B}}^2}{kT} \frac{\sum\limits_{J=|L-S|}^{L+S} g_J^2 \sum\limits_{M=-J}^{+J} M^2}{\sum\limits_{J=|L-S|}^{L+S} \sum\limits_{M=-J}^{+J} 1}$$

$$= \frac{N_{\text{A}}\mu_0\mu_{\text{B}}^2}{kT} \frac{\sum\limits_{J=|L-S|}^{L+S} \left[\frac{3J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}\right]^2 \times \frac{J(J+1)(2J+1)}{3}}{\sum\limits_{J=|L-S|}^{L+S} (2J+1)}$$

which finally yields

$$\chi_{\text{mol}} = \frac{N_{\text{A}}\mu_0\mu_{\text{B}}^2}{3kT} [4S(S+1)+L(L+1)]$$

This formula is applicable for a free ion at sufficiently high temperature.

11.5. Multiplets of intermediate width

In this most realistic case the van Vleck formula adopts the form of

$$\chi_{\text{mol}} = N_{\text{A}}\mu_0 \frac{\sum\limits_{J=|L-S|}^{L+S} \sum\limits_{M=-J}^{+J} \left[\frac{(E_{J,M}^{(1)})^2}{kT} - 2E_{J,M}^{(2)}\right] \exp[-E_J^{(0)}/kT]}{\sum\limits_{J=|L-S|}^{L+S} \sum\limits_{M=-J}^{+J} \exp[-E_J^{(0)}/kT]}$$

By introducing the particular susceptibility function common for a multiplet

$$\chi_J = N_{\text{A}}\mu_0 \frac{\sum\limits_{M=-J}^{+J} \left[\frac{(E_{J,M}^{(1)})^2}{kT} - 2E_{J,M}^{(2)}\right]}{2J+1}$$

the molar susceptibility can be expressed as

$$\chi_{\text{mol}} = \frac{\sum\limits_{J=|L-S|}^{L+S} (2J+1)\chi_J \exp[-E_J^{(0)}/kT]}{\sum\limits_{J=|L-S|}^{L+S} (2J+1) \exp[-E_J^{(0)}/kT]}$$

The zero-order van Vleck coefficients are determined as the relative energies of levels of the ${}^{2S+1}L_J$ multiplet as

$$E_J^{(0)} = \frac{\lambda}{2} J(J+1)$$

where we omitted the remainder $O = -(\lambda/2)[L(L+1)+S(S+1)]$ which is constant within the term.

The first-order van Vleck coefficients are simply

$$E_{J,M}^{(1)} = \mu_B g_J M$$

and then

$$\sum_{M=-J}^{+J} (E_{J,M}^{(1)})^2 = (\mu_B g_J)^2 \sum_{M=-J}^{+J} M^2 = (\mu_B g_J)^2 \frac{J(J+1)(2J+1)}{3}$$

The determination of the second-order van Vleck coefficients $E_{J,M}^{(2)}$ is the most laborious step. The magnetic field gives rise to matrix elements between different multiplets of a term: the non-vanishing matrix elements are of the form

$$\begin{aligned}\langle J'M|\hat{H}'|JM\rangle &= \langle J'M|\hat{H}_z^Z|JM\rangle = \mu_B B_z \langle J'M|2\hat{J}_z - \hat{L}_z|JM\rangle[\hbar^{-1}] \\ &= \mu_B B_z 2M\delta_{J,J'}[\hbar^{-1}] - \mu_B B_z \langle J'M|\hat{L}_z|JM\rangle[\hbar^{-1}]\end{aligned}$$

and they can be simply evaluated as follows

$$\langle J-1, M|\hat{L}_z|JM\rangle = \langle J-1\|\boldsymbol{L}\|J\rangle(J^2-M^2)^{1/2} = -(J^2-M^2)^{1/2} f(SLJ)[\hbar]$$

with the function

$$f(SLJ) = -\langle J-1\|\boldsymbol{L}\|J\rangle[\hbar^{-1}] = \left\{\frac{[J^2-(L-S)^2][(L+S+1)^2-J^2]}{4J^2(4J^2-1)}\right\}^{1/2}$$

The energy contribution in the second-order perturbation theory is

$$\begin{aligned}E_2(J, M) &= -\sum_{j\neq i} \frac{\langle j|\hat{H}'|i\rangle^2}{E_j - E_i} = -\sum_{J'\neq J} \frac{\langle J'M|\hat{H}^Z|JM\rangle^2}{E_0(J') - E_0(J)} \\ &= -(\mu_B B_z)^2 \sum_{J'=J\pm 1} \frac{\langle J'M|\hat{L}_z|JM\rangle^2}{E_0(J') - E_0(J)} [\hbar^{-2}]\end{aligned}$$

With the help of the energy differences

$$E_0(J+1) - E_0(J) = \frac{\lambda}{2}(J+1)(J+2) - \frac{\lambda}{2}J(J+1) = \lambda(J+1)$$

$$E_0(J-1) - E_0(J) = \frac{\lambda}{2}(J-1)J - \frac{\lambda}{2}J(J+1) = -\lambda J$$

and

$$\langle J+1, M|\hat{L}_z|JM\rangle = \langle JM|\hat{L}_z|J+1, M\rangle = -[(J+1)^2-M^2]^{1/2} f(SL, J+1)[\hbar]$$

the second-order van Vleck coefficients result as follows

$$E^{(2)}_{J,M} = -\mu_B^2\left\{\frac{\langle J+1\|\boldsymbol{L}\|J\rangle^2[(J+1)^2-M^2]}{\lambda(J+1)} - \frac{\langle J-1\|\boldsymbol{L}\|J\rangle^2(J^2-M^2)}{\lambda J}\right\}[\hbar^{-2}]$$

$$= -\mu_B^2\left\{\frac{[f(SL, J+1)]^2[(J+1)^2-M^2]}{\lambda(J+1)} - \frac{[f(SLJ)]^2(J^2-M^2)}{\lambda J}\right\}$$

These can be further summed up to give

$$\sum_{M=-J}^{+J} E^{(2)}_{J,M} = -\mu_B^2 \sum_{M=-J}^{+J}\left\{\frac{[f(SL, J+1)]^2[(J+1)^2-M^2]}{\lambda(J+1)} - \frac{[f(SLJ)]^2(J^2-M^2)}{\lambda J}\right\}$$

$$= -\frac{\mu_B^2}{\lambda}\{[f(SL, J+1)]^2(J+1) - [f(SLJ)]^2 J\}\left(\sum_{M=-J}^{+J} 1\right)$$

$$-\frac{\mu_B^2}{\lambda}\left\{-\frac{[f(SL, J+1)]^2}{J+1} + \frac{[f(SLJ)]^2}{J}\right\}\left(\sum_{M=-J}^{+J} M^2\right)$$

After simple algebraic manipulations we get

$$\sum_{M=-J}^{+J} E^{(2)}_{J,M} = -\frac{\mu_B^2}{3\lambda}(2J+1)3\{[f(SL, J+1)]^2(J+1) - [f(SLJ)]^2 J\}$$

$$-\frac{\mu_B^2}{3\lambda}(2J+1)(J+1)J\left\{-\frac{[f(SL, J+1)]^2}{J+1} + \frac{[f(SLJ)]^2}{J}\right\}$$

$$= \frac{\mu_B^2}{3\lambda}(2J+1)\{[f(SL, J+1)]^2[3(J+1)-J] - [f(SLJ)]^2[3J-(J+1)]\}$$

$$\sum_{M=-J}^{+J} E^{(2)}_{J,M} = -\frac{\mu_B^2}{3\lambda}(2J+1)\{[f(SL, J+1)]^2(2J+3) - [f(SLJ)]^2(2J-1)\}$$

It is understood that $f(SLJ)=0$ for $J=0$. A further simplification is obtained when the following identity is utilized:

$$[f(SL, J+1)]^2(2J+3) - [f(SLJ)]^2(2J-1)$$

$$= \frac{[(S+L+1)(S-L)]^2 - [J(J+1)]^2}{[2J(J+1)]^2} = (g_J-1)(g_J-2)$$

which can be easily proven after insertions for g_J, $f(SLJ)$ and $f(SL, J+1)$. Then the second-order van Vleck coefficients are summed up to

$$\sum_{M=-J}^{+J} E_{J,M}^{(2)} = -\frac{\mu_B^2}{3\lambda}(2J+1)(g_J-1)(g_J-2)$$

The expressions derived for the van Vleck coefficients allow us to construct the particular susceptibility function for a multiplet

$$\begin{aligned}\chi_J &= N_A\mu_0 \frac{\sum_{M=-J}^{+J}\left[\frac{(E_{J,M}^{(1)})^2}{kT} - 2E_{J,M}^{(2)}\right]}{2J+1}\\ &= \frac{N_A\mu_0}{2J+1}\left[\frac{1}{kT}\sum_{M=-J}^{+J}(E_{J,M}^{(1)})^2 - 2\sum_{M=-J}^{+J}E_{J,M}^{(2)}\right]\\ &= \frac{N_A\mu_0}{2J+1}\left[\frac{\mu_B^2 g_J^2}{kT}\frac{J(J+1)(2J+1)}{3} + 2\frac{\mu_B^2}{3\lambda}(2J+1)(g_J-1)(g_J-2)\right]\\ &= \frac{N_A\mu_0\mu_B^2}{3}\left[\frac{g_J^2}{kT}J(J+1) + \frac{2}{\lambda}(g_J-1)(g_J-2)\right]\end{aligned}$$

and the final molar magnetic susceptibility becomes

$$\chi_{\text{mol}} = \frac{\sum_{J=|L-S|}^{L+S}(2J+1)\chi_J \exp[-\lambda J(J+1)/2kT]}{\sum_{J=|L-S|}^{L+S}(2J+1)\exp[-\lambda J(J+1)/2kT]}$$

or alternatively

$$\chi_{\text{mol}} = \frac{N_A\mu_0\mu_B^2}{3kT}\frac{\sum_{i=|L-S|}^{L+S} a_i(c_i + d_i/x)\exp(-b_i x)}{\sum_{i=|L-S|}^{L+S} a_i \exp(-b_i x)}$$

with

$$a_i = 2J+1$$

$$b_i = \tfrac{1}{2}J(J+1) - b_1$$

$$c_i = g_J^2 J(J+1)$$

$$d_i = 2(g_J-1)(g_J-2)$$

and

$$x = \frac{\lambda}{kT} = \pm\frac{\xi}{2S}\frac{1}{kT}$$

where the positive sign applies for the half-filled shells and the negative sign in the opposite case. These constants are collected in Table 20.

Representative plots of the product functions $\chi_{\mathrm{mol}}T$ versus the reduced parameter $1/x = kT/\lambda$ are given in Fig. 21. The main difference between the left- and right-part of Fig. 21 lies in the fact that the inverted multiplets (on the right) have their ground states of the maximum J. This results in the high-spin state which is little affected as temperature increases.

The real magnetic behaviour of the lanthanide compounds is affected by a magnetic anisotropy which becomes significant upon cooling. Moreover, a reduction of the orbital angular momentum and the crystal field splitting may become important.

For completeness, Table 21 provides data for the susceptibility function of transition metal ions; these are displayed in Fig. 22. However, the crystal field splitting of energy levels is very important for 3d-metal ions, so that a more elaborate approach is necessary.

11.6. Reduction factor

The experimental data in accordance with theoretical predictions show that the orbital angular momentum in real metal complexes is somehow reduced so that it is legitimate to operate with $\hat{L} \rightarrow \kappa\hat{L}$, $0 < \kappa \leqslant 1$ being an orbital reduction factor. There are two sources of the orbital reduction:

(1) covalency, due to bond formation;
(2) configuration interaction (CI).

In metal complexes a set of molecular orbitals can be written in the form

$$\varphi_i = c_i^{\mathrm{M}} \mathrm{d}_i^{\mathrm{M}} + c_i^{\mathrm{L}} \chi_i^{\mathrm{L}}$$

where χ_i^{L} are appropriate symmetry combinations of ligand orbitals (group orbitals), $\mathrm{d}_i^{\mathrm{M}}$ being the metal d-orbitals. The LCAO coefficients obey the normalization condition

$$\begin{aligned}\langle\varphi_i|\varphi_i\rangle &= (c_i^{\mathrm{M}})^2\langle \mathrm{d}_i^{\mathrm{M}}|\mathrm{d}_i^{\mathrm{M}}\rangle + (c_i^{\mathrm{L}})^2\langle\chi_i^{\mathrm{L}}|\chi_i^{\mathrm{L}}\rangle + 2c_i^{\mathrm{M}}c_i^{\mathrm{L}}\langle \mathrm{d}_i^{\mathrm{M}}|\chi_i^{\mathrm{L}}\rangle \\ &= (c_i^{\mathrm{M}})^2 + (c_i^{\mathrm{L}})^2 + 2c_i^{\mathrm{M}}c_i^{\mathrm{L}}S_{i,i}^{\mathrm{M,L}} = 1\end{aligned}$$

The molecular spinorbitals

$$\phi_i = \begin{cases}\varphi_i\alpha \\ \varphi_i\beta\end{cases}$$

constitute a determinantal wave function

$$|\Psi_\mu\rangle = \hat{A}_n\{\phi_1(1)\ldots\phi_n(n)\}$$

Table 20
Terms of the magnetic susceptibility formula for multiplets of intermediate width

Ion	Multiplet		g_J	a_i	b_i	c_i	d_i
Ce(III)	1	$^2F_{5/2}$	6/7	6	0	6.42857	0.32653
	2	$^2F_{7/2}$	8/7	8	7/2	20.57143	−0.24490
Pr(III)	1	$^3H_4$	4/5	9	0	12.8	0.48
	2	$^3H_5$	31/30	11	5	32.03333	−0.06444
	3	$^3H_6$	7/6	13	11	57.16667	−0.27778
Nd(III)	1	$^4I_{9/2}$	8/11	10	0	13.09091	0.69421
	2	$^4I_{11/2}$	138/143	12	11/2	33.29371	0.07238
	3	$^4I_{13/2}$	216/195	14	12	59.81538	−0.19219
	4	$^4I_{15/2}$	306/255	16	39/2	91.8	−0.32
Pm(III)	1	$^5I_4$	3/5	9	0	7.2	1.12
	2	$^5I_5$	9/10	11	5	24.3	0.22
	3	$^5I_6$	15/14	13	11	48.21429	−0.13265
	4	$^5I_7$	33/28	15	18	77.78571	−0.29337
	5	$^5I_8$	5/4	17	26	112.5	−0.375
Sm(III)	1	$^6H_{5/2}$	2/7	6	0	0.71429	2.44898
	2	$^6H_{7/2}$	52/63	8	7/2	10.73016	0.41018
	3	$^6H_{9/2}$	106/99	10	8	28.37374	−0.13142
	4	$^6H_{11/2}$	172/143	12	27/2	51.72028	−0.32334
	5	$^6H_{13/2}$	50/39	14	20	80.12821	−0.40500
	6	$^6H_{15/2}$	4/3	16	55/2	113.33333	−0.44444
Eu(III)	1	$^7F_0$	5	1	0	0	24.0
	2	$^7F_1$	3/2	3	1	4.5	−0.5
	3	$^7F_2$	3/2	5	3	13.5	−0.5
	4	$^7F_3$	3/2	7	6	27.0	−0.5
	5	$^7F_4$	3/2	9	10	45.0	−0.5
	6	$^7F_5$	3/2	11	15	67.5	−0.5
	7	$^7F_6$	3/2	13	21	94.5	−0.5
Gd(III)	1	$^8S_{7/2}$	2	8	0	63.0	0
Tb(III)	1	$^7F_6$	3/2	13	0	94.5	−0.5
	2	$^7F_5$	3/2	11	−6	67.5	−0.5
	3	$^7F_4$	3/2	9	−11	45.0	−0.5
	4	$^7F_3$	3/2	7	−15	27.0	−0.5
	5	$^7F_2$	3/2	5	−18	13.5	−0.5
	6	$^7F_1$	3/2	3	−20	4.5	−0.5
	7	$^7F_0$	5	1	−21	0	24.0
Dy(III)	1	$^6H_{15/2}$	4/3	16	0	113.33333	−0.44444
	2	$^6H_{13/2}$	50/39	14	−15/2	80.12821	−0.40500
	3	$^6H_{11/2}$	172/143	12	−14	51.72028	−0.32334
	4	$^6H_{9/2}$	106/99	10	−39/2	28.37374	−0.13142
	5	$^6H_{7/2}$	52/63	8	−24	10.73016	0.41018
	6	$^6H_{5/2}$	2/7	6	−55/2	0.71429	2.44898
Ho(III)	1	$^5I_8$	5/4	17	0	112.5	−0.375
	2	$^5I_7$	33/28	15	−8	77.78571	−0.29337
	3	$^5I_6$	15/14	13	−15	48.21429	−0.13265
	4	$^5I_5$	9/10	11	−21	24.3	0.22
	5	$^5I_4$	3/5	9	−26	7.2	1.12
Er(III)	1	$^4I_{15/2}$	306/255	16	0	91.8	−0.32
	2	$^4I_{13/2}$	216/195	14	−15/2	59.81538	−0.19219
	3	$^4I_{11/2}$	138/143	12	−14	33.29371	0.07238
	4	$^4I_{9/2}$	8/11	10	−39/2	13.09091	0.69421
Tm(III)	1	$^3H_6$	7/6	13	0	57.16667	−0.27778
	2	$^3H_5$	31/30	11	−6	32.03333	−0.06444
	3	$^3H_4$	4/5	9	−11	12.8	0.48
Yb(III)	1	$^2F_{7/2}$	8/7	8	0	20.57143	−0.24490
	2	$^2F_{5/2}$	6/7	6	−7/2	6.42857	0.32653

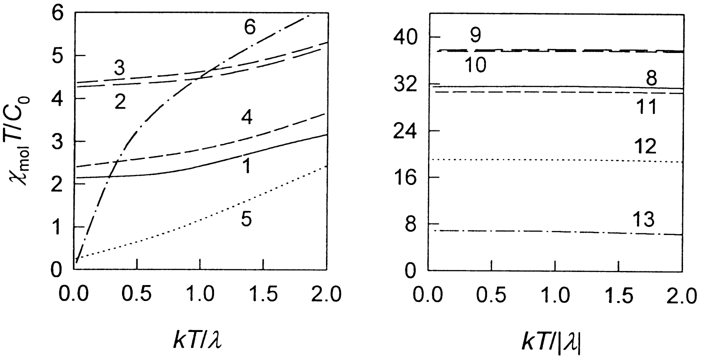


Fig. 21. The product function $\chi_{mol}T$ versus kT/λ for lanthanide trivalent ions: (left) less than half-filled shells, (right) more than half-filled shells ($\lambda < 0$); numbers correspond to the f^n configuration.

Table 21
Terms of the magnetic susceptibility formula for multiplets of d^n-metal ions

Ion	Multiplet		g_J	a_i	b_i	c_i	d_i
d^1	1	$^2D_{3/2}$	4/5	4	0	2.4	0.48
	2	$^2D_{5/2}$	6/5	6	5/2	12.6	−0.32
d^2	1	$^3F_2$	2/3	5	0	2.66667	0.88880
	2	$^3F_3$	13/12	7	3	14.08333	−0.15278
	3	$^3F_4$	5/4	9	7	31.25	−0.375
d^3	1	$^4F_{3/2}$	2/5	4	0	0.6	1.92
	2	$^4F_{5/2}$	36/35	6	5/2	9.25714	−0.05551
	3	$^4F_{7/2}$	26/21	8	6	24.14286	−0.36281
	4	$^4F_{9/2}$	4/3	10	21/2	44.0	−0.44444
d^4	1	$^5D_0$	4	1	0	0	12.0
	2	$^5D_1$	3/2	3	1	4.5	−0.5
	3	$^5D_2$	3/2	5	3	13.5	−0.5
	4	$^5D_3$	3/2	7	6	27.0	−0.5
	5	$^5D_4$	3/2	9	10	45.0	−0.5
d^5	1	$^6S_{5/2}$	2	6	0	35.0	0.0
d^6	1	$^5D_4$	3/2	9	0	45.0	−0.5
	2	$^5D_3$	3/2	7	−4	27.0	−0.5
	3	$^5D_2$	3/2	5	−7	13.5	−0.5
	4	$^5D_1$	3/2	3	−9	4.5	−0.5
	5	$^5D_0$	4	1	−10	0	12.0
d^7	1	$^4F_{9/2}$	4/3	10	0	44.0	−0.44444
	2	$^4F_{7/2}$	26/21	8	−9/2	24.14286	−0.36281
	3	$^4F_{5/2}$	36/35	6	−8	9.25714	−0.05551
	4	$^4F_{3/2}$	2/5	4	−21/2	0.6	1.92
d^8	1	$^3F_4$	5/4	9	0	31.25	−0.375
	2	$^3F_3$	13/12	7	−4	14.08333	−0.15278
	3	$^3F_2$	2/3	5	−7	2.66667	0.88880
d^9	1	$^2D_{5/2}$	6/5	6	0	12.6	−0.32
	2	$^2D_{3/2}$	4/5	4	−5/2	2.4	0.48

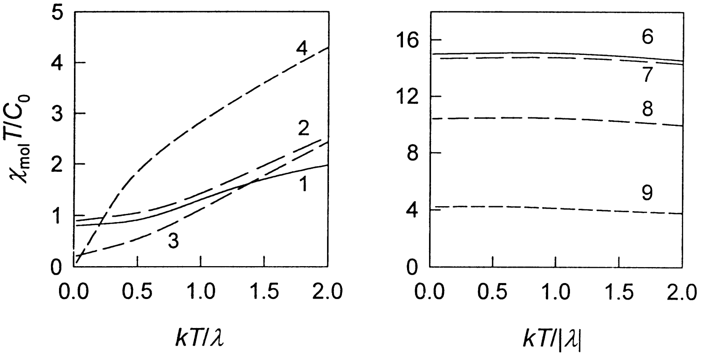


Fig. 22. The product function $\chi_{\mathrm{mol}}T$ versus kT/λ for transition metal ions: (left) less than half-filled shells, (right) more than half-filled shells ($\lambda<0$); numbers correspond to the d^n configuration.

and thus the integrals of the total angular momentum between the determinantal wave functions are expressed through a sum of one-electron terms

$$\langle \Psi_\mu | \boldsymbol{L} | \Psi_\nu \rangle = \sum_{i=1}^{n} \langle \Psi_\mu | \boldsymbol{l}_i | \Psi_\nu \rangle$$

$$= \begin{cases} \sum_{i=1}^{n} \langle \phi_i | \boldsymbol{l}_1 | \phi_i \rangle & \text{for identical determinants} \\ \langle \phi_i | \boldsymbol{l}_1 | \phi_j \rangle & \text{for determinants differing in one spinorbital} \end{cases}$$

The one-electron integrals are expanded as follows

$$L_{ij,a} = \langle \varphi_i | \hat{l}_{1a} | \varphi_j \rangle = c_i^{\mathrm{M}} c_j^{\mathrm{M}} \langle \mathrm{d}_i^{\mathrm{M}} | \hat{l}_{1a} | \mathrm{d}_j^{\mathrm{M}} \rangle + c_i^{\mathrm{M}} c_j^{\mathrm{L}} \langle \mathrm{d}_i^{\mathrm{M}} | \hat{l}_{1a} | \chi_j^{\mathrm{L}} \rangle$$
$$+ c_i^{\mathrm{L}} c_j^{\mathrm{M}} \langle \chi_i^{\mathrm{L}} | \hat{l}_{1a} | \mathrm{d}_j^{\mathrm{M}} \rangle + c_i^{\mathrm{L}} c_j^{\mathrm{L}} \langle \chi_i^{\mathrm{L}} | \hat{l}_{1a} | \chi_j^{\mathrm{L}} \rangle$$

To a further approximation we expect the validity

$$c_i^{\mathrm{M}} \approx c_j^{\mathrm{M}} = c^{\mathrm{M}}$$

and

$$c_i^{\mathrm{L}} \approx c_j^{\mathrm{L}} = c^{\mathrm{L}}$$

so that we get

$$L_{ij,a} \approx (c^{\mathrm{M}})^2 \langle \mathrm{d}_i^{\mathrm{M}} | \hat{l}_{1a} | \mathrm{d}_j^{\mathrm{M}} \rangle + 2 c^{\mathrm{M}} c^{\mathrm{L}} \langle \mathrm{d}_i^{\mathrm{M}} | \hat{l}_{1a} | \chi_j^{\mathrm{L}} \rangle + (c^{\mathrm{L}})^2 \langle \chi_i^{\mathrm{L}} | \hat{l}_{1a} | \chi_j^{\mathrm{L}} \rangle$$

Since the action of the angular momentum operator on a ket $|\mathrm{d}_j^{\mathrm{M}}\rangle$ yields a (complex) number ϵ_j and another ket, say $|\mathrm{d}_k^{\mathrm{M}}\rangle$

$$\hat{l}_{1a} | \mathrm{d}_j^{\mathrm{M}} \rangle = \epsilon_j | \mathrm{d}_k^{\mathrm{M}} \rangle [\hbar]$$

then

$$L_{ij,a} = \epsilon_j[(c^{\mathrm{M}})^2 \delta_{i,k} + 2c^{\mathrm{M}} c^{\mathrm{L}} S_{i,k}^{\mathrm{L,M}}][\hbar] + (c^{\mathrm{L}})^2 \langle \chi_i^{\mathrm{L}} | \hat{l}_{1a} | \chi_j^{\mathrm{L}} \rangle$$

The last term can be neglected owing to the combined effect of small coefficient $(c^{\mathrm{L}})^2$ and small integral $\langle \chi_i^{\mathrm{L}} | \hat{l}_{1a} | \chi_j^{\mathrm{L}} \rangle$. Using the normalization condition for molecular orbitals

$$(c^{\mathrm{M}})^2 + 2c^{\mathrm{M}} c^{\mathrm{L}} S^{\mathrm{M,L}} = 1 - (c^{\mathrm{L}})^2$$

we arrive at the expression

$$L_{ij,a} = \epsilon_j[1 - (c^{\mathrm{L}})^2][\hbar] = \epsilon_j \kappa [\hbar]$$

with the orbital reduction factor introduced by Stevens

$$\kappa = [1 - (c^{\mathrm{L}})^2] \leqslant 1$$

Now one can see that owing to the covalency effect (the involvement of the ligand orbitals into the molecular orbitals) the angular momentum is reduced in the extent of κ. For pure metal d-orbitals $\kappa = 1$ holds true (no reduction).

The orbital reduction factor used to be considered as an empirical parameter and the spin Hamiltonian is rewritten in the form

$$\hat{H}^{\mathrm{S}} = \mu_{\mathrm{B}}(\kappa \boldsymbol{L} + g_{\mathrm{e}} \boldsymbol{S}) \cdot \boldsymbol{B}[\hbar^{-1}] + \kappa \lambda_0 \boldsymbol{L} \cdot \boldsymbol{S}[\hbar^{-2}]$$

where λ_0 is a free-atom (or ion) SO splitting parameter. Then the actual SO splitting parameter in a complex is reduced as follows:

$$\lambda = \kappa \lambda_0$$

The orbital reduction in metal complexes reaches a value of $\kappa = 0.8$.

Within the variational CI a limited CI expansion is written as follows

$$|\Psi_i\rangle = C_0 |\Phi_0\rangle + C_1 |\Phi_1\rangle$$

and the matrix elements of the angular momentum operator can be expressed as

$$L_{ij} = \langle \Psi_i | \boldsymbol{L} | \Psi_j \rangle = C_0^2 \langle \Phi_0 | \boldsymbol{L} | \Phi_0 \rangle + 2C_0 C_1 \langle \Phi_1 | \boldsymbol{L} | \Phi_0 \rangle + C_1^2 \langle \Phi_1 | \boldsymbol{L} | \Phi_1 \rangle$$

After the action of the angular momentum operator to the kets

$$\boldsymbol{L} |\Phi_i\rangle = \epsilon_i |\Phi_i'\rangle [\hbar]$$

one obtains

$$L_{ij} = [C_0^2 \epsilon_0 \langle \Phi_0 | \Phi_0' \rangle + 2C_0 C_1 \epsilon_0 \langle \Phi_1 | \Phi_0' \rangle + C_1^2 \epsilon_1 \langle \Phi_1 | \Phi_1' \rangle][\hbar]$$

For example, in tetrahedral complexes the following mixing of kets is possible

$$|XZ\rangle = C_0 |\mathrm{d}_{xz}\rangle + C_1 |\mathrm{p}_y\rangle$$

$$|YZ\rangle = C_0 |\mathrm{d}_{yz}\rangle + C_1 |\mathrm{p}_x\rangle$$

since the kets $|\mathrm{d}_{xy}\rangle$, $|\mathrm{d}_{xz}\rangle$, $|\mathrm{d}_{yz}\rangle$, $|\mathrm{p}_x\rangle$, $|\mathrm{p}_y\rangle$ and $|\mathrm{p}_z\rangle$ transform according to the representation T_2 of the T_d group. It follows that

$$\begin{aligned}\langle XZ|\hat{L}_z|YZ\rangle = {} & C_0^2\langle \mathrm{d}_{xz}|\hat{L}_z|\mathrm{d}_{yz}\rangle + C_0C_1\langle \mathrm{d}_{xz}|\hat{L}_z|\mathrm{p}_x\rangle + C_0C_1\langle \mathrm{p}_y|\hat{L}_z|\mathrm{d}_{yz}\rangle \\ & + C_1^2\langle \mathrm{p}_y|\hat{L}_z|\mathrm{p}_x\rangle = [C_0^2(-\mathrm{i}) + C_0C_1(0) \\ & + C_0C_1(0) + C_1^2(\mathrm{i})][\hbar] = -\mathrm{i}(C_0^2 - C_1^2)[\hbar] = -\mathrm{i}\kappa[\hbar]\end{aligned}$$

Then the CI reduction factor becomes

$$\kappa = C_0^2 - C_1^2$$

and using the normalization condition

$$\langle \Psi_i|\Psi_i\rangle = C_0^2\langle \Phi_0|\Phi_0\rangle + 2C_0C_1\langle \Phi_0|\Phi_1\rangle + C_1^2\langle \Phi_1|\Phi_1\rangle = C_0^2 + C_1^2 = 1$$

one gets the CI reduction factor in the form of

$$\kappa = 1 - 2C_1^2 \leqslant 1$$

For a single determinantal wave function $\kappa = 1$ holds true (no reduction).

11.7. T–P isomorphism

The angular momentum operators acting on the set of complex $(\mathrm{p}_1, \mathrm{p}_0, \mathrm{p}_{-1})$ functions yield

$$\hat{l}_x\begin{pmatrix}\mathrm{p}_1\\ \mathrm{p}_0\\ \mathrm{p}_{-1}\end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\mathrm{p}_1\\ \mathrm{p}_0\\ \mathrm{p}_{-1}\end{pmatrix}[\hbar]$$

$$\hat{l}_y\begin{pmatrix}\mathrm{p}_1\\ \mathrm{p}_0\\ \mathrm{p}_{-1}\end{pmatrix} = \frac{\mathrm{i}}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{pmatrix}\begin{pmatrix}\mathrm{p}_1\\ \mathrm{p}_0\\ \mathrm{p}_{-1}\end{pmatrix}[\hbar]$$

$$\hat{l}_z\begin{pmatrix}\mathrm{p}_1\\ \mathrm{p}_0\\ \mathrm{p}_{-1}\end{pmatrix} = \begin{pmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{pmatrix}\begin{pmatrix}\mathrm{p}_1\\ \mathrm{p}_0\\ \mathrm{p}_{-1}\end{pmatrix}[\hbar]$$

Except for the sign, equivalent results are obtained for the set of t_2 functions forming the basis of the T_2 term

$$\begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = \begin{pmatrix} |2, -1\rangle \\ (1/\sqrt{2})(|2, 2\rangle - |2, 2\rangle) \\ -|2, 1\rangle \end{pmatrix}$$

Namely

$$\hat{l}_x \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = -\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} [\hbar]$$

$$\hat{l}_y \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = -\frac{i}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} [\hbar]$$

$$\hat{l}_z \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} = -\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} T_2(1) \\ T_2(0) \\ T_2(-1) \end{pmatrix} [\hbar]$$

Thus it is legitimate to claim that the transformation matrix of $\boldsymbol{l}$ within the t_2 representation of d-functions is equal to the matrix of $(-\boldsymbol{l})$ for p-functions (see Table 22).

As far as the SO coupling for a one-electron system is concerned, one can use an equivalence

$$\hat{H}^{\mathrm{so}} = \xi_{\mathrm{d}} \boldsymbol{l}_{t_{2g}} \cdot \boldsymbol{s}[\hbar^{-2}] = -\xi_{\mathrm{d}} \boldsymbol{l}_{\mathrm{p}} \cdot \boldsymbol{s}[\hbar^{-2}]$$

Table 22
T–P isomorphism

O_h group	T_d group
$^2T_{2g}(d^1,t_2^1) \leftrightarrow {}^2P(p^5)$	$^2T_2(d^9,[t_2^1]) \leftrightarrow {}^2P(p^5)$
$^3T_{1g}(d^2,t_2^2) \leftrightarrow {}^3P(p^4)$	$^3T_1(d^8,[t_2^2]) \leftrightarrow {}^3P(p^4)$
$^3T_{1g}(d^4,t_2^4) \leftrightarrow {}^3P(p^2)$	
$^2T_{2g}(d^5,t_2^5) \leftrightarrow {}^2P(p^1)$	
$^5T_{2g}(d^6,t_2^4\,e_g^2) \leftrightarrow {}^5P(p^2)$[a]	$^5T_2(d^4,e_2t_2^2) \leftrightarrow {}^5P(p^4)$[a,b]
$^4T_{1g}(d^7,t_2^5\,e_g^2) \leftrightarrow {}^4P(p^1)$[a]	$^4T_1(d^3,e_2t_2^1) \leftrightarrow {}^4P(p^5)$[a,b]

[a] Hypothetical terms with required spin multiplicity.

[b] $[t_2^n]$ Holes in the filled d^{10} shell.

and the spin Hamiltonian is of the form

$$\hat{H}^S = v_\xi \boldsymbol{l}_\mathrm{p} \cdot \boldsymbol{s}[\hbar^{-2}] + \mu_\mathrm{B} \boldsymbol{B} \cdot (\gamma \boldsymbol{l}_\mathrm{p} + g_\mathrm{e} \boldsymbol{s})[\hbar^{-1}]$$

with the equivalence coefficients

$$\gamma = -1$$

and

$$v_\xi = -\xi_\mathrm{d}$$

For a many-electron problem the spin-Hamiltonian is written as

$$\hat{H}^S = v_\xi \boldsymbol{L}_\mathrm{p} \cdot \boldsymbol{S}[\hbar^{-2}] + \mu_\mathrm{B} \boldsymbol{B} \cdot (\gamma \boldsymbol{L}_\mathrm{p} + g_\mathrm{e} \boldsymbol{S})[\hbar^{-1}]$$

A proper determination of the equivalence coefficients depends upon which set of the crystal field functions is actually used [28–30]:
(1) the strong-field functions (for low-spin complexes), $\gamma = -1$;
(2) the weak-field functions (for high-spin complexes), $\gamma = -3/2$;
(3) the intermediate-field functions, $-3/2 < \gamma < -1$.

In the strong-field limit one can include a mixing of terms arising from different electron configurations as follows:

$$\begin{aligned} |\Psi'(^3\mathrm{T}_1)\rangle &= C_0 |\Psi(^3\mathrm{T}_1; \mathrm{t}_2^1)\rangle + C_1 |\Psi(^3\mathrm{T}_1; \mathrm{t}_2^1\, \mathrm{e}^1)\rangle \\ &= \cos\alpha |\Psi(^3\mathrm{T}_1; \mathrm{t}_2^2)\rangle + \sin\alpha |\Psi(^3\mathrm{T}_1; \mathrm{t}_2^1\, \mathrm{e}^1)\rangle \end{aligned}$$

and thus

$$\begin{aligned} \left\langle \Psi'(^3\mathrm{T}_1) \middle| \sum_i \hat{l}_{iz} \middle| \Psi'(^3\mathrm{T}_1) \right\rangle &= \cos^2\alpha \left\langle \Psi(^3\mathrm{T}_1; \mathrm{t}_2^2) \middle| \sum_i \hat{l}_{iz} \middle| \Psi(^3\mathrm{T}_1; \mathrm{t}_2^2) \right\rangle \\ &+ \sin^2\alpha \left\langle \Psi(^3\mathrm{T}_1; \mathrm{t}_2^1\, \mathrm{e}^1) \middle| \sum_i \hat{l}_{iz} \middle| \Psi(^3\mathrm{T}_1; \mathrm{t}_2^1\, \mathrm{e}^1) \right\rangle \\ &+ 2\cos\alpha \sin\alpha \left\langle \Psi(^3\mathrm{T}_1; \mathrm{t}_2^2) \middle| \sum_i \hat{l}_{iz} \middle| \Psi(^3\mathrm{T}_1; \mathrm{t}_2^1\, \mathrm{e}^1) \right\rangle \end{aligned}$$

Knowing the exact form of the strong-field kets $|\Psi(^3\mathrm{T}_1; \mathrm{t}_2^2, S, M_S)\rangle$ we arrive at the result [29]

$$\begin{aligned} \left\langle \Psi'(^3\mathrm{T}_1) \middle| \sum_i \hat{l}_{iz} \middle| \Psi'(^3\mathrm{T}_1) \right\rangle &= [\cos^2\alpha \cdot (-1) + \sin^2\alpha \cdot (1/2) \\ &+ 2\cos\alpha \sin\alpha \cdot (+1)][\hbar] \end{aligned}$$

On the other hand, the T–P isomorphism says that the following correspondence of the functions $|JM\rangle = |2, 2\rangle$ of the ^{3}p-term and $|\Psi'(^3\mathrm{T}_1)\rangle$ exists

$$\langle \Psi'(^3\mathrm{T}_1) | \boldsymbol{L} | \Psi'(^3\mathrm{T}_1) \rangle = \langle 2, 2 | \gamma \boldsymbol{L} | 2, 2 \rangle = \gamma \cdot (+1)[\hbar]$$

yielding the equivalence coefficient

$$\gamma = -\cos^2\alpha + \tfrac{1}{2}\sin^2\alpha + 2\cos\alpha\sin\alpha$$

For a very strong field (when the $10Dq$ parameter is very large) the sine component vanishes, $\cos\alpha = 1$, and then $\gamma = -1$.

Analogously we can write the second equivalence equation

$$\left\langle \Psi'(^3\mathrm{T}_1) \middle| \xi_\mathrm{d} \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \middle| \Psi'(^3\mathrm{T}_1) \right\rangle = \langle 2, 2 | v_\xi \boldsymbol{L} \cdot \boldsymbol{S} | 2, 2 \rangle v_\xi (+1)[\hbar^2]$$

and since

$$\left\langle \Psi'(^3\mathrm{T}_1) \middle| \xi_\mathrm{d} \sum_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \middle| \Psi'(^3\mathrm{T}_1) \right\rangle = \frac{\gamma}{2}[\hbar^2]$$

(this arises from knowing the exact forms of the strong-field kets) we obtain

$$v_\xi = \frac{\gamma}{2}\,\xi_\mathrm{d}$$

For the very strong field

$$v_\xi = -\frac{1}{2}\,\xi_\mathrm{d}$$

An analogous procedure for the known form of the weak-field kets $|\Psi(^3\mathrm{T}_1;\,^3\mathrm{F}, S, M_S)\rangle$ yields $\gamma = -3/2$ and $v_\xi = -(3/4)\xi_\mathrm{d}$.

The relevant equivalence coefficients for T_1 and T_2 terms of the d^n configurations are collected in Table 23.

11.8. Multiplets with magnetic angular momentum

The zero-order energy accounting for the equivalence coefficients has the form

$$\begin{aligned} E_0(J) &= \langle JM | v_\xi \boldsymbol{L} \cdot \boldsymbol{S} | JM \rangle [\hbar^{-2}] = v_\xi \tfrac{1}{2} \langle JM | \hat{J}^2 - \hat{L}^2 - \hat{S}^2 | JM \rangle [\hbar^{-2}] \\ &= v_\xi \tfrac{1}{2} [J(J+1) - L(L+1) - S(S+1)] \end{aligned}$$

This leads to the following zero-order van Vleck coefficient:

$$E_J^{(0)} = v_\xi \tfrac{1}{2} J(J+1)$$

The first-order perturbation correction to the energy is given by the electronic Zeeman term as follows:

$$\begin{aligned} E_1(J, M) &= \langle JM | \hat{H}^Z | JM \rangle = \mu_\mathrm{B} \boldsymbol{B} \cdot \langle JM | \gamma \boldsymbol{L} + g_\mathrm{e} \boldsymbol{S} | JM \rangle [\hbar^{-1}] \\ &= \mu_\mathrm{B} \boldsymbol{B} \cdot \langle JM | g_\mathrm{e} \boldsymbol{J} + (\gamma - g_\mathrm{e}) \boldsymbol{L} | JM \rangle [\hbar^{-1}] \\ &\approx \mu_\mathrm{B} \boldsymbol{B} \cdot \langle JM | 2\boldsymbol{J} + (\gamma - 2) \boldsymbol{L} | JM \rangle [\hbar^{-1}] \end{aligned}$$

Table 23
Coefficients of the susceptibility formula for octahedral d^n complexes

d^n	Term	γ	v_ξ	J	g_J^γ	A_J	B_J
d^1	${}^2T_2(t_1^2)$	-1	$-\xi_d$	1/2	-2	3	-8
				3/2	0	0	4
d^2	${}^3T_1(t_2^2)$	-1	$-(1/2)\xi_d$	0	5	0	-72
				1	1/2	1/2	9
				2	1/2	3/2	9
d^2	${}^3T_1({}^3F)$[a]	$-3/2$	$-(3/4)\xi_d$	0	11/2	0	$-196/3$
				1	1/4	1/8	49/6
				2	1/4	3/8	49/6
d^4	${}^3T_1(t_2^4)$	-1	$(1/2)\xi_d$	0	5	0	72
				1	1/2	1/2	-9
				2	1/2	3/2	-9
d^5	${}^2T_2(t_2^5)$	-1	ξ_d	1/2	-2	3	8
				3/2	0	0	-4
d^6	${}^5T_2(t_2^4\,e^2)$	-1	$(1/4)\xi_d$	1	7/2	49/2	54
				2	3/2	27/2	-10
				3	1	12	-16
d^7	${}^4T_1(t_2^5\,e^2)$	-1	$(1/3)\xi_d$	1/2	4	12	60
				3/2	6/5	27/5	$-264/25$
				5/2	4/5	28/5	$-324/25$
d^7	${}^4T_1({}^2F)$[a]	$-3/2$	$(1/2)\xi_d$	1/2	13/3	169/12	490/9
				3/2	16/15	64/15	$-2156/225$
				5/2	3/5	63/20	$-294/25$

[a] Weak-field reference; otherwise, strong-field reference.

and for the z-component of the magnetic field it is

$$E_1(J,M)=\mu_B B_z\langle JM|2\hat{J}_z+(\gamma-2)\hat{L}_z|JM\rangle[\hbar^{-1}]$$

$$=\mu_B B_z\left[2+(\gamma-2)\frac{J(J+1)+L(L+1)-S(S+1)}{2J(J+1)}\right]M$$

Then the comparison with

$$E_1(J,\,M)=\mu_B B_z g_J^\gamma\langle JM|\hat{J}_z|JM\rangle[\hbar^{-1}]=\mu_B B_z g_J^\gamma M$$

yields the Landé factor modified to the form

$$g_J^\gamma=\gamma+(2-\gamma)\frac{J(J+1)-L(L+1)+S(S+1)}{2J(J+1)}$$

Consequently, the first-order van Vleck coefficients become

$$E_{J,M}^{(1)}=\mu_B g_J^\gamma M_J$$

In the derivation of the second-order energy the perturbation operator is

$$\langle J'M|\hat{H}'|JM\rangle=\langle J'M|\hat{H}_z^Z|JM\rangle=2\mu_B B_z\langle J'M|\hat{J}_z|JM\rangle[\hbar^{-1}]$$

$$+(\gamma-2)\mu_B B_z\langle J'M|\hat{L}_z|JM\rangle[\hbar^{-1}]$$

where the first term vanishes. This yields the result

$$E_2(J, M) = -(\gamma-2)^2(\mu_B B_z)^2 \sum_{J'=J\pm 1} \frac{\langle J'M|\hat{L}_z|JM\rangle^2}{E_0(J')-E_0(J)} \, [\hbar^{-2}]$$

and thus the second-order van Vleck coefficients

$$E^{(2)}_{J,M} = -(\gamma-2)^2 \mu_B^2 \left\{ \frac{[f(SL, J+1)]^2[(J+1)^2-M^2]}{v_\xi(J+1)} - \frac{[f(SLJ)]^2(J^2-M^2)}{v_\xi J} \right\}$$

are summed up as follows

$$\sum_{M=-J}^{+J} E^{(2)}_{J,M} = -(\gamma-2)^2 \mu_B^2 \sum_{M=-J}^{+J} \left\{ \frac{[f(SL, J+1)]^2[(J+1)^2-M^2]}{v_\xi(J+1)} - \frac{[f(SLJ)]^2(J^2-M^2)}{v_\xi J} \right\}$$

yielding

$$\sum_{M=-J}^{+J} E^{(2)}_{J,M} = -\frac{(\gamma-2)^2\mu_B^2}{3v_\xi}(2J+1)\{[f(SL, J+1)]^2(2J+3) - [f(SLJ)]^2(2J-1)\}$$

Finally using

$$(2-\gamma)^2\{[f(SL, J+1)]^2(2J+3)-[f(SLJ)]^2(2J-1)\} = (2-\gamma)^2 \frac{[(S+L+1)(S-L)]^2-[J(J+1)]^2}{[2(J+1)]^2} = (g_J^\gamma-\gamma)(g_J^\gamma-2)$$

we arrive at the simple expression

$$\sum_{M=-J}^{+J} E^{(2)}_{J,M} = -\frac{\mu_B^2}{3v_\xi}(2J+1)(g_J^\gamma-\gamma)(g_J^\gamma-2)$$

yielding the particular susceptibility function for a given multiplet

$$\chi_J = \frac{N_A\mu_0\mu_B^2}{3}\left[\frac{(g_J^\gamma)^2}{kT}J(J+1) + \frac{2}{v_\xi}(g_J^\gamma-\gamma)(g_J^\gamma-2)\right] = \frac{N_A\mu_0\mu_B^2}{3kT}\left[A_J + \frac{B_J}{x}\right]$$

with the coefficients

$$A_J = (g_J^\gamma)^2 J(J+1)$$

$$B_J = \frac{2}{(v_\xi/\xi_d)}(g_J^\gamma-\gamma)(g_J^\gamma-2)$$

and

$$x = \xi_d / kT$$

Then the molar magnetic susceptibility is

$$\chi_{\mathrm{mol}} = \frac{\sum_{J=|L-S|}^{L+S} (2J+1)\chi_J \exp[-v_\xi J(J+1)/2kT]}{\sum_{J=|L-S|}^{L+S} (2J+1)\exp[-v_\xi J(J+1)/2kT]}$$

In the above formulae, we have to use $L=1$ as a consequence of the T–P isomorphism. Hence

$$g_0^\gamma = 4 - \gamma$$

$$g_J^\gamma = \gamma + (2-\gamma)\frac{J(J+1) - 2 + S(S+1)}{2J(J+1)}$$

The corresponding coefficients for the susceptibility formula are collected in Table 23 and the product functions $\chi_{\mathrm{mol}}T$ versus x^{-1} are displayed in Fig. 23.

11.9. Inclusion of term interaction

According to Figgis [30] one can consider a limited configuration interaction starting from the weak-field kets

$$|\Psi'({}^3\mathrm{T}_1))\rangle = C_0|\Psi({}^3\mathrm{T}_1;\, {}^3\mathrm{F}))\rangle + C_1|\Psi({}^3\mathrm{T}_1;\, {}^3\mathrm{P}))\rangle$$
$$= \frac{1}{\sqrt{1+C^2}}[|\Psi({}^3\mathrm{T}_1;\, {}^3\mathrm{F}))\rangle + C|\Psi({}^3\mathrm{T}_1;\, {}^3\mathrm{P}))\rangle]$$

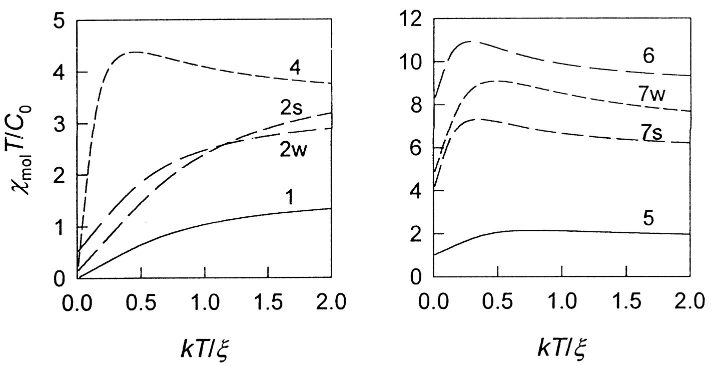


Fig. 23. The product function $\chi_{\mathrm{mol}}T$ versus x^{-1} for T_1 and T_2 terms of octahedral d^n complexes: s, strong-field reference; w, weak-field reference.

The corresponding secular equation is

$$\det\begin{pmatrix} \langle \Psi(^3\mathrm{T}_1;\,^3\mathrm{F})|\hat{V}^{\mathrm{cf}}|\Psi(^3\mathrm{T}_1;\,^3\mathrm{F})\rangle-\epsilon & \langle \Psi(^3\mathrm{T}_1;\,^3\mathrm{F}|\hat{V}^{\mathrm{cf}}|\Psi(^3\mathrm{T}_1;\,^3\mathrm{P})\rangle \\ \langle \Psi(^3\mathrm{T}_1;\,^3\mathrm{P})|\hat{V}^{\mathrm{cf}}|\Psi(^3\mathrm{T}_1;\,^3\mathrm{F})\rangle & \langle \Psi(^3\mathrm{T}_1;\,^3\mathrm{P})|\hat{V}^{\mathrm{cf}}|\Psi(^3\mathrm{T}_1;\,^3\mathrm{P})\rangle-\epsilon \end{pmatrix}=0$$

which after evaluation of matrix elements relaxes to

$$\det\begin{pmatrix} -6Dq-\epsilon & 4Dq \\ 4Dq & 15B-\epsilon \end{pmatrix}=0$$

where $10Dq$ is the crystal-field splitting and B is the Racah parameter. Then the secular equation

$$\epsilon^2+(6Dq-15B)\epsilon-16(Dq)^2-90(Dq)B=0$$

has two eigenvalues ϵ. The lower one is used to determine the CI-expansion coefficient as

$$C=\frac{6Dq+\epsilon}{4Dq}=\frac{3}{2}-\frac{15}{2}\left(\frac{B}{Dq}\right)-\sqrt{25+45\left(\frac{B}{Dq}\right)+\frac{225}{4}\left(\frac{B}{Dq}\right)^2}$$

In the weak-field limit with $\epsilon=-6Dq$ one gets $C=0$. On the contrary, the strong-field limit with $\epsilon=-8Dq$ yields $C=1/2$ (Fig. 24).

In the case of the intermediate field Figgis et al. [30] derived the magnetic

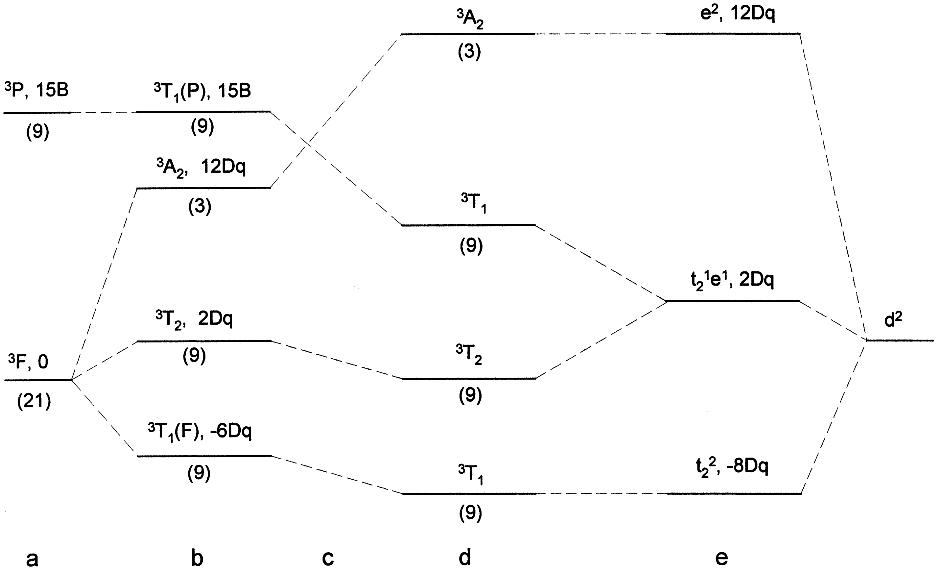


Fig. 24. Correlation diagram for the triplet terms of d^2 configuration in the octahedral crystal field: (a) free ion terms ($\hat{H}_0$ includes $\hat{V}^{\mathrm{ee}}$); (b) weak field limit ($\hat{H}'=\hat{V}^{\mathrm{cf}}$); (c) intermediate field ($\hat{H}'=\hat{V}^{\mathrm{ee}}+\hat{V}^{\mathrm{cf}}$); (d) strong field limit ($\hat{H}'=\hat{V}^{\mathrm{ee}}$); (e) strong field configurations ($\hat{H}_0$ includes $\hat{V}^{\mathrm{cf}}$).

susceptibility formula in the form (Table 24)

$$\chi_{\mathrm{mol}} = N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2 \frac{\sum_{J=|L-S|}^{L+S} \left[\frac{(g_J^A)^2 J(J+1)(2J+1)}{3kT} - 2F_{J,J+1} + 2F_{J-1,J} \right] \exp(-E_J^{(0)}/kT)}{\sum_{J=|L-S|}^{L+S} (2J+1)\exp(-E_J^{(0)}/kT)}$$

with

$$g_J^A = 1 - \frac{A}{2} + (2+A)\frac{S(S+1)-2}{2J(J+1)}$$

and the second-order factors for the adjacent terms

$$F_{J,J+1} = \frac{(2+A)^2}{A} F_{J,J+1}^{[\text{free ion } P \text{ term}]}$$

$$= \frac{(2+A)^2}{A} \frac{(J+L+S+2)(-J+L+S)(J-L+S+1)(J+L-S+1)}{12(J+1)^2\lambda}$$

with $L=1$. This yields the final formula in the form

$$\chi_{\mathrm{mol}} = \frac{N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2}{3kT}\mu_{\mathrm{eff}}^2 = \frac{N_{\mathrm{A}}\mu_0\mu_{\mathrm{B}}^2}{3kT}\frac{N}{D} = \frac{C_0}{3T}\frac{N}{D}$$

where the numerators and denominators are:

(a) for the $^3\mathrm{T}_1$ terms

$$N = 3\left\{ \frac{5(A-2)^2}{2} + \frac{5(A+2)^2}{6Ax} + \left[\frac{(A-2)^2}{2} + \frac{(A+2)^2}{2Ax} \right] \times \exp(-2Ax) - \frac{4(A+2)^2}{3Ax}\exp(-3Ax) \right\}$$

$$D = 5 + 3\exp(-2Ax) + \exp(-3A)$$

Table 24
Terms of the susceptibility formula for intermediate crystal field

d^n	Term	J	g_J^A	$E_J^{(0)}$	$F_{J,J+1}$
d^2	$^3\mathrm{T}_{1g}$	0	0	$3A\lambda$	$(2/3)(2+A)^2/A\lambda$
		1	$1-(1/2)A$	$2A\lambda$	$(5/12)(2+A)^2/A\lambda$
		2	$1-(1/2)A$	0	
d^3	$^4\mathrm{T}_{1g}$	1/2	$(10+2A)/3$	$4A\lambda$	$(20/27)(2+A)^2/A\lambda$
		3/2	$(22-4A)/15$	$(5/2)A\lambda$	$(12/25)(2+A)^2/A\lambda$
		5/2	$(6-2A)/5$	0	

(b) for the $^4T_1$ terms:

$$N=3\left\{\frac{7(3-A)^2}{5}+\frac{12(A+2)^2}{25Ax}+\left[\frac{2(11-2A)^2}{45}+\frac{176(A+2)^2}{675Ax}\right]\right.$$
$$\left.\times\exp[-(5/2)Ax]+\left[\frac{(A+5)^2}{9}-\frac{20(A+2)^2}{27Ax}\right]\exp(-4Ax)\right\}$$

$$D=3+2\exp[-(5/2)Ax]+\exp(-4Ax)$$

with the parameters

$$x=\lambda/kT$$

$$A=\langle\Psi'(^3T_1)|\hat{L}_z|\Psi'(^3T_1)\rangle=\frac{(3/2)-C^2}{1+C^2}$$

and

$$C=\frac{6Dq+\epsilon}{4Dq}$$

where ϵ being a lower root of the equation

$$\epsilon^2+(6Dq-15B)\epsilon-16(Dq)^2-90(Dq)B=0$$

Then

$$1<A<3/2$$

holds true between the strong-field and weak-field limits.

11.10. Symmetry lowering

It is unlikely that the ground states of real metal complexes are degenerate (T or E terms) for three reasons.

(1) The actual crystal packing may require lower than cubic symmetry.

(2) The relativistic double group approach allows only the doubly degenerate levels and in the case of the cubic symmetry the maximum degeneracy of Γ_8 is four; consequently, no orbital triplets are allowed, only spinorbital quadruplets.

(3) The Jahn–Teller effect excludes the ground state being orbitally degenerate: there exists an internal disposition of the complex for a geometrical distortion that removes the orbital degeneracy. Among the cubic systems the distortion applies either along the $e_{(g)}$ mode, which results in an axial (or rhombic) symmetry, or along the $t_{2(g)}$ mode which leads to a trigonal symmetry.

Consequently, the complex has a lower than cubic symmetry, which is equivalent to the addition of a low-symmetry crystal field potential to the spin Hamiltonian.

The most common axial distortion can be described by the operator equivalent

$$\hat{V}^{\rm dis}=\Delta\{\hat{L}_z^2[\hbar^{-2}]-L(L+1)/3\}$$

The basis set consists of all combinations of the orbital kets $|L, M_L\rangle$ and the spin kets $|S, M_S\rangle$ yielding the number $N=(2L+1)(2S+1)$. The perturbation operator includes the crystal field distortion $\hat{V}^{\rm dis}$ and the SO coupling $\hat{H}^{\rm so}$ terms

$$\hat{H}'=\hat{V}^{\rm dis}+\hat{H}^{\rm so}$$

Then the interaction matrix of the perturbation operator

$$H'_{ij}=\langle M_L M_S|\hat{H}'|M_L M_S\rangle$$

for a given value of L and S has the dimension of $N\times N$.

The matrix associated with $\hat{V}^{\rm dis}$ is diagonal in the $|M_L M_S\rangle$ basis set, viz.

$$\langle M_L M_S|\hat{V}^{\rm dis}|M_L M_S\rangle=\Delta(M_L^2-2/3)$$

where we applied $L=1$.

The operator of the SO interaction can be manipulated using the escalator operators as follows

$$\boldsymbol{L}\cdot\boldsymbol{S}=\hat{L}_x\hat{S}_x+\hat{L}_y\hat{S}_y+\hat{L}_z\hat{S}_z=(1/2)(\hat{L}_+\hat{S}_-+\hat{L}_-\hat{S}_+)+\hat{L}_z\hat{S}_z$$

Then the non-zero matrix elements are

$$\langle M_L M_S|\lambda\boldsymbol{L}\cdot\boldsymbol{S}|M_L M_S\rangle[\hbar^{-2}]=\lambda M_L M_S$$

$$\langle M_L M_S|\lambda\boldsymbol{L}\cdot\boldsymbol{S}|M_L+1, M_S-1\rangle[\hbar^{-2}]=\langle M_L+1, M_S-1|\lambda\boldsymbol{L}\cdot\boldsymbol{S}|M_L M_S\rangle[\hbar^{-2}]$$
$$=(\lambda/2)[(L-M_L)(L+M_L+1)]^{1/2}[(S+M_S)(S-M_S+1)]^{1/2}$$

and

$$\langle M_L M_S|\lambda\boldsymbol{L}\cdot\boldsymbol{S}|M_L-1, M_S+1\rangle[\hbar^{-2}]=\langle M_L-1, M_S+1|\lambda\boldsymbol{L}\cdot\boldsymbol{S}|M_L M_S\rangle[\hbar^{-2}]$$
$$=(\lambda/2)[(L+M_L)(L-M_L+1)]^{1/2}[(S-M_S)(S+M_S+1)]^{1/2}$$

Owing to the T–P isomorphism, we have to substitute $L=1$ when dealing with T-term kets.

There are two possible routes in determining the magnetic susceptibility.

(1) The interaction matrix

$$H'_{ij}=\langle\Psi_i|\hat{V}^{\rm dis}+\hat{H}^{\rm so}|\Psi_j\rangle$$

is diagonalized yielding the set of the zero-field eigenvalues

$$\epsilon_i=\langle\Psi'_i|\hat{V}^{\rm dis}+\hat{H}^{\rm so}|\Psi'_j\rangle\delta_{ij}$$

and eigenvectors $|\Psi'_i\rangle$. Using these eigenvectors as a new basis set (of coupled angular momenta kets) the matrix elements of the Zeeman operator $\hat{H}^Z$ are evaluated, for B parallel and perpendicular to the z (distortion) axis

$$H''_{ij} = \langle \Psi'_i | \hat{V}^{\rm dis} + \hat{H}^{\rm so} | \Psi'_j \rangle = \epsilon_i \delta_{ij} + \langle \Psi'_i | \hat{H}^Z | \Psi'_j \rangle$$

(Notice that in the transformed basis set the z-component of the Zeeman operator is no longer diagonal: there are off-diagonal matrix elements of the type $\langle \Psi'_i | \hat{H}^Z_z | \Psi'_j \rangle$.) The full spin Hamiltonian matrix H''_{ij} is then diagonalized. The eigenvalues $\epsilon_i(B)$ obtained are expanded in powers of B yielding the van Vleck coefficients.

(2) Alternatively, the matrix elements of the Zeeman operator are included into the spin Hamiltonian on the original basis set (of uncoupled angular momenta kets)

$$H'_{ij} = \langle M_L M_S | \hat{V}^{\rm dis} + \hat{H}^{\rm so} + \hat{H}^Z | M_L M_S \rangle$$

and this matrix is diagonalized.

Normally a numerical treatment on computers is required.

In the case of the ${}^2{\rm T}_{2(\rm g)}$ term the orbital kets appropriate for $\hat{V}^{\rm dis}(D_{4\rm h})$ can be defined as follows:

$$|\Psi({}^2{\rm T}_2)\rangle = \begin{cases} |a\rangle = {\rm d}_{+1} \\ |b\rangle = (1/\sqrt{2})({\rm d}_{+2} - {\rm d}_{-2}) = |0\rangle \\ |c\rangle = {\rm d}_{-1} = |-a\rangle \end{cases}$$

and those appropriate for $\hat{V}^{\rm dis}(D_{3\rm d})$ can be

$$|\Psi({}^2{\rm T}_2)\rangle = \begin{cases} |a\rangle = \sqrt{2/3}{\rm d}_{-2} + \sqrt{1/3}{\rm d}_{+1} \\ |b\rangle = {\rm d}_0 \\ |c\rangle = \sqrt{2/3}{\rm d}_{+2} + \sqrt{1/3}{\rm d}_{-1} \end{cases}$$

The perturbation Hamiltonian, in the form that properly accounts for the T–P isomorphism, is

$$\hat{H}' = \hat{V}^{\rm dis} + v_\xi \boldsymbol{L} \cdot \boldsymbol{S} [\hbar^{-2}]$$

with the equivalence coefficient $v_\xi = -1\xi_{\rm d} = -\lambda$. We used v_ξ for the equivalence coefficient not to be confused with an axial splitting parameter v introduced as follows

$$v = \Delta / \lambda$$

The matrix elements in the basis set of $^2T_{2(g)}$ kets are

$$H'_{ij}=\lambda\begin{pmatrix} \frac{v}{3}+\frac{1}{2} & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{v}{3}-\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{2v}{3} & 0 & 0 & -\frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & 0 & 0 & -\frac{2v}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{v}{3}-\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{\sqrt{2}} & 0 & 0 & \frac{v}{3}+\frac{1}{2} \end{pmatrix}$$

The corresponding 6×6 secular equation

$$\det\{H'_{ij}-\epsilon\delta_{ij}\}=0$$

can be factorized into a set of secular equations of the lower dimensions, namely

$$\det\begin{Bmatrix} \lambda\left(\frac{v}{3}+\frac{1}{2}\right)-\epsilon & \lambda\left(-\frac{1}{\sqrt{2}}\right) \\ \lambda\left(-\frac{1}{\sqrt{2}}\right) & \lambda\left(-\frac{2v}{3}\right)-\epsilon \end{Bmatrix}=0$$

$$\det\begin{Bmatrix} \lambda\left(-\frac{2v}{3}\right)-\epsilon & \lambda\left(-\frac{1}{\sqrt{2}}\right) \\ \lambda\left(-\frac{1}{\sqrt{2}}\right) & \lambda\left(\frac{v}{3}+\frac{1}{2}\right)-\epsilon \end{Bmatrix}=0$$

$$\det\left\{\lambda\left(\frac{v}{3}-\frac{1}{2}\right)-\epsilon\right\}=0,\quad \text{[twice]}$$

The resulting zero-field eigenvalues are listed in Table 25 and plotted in Fig. 25.

In the case of the $^5T_{2(g)}$ term the orbital kets are the same as for the $^2T_{2(g)}$ term. A higher spin multiplicity makes the dimension of the interaction matrix enlarged

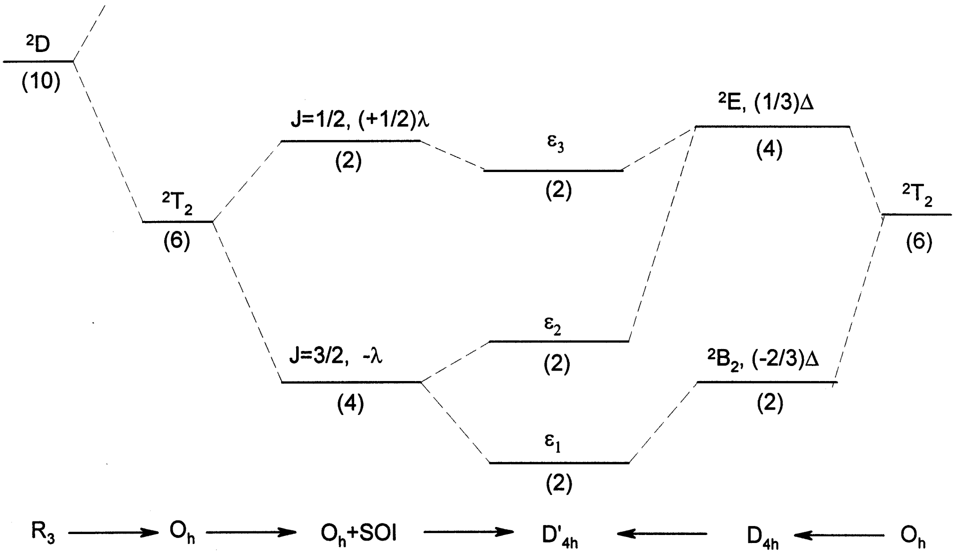


Fig. 25. Splitting pattern for the $^2T_{2(g)}$ term on reduction of symmetry.

to $N=3\cdot 5=15$. The secular equation can be split into a set of secular equations of lower dimension (Table 25). The zero-field energy levels are shown in Fig. 26.

In the case of the $^3T_{1(g)}$ term the non-interacting term functions are proper combinations of the determinantal functions $|L, M_L\rangle$, hence

$$|\Psi(^3T_1, {^3F})\rangle=\begin{cases} |a\rangle=\sqrt{15/24}|3, +3\rangle-\sqrt{9/24}|3, -1\rangle \\ |b\rangle=|3, 0\rangle \\ |c\rangle=\sqrt{15/24}|3, -3\rangle-\sqrt{9/24}|3, +1\rangle \end{cases}$$

and

$$|\Psi(^3T_1, {^3P})\rangle=\begin{cases} |1, +1\rangle \\ |1, 0\rangle \\ |1, -1\rangle \end{cases}$$

The perturbed kets accounting for the limited configuration interaction become

$$|\Psi'(^3T_1)\rangle=\begin{cases} |+A\rangle=(1+C^2)^{-1/2}(|a\rangle+C|1, +1\rangle) \\ |0\rangle=(1+C^2)^{-1/2}(|b\rangle+C|1, 0\rangle) \\ |-A\rangle=(1+C^2)^{-1/2}(|c\rangle+C|1, -1\rangle) \end{cases}$$

Table 25
Relationships for T-type terms under symmetry lowering

^{m}T	Kets $\lvert M_L\rangle\lvert M_S\rangle$	Factorized interaction matrix	Zero-field eigenvalues[a]
^{2}T$_2$	$\lvert\pm a\rangle\lvert\mp 1/2\rangle$ $\lvert 0\rangle\lvert\pm 1/2\rangle$	$\lambda\begin{pmatrix} v/3+1/2 & -1/\sqrt{2} \\ -1/\sqrt{2} & -2v/3 \end{pmatrix}$	$\epsilon_{1,3}=\lambda[-v/3+1/2\pm(v^2+v+\frac{9}{4})^{1/2}]/2$
	$\lvert\pm a\rangle\lvert\pm 1/2\rangle$	$\lambda(v/3-1/2)$	$\epsilon_2=\lambda(v/3-1/2)$
^{5}T$_2$	$\lvert\pm a\rangle\lvert\pm 2\rangle$ $\lvert 0\rangle\lvert\pm 1\rangle$ $\lvert\mp a\rangle\lvert 0\rangle$	$\lambda\begin{pmatrix} v/3+2 & \pm\sqrt{2} & 0 \\ \pm\sqrt{2} & -2v/3 & \mp\sqrt{3} \\ 0 & \mp\sqrt{3} & v/3 \end{pmatrix}$	$\epsilon_{3,7,9}=\lambda[v/3-\text{roots}_x\{x^3+x^2(2-v)+x(-5-2v)-6=0\}]$
	$\lvert +a\rangle\lvert +1\rangle$ $\lvert 0\rangle\lvert 0\rangle$ $\lvert -a\rangle\lvert -1\rangle$	$\lambda\begin{pmatrix} v/3+1 & +\sqrt{3} & 0 \\ +\sqrt{3} & -2v/3 & -\sqrt{3} \\ 0 & -\sqrt{3} & v/3+1 \end{pmatrix}$	$\epsilon_{8,2}=\lambda[-v/3+1\pm(v^2+2v+25)^{1/2}]/2$ $\epsilon_6=\lambda(v/3+1)$
	$\lvert\pm a\rangle\lvert\mp 1\rangle$ $\lvert 0\rangle\lvert\mp 2\rangle$	$\lambda\begin{pmatrix} v/3-1 & \pm\sqrt{2} \\ \pm\sqrt{2} & -2v/3 \end{pmatrix}$	$\epsilon_{5,1}=\lambda[-v/3-1\pm(v^2-2v+9)^{1/2}]/2$
	$\lvert\pm a\rangle\lvert\mp 2\rangle$	$\lambda(-v/3-2)$	$\epsilon_1=\lambda(-v/3-2)$
^{3}T$_1$	$\lvert +A\rangle\lvert 1\rangle$ $\lvert 0\rangle\lvert 0\rangle$ $\lvert -A\rangle\lvert -1\rangle$	$\lambda\begin{pmatrix} v/3+A & -A & 0 \\ -A & -2v/3 & -A \\ 0 & -A & v/3+A \end{pmatrix}$	$\epsilon_{6,2}=\lambda[-v/3+A\pm(v^2+2Av+9A^2)^{1/2}]/2$ $\epsilon_5=\lambda(v/3+A)$
	$\lvert\pm A\rangle\lvert 0\rangle$ $\lvert 0\rangle\lvert\mp 1\rangle$	$\lambda\begin{pmatrix} v/3 & -A \\ -A & -2v/3 \end{pmatrix}$	$\epsilon_{4,1}=\lambda[-v/3\pm(v^2+4A^2)^{1/2}]/2$
	$\lvert\pm A\rangle\lvert\mp 1\rangle$	$\lambda(v/3-A)$	$\epsilon_3=\lambda(v/3-A)$
^{4}T$_1$	$\lvert\pm A\rangle\lvert\mp 3/2\rangle$ $\lvert 0\rangle\lvert\pm 1/2\rangle$ $\lvert\mp A\rangle\lvert\mp 1/2\rangle$	$\lambda\begin{pmatrix} v/3+3A/2 & \sqrt{3/2}A & 0 \\ \sqrt{3/2}A & -2v/3 & \sqrt{2}A \\ 0 & \sqrt{2}A & v/3+A/2 \end{pmatrix}$	$\epsilon_{2,4,6}=\lambda[v/3+3A/2-\text{roots}_x\{x^3+x^2(-v-5A/2)+x(Av-2A^2)+3A^3/2=0\}]$
	$\lvert\pm A\rangle\lvert\mp 1/2\rangle$ $\lvert 0\rangle\lvert\mp 3/2\rangle$	$\lambda\begin{pmatrix} v/3-A/2 & \sqrt{3/2}A \\ \sqrt{3/2}A & -2v/3 \end{pmatrix}$	$\epsilon_{5,1}=\lambda[-v/3-A/2\pm(v^2-vA+\frac{25}{4}A^2)^{1/2}]/2$
	$\lvert\pm A\rangle\lvert\mp 3/2\rangle$	$\lambda(v/3-3A/2)$	$\epsilon_3=\lambda(v/3-3A/2)$

[a] Roots$_x$ $\{x^3+bx^2+cx+d=0\}$ are the three real roots of the cubic equation.

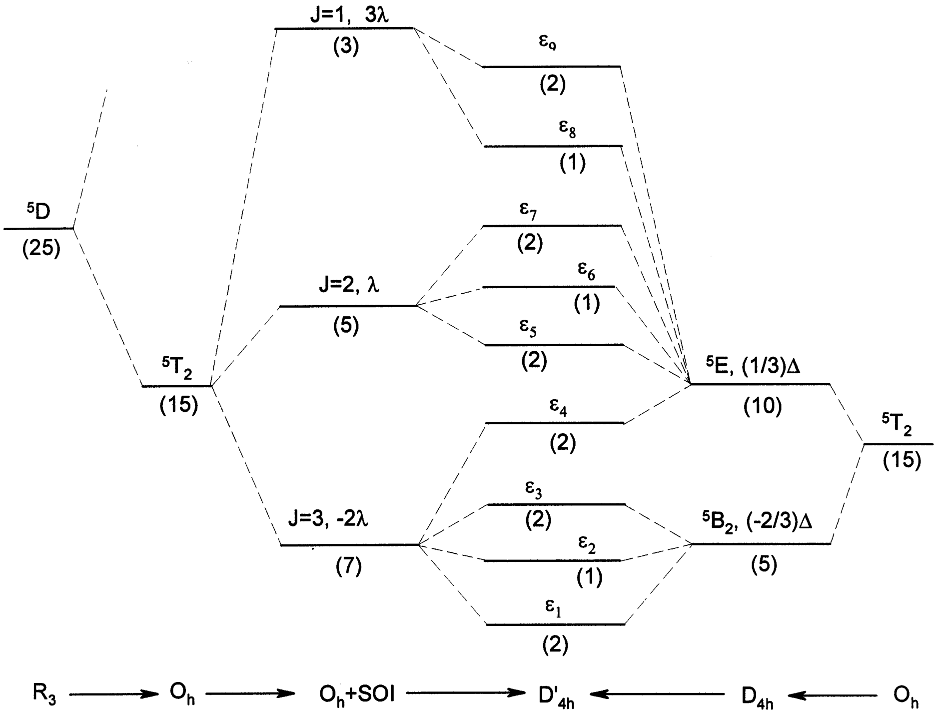


Fig. 26. Splitting pattern for the $^5T_{2(g)}$ term on reduction of symmetry.

These functions produce an interaction matrix of the perturbation operator

$$\hat{H}'\hat{V}^{\mathrm{dis}} + A\hat{H}^{\mathrm{so}}$$

whose dimension is 9 × 9; the mixing parameter is

$$A = \frac{(3/2) - C^2}{1 + C^2}$$

In evaluating the matrix elements the orbital kets obey the relationships

$$\langle \pm A|\hat{L}_z|\pm A\rangle = \pm A[\hbar]$$

$$\langle \pm A|\hat{L}_x|0\rangle = -(1/\sqrt{2})A[\hbar]$$

and

$$\langle \pm A|\hat{L}_y|0\rangle = -\mathrm{i}(1/\sqrt{2})A[\hbar]$$

Fortunately the secular equation can be factorized into a set of secular equations of lower dimensions having analytical solutions (Table 25). The zero-field energy levels are displayed in Fig. 27.

An analogous procedure can be applied for the $^4T_{1(g)}$ term on reduction of

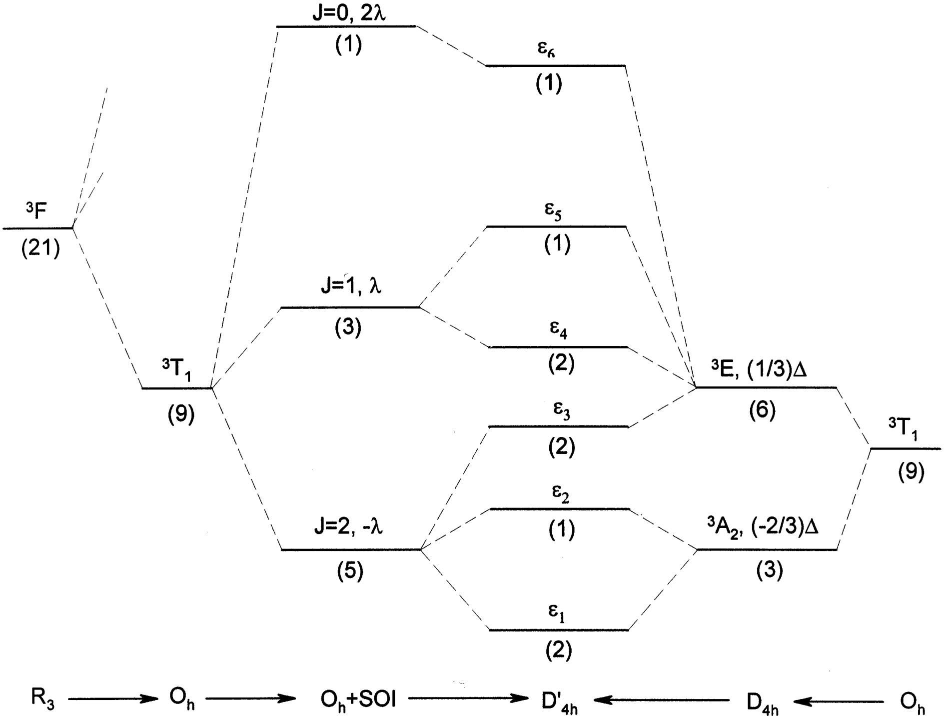


Fig. 27. Splitting pattern for the ${}^3T_{1(g)}$ term on reduction of symmetry.

symmetry. The orbital parts of the wave functions are identical to those for the ${}^3T_{1(g)}$ term and only the spin functions alter. The secular equation of order 12×12 is factorized into a set of lower-dimension problems again having analytical solutions (Table 25). The zero-field energy levels are shown in Fig. 28.

The addition of the Zeeman term makes the problem more complex, since no factorization of the secular equation may appear. However, the problem is tractable numerically, using computers. The complete spin Hamiltonian is of the form

$$\hat{H}^S = \Delta\{\hat{L}_z^2[\hbar^{-2}] - L(L+1)/3\} + \kappa v_\xi^{[\text{strong field}]} A\boldsymbol{L}\cdot\boldsymbol{S}[\hbar^{-2}]$$
$$+ \mu_B(\kappa\gamma^{[\text{strong field}]} A\boldsymbol{L} + g_e\boldsymbol{S})\cdot\boldsymbol{B}[\hbar^{-1}]$$

and parameters entering the theoretical relationships cover the axial splitting parameter $v = \Delta/\lambda$, the orbital reduction factor κ and eventually the CI mixing parameter A, the last one originating in the CI form of the orbital kets. The effective magnetic moment becomes an implicit function of the reduced variable $x^{-1} = kT/\lambda$, hence

$$\mu_{\text{eff}}/\mu_B = f(v, \kappa, A; x^{-1})$$

for fixed equivalence coefficients γ and v_ξ associated with the particular term. An extensive tabulation of these functions was provided by Figgis and coworkers [31–34]. These are given in Figs. 29 and 30.

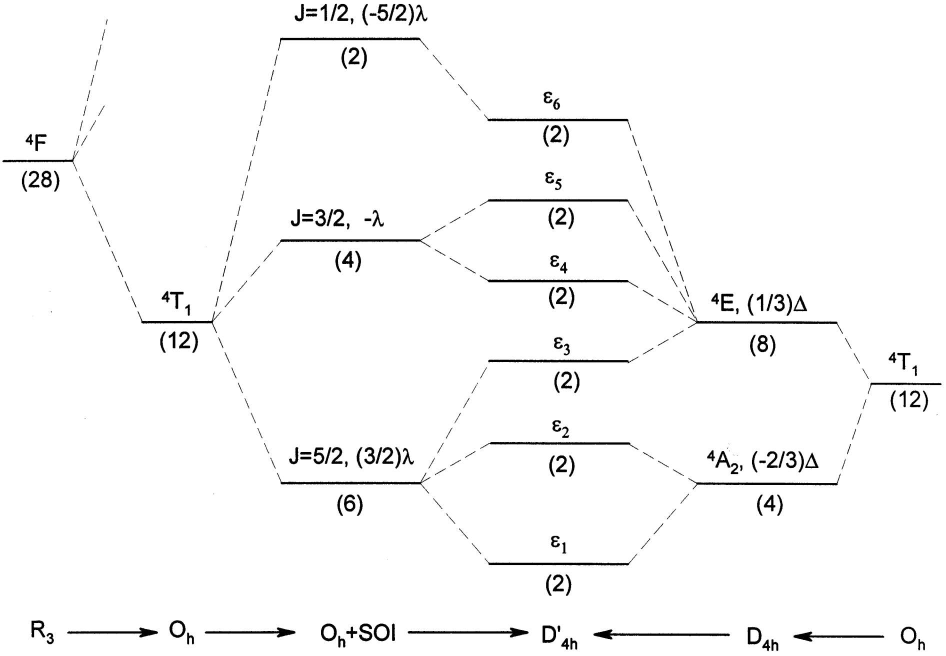


Fig. 28. Splitting pattern for the $^4T_{1(g)}$ term on reduction of symmetry.

One trivial note should be added: in dealing with the reduced parameter $x^{-1}=kT/\lambda$ the value of the SO splitting parameter should be given in Kelvin units: λ/k has dimension of [K]; the usual tabulation of the SO splitting parameter corresponds to the wave number λ/hc and has dimension of [cm^{-1}]. Then the conversion is

$$\lambda \text{ (in the meaning of } \lambda/hc\text{) in [cm}^{-1}]$$
$$=1/1.438\,769\,[\mathrm{K\,cm^{-1}}]\cdot(\lambda/k) \text{ in [K]}$$

However, the reduced parameter alters the sign when passing from the less than half-filled shells to more than half-filled ones (since λ alters the sign); then also the axial splitting parameter $v=\Delta/\lambda$ alters the sign.

A more detailed inspection is given by Fig. 31 where the case of an octahedral d^7 complex, e.g. Co^{2+}, with $^4T_{1g}$ ground term is analysed. The set of parameters entering the spin Hamiltonian was: $v_\xi^{[\text{strong field}]}=(1/3)\xi_d=540/3\ \mathrm{cm^{-1}}=180\ \mathrm{cm^{-1}}$; $\kappa=\underline{1.0}$, 0.8 and 0.6; $A=\underline{1.0}$, 1.25 and 1.5; the default parameters for the other combinations are underlined.

On the basis of these figures one can conclude:

(1) the orbital reduction factor leads to lowering of the effective magnetic moment;
(2) the CI mixing parameter A increases the effective magnetic moment, when passing from the strong-field limit ($A=1$) to the weak-field one ($A=1.5$);

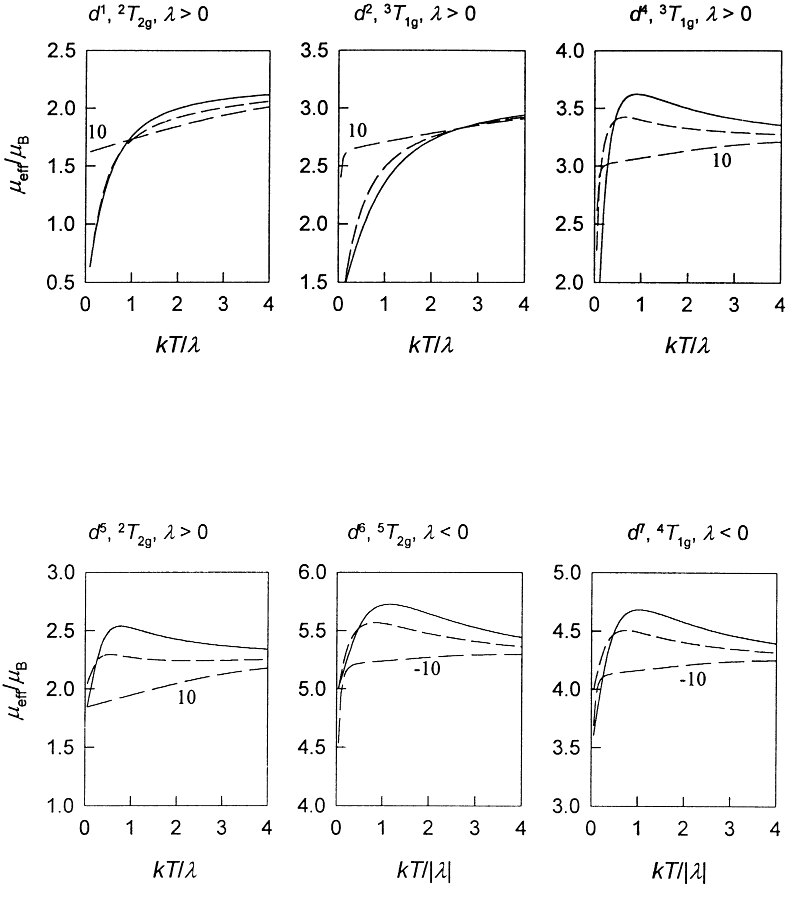


Fig. 29. Effective magnetic moment versus the reduced temperature for octahedral complexes: full line, $v=0$; dashed line, $v=\pm 10$.

(3) the axial splitting parameter reduces the effective magnetic moment, irrespective of its sign; the reduction, however, is different for positive and/or negative v;

(4) there is a pronounced magnetic anisotropy at relatively high temperatures.

An interesting point is that the spin Hamiltonian appropriate for the mononuclear complexes with the first-order angular momentum has a form analogous to the spin Hamiltonian that describes an isotropic binuclear exchange

$$\hat{H}^S = -J\boldsymbol{S}_1 \cdot \boldsymbol{S}_2[\hbar^{-2}] + \mu_B(g_1\boldsymbol{S}_1 + g_2\boldsymbol{S}_2) \cdot \boldsymbol{B}[\hbar^{-1}]$$

with the correspondences

$$\boldsymbol{L} \leftrightarrow \boldsymbol{S}_1$$

$$\boldsymbol{S} \leftrightarrow \boldsymbol{S}_2$$

$$-J \leftrightarrow v_{\xi}\kappa A$$

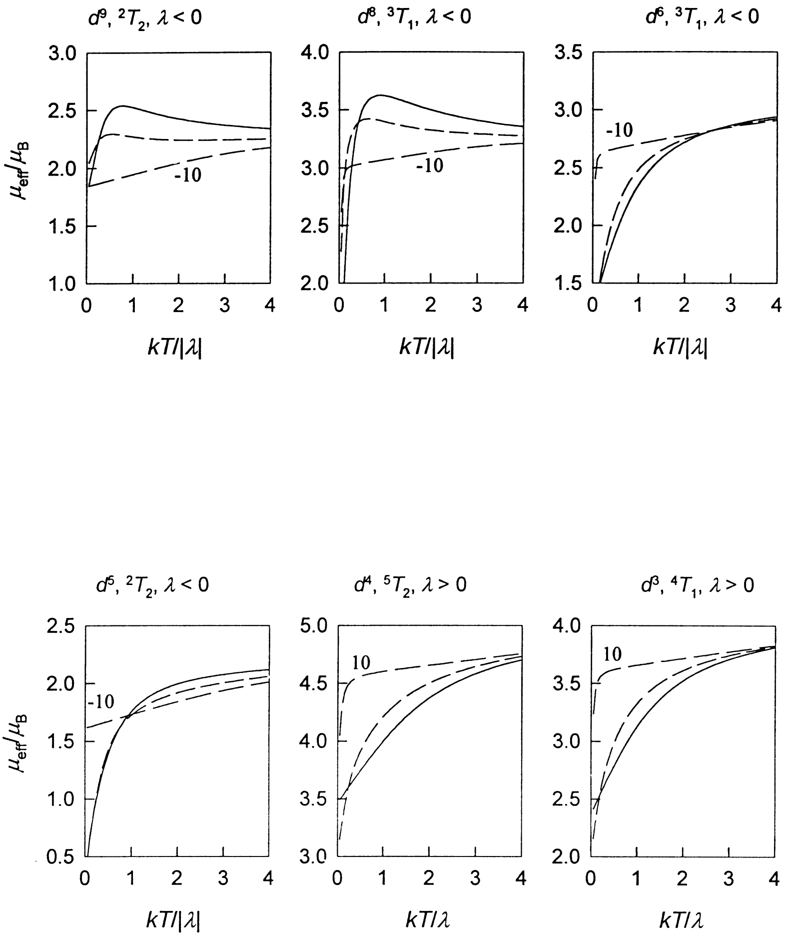


Fig. 30. Effective magnetic moment versus the reduced temperature for tetrahedral complexes: full line, $v=0$; dashed line, $v=\pm 10$.

$$g_1 \leftrightarrow \gamma\kappa A$$

$$g_2 \leftrightarrow g_e$$

Therefore, the transformation matrix C which diagonalizes the SO coupling operator can be generated by the well-known techniques for coupling of two angular momenta, one of them having $S_1 = 1$.

However, this procedure just described still suffers from several simplifications, among which the following may be important:

(1) a component of the symmetry lowering is not necessarily oriented along the C_4 and/or C_3 axis of the cubic group;

(2) the orbital reduction factor κ appearing in $\hat{H}^{so}$ and $\hat{H}^{Z}$ can be anisotropic;

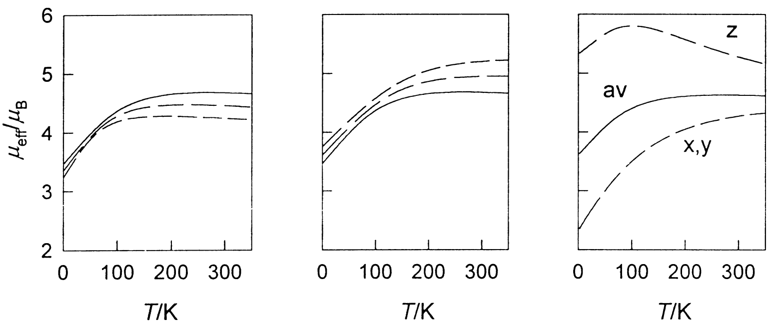


Fig. 31. Temperature variation of the magnetic functions for an octahedral complex with $^4T_{1g}$ ground term: (a) $\kappa = 1.0$ (solid), 0.8 and 0.6; (b) $A = 1.0$ (solid), 1.25 and 1.5; (c) $\Delta = -500\,\mathrm{cm}^{-1}$.

(3) the SO splitting parameter λ can be anisotropic as well;
(4) there is a mixing of the ground and excited terms through the SO operator since some matrix elements in fact are non-zero, e.g. $\langle {}^3T_1|\hat{H}^{so}|{}^3T_2\rangle \neq 0$.

11.11. A magneto-theoretical hierarchy

We have seen that the mononuclear complexes, with or without the first-order angular momentum, can be theoretically treated with different degrees of complexity. Thus we can speak about some magneto-theoretical hierarchy (Table 26). Depending on the basic postulate about the extent of the active space (a space of kets involved in the zero-order Hamiltonian) various levels of the theory can be distinguished.

In the most complete treatment (as in the theory of König and Kremer) there is almost nothing to be included by the perturbation theory, except the Zeeman term. Therefore, the differential g-tensor, the temperature-independent paramagnetic tensor and the spin–spin interaction tensor are blank: $\overline{\overline{\Delta g}} = 0$, $\overline{\overline{\kappa}}^{para}$, $\overline{\overline{D}}$. Only higher excited kets can bring some contribution which is, however, assumed negligible since the energy denominator is then large

$$\Lambda_{ab} \approx (E_n - E_0)^{-1} \approx 0$$

In contrast, when the active space is restricted to the spin-only kets, the influence of all attainable excited states contributes to magnitudes of the magnetic parameters (tensors). In such a case the g-tensor deviates considerably from the free-electron value, the temperature-independent paramagnetism appears substantial and the spin–spin interaction tensor transforms to high values of the ZFS parameters (D and E).

A direct comparison of the “magneto-chemical” g-values with the spectroscopic EPR values may have little sense. This can work only when the effective spin approach is of use, for systems where a Kramers doublet is the only relevant active space (e.g. Cu^{2+} and V^{4+} complexes).

Table 26
Magneto-theoretical hierarchy

Level	Description	Active space	Free parameters	Magnetic parameters
7		All terms of $f^k d^n s^m p^l$	ξ_d, ξ_f, …	
6	König and Kremer [23,35–38]	All terms of d^n	ξ_d, Dq, (or D_s, D_t, …)	$\overline{\overline{\Delta g}}=0$ $\overline{\overline{\kappa}}^{\mathrm{para}}=0$ $\overline{\overline{D}}^{\mathrm{para}}=0$
5	Figgis and coworkers [31–34]	Limited CI, kets of lowered symmetry	λ, A, κ, $\varDelta$ (or v)	$\overline{\overline{\Delta g}}=0$ $\overline{\overline{k}}^{\mathrm{para}}\neq 0$
4	Figgis [30]	Limited CI	λ, A, κ	$\overline{\overline{\Delta g}}=0$ $\overline{\overline{k}}^{\mathrm{para}}\neq 0$
3	Kotani [39]	Ground term $^{2S+1}\mathrm{T}$, kets $\vert L, M_L, S, M_S\rangle$ or $\vert J, M\rangle$	λ, κ	$\overline{\overline{\Delta g}}=0$ $\overline{\overline{k}}^{\mathrm{para}}=0$
2	ZFS	Ground term $^{m}\mathrm{S}$, kets $\vert S, M_S\rangle$	g_{aa}, D, E, (a, F), χ^{TIP} (or $\varLambda_{aa}$)	$\overline{\overline{\Delta g}}\neq 0$ $\overline{\overline{k}}^{\mathrm{para}}\neq 0$ $\overline{\overline{D}}^{\mathrm{para}}\neq 0$
1	Effective spin	Lowest Kramers doublet $\vert\tilde{S}, \pm 1/2\rangle$	g_{aa}^{eff}	$\overline{\overline{\Delta g}}\neq 0$ $\overline{\overline{k}}^{\mathrm{para}}\neq 0$

11.12. Magnetic field influence

According to König and Kremer [23] the magnitude of the magnetic field has an influence on the magnetic susceptibility and, consequently, on the effective magnetic moment at low temperature. This applies for A-terms, such as $^6A_{1g}$ for Mn(II) complexes, as well as for T-terms, such as $^4T_{1g}$ for Co(II) complexes.

Fig. 32 shows that the effective magnetic moment for the $^4T_{1g}$ term tends to decrease rapidly on cooling with the ramping field. At an intermediate field of $B=5$ T the onset of the decrease appears at ca $T=20$ K; thus the effect is well pronounced. The data in that figure have been generated on the basis of the mean magnetic susceptibility which was simply a ratio $\bar{\chi}=\mu_0 M/B$; the mean susceptibility has been obtained by a "polynomial fit formula" for eigenvalues (Section 8.6) with the subsequent application of the van Vleck formula. This, in fact, is equivalent to the original "finite difference formula" of König and Kremer [23].

It should be noted that the interpretation of the decrease of the effective magnetic moment at low temperature as an "intermolecular antiferromagnetic interaction", giving rise to the negative Weiss constant Θ within the Curie–Weiss law, can in fact be incorrect owing to ignorance of the non-linear magnetic behaviour.

The field dependence of the magnetization is better described by applying the "polynomial magnetization formula" (Section 8.8): the M versus B function is fitted to a quadratic equation

$$M(B)=d^{(0)}+d^{(1)}B+d^{(2)}B^2$$

from which the expansion coefficients $d^{(0)}$, $d^{(1)}$ and $d^{(2)}$ result. These are displayed in Fig. 33. The important observations are:

(1) the magnitude of the magnetization increases with the magnetic field;

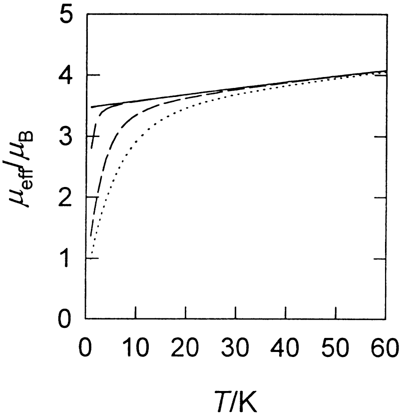


Fig. 32. Effective magnetic moment based on the mean magnetic susceptibility versus temperature for the $^4T_{1g}$ term at different magnetic fields: $B=0.001$ T (solid), $B=1$ T (long dashed), $B=5$ T (medium dashed), $B=10$ T (short dashed).

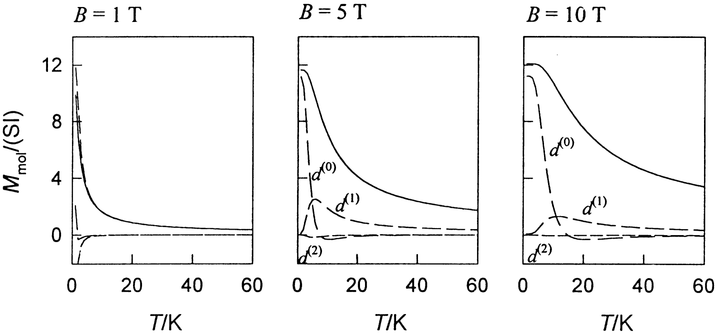


Fig. 33. Temperature dependence of the magnetization and its expansion coefficients for the $^4T_{1g}$ term at different magnetic fields.

(2) its first derivative, which is proportional to the differential susceptibility

$$\tilde{\chi}=\mu_0\frac{\partial M}{\partial B}=\mu_0 d^{(1)}$$

starts from zero, passes through a maximum and then escapes continuously; the higher the applied field, the lower the differential susceptibility; its maximum is shifted to higher temperature with increasing field.

Evidently, the differential susceptibility deviates considerably from the Curie law at low temperature and a higher field.

The mean and the differential magnetic susceptibilities are compared in Fig. 34. Their difference becomes dramatic at low temperature: the differential susceptibility approaches zero whereas the mean susceptibility has a non-zero value. It is worth noting that at $T=4.2$ K the difference may already be substantial.

Even more surprising is the difference between the effective magnetic moments when generated from the mean and/or differential magnetic susceptibilities (Fig. 35).

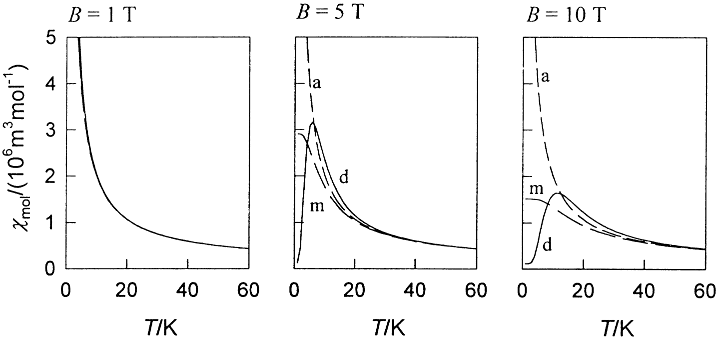


Fig. 34. Temperature dependence of the magnetic susceptibilities for the $^4T_{1g}$ term at different applied fields: m, mean magnetic susceptibility; d, differential magnetic susceptibility; a, approximate magnetic susceptibility based on the van Vleck equation.

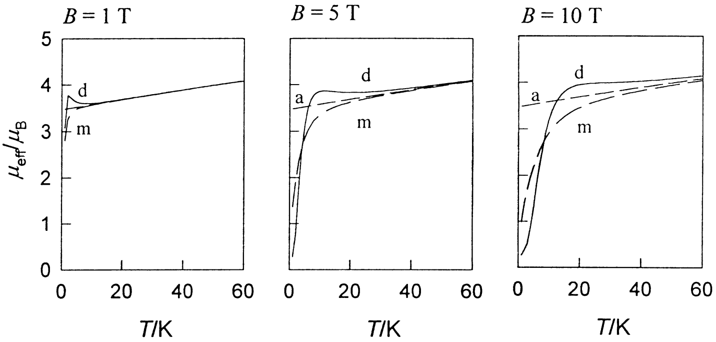


Fig. 35. Temperature dependence of the effective magnetic moments for the $^4T_{1g}$ term at different applied fields: m, based on the mean magnetic susceptibility; d, based on the differential magnetic susceptibility; a, based on the approximate magnetic susceptibility via the van Vleck equation.

This implies a conclusion that dealing with the mean magnetic susceptibilities at low temperature is, in principle, incorrect. The mean magnetic susceptibility is apparently a wrong approximation to the differential magnetic susceptibility; the latter represents a true thermodynamic quantity and, when taken at constant temperature, it becomes the isothermal magnetic susceptibility

$$\tilde{\chi} = \mu_0 \left(\frac{\partial M}{\partial B} \right)_T = \chi_T$$

12. Insight into polynuclear systems

The spin Hamiltonian that describes the exchange interaction in a binuclear system is

$$\hat{H}^{bi} = \boldsymbol{s}_1 \cdot \overline{\overline{D}} \cdot \boldsymbol{s}_2 [\hbar^{-2}]$$

The Cartesian spin–spin interaction tensor, however, can be decomposed into its irreducible components and the spin Hamiltonian rewritten as

$$\hat{H}^{bi} = [J_0 \boldsymbol{s}_1 \cdot \boldsymbol{s}_2 + \boldsymbol{A} \cdot (\boldsymbol{s}_1 \times \boldsymbol{s}_2) + \boldsymbol{s}_1 \cdot \overline{\overline{S}}_0 \cdot \boldsymbol{s}_2][\hbar^{-2}]$$

where the first term represents an isotropic exchange, the second an the antisymmetric exchange, and the last the anisotropic exchange with:

(1) the scalar constant

$$J_0 = \tfrac{1}{3}\,\mathrm{Tr}(\boldsymbol{D}) = \tfrac{1}{3}(D_{xx} + D_{yy} + D_{zz})$$

(2) antisymmetric vector

$$A_{ab} = \tfrac{1}{2}\,(D_{ab} - D_{ba}) = -A_{ba}$$

(3) a traceless symmetric tensor

$$S_{0,ab} = \tfrac{1}{2}(D_{ab} - D_{ba}) - J_0 = S_{0,ba}$$

In the most simple case of an isotropic exchange one has

$$\hat{H}^{\mathrm{bi}} \approx J_0 \boldsymbol{s}_1 \cdot \boldsymbol{s}_2[\hbar^{-2}] = -J\boldsymbol{s}_1 \cdot \boldsymbol{s}_2[\hbar^{-2}] = -2j\boldsymbol{s}_1 \cdot \boldsymbol{s}_2[\hbar^{-2}]$$

(One should be careful in definition of the constant factor since other numerical and sign conventions are common.)

Restricting ourselves only to pair interactions, the spin Hamiltonian appropriate for the exchange interaction in polynuclear systems becomes

$$\hat{H}^{\mathrm{poly}} = \sum_{A}^{N} \sum_{B<A}^{N} -J_{AB}\boldsymbol{s}_A \cdot \boldsymbol{s}_B[\hbar^{-2}]$$

where we applied one of the possible conventions for the sign and a numerical factor in front of the isotropic exchange constants. The number of magnetic energy levels varies from a few ($M = 2^2 = 4$ for two centres with $s_1 = s_2 = 1/2$) to several millions ($M = 6^8$ for eight centres with $s_A = 5/2$). The spacing of the magnetic energy levels (the density of states) is predetermined by the values of the exchange constants; for J small enough ($J < 5\,\mathrm{cm}^{-1}$) there would be a dense spacing of magnetic energy levels. Thus one can expect that the substance will exhibit a non-linear magnetic behaviour where the difference between the mean and differential susceptibilities could be substantial. We are not so ambitious as to cover this subject in detail. Rather we will present a few examples where the effect would be observable.

The exchange coupling in the $s_1 = s_2 = 1/2$ system leads to the singlet ground-state ($S = 0$) and a triplet excited state ($S = 1$, $M_S = 0, \pm 1$) when the exchange constant, according to our definition, is negative: $J < 0$ (antiferromagnetic coupling). The situation somehow resembles the behaviour which we have already met for the ZFS systems (see Fig. 17). With increasing applied field the magnetically more productive state ($M_S = -1$) becomes a ground state which manifests itself in a step increase of the magnetization.

For the exchange coupling of homospin systems the allowed molecular states lie

Table 27
Energy levels ϵ_S for a binuclear homospin system in the zero field[a]

S	n_S	$\epsilon_S = -n_S J$
0	0	0
1	1	$-J$
2	3	$-3J$
3	6	$-6J$
4	10	$-10J$
5	15	$-15J$

[a] n_s Multiplication factor.

between

$$S_{\min} = |s_1 - s_2|$$

and

$$S_{\max} = s_1 + s_2$$

In this fortunate case the zero-field Hamiltonian is diagonal, giving rise to energy levels according to Table 27.

Since the (spin) Zeeman operator in the basis set of coupled spin angular momenta functions $|S, M_S\rangle$ is diagonal as well, then the magnetic energy levels are easy to generate

$$\epsilon_{S,M_S}(B) = \epsilon_S(B=0) + \mu_B \mathrm{gBM}_S = -n_S J + \mu_B g B M_S$$

and then the partition function becomes

$$Z = \sum_{S=S_{\min}}^{S_{\max}} Z(S) = \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} \exp[(n_S J - \mu_B g B M_S)/kT]$$

In evaluating the magnetic susceptibility one can apply the "magnetization formula" (Section 8.1) according to which

$$M = N_A \frac{1}{Z} \sum_i \left(-\frac{\partial \epsilon_i}{\partial B} \right) \exp(-\epsilon_i/kT)$$

and

$$\tilde{\chi} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} \left\{ \left[\sum_i \left(\frac{\partial \epsilon_i}{\partial B} \right)^2 \exp(-\epsilon_i/kT) - (kT) \sum_i \left(\frac{\partial^2 \epsilon_i}{\partial B^2} \right) \right. \right.$$
$$\left. \left. \times \exp(-\epsilon_i/kT) \right] Z - \left[\sum_i \left(\frac{\partial \epsilon_i}{\partial B} \right) \exp(-\epsilon_i/kT) \right]^2 \right\}$$

Because the second-order derivatives are zero for the isotropic exchange model, a simplification is obtained:

$$\tilde{\chi} = \frac{N_A \mu_0}{kT} \frac{1}{Z^2} (T_2 Z - T_1^2)$$

and

$$M = N_A \frac{1}{Z} T_1$$

The terms of the magnetization and the susceptibility are

$$T_1 = \sum_i \left(-\frac{\partial \epsilon_i}{\partial B} \right) \exp(-\epsilon_i/kT)$$
$$= \mu_B g \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S \exp[(n_S J - \mu_B g B M_S)/kT]$$

and

$$T_2 = \sum_i \left(\frac{\partial \epsilon_i}{\partial B}\right)^2 \exp(-\epsilon_i/kT)$$

$$= (\mu_B g)^2 \sum_{S=S_{\min}}^{S_{\max}} \sum_{M_S=-S}^{+S} M_S^2 \exp[(n_S J - \mu_B g B M_S)/kT]$$

and these are collected in Table 28. The corresponding plots are given in Figs. 36 and 37.

The second selected example is represented by an exchange coupling within a tetranuclear cluster of $s_1 = s_2 = s_3 = s_4 = 1/2$ (Figs. 38–40). The 16 energy levels ($M = 2^4 = 16$) at the tetrahedral arrangement of centres and the zero field are represented by two singlets, three triplets and one quintet; their spacing is

$$\epsilon_{S=0} = 0, \quad \text{[twice]}$$

$$\epsilon_{S=1} = -J, \quad \text{[three } \times\text{]}$$

$$\epsilon_{S=2} = -3J, \quad \text{[once]}$$

As far as the magnetic field is applied, they become

$$\epsilon_{S=0,M_S=0}(B) = 0$$

$$\epsilon_{S=1,M_S=0,\pm1}(B) = -J + \mu_B g B M_S$$

$$\epsilon_{S=2,M_S=0,\pm1,\pm2}(B) = -3J + \mu_B g B M_S$$

Then the terms of the magnetic susceptibility are given by Table 29.

According to Fig. 38 the magnetization per cluster, depending upon the magnitude of the (negative) exchange constant, may exhibit two steps with the increasing applied field.

13. Conclusions

The main messages given by this article are summarized below.

(1) The magnetic susceptibility is introduced as a thermodynamic quantity which requires a partial differentiation of the magnetization according to the applied field. This differential (isothermal) magnetic susceptibility differs from the frequent definition of the mean magnetic susceptibility if the behaviour of the magnetic material is non-linear.

(2) Different experimental techniques, depending on whether they register a mag-

Table 28
Terms of the magnetic susceptibility for binuclear homospin systems[a]

$s_1=s_2$	$S_{\max}$	$Z(S)$	$T_1(S)/(\mu_B g)$	$T_2(S)/(\mu_B g)^2$
1/2	1	$1+\exp(x+By)+\exp(x)+\exp(x-By)$	$+1\cdot\exp(x+By)-1\cdot\exp(x-By)$	$+1^2\cdot\exp(x+By)+1^2\cdot\exp(x-By)$
1	2	$Z(S-1)+\exp(3x+2By)+\exp(3x+By)$ $+\exp(3x)+\exp(3x-By)+\exp(3x-2By)$	$T_1(S-1)+2\cdot\exp(3x+2By)+1\cdot\exp(3x+By)$ $-1\cdot\exp(3x-By)-2\cdot\exp(3x-2By)$	$T_2(S-1)+2^2\cdot\exp(3x+2By)$ $+1^2\cdot\exp(3x+By)+1^2\cdot\exp(3x-By)$ $+2^2\cdot\exp(3x-2By)$
3/2	3	$Z(S-1)+\exp(6x+3By)+\exp(6x+2By)$ $+\exp(6x+By)+\exp(6x)+\exp(6x-By)$ $+\exp(6x-2By)+\exp(6x-3y)$	$T_1(S-1)+3\cdot\exp(6x+3By)+2\cdot\exp(6x+2By)$ $+1\cdot\exp(6x+By)-1\cdot\exp(6x-By)$ $-2\cdot\exp(6x-2By)-3\cdot\exp(6x-3By)$	$T_2(S-1)+3^2\cdot\exp(6x+3By)$ $+2^2\cdot\exp(6x+2By)+1^2\cdot\exp(6x+By)$ $+1^2\cdot\exp(6x-By)+2^2\cdot\exp(6x-2By)$ $+3^2\cdot\exp(6x-3By)$
2	4	$Z(S-1)+\exp(10x+4By)$ $+\exp(10x+3By)+\exp(10x+2By)$ $+\exp(10x+By)+\exp(10x)+\exp(10x-By)$ $+\exp(10x-2By)+\exp(10x-3y)$ $+\exp(10x-4By)$	$T_1(S-1)+4\cdot\exp(10x+4By)+3\cdot\exp(10x+3By)$ $+2\cdot\exp(10x+2By)+1\cdot\exp(10x+By)$ $-1\cdot\exp(10x-By)-2\cdot\exp(10x-2By)$ $-3\cdot\exp(10x-3By)-4\cdot\exp(10x-4By)$	$T_2(S-1)+4^2\cdot\exp(10x+4By)$ $+3^2\cdot\exp(10x+3By)+2^2\cdot\exp(10x+2By)$ $+1^2\cdot\exp(10x+By)+1^2\cdot\exp(10x-By)$ $+2^2\cdot\exp(10x-2By)+3^2\cdot\exp(10x-3By)$ $+4^2\cdot\exp(10x-4By)$
5/2	5	$Z(S-1)+\exp(15x+5By)+\exp(15x+4By)$ $+\exp(15x+3By)+\exp(15x+2By)$ $+\exp(15x+By)+\exp(15x)+\exp(15x-By)$ $+\exp(15x-2By)+\exp(15x-3By)$ $+\exp(15x-4By)+\exp(15x-5By)$	$T_1(S-1)+5\cdot\exp(15x+5By)+4\cdot\exp(15x+4By)$ $+3\cdot\exp(15x+3By)+2\cdot\exp(15x+2By)$ $+1\cdot\exp(15x+By)-1\cdot\exp(15x-By)$ $-2\cdot\exp(15x-2By)-3\cdot\exp(15x-3By)$ $-4\cdot\exp(15x-4By)-5\cdot\exp(15x-5By)$	$T_2(S-1)+5^2\cdot\exp(15x+5By)$ $+4^2\cdot\exp(15x+4By)+3^2\cdot\exp(15x+3By)$ $+2^2\cdot\exp(15x+2By)+1^2\cdot\exp(15x+By)$ $-1^2\cdot\exp(15x-By)-2^2\cdot\exp(15x-2By)$ $-3^2\cdot\exp(15x-3By)-4^2\cdot\exp(15x-4By)$ $-5^2\cdot\exp(15x-5By)$

[a] Substitution $x=J/kT$, $y=\mu_B g/kT$.

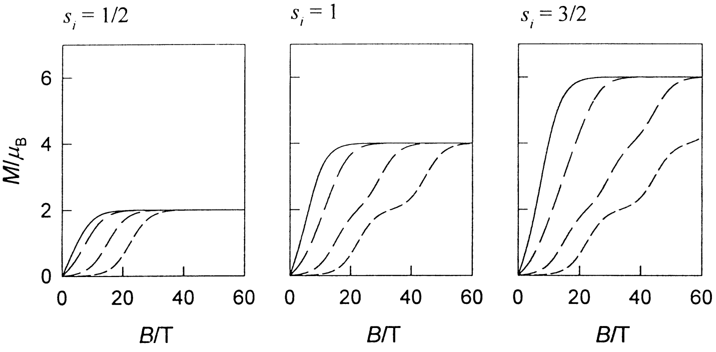


Fig. 36. Magnetization per dimer versus the applied field for binuclear homospin systems at T=4.2 K; J/k= −5 K (solid), J/k= −10 K (long dashed), J/k= −20 K (medium dashed), J/k= −30 K (short dashed).

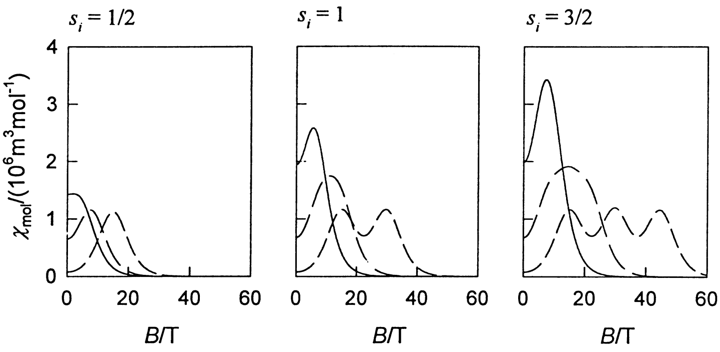


Fig. 37. Differential magnetic susceptibility per dimer versus the applied field for binuclear homospin systems at T=4.2 K; J/k= −5 K (solid), J/k= −10 K (long dashed), J/k= −20 K (medium dashed).

netic response in static or alternating fields, yield different types of magnetic susceptibility. In certain situations a correction to demagnetization effects is necessary.

(3) A linkage between the quantum theory (Hamiltonian, active space of state kets) and the macroscopic thermodynamical quantities (magnetization, magnetic heat capacity, magnetic susceptibility) is given by statistical thermodynamics in which the partition function adopts a key role.

(4) For Curie paramagnets a non-linear behaviour is observed at low temperature and high fields, i.e. when the linear approximation to the Brillouin function is violated.

(5) For systems with the spin $S \geqslant 1$ the ZFS of energy levels appears. These substances may exhibit a step increase of the magnetization (the temperature should be low and the magnetic field high). Consequently, the mean and differential magnetic susceptibilities differ substantially.

(6) Transition metal centres with magnetic angular momentum, i.e. systems with

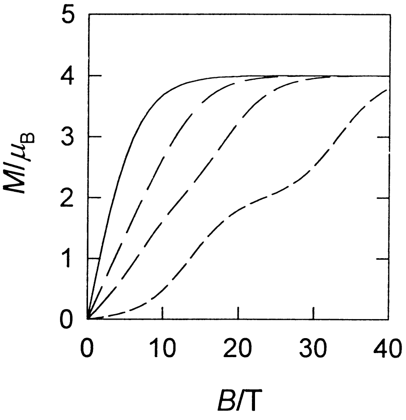


Fig. 38. Magnetization per cluster for an $s_1=s_2=s_3=s_4=1/2$ system versus the applied field at $T=4.2$ K. The individual curves correspond to $J=0$ (solid), $J/k=-5$ K (long dashed), $J/k=-10$ K (medium dashed), and $J/k=-20$ K (short dashed).

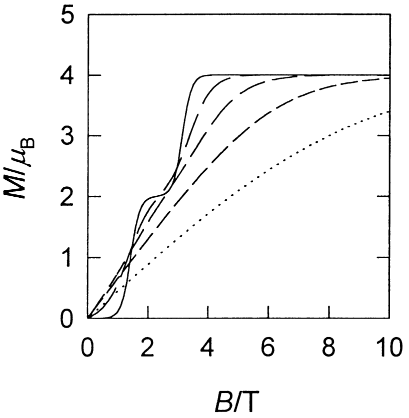


Fig. 39. Magnetization per cluster for an $s_1=s_2=s_3=s_4=1/2$ system versus the applied field for $J/k=-2$ K. The individual curves correspond to $T=0.2$ K (solid), $T=0.5$ K (long dashed), $T=1$ K (medium dashed), $T=2$ K (short dashed), and $T=4.2$ K (dotted).

ground T-terms, exhibit a complicated variance of the magnetic susceptibility which is better visualized when the product function $(\chi_{\mathrm{mol}}T)$ and/or the effective magnetic moment μ_{eff} is plotted versus the temperature. Its field dependence becomes pronounced with increasing magnetic field at low temperature.

(7) A departure from cubic symmetry may generate a more dense spacing of relevant, temperature-populated energy levels and a non-linear magnetic response tends to be more pronounced.

(8) Several levels of theory can be distinguished which more or less completely cover the active space of the state kets. When the active space is extended to all

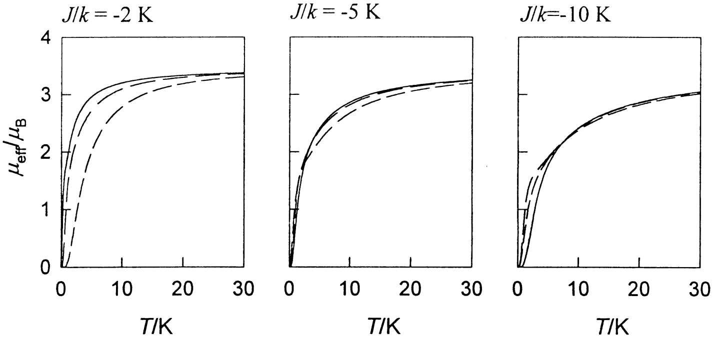


Fig. 40. Effective magnetic moment for an $s_1 = s_2 = s_3 = s_4 = 1/2$ cluster versus temperature. The individual curves correspond to $B = 1$ T (solid), $B = 5$ T (long dashed), and $B = 10$ T (medium dashed).

Table 29
Terms of the magnetic susceptibility for a tetranuclear cluster withs $s_i = 1/2$[a]

Z	$T_1/(\mu_B g)$	$T_2/(\mu_B g)^2$
$2+3\exp(x+By)+3\exp(x)$	$+3\cdot\exp(x+By)-3\cdot\exp(x-By)$	$+3\cdot 1^2\cdot\exp(x+By)$
$+3\exp(x-By)$	$+2\cdot\exp(3x+2By)+1\cdot\exp(3x+By)$	$+3\cdot 1^2\cdot\exp(x-By)$
$+\exp(3x+2By)$	$-1\cdot\exp(3x-By)-2\cdot\exp(3x-2By)$	$+1\cdot 2^2\cdot\exp(3x+2By)$
$+\exp(3x+By)+\exp(3x)$		$+1\cdot 1^2\cdot\exp(3x+By)$
$+\exp(3x-By)$		$+1\cdot 1^2\cdot\exp(3x-By)$
$+\exp(3x-2By)$		$+1\cdot 2^2\cdot\exp(3x-2By)$

[a] Substitution $x = J/kT$, $y = \mu_B g/kT$.

(relevant) terms of the given d^n electron configuration, then the magnetic parameters, i.e. the $\overline{\overline{\Delta g}}$, $\overline{\overline{D}}$ and $\overline{\overline{\kappa}}^{\mathrm{para}}$ tensors are blank. As long as the active space is more restricted to only a few magnetic levels, contributions to the magnetic parameters become significant. Thus, in magnetochemistry no match of the g-factors with the EPR readings is necessary: for a Co(II) system the magnetochemical g-values may be either close to the free-electron value of $g_e = 2.0023$ (when the active space is extended enough) or close to EPR values ($g_{\mathrm{eff}} = 4$–13) when only a few magnetic levels are included into the active space.

(9) A dense spacing of energy levels for dinuclear systems and polynuclear clusters manifests itself in a step increase of the magnetization if the temperature is low and the applied field high. Again, a pronounced difference between the mean and differential magnetic susceptibilities appears.

Nomenclature

$\boldsymbol{B}$	magnetic induction vector
$B_J(\eta)$	Brillouin function
C	Curie constant

C_0	reduced Curie constant ($C_0 = N_A \mu_0 \mu_B^2 / k$)
D	axial zero-field splitting parameter
E	rhombic zero-field splitting parameter
F	free energy (Helmholtz energy)
g_a	Cartesian component of the g-tensor
g_e	electronic g-factor
$\hat{H}$	Hamiltonian
$\hat{H}^{zfs}$	zero-field splitting Hamiltonian
$\hat{H}^{so}$	spin–orbit Hamiltonian
$\boldsymbol{H}$	magnetic field strength vector
$\boldsymbol{H}_a$	applied magnetic field
$\boldsymbol{H}_d$	demagnetizing field
k	Boltzmann's constant
$\boldsymbol{L}$	orbital angular momentum vector
m	sample mass
$\boldsymbol{M}$	magnetization (volume, molar) vector
M_a	Cartesian component of the magnetization
M_{av}	averaged (powder) magnetization
M_r	molar mass
N	demagnetization factor
N_A	Avogadro's number
S	entropy
S	spin quantum number
$\boldsymbol{S}$	spin angular momentum vector
$\hat{S}_a$	spin angular momentum operator for the coordinate a ($a = x, y, z$)
T	(thermodynamic) temperature
U	internal energy
V	volume of the specimen
Z	partition function
δ_{ij}	Kronecker symbol
$\boldsymbol{\mu}$	magnetic moment vector
μ_0	permeability of the vacuum
μ_B	Bohr magnetron ($\mu_B = e\hbar / 2m_e$)
χ, $\tilde{\chi}$	differential (volume) magnetic susceptibility
$\underline{\bar{\chi}}$	mean (volume) magnetic susceptibility
$\overline{\overline{\chi}}$	magnetic susceptibility tensor
χ'	real component of AC susceptibility (dispersion)
χ''	imaginary component of AC susceptibility (absorption)
χ_{av}	averaged (powder) magnetic susceptibility
χ_{mol}	molar magnetic susceptibility
χ_S	adiabatic susceptibility
χ_T	isothermal susceptibility
χ_ρ	mass magnetic susceptibility
ρ	sample density
$\hbar$	reduced Planck constant ($\hbar = h / 2\pi$)

References

[1] J.H. van Vleck, Theory of Electric and Magnetic Susceptibilities, Oxford University Press, 1932.
[2] P.W. Selwood, Magnetochemistry, 2nd edition, Interscience, New York, 1956.
[3] D.E.G. Williams, The Magnetic Properties of Matter, Longmans, London, 1965.
[4] A. Weiss, H. Witte, Magnetochemie, Verlag Chemie, Weinheim, 1973.
[5] F.E. Mabbs, D.J. Machin, Magnetism and Transition Metal Complexes, Chapman and Hall, London, 1973.
[6] A.S. Chakravarty, Introduction to Magnetic Properties of Solids, Wiley, New York, 1980.
[7] V.T. Kalinnikov, J.V. Rakitin, Vvedeniye v magnetochimiyu, Nauka, Moscow, 1980.
[8] R.L. Carlin, A.J. van Duyneveldt, Magnetic Properties of Transition Metal Compounds, Springer, New York, 1977.
[9] R.L. Carlin, Magnetochemistry, Springer, Berlin, 1986.
[10] D. Gignoux, in: K.H.J. Buschow (Ed.), Materials Science and Technology, vol. 3A, part I, VCH, Weinheim, 1991.
[11] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
[12] D. Craik, Magnetism, Wiley, Chichester, 1995.
[13] T. Ishida, R.B. Goldfarb, Phys. Rev. B 41 (1990) 8937.
[14] E.C. Stoner, Philos. Mag. 36 (1945) 803.
[15] J.A. Osborne, Phys. Rev. 67 (1954) 351.
[16] R.B. Goldfarb, J.V. Minervini, Rev. Sci. Instrum. 55 (1984) 761.
[17] T.T. Taylor, J. Res. Nat. Bur. Stand. Sect. B: 64 (1960) 199.
[18] D.C. Mattis, The Theory of Magnetism II, Springer Series in Solid-State Sciences 55, Springer, Berlin, 1985.
[19] A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970.
[20] M. Gerloch, R.F. McMeeking, J. Chem. Soc. Dalton Trans. (1975) 2443.
[21] S.W. Gordon-Wylie, E.L. Bominaar, T.J. Collins, J.M. Workman, B.L. Claus, R.E. Patterson, S.A. Williams, B.J. Conklin, G.T. Yee, S.T. Weintraub, Chem. Eur. J. 1 (1995) 528.
[22] R. Boča, P. Baran, L. Dlháò, M. Hvastijová, G. Wltschek, Chem. Phys. Lett. 284 (1998) 254.
[23] E. König, S. Kremer, Ber. Bunsenges. Phys. Chem. 78 (1974) 268.
[24] C.P. Poole Jr., H.A. Farach, The Theory of Magnetic Resonance, Wiley, New York, 1972.
[25] H.H. Wickmann, M.P. Klein, D.A. Shirley, J. Chem. Phys. 42 (1965) 2113.
[26] J.R. Pilbrow, Transition Ion Electron Paramagnetic Resonance, Claredon, Oxford, 1990.
[27] H. Appel, in: Landolt–Börnstein, Neue Serie, Band 3, Springer, Berlin, 1968.
[28] J.S. Griffith, The Theory of Transition Metal Ions, University Press, Cambridge, 1964.
[29] W. Haberditzl, Quantenchemie, Band 4, Hüthig, Heidelberg, 1979.
[30] B.N. Figgis, Introduction to Ligand Fields, Wiley, New York, 1966.
[31] B.N. Figgis, J. Lewis, F.E. Mabbs, G.A. Webb, J. Chem. Soc. A: (1966) 1411.
[32] B.N. Figgis, M.Gerloch, J. Lewis, F.E. Mabbs, G.A. Webb, J. Chem. Soc. A: (1968) 2086.
[33] B.N. Figgis, J. Lewis, F.E. Mabbs, G.A. Webb, J. Chem. Soc. A: (1967) 442.
[34] B.N. Figgis, Trans. Faraday Soc. 57 (1961) 198.
[35] E. König, S. Kremer, Ber. Bunsenges. Phys. Chem. 76 (1972) 870.
[36] E. König, S. Kremer, Ber. Bunsenges. Phys. Chem. 78 (1964) 786.
[37] E. König, S. Kremer, Ligand Field Energy Diagrams, Plenum Press, New York, 1977.
[38] E. König, S. Kremer, Magnetism Diagrams for Transition Metal Ions, Plenum Press, New York, 1979.
[39] M. Kotani, J. Phys. Soc. Jpn. 4 (1949) 293.