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PARAMAGNETIC ANISOTROPY

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A. INTRODUCTION

The usefulness of magnetic susceptibility data in coordination chemistry has long been realized. This is particularly true for paramagnetic substances which exhibit magnetic moments owing to the spin-, and in some cases the orbital-, angular momentum of their unpaired electrons. While this review is concerned primarily with paramagnetism, the experimental methods described may be applied with only minor modifications to measurements on diamagnetic substances. In any case the underlying diamagnetism necessarily present in all matter must be kept in mind and appropriate corrections applied when analyzing the susceptibility data of paramagnetic substances. A fairly recent compendium[66K2] reveals how large indeed is the number of measurements made on paramagnetic substances over the years. The vast majority of these measurements have been made on powders or solutions. Only a relatively small number of investigations of the principal magnetic susceptibilities of single crystals have been reported. This is unfortunate since considerably more can be learned of the electronic structure of a complex if its principal molecular susceptibilities are known than if only the average susceptibility is available.

When compared to various spectroscopic measurements, a magnetic susceptibility determination has, on the face of it, a relatively low information content. The average susceptibility is a single number which may be measured as a function of temperature. A typical spectroscopic measurement yields a large number of observables (i.e. fundamental frequencies, chemical shifts, coupling constants, g-values, hyperfine constants, band widths, extinction coefficients, etc.). It is important, therefore, to extract as much information as possible from susceptibility measurements. This can be achieved through anisotropy studies.

Knowledge of anisotropy is particularly important when it comes to a theoretical interpretation of magnetic susceptibility in terms of the electronic structure of a complex. Alternative sets of theoretical parameters (ligand field, Racah, spin–orbit coupling and orbital reduction) often account equally well for average susceptibility findings[69W1]. Anisotropy data generally resolves any such ambiguity. It is becoming increasingly apparent[69G1–2] that the actual values of derived theoretical parameters are quite sensitive to the nature of the approximations involved in the theory applied to any particular case. This point is further amplified in the illustrative example provided in Section C.

This review is concerned with susceptibility anisotropy rather than electron paramagnetic resonance (*epr*) measurements which yield related and to some extent complementary information. The former method is of somewhat more generality for while the susceptibility of any paramagnetic substance can be measured, *epr* experiments may fail for one or more of a variety of reasons (unfavorable spin-lattice relaxation time, large zero field splitting, excessive dipolar broadening, etc.). *Epr* measurements on transition metal complexes have been reviewed fairly recently[66M1]. The complementary relationship between *epr* and susceptibility anisotropy data will be illustrated in conjunction with the example described in Section C.

While fairly recent reviews of paramagnetic susceptibility data are available[66K2,64F2], each treats magnetic anisotropy only peripherally. The present article is intended to serve as a key to the literature on anisotropy measurements, many of which are reported in Indian journals and thus may not have come to the attention of most coordination chemists. This key is provided in the form of a comprehensive listing (by periodic group) of all compounds upon which such measurements have been made. No attempt is made here to discuss the various results or their interpretation. Rather, an outline of the basic theory of anisotropy measurements and their interpretation is given with an illustrative example. In the judgement of the present authors, Krishnan's critical torque (flip-angle) method is the most widely applicable and generally satisfactory method of anisotropy measurement available to inorganic chemists. Since there is no discussion of this method in the readily accessible literature, a fairly detailed analysis is presented here (Section D). This article should provide a useful starting point for those searching for available anisotropy data or planning to embark on such studies themselves.

Finally, the opportunity is taken in this review (see section B) to propose a unified and rational system of notation for magnetic susceptibility quantities and a unit of susceptibility to replace the clumsy notation presently in use.

B. BASIC RELATIONS OF DIA- AND PARAMAGNETISM

This section will review the basic relationships and formulae applicable to dia- and paramagnetic substances. Ferromagnetic substances which may exhibit net magnetizations in the absence of an applied field are not treated. The magnetic induction **B** within a substance differs from that of the field strength **H** outside by the relationship:

$$\mathbf{B} = \mathbf{H} + 4\pi\mathbf{I} \tag{1}$$

where **I** is the intensity of magnetization (the magnetic moment per unit volume). The vector quantities **B**, **H**, and **I** are shown in bold face. **I** does not vary throughout a homogeneous substance except as **H** varies. For isotropic substances **I** depends only on **H** and is independent of direction,

$$\mathbf{I} = {}^{V}\chi\mathbf{H} \tag{2}$$

where ${}^{V}\chi$ is the volume susceptibility and is a scalar quantity for isotropic substances. Eqn. (1) may be rewritten:

$$\mathbf{B} = \mathbf{H} + 4\pi\,{}^{V}\chi\mathbf{H} = (1 + 4\pi\,{}^{V}\chi)\mathbf{H} \tag{3}$$

$$\mathbf{B} = \mu\mathbf{H} \tag{4}$$

where μ is the permeability. Paramagnetic substances have ${}^{V}\chi > 0$, while diamagnetic ones have ${}^{V}\chi < 0$. Typical room temperature volume susceptibilities of paramagnetic substances are 10^{-4}–10^{-5} c.g.s.u./cm^3 and generally exhibit a $1/T$ temperature dependence. Volume susceptibilities of diamagnetic substances are of the order of -10^{-8} c.g.s.u./cm^3. From Eqns. (3) and (4) it is seen that the permeabilities of such substances are quite close to unity. In other words, the field within a dia- or paramagnetic material is practically identical to the applied field.

In homogeneous but *anisotropic* substances (i.e. almost any noncubic crystal), **I** depends on the direction as well as the magnitude of **H**. In such cases χ is a tensor quantity and Eqn. (2) becomes

$$\mathbf{I} = \mathbb{X}\mathbf{H} \quad \text{or} \tag{5}$$

$$\begin{bmatrix} I_1 \\ I_2 \\ I_3 \end{bmatrix} = \begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{12} & \chi_{22} & \chi_{23} \\ \chi_{13} & \chi_{23} & \chi_{33} \end{bmatrix} \begin{bmatrix} H_1 \\ H_2 \\ H_3 \end{bmatrix} \tag{6}$$

where the vector components $I_1, I_2, I_3, H_1, \ldots$ etc. refer to an *orthogonal* coordinate system fixed in the crystal. $\mathbb{X}$ is then a symmetric tensor with six independent elements. The intensity of magnetization in the ith direction ($i = 1, 2,$ or 3) is given by

$$I_i = \chi_{i1}H_1 + \chi_{i2}H_2 + \chi_{i3}H_3 \tag{7}$$

It is always possible to find an orthogonal coordinate system in which the only non-vanishing elements of $\mathbb{X}$ are along the diagonal.

$$\begin{bmatrix} \chi_1 & 0 & 0 \\ 0 & \chi_2 & 0 \\ 0 & 0 & \chi_3 \end{bmatrix} = \mathbb{X}_P \tag{8}$$

The elements χ_1, χ_2, and χ_3 are known as the principal susceptibilities and their directions (i.e. the coordinate axes) are the principal magnetic axes. The principal anisotropies of a crystal are the differences $(\chi_1 - \chi_2)$, $(\chi_1 - \chi_3)$, $(\chi_2 - \chi_3)$.

Except for triclinic and monoclinic crystals the directions of the principal magnetic axes are completely determined by crystal symmetry. Cubic crystals are of course isotropic. In the axial crystal systems (tetragonal, trigonal, hexagonal) one principal axis ($\chi_\parallel$) coincides with the C_4 or C_3 symmetry axis of the crystal lattice. The other two ($\chi_\perp$) are perpendicular to this and may be arbitrarily specified. The principal susceptibilities of orthorhombic crystals are in general all different and their directions coincide with the *a, b* and *c* crystallographic axes. The direction of the unique (C_2, *b*) axis of a monoclinic crystal defines one principal susceptibility axis (say χ_1) the other two axes (χ_2 and χ_3) lie in the (010) plane, but their directions must be experimentally determined (see section D). In the triclinic case none of the principal magnetic axes are crystallographically determined and the situation is more complex. With a knowledge of the six unique elements of the susceptibility tensor, referred to an arbitrary crystal-fixed orthogonal coordinate system, the determination of the principal susceptibilities and their directions becomes a simple eigenvalue problem:

$$\begin{bmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{12} & \chi_{22} & \chi_{23} \\ \chi_{13} & \chi_{23} & \chi_{33} \end{bmatrix} \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{bmatrix} \begin{bmatrix} \chi_1 & 0 & 0 \\ 0 & \chi_2 & 0 \\ 0 & 0 & \chi_3 \end{bmatrix} \quad (9)$$

or

$$\mathbb{X}\mathbb{C} = \mathbb{C}\mathbb{X}_{\mathrm{P}} \quad (10)$$

where $\mathbb{C}$ is the transformation matrix from the original coordinate system to that in which $\mathbb{X}$ is diagonal. The problem of finding the principal susceptibilities becomes a simple one of diagonalizing the susceptibility matrix. The eigenvalues are the principal susceptibilities (χ_1, χ_2, and χ_3) and the eigenvectors represent the transformation matrix. This may be accomplished by standard methods. Use of this general procedure should only be necessary in the triclinic case. Further discussion is reserved for section D.

Nomenclature and notation

The above discussion applies to all forms of susceptibility (volume, gram, molar) however Eqns. (1)–(4) refer to volume susceptibilities. At this point the relationships between the various types of susceptibility will be reviewed and a proposal for a new standard notation made. We suggest that all types of susceptibility be symbolized by the Greek letter χ, with a left superscript indicating the type. Thus volume susceptibilities are ${}^{\mathrm{V}}\chi$ (as opposed to κ sometimes used in the literature). The gram susceptibility ${}^{\mathrm{g}}\chi$ of a substance is by definition

$${}^{\mathrm{g}}\chi = \frac{{}^{\mathrm{V}}\chi}{d} \quad (11)$$

where d is the density. The molar susceptibility ${}^{M}\chi$ is then

$$ {}^{M}\chi = {}^{g}\chi M \qquad (12) $$

where M is the molecular weight of a substance.

Unit of magnetic susceptibility

It is customary to express ${}^{g}\chi$ in units of 10^{-6} c.g.s.u./g and ${}^{M}\chi$ in units of 10^{-6} c.g.s.u./mole. We propose a simplification of this clumsy notation by introducing a new unit of susceptibility. Its name is chosen to honor the man who laid the foundations of the atomic and molecular basis of paramagnetism, Professor J. H. Van Vleck of Harvard. The new unit, the Van Vleck (VVk) has by definition the following value

$$ 1\ \mathrm{VVk} \equiv 10^{-6}\ \mathrm{c.g.s.u.} \qquad (13) $$

Molar susceptibilities may be expressed in units of VVk/mole. The necessity to use the lengthy $\times 10^{-6}$ c.g.s.u. is eliminated.

The presently proposed notation leaves the right subscript position free for the additional notation necessary to specify tensor quantities. The principal susceptibilities of a crystal will be referred to with the numerical subscripts 1, 2, or 3: χ_1, χ_2, or χ_3, while for axial crystals $\chi_\parallel$ and $\chi_\perp$ may be used. The less useful quantities, the susceptibilities along the crystallographic axes will carry the axis designation as a subscript i.e. χ_a, χ_b, χ_c. It should be noted that when referred to the non-orthogonal coordinate systems of monoclinic and triclinic crystals, the susceptibility tensor is in general neither diagonal nor symmetric. The mathematics of such tensors has been discussed at length by Ghose[64G1,66G2-4], but their use is unnecessary and will not be considered further here. Of course the crystal axis susceptibilities can be obtained from Eqn. (6) and the principal susceptibility tensor provided the direction cosines of the particular axis with respect to the coordinate system of the principal magnetic axes is known. (Evaluate the magnitude of **I** and divide by the magnitude of **H**).

Principal molecular susceptibilities

From the chemical point of view the quantities of interest are the principal *molecular* susceptibilities. These are the susceptibilities of the individual molecules, ions or coordination complexes in the crystal referred to a molecule-fixed coordinate system. The subscripts x, y, and z will be reserved for principal molecular susceptibilities, χ_x, χ_y, and χ_z. For axially symmetric molecules the symbols $\chi_\parallel$ and $\chi_\perp$ may be used. These can be distinguished from the principal crystal susceptibilities $\chi_\parallel^{\mathrm{cryst}}$ and $\chi_\perp^{\mathrm{cryst}}$ by using a right superscript in the latter case if any confusion might result.

Triclinic case—A triclinic unit cell contains either a single assymmetric unit ($P1$) or two such units related by a center of symmetry ($P\bar{1}$). Except in extraordinary circumstances the assymmetric unit will consist of a single (or perhaps half a) magnetic unit (molecule). Since the direction cosines of the molecule-fixed coordinate axes with respect to a crystal lattice-fixed coordinate system for molecules related by a center of symmetry are identical, the principal molecular susceptibility axes coincide with the principal crystal susceptibility axes. The latter must be determined experimentally. This is generally more difficult for triclinic than for other crystal classes (see section D). Principal molecular susceptibilities may be determined for substances crystallizing in the triclinic system without a detailed knowledge of the crystal structure. However, the relationship between the principal molecular susceptibilities and the molecular structure cannot be known without complete structural information.

Monoclinic case.—Details of the relationships between the principal molecular and crystal susceptibilities for the various crystal classes have been discussed at length by Lonsdale and Krishnan[36L1]. Details of their treatment, which involves coordinate transformation matrices and a consideration of space group symmetry (equivalent position relationships), will not be repeated here. Only the results will be presented. It is convenient to consider an orthogonal crystal-fixed coordinate system. For monoclinic crystals *a*, *b*, and *c** form an appropriate reference system, where *c** is the reciprocal axis perpendicular to both real axes *a* and *b*. Relative to these axes the direction cosines of the principal molecular susceptibility axes χ_x, χ_y, and χ_z are:

$$\begin{array}{c} \\ \chi_x \\ \chi_y \\ \chi_z \end{array}\begin{array}{c} \begin{array}{ccc} a & b & c^* \end{array} \\ \begin{bmatrix} \alpha_x & \beta_x & \gamma_x \\ \alpha_y & \beta_y & \gamma_y \\ \alpha_z & \beta_z & \gamma_z \end{bmatrix} \end{array} \tag{14}$$

In terms of the above direction cosines the relationship between the principal molecular and crystal susceptibilities may be expressed in terms of three equations in three unknowns:

$$\begin{aligned} \chi_1 &= \tfrac{1}{2}\{a\chi_x + b\chi_y + c\chi_z + [(d\chi_x + e\chi_y + f\chi_z)^2 + (l\chi_x + m\chi_y + n\chi_z)^2]^{1/2}\} \\ \chi_2 &= \tfrac{1}{2}\{a\chi_x + b\chi_y + c\chi_z - [(d\chi_x + e\chi_y + f\chi_z)^2 + (l\chi_x + m\chi_y + n\chi_z)^2]^{1/2}\} \\ \chi_1 + \chi_2 + \chi_3 &= \chi_x + \chi_y + \chi_z \end{aligned} \tag{15}$$

where

$$\begin{array}{lll} a = \alpha_x{}^2 + \gamma_x{}^2 & d = \alpha_x{}^2 - \gamma_x{}^2 & l = 2\alpha_x\gamma_x \\ b = \alpha_y{}^2 + \gamma_y{}^2 & e = \alpha_y{}^2 - \gamma_y{}^2 & m = 2\alpha_y\gamma_y \\ c = \alpha_z{}^2 + \gamma_z{}^2 & f = \alpha_z{}^2 - \gamma_z{}^2 & n = 2\alpha_z\gamma_z \end{array} \tag{16}$$

The final equation of set (15) merely states the fact that the average molecular susceptibility is identical to the average crystal susceptibility. Eqns. (15) further assume that there is but a single molecule per assymmetric unit. Alternative solutions will occur and the correct one must be chosen on the basis of physical reasonableness.

Orthorhombic case.—The orthogonal coordinate system of the crystallographic axes is appropriate here. The direction cosines of the molecular coordinate system are defined as in Eqn. (14), except that c^* is replaced by c. The relationship between principal molecular and crystal susceptibilities is simply expressed

$$\begin{aligned} \chi_1 &= \chi_a = \sum (\chi_x {\alpha_x}^2 + \chi_y {\alpha_y}^2 + \chi_z {\alpha_z}^2) \\ \chi_2 &= \chi_b = \sum (\chi_x {\beta_x}^2 + \chi_y {\beta_y}^2 + \chi_z {\beta_z}^2) \\ \chi_3 &= \chi_c = \sum (\chi_x {\gamma_x}^2 + \chi_y {\gamma_y}^2 + \chi_z {\gamma_z}^2) \end{aligned} \tag{17}$$

where the summation is taken over all independently oriented molecules (not connected by symmetry operations inherent in the space group). In the usual case with one molecule in the assymmetric unit no summation is involved. Eqns. (17) provide three equations in three unknowns which may be solved for the principal molecular susceptibilities provided the crystal structure is known.

Axial crystal classes.—Unlike the triclinic, monoclinic and orthorhombic cases where three principal crystal susceptibilities are measurable, axial crystals provide only ${\chi_\parallel}^{\mathrm{cryst}}$ and ${\chi_\perp}^{\mathrm{cryst}}$. If the molecular magnetic unit has less than axial symmetry there is insufficient information available to determine χ_x, χ_y, and χ_z. Fortunately most axial crystals reflect the axial symmetry of the molecular subunit which generally has its principal axis aligned parallel to that of the crystalline lattice. In this case

$${\chi_\parallel}^{\mathrm{cryst}} = {\chi_\parallel}^{\mathrm{mol}} \text{ and } {\chi_\perp}^{\mathrm{cryst}} = {\chi_\perp}^{\mathrm{mol}} \tag{18}$$

For completeness we give here the general equations of Lonsdale and Krishnan for tetragonal, trigonal, and hexagonal crystal classes.

$$\begin{aligned} \chi_1 &= \chi_c = \chi_x {\gamma_x}^2 + \chi_y {\gamma_y}^2 + \chi_z {\gamma_z}^2 \\ \chi_2 &= \chi_3 = \chi_a = \chi_b = \frac{\chi_x}{2}({\alpha_x}^2 + {\beta_x}^2) + \frac{\chi_y}{2}({\alpha_y}^2 + {\beta_y}^2) + \frac{\chi_z}{2}({\alpha_z}^2 + {\beta_z}^2) \\ &= \tfrac{1}{2}(\chi_x - \chi_y - \chi_z - \chi_1) \end{aligned} \tag{19}$$

C. THEORY: THE MOLECULAR BASIS OF PARAMAGNETISM

The proper interpretation of magnetic anisotropy data requires the application of valid theory. The present section is concerned with developing the basic, generally applicable theory of paramagnetism of discrete molecular units. Magnetic dilution will be assumed and exchange interactions and antiferromagnetism will be ignored.

It is perhaps appropriate here to point out that magnetic anisotropy arises only in systems exhibiting appreciable orbital contributions to their magnetic moments. Very little can be learned from studies of systems whose effective magnetic moments correspond to "spin-only" values. For this reason the present discussion will be illustrated with the theory applicable to axially distorted cobalt(II) complexes. Complexes of this type exhibit the largest anisotropies found in the first transition series.

Van Vleck's Equation

In his classic 1932 book[32V1] Van Vleck laid the foundation of the molecular basis of paramagnetism. He developed a general equation applicable to almost any paramagnetic susceptibility or anisotropy experiment.

The magnetic moment μ_n of a molecule in electronic state n of energy E_n in a magnetic field H is by definition

$$\mu_n = -\frac{\partial E_n}{\partial H} \tag{20}$$

The standard statistical mechanical formula for the probability P_n that a molecule will be in state n is

$$P_n = \frac{\exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \tag{21}$$

where the summation is taken over all possible energy levels n, and it is assumed that all degeneracies are lifted making degeneracy factors unnecessary.

The molar intensity of magnetization ${}^{M}I$ is in effect the magnetic moment per mole and is thus given by

$${}^{M}I = \frac{N \sum_n \mu_n \exp(-E_n/kT)}{\sum_n \exp(-E_n/kT)} \tag{22}$$

where N is Avogadro's number and the energy of state n is expressed as a power series in the magnetic field strength.

$$E_n = E_n^{(0)} + E_n^{(1)} H + E_n^{(2)} H^2 + \cdots \tag{23}$$

Here $E_n^{(0)}$ is the energy of a state in the absence of an applied magnetic field, $E_n^{(1)}$ is the first order Zeeman (FOZ) coefficient.

$$E_{n,\alpha}^{(1)} = \beta\langle n|\hat{L}_\alpha + 2\hat{S}_\alpha|n\rangle \tag{24}$$

where α is in general x, y, or z; for axial symmetry $\alpha = \parallel$ or $\perp$, $\hat{L}_\alpha$ and $\hat{S}_\alpha$ are the orbital and spin angular momentum operators respectively, β is the Bohr magneton, and $|n\rangle$ represents the wave function of state n.

$E_n^{(2)}$, the second order Zeeman (SOZ) coefficient, is given by

$$E_{n,\alpha}^{(2)} = \sum_{m \neq n} \frac{\beta^2 \langle n|\hat{L}_\alpha + 2\hat{S}_\alpha|m\rangle^2}{E_n - E_m} \tag{25}$$

where the sum is taken over all states m other than n, and excludes states degenerate with

n in the absence of an applied field. Therefore from Eqn. (20)

$$\mu_n = -E_n^{(1)} - 2HE_n^{(2)} - \ldots \tag{26}$$

and

$${}^{\mathrm{M}}I = \frac{N\sum_n [-E_n^{(1)} - 2HE_n^{(2)}]\,[1-(HE_n^{(1)}/kT)]\exp(-E_n^{(0)}/kT)}{\sum_n \exp(-E_n^{(0)}/kT)\,[1-(HE_n^{(1)}/kT)]} \tag{27}$$

where the assumption is made that $HE_n^{(1)} \ll kT$ which allows the approximation:

$$\exp(-HE^{(1)}/kT) \simeq 1-(HE^{(1)}/kT) \tag{28}$$

Since paramagnetic systems exhibit no net magnetization in the absence of an applied magnetic field, ${}^{\mathrm{M}}I = 0$ at $H = 0$ leading to:

$$\sum_n E_n^{(1)}\exp(-E_n^{(0)}/kT) = 0 \tag{29}$$

Dropping terms in H^2 and higher, the result for the susceptibility Eqn. (2) is

$${}^{\mathrm{M}}\chi = \frac{{}^{\mathrm{M}}I}{H} = \frac{N\sum_n [((E_n^{(1)})^2/kT) - 2E_n^{(2)}]\exp(-E_n^{(0)}/kT)}{\sum_n \exp(-E_n^{(0)}/kT)} \tag{30}$$

In terms of the FOZ and SOZ coefficients Eqn. (30) becomes

$${}^{\mathrm{M}}\chi_\alpha = \frac{N\beta^2\sum_n\left\{\frac{\langle n|\hat{L}_\alpha + 2\hat{S}_\alpha|n\rangle^2}{kT} - 2\sum_{m\neq n}\frac{\langle n|\hat{L}_\alpha + 2\hat{S}_\alpha|m\rangle^2}{E_n - E_m}\right\}\exp(-E_n^{(0)}/kT)}{\sum_n \exp(-E_n^{(0)}/kT)} \tag{31}$$

In cases with no ground state orbital angular momentum and in which the ground multiplet is well separated from all excited states, i.e. the SOZ terms (Eqn. (25)) are negligible, it is easy to show that Eqn. (31) reduces to the well known spin-only formula

$$\chi_\alpha = \frac{N\beta^2 g_\alpha^2 S(S+1)}{3kT} \tag{32}$$

from which the common expression for the effective magnetic moment μ_{eff} derives:

$$\mu_{\mathrm{eff}} = 2.828[{}^{\mathrm{M}}\chi T]^{1/2} \tag{33}$$

where

$$\mu_{\text{eff}} = g[S(S+1)]^{1/2} \text{(in units of } \beta) \tag{34}$$

For the exactly spin-only case $g = 2$ and the magnetic moment and susceptibility are isotropic.

More interesting from the magnetic anisotropy point of view are cases where ground state orbital angular momentum does not vanish. Thermal population of excited levels often occurs and SOZ terms can make a heavy and temperature *dependent* contribution to the susceptibility and its anisotropy. Van Vleck's equation in its most general form must be used to interpret such susceptibility data. This is well illustrated by the example of trigonally distorted hexacoordinate cobalt(II).

The problem of calculating a susceptibility becomes one of evaluating matrix elements of the type $\langle n|\hat{L}_\alpha + 2\hat{S}_\alpha|n\rangle$ and $\langle n|\hat{L}_\alpha + 2\hat{S}_\alpha|m\rangle$ between wave functions appropriate to molecular orbitals (MO's) containing the unpaired electrons. Application of the phenomenological ligand field theory (or adjusted crystal field theory) is the most practical approach. This will be illustrated here. Matrix elements of the above type can be readily calculated for wave functions based on d^n free ion configurations, however this neglects the fact that the electrons are in MO's and spend some of their time on the ligand. This can be adequately taken into account by the orbital reduction factor k introduced by Stevens[53S1] and recently discussed at length by Gerloch and Miller[68G1]. By definition k is

$$k_\alpha = \frac{\langle\psi|\hat{L}_\alpha|\psi\rangle}{\langle\varphi|\hat{L}_\alpha|\varphi\rangle} \tag{35}$$

where ψ represents a MO and φ the metal atomic orbital (AO) which contributes to the MO. For an "ionic" complex where the magnetic electrons occupy pure AO's, $k_\alpha = 1.0$, while for real systems k_α will be somewhat below this value, generally in the range 0.6–1.0. The orbital reduction factor is a measure of covalency, however it is not accurately determined by most experiments and is sensitive to the details and approximations of the theory used to analyze the data. It is becoming increasingly evident that theoretical approximations of any sort severely affect the derived phenomenological parameters and in some cases the quality of fit of theory to experiment[69G1-2]. The present section will therefore be illustrated with a generally applicable and reasonably approximation free theory.

Weak field calculations. Trigonal cobalt(II) d^7 example.—The principal susceptibilities of the complex anion Co(acac)_3^- (acac = acetylacetonate anion) of D_3 symmetry have been measured in our laboratory[70H1]. This is basically a trigonally distorted octahedral d^7 system. Weak field calculations analogous to those to be described here may be readily made for other symmetries and electronic ground states.

The free ion wave functions for the ^4F and ^4P states of the form $|L,M_L,S,M_S\rangle$ are chosen as a basis set. The octahedral field, trigonal distortion, and spin-orbit coupling perturbations are then applied simultaneously and the resulting 40 x 40 matrix is diagonalized yielding 20 Kramers doublets and their wave functions. The effect of successive application of these perturbations is illustrated in Fig. 1. The matrix elements for the various perturbations between the basis set wave functions are obtained as follows.

Trigonally distorted octahedral field.—The matrix elements for the one electron d orbitals $[m_l = \pm 2, \pm 1, 0]$ are given by Ballhausen[62B1] for an octahedral field with a trigonal distortion (V_T), and involve the three phenomenological parameters Dq, $D\sigma$ and $D\tau$ as indicated below $\langle m_l | V_T | m_l \rangle$:

$$
\begin{aligned}
\langle \pm 2 | V_T | \pm 2 \rangle &= -(2/3)\, Dq + 2D\sigma - D\tau \\
\langle \pm 1 | V_T | \pm 1 \rangle &= (8/3)\, Dq - D\sigma + 4D\tau \\
\langle 0 | V_T | 0 \rangle &= -4Dq - 2D\sigma - 6D\tau \\
\langle \pm 2 | V_T | \mp 1 \rangle &= \langle \mp 1 | V_T | \pm 2 \rangle = \pm(10/3)\sqrt{2}\, Dq
\end{aligned}
\tag{36}
$$

Here Dq describes the splitting by the octahedral field, while $D\sigma$ and $D\tau$ account for the trigonal distortion.

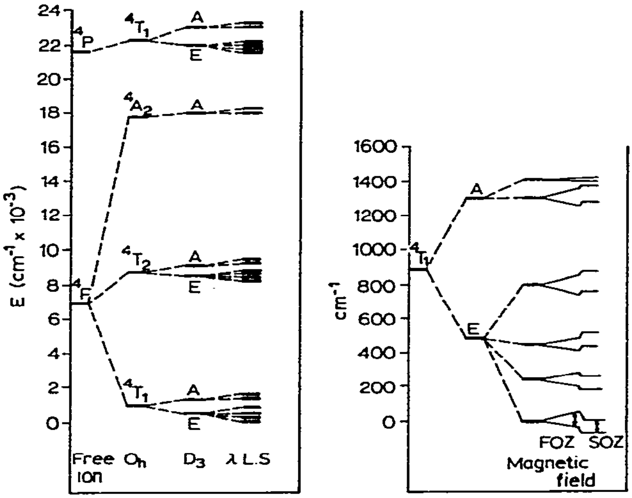


Fig. 1. Energy level diagram for trigonally distorted octahedral d^7 configuration showing the effect of successive perturbations. The parameter δ is the energy difference between the lowest A and E states (D_3). Detail of the splitting of the lowest $^4T_1$ level is shown on the right. The first order Zeeman (FOZ) and second order Zeeman (SOZ) effects of the applied magnetic field are shown schematically on an exaggerated scale.

The matrix elements for the many electron basis functions for the electrostatic interaction are readily calculated by expanding them as linear combinations of Slater determinants of the three hole configuration $(m_l^{(1)}, m_l^{(2)}, m_l^{(3)})$. These may be readily generated by ladder operator techniques[62B1]. Spin variables may be ignored for an electrostatic calculation so for $|L,M_L\rangle$ one has

$$\begin{aligned}
&{}^4F, L = 3\\
&|M_L\rangle\\
&|3\rangle = (2,1,0)\\
&|2\rangle = (2,1,-1)\\
&|1\rangle = (2/5)^{1/2}(2,1,-2) + (3/5)^{1/2}(2,0,-1)\\
&|0\rangle = (4/5)^{1/2}(2,0,-2) + (1/5)^{1/2}(1,0,-1)\\
&|-1\rangle = -(2/5)^{1/2}(-2,-1,2) - (3/5)^{1/2}(-2,0,1) \qquad (37)\\
&|-2\rangle = -(-2,-1,1)\\
&|-3\rangle = -(-2,-1,0)
\end{aligned}$$

$$\begin{aligned}
&{}^4P, L = 1\\
&|1\rangle = -(3/5)^{1/2}(2,1,-2) + (2/5)^{1/2}(2,0,-1)\\
&|0\rangle = -(1/5)^{1/2}(2,0,-2) + (4/5)^{1/2}(1,0,-1)\\
&|-1\rangle = (3/5)^{1/2}(-2,-1,2) - (2/5)^{1/2}(-2,0,1)
\end{aligned}$$

This yields a 10 x 10 perturbation matrix of the electrostatic interaction. It may be noted that the corresponding matrix for the d^2 configuration is identical save for a change in sign of all elements. A small amount of labor can be saved by generating it rather than the d^3 case. The quantity 15B (where B is the Racah interelectronic repulsion parameter) is added to the diagonal elements of the ${}^4P$ excited state. Its value may be varied with the stipulation only that it be less than the free ion value (B_0 for Co(II) = 1115 cm^{-1}).

Spin-orbit coupling.—The 40 x 40 matrix of spin-orbit coupling is readily written down for an interaction of the form,

$$\begin{aligned}
\lambda k \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} &= \lambda k_{\parallel} \hat{L}_z \hat{S}_z + \lambda k_{\perp}[\hat{L}_x \hat{S}_x + \hat{L}_y \hat{S}_y]\\
&= \lambda k_{\parallel} \hat{L}_z \hat{S}_z + \frac{\lambda k_{\perp}}{2}[\hat{L}_+ \hat{S}_- + \hat{L}_- \hat{S}_+]
\end{aligned} \qquad (38)$$

since the results of operating on $|L,M_L,S,M_S\rangle$ wave functions by the operators $\hat{L}_z, \hat{S}_z, \hat{L}_+, \hat{L}_-, \hat{S}_+$ and $\hat{S}_-$ are known[62B1]. The spin-orbit coupling constant λ is treated as a parameter in that it can assume values reduced in absolute magnitude from that of the free ion ($\lambda_0 = -172$ cm^{-1} for Co(II)). Provision is made for anisotropy in the orbital reduction factor by allowing independent variation of $k_\parallel$ and $k_\perp$ for the parallel and perpendicular direction respectively.

Energies of the twenty Kramers doublets.—These are obtained by diagonalizing the 40 x 40 matrix obtained by adding the 10 x 10 electrostatic matrix to the 40 x 40 spin-orbit matrix in such a way that the electrostatic matrix elements only connect functions with the same M_S values. The wave functions for the components of these Kramers doublets are given by the eigenvectors generated by standard digital computer diagonalization techniques.

Evaluation of magnetic properties.—In the calculation of $\chi_\parallel$ and $\chi_\perp$, matrix elements of the magnetic moment operators $\hat{\mu}_\parallel$ and $\hat{\mu}_\perp$ must be evaluated where

$$\hat{\mu}_\parallel = k_\parallel \hat{L}_z + 2\hat{S}_z$$

and

$$\hat{\mu}_\perp = k_\perp \hat{L}_x + 2\hat{S}_x = \frac{k_\perp}{2}(\hat{L}_+ + \hat{L}_-) + (\hat{S}_+ + \hat{S}_-)$$

Degenerate perturbation theory must again be applied, this time to the two components of each Kramers doublet. The magnetic moment operator serves as a perturbation in order to generate wave functions appropriate to a magnetic field applied respectively parallel and perpendicular to the molecular symmetry axis. Only the 2 x 2 matrices of the six lowest lying Kramers doublets need be diagonalized. These arise from the ${}^4T_1$ state of the octahedral complex and are the only ones which become thermally populated at ordinary temperatures. These operations are all readily accomplished by high speed digital computation. The matrix elements of Van Vleck's equation (31) are evaluated and the appropriate summations carried out also by computer. In this way $\chi_\parallel$ and $\chi_\perp$ are calculated as a function of the semiempirical phenomenological variables Dq, $D\sigma$, $D\tau$, B, λ, $k_\parallel$ and $k_\perp$. The parameters Dq and B, and to a lesser extent $D\sigma$, and $D\tau$ may be fixed to within reasonable limits by the electronic spectra. Values of λ and the orbital reduction factors $k_\parallel$ and $k_\perp$ must be chemically reasonable.

One desires to fit $\chi_\parallel$, $\chi_\perp$ and their temperature dependencies by suitable manipulation of the adjustable parameters. Unfortunately a unique set is not always obtainable. For instance a reasonable fit for the susceptibility anisotropy data of $\mathrm{Co(acac)_3}^-$ is found for the parameter set $Dq = 900, D\sigma = 300, D\tau = 50, B = 980$, $\lambda = -172$ (all in cm^{-1}), $k_\parallel = k_\perp = 1.0$. This fit is shown in Fig. 2. It predicts a trigonal field splitting δ of the ${}^4T_1$ state of 819 cm^{-1} with the E state lying lower. Alternatively, the same set of parameters except for $D\sigma = 400, D\tau = 500$ yields δ of 955 cm^{-1} and again results in reasonable agreement (see Fig. 2). Both of these are essentially "ionic" models using the free ion value of the spin-orbit coupling constant and no orbital reduction. This does not seem entirely reasonable chemically. Nevertheless the sense of the splitting, δ, of ${}^4T_1$ state and its approximate magnitude can be fairly confidently determined from this analysis. Even a detailed study of the electronic spectra would probably not yield this information[66P1].

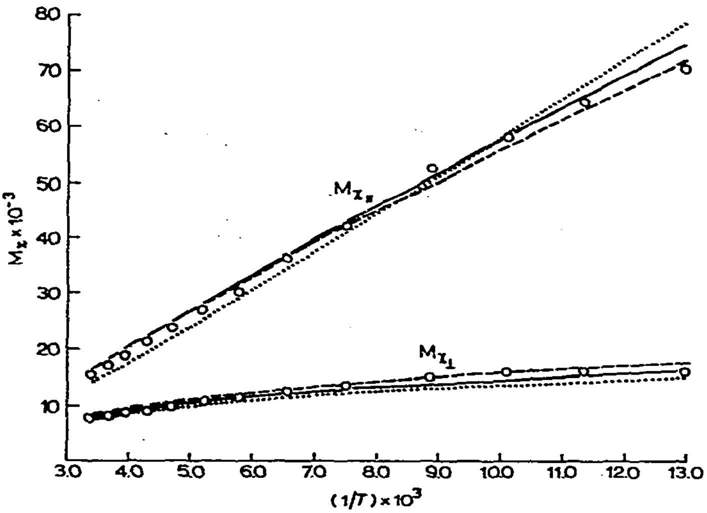


Fig. 2. Plots of $M_{\chi_\parallel}$ and $M_{\chi_\perp}$ versus $1/T$. The circles represent experimental points, the curves are calculated from theory for the following sets of phenomenological parameters (all energy quantities are in cm^{-1}). ——— : $Dq = 920, D\sigma = 500, D\tau = 50, B = 920, \lambda = -172, k_\parallel = k_\perp = 1.0$ ($\delta^{\mathrm{calc}} = 1175$, $g_\parallel^{\mathrm{calc}} = 7.45, g_\perp^{\mathrm{calc}} = 2.38$); -------- : $Dq = 900, D\sigma = 300, D\tau = 50, B = 980, \lambda = -172$, $k_\parallel = k_\perp = 1.0$ ($\delta^{\mathrm{calc}} = 819, g_\parallel^{\mathrm{calc}} = 7.18, g_\perp^{\mathrm{calc}} = 2.67$); .... : $Dq = 900, D\sigma = 50, D\tau = 100$, $B = 900, \lambda = -120, k_\parallel = k_\perp = 0.85$ ($\delta^{\mathrm{calc}} = 975, g_\parallel^{\mathrm{calc}} = 8.01, g_\perp^{\mathrm{calc}} = 1.40$). $g_\parallel^{\mathrm{exp}} = 8.01$, $g_\perp^{\mathrm{exp}} = 1.37$.

Relation to the g-values of an electron spin resonance experiment.—An *epr* experiment measures the energy separation ΔE of the components of a Kramers doublet when a magnetic field of a particular strength is applied in a given direction. When a magnetic field is applied, one component of the doublet, say a, with a negative μ increases in energy

$$E_a = -\mu_a H = \beta \langle a | k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha | a \rangle H$$

while the other, b, with a positive μ decreases in energy:

$$E_b = -\mu_b H = \beta \langle b | k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha | b \rangle H$$

Standard convention defines the g value

$$\Delta E = h\nu = g\beta H = E_a - E_b$$

so

$$g = \langle a | k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha | a \rangle - \langle b | k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha | b \rangle$$

or, in general, since

$$|\langle a | k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha | a \rangle| = |\langle b | k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha | b \rangle|$$

one has

$$g = 2|\langle n|k_\alpha \hat{L}_\alpha + 2\hat{S}_\alpha|n\rangle|$$

where $n = a$ or b, either component of the Kramers doublet. The FOZ contribution of the ith Kramers doublet to the susceptibility can be written as $[g_\alpha(i)]^2/4kT$ where this contribution is weighted by the fractional population of the doublet in question at a particular temperature. Thus a knowledge of the g-values of *all* the thermally populated doublets is equivalent to a knowledge of the FOZ contribution to the susceptibility. g-values, however, contain no information about the SOZ contributions to the susceptibility which turn out to be extremely important. In the examples cited SOZ contributes about 25% to the parallel and 82% to the perpendicular susceptibility at room temperature. The SOZ effect results in identical energy displacements for *both* components of each Kramers doublet upon application of a magnetic field, it therefore does not affect the resonance experiment. Thus there is an important difference in the information that can be obtained from *epr* and susceptibility experiments. Generally for hexacoordinate cobalt(II) complexes only the lowest lying Kramers doublet can be observed in an *epr* experiment. This occurs because in order to achieve a long enough electron spin-lattice relaxation time to observe a resonance signal, the experiment must be performed at liquid helium temperatures where only the lowest doublet is populated. The *epr* spectrum of the $Co(acac)_3^-$ ion as a dilute substitutional impurity in a diamagnetic host has been observed with the results: $g_\parallel = 8.01$ and $g_\perp = 1.37$. Using the theory described above with the following parameters:

$$Dq = 900, D\sigma = 50, D\tau = 100, B = 900, \lambda = -120, k_\parallel = k_\perp = 0.85$$

yields

$$g_\parallel^{\text{calc}} = 8.01, \quad g_\perp^{\text{calc}} = 1.40.$$

Unfortunately the fit to the susceptibility data using these parameters is inferior to those reported above as is shown in Fig. 2. It is of course quite possible that a set of parameters can be found that would produce better agreement between the two independent experiments, however as of this writing such a set has not been found.

Critique

The lack of satisfactory agreement between the phenomenological parameter sets necessary to describe both the susceptibility and *epr* experiments may arise from a number of sources. First of all there is no really satisfactory way to obtain a best fit since changes in the various parameters affect the calculated properties in highly coupled and non-linear ways. Secondly, although the phenomenological theory presented here is relatively assumption free, it is necessarily a *static* theory. The parameters themselves are not permitted to be functions of temperature. In a real complex the ligand atoms are undergoing vibrational motion which is affected by temperature and is ignored in the *static* theory. Indeed the breadth of the "*d–d*" electronic spectral bands arises largely from this source. At this stage of development it is clear that it is impossible to predict liquid helium *epr* spectra (*g*-values) from higher temperature susceptibility data or vice versa.

Despite this moderately pessimistic report on the theory, paramagnetic anisotropy studies can yield a great deal of information, much of which cannot be obtained in any other way. Paramagnetic anisotropy investigations are important in their own right in the direct evaluation of dipolar nuclear magnetic resonance shifts[70H2].

D. MEASUREMENT: DETAILED ANALYSIS OF THE CRITICAL TORQUE METHOD

Clearly almost any experimental method capable of measuring the magnetic susceptibility of solids could be adapted to the measurement of the principal susceptibilities of single crystals. These methods fall into two general categories (1) force methods such as Faraday or Gouy and (2) inductance methods such as the vibrating sample magnetometer. Recent reviews[63M2,64M2,68M2] of general methods in magnetochemistry are available and no extended discussion will be given here. Suffice it to say that sensitivity is a problem, considering the necessarily small sample size represented by a single crystal. The Gouy method generally employs macro samples and inductance methods tend to have low sensitivity as well as involving extensive instrumentation. Inductance methods have nevertheless been used to measure anisotropies in ferromagnetic and other substances, particularly at low temperatures. At present, however, they appear to be less satisfactory for measurements on paramagnetic substances over a large temperature range. The Faraday method, which measures directly the susceptibility in the direction of the magnetic field gradient of a crystal suspended in a region of constant $H(\partial H/\partial x)$ has been successfully adapted to measurements on single crystals, but an extremely sensitive force measuring device must be employed. The above cited reviews provide references to a number of suitable balances.

One of the most ingenious force methods adapted for the measurement of single crystal susceptibilities was invented by Rabi[27R1]. The method involves balancing out the translation tendency of a crystal suspended in a non-uniform magnetic field by immersing it in a bath, the susceptibility of which can be adjusted. At the balance point the susceptibility of the crystal in the direction of the magnetic field gradient and the bath fluid are identical, the susceptibility of the latter can be measured accurately by, say, the Gouy method. The requirement that the crystal be immersed in a bath poses technical problems (generally a solution saturated with respect to the substance being measured was employed) and severely limits the temperature range over which it can be employed. These practical considerations render this clever method unsuitable for general application.

When an arbitrarily oriented magnetically anisotropic sample is suspended in a uniform magnetic field it will generally experience a torque tending to align a direction of maximum susceptibility with the applied field. The measurement of such torques provides the basis for the determination of differences between principal susceptibilities and, when coupled with an average susceptibility measurement, the principal susceptibilities themselves. As described in some detail below, the measurement of the maximum magnetic torque acting on a suitably oriented crystal yields directly a principal anisotropy. Any appropriately sensitive torque measuring device would serve, with quartz torsion fibres representing extremely sensitive and readily available examples. The remainder of this section will be devoted to a method in which these are employed.

In our view Krishnan's critical torque or flip-angle method is the most satisfactory of the various techniques for measuring paramagnetic anisotropy in single crystals, at least at liquid nitrogen temperatures and above. The apparatus is simple and the method is sensitive. Differences in principal susceptibilities are observed directly, enabling even small anisotropies to be measured accurately. Although the method has been in use since the 1930's when it was introduced by Krishnan and Bannerjee[35K3], there is no readily available detailed discussion of the theory or technique of this method in the literature. Indeed, most papers reporting such measurements are practically devoid of experimental details. This section will develop the theory of the method, following in large measure the presentation of Gordon[58G1], and will outline the technique of measurement developed in our laboratories. The apparatus will be briefly described and the strategy employed for the various crystal classes will be detailed.

Theory

As a starting point the general equation[53P1,58G1] for the magnetic torque L_H exerted on an arbitrarily oriented body in a magnetic field will be taken.

$$L_H = -\int_{\text{vol.}} (\nabla\cdot\mathbf{I})(\mathbf{r}\times\mathbf{H})\,\mathrm{d}V + \int_{\text{surf.}} (\mathbf{r}\times\bar{\mathbf{H}})(\mathbf{I}\cdot\mathrm{d}S) \tag{39}$$

Here **I** is the intensity of magnetization, **r** a vector representing the position of a volume or surface element with respect to the origin, **H** the magnetic field, dV the differential volume element, and dS the differential element of surface. An anisotropic substance may experience a torque even if it is spherical or cylindrical in shape. The torque acting about a principal susceptibility axis on a sphere oriented with the external field $\mathbf{H}_0$ perpendicular to this axis is given by

$$L_H = \frac{V}{2}\left(\frac{3H_0}{\mu_1+2}\right)\left(\frac{3H_0}{\mu_2+2}\right)({}^V\chi_2 - {}^V\chi_1)\sin 2\theta \tag{40}$$

while that for a cylinder with $\mathbf{H}_0$ perpendicular to the cylinder axis which is also a principal magnetic axis is

$$L_H = \frac{V}{2}\left(\frac{2H_0}{\mu_1+1}\right)\left(\frac{2H_0}{\mu_2+1}\right)({}^V\chi_2 - {}^V\chi_1)\sin 2\theta \tag{41}$$

where in both Eqns. (40) and (41) V is the volume of the body, μ_1 and μ_2 and ${}^V\chi_1$ and ${}^V\chi_2$ are the principal permeabilities and volume susceptibilities in the plane perpendicular to the axis of torque, respectively, and θ is the angle the ${}^V\chi_1$ axis makes with the field direction. For dia- and paramagnetic substances the difference between the permeabilities μ_1 and μ_2 and unity may be neglected so both Eqns. (40) and (41) become

$$L_H = \frac{VH_0^2}{2}({}^V\chi_2 - {}^V\chi_1)\sin 2\theta \tag{42}$$

Thus there will be no magnetic torque for any orientation of a crystal if ${}^V\chi_1 = {}^V\chi_2$; when these quantities are unequal L_H vanishes at $\theta = 0$ and $\pi/2$ and is maximum at $\theta = \pi/4 = 45°$. Eqn. (42) holds strictly only for spheres and cylinders.

A typical critical torque experiment may be readily visualized by reference to Eqn. (42). The crystal is suspended from a quartz torsion fiber with a principal magnetic axis (χ_3) parallel to the fiber. With the magnetic field on (assuming $\chi_1 > \chi_2$) the crystal is allowed to come to its equilibrium position with the direction of χ_1 parallel to $H(\theta = 0°)$. A fiber torque L_f is then applied to the crystal by turning the torsion head to which the upper end of the fiber is affixed (though an angle α from its original point). This fiber torque is opposed by the magnetic torque L_H, however the crystal will turn through some angle θ as a result of this and will be in stable equilibrium with $L_H = L_f$ for $\theta < \pi/4$. Continued increase of L_f by increasing α causes θ to increase until at $\theta = \pi/4$, L_H begins to decrease while L_f continues to increase. At this point stable equilibrium is no longer maintained, the crystal begins to turn rapidly in the direction of increasing α (and θ), kinetic energy causes the crystal to spin until the fiber is partially or completely unwound and the crystal is again caught in a stable situation with $L_H = L_f$. The magnetic anisotropy is quantitatively related to α_{cr}, the critical value of α at which the flipping occurred as described below.

The general case.—Consider a spherical crystal (volume V, mass m) of anisotropic dia- or paramagnetic substance residing in a homogeneous magnetic field **H**. Differences in the direction and magnitude of the magnetic field within and without the crystal are considered negligible for the present purposes, the principal volume magnetic susceptibilities ${}^V\chi_1$, ${}^V\chi_2$, ${}^V\chi_3$, being small compared with unity. Integration of Eqn. (39) yields

$$\mathbf{L} = V({}^V\mathbf{I} \times \mathbf{H}) \tag{43}$$

or in terms of molar quantities

$$\mathbf{L} = (m/M)({}^M\mathbf{I} \times \mathbf{H}) \tag{44}$$

where M is the molecular weight of the substance in question.

Let vectors **1**, **2**, and **3** be the mutually orthogonal principal magnetic axes of the crystal sphere (see Section B). Let **i**, **j**, and **k** be three other orthogonal unit vectors with **k** vertical (fiber axis), **i** is in the direction of the magnetic field **H**, and **j** completes a right handed coordinate system. Σ is the plane containing the **i** and **j** axes and Π is the plane containing the **1** and **2** axes. Let Ψ, φ and θ be the Eulerian angles defining the orientation of the **1**-**2**-**3** coordinate system with respect to the **i**-**j**-**k** system. These relationships are shown in Fig. 3. In general Ψ and φ will be fixed for a given crystal mounting and θ will vary during the experiment corresponding to a rotation of the spherical crystal

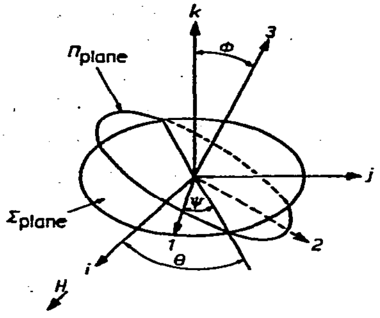


Fig. 3. Coordinate system relationships.

about the k axis. The magnetic torque tending to turn the sphere about the vertical k axis is given by Eqn. (45).

$$\begin{aligned}
&L_H = (mH^2/2M)(\mathrm{A}\sin 2\theta + \mathrm{B}\cos 2\theta)\\
&\mathrm{A} = {}^{\mathrm{M}}\chi_1(\cos^2\varphi\sin^2\Psi - \cos^2\Psi) + {}^{\mathrm{M}}\chi_2(\cos^2\varphi\cos^2\Psi - \sin^2\Psi) + {}^{\mathrm{M}}\chi_3\sin^2\varphi\\
&\mathrm{B} = ({}^{\mathrm{M}}\chi_1 - {}^{\mathrm{M}}\chi_2)\cos\varphi\sin 2\Psi
\end{aligned} \tag{45}$$

It is apparent that if the principal magnetic axis 3 is coincident with k (i.e. vertical) that $\varphi = 0$, $\Psi = 0\,({}^{\mathrm{M}}\chi_1 > {}^{\mathrm{M}}\chi_2)$, and Eqn. (45) reduces to Eqn. (42).

The critical torque experiment.—Let the spherical crystal be suspended by an untwisted quartz fiber of torsion constant K, let the initial position of the sphere designated $\theta = \theta_0$, be the position at which the magnetic torque L_H is zero. Then from Eqn. (45):

$$\tan 2\theta = -\frac{\mathrm{B}}{\mathrm{A}} \tag{46}$$

When the free end of the fiber is twisted through an angle α, measured positively in the same direction as θ, the quartz fiber then exerts a torque L_f on the sphere about the k axis given by

$$L_f = K(\alpha - \theta + \theta_0) \tag{47}$$

The total torque L_t tending to turn the sphere about the k axis is the sum $L_H + L_f$. If L_t is positive the sphere tends to turn in the direction of increasing θ, if negative in the opposite direction. In order for a stable equilibrium to exist not only must L_t vanish but its partial derivative with respect to θ, α being kept constant, must be negative. Expressed mathematically this amounts to

$$\left(\frac{\partial L_t}{\partial\theta}\right)_\alpha = -K + \frac{mH^2}{M}(\mathrm{A}\cos^2 2\theta - \mathrm{B}\sin^2 2\theta) \leqslant 0 \tag{48}$$

If the sphere is initially at equilibrium ($L_t = 0$) and α is increased by turning the torsion head at the top of the fiber, the sphere will turn (increasing θ) in order to reduce the net torque to zero. As θ is increased in this manner a point will be reached at which the derivative in Eqn. (48) becomes zero, a further slight increase causes the derivative to become positive. Since L_H is now beginning to decrease, a positive torque will act on the crystal tending to make θ still larger. The crystal will begin to spin at this point and owing to kinetic energy this spinning will continue until the fiber is partially or completely unwound and a new stable equilibrium is attained. The critical values of the angles α and θ at which this spinning or flipping begins will be designated α_{cr} and θ_{cr}. At this point the fiber is exerting maximum torque, and the following relations hold.

$$\left(\frac{\partial L_t}{\partial \theta}\right)_\alpha = 0;\ L_t = 0 \text{ at } \alpha = \alpha_{cr} \text{ and } \theta = \theta_{cr} \tag{49}$$

$$\tan 2\theta_{cr} = \frac{B + 2A(\alpha_{cr} - \theta_{cr} + \theta_0)}{-A + 2B(\alpha_{cr} - \theta_{cr} + \theta_0)} \tag{50}$$

The special cases of Eqn. (45) useful in determining principal crystal susceptibilities will now be considered.

First special case. Principal axis parallel to the axis of rotation.—Let principal axis 3 be parallel to the rotation axis k (see Fig. 3) so that $\Phi = 0$. The angle θ may now be defined as the angle between the field direction i and the 1 axis, making Ψ zero. Since $L_t = L_H + L_f$ one has from Eqn. (45), noting that $B = 0$

$$L_t = K(\alpha - \theta + \theta_0) + \frac{mH^2}{2M}({}^{M}\chi_2 - {}^{M}\chi_1)\sin 2\theta \tag{51}$$

and from the general relations (49) and (50) at critical torque it follows that

$$\cos 2\theta_{cr} = \frac{KM}{mH^2({}^{M}\chi_2 - {}^{M}\chi_1)} \tag{52}$$

and

$$\tan 2\theta_{cr} = -2(\alpha_{cr} - \theta_{cr} + \theta_0) \tag{53}$$

Since $(\chi_2 - \chi_1)$ is negative and $\alpha_{cr} > \theta_{cr}$ it is clear that θ_{cr} lies between $\pi/4$ and $\pi/2$. In practice the numerator of Eqn. (52) is small compared with the denominator and little error is introduced in assuming $\theta_{cr} = \pi/4$. Eqn. (53) shows that the difference between θ_{cr} and $\pi/4$ may be neglected safely when α_{cr} is greater than 4π or so.

In the first special case the axis of suspension is parallel to a principal susceptibility and the anisotropy is given by:

$$({}^{M}\chi_1 - {}^{M}\chi_2) = \frac{2KM(\alpha_{cr} - \pi/4)}{mH^2} \tag{54}$$

where it is assumed that ${}^{\mathrm{M}}\chi_1 > {}^{\mathrm{M}}\chi_2$ and α_{cr} is measured from a zero point where the crystal is in equilibrium (the 1 axis parallel to the field with no applied fiber torque, i.e. $\theta_0 = \alpha_0 = 0$).

Eqn. (54) is useful for all measurements on crystals suspended from the unique (C_2, b) axis of a monoclinic crystal. In such cases the principal magnetic axis is determined by crystal symmetry and the crystal may be conveniently oriented by X-ray methods.

Second special case. Principal axis perpendicular to the axis of rotation.—In this case φ is not necessarily zero, but Ψ is. Let the axis of rotation be somewhere between the 2 and 3 axes and perpendicular to the 1 axis. Then from Eqns. (45) and (47) the total torque becomes

$$L_t = K(\alpha - \theta + \theta_0) + \frac{mH^2}{2M}({}^{\mathrm{M}}\chi_2 \cos^2\varphi + {}^{\mathrm{M}}\chi_3 \sin^2\varphi - {}^{\mathrm{M}}\chi_1) \sin 2\theta \tag{55}$$

The value of θ_{cr} is determined by Eqns. (49) and (50), and one obtains:

$$({}^{\mathrm{M}}\chi_2 \cos^2\varphi + {}^{\mathrm{M}}\chi_3 \sin^2\varphi - {}^{\mathrm{M}}\chi_1) = -\frac{2KM(\alpha_{\mathrm{cr}} - \pi/4)}{mH^2 \sin 2\theta_{\mathrm{cr}}} \tag{56}$$

If the $L_H = 0$, $L_f = 0$ stable equilibrium position θ_0 corresponds to the 1 principal axis parallel to the field ($\theta_0 = 0$) then $\theta_{\mathrm{cr}} = \pi/4$ and $\sin 2\theta_{\mathrm{cr}} = +1$, but if the 1 principal axis aligns itself perpendicular to the field ($\theta_0 = \pi/2$) then $\theta_{\mathrm{cr}} = 3\pi/4$ and $\sin 2\theta_{\mathrm{cr}} = -1$. Direct use of Eqn. (56) requires the knowledge of the value of the angle φ, the determination or the elimination of which is discussed in the section on strategy for monoclinic crystals.

Method of obtaining principal susceptibilities from critical torque data

Before discussing the apparatus or experimental techniques, an outline of the approach to determining principal *crystal* susceptibilities from critical torque data will be outlined. Since this method directly provides only differences in principal susceptibility values some additional information is required. This is provided by an independent measurement of the average susceptibility $\bar{\chi}$, which may be obtained by a Gouy or Faraday measurement on a powdered sample of the substance involved. Eqn. (57) provides the additional information necessary to yield the principal susceptibilities:

$${}^{\mathrm{M}}\bar{\chi} = \tfrac{1}{3}({}^{\mathrm{M}}\chi_1 + {}^{\mathrm{M}}\chi_2 + {}^{\mathrm{M}}\chi_3) \tag{57}$$

Strategy for axially symmetric crystals.—Tetragonal, trigonal, and hexagonal crystals require only measurement of ${}^{\mathrm{M}}\bar{\chi}$ and $({}^{\mathrm{M}}\chi_\parallel - {}^{\mathrm{M}}\chi_\perp)$. The latter quantity is obtained by mounting the crystal with the axis of suspension perpendicular to the principal crystallographic axis (i.e. the a or b axis of a tetragonal crystal vertical). ${}^{M}\chi_{\parallel}$ and ${}^{M}\chi_{\perp}$ are the two unknowns which may be obtained from a simultaneous solution of Eqns. (58),

$$\begin{aligned} &\tfrac{1}{3}({}^{M}\chi_{\parallel} + 2\,{}^{M}\chi_{\perp}) = {}^{M}\bar{\chi} \\ &{}^{M}\chi_{\parallel} - {}^{M}\chi_{\perp} = a \end{aligned} \tag{58}$$

where the value a is obtained from the critical torque experiment by application of Eqn. (54).

Strategy for orthorhombic crystals.—The principal magnetic axes are again all crystallographically determined. From the average susceptibility and critical torque measurements with the crystal mounted parallel to each of the three crystallographic axes, four equations are obtained:

$$\begin{aligned} &\tfrac{1}{3}({}^{M}\chi_{a} + {}^{M}\chi_{b} + {}^{M}\chi_{c}) = {}^{M}\bar{\chi} \\ &({}^{M}\chi_{a} - {}^{M}\chi_{b}) = a \\ &({}^{M}\chi_{a} - {}^{M}\chi_{c}) = b \\ &({}^{M}\chi_{b} - {}^{M}\chi_{c}) = c \end{aligned} \tag{59}$$

The first and any two of the remaining three serve to determine the three unknowns, the remaining measurement can serve as a useful check.

Strategy for monoclinic crystals.—Since the only convenient and accurate method of aligning crystals is by X-ray crystallographic techniques, it is desirable to mount crystals with a real crystallographic axis parallel to the axis of suspension. For monoclinic crystals there are three unknowns, ${}^{M}\chi_1$, ${}^{M}\chi_2$ and ${}^{M}\chi_3$. For the purpose of the present discussion let the 1 axis be parallel to the unique (*b*) monoclinic axis. The crystal may be suspended with the *b* axis perpendicular and the $({}^{M}\chi_3 - {}^{M}\chi_2)$ difference determined via Eqn. (54). An additional measurement is necessary in order to determine the unknowns. One possibility is to suspend the crystal from the *a* or *c* crystallographic axis (which are each perpendicular to the principal axis $b \equiv 1$), and employ Eqn. (56). An accurate knowledge of the angle φ is necessary in this case. This may be obtained by suspending the crystal with the *b* axis vertical and directly observing the angle between 3 (either parallel or perpendicular to the field direction when no fiber torque is applied) and the *a* or *c* crystal axis about which suspension is to be made in the second measurement. An arrangement involving a set of mirrors (sides of a right hexagonal prism mounted coaxially with the fiber) has been described[66T1] and should be useful in measuring this angle accurately with the aid of a collimated beam of light.

An alternative method has been outlined[58G1] which eliminates the necessity of measuring the angle φ. Again the crystal is mounted with the *b* axis vertical to yield $({}^{M}\chi_3 - {}^{M}\chi_2)$. Then it is mounted with $b \equiv 1$ horizontal, φ having some arbitrary value, it is then remounted, again with *b* horizontal, but with φ altered by exactly 90°. The three measurements yield the three equations:

$$\begin{aligned} &{}^{M}\chi_3 - {}^{M}\chi_2 = a \\ &{}^{M}\chi_2 \cos^2\varphi + {}^{M}\chi_3 \sin^2\varphi - {}^{M}\chi_1 = b \\ &{}^{M}\chi_2 \sin^2\varphi + {}^{M}\chi_3 \cos^2\varphi - {}^{M}\chi_1 = c \end{aligned} \tag{60}$$

which along with the ${}^{M}\bar{\chi}$ measurement yield four independent equations determining ${}^{M}\chi_1$, ${}^{M}\chi_2$, ${}^{M}\chi_3$ and the angle φ.

$$\begin{aligned} &\tfrac{1}{3}({}^{M}\chi_1 + {}^{M}\chi_2 + {}^{M}\chi_3) = {}^{M}\bar{\chi} \\ &({}^{M}\chi_3 - {}^{M}\chi_1) = \tfrac{1}{2}(a + b + c) \\ &({}^{M}\chi_2 - {}^{M}\chi_1) = \tfrac{1}{2}(b + c - a) \\ &\cos 2\varphi = (c - b)/a \end{aligned} \tag{61}$$

This latter method requires that one be able to mount accurately a crystal at exactly 90° from a previous setting and still perpendicular to the *b* axis.

Strategy for triclinic crystals.—In this case none of the principal magnetic axes are crystallographically determined and the problem is more complex. Krishnan and Mookherjee[36K2,38K5] describe a trial and error method, but such procedures are not recommended. Ghose, in an extensive series of papers[64G1,66G2–5], describes some tensor methods which may be applied to triclinic crystals. The methods described in Refs. 64G1, 66G2 and 66G3 all require a knowledge of the magnitude of one principal susceptibility, this quantity cannot be obtained by the critical torque method. The procedure described in Ref. 66G4 is a general one by which both the directions and magnitudes of the principal susceptibilities may be obtained from critical torque measurements and a knowledge of the average susceptibility. Space does not permit a complete exposition of the theory of the method here, however a brief description will be given. The magnetic susceptibility tensor in an arbitrary orthogonal coordinate system is symmetric and has six unique elements (see section B): χ_{11}, χ_{12}, χ_{13}, χ_{22}, χ_{23}, and χ_{33}. Their measurement in general requires at least six experimental observations. Ghose[66G4] has shown that they may be determined from the bulk susceptibility and five anisotropy measurements. If *x* and *y* represent a crystal fixed coordinate system (say *a* and *b** of a triclinic crystal), then the elements of the susceptibility tensor may be obtained by measurement of the anisotropy in five different planes, the normals (axes of suspension) to which all lie in the *xy* plane. For maximum accuracy adjacent normals should make angles of 36° with one another. The principal susceptibilities can be obtained by diagonalizing the general susceptibility tensor, this procedure also yields their directions. This method appears to be the best so far derived for triclinic crystals, however no examples of its application appear in the literature.

Ghose[66G5] has also described a method for triclinic crystals which contain axially symmetric molecules or ions. This method can be employed if the orientation of these magnetic subunits is known from X-ray data. Similar procedures have been employed for monoclinic crystals[68F1]. They are not to be recommended since they prejudice the experimentalist. Methods which do not involve any assumptions about molecular magnetic axes are much to be preferred. A check is then provided when the molecular quantities are obtained and compared with the expectations of chemical intuition.

Apparatus

The apparatus necessary for critical torque measurements is extremely simple and a number of adequate descriptions appear in the literature[66T1,58G2,66F1]. Only a brief description of the apparatus used in the authors' laboratory will be given here. It consists of a torsion head, calibrated in hundreths of a revolution mounted coaxially with a drill chuck whose height is adjustable, the upper bearing of the torsion head is a revolution counter. Just below the torsion head is a pulley which allows the head to be turned via an O-ring belt from a variable slow speed electric motor which is mounted separately on an adjacent wall to minimize vibrations. The quartz torsion fiber and crystal mounting assembly are hung from the drill chuck as will be described in more detail in the section on technique. The crystal hangs in a region of homogeneous magnetic field produced by a 4 in. electromagnet. A draft shield is arranged to enclose completely the fiber and crystal mounting assembly. The upper part of this shield consists of a plexiglass box while the lower portion is a 2 in. diameter glass tube closed at the lower end. No problems with electrostatic charges are encountered with the crystal and fiber suitably far away from the shield. For variable temperature work the lower part of the draft shield is replaced by a cryostat of published design[59F1] which also serves for Gouy measurements.

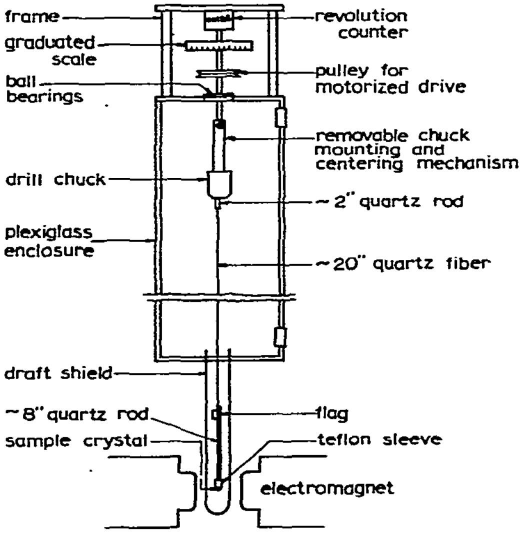


Fig. 4. Critical torque apparatus.

Technique

While the critical torque experiment is one of the simplest conceivable, it is nevertheless an extremely delicate one. Considering the grief to be caused by the destruction of a calibrated fiber, it is worthwhile to follow a technique designed to minimize the danger of accidental fiber breakage. The methods developed in our laboratory have proved quite successful (as of this writing we have yet to break a fiber) and will be described in some detail. The literature is virtually devoid of helpful experimental hints.

The crystal mounting-fiber assembly consists of the following (starting at the top): a quartz rod (5 cm long, 1 mm diameter) which is held in the drill chuck, the fiber (20 in. long, 10–20 μ diameter), a second quartz rod (20 cm long, 1 mm diameter), a cylindrical teflon sleeve (1.1 cm long, 1 mm internal, 3 mm outer diameter). The quartz fiber (supplied by Worden Laboratories, Houston, Texas) is attached to the quartz rods at both ends with a thermoplastic adhesive (Apiezon "W" wax) in the following manner. The fiber is stretched out on a soapstone slab and held down with two bits of masking tape. The Apiezon wax is applied to the rods with the aid of a hand held torch. The rod is placed coaxially with the fiber which is made to adhere to the rod with the aid of additional heating. With the quartz rods attached to each end of the fiber the upper rod is placed in the drill chuck. The whole assembly is held in a clamp so that the bottom hangs free just over a table top. A particularly convenient and safe means of mounting and demounting crystals is then possible.

The crystal to be measured is mounted on one end of the teflon sleeve with the aid of glyptal or other cement. This sleeve is constructed to fit snugly over a brass jig which seats coaxially into a standard goniometer head (with both adjustable arcs set to 0°). An oscillation photograph taken on a Weissenberg camera serves as a check on the crystal alignments in its final mounting configuration. The sleeve and affixed crystal are mounted on the lower quartz rod by the following procedure. The tension on the fiber is removed by a slight upward pressure on the bottom of the lower rod which is then clamped securely. The teflon sleeve upon which the crystal is mounted is slipped over the rod and held by friction and a little silicone grease. In this way the crystal-sleeve axis is positioned accurately parallel to the fiber direction. The lower quartz rod is carefully unclamped and the mounted crystal allowed to hang freely. The whole assembly is transferred to the torsion apparatus and the drill chuck is secured to the torsion-head axis with a nylon set screw. The door in the upper draft shield is closed and the tubular glass shield brought carefully up from below and clamped into position. Alternatively, the variable temperature cryostat, mounted in a wooden stand secured to a laboratory jack is carefully raised from below the crystal and securely clamped in its final position. The jack and wooden stand are then lowered and removed. All of these operations are accomplished with the magnet wheeled out of the way on a short railway designed for this purpose. The magnet is then moved into position and the experiment may proceed. The movable magnet feature is essential, since a successful "threading" of the fiber and crystal down the orifice of the cryostat would be virtually impossible. The above described procedure is reversed for demounting the crystal.

Calibration.—An absolute calibration of a torsion fiber can be achieved by causing it to act as a torsion pendulum. Elaborate instructions for such procedures are available[58G1,53D1]. Such an undertaking is tedious and unless elaborate precautions are taken and it is accomplished in vacuo it is fraught with errors. A more satisfactory procedure is to determine the fiber constant, K, by performing the experiment on a crystal of known anisotropy. Such a calibrant crystal can be kept permanently mounted on a sleeve for use in calibrating a number of fibers.

For measurements on paramagnetic unknowns it is desirable to use a paramagnetic calibrant in order for the anisotropies to be of the same order of magnitude, however, diamagnetic crystals have sometimes been used.

$NiSO_4 \cdot 6H_2O$ has been used by us as a calibrant. Its anisotropy has been measured in a number of laboratories with good agreement among recent measurements. It has the added advantages of being readily available and tetragonal so that a mounting on the a or b axes is easily achieved. The value[58B1] $\Delta^M\chi = 80.8$ VVk/mole appears to be the most reliable. Any substance of accurately known anisotropy may of course be used.

Before any calibration or measurements can be done it must be determined to what extent the fiber-rod-sleeve assembly possesses anisotropy. By boiling the teflon sleeve in hydrochloric acid such anisotropy was generally reduced to below one revolution ($\alpha_{cr} < 2\pi$). Corrections for these non-negligible flip angles were made by adding the quantity $-\alpha_0 \cos 2\epsilon$ to the α_{cr} obtained with a crystal mounted on the assembly. Here ϵ is the angle ($\leqslant \pi/2$) between the equilibrium angles (θ_0) for the assembly alone and for the assembly with affixed crystal. Since α_{cr} values for crystals are generally in excess of 20 turns (40π) and often in the hundreds, this form of correction is sufficiently accurate.

The experiment

In essence this consists of finding α_{cr}. First of all the fiber torque free equilibrium position must be determined. Both this and the moment of flip observation are aided by having a small flag (a piece of masking tape has been found satisfactory) affixed to the top of the lower quartz rod. The angular setting of the torsion head at which no motion of the flag is observed upon turning the field on and off serves to determine this equilibrium position ($\theta = \theta_0$), $\alpha = \alpha_0 = 0$. With the field on a rough value of α_{cr} is determined by driving the torsion head with the motor until flipping occurs as detected by the motion of the flag. With the field off the crystal is returned to the fiber torque free equilibrium position, the field is turned on and the experiment repeated. This time the torsion head is motor driven until within about two revolutions of α_{cr}, it is then turned slowly by hand, until flipping occurs. Care must be taken to avoid vibrations and oscillations which occasion premature flips. Values of α_{cr} are generally reproducible to within 15 or 20 degrees which is entirely satisfactory for values of α_{cr} of several revolutions.

Errors.—The determination of principle susceptibility values by the critical torque method involves a great many sources of error. A rigorous error analysis is virtually impossible, but it is useful to be aware of the principal causes of uncertainty in the final result. These are outlined below.

(a) Orientation errors. Gordon[58G1] has given expressions by which the magnitude of error introduced by a slight misalignment in the suspension of the crystal may be obtained. For a principal axis vertical (Eqn. (54)) the error E is given by

$$\begin{aligned} E &= \varphi^2({}^{M}\chi_1 \sin^2 \Psi + {}^{M}\chi_2 \cos^2 \Psi - {}^{M}\chi_3) \\ E &\leqslant \varphi^2(\Delta^{M}\chi_{\max}) \end{aligned} \qquad (62)$$

where $\Delta^{M}\chi_{\max}$ is the numerically largest anisotropy. For a suspension with a principal axis horizontal (Eqn. (56)) the estimated error is

$$\begin{aligned} E &= \Delta\varphi({}^{M}\chi_3 - {}^{M}\chi_2) \sin 2\varphi + \Psi^2({}^{M}\chi_1 - {}^{M}\chi_2)(1 + \cos^2 \varphi) \\ E &\leqslant (\Delta\varphi + 2\Psi^2) \ (\Delta^{M}\chi_{\max}) \end{aligned} \qquad (63)$$

where $\Delta\varphi$ is a slight error in φ. For small angular errors ($< 3°$) such errors will generally amount to less than a percent. Using X-ray techniques and the coaxial suspension method described in the *technique* section such errors will be negligible.

(b) Shape anisotropy. All of the equations given above are strictly valid only for spherical crystals. In practice it is rarely feasible to obtain crystals of this shape. Shape anisotropy has been investigated experimentally by Majumdar[62M1] using magnetically isotropic crystals of nonspherical shape and various dimensions. Gordon[58G1] has considered the same problem theoretically. Such errors are expected to be small in any case and can be minimized by choosing regular crystals with approximately equal dimensions in all directions. Thin plates and needles mounted crosswise are to be avoided.

(c) Ferromagnetic impurities. These can be a problem, particularly if the crystal suspension assembly (rod and sleeve) contains a considerable mass of quartz. The symptoms are: non-negligible flip angles with the crystal absent, unusual field strength dependence ($H^{\frac{1}{2}}$ at low field strengths and constant at higher fields), and, in our experience, significantly different flip angles for clockwise and counter-clockwise rotation of the crystal and/or the assembly. Manufacture of the crystal mounting sleeves from teflon followed by washing with hydrochloric acid reduced this problem to tolerable proportions which could be adequately corrected for (see *The experiment* section above).

(d) Weighing and composition of the single crystal. Since crystals suitable for flip-angle experiments generally weigh between 1 and 20 mg, it is necessary to weigh masses of this size accurately to as many significant figures as possible. A quartz torsion balance (i.e. Precision Torque Balance (± 0.002 mg) by Vereenigde Draadfabrieken Nijmegen, Holland) is quite satisfactory. Any given crystal may not be representative of the sample from which it is taken. The error introduced by such minor variations can be estimated by performing measurements on several different crystals.

(e) Magnetic field. The magnetic field must be homogeneous and accurately reproducible from experiment to experiment. The flip-angle depends on H^2 making this factor critical. The calibrations and all measurements must be performed in the same homogeneous magnetic field. The use of high quality electromagnets and stabilized power supplies is a must.

(f) Average susceptibility. Since the principal susceptibility values cannot be obtained without a knowledge of this quantity they are no more accurate than this. All

the sources of error which contribute to the Gouy or Faraday methods of measuring $\bar{\chi}$ affect the principal susceptibility values.

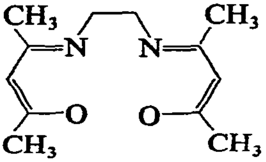
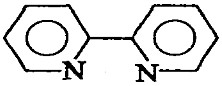
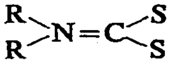
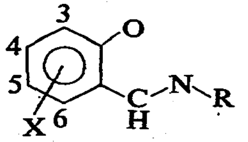
While the many sources of error can be minimized or estimated, it is doubtful whether principal susceptibility values can be obtained with less than about 3% error. Of course the absolute accuracy can be no better than that of the substance taken as calibrant.

E. TABULATION OF ANISOTROPY DATA

This section provides a list of compounds and references to paramagnetic anisotropy data reported in the literature. It is believed to be reasonably complete through 1969*. Mention is made only of quantitative work; all the early qualitative research has been excluded. The literature search was restricted to paramagnetic substances. The fairly extensive literature on diamagnetic, ferromagnetic, and anti-ferromagnetic substances is excluded, although certain materials in the last category are mentioned if measurements on a paramagnetic region were reported.

The compounds are listed according to the central metal, in the order of increasing atomic number for the transition and lanthanide elements, a brief listing of minerals then follows. No references were found to measurements on compounds of the actinides. The order of compound listing under a particular element and the reference format is analogous to that used by König in his compilation of magnetic data[66K2].

The abbreviations employed are listed below.

acac	acetylacetonate anion [$CH_3COCHCOCH_3$]
baed	bis(acetylacetone)ethylenediimine anion 
bipy	2,2′-bipyridyl 
R_2-dtc	*N,N*-dialkyldithiocarbamate 
en	ethylenediamine, $NH_2CH_2CH_2NH_2$
mesityl	$(CH_3)_3C_6H_2-$
N-t-butyl-sal	 R = t-butyl X = H

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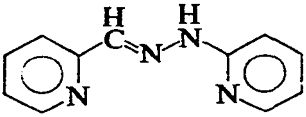
* Note added in proof: The authors have inserted some additional references in proof to bring the tabulation more up to date.

N-i-propyl-sal	R = i-propyl X = H
5-Cl-N-B-sal	R = β-(diethylamino)ethyl, $-CH_2CH_2N(CH_2CH_3)_2$ X = 5-Cl
paphy	pyridine-2-aldehyde-2-pyridylhydrazone



ph	phenyl, C_6H_5-
sacsac	dithioacetylacetonate anion $[CH_3CSCHCSCH_3]$

VANADIUM

V^{III} *(Argon)* $3d^2$

$V_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	59C1, 62B2
$V(KC_2O_4)_3 \cdot 3H_2O$	64B3
$V^{3+}:Al_2O_3$	63B2, 68S2, 68S3

CHROMIUM

Cr^{III} *(Argon)* $3d^3$

$K_2SO_4Cr_2(SO_4)_3 \cdot 24H_2O$	55B2, 62M1
$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	39K3, 56D1, 67S1, 68S4
$(NH_4)_3Cr(C_2O_4)_3 \cdot 3H_2O$	39K3, 48B2, 51G1, 56D1
$Cr(acac)_3$	51G1

Cr^{VI}*(Argon)* $3d^0$

$Na_2(CrO_4) \cdot 4H_2O$	63S1
$K_2(CrO_4)$	38K4, 63S1
$(NH_4)_2(CrO_4)$	38K4, 63S1
$Na_2(Cr_2O_7) \cdot 2H_2O$	62S2
$(NH_4)_2(Cr_2O_7)$	38K4, 62S2

MANGANESE

Mn^{II} *(Argon)* $3d^5$

$MnSO_4 \cdot 4H_2O$	21F1, 33J1
$MnSO_4 \cdot 5H_2O$	33J1

$K_2Mn(SO_4)_2 \cdot 4H_2O$	36K1
$Rb_2Mn(SO_4)_2 \cdot 6H_2O$	35K1, 36K1
$Cs_2Mn(SO_4)_2 \cdot 6H_2O$	35K1, 36K1
$Tl_2Mn(SO_4)_2 \cdot 6H_2O$	35K1, 36K1
$(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$	26J1, 27R1, 33K1, 35K1, 36K1, 39K3, 51G1
$(NH_4)_2(Mn,Mg)(SO_4)_2 \cdot 6H_2O$	36K1
$(NH_4)_2(Mn,Zn)(SO_4)_2 \cdot 6H_2O$	36K1
$Rb_2Mn(SeO_4)_2 \cdot 6H_2O$	35K1, 36K1
$Tl_2Mn(SeO_4)_2 \cdot 6H_2O$	35K1, 36K1
$(NH_4)_2Mn(SeO_4)_2 \cdot 6H_2O$	35K1, 36K1
$Mn(CH_3COO)_2 \cdot 4H_2O$	67M2
Mn(phthalocyanine)	70B1

Mn^{VII} (Argon) $3d^0$

$KMnO_4$	51G1, 62S1

IRON

Fe^{II} (Argon) $3d^6$

$FeCl_2 \cdot 4H_2O$	64S1
$FeSO_4 \cdot 7H_2O$	10F1, 33K1, 51G1, 54D1
$LiFePO_4$	70C1
$K_2Fe(SO_4)_2 \cdot 6H_2O$	27R1, 33K1, 48B1, 48B4, 54D1, 64B1, 66T1, 67K1
$Rb_2Fe(SO_4)_2 \cdot 6H_2O$	38K4
$Cs_2Fe(SO_4)_2 \cdot 6H_2O$	38K4
$Tl_2Fe(SO_4)_2 \cdot 6H_2O$	38K4
$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	10F1, 33K1, 38J2, 48B1, 48B4, 54D1, 57O1, 58C1, 61B2, 62B2, 62M1, 64B1, 66T1, 67K1, 68I1
$(NH_4)_2(Fe,Mg)(SO_4)_2 \cdot 6H_2O$	38J2
$(NH_4)_2(Fe,Zn)(SO_4)_2 \cdot 6H_2O$	38J2
$Tl_2Fe(SeO_4)_2 \cdot 6H_2O$	38K4
$FeSiF_6 \cdot 6H_2O$	57P1, 59J1, 59O1, 65B5, 67K1, 67M1, 70G2
$FeGeF_6 \cdot 6H_2O$	70G2
$(Fe,Zn)SiF_6 \cdot 6H_2O$	67M1
$[(C_2H_5)_4N]_2FeCl_4$	68B5
Fe(phthalocyanine)	70B2

Fe^{III} (Argon) $3d^5$

$K_3Fe(CN)_6$	33J1, 35H1, 38J1, 38K4, 47M1, 51G1, 58S1, 69F1
$Na_3Fe(C_2O_4)_3 \cdot 5H_2O$	36K1
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	33J1, 36K1, 51G1, 68B5, 69G1
$Fe(acac)_3$	33J1, 51G1, 69G1
$Fe(salen)Cl(CH_3NO_2)_x$	66G1
Fe(salen)Cl	68B5
Acid ferrimyoglobin	61M2, 65M6, 68U1
Ferrimyoglobin fluoride	68U1

COBALT

Co^{II} (Argon) $3d^7$

$CoF_2 \cdot 5HF \cdot 6H_2O$	68D1, 69D1
$CoCl_2 \cdot 6H_2O$	60H1, 64N1, 65N1, 66K1, 69L1
$CoBr_2 \cdot 6H_2O$	68M3
$CoSO_4 \cdot 7H_2O$	10F1, 32B1, 33B1, 33J1, 33K1, 51G1, 54D1
$K_2Co(SO_4)_2 \cdot 6H_2O$	10F1, 26J1, 27R1, 32B1, 33B1, 33K1, 48B1, 48B3, 54D1, 61B1, 62B2, 66T1, 67N1
$Rb_2Co(SO_4)_2 \cdot 6H_2O$	27R1, 38K4, 51G1
$Cs_2Co(SO_4)_2 \cdot 6H_2O$	38K4, 51G1
$Tl_2Co(SO_4)_2 \cdot 6H_2O$	38K4, 51G1
$(NH_4)_2Co(SO_4)_2 \cdot 6H_2O$	10F1, 23J1, 27R1, 32B1, 33B1, 33K1, 38J2, 48B1, 48B3, 54D1 56U1, 61B1, 62B2, 66T1
$(NH_4)_2(Co,Mg)(SO_4)_2 \cdot 6H_2O$	38J2
$(NH_4)_2(Co,Zn)(SO_4)_2 \cdot 6H_2O$	38J2
$CuCo(SO_4)_2 \cdot 6H_2O$	10F1
$CuCo(SO_4)_2 \cdot 7H_2O$	33K1
$Co(SeO_4) \cdot 6H_2O$	38K4, 51G1
$K_2Co(SeO_4)_2 \cdot 6H_2O$	38K4
$Rb_2Co(SeO_4)_2 \cdot 6H_2O$	38K4, 51G1
$Tl_2Co(SeO_4)_2 \cdot 6H_2O$	38K4
$(NH_4)_2Co(SeO_4)_2 \cdot 6H_2O$	38K4
$K_2Co(SO_4)(SeO_4) \cdot 6H_2O$	38K4
$CoSiF_6 \cdot 6H_2O$	65B2, 65M1
$(NH_4)_2Co(BeF_4)_2 \cdot 6H_2O$	38K4, 48B1, 48B3, 61B1, 62B2
$CoWO_4$	69Z1
$Zn_{0\cdot98}Co_{0\cdot02}WO_4$	69Z1
$LiCoPO_4$	70C1
$Co(CH_3COO)_2 \cdot 4H_2O$	46M1, 59G1, 65M5
$Cs_2(CoCl_4)$	37K3, 37K4, 38K4, 48B1, 48B3, 64F1, 68M4
Cs_3CoCl_5	37K4, 38K4, 64F1, 64K1, 64D1, 65B4, 66B3, 68B5
$K_2Co(NCS)_4 \cdot 4H_2O$	64F1
$Co(acac)_2 \cdot 2H_2O$	68B5
$Co(mesityl)_2[P(C_2H_5)_2Ph]_2$	69B1
β-Co(paphy)Cl_2	68B5
$Co(Ph_2CH_3AsO)_4(NO_3)_2 \cdot H_2O$	68B5
β-Co(pthalocyanine)	69M1
$Co(bipy)_3Br_2 \cdot 6H_2O$	70H1, 70H2
$NaCo(acac)_3 \cdot p$-dioxane	70H1
$Co(thiourea)_4Cl_2$	70H1
$Copy_2(acac)_2$	70H1
$Co(sacsac)_2$	70G1

NICKEL

Ni^{II} (Argon) $3d^8$

$NiF_2 \cdot 5HF \cdot 6H_2O$	68D1, 69D1

$NiSO_4 \cdot 6H_2O$	33K1, 38K3, 39K3, 46M1, 50S1, 51G1, 54D1, 55B2, 57B1, 58B1, 63B1, 68B5, 68F2
$NiSO_4 \cdot 7H_2O$	10F1, 23J1, 31G1, 33K1, 46M1, 51G1, 54D1, 63B1
$K_2Ni(SO_4)_2 \cdot 6H_2O$	27R1, 33K1, 48B1, 48B2, 54D1, 57B1, 58B1, 59H1, 63B1, 67N1
$Rb_2Ni(SO_4)_2 \cdot 6H_2O$	27R1, 38K4, 51G1, 54D1, 57B1, 58B1
$Cs_2Ni(SO_4)_2 \cdot 6H_2O$	38K4, 51G1, 54D1, 57B1, 58B1
$Tl_2Ni(SO_4)_2 \cdot 6H_2O$	38K4, 51G1, 54D1, 57B1, 58B1, 63B1,
$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$	26J1, 27R1, 32B1, 33B1, 33K1, 38J2, 48B1, 48B2, 54D1, 57B1, 58B1, 63B1
$(NH_4)_2(Ni,Mg)(SO_4)_2 \cdot 6H_2O$	38J2
$(NH_4)_2(Ni,Zn)(SO_4)_2 \cdot 6H_2O$	38J2
$NiSeO_4 \cdot 6H_2O$	38K3, 38K4, 39K3, 51G1, 54D1, 57B1, 58B1
$K_2Ni(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B1, 58B1
$Rb_2Ni(SeO_4)_2 \cdot 6H_2O$	38K4, 51G1, 54D1, 57B1, 58B1
$Cs_2Ni(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B1, 58B1
$Tl_2Ni(SeO_4)_2 \cdot 6H_2O$	38K4, 51G1, 54D1, 57B1, 58B1
$(NH_4)_2Ni(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B1, 58B1, 63B1
$(NH_4)_2Ni(SO_4)(SeO_4) \cdot 6H_2O$	38K4, 51G1
$K_2Ni(BeF_4)_2 \cdot 6H_2O$	54D1, 57B1, 58B1
$Rb_2Ni(BeF_4)_2 \cdot 6H_2O$	54D1, 57B1, 58B1
$Cs_2Ni(BeF_4)_2 \cdot 6H_2O$	54D1, 57B1, 58B1
$Tl_2Ni(BeF_4)_2 \cdot 6H_2O$	54D1, 57B1, 58B1
$(NH_4)_2Ni(BeF_4)_2 \cdot 6H_2O$	38K4, 48B1, 48B2, 54D1, 57B1, 58B1
$Ni(SiF_6) \cdot 6H_2O$	54D1, 66B2
$Ni(SnCl_6) \cdot 6H_2O$	66B2
$Ni(CH_3COO)_2 \cdot 4H_2O$	46M1, 65M4
$[(C_2H_5)_4N]_2NiCl_4$	69G3
$[(C_2H_5)_4N]_2NiBr_4$	65B4
$Ni(PhCH_3AsO)_4(NO_3)_2H_2O$	68B5
$Ni(\textit{N}\text{-i-propyl-sal})_2$	68B5, 68L1, 69G3
$Ni(5\text{-Cl-N-B-sal})_2$	68B5
$Ni(\text{thiourea})_4Cl_2$	69P1
$Ni(\text{thiourea})_6Br_2$	69P1
$Ni^{2+}:ZnO$	64B2
$Ni^{2+}:CdS$	64B2

COPPER

Cu^{II} (Argon) $3d^9$

$CuF_2 \cdot 2H_2O$	65T1
$CuCl_2 \cdot 2H_2O$	52V1

$CuSO_4 \cdot 5H_2O$	36K2, 37K2, 38K5, 38K6, 42P1 48B4, 52B1, 57B2
$K_2Cu(SO_4)_2 \cdot 6H_2O$	27R1, 32B1, 33B1, 33K1, 42H1, 48B4, 54D1, 55B2, 57B2, 67N1, 70M2
$K_2(Cu,Zn)(SO_4)_2 \cdot 6H_2O$	62M2, 65B1, 65M2
$Rb_2Cu(SO_4)_2 \cdot 6H_2O$	27R1, 38K4, 51G1, 54D1, 57B2
$Cs_2Cu(SO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B2
$Tl_2Cu(SO_4)_2 \cdot 6H_2O$	38K4, 51G1, 54D1, 57B2
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$	27R1, 32B1, 33B1, 33K1, 38J2, 48B4, 54D1, 57B2
$(NH_4)_2(Cu,Mg)(SO_4)_2 \cdot 6H_2O$	38J2
$(NH_4)_2(Cu,Zn)(SO_4)_2 \cdot 6H_2O$	38J2
$CoCu(SO_4)_2 \cdot 6H_2O$	10F1
$CoCu(SO_4)_2 \cdot 7H_2O$	33K1
$CuSeO_4 \cdot 5H_2O$	39M1, 57B2
$K_2Cu(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B2
$Rb_2Cu(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B2
$Tl_2Cu(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B2
$(NH_4)_2Cu(SeO_4)_2 \cdot 6H_2O$	38K4, 54D1, 57B2
$CuSiF_6 \cdot 6H_2O$	68B3
$Cu(HCOO)_2 \cdot 4H_2O$	60F1, 62H1, 63F1, 63K1, 63M3, 67M3, 69G6
$Cu(HCOO)_2 \cdot 4D_2O$	63F1
$Cu(CH_3COO)_2 \cdot H_2O$	45M1, 51G1, 62M3, 62S1, 63M1, 63N2, 65G1, 65M4, 66B1, 66G6, 68B4
$CaCu(CH_3COO)_2 \cdot 6H_2O$	68B2, 68F1, 69G5, 70B3
$K_2(CuCl_4) \cdot 2H_2O$	39K3, 45M1, 54D1, 62C1
$Rb_2(CuCl_4) \cdot 2H_2O$	39K3, 45M1, 54D1
Cs_2CuCl_4	64M1, 64S1, 65B4, 65C2, 65C3, 66L1, 68F1
$(NH_4)_2CuCl_4 \cdot 2H_2O$	39K3, 45M1, 51G1, 54D1
$[(CH_3)_4N]_2CuCl_4$	66L1
$Cs_2(CuBr_4)$	66L1, 68F1
$(NH_4)_2(CuBr_4) \cdot 2H_2O$	54D1, 62C1
$[(CH_3)_4N]_2CuBr_4$	66L1
$Cu(en)Cl_2$	69B2
Cu(baed)	68F1
Cu(*N*-t-butyl-sal)$_2$	68F1, 68L1
Cu(*N*-i-propyl-sal)$_2$	68F1, 68L1
β-CuH(phthalocyanine)	70M1
Cu(R$_2$-dtc)$_2$, R = ethyl, n-propyl, n-butyl	68G2, 68P1
Cu(acac)$_2$	70B3

RUTHENIUM

Ru^{III} (Krypton) 4d^5

Ru(acac)$_3$	68S1, 69G4

CERIUM

Ce^{III} (Xenon) $4f^1$

$Ce(NH_4)(SO_4)_2 \cdot 4H_2O$	38K4, 49M1
$Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O$	38K4, 49M1, 61H1
$Ce_2Zn_3(NO_3)_{12} \cdot 24H_2O$	38K4
$Ce_2(C_2H_5SO_4)_6 \cdot 18H_2O$	35F1, 38K4, 49M1, 51B1

PRASEODYMIUM

Pr^{III} (Xenon) $4f^2$

$Pr_2(SO_4)_3 \cdot 8H_2O$	37K1, 38K4, 49M2
$Pr_2Mg_3(NO_3)_{12} \cdot 24H_2O$	38K4, 49M2
$Pr_2Zn_3(NO_3)_{12} \cdot 24H_2O$	38K4
$Pr_2(C_2H_5SO_4)_6 \cdot 18H_2O$	35F1, 38K4, 39K3, 51M1

NEODYMIUM

Nd^{III} (Xenon) $4f^3$

$NdCl_3$	68T1
$NdCl_3 \cdot 6H_2O$	39K3
$Nd_2(SO_4)_3 \cdot 8H_2O$	37K1, 38K4, 49M3, 61M1, 65C1
$Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$	38K4, 49M3
$Nd_2Zn_3(NO_3)_{12} \cdot 24H_2O$	38K4
$Nd_2(C_2H_5SO_4)_6 \cdot 18H_2O$	35F1, 38K4, 42V1, 53E1, 66M2 68M1
$NdGaO_3$	68B1

SAMARIUM

Sm^{III} (Xenon) $4f^5$

$SmCl_3 \cdot 6H_2O$	39K3
$Sm_2(SO_4)_3 \cdot 8H_2O$	37K1, 38K4, 49M4
$Sm_2Mg_3(NO_3)_{12} \cdot 24H_2O$	38K4, 49M4
$Sm_2(C_2H_5SO_4)_6 \cdot 18H_2O$	38K4, 39K3, 53E1

EUROPIUM

Eu^{III} (Xenon) $4f^6$

$EuAlO_3$	69H1
$Eu_2(SO_4)_3 \cdot 8H_2O$	59M2, 63N1, 65N2

GADOLINIUM

Gd^{III} *(Xenon)* $4f^7$

$Gd_2(SO_4)_3 \cdot 8H_2O$	39K3, 41K1
$NaGd(MoO_4)_2$	68H1, 68H2
$Gd_2(C_2H_5SO_4)_6 \cdot 18H_2O$	53E1

TERBIUM

Tb^{III} *(Xenon)* $4f^8$

$NaTb(MoO_4)_2$	68H1, 68H2

DYSPROSIUM

Dy^{III} *(Xenon)* $4f^9$

$DyCl_3$	70T1
$Dy_2(SO_4)_3 \cdot 8H_2O$	63N1, 65C2, 65N4
$NaDy(MoO_4)_2$	68H1, 68H2
$Dy_2(C_2H_5SO_4)_6 \cdot 18H_2O$	53E1, 69M2

HOLMIUM

Ho^{III} *(Xenon)* $4f^{10}$

$HoCl_3$	70T1
$NaHo(MoO_4)_2$	68H1, 68H2
$Ho_2(C_2H_5SO_4)_6 \cdot 18H_2O$	65C3

ERBIUM

Er^{III} *(Xenon)* $4f^{11}$

$ErCl_3$	69T1
$ErCl_3 \cdot 6H_2O$	39K3
$Er_2(SO_4)_3 \cdot 8H_2O$	37K1, 38K4, 61M1, 63N1, 65N3
$NaEr(MoO_4)_2$	68H1, 68H2
$Er_2(C_2H_5SO_4)_6 \cdot 18H_2O$	35F1, 38K4, 53E1, 64M3, 65C3

THULIUM

Tm^{III} *(Xenon)* $4f^{12}$

$NaTm(MoO_4)_2$	68H1, 68H2

YTTERBIUM

Yb^{III} (Xenon) $4f^{13}$

$Yb_2(SO_4)_3 \cdot 8H_2O$	62M4, 63N1, 63N2
$Yb(C_2H_5SO_4)_3 \cdot 9H_2O$	69C1
$NaYb(MoO_4)_2$	68H1, 68H2

MINERALS

Augit, $CaMg(SiO_3)_2(Mg,Fe)(AlFe)_2SiO_6$	10F1
Biotite, $(K,H)_2(Mg,Fe)_2(AlFe)_2(SiO_4)_3$	40N1
Braunite, $3Mn_2O_3 \cdot MnSiO_3$	39K2
Epidote, $4CaO \cdot 3(AlFe)_2O_3 6SiO_2 \cdot H_2O$	10F1, 44S1
Hornblende, $Ca(Mg,Fe)_3(SiO_2)_4, Al_2(Mg,Fe)_2$-$(AlO_3)_2(SiO_3)_2, Fe(Mg,Fe)_2(FeO_3)_2(SiO_3)_2$	10F1
Manganite, $MnO(OH)$	38K1, 39K1
Rhodochrosite, $MnCO_3$	31D1, 38K2, 55B1
Siderite, $FeCO_3$	21F1, 31D1, 33K1, 59M1, 65M3
Tourmaline, $(H,Li,Na,K)_9Al_3[BOH]_2Si_4O_{19}$-$(+Fe_2O_3,FeO,MgO,MnO)$?	44S1, 59V1
Tungstenite, WS_2	49D1

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