

GRAPH PLOTTING PROGRAM: TRAJECTORIES

```

C THIS PROGRAM WILL PLOT OUT THE WIRE AND THE PATHS OF THE PARTICLES.
C THE POINTS FOR THE WIRE SHOULD BE READ IN VIA CHANNEL NO.5.
C THE DATA FOR THE PATHS SHOULD BE READ IN VIA CHANNEL NO.6.
C
  INTEGER Q
  DIMENSION X(1000),Y(1000),IPLOT(19)
  DATA IPLOT/22,22H PARTICLE TRAJECTORIES,20,20HX-AXIS IN UNITS OF A
  *,20,20HY-AXIS IN UNITS OF A/
  I=0
  READ(1,1001)IO
  READ(5,1000)(X(N),Y(N),N=1,120)
  CALL NARROW
  CALL RSIZE(150.0,150.0)
  CALL FIXAXS(-9.99,10.0,-9.99,10.0)
  CALL FGPLT(X,Y,120,5,0,1,0,IPLOT)
1  I=I+1
  READ(6,999)Q
  READ(6,1000)(X(N),Y(N),N=1,Q)
  CALL FGPLT(X,Y,Q,15,0,1,1,IPLOT)
  IF(I.EQ.IO)GOTO 100
  GOTO 1
100 CALL DEUFIN
  STOP
999 FORMAT(I10)
1000 FORMAT(1X,F10.5,F20.5)
1001 FORMAT(15)
  END

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GRAPH PLOTTING PROGRAM: VELOCITIES

C THIS PROGRAM WILL PLOT OUT THE LINE REPRESENTING THE
 C VELOCITIES OF THE PARTICLES AS A FUNCTION OF X-DISTANCE FROM
 C THE WIRE, BUT NOT THE WIRE ITSELF AS THE SCALE IS TOO LARGE.
 C THE POINTS FOR THE CURVE SHOULD BE READ IN VIA CHANNEL NO.6.
 C

```

      INTEGER Q
      DIMENSION X(1000),Y(1000),R(1000),U(1000),IPLOT(22)
      DATA IPLOT/19,19HPARTICLE VELOCITIES,22,22HPOSITION IN UNITS OF A,
      *31,31HVELOCITY IN UNITS OF A PER SEC./
      I=0
      READ(1,1001)IO,Z,ALPHA
      READ(6,999)Q
      N=1
2  READ(6,1000)X(N),Y(N),U(N)
      THETA=ATAN2(Y(N),X(N))
      R(N)=SQRT(X(N)*X(N)+Y(N)*Y(N))*COS(THETA-ALPHA)
      N=N+1
      IF(N.LE.Q)GOTO 2
      CALL NARROW
      CALL RSIZE(200.0,100.0)
      CALL FIXAXS(-9.99,10.0,0.0,Z)
      CALL CHAPEN(2)
      CALL FGPLT(R,U,Q,15,0,1,0,IPLOT)
      I=I+1
      IF(I.EQ.I)GOTO 1
      DO 1 I=2,IO
      READ(6,999)Q
      N=1
3  READ(6,1000)X(N),Y(N),U(N)
      THETA=ATAN2(Y(N),X(N))
      R(N)=SQRT(X(N)*X(N)+Y(N)*Y(N))*COS(THETA-ALPHA)
      N=N+1
      IF(N.LE.Q)GOTO 3
      CALL CHAPEN(2)
      CALL FGPLT(R,U,Q,15,0,1,1,IPLOT)
1  CONTINUE
      CALL DEUFIN
      STOP
999 FORMAT(I10)
1000 FORMAT(1X,F10.5,2F20.5)
1001 FORMAT(15,2F15.5)
      END

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CHAPTER 6

Magnetization in the Crystal Field System Praseodymium

J. A. G. TEMPLE

1. INTRODUCTION

The rare earth metals, atomic numbers 58–71, have unfilled 4f shells lying inside closed 5s 5p shells. The outermost electrons, that is $5d^1 6s^2$, are lost to the conduction band and become a part of the nearly free electron sea. The small spatial extent of the 4f wavefunctions makes overlap of these wave functions on neighbouring ions very unlikely in the solid. This implies a magnetic moment which is well localized on the ionic site. This situation is very different from the more conventional magnetic systems (Fe, Co, Ni, etc.), in which the magnetism is due entirely to the free electrons, and cannot be attributed to well-localized magnetic moments. For this reason the rare earths are intrinsically interesting, especially so when the range and type of magnetic orderings (ferromagnetic, antiferromagnetic, helical, fan, and spiral types often with magnetic unit cells many times larger than the crystal unit cell) are noted. They are becoming increasingly important in technology too, with uses in high-power permanent magnets and in lasers.

This localized magnetic moment is, to some extent, screened by the 5s 5p electrons and does not experience the full effect of the Coulomb interaction due to the periodic array of ions. Another way of describing this is to say that the crystalline electric field is weaker. Each of the localized magnetic moments experiences the effect of many others in the crystal through a double interaction with the conduction electrons. A local moment will scatter a conduction electron with a spin-dependent interaction so that the conduction electron carries away with it a 'memory' of the orientation of the first moment. This electron, on a second scattering, with a, presumably, different local moment, conveys this memory to the second moment. Thus it appears as though there is a direct interaction between local moments i and j of the form $F(\mathbf{R}_{ij})(\mathbf{J}_i \cdot \mathbf{J}_j)$. $F(\mathbf{R}_{ij})$ oscillates rapidly with the distance \mathbf{R}_{ij}

between total ionic angular momenta \mathbf{J}_i and \mathbf{J}_j . This is the well-known RKKY interaction (Rudermann and Kittel,¹ Kasuya,² Yosida³) which dominates the magnetic behaviour of the 14 rare earth elements. In its simplest form, this interaction may be represented by an internal local magnetic field at each site.

Hund's rules give the ground state of the 4f configuration. This is separated from the other multiplets of total angular momentum by an energy which is typically of the order of 1000 K. At low temperatures (i.e. a few kelvin) therefore, only the lowest J -multiplet is occupied; J being the total angular momentum of the ion. This multiplet is $(2J+1)$ -fold degenerate in the absence of an internal magnetic field and a crystalline electric field. In the presence of a crystal field, the multiplet is split into a series of singlets, doublets and triplets depending on the symmetry of the charge distributions of neighbouring ions.

At low temperatures (i.e. tens of kelvin) when only a few of these singlets, doublets, and triplets are occupied the system will, in general, be magnetically ordered with all the localized moments arranged in some well-defined pattern. The free electrons, that is those responsible for the electrical conductivity, will sense this ordering and will be scattered differently in the ordered state to the disordered state. There will thus be, possibly, interesting anomalies in the conductivity, or its reciprocal the resistivity, at low temperatures, as well as the magnetization itself. These anomalies reflect the competition between the internal magnetic fields at each lattice site and the local electrical fields due to the Coulomb interaction with neighbouring ions. For praseodymium this competition is finely balanced and, as explained in section 2, no other metal is known to sit so close to a threshold between the ability to order spontaneously as the temperature is reduced and the ability to remain paramagnetic even towards the absolute zero of temperature. The magnetization anomalies may thus be expected to be rather interesting in the presence of an externally applied magnetic field.

2. THE MODEL

Praseodymium (Pr) is element number 59 and has therefore a $4f^2$ configuration for which Hund's rules give the quantum numbers $S=1$, $L=5$ and, since the shell is less than half full, $J=L-S=4$. The ground state is denoted 3H_4 and is ninefold degenerate in the absence of a crystalline electric field or internal magnetic field. Other ways of adding together the total orbital angular momentum L and the total spin S would give the configurations 3H_5 , 3H_6 . These lie at much greater energies; in praseodymium it requires at least 1000 K to excite the ions into these higher energy states. Because of this large energy requirement it is safe to assume only the lowest multiplet, namely 3H_4 , is populated at room temperature or below.

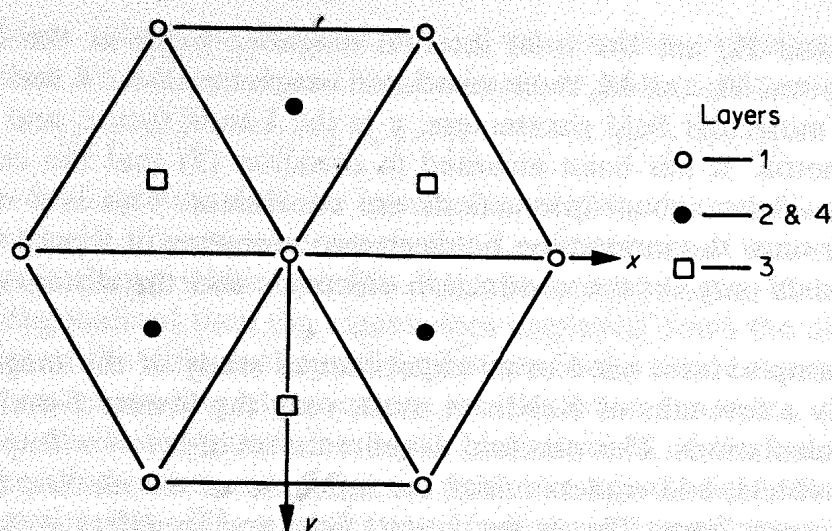


Figure 1. Plan view of dhcp crystal structure showing layers of ions in the planes perpendicular to the crystal c -axis. Ions in successive layers are denoted by 1, 2, 3, and 4

The solid-state form of Pr has the double hexagonal close-packed structure (dhcp) as shown in Figure 1. This is usually denoted as a stacking sequence ABCB of hexagonal layers. In a material with cubic symmetry the layer sequence is ABC and in a hexagonal material the sequence is ABAB. It is clear that, based on the nearest-neighbour environments, the dhcp structure has layers of alternate designation, cubic or hexagonal. Two types of crystallographic symmetry imply that there are two different magnetic behaviours; in this material two interpenetrating sublattices each with its own molecular field.

Suppose that there is an externally applied magnetic field. This acts at each lattice site, together with an additional magnetic field due to an extra alignment of all the magnetic moments on the neighbouring lattice sites, since each ion responds to the applied field by a tendency to align with it. This additional internal field is called a 'molecular field' after the original concept of Weiss.⁴ In this approximation, the magnetic field due to the partial alignment of neighbouring moments is linearly related to this alignment or magnetization. Although the applied field will be the same at all lattice sites, the internal field will vary according to the physical arrangement of the neighbours, that is to the symmetry and number of neighbouring ions and their magnetization, i.e.

$$\begin{aligned} \mathbf{H}_c &= \frac{\lambda}{g^2 \mu_B^2} \mathbf{M}_c + \frac{\mu}{g^2 \mu_B^2} \mathbf{M}_h + \mathbf{H}_{\text{applied}}, \\ \mathbf{H}_h &= \frac{\lambda}{g^2 \mu_B^2} \mathbf{M}_h + \frac{\mu}{g^2 \mu_B^2} \mathbf{M}_c + \mathbf{H}_{\text{applied}}, \end{aligned} \quad (1)$$

where \mathbf{H}_c and \mathbf{H}_h are the total internal magnetic fields at the cubic and hexagonal sites, \mathbf{M}_c and \mathbf{M}_h their associated magnetizations, λ and μ are the two Weiss molecular field parameters, g is the Landé factor, and μ_B is the Bohr magneton. It has been assumed in equation (1) that the cubic-cubic and hexagonal-hexagonal interactions are equivalent. This is a reasonable assumption since the interaction between two moments of a pure rare earth metal depends only on the conduction electrons and the distance between the ions.

As the temperatures used in an experimental study of the magnetization will be only a few tens of Kelvin at most, only the lowest J -multiplet will enter the calculations. This ninefold degenerate set of levels will split up into singlets, doublets, and triplets under the influence of the electric field of all the neighbouring ions. This is the crystal field and its effect is determined principally by the symmetry of the neighbouring ions. As we are concerned only with a set of levels, all of which possess the same total angular momentum J , it is possible to calculate the effect of the Coulomb interaction of all the ions on each other; a kind of Stark effect, by using the method of Stevens operators. These make easier the task of determining the splitting of the levels with the same J but differing J_z through the first-order perturbation caused by the electric field of neighbouring ions. Using these Stevens operator equivalents (Stevens⁵), the ionic Hamiltonian, or total energy operator, becomes

$$\mathcal{H}_\alpha = V_\alpha - g\mu_B \mathbf{H} \cdot \mathbf{J}, \quad (2)$$

where α = cubic or hexagonal, V_α is the energy in the crystal field, and \mathbf{H} is the total internal magnetic field.

$$V_{\text{cubic}} = B_2 O_2^0 + B_4 (O_4^0 + 20\sqrt{2} O_4^3) + B_6 \left(O_6^0 - \frac{35}{\sqrt{8}} O_6^3 + \frac{77}{8} O_6^6 \right), \quad (3)$$

$$V_{\text{hexagonal}} = B_2 O_2^0 + B_4 O_4^0 + B_6 (O_6^0 + \frac{77}{8} O_6^6), \quad (4)$$

where B_l are constants with dimensions of energy and the O_l^m are the Stevens operators that are polynomials of degree l in the quantum mechanical operators J_z , $J+$, $J-$. Some typical Stevens operators are:

$$\begin{aligned} O_2^0 &= 3J_z^2 - J(J+1), \\ O_6^0 &= \frac{1}{2} \{ (J+)^6 + (J-)^6 \}, \end{aligned} \quad (5)$$

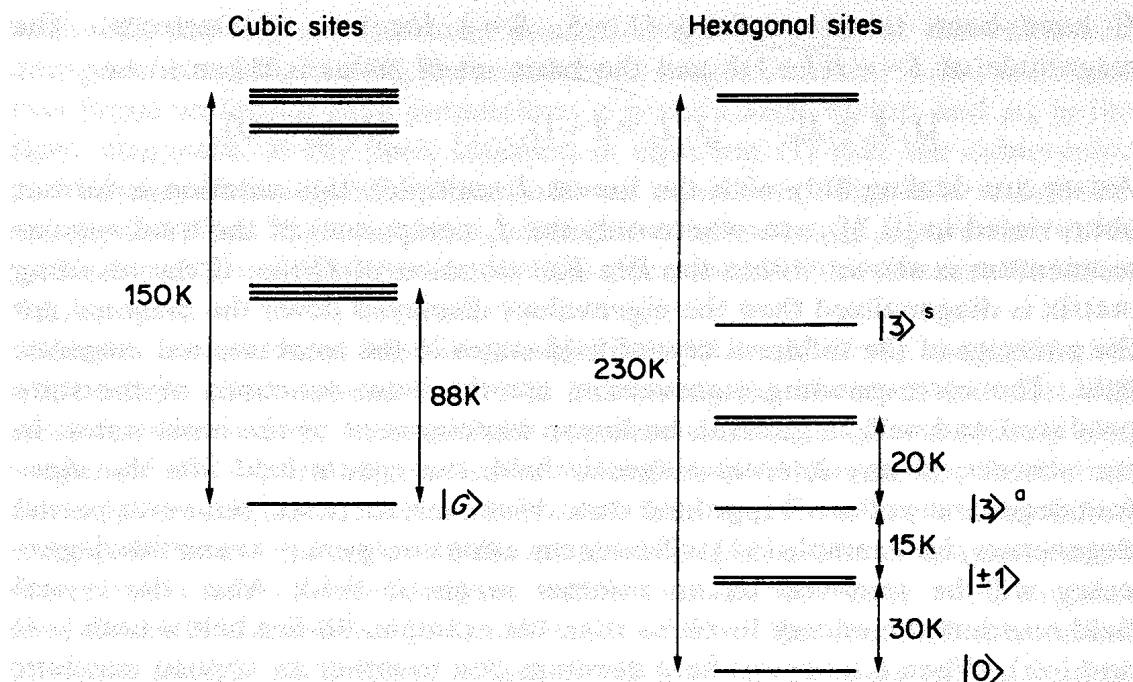
and a full list of them may be found in Hutchings.⁶ The resulting operator \mathcal{H}_α may be expressed as a matrix whose elements are the numbers obtained from $\langle i | \mathcal{H}_\alpha | j \rangle$, where $|i\rangle$ and $|j\rangle$ are states of total angular momentum J and z -component J_z . That is, a state of the system is written $|J; J_z\rangle$ where L and

S have been taken as fixed ($L=5$, $S=1$ for two 4f electrons). The magnitude of $J=\sqrt{J(J+1)}\hbar$ and the basis set of states is taken to be

$$|J; J_z = J\rangle, \quad |J; J_z = J-1\rangle, \dots, \quad |J; J_z = -J\rangle.$$

As we are dealing only with the lowest J multiplet, this notation is further abbreviated to $|i\rangle$, $|j\rangle$, etc. where only the J_z component of the total angular momentum is shown within the Bra-Ket notation of Dirac. If the resulting matrix is diagonalized then the eigenvalues displayed down the diagonal are the energies of the different crystal field states in the total internal magnetic field. The corresponding eigenvectors are the wave functions of the state produced and will, in general, be linear combinations of the basis states. In the absence of any internal magnetic field, the crystal field lifts the nine-fold degeneracy of the 3H_4 ground state. However, there still remains a partial degeneracy, for example $|+1\rangle$ will have the same energy as $|-1\rangle$ and this degeneracy will be removed by an internal magnetic field. Also, the crystal field reorders the energy levels so that, for example, $|0\rangle$ lies below both $|+1\rangle$ and $|-1\rangle$. When a magnetic field develops due to either an applied magnetic field or spontaneous ordering, this level scheme will change and in the limit of very large internal magnetic fields the levels will be, in ascending order: $|-4\rangle$, $|-3\rangle$, $|-2\rangle$, $|-1\rangle$, $|0\rangle$, $|1\rangle$, $|2\rangle$, $|3\rangle$, $|4\rangle$.

The ground state, which is the state of lowest energy, may be a pure $|J_z\rangle = |0\rangle$ state and is then an example of a 'singlet ground state system'. A characteristic of such a system is that it will not order even at the lowest obtainable temperature because the magnetic moment operator vanishes identically (i.e. $\langle 0 | J_z | 0 \rangle = 0$). Such a system may exist if the ratio of crystal field energy to internal magnetic energy exceeds a certain threshold value. Praseodymium is a unique metal because the ratio of exchange energy (the magnetic interaction between two local moments), to the energy of the ions in the crystal field is found to be about 0.96, whereas the threshold value is 1.0. For a ratio greater than 1.0 Pr would order spontaneously at some small non-zero temperature, but for ratios less than 1.0 it will remain paramagnetic until temperatures of a few millikelvin at which the hyperfine interaction becomes important. No other metal is known to sit so close to this threshold value. The level schemes, from neutron-scattering experiments, in dhcp Pr are shown in Figure 2. From this figure it will be observed that the cubic sites may be expected to play a rather small role in the magnetization at low temperatures since no significant population of levels with resultant moments can occur until temperatures of about 80 K are reached. It is, therefore, instructive to look at the bottom three levels on the hexagonal sites and investigate their behaviour in magnetic fields applied parallel to the z - or x -axes. This will give physical insight into the behaviour of the system as a whole.



$$|G\rangle = 0.609(|3\rangle - |-3\rangle) - 0.509|0\rangle$$

not to scale

$$|3\rangle^a = \frac{1}{\sqrt{2}} \{ |3\rangle - |-3\rangle \}$$

$$|3\rangle^s = \frac{1}{\sqrt{2}} \{ |3\rangle + |-3\rangle \}$$

Figure 2. Praseodymium: energy levels in zero applied magnetic field

2.1 Example of way model is used

Ignoring, for the present, any molecular field, we may consider the artificial system of a $J = 1$ spin sitting in a crystal field of axial symmetry. If instead of V_α we write \mathcal{H}_{cf} for the effect of the crystalline electric field, then equation (2) becomes

$$\mathcal{H} = \mathcal{H}_{cf} - g\mu_B \mathbf{H} \cdot \mathbf{J}, \quad (6)$$

where \mathbf{H} is the applied magnetic field only. Considering first the field applied parallel to the z -axis, then $\mathbf{H} \cdot \mathbf{J} = H_z J_z$. Hence, if we write $\alpha = g\mu_B$ and the familiar result for \mathcal{H}_{cf} we may express (6) as

$$\mathcal{H} = DJ_z^2 - \alpha J_z, \quad (7)$$

where D and α are numbers with dimensions of energy and D represents the crystal field splitting in a system of uniaxial symmetry. For a $J = 1$ system

the corresponding matrix Hamiltonian becomes (see for example Dicke and Wittke⁷)

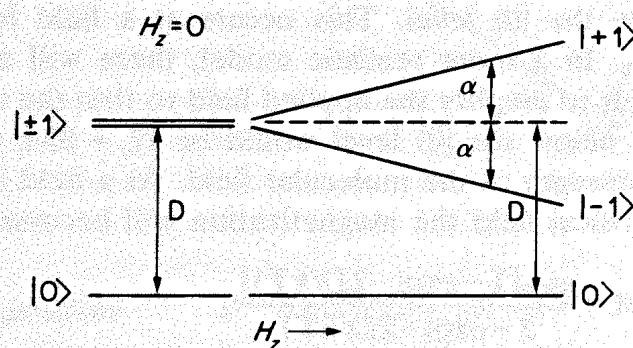
$$\mathcal{H} = \begin{pmatrix} D - \alpha & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D + \alpha \end{pmatrix},$$

where we have used a quantization scheme along the z-axis with eigenvalues 0, $D - \alpha$, $D + \alpha$, so that the energy level diagram has the form shown in Figure 3.

The magnetization is calculated from

$$M = -g\mu_B \langle \langle J_z \rangle \rangle, \quad (8)$$

where $\langle \langle A \rangle \rangle$ denotes the thermal average of the expectation value of the operator A . It is necessary to use the thermal average as the energy splitting of the levels caused by either crystal field or magnetic field is of the same order as the temperature and therefore there will be a statistical population of the levels throughout the 10^{23} sites in a macroscopic crystal.



Eigenvalues	0	$D + \alpha$	$D - \alpha$
Eigenvectors	$\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$	$\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$	$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$

Figure 3. Energy levels of a $J = 1$ system with uniaxial crystal field showing how the levels split with a magnetic field applied along the z-axis.

With the eigenvalues and eigenvectors given in Figure 3 we have

$$\begin{aligned} \langle J_z \rangle = & \left[\langle 0 | J_z | 0 \rangle + \langle -1 | J_z | -1 \rangle \exp \left\{ -\frac{(D-\alpha)}{kT} \right\} \right. \\ & \left. + \langle +1 | J_z | +1 \rangle \exp \{ -(D+\alpha)/kT \} \right] Z^{-1}, \end{aligned} \quad (9)$$

where Z , the partition function, is given by

$$Z = 1 + \exp \{ -(D-\alpha)/kT \} + \exp \{ -(D+\alpha)/kT \}, \quad (10)$$

k is Boltzmann's constant and T is the temperature in kelvin. Clearly, when $\alpha = 0$ ($H_z = 0$) then $\langle J_z \rangle = 0$ and the system can never order no matter how low the temperature to which it is subjected. This is characteristic of a singlet ground state system. However, when $\alpha \neq 0$ (since $\langle 0 | J_z | 0 \rangle = 0$) the magnetization looks like

$$M = -\frac{g\mu_B}{Z} [-\exp \{ -(D-\alpha)/kT \} + \exp \{ -(D+\alpha)/kT \}], \quad (11)$$

This is very small for $\alpha \ll D$, (i.e. energy of the spin in the applied magnetic field is very much less than the crystal field splitting), showing that the initial susceptibility is small. If the applied field is increased, then, eventually, the $|-1\rangle$ level will fall below the $|0\rangle$ level. This occurs at a field for which $D - \alpha = 0$ or $H_z = D/g\mu_B$. In a more realistic model, there will also be a molecular field which tends to amplify the applied field so that the condition for the $|-1\rangle$ level to fall below the $|0\rangle$ level would be $H_z + \beta M_z = D/g\mu_B$, where β represents the strength of the molecular field. At a field infinitesimally greater than this critical field the magnetization will become

$$M = \frac{g\mu_B [1 - \exp(-2D/kT)]}{2 + \exp(-2D/kT)}, \quad (12)$$

which for very small temperatures tends to $M = (\frac{1}{2})g\mu_B$. This appears as a jump discontinuity in the magnetization, i.e. for α just smaller than D , as the temperature tends to zero, the magnetization remains zero; but for α just larger than D , under the same circumstances, the magnetization is $(\frac{1}{2})g\mu_B$.

Now consider what happens if the field is applied along the x -direction, in the simple model. If we put $\alpha = g\mu_B H_x$ then

$$\mathcal{H} = DJ_z^2 - \alpha J_x, \quad (13)$$

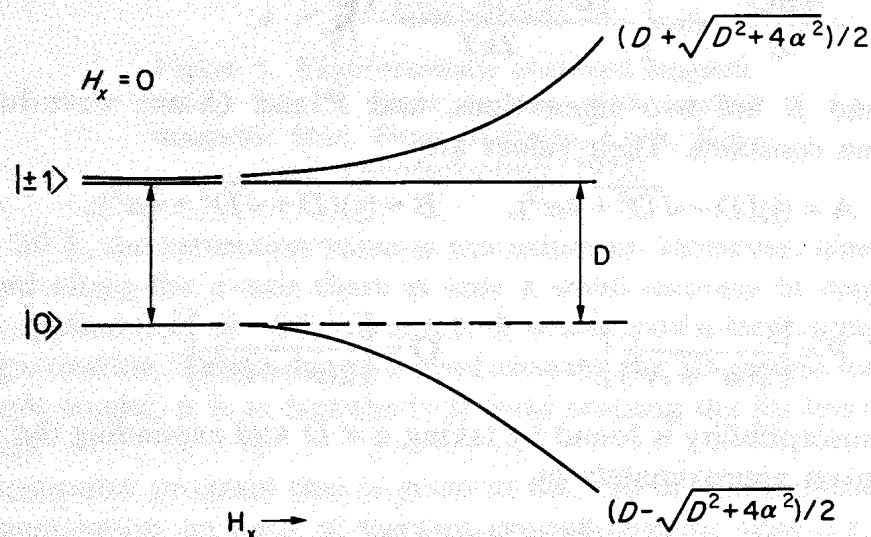
or in matrix form, still using quantization along the z -axis,

$$\mathcal{H} = \begin{pmatrix} D & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & D \end{pmatrix} - \frac{\alpha}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}.$$

The resultant matrix has eigenvalues, found in the usual way from the characteristic equation,

$$D, \frac{1}{2}\{D \pm \sqrt{D^2 + 4\alpha^2}\}.$$

This gives the form of energy level diagram shown in Figure 4 together with the corresponding eigenvectors. The magnetic behaviour in this case is rather different from applying a field parallel to the z -axis. Applying the field along the x -axis polarizes the ground state and induces a moment on it.



$$\text{Eigenvalues} \quad D \quad B \equiv (1/2)(D + \sqrt{D^2 + 4\alpha^2}) \quad A \equiv (1/2)(D - \sqrt{D^2 + 4\alpha^2})$$

$$\text{Eigenvectors} \quad \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} \quad P \begin{bmatrix} 1 \\ -\frac{A\sqrt{2}}{\alpha} \\ 1 \end{bmatrix} \quad Q \begin{bmatrix} 1 \\ -\frac{B\sqrt{2}}{\alpha} \\ 1 \end{bmatrix}$$

$$P^2 = \frac{\alpha^2}{2(\alpha^2 + A^2)} \quad Q^2 = \frac{\alpha^2}{2(\alpha^2 + B^2)}$$

Figure 4. Energy levels of a $J = 1$ system with uniaxial crystal field showing how the levels split with a magnetic field applied along the x -axis

Since we have chosen the crystallographic c -axis as the axis of quantization, and the particular form for the crystal field energy given in equation (13), the required magnetic moment operator is J_x . Hence the magnetization is

$$M = -g\mu_B \langle J_x \rangle. \quad (14)$$

From the eigenvectors and eigenvalues given in Figure 4 this expression is, for small non-zero fields ($0 < \alpha \ll D$),

$$M = -\frac{g\mu_B}{Z} \left\{ 0 \cdot \exp\left[-\frac{D}{kT}\right] - \frac{4AP^2}{\alpha} \cdot \exp\left[-\frac{(D + \sqrt{D^2 + 4\alpha^2})}{2kT}\right] - \frac{4BQ^2}{\alpha} \cdot \exp\left[-\frac{(D - \sqrt{D^2 + 4\alpha^2})}{2kT}\right] \right\}, \quad (15)$$

where A and B are two eigenvalues, and P and Q are wave-function normalization constants. Their values are

$$A = \left(\frac{1}{2}\right)\{D - \sqrt{D^2 + 4\alpha^2}\}, \quad B = \left(\frac{1}{2}\right)\{D + \sqrt{D^2 + 4\alpha^2}\},$$

and

$$P = \left[\frac{\alpha^2}{2(\alpha^2 + A^2)} \right]^{\frac{1}{2}}, \quad Q = \left[\frac{2}{2(\alpha^2 + B^2)} \right]^{\frac{1}{2}}.$$

The initial susceptibility is found by taking $\alpha \ll D$ and expanding the square root. It is given approximately by

$$M \sim 2g\mu_B \alpha / DZ, \quad (16)$$

where

$$Z = \exp[-D/kT] + \exp[-(D + \sqrt{D^2 + 4\alpha^2})/2kT] + \exp[-(D - \sqrt{D^2 + 4\alpha^2})/2kT].$$

The magnetization, although small, for small α , is in fact much larger than the case when the field is applied along the z -axis.

2.2 Application to the real system

The behaviour of the simple $J=1$ system gives the clue to the observed magnetization of Pr at low temperatures and high fields. The experimental magnetization, for fields along the [001] axis and the [110] axis is shown in Figure 5 and is taken from McEwan *et al.*⁸ The z -axis of the model is the [001] axis, whereas the x -axis of Figure 1 corresponds to the [110] axis of the experimental work. For Pr the Landé g -factor is (4/5), so therefore the saturated magnetic moment is 3.2 Bohr magnetons per atom. Applying the field along the x -axis causes the magnetization to rise rapidly, although,

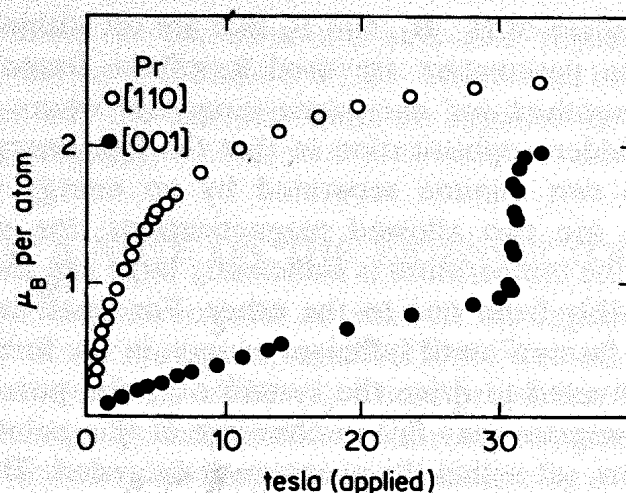


Figure 5. Experimentally observed magnetization of Pr single crystals with applied magnetic field. From McEwen, Cock, Roeland, and Mackintosh (1973)

even in 30 T, the saturation value is not achieved. However, when the field is applied along the z -axis there is only a small increase in magnetization until an applied field of ~ 32 T is reached, whereupon a large jump occurs in the magnetization. This is due to a level crossing the $|0\rangle$ ground state. Unlike our simple model, it is in fact the $|-3\rangle$ level crossing the $|0\rangle$ level that gives this jump.

The computer program that is given at the end of this chapter calculates the magnetization on each of the two crystallographic sites (i.e. the cubic and hexagonal sites of the dhcp structure) for a given applied field and temperature. This is achieved by setting up the matrix Hamiltonian of equation (2) for the given applied field and diagonalizing it. The eigenvalues and eigenvectors are then used in equations (14) or (8) to calculate a magnetization at each site. This magnetization is converted to an internal field by equation (1) and this new total internal field is compared with that obtained on the previous iteration for the same applied field. If they are not close enough the program iterates these steps until the self-consistent solution is found. This is stored and a new field is chosen by adding on a certain amount, decided from the input data, and the whole process repeated for a particular temperature. When all the field steps have been calculated a table of results is printed on the line printer, then simple graphs are drawn on the line printer of the magnetization of the cubic sites, the hexagonal sites, and their average against the applied field. More temperatures may be requested and the entire process is repeated until a negative temperature is encountered, whereupon the program terminates.

The experimental magnetization can be reproduced reasonably well by choosing the values of the molecular field parameters $\lambda = -1.20$, $\mu = 4.14$ K,

together with the values of B_2 , B_4 , and B_6 that are set within the program. If these values of the parameters are used it will be found that the jump discontinuity is 'smoothed out' over some range ΔH where $\Delta H \sim (kT/g\mu_B)$. This is due to a hidden sophistication in that the free energy curve against magnetization has two minima separated by an energy barrier. At the critical field there are two allowed magnetizations, the smaller and the larger, and only if the temperature is sufficiently large can the system sample both and go smoothly from one to the other. For small temperatures the second state is not 'sensed' until sufficient energy, in the form of the applied field, has been delivered to drive the system over the potential barrier. In certain cases the program may fail to converge at this point as the allowed number of iterations, set within the program, is exceeded. The program then lists the results obtained up to that point and proceeds with the next temperature.

3. THE PROGRAM DATA

The necessary data to be presented to the program take the following form where each FORMAT refers to a new line of data. An integer number of field steps (FORMAT I3) is used. If this number is negative the graphs produced on the line printer will be approximately 7 in wide. This is a useful feature if the graphs are to be returned to a teletype, or are to form part of a report. The next data are the lowest field in tesla and the increment (FORMAT 2F6.2), two molecular field parameters λ , μ in kelvin (FORMAT 2F7.2) and an integer (FORMAT I1) that must be either a 0 or 1. If it is desired to apply the field along the z -axis use zero and if the field is to be applied along the x -axis use unity. Next there is an integer (FORMAT I1) which, if zero, inhibits the printing of all the eigenvalues and eigenvectors; it is this form that should generally be used. If the eigenvectors are desired, inputting unity here will print out nine eigenvalues across the page, followed underneath by the eigenvectors. These latter will each be columns of nine numbers and are to be interpreted as the coefficients of successively smaller $|J_z\rangle$ values. Thus, for example, in zero applied field, on the cubic sites the lowest eigenvalue would have below it (see Figure 2):

```

0.000
0.609
0.000 which is interpreted as
0.000 0.609  $|+3\rangle - 0.509 |0\rangle - 0.609 |-3\rangle$ 
-0.509
0.000
0.000
-0.609
0.000
```


The next numbers in the data are real and represent the required temperatures in kelvin (FORMAT F7.2). There can be any (reasonable) number of these, but the last one must be negative in order to stop the execution of the program.

4. A NOTE ON THE EIGENVECTORS

The eigenvectors are normalized so that, if V_i represents a nine-tuple eigenvector, V_i^T is its transpose, and $V_i^T V_i = 1$ for all i . They are also orthogonal in the sense that $V_i^T V_j = \delta_{ij}$. These properties are readily demonstrated in simple cases by examination of the eigenvectors produced by the program (to an accuracy of three decimal places). In a very large applied magnetic field the energy level scheme on both sites will tend towards nine levels, equally spaced, the lowest being the $|-4\rangle$ state, then $|-3\rangle$, and so on up to the $|+4\rangle$ state. If one was interested in a neutron-scattering experiment then the intensity of neutrons scattered with momentum change along the z -axis is proportional to the Boltzmann population of the initial energy level $|i\rangle$ and to the square of matrix elements connecting initial and final states $|f\rangle$, that is

$$I(E_{if}) \propto \frac{\exp(-E_i/kT)}{Z} \cdot |\langle i | J_z | f \rangle|^2,$$

where E_{if} is the energy lost or gained by the neutron beam. With the subroutines provided with the program it is fairly simple to produce intensity spectra for different level schemes and different temperatures.

5. RUNNING THE PROGRAM

The data required to run the program and the input formats required were discussed in section 3. A useful starting point will be to use the program in an attempt to reproduce some recent experimental data (McEwan *et al.*⁸). The experiments were done at the temperature of liquid helium, 4.2 K, and with applied magnetic fields up to about 34 T. These fields were applied to the x - and z -axes in turn. This range of applied magnetic field represents the limit of high field experimental equipment currently available. Fields in excess of this may be applied in the program. It may be interesting to determine at what field you would expect to obtain magnetic saturation of a pure crystal of praseodymium. Choosing molecular field parameters $\lambda = -1.20$, $\mu = 4.14$ K and a temperature of 4.2 K gives reasonable representation of the experimental results. For convenience, only the regions where the curves begin to become asymptotic are drawn at the end of the chapter, although the computer program will always give the complete curves, starting at 0 tesla. The deviations from experiment are discussed briefly in section 2.2.

Keeping λ and μ fixed, for the present, the temperature should be varied. By pumping on the vapour above the liquid helium, temperatures down to 1 K are possible experimentally so temperatures down to this should be tried in the simulation. Lower temperatures may also be used, the effect being to sharpen up the transition that occurs for magnetic fields applied parallel to the z -axis. However, even though a temperature as low as a few millikelvin (~ 50 mK) may be produced by using the technique of magnetic cooling (a good description may be found in Mendelssohn⁹), temperatures as low as this are not recommended for the program for two reasons. Firstly, at these very low temperatures some new physics occurs; the magnetic moments of the nuclei may become aligned through the hyperfine interaction and would, therefore, add an extra contribution to the molecular field. The approximations made in setting up the model used here are inadequate to represent this effect correctly. Secondly, overflows may occur when calculating the exponential factors, thus causing the program to end abnormally, the exact effect will depend on the computer operating system under which the job is being run.

Higher temperatures are also well worth investigating. The next convenient experimental temperature would be 77 K, the temperature of liquid nitrogen. Increasing the temperature allows more of the energy levels to be populated in proportion to the usual Boltzmann factor. This changes the averaged magnetic moment of each ion and smears out the magnetic ordering over a greater range of applied magnetic fields. For higher temperatures, stronger magnetic fields will be required to induce the ordering. Note that praseodymium melts at about 1300 K so temperatures larger than this would not be sensible.

Having investigated the role of temperature, the other parameters easily varied are the two molecular field constants λ and μ . Equation (1) of section 2 shows how these parameters are related to the strengths of the internal magnetic fields. By applying a large hydrostatic pressure to the crystal one might expect to change the lattice spacings and hence alter λ and μ . Because the interaction between two local magnetic moments has the oscillatory RKKY form, changing the lattice spacing by small amounts may change both the magnitude and the sign of either λ or μ , or both. Unfortunately, the way in which this would happen is rather complex, and lies on the frontiers of current research, so it is difficult to give an easy physical picture. Nevertheless it is instructive to vary both λ and μ . Try varying them one at a time, in small steps, to build up a picture of the behaviour of the system you have created within a parameter space limited by, say, $-5 \leq \lambda, \mu \leq 5$ K. This will represent a lot of computing and may well need more than one session to do it properly.

As an extension to the work, there is the possibility of building up the sort

of pictures you would get from a neutron diffraction experiment. This was discussed briefly in section 4.

Not only are there anomalies in the magnetization curves, there are also associated anomalies in the resistivity curves or magneto-resistance, if it is measured as a function of applied magnetic field. For those who would like to study this aspect, and who are willing to write their own programs it is an easy matter. The equations necessary may be found in either of the two references¹⁰ at the end of this chapter, the only extra ones required are those to calculate two matrices that contain the scattering probability information.

Another extension of the work, which requires no extra programming, is to keep $\lambda = -1.20$, $\mu = 4.14$ and to reset the constants BH2, BH4, BH6, BC2, BC4, BC6 used in the program. These are the constants multiplying the various Stevens operators and represent the strengths of each of the terms of different symmetry in the electric crystal field. Altering their values will have the effect of altering the energy levels and the order in which they occur in the absence of an applied magnetic field. Thus a hypothetical praseodymium may be 'produced' in which a completely different arrangement of the levels is investigated. This extension will be most suitable for those who wish to delve into the current research literature to obtain the most up-to-date values for the crystal field constants in a point charge model.

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PRASEODYMIUM

```

      DIMENSION RHH(9,9),RHC(9,9),EVALC(9),EVALHK(9)
      DIMENSION RZ0(9,9),RMO(9,9),RPO(9,9),RES(50,5)
      DIMENSION RX0(9,9),USE(9)
      LOGICAL A4
      A4=.FALSE.
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C   THE LOGICAL VARIABLE A4 GOVERNS THE SIZE OF THE GRAPHS PRODUCED ON
C 120 COLUMNS THAT IS 12 INCHES. A4=TRUE GIVES GRAPHS OCCUPYING
C ONLY 71 COLUMNS WIDTH AND IS THEREFORE SUITABLE FOR OUTPUTTING
C RESULTS TO NORMAL TELETYPES
C A4 IS SET TRUE IF THE NUMBER OF FIELD STEPS (THE FIRST DATA ITEM)
C IS NEGATIVE, OTHERWISE IT REMAINS FALSE.
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C SET THE OPERATOR MATRICES TO ZERO BEFORE SETTING THEIR
C NON ZERO ELEMENTS
C
      DO 100 I=1,9
      DO 100 J=1,9
      RZ0(I,J)=0.0
      RMO(I,J)=0.0
      RX0(I,J)=0.0
      RPO(I,J)=0.0
100 CONTINUE
C
C SET THE NON ZERO ELEMENTS OF THE FOUR OPERATOR MATRICES
C
      DO 200 I=1,9
      FI=FLOAT(5-I)
      RZ0(I,I)=FI
200 CONTINUE
      DO 205 I=2,9
      J=I-1
      FJ=FLOAT(J)
      FI=FLOAT(10-I)
      XX=FI*FJ
      XX=SQR1(XX)
      RPO(J,I)=XX
      RMO(I,J)=XX
205 CONTINUE
      DO 210 I=1,9
      DO 210 J=1,9
      RX0(I,J)=0.50*(RPO(I,J)+RMO(I,J))
210 CONTINUE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C DATA IS READ IN WITH THE FOLLOWING FORMATS
C
C NUMBER OF FIELD STEPS FOR EACH TEMPERATURE   FORMAT  I3
C IF NUMBER OF FIELD STEPS IS NEGATIVE
C THEN THE LINEPRINTER GRAPHS ARE PRODUCED A4 SIZE.
C
C LOWEST FIELD AND FIELD INCREMENT IN TESLA   FORMAT 2F6.2
C TWO MOLECULAR FIELD PARAMETERS IN KELVIN    FORMAT 2F7.2

```

PRASEODYMIUM

C (FOR DETAILS OF MOLECULAR FIELD CONSTANTS SEE EQN.(1) AND ASSOCIATED
C TEXT).

C INTEGER=0 FOR FIELD PARALLEL TO THE Z-AXIS FORMAT 11

C =1 FOR FIELD PARALLEL TO THE X-AXIS

C INTEGER=0 FOR NO PRINTING OF EIGENVECTORS FORMAT 11

C =1 FOR PRINTING OF ALL EIGENVECTORS

C SERIES OF TEMPERATURES THE LAST OF WHICH MUST

C BE NEGATIVE.

FORMAT F7.2

CC

READ(1,1008) NHS
IF(NHS.LT.0) A4=.TRUE.

NHS=IABS(NHS)

IF(NHS.GT.50) NHS=50

READ(1,1010) PHL,RHS

READ(1,1011) RM1,RM2

READ(1,1009) ID

READ(1,1009) IP

WRITE(2,1200)

WRITE(2,1201) RHL

WRITE(2,1202) NHS,RHS

IF(ID.EQ.0) GOTO 220

WRITE(2,1203)

GOTO 230

220 WRITE(2,1204)

230 CONTINUE

WRITE(2,1205) RM1,RM2

CRYSTAL FIELD PARAMETER ARE SET

BH2=4.920

BH4=1.390

BH6=1.240

BC2=0.0

BC4=BH4

BC6=BH6

300 READ(1,1012) T

IF(T.LT.0.0) GOTO 940

IM=30

DO 120 I=1,5

DO 120 J=1,50

RES(J,I)=0.0

120 CONTINUE

IH=0

RMAGC=0.0

RMAGH=0.0

CU IS CONVERSION FACTOR FROM TESLA TO KELVIN

CU=(0.8000092730)/1.38060

IF(RHL.GT.0.0) IM=100

310 IT=0

IH=IH+1

320 IT=IT+1

IF(IT.LT.IM) GO TO 325

WRITE(2,2900)

WRITE(2,2901) IH,II,IM