Rare Earth Ions in a Hexagonal Field. II*

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Energy levels, eigenfunctions and magnetic moments of rare earth ions in a crystal field of hexagonal symmetry have been obtained using a Hamiltonian of the form, $\mathcal{H} = \mu_B g J \cdot H + B_4^0 O_4^0 + B_6^0 (O_6^0 + 77/8 \ O_6^6)$. Results are presented for all J values appearing in the rare earth series and for values of the parameters covering the situations in which the crystal field interaction is dominant, in which the interaction with the magnetic field is dominant and in which the two interactions are comparable in magnitude.

I. Introduction

In the first paper of this series (*1*) hereafter referred to as SWI, energy levels, eigenfunctions and magnetic moments were obtained and presented for rare earth ions in a hexagonal field using the Hamiltonian, $\mathcal{H} = B_4^0 O_4^0 + B_6^0 (O_6^0 + 77/8 \ O_6^6)$. These zero-field results are useful in assessing the influence of the crystal field interaction on the heat capacity behavior of rare earth systems, an area of investigation being actively pursued in this laboratory. The earlier results are not useful in determining the magnetic characteristics (susceptibilities, etc.) of rare earth systems, another area of inquiry engaging the attention of investigators in this laboratory. The present work, which supplies the information needed in this latter connection, is like SWI in that it is for a crystal with an ideal axial ratio so that the second order interaction vanishes and, moreover, B_6^0/B_6^6 is taken as 8/77, the value expected from the point charge model for a crystal in which the axial ratio is ideal. In paper III of this series the stipulation of an ideal axial ratio will be relaxed and the second order interaction will be included.

Recent calculations made (*2*) for $J = 4$ indicate that the parallel component is the dominant contribution to the susceptibility. Hence present calculations have been limited to the case in which H is applied along the hexagonal axis. There may be instances in which the perpendicular component is important. In this case the present results will have to be supplemented by similar calculations made with H applied perpendicular to the hexagonal axis to deal with the susceptibility behavior of polycrystalline materials.

II. The Calculations

A. The Hamiltonian

The general Hamiltonian for a paramagnetic ion situated in a combined hexagonal crystal field and a uniform magnetic field is:

$$\mathcal{H} = \mu_B g J \cdot H + B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6. \tag{1}$$

When the assumptions of SWI (*1*) are valid, this Hamiltonian reduces to:

$$\mathcal{H} = \mu_B g J \cdot H + B_4^0 O_4^0 + B_6^0 (O_6^0 + 77/8 \ O_6^6) \tag{2}$$

or

$$\mathcal{H} = \mu_B g J \cdot H + W \left[x \frac{O_4}{F_4} + (1 - |x|) \frac{O_6}{F_6} \right]. \tag{3}$$

Results are obtained in terms of three parameters: W, x and c. W is the energy scaling factor used in SWI. x is a parameter which establishes the relative importance of the fourth and sixth order crystal field interactions. x and W are the same as the parameters originally introduced by Lea, Leask and Wolf (3) in their treatment of rare earth ions in a cubic field. c is newly introduced. $c = E_{mag}/E_{cr}$ where E_{mag} and E_{cr} are splittings of the energy of the ion by the magnetic and crystal field interactions, respectively, acting separately and alone. $E_{mag} = 2\mu \cdot H = 2\mu_B gJ \cdot H$. E_{cr} is denoted as W_{cr}, where W_{cr} is the overall splitting of the energy states due to the crystal field interaction, expressed in units of the parameter W. Values of W_{cr} can be obtained in the tables and graphs of SWI.

In the present calculations, as noted above, the magnetic field is assumed to be applied along the hexagonal axis. Thus:

$$J \cdot H = J_x H_x + J_y H_y + J_z H_z = J_z H_{\parallel}, \quad (4)$$

where $H_{\parallel} = |H|$.

Introducing c and Eq. (4) into Eq. (3) the Hamiltonian becomes:

$$\mathscr{H} = W \left[c \frac{W_{cr}}{2J} J_z + x \frac{O_4}{F_4} + (1 - |x|) \frac{O_6}{F_6} \right]. \quad (5)$$

This is the form of the Hamiltonian used in the calculations. It is taken to be applicable not only for an applied magnetic field but also for ferromagnetic or ferrimagnetic materials with H representing the exchange interactions via the molecular field approximation. In this case the field strength $H = H_W = 2[(g - 1)/g]H_{exch}$. Here H_W is the Weiss field, H_{exch} is the exchange field acting between the paramagnetic ions and g is the g-factor of the ionic level involved.

B. Eigenfunctions and Magnetic Moments

In the Hamiltonian in Eq. (5) we are assuming that the spin orbit coupling energy is strong compared to both the crystal field and magnetic energies. Eigenfunctions are then presented in the LSJM scheme and are given in the form:

$$\psi = \sum_{M=-J}^{J} a_{iM} |M\rangle \quad (6)$$

where $|M\rangle = |LSJM\rangle$. The nomenclature of the levels and eigenfunctions are identical with that of SWI.

The magnetic moment is given by:

$$\mu = \frac{1}{gJ} \langle \psi | gJ | \psi \rangle = \frac{1}{J} \langle \psi | J | \psi \rangle. \quad (7)$$

The division by gJ allows the magnetic moment to be given in "free ion" units. The magnetic field induces in each of the energy levels a magnetic moment parallel to its direction. The combined permanent and induced magnetic moment of the energy level is obtained from Eq. (7) and is given by the expression:

$$\mu_{\parallel} = \frac{1}{J} \sum_{M=-J}^{J} M a_M{}^2. \quad (8)$$

The degenerate levels will split under the influence of the magnetic field. Since there are no levels which contain cross terms corresponding to $\triangle M = \pm 1$, such as occurs in the pure crystal field case, permanent moments perpendicular to the hexagonal c-axis will vanish.

Singlets which have no magnetic moment in the pure crystal field case will develop an induced moment under the influence of a magnetic field. This leads to the Van Vleck paramagnetism if the singlet is the ground state. A singlet composed of only $|M = 0\rangle$ component is not polarized by a magnetic field applied along the hexagonal axis. If $|M = 0\rangle$ is the ground state, the susceptibility along the hexagonal axis will vanish at low temperatures.

III. Results and Discussion

Results are summarized in Tables II through VII[1] and in Figs. 1 through 30. Information is given concerning the energy levels, nature of the eigenfunctions and the magnetic moments. The data in the tables are copied directly from the computer sheets. The presentation of results has been arranged to conform as far as possible with the practice employed in SWI.

A. The Tabular Data

Calculations have been made for all J values appearing in the ground state multiplets of the rare earth series. The parameter x gives the relative importance of the fourth and sixth order interactions [see Eq. (3)]. $c - 2\mu H/CFOAS = 2\mu H/W_{cr}$; it defines the relative importance of the magnetic and electrostatic perturbations. In
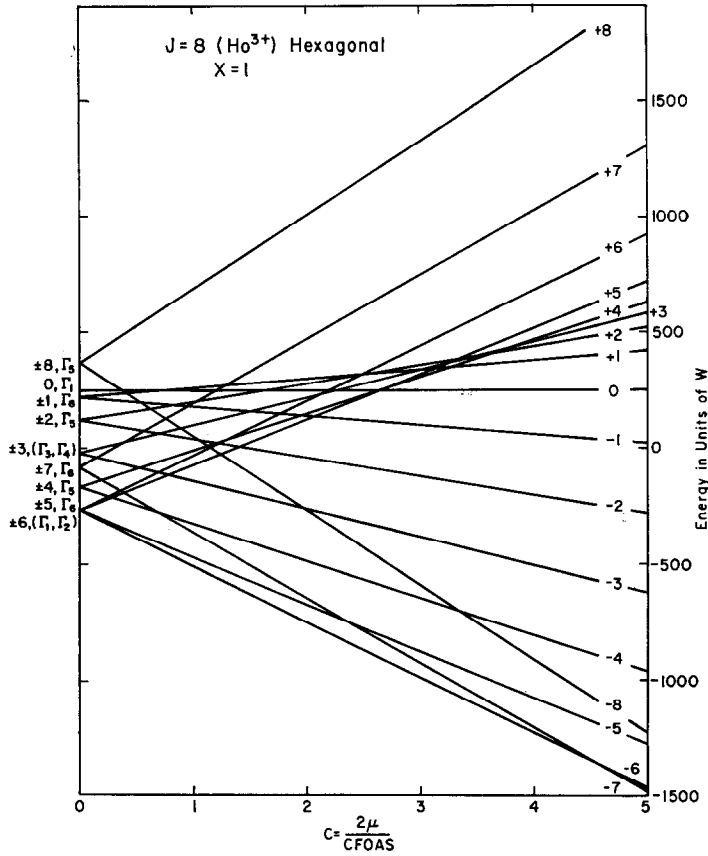
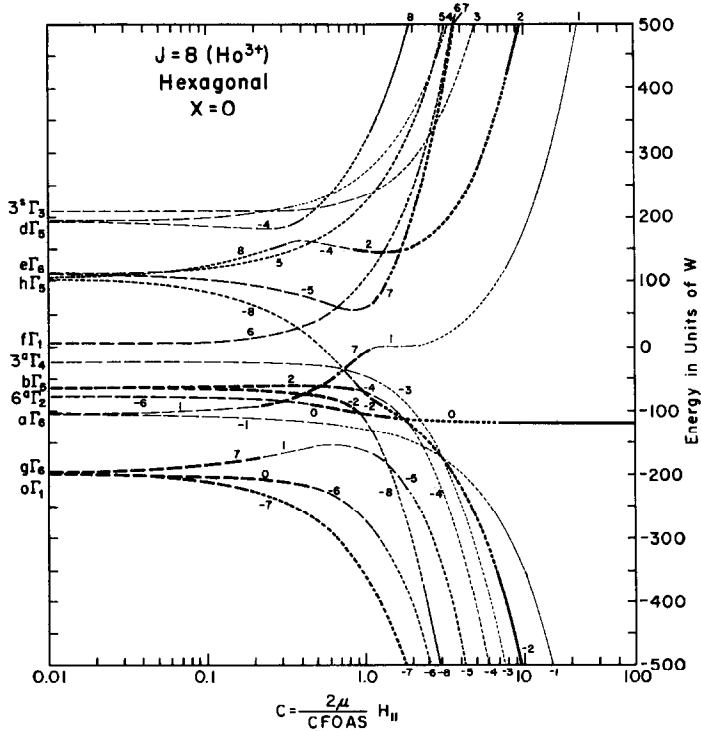FIG. 1. Energies versus c for $J = 8$, $x = 1$.

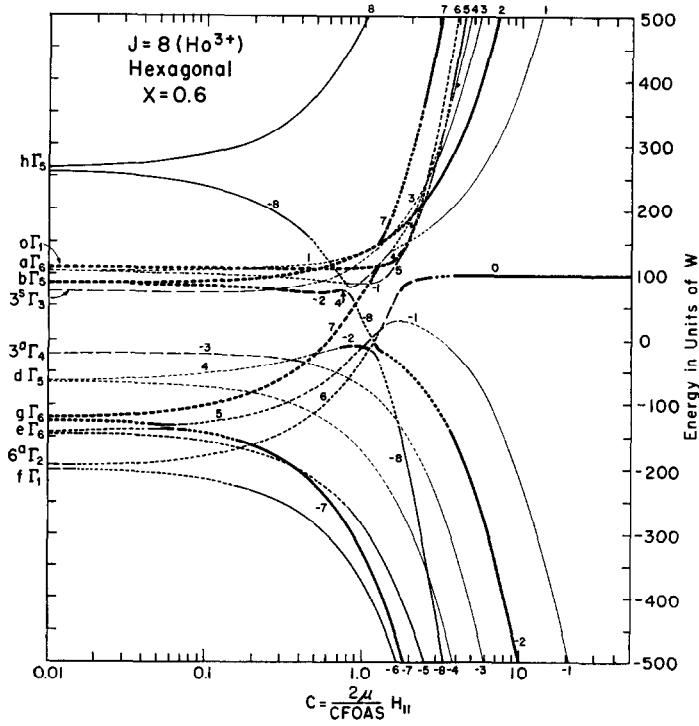FIG. 2. Energies versus c for $J = 8$, $x = 0$.

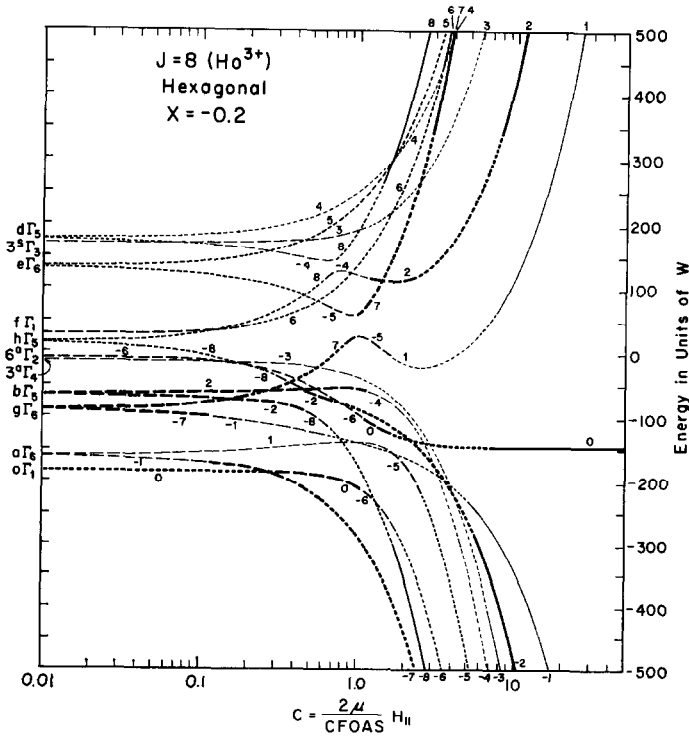FIG. 3. Energies versus c for $J = 8$, $x = 0.6$.

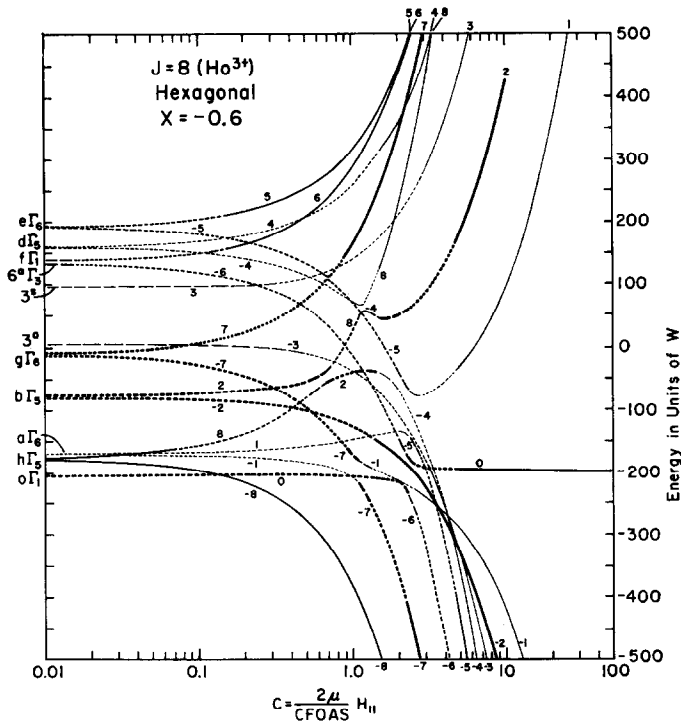FIG. 4. Energies versus c for $J = 8$, $x = -0.2$.

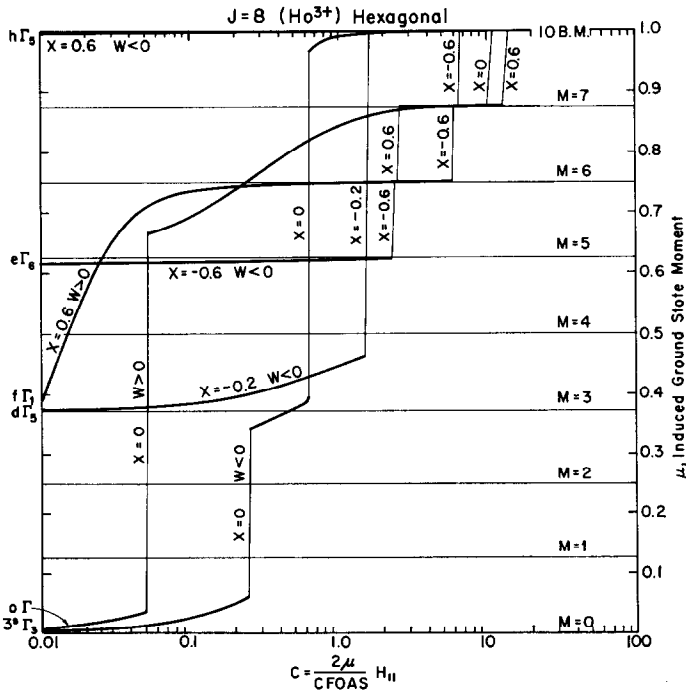FIG. 5. Energies versus c for $J = 8$, $x = -0.6$.

FIG. 6. Ground state magnetic moments versus c for $J = 8$.
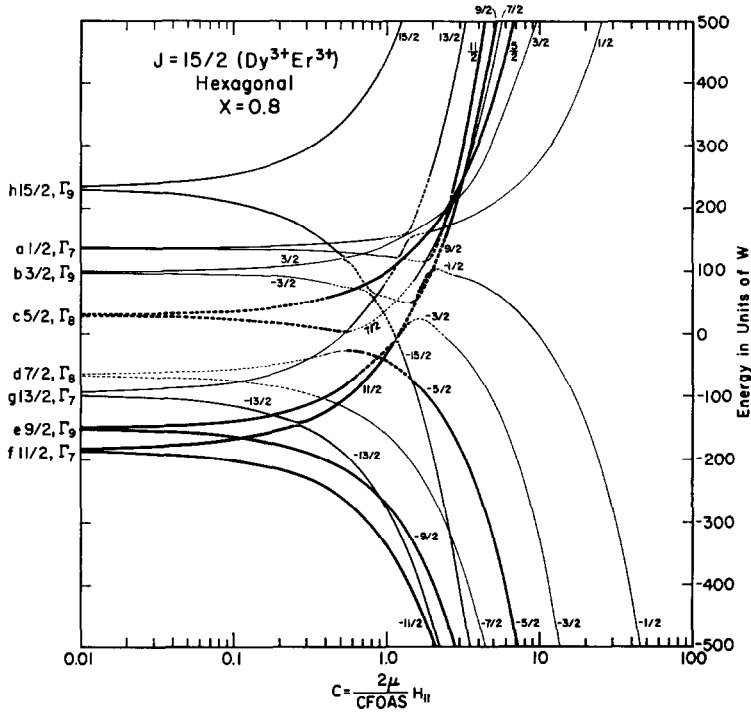
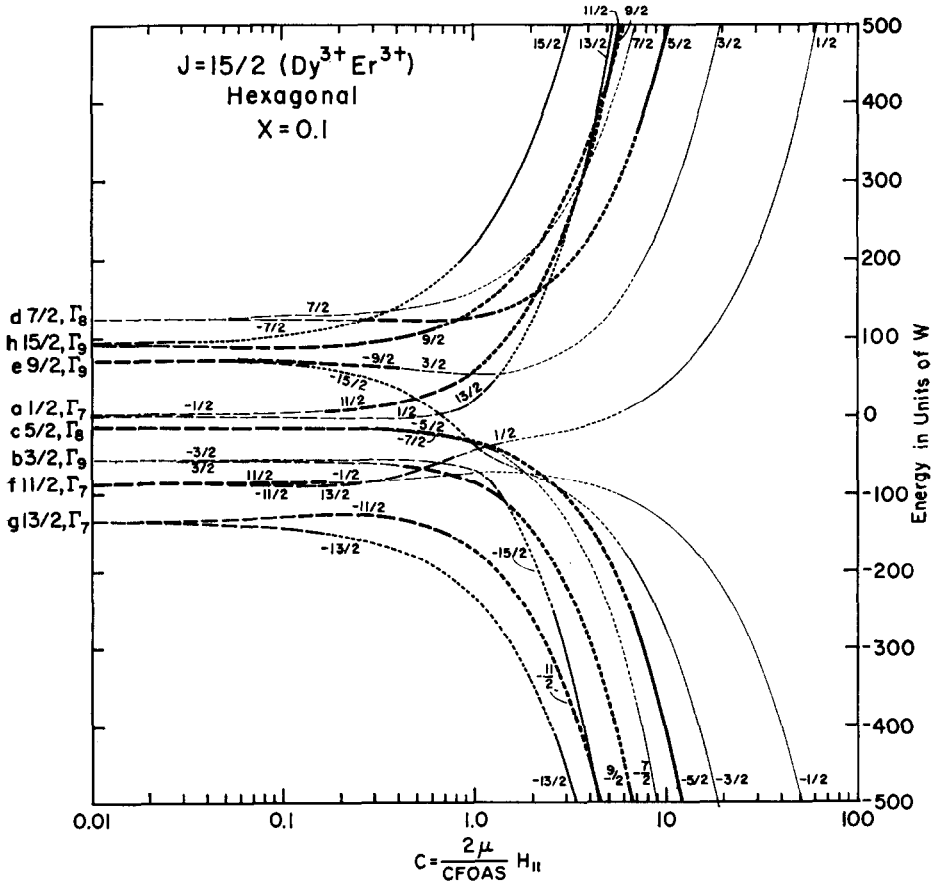FIG. 7. Energies versus c for $J = 15/2$, $x = 0.8$.

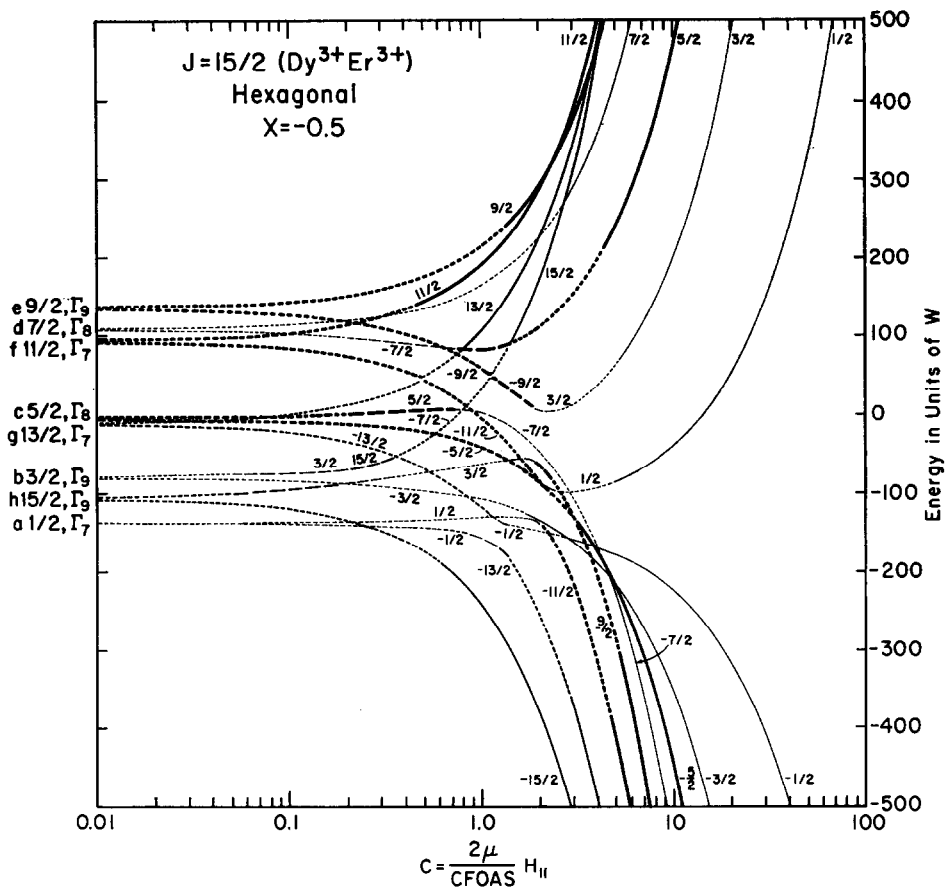FIG. 8. Energies versus c for $J = 15/2$, $x = 0.1$.

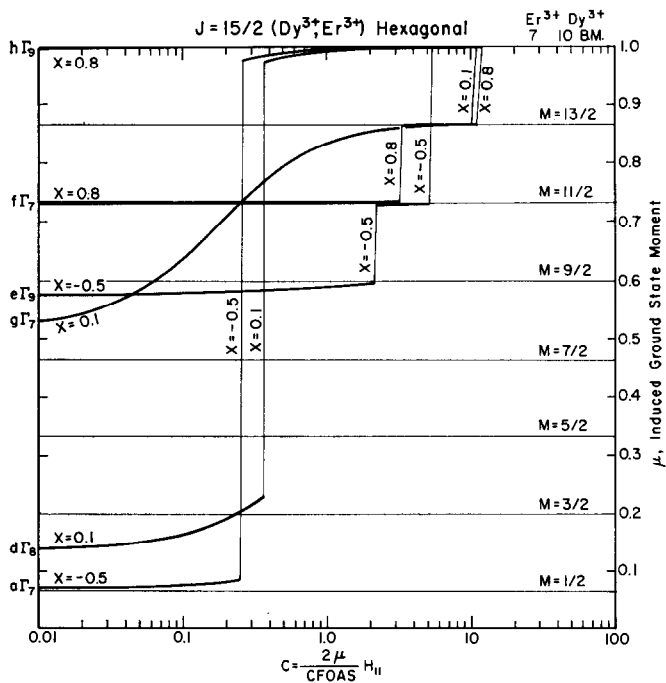FIG. 9. Energies versus c for $J = 15/2$, $x = -0.5$.

FIG. 10. Ground state moments versus c for $J = 15/2$.

FIG. 11. Energies versus c for $J = 6$, $x = 1$.

FIG. 12. Energies versus c for $J = 6$, $x = 0$.

FIG. 13. Energies versus c for $J = 6$, $x = 0.8$.

FIG. 14. Energies versus c for $J = 6$, $x = -0.6$.

FIG. 15. Ground state moments versus c for $J = 6$.

FIG. 16. Energies versus c for $J = 9/2$, $x = 1$.

FIG. 17. Energies versus c for $J = 9/2$, $x = 0.6$.

FIG. 18. Energies versus c for $J = 9/2$, $x = 0.2$.

FIG. 19. Energies versus c for $J = 9/2$, $x = -0.8$.

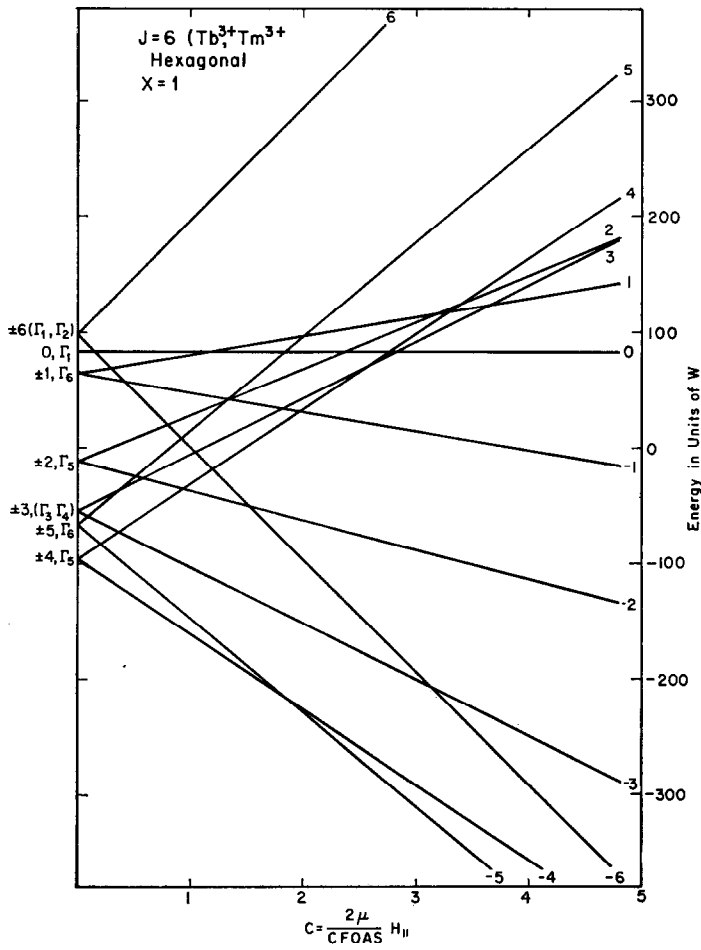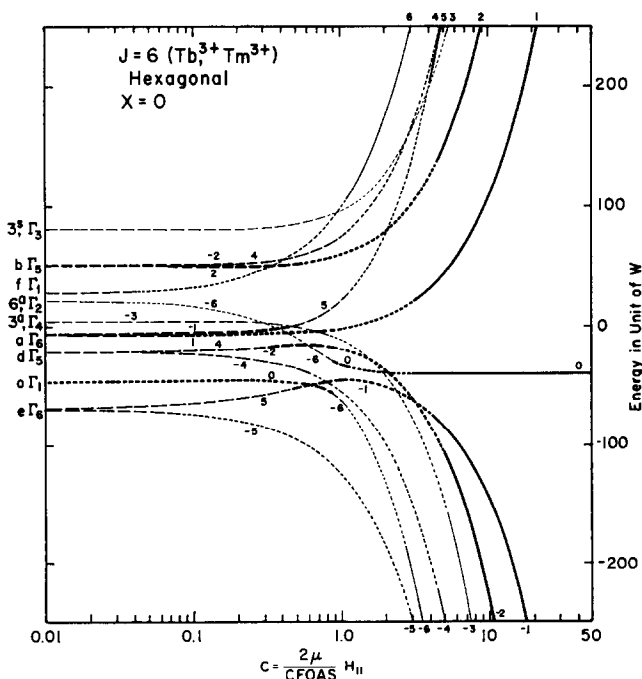

FIG. 20. Ground state moments versus c for $J = 9/2$.

FIG. 21. Energies versus c for $J = 4$, $x = 1$.

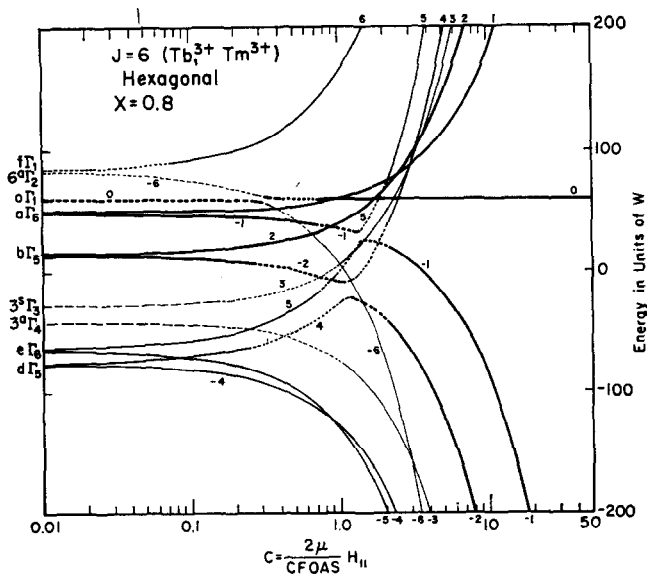FIG. 22. Energies versus c for $J = 4$, $x = 0$.
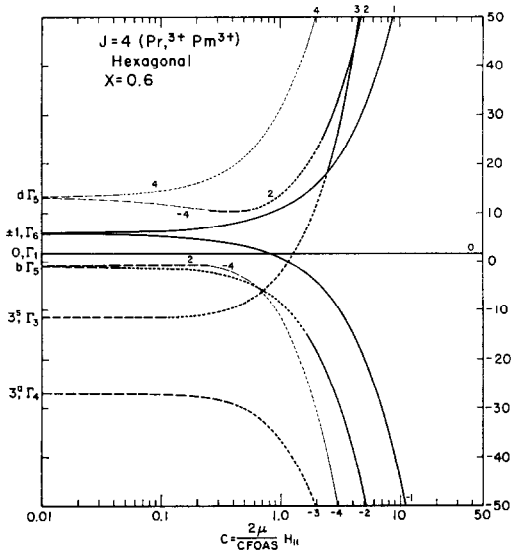
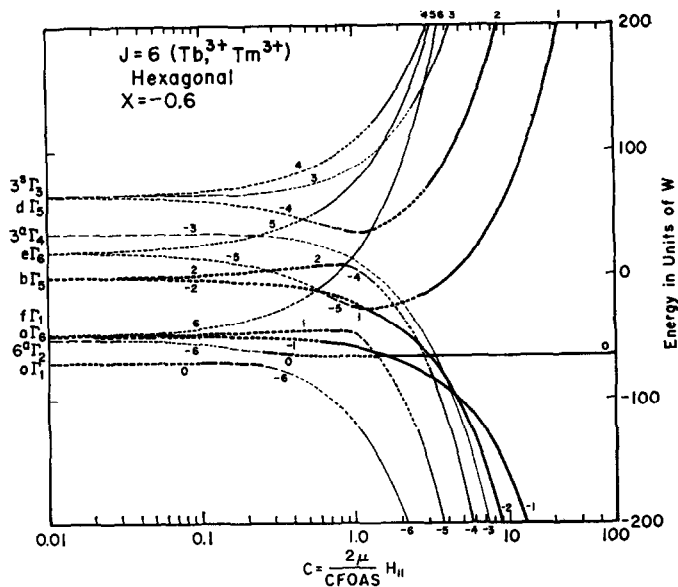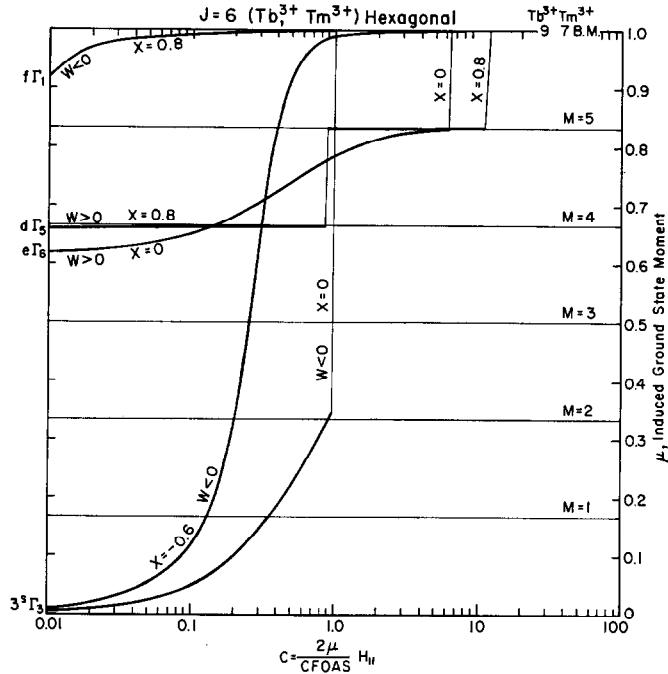FIG. 23. Energies versus c for $J = 4$, $x = 0.6$.

FIG. 24. Energies versus c for $J = 4$, $x = -0.8$.
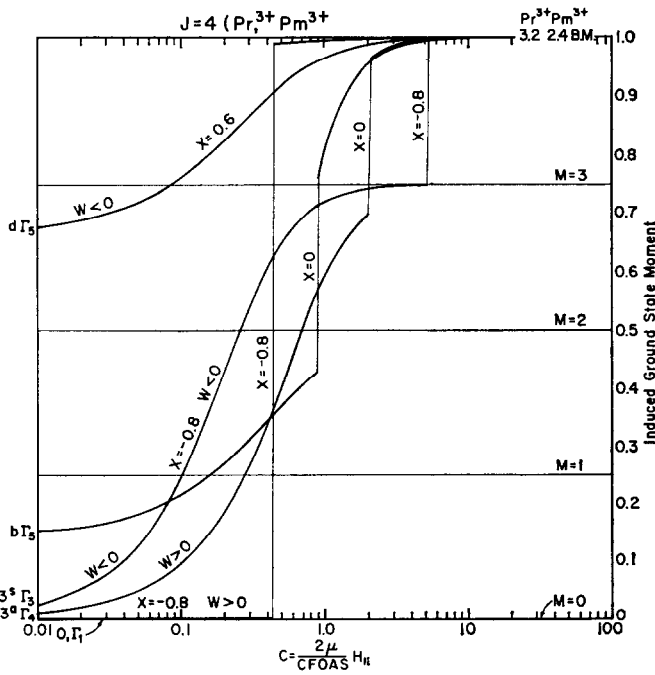
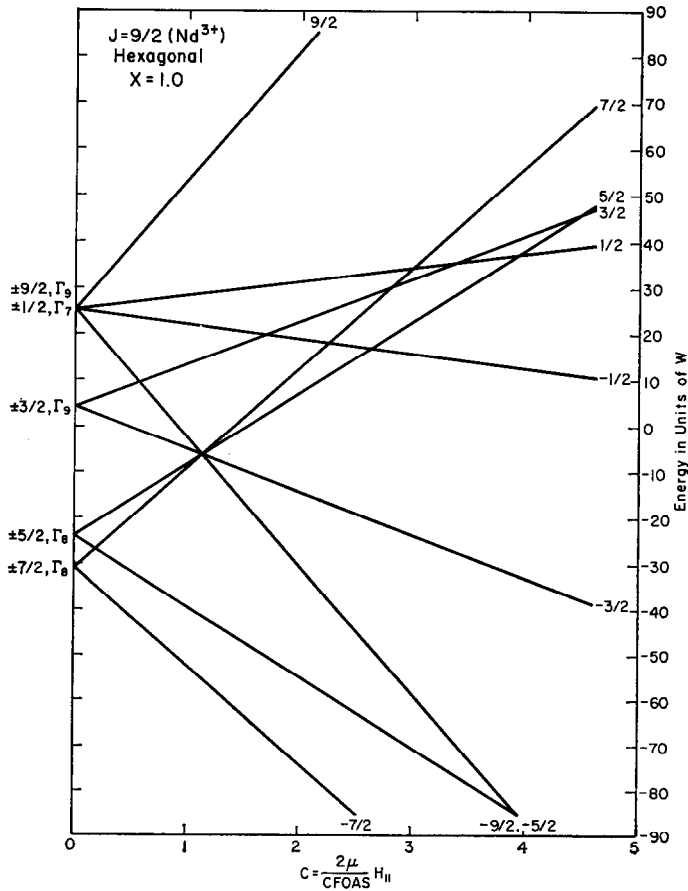FIG. 25. Ground state moments versus c for $J = 4$.
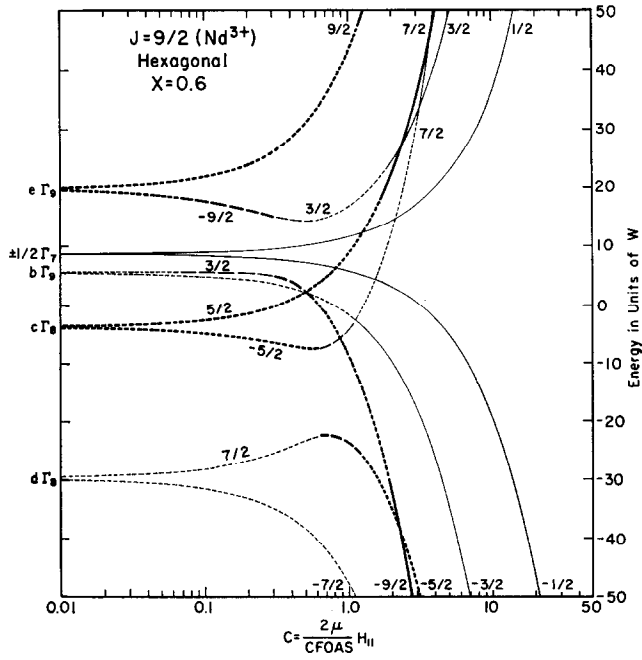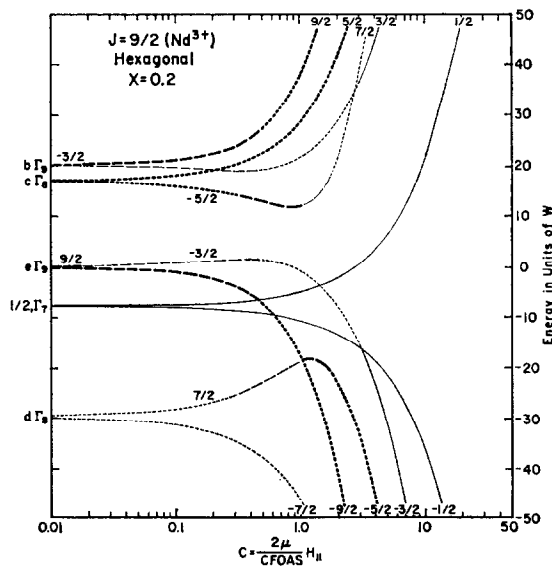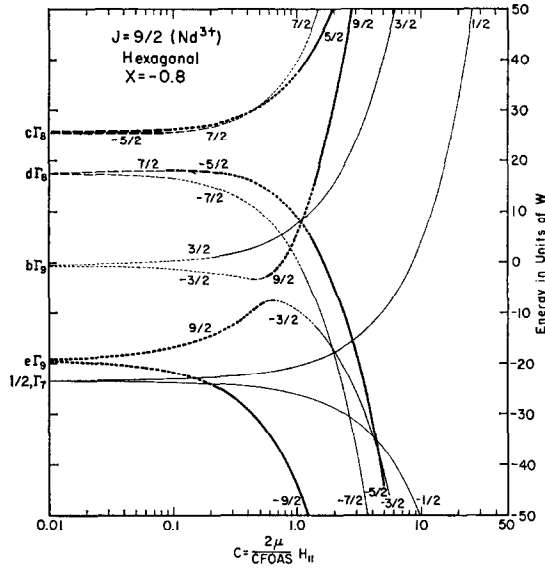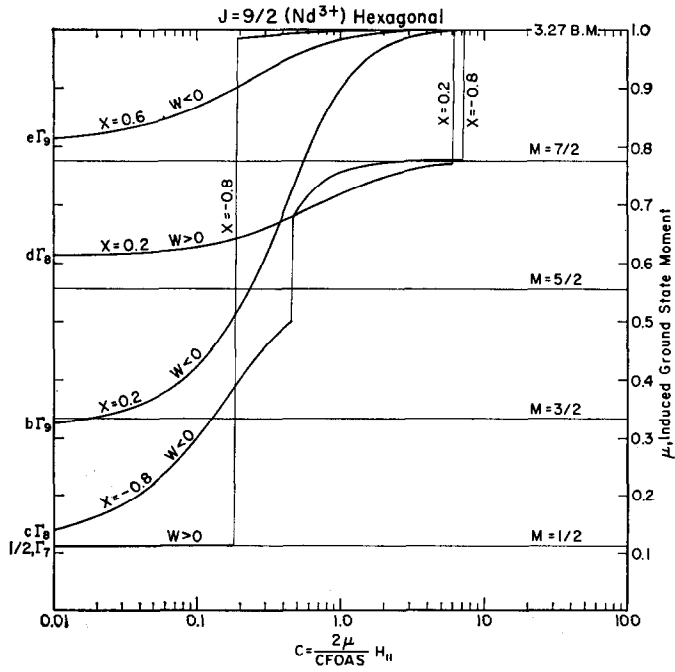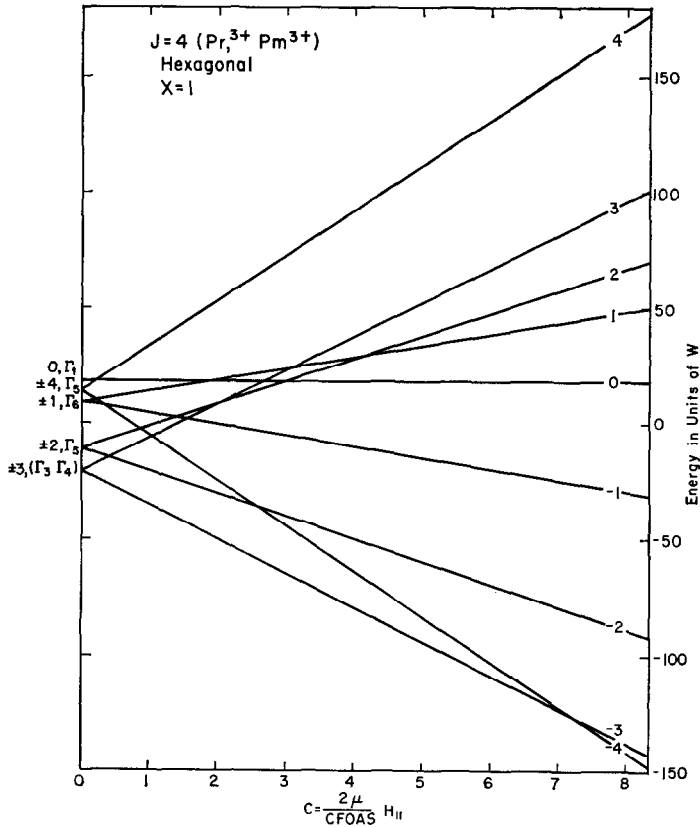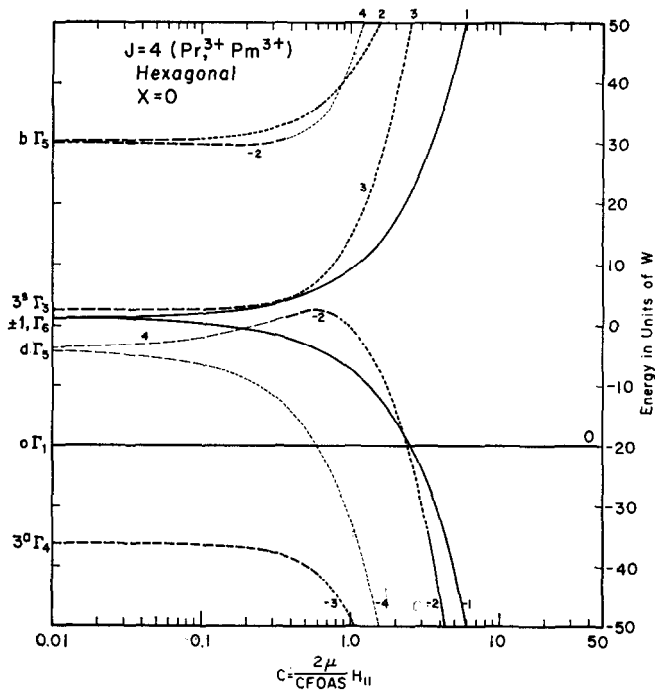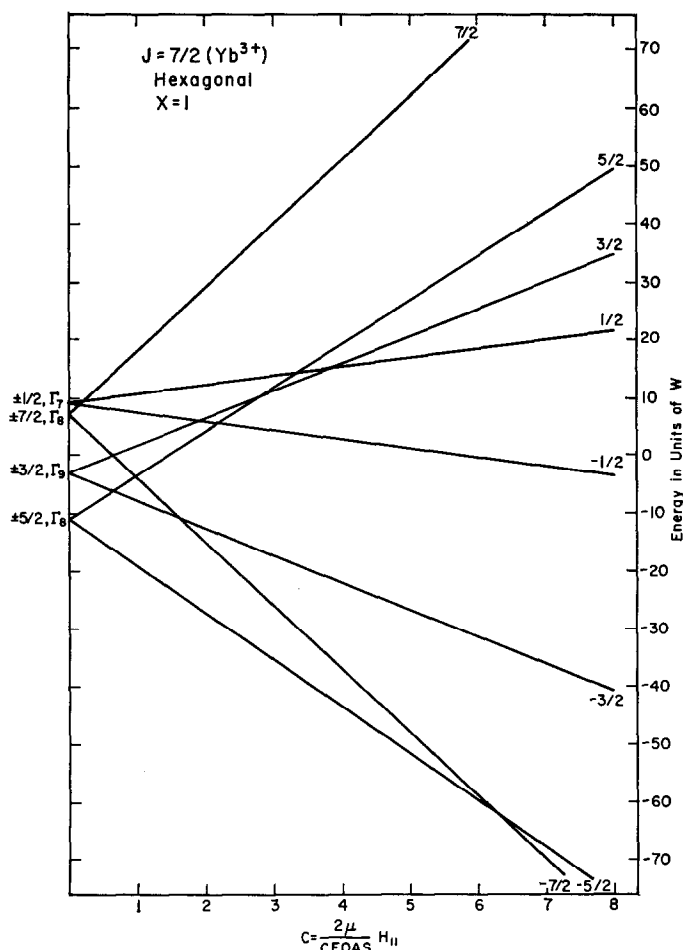
FIG. 26. Energies versus c for $J = 7/2$, $x = 1$.

column 1 of Tables II–VII energy in units of W are given for the $2J + 1$ crystal field states. Column 2, headed "HEPAL" or "HEFF," gives the corresponding magnetic moment in units of $gJ\mu_B$. The remaining columns under M_i (M_i ranging from $-J$ to $+J$) give the normalized coefficients in the eigenfunction $= \sum_{M=-J}^{J} a_{iM} |M\rangle$.

No tabular data for $J = 5/2$ are given. In this case the Hamiltonian given in Eq. (9) (*vide infra*)

TABLE I

OVERALL CRYSTAL FIELD SPLITTINGS $(W_{cr})^a$

J	8	15/2	6	9/2	4	7/2	5/2
W_{cr}	637	494	195	56	39	22	5

^{a} This is the quantity E_{cr} expressed in units of W. W_{cr} is designated CFOAS in the legend of the diagrams.

applies and energies are linear with c, moments are constant (see Fig. 30) and the eigenfunctions are independent of c.

B. Graphical Presentations

For cases in which $x \neq \pm 1$, a logarithmic scale for c, which is proportional to the magnetic field strength, is used in the graphical presentations to enable a wide range of this parameter to be included—from a dominant crystal field ($c = 0.01$) to a dominant magnetic field ($c = 100$). When $x = \pm 1$ the Hamiltonian is diagonal:

$$\mathcal{H} = W\left[\frac{O_4}{F_4} + \frac{W_{cr}}{2J}J_z c\right] = \mu_B g H_{\parallel} J_z + W\frac{O_4}{F_4}. \quad (9)$$

With the Hamiltonian of Eq. (9), the eigenfunctions do not depend on c and energies are linear with c. In this case, the crystal field doublets are of the form $|\pm M\rangle$ and under the influence of

FIG. 27. Energies versus c for $J = 7/2$, $x = 0.6$.

a magnetic field the degeneracy is lifted, forming two levels corresponding to $+M$ and $-M$. A linear scale for c is used when $x = \pm 1$ to emphasize the linear dependence of energy on magnetic field.

Since the Hamiltonian in Eq. (9) is diagonal, the energies, eigenfunctions and magnetic moments are very easily obtained. For convenience, the values of W_{cr} energy in units of W, are given in Table I. These are obtained from SWI. $F_4 = 60$ for all J values. The J_z matrices are, of course,

$$
\begin{pmatrix}
-J & & & & \\
 & \ddots & & & \\
 & & -M & & O \\
 & & & \ddots & \\
 & O & & M & \\
 & & & & \ddots \\
 & & & & & J
\end{pmatrix}
$$

The O_4 matrices are readily constructed from tables given by Hutchings (4).

As noted above, the nomenclature and presen-

tation of data are in conformity with the procedure in SWI insofar as possible. Specifically we note, in respect to the diagrams, the following practice is employed:

1. When the eigenfunction of a level does not depend on c or when there is a dominant M value for which $a_M^2 \geqslant 0.99$ ($a_M \gtrsim 0.995$), a solid line follows the level and the dominant M is indicated on it. Otherwise the line is broken. If the eigenfunction is composed of more than 80% of a certain M ($a_M \geqslant 0.9$), the dashes are short and dense. When the eigenfunction is less than 80%, the dashes are long.

2. The lines in the graphs follow the dominant M value. In this case of combined crystal and magnetic fields the Γ_i are no longer good quantum states. Although M is also not a good quantum number we use the dominant M value in characterizing the energy levels since this turns out to be simpler and more useful, in the sense of being more directly related to physical properties of
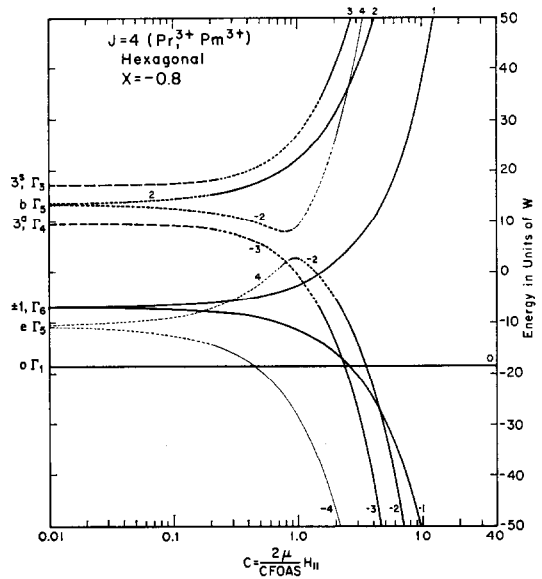
FIG. 28. Energies versus c for $J = 7/2$, $x = -0.4$.

FIG. 29. Ground state moments for $J = 7/2$.
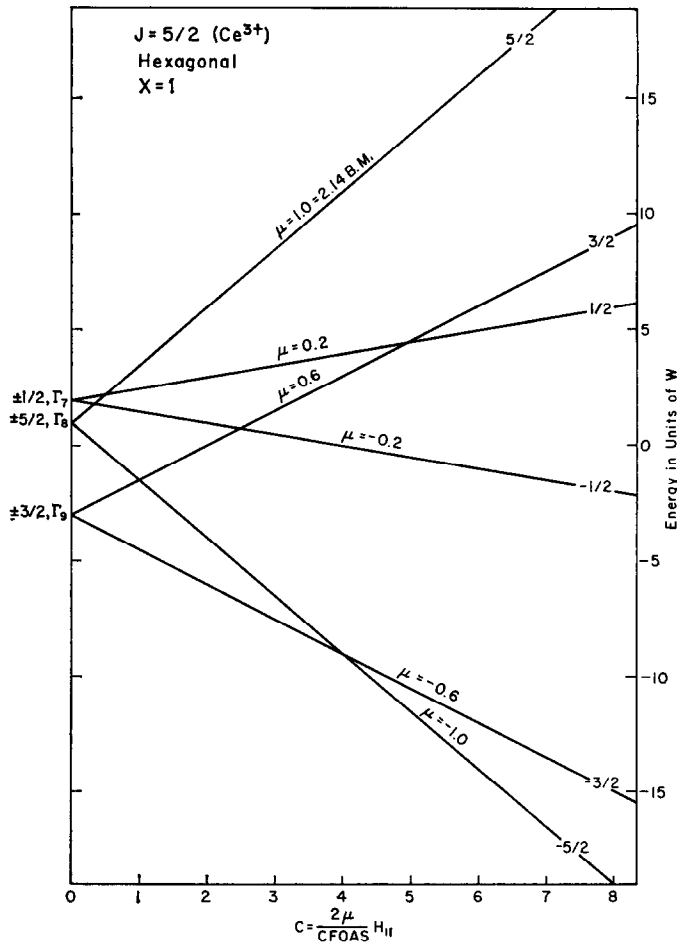
FIG. 30. Energies versus c for $J = 5/2$. Moments, which are independent of c, are also shown.

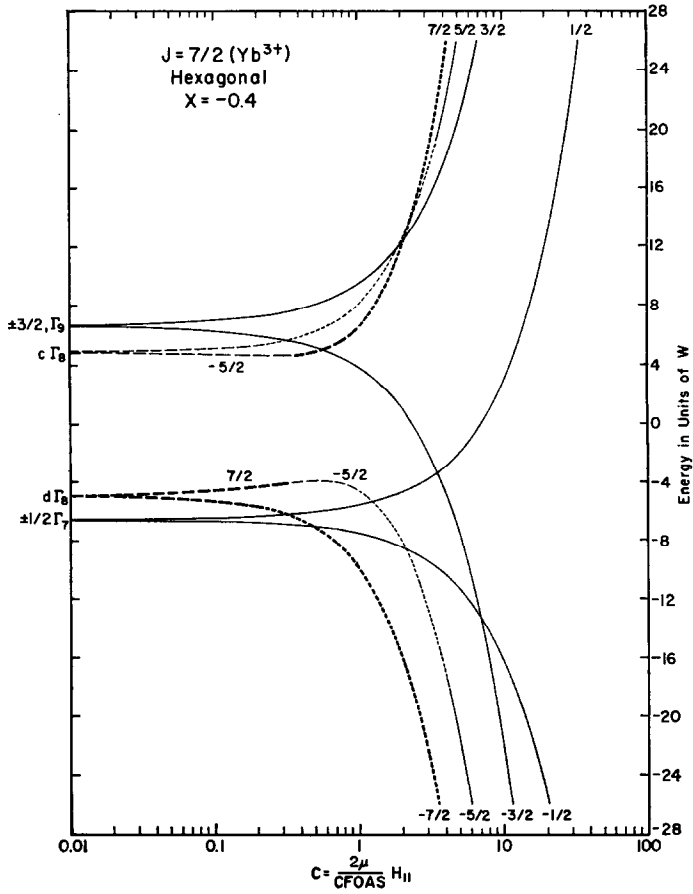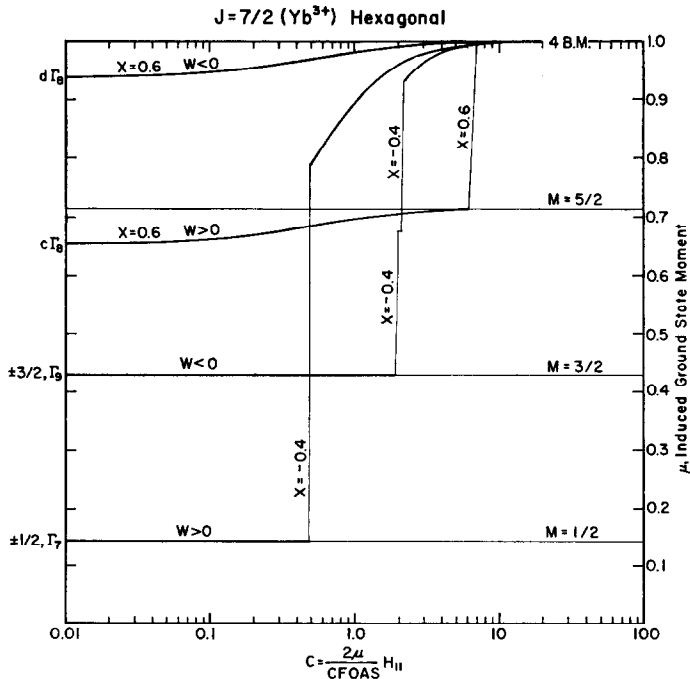the system, than other procedures that might be employed. With this procedure of characterizing states it sometimes becomes necessary to jump from one energy level to another. For example, in Fig. 5 for $J = 8$ the level $M = +8$ (which originated in $\Gamma_5 h$) jumps at $c = 0.66$ from $E = -60W$ to $E = -40W$, continuing at the level $M = +2$ (which originated in $\Gamma_5 b$). Then the same level $M = +8$ jumps once more at $c = 1.2$ from $E = 56W$ to $E = 67W$ continuing at the level $M = -4$ (which originated in $\Gamma_5 d$).

It is not possible to present results obtained for all values of the parameters c and x. Only a sampling is presented of the results of the calculations. These have been chosen with the aim of maximizing utility to experimentalists. Since crystal field effects are most noticeable at reduced temperatures at which the ground state is preferentially populated, we focus attention in the results presented on the ground state. Values of x were chosen so that all ground state possibilities are covered. For instance, an ion with $J = 15/2$ in a hexagonal crystal may theoretically have as ground state the levels h, a, g, f, e and d, but the two levels b and c can never be the ground state. In this case, i.e., $J = 15/2$, we have chosen $x = 0.8$, which covers possibilities f or h as the ground state, $x = 0.1$, which covers g or d, and $x = -0.5$, which would make a or e the ground state.

It would be too cumbersome to present diagrams for the magnetic moments of all the levels computed. Only the ground state moments were drawn; these are, of course, the moments which are relevant when the substance is at low temperature. For every J value the moments of all possible ground states were drawn as a function of the parameter c. At low c, the value

of the magnetic moment of the ion in the substance is characterized by the crystal field ground state. At high values of c, in all cases the free ion value is attained because the levels cross with the increasing magnetic field until at very strong magnetic fields the level $+J$ or $-J$ (depending on the sign of W) is the ground state. Once the magnetic moment of a substance at low temperature is known, the magnetic moment diagrams enable one to ascertain possible combinations for the parameters x and c and to establish the sign of W. These graphs are calculated for 0 K. At finite (but low) temperatures the graphs would appear continuous.

A simple computer program is given in the Appendix to calculate the energy levels, magnetic moments and eigenfunctions in the LSJM scheme, for any desired J, x and c values not given in the tables or graphs. The program is divided into the following steps:

1. The data, including the matrices, is placed into the computer. (The program given is for $J = 8$. For other J values one should put in the matrix elements of the appropriate J value (4). At this point the cards indicated by "$J = 8$" may need to be changed.)

2. A diagonalization program. This portion computes the energy levels and the eigenfunctions.

3. Computation of the magnetic moment.

4. Printing of the results. The results are printed in the form given in Tables II–VII.

References

1. E. SEGAL AND W. E. WALLACE, J. Solid State Chem. 2, 347 (1970).
2. R. S. CRAIG, S. G. SANKAR, V. U. S. RAO, W. E. WALLACE, AND E. SEGAL, J. Phys. Chem. Solids, in press.
3. K. R. LEA, M. J. M. LEASK, AND W. P. WOLF, J. Phys. Chem. Solids 23, 1381 (1962).
4. M. T. HUTCHINGS, Solid State Phys. 16, 277 (1966).

Appendix. Program for Computing Energies, Eigenvalues and Magnetic Moments

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      PIMENSICN A(17,17),HAMILT(17,17),S(17,17),VS(8,17)
     1,HPAL(17),ILCC(17),OU(A),RCOT(17),C(RO),HCR(3C),X(30)
C                          CATA INPLT
C   G=J VALLE. F4,F6=L.L.W. CONSTANTS. NC=NCMREF OF C VALLES. NX=NO. OF X VALUES.
C   H=ENERGY SCALF. HCP=CRYSTALFIELC CVERALL SPLITINGS IN UNITS OF H.
C   THE VALLES CF HCR SHOULD RE TAKEN FOR EACH VALUE OF X, FROM S.H.1 .
C                  THE $ SIGN INCICATES A NEW STATMENT
      G=8. $ F4=60. $ F6=13860.                                      J=8
      N=2.*G+1.5 $ AN=N $ NM1=N-1 $ NF1=N+1 $ J=NM1/2 $ JP=NF1/2
      JM3=J-6/2 $ JFM3=JP-6/2 $ H=1. $ NC=3 $ IX=1 $ PRINT 1F1
      REAC 2C1, (C(IC),IC=1,NC) $ PRINT 201, (C(IC),IC=1,NC)
      REAO 2C1, (HCR(IX),IX=1,NX) $ PPINT 201, (HCR(IX),IX=1,NX)
      REAC 2C1, (X(IX),IX=1,NX) $ FRINT 2C1, (X(IX),IX=1,NX) $ PRINT 1C2
      DO 40 IX=1,NX
      B4F4=H*X(IX) $ B6F6=H*(1.-ARSF(X(IX))) $ CFOAS=H*HCR(IX)
      DO 3C IC=1,NC $ WHPAL=C(IC)*CFOAS/(2.*G)
      DO 24 I=1,NM1 $ IP1=I+1 $ CO 24 K=IP1,N $ HAMILT(I,K)=C.
   24 CONTINLE
C                          THE MATPIX ELEMENTS
      OO(1)=364.*B4F4+104.*96F6 $ CO(2)=- 51.*P4F4-169.*E6F6      J=8
      OO(3)=-273.*E4F4- 78.*B6F6 $ OO(4)=-273.*B4F4+ 6F.*P6FE     J=8
      OO(5)=-168.*F4F4+128.*B6F6 $ OO(6)=- 21.*B4F4+ 92.*P6F6     J=8
      OO(7)=115.*B4F4+ 2.*96FE $ OO(8)=217.*P4F4- 85.*E6F6        J=8
      HAMILT(9,9)=     252.*B4F4-120.*P6F6          ·             J=8
C     DC 25 IA=1,JP                                               J ODD
      DC 25 IA=1,J                                                J EVEN
      AI=IA $ NP1=IA=NP1-IA $ WHPALM=(G+1.-AI)*WHPAL
      HAMILT(IA,IA)=-WHPALM+OO(IA) $ HAMILT(NP1=IA,NF1+IA)=WHPALM+CO(IA)
   25 CONTINLE
      O=(77./8.)*(360./F6)*B6FE                                   J=8
      HAMILT(1,7)=C*2.*SQRT(14.*143.) $ HAMILT(2,8)=C*7.*SCRT(13.*55.)  J=8
      HAMILT(3,9)=C*14.*SQRT(3.*143.) $ HAMILT(4,10)=C*12.*SCPT(13.*77.) J=8
      HAMILT(5,11)=C*42.*SQRT(11C.) $ HAMILT(6,12)=D*4E2.         J=8
C     DO 26 I=1,J*P3                                              J CDD
      DO 26 I=1,J*3                                               J EVEN
      NP1P1=NP1-I $ HAMILT(NP1P1-6,NP1P1)=HAMILT(I,I+6)
   26 CONTINLE
      DO 27 I=2,N $ IM1=I-1 $ DO 27 K=1,IM1 $ HAMILT(I,K)=HAMILT(K,I)
   27 CONTINUE
      DO 28 I=1,N $ DO 28 K=1,N $ A(I,K)=HAMILT(I,K)
   28 CONTINUE
   29 CONTINUE
```

Appendix, *continued*

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C                               DIAGONALIZATICN PROGRAM
      SQ=0. $ S(1,1)=1. $ DO 3 I=2,N $ S(I,I)=1. $ IM=I-1 $ CO 3 K=1,IM
      IF(ABSF(A(I,K))-10.E-15) 2,2,1
    1 SQ=SC+A(I,K)*A(I,K)
    2 S(I,K)=0.
    3 S(K,I)=0. $ V=SQRTF(SQ+SQ) $ TCL=V*1.E-9 $ FN=N $ IF (V) 14,14,4
    4 V=V/FN
    5 JJ=0 $ DC 12M=2,N $ MM=M-1 $ DC12L=1,MM $ IF(ABSF($(L,M))-V)12,6,6
    6 ALM=-A(L,M) $ UM=.5*(A(L,L)-A(M,M)) $ OMGA=ALM/SCRT(ALM*ALM+LM*UM)
      IF(ABSF(CMGA)-10.E-15) 12,12,7
    7 JJ = 1 $ IF(UM) 8,9,9
    8 OMGA=-CMGA
    9 SNT=CMGA/SCRTF(2.*(1.+SQRTF(1.-OMGA*CMGA))) $CST=SCRTF(1.-SNT*SNT)
      DO 10 I=1,N $ COM1=A(I,L) $ COM2=A(I,M) $ A(I,L)=CCM1*CST-CCM2*SNT

      A(I,M)=CCM1*SNT+COM2*CST $ CCM1=S(I,L) $ COM2=S(I,M)
      S(I,L)=CCM1*CST-COM2*SNT
   10 S(I,M)=CCM1*SNT+COM2*CST
      A(L,L)=A(L,L)*CST-A(M,L)*SNT $ A(M,M)=A(M,M)*CST+A(L,M)*SNT
      A(L,M)=0. $ A(M,L)=A(L,M) $ DO 11 I=1,N $ A(L,I)=A(I,L)
   11 A(M,I)=A(I,M)
   12 CONTINUE $ IF (JJ-1) 13,5,13
   13 IF(V-TCL) 14,14,4
   14 CCNTINUE $ DC 15 I=1,N $ ROOT(I)=A(I,I)
   15 ILCC(I)=I $ CC 18 I=1,NM1 $ IP1=I+1 $ IL=ILOC(I) $ TEMP=ROOT(IL)
      DO 17 K=IP1,N $ KL=ILOC(K) $ IF(TEMP-ROOT(KL)) 16,17,17
   16 TEMP=RCCT(KL) $ ITEMP=ILCC(I) $ ILCC(I)=ILOC(K) $ ILOC(K)=ITEMP
   17 CONTINUE
   18 CONTINUE $ IMAX=ILOC(1) $ IMIN=ILOC(N)

C
      OAS=RCCT(IMAX)-ROOT(IMIN)
C                          CALCULATING THE MAGNETIC MOMENTS
      DC 34 L=1,N $ SUMZ=0.
      DC 31 I=1,N $ AI=I $ SUMZ=SUMZ+S(I,L)**2*(AI-(G+1.))
   31 CCNTINUE $ HFAL(L)=SUMZ/G
C                          PRINTING THE RESULTS
   34 CONTINUE $ PRINT 103, X(IX),C(IC),MCR(IX),OAS $ PRINT 104
      DO 35 I=1,N $ DO 35 L=1,J $ NP1ML=NP1-L $ VS(L,I)=S(NP1ML,I)     J=8
   35 CCNTINUE $ DC 36 I=1,N $ II=ILCC(I)
      PRINT 105, RCCT(II),HPAL(II),(S(K,II),K=1,JP),(VS(L,II),L=1,J)    J=8
   36 CONTINUE $ PRINT 104 $ PRINT 106
   30 CONTINUE                                                          IC
      PRINT 106 $ PRINT 106
  101 FORMAT(//////)
  102 FCRMAT(1H1)
  103 FORMAT(1H ,2HX=,F6.3,5X,2HC=F7.2,10X,6HCFOAS=,F8.3,2H*N,3X
     1,4HCAS=,E13.6,2H*N)
  104 FORMAT(1H ,4X,6HENERGY,7X,4HHPAL,10X,3HM=8,7X,3HM=7,7X          J=8
     1,3HM=6,7X,3HM=5,7X,3HM=4,7X,3HM=3,7X,3HM=2,7X,3HM=1,7X,3HM=0)    J=8
  105 FORMAT(1H ,E11.4,3X,F7.4,4X,2H-M,F9.6,8F10.6,2H-M/1H ,24X        J=8
     1,2H+M,F9.6,7F10.6,10X,2H+M)                                      J=8
  106 FORMAT(1H0)
  201 FORMAT(8F10.5)
   40 CONTINUE $ STCP $ END                                            IX
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