

## Rare Earth Ions in a Hexagonal Field IV\*

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Energy levels and eigenfunctions of rare earth ions in a crystal field of hexagonal symmetry have been obtained using a Hamiltonian of the form  $\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0$ . Results are presented for all  $J$  values appearing in the rare earth series. The order of the energy levels has been determined for all relative values of the second and fourth order crystal field intensity parameters,  $B_2^0$  and  $B_4^0$ . This, of course, includes information for the commercially significant  $\text{RCO}_5$  compounds, for which the second order term is dominant. The eigenfunctions are pure  $M$  states with permanent magnetic moments  $\pm Mg \mu_B$ . The moments are unchanged by a field applied along the  $c$  axis.

### I. Introduction

The perturbing influence of the crystalline electric field on a rare earth ion can be dealt with using the Hamiltonian.

$$\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6. \quad (1)$$

Here the  $B_n^m$  quantities are the so-called crystal field intensity parameters and  $O_n^m$  represent operators which are well-known polynomials in the angular momentum operators. They are tabulated by Hutchings for various values of  $J$  ( $I$ ). In paper I of this series ( $2$ ) the Hamiltonian was solved for the special case in which the axial ratio is ideal. Under these circumstances  $B_2^0$  vanishes. The point charge model was made use of to estimate the ratio of  $B_6^0/B_6^6$ . Using the value obtained, namely  $8/77$ , the above Hamiltonian can be put in form

$$\mathcal{H} = W \left[ x \frac{O_4^0}{F_4} + (1 - |x|) \frac{O_6^0}{F_6} \right]. \quad (2)$$

In this,  $O_6^0 = O_6^0 + 77/8 O_6^6$  and  $W/F_4$  and  $W/F_6$  are related to  $B_4^0$ ,  $B_6^0$  and  $x$  in a simple way. The Hamiltonian was used in this form for convenience in calculation.

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Compounds represented by the formula  $\text{RCO}_5$ , where R is a rare earth, are assuming considerable practical significance as permanent magnet materials ( $3$ ). Their utility stems primarily from their powerful magnetocrystalline anisotropy which in turn originates with the influence of the crystalline electric field. The  $\text{RCO}_5$  compounds do not have an ideal axial ratio and hence  $B_2^0$  for them does not vanish. In fact, it has recently become clear ( $4-6$ ) that  $B_2^0 O_2^0$  is the dominant term in the Hamiltonian given in Eq. ( $1$ ).

In paper I of this series the Hamiltonian was solved for various values of  $x$ , which represents the relative importance of the fourth and sixth, order terms. Since the second order term is dominant for the important  $\text{RCO}_5$  series, it appears that results of corresponding calculations in terms of  $y$ , the relative importance of the fourth and second order interactions, would be useful. These are presented in the present paper.

### II. Results of Calculations

Actual calculations were made with the Hamiltonian in the form

$$\mathcal{H} = W_{24} \left[ \frac{(1 - |y|)}{F_2} O_2^0 + \frac{y}{F_4} O_4^0 \right], \quad (3)$$

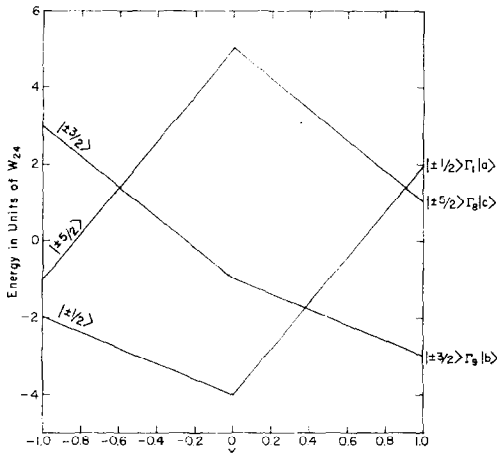


FIG. 1. Energy levels for various values of  $\gamma$  for  $J = 5/2$ .

where  $B_4^0 F_4 = W_{24} \gamma$  and  $B_2^0 F_2 = W_{24} (1 - |\gamma|)$ .  $F_2$  and  $F_4$  are the well-known Stevens (7) multiplier factors. Since only operators of the form  $O_n^0$  are involved the matrix corresponding to the Hamiltonian is diagonal and the eigenvectors are pure  $M$  states. The eigenvalues for various  $J$  values in terms of the scaling factor  $W_{24}$  are displayed graphically in Figs. 1-7. The eigenvectors are also given so that the nature

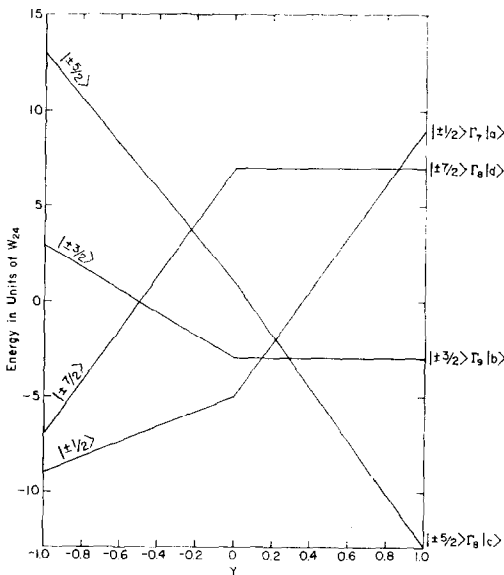


FIG. 2. Energy levels for  $J = 7/2$ .

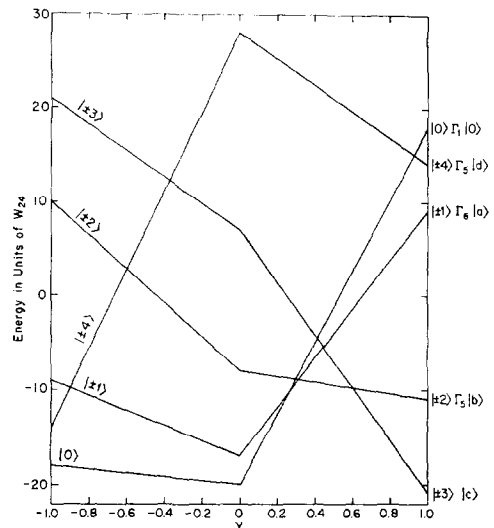


FIG. 3. Energy levels for  $J = 4$ .

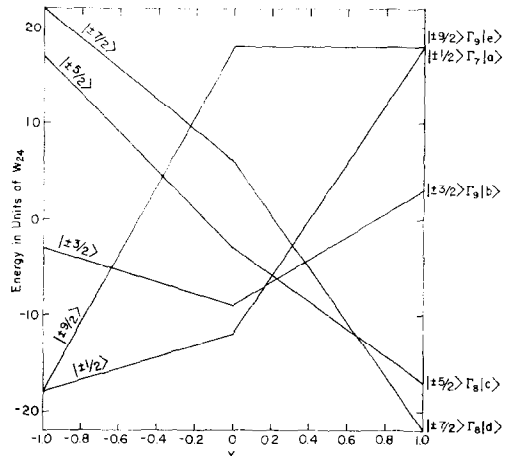


FIG. 4. Energy levels for  $J = 9/2$ .

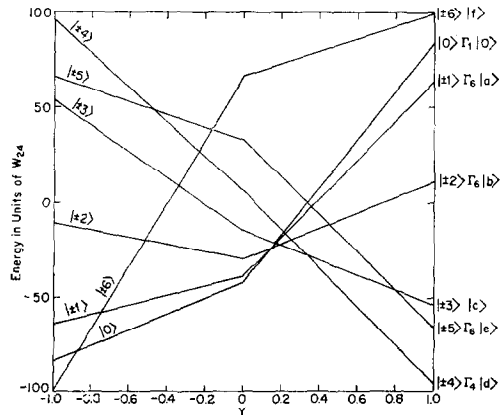
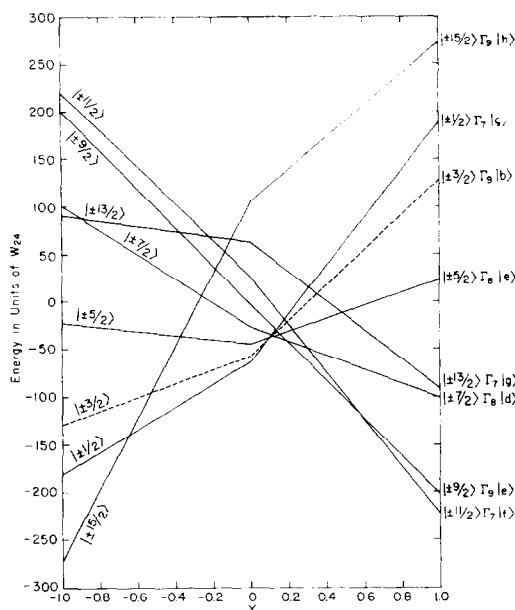
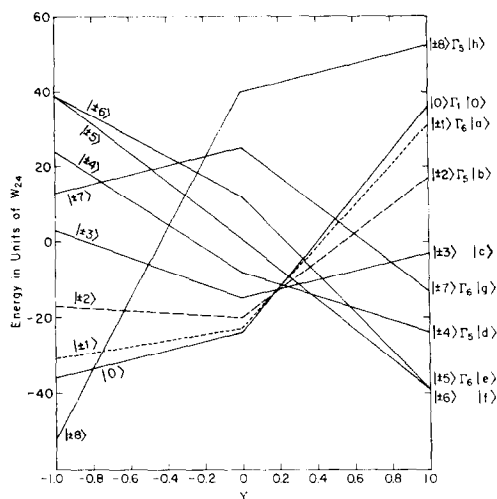


FIG. 5. Energy levels for  $J = 6$ .

FIG. 6. Energy levels for  $J = 15/2$ .

of the ground state for various values of  $\gamma$  can be identified.

The permanent moments of the several crystal field states are  $\pm Mg \mu_B$ . For example, for  $Ce^{3+}$  ( $J = 5/2$ ) the ground state moment is  $\pm \frac{1}{2}g \mu_B$  if  $W_{24}$  is positive and the interaction is pure second order. These moments ( $\pm Mg \mu_B$ ) are unmodified by an applied magnetic field if it is directed along the  $c$  axis. If, however, the field is applied  $\perp$  to the  $c$  axis, the matrix contains off diagonal terms and the eigenvectors are no longer pure  $M$  states. Calculations in these cases have been made (8, 9) for  $Ce^{3+}$  and  $Pr^{3+}$  with  $J = 5/2$  and 4 but not for the other  $J$  values appearing in the rare earth series.

FIG. 7. Energy levels for  $J = 8$ .

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