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Anisotropic exchange effects in optical spectra: Er^{3+} in ferromagnetic $Tb(OH)_3$

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The theory of spontaneous splittings of impurity levels in magnetic insulators below their ordering temperatures has been examined, with particular consideration of the anisotropies of the interactions and possible collective excitation effects. Under appropriate realistic conditions these splittings are *accurately* described by a first-order analysis, with the result that the contribution of the exchange interaction may be isolated and its orbital anisotropy determined empirically. As an illustration of the effectiveness of this method for studying the nature of the exchange interaction, the splittings of isolated Er^{3+} impurities have been investigated in ferromagnetic $Tb(OH)_3$. This is a system for which a number of the simplifying conditions can be shown to apply quite accurately, so that the exchange contribution can be isolated unambiguously from the competing effects of the crystal field, electric multipole, virtual phonon exchange, and magnetic dipole-dipole interactions. An effective exchange operator for the Er^{3+} ion has been derived in terms of single-electron spherical tensor operators which are applicable to all levels of the ground $4f^{11}$ configuration. A least-squares fit of 11 observed splittings using eight parameters has provided a good description of both the signs and magnitudes of the splittings. The results show that the contributions of the anisotropic terms are generally one order of magnitude larger than the contribution of the isotropic term, indicating that any realistic analysis of ion-ion interaction effects involving ions with large orbital admixtures must consider the effects of anisotropy in the exchange interaction as a major factor.

I. INTRODUCTION

It is well known that the exchange interaction which arises from the quantum-mechanical treatment of the electrostatic interaction between electrons can be considered as an effective spin-spin interaction.[1] For ions in pure orbitally nondegenerate S states or orbitally quenched states the form is[2]

$$\mathcal{H}_{\text{exch}} = -2J\vec{S}_1 \cdot \vec{S}_2 \ , \tag{1}$$

where J is a linear combination of "two-electron" exchange integrals and $\vec{S}_1$ and $\vec{S}_2$ are the real ionic spins of the individual ions. Such an interaction is valid for the ground states of a number of transition-metal ions in appropriate symmetries; but among all of the lanthanide ions, it provides a complete description of the exchange interaction only for the ground states of Gd^{3+} and Eu^{2+}, which have no orbital angular momentum.

Although a number of early investigators[3-7] were aware that the individual "two-electron" exchange integrals[8] depended on the orbital states of the electrons, and that this orbital dependence could result in a considerable amount of anisotropy for nonsinglet orbital states, the simple isotropic form above has been widely used in the analysis of data. Throughout the past few years, however, a considerable amount of experimental evidence has accumulated for a *significantly anisotropic* exchange interaction in cases where orbital angular momentum is not quenched. The first striking illustration was found in the anisotropy of the exchange splittings of Yb^{3+} levels in Yb iron garnet by Wickersheim and White.[9-11] Other examples have been provided by Ce^{3+} pair interactions in $LaCl_3$,[12-15] Er^{3+} splittings in Er iron garnet,[16-18] $Eu^{3+}-Cr^{3+}$ and $Eu^{3+}-Fe^{3+}$ interactions in the garnets,[19-23] $Ho^{3+}-Fe^{3+}$ interactions in yttrium iron garnet,[24] $Eu^{3+}-Eu^{3+}$ interactions,[25] and Cr^{3+} and V^{2+} pair interactions in several hosts.[26-30] More extensive lists have been given by Wolf[31] and Baker.[32]

While the results cited above have clearly shown the presence of anisotropic exchange in a wide range of systems, detailed treatment of these effects is difficult. Whether the theory is formulated in terms of "two-electron" exchange integrals,[2,27-29,33] or the generally more convenient two-electron tensor-operator expansions of Levy,[34,35] Elliot and Thorpe,[36] Huang and Van Vleck,[20,25] Nikiforov *et al.*,[30] or Copland and Newman,[37] as many as 1225 different parameters are required for a general description of rare-earth exchange.[35] (A model which describes interactions of this type has been given by Stevens.[38]) The analysis of experimental results is further complicated by competing effects from other interactions, such as the electric multipole interaction, which are often hard to distinguish from those due to exchange.[39]

The problem is thus to find a system for which the properties of the electronic states and the symmetry operations of the ions can be used to limit the number of parameters required to characterize the anisotropic exchange interaction in a completely general way. At the same time, it must be possible to isolate the effects of the exchange interaction from those of other interactions.

The purpose of the present paper is to demonstrate that a detailed analysis of anisotropic exchange effects is possible for the exchange splittings of isolated doublet energy levels of impurity ions in a magnetically ordered crystal and thus to provide information on the nature of the exchange anisotropy. The method of analysis employed here is also applicable to the exchange splitting of exciton levels in pure systems when the resonant energy transfer between neighboring ions and the resulting dispersion are known.[40]

In Sec. II, we consider systems for which an excitation is highly localized on the impurity ion and use the tensor operator description of the exchange interaction to derive a *unique* exchange potential[41] which is applicable to *all* levels in the $4f^n$ configuration of the impurity ion *under such circumstances.* The number of unknown parameters in this potential is determined by the magnetic point symmetry of the impurity site, resulting in a much greater reduction in the number of parameters than can be obtained on the basis of ion-pair symmetry alone. Moreover, if the magnetic system is *chosen* so that the splittings of the impurity ion are a first-order effect, with higher-order terms negligible,[42] the splittings of the impurity doublets will be due *only* to the exchange interaction and the magnetic dipole-dipole interaction. The magnetic-dipole contributions to the splittings may then be calculated and directly subtracted from the experimental splittings to yield the exchange contributions. It thus becomes feasible to *isolate* the exchange effects for a number of states of the impurity ion, and to gain enough information from optical studies of the splittings to completely determine the parameters in the theory.

It should be emphasized that the system is *chosen* to have the simple properties described above, not just assumed to have them. The validity of this approach is discussed in detail in Sec. II, and it will be shown that a number of real systems should meet the appropriate conditions.

The splittings of the Er^{3+} impurity levels in the Ising-like ferromagnet $Tb(OH)_3$ can be shown to fulfill all the necessary conditions, and measurements on this system are analyzed in detail in Sec. III. Both the signs and magnitudes of the experimental splittings are determined, and fitting them to a Hamiltonian of the appropriate form provides a rigorous test of the theory. The results illustrate dramatically the importance of anisotropic terms in the exchange interaction, as one might expect for ions with large orbital moments. A preliminary report of this work has been given earlier.[43]

II. THEORY OF IMPURITY SPECTRA IN MAGNETICALLY ORDERED CRYSTALS

Although the single-ion picture using an effective field to represent the spin-spin interactions has been fairly successful in explaining the results of optical experiments in magnetic insulators,[44] a rather more-detailed analysis is required to explain all features which are observed in some spectra.

Two kinds of refinements may be considered. One involves improvements in the statistical approximations used to represent the effects of the interactions and the possible effects of collective excitations. The other type of refinement involves improved characterization of the microscopic interactions, including contributions from the magnetic dipole-dipole interaction, the electric multipole interaction, and virtual phonon exchange, as well as possible anisotropic contributions to the electronic exchange interaction.

In the past, most of the emphasis has been placed on the cooperative effects, assuming the microscopic interactions to be represented adequately by the Heisenberg form of Eq. (1). This was often quite appropriate since ions with either orbital *S* states or quenched orbital angular momentum were involved, but in many cases possible anisotropy effects were neglected without any reasonable justification.

In the sections below, we shall consider the different interactions in more detail and describe the simplifications which can be made in the case of highly localized excitations involving impurities *without* reducing the generality of the interactions or invoking molecular-field theory. In particular, in Sec. II A we shall consider the types of excitations which can occur when an impurity ion is added to a magnetic crystal, and we shall describe briefly the general complexities of localized exciton and magnon modes. In Sec. II B we shall then discuss the physical conditions under which highly localized excitations may be expected and readily observed. Under these conditions a simple analysis of the impurity spectrum in terms of an effective single-ion Hamiltonian allows the isolation of the exchange contribution and the determination of the exchange anisotropy. Section II C will describe the single-ion Hamiltonian approach in more detail and discuss the contributions to it by the four types of electronic interactions mentioned above. The analysis is carried out in terms of spherical tensor operators acting on *individual* electrons, so that the Hamiltonian will be applicable to all electronic states of the impurity ion arising from a given electronic configuration and not just the lowest term. To complete the discussion of the general theory, we shall describe in Sec. II D the evaluation of the matrix elements of the relevant spherical tensor operators.

Many of the results of this section are directly applicable also to pure concentrated magnetic materials in which anisotropic interactions are important. However in such systems the excitations are generally not localized and the additional effects of exciton dispersion due to resonant energy transfer and translational symmetry must be included.[40]

A. Excitations involving impurity ions

A significant amount of work has been done on the collective excitations associated with impurity ions in a magnetic crystal, and reviews have been given by Dietz and Misetich,[45] Svensson *et al.*,[46] and by Cowley and Buyers.[47] Three general classes of excitations may exist: (a) excitations which are highly localized on the impurity, (b) so-called shell modes where the excitation spreads over a shell of the magnetic "host" ions surrounding the impurity, and (c) propagating modes where the excitation extends over a range comparable to the distance between impurities.

The propagating modes occur only for relatively high concentrations of impurity ions, so that for dilute systems of the type with which we shall be concerned only the first two classes of localized modes are important. Analysis of even these more localized modes may in general be quite complicated, however, due to energy transfer effects which require a collective excitation treatment. Both cluster calculations and Green's-function techniques have been used to describe these effects in transition metal compounds where the exchange interaction is of the isotropic Heisenberg form (for example, Mn-Ni exchange).[45–49] There is no reason to believe that similar effects would not also be important for rare-earth systems.

Since the main emphasis of the present work was a detailed study of the nature of the anisotropic exchange, it was desirable to *choose* systems for which the additional complexities of the collective or shell modes can be avoided. Under the conditions given in Sec. II B, the shell modes can be shown to be distinct from the highly localized modes and not appreciably excited, so that they will not be important in the analysis of the spectra which lead to information concerning the exchange interactions of interest.

B. Requirements for a simple analysis of impurity-ion exchange splittings

As we pointed out in Sec. I, one of the simplest cases to analyze in order to obtain information regarding the anisotropic nature of the exchange interaction is the so-called exchange splitting of isolated Kramers-doublet levels of a magnetic ion in a fixed environment of magnetically ordered neighbors. Such a simple description is generally only a first approximation in a real case, due to complications from collective effects. However, as we shall show, it may in fact be an excellent description of certain chosen systems under appropriate conditions without any uncertainty involving unjustified approximations.

1. Highly localized excitations involving only the impurity ion

In order for the highly localized excitation picture to be valid, we must ensure that such excitations are distinct from the shell modes, that is, that they are eigenstates of the system. The first and most important requirement is that the excited levels of the impurity ion to be studied are not degenerate with excited levels of the magnetic host. In such a case it would clearly be unreasonable to expect highly localized excitations, since resonant coupling would occur between the impurity ion and its magnetic neighbors.

In considering further requirements, it is useful to construct a basis of product states involving various states of the magnetic host crystal and zeroth-order (crystal-field) states of the impurity ion. Such product states may be constructed involving (a) the impurity and completely ordered magnetic host ions, (b) excitations of host ions only, and (c) excitations involving both the impurity and host ions. In general, all of these product states will be coupled by the interactions between the magnetic host ions and the impurity ion, and the resulting eigenstates will be linear combinations. In order for a product state labeled i involving the impurity in a completely ordered magnetic host to be regarded as an eigenstate of the crystal the condition

$$V_{ij}' \ll \delta E_{ij} \tag{2}$$

must be satisfied for all j, where δE_{ij} is the zeroth-order energy difference between the highly localized excitation i of the impurity [type (a) above] and one of the product states labeled j involving an excitation of magnetic host ions [types (b) and (c) above], and where V_{ij}' represents the *off-diagonal* terms in the interaction potential coupling these states.

If condition (2) is not satisfied, "feedback" to neighbors occurs; the magnetic neighbors then "adjust" to the state of the impurity, and the excitation is thus not completely localized on the impurity ion. Any effective single-ion operator used to describe such a situation would then depend on the state of the impurity; that is, a *universal* operator would not be obtained.

If, on the other hand (2) is satisfied, highly localized excitations will approximate to the eigenstates of the system as required for a simple analysis. Even if this is the case, however, we must still ensure that the optical transitions observed between these states are separable from those involving thermally populated shell modes. In constructing the shell modes, two types of magnetic host states need to be considered: low-lying magnetic excitations and higher crystal-field states. Shell modes involving higher crystal-field states of the magnetic host ions will generally be at sufficiently higher energies to have negligible thermal populations compared to those involving only excitations of the magnetic ground state. We can thus concentrate on the shell modes arising from magnetic excitation of the magnetic host ions.

If, as is frequently the case, the low-lying magnetic excitations in the pure host lattice have an energy gap Δ above the ground state, and if the coupling between the impurity and the host is not significantly greater than the coupling between the host lattice ions, it is reasonable to estimate the energy of the shell modes to be also of the order of Δ. If experiments are now performed at temperatures such that

$$kT \ll \Delta \ , \qquad (3)$$

the shell modes will not be appreciably populated, and hence they will not give rise to additional contributions to the absorption spectrum which might confuse the analysis of the highly localized excitations.

Conditions (2) and (3) are in fact reasonable for real systems. We shall see in Sec. II C that the interactions may be expressed in terms of spherical tensor operators, and that for f electrons, the rank of the operators is less than or equal to seven. Within isolated doublet ground states for rare-earth ions described by $|J, \pm J_z\rangle$ for which $J_z \geq 4$, *all* off-diagonal elements of the interactions will be zero, and (2) will be satisfied with $V' \equiv 0$. Thus, an Ising-like material such as $Tb(OH)_3$, which has a ground state closely approximated by $|J_z = \pm 6\rangle$, may provide an ideal choice for the magnetic host satisfying (2). In a highly anisotropic system such as this, condition (3) is roughly equivalent to

$$T \ll T_C \ , \qquad (3')$$

which can generally be satisfied. For $Tb(OH)_3$, $T_C = 3.72$ K,[50] and with our apparatus experiments could be performed down to 1.3 K, so that thermal population effects could readily be avoided.

For many other systems in which the off-diagonal coupling by V' is not identically zero, the energy gap Δ might be made sufficiently large to satisfy condition (2) by the application of a large external field.[40, 51]

In the above discussion, possible effects of the probe on the ground state of the magnetic crystal were assumed to be negligible. Such effects could arise from distortion of the crystal field at the neighboring magnetic host-ion sites or disruption of the magnetic order. If, as is usually the case, the impurity has the same electrical charge as that of the magnetic host ions and a similar ionic radius, crystal-field distortion should be relatively small. Unless some of the crystal-field splittings in the unperturbed host ions are accidentally small only a small amount of mixing will occur and changes in the ground-state wave function may be expected to have a negligible effect. As we shall discuss in Sec. III, $Tb(OH)_3$ is far from such a near-degenerate situation while Er^{3+} is only slightly smaller than Tb^{3+}. We may thus expect negligible changes in the host-lattice crystal-field ground state for that system. Similarly, the effect of a small concentration of impurities (<1%) should not affect the magnetic order of the host lattice significantly, especially if the system has no relatively low-lying excitations, i.e., if (2) is satisfied. This will certainly apply in our case of $Tb(OH)_3{:}Er^{3+}$, but each system must be considered individually since local perturbations of the host-lattice order *may* occur in some cases.

2. *Determination of the exchange contribution to the observed splittings*

Under the conditions (2) and (3) discussed above, corrections to the zeroth-order (crystal-field) energies of the impurity due to its presence in a magnetically ordered crystal will be a first-order effect, with all higher-order terms negligible to a good approximation. Moreover, the effects of the four different types of interaction will be simply *additive*. If the impurity is an odd electron ion with Kramers-doublet crystal-field levels there is a further simplification in that neither the electric multipole interaction nor the virtual phonon exchange will produce a first-order splitting of such a doublet, (due to time-reversal symmetry), while higher-order splittings may be expected to be quite small. The experimental splittings will thus be due only to the exchange interaction and magnetic dipole-dipole interaction. Since the contribution of the magnetic dipole-dipole interaction can be calculated accurately, the contributions of the exchange interaction to the splittings can be readily isolated.

For a rigorous comparison of the observed exchange splittings with the theory described in Sec. II C, we need to know both the magnitude and sign of the observed splittings. This gives rise to a practical consideration regarding the choice of a magnetic-host crystal. In the general case of two split doublets, four transitions are possible. If the probe-ion site symmetry results in selection rules for linearly polarized light, these can readily be used in conjunction with the line intensities to determine both the magnitudes and relative *signs* for the splittings of each doublet. While in principle, these could also be determined using the relative intensities of absorption of positive and negative circularly polarized light in cases where selection rules for linear polarization do not exist, this requires fairly detailed knowledge of the various wave functions involved which is not always available. In cases in which the relative signs of the splittings cannot be determined the analysis is very much more complicated, since all possible permutations of signs must then be considered in fitting the measured splittings to the theoretical model. Such difficulties were experienced, for example, by Orlich and Hüfner in their very detailed work on erbium iron garnet.[17] Even though they were able to find a reasonable fit to their data, there was no conclusive way to show that the particular choices of signs which produced the fit actually corresponded to the physical situation.

C. Contributions of the individual impurity-host pair interactions to the effective single-ion Hamiltonian for the impurity

When the excitation is completely localized on the impurity ion, an effective single-ion Hamiltonian may be obtained for the impurity ion by evaluation of the matrix elements of the operators on the host-ion sites. We shall first discuss some general aspects of this procedure and shall then consider the contributions of the individual interactions. While it may seem that the same form of effective Hamiltonian could also be written phenomenologically using symmetry arguments, it is in fact desirable to relate the effective Hamiltonian to the microscopic nature of the interactions for three reasons. First, it is necessary to consider the interactions individually to ensure that the assumption of highly localized excitations is valid. Second, a microscopic approach provides justification for assuming the effective single-ion interaction parameters to be the same for different J manifolds of the impurity; and third, it will allow us to eliminate some terms in the Hamiltonian, using properties of the host ion states. The latter reason turns out to be quite important in practice, as we shall see in Sec. III.

1. *Effective single-ion Hamiltonian approximation*

The interaction of an impurity or "probe" ion with the crystal can be written as a sum over ion-pair interactions between the impurity ion (a) and the individual magnetic host lattice ions (b):

$$V_{\text{int}} = \sum_b V_{\text{int}}(a,b) \quad . \tag{4}$$

Concentrating on a single term in this sum, the interaction of ions a and b may be written as a sum over products of operators acting on ion a (the impurity) and operators acting on ion b (a magnetic host ion):

$$V_{\text{int}}(a,b) = \sum_{c,d} A_{cd}(a,b)\, V_c(a)\, V_d(b) \quad , \tag{5}$$

where the subscripts c and d indicate possibly different operators V and the $A_{cd}(a,b)$ are arbitrary coefficients.

If an excitation involves *only* the impurity ion a, the operators $V_d(b)$ may be replaced by their diagonal matrix elements for the ground state $\langle g | V_d(b) | g \rangle$, resulting in an effective single-ion Hamiltonian acting on the impurity ion a. (The exchange contribution will be called the exchange potential.) That is,

$$V_{\text{int}} \rightarrow H_{\text{eff}} = \sum_c \alpha_c V_c(a) \quad , \tag{6}$$

where

$$\alpha_c = \sum_{b,d} A_{cd}(a,b) \langle g | V_d(b) | g \rangle \quad . \tag{7}$$

In replacing the operators $V_d(b)$ by their matrix elements in the ground state, we also implicitly neglect *virtual* excitations of the b-type ions, that is the possible effects of off-diagonal matrix elements of V_d. The condition for this to be valid is condition (2) given above, and it can be satisfied in practice by ensuring either that the effective interactions are weak relative to the b-site excitation energies, or that selection rules for the b-site states make the corresponding matrix elements zero or small.

The operator H_{eff} obtained in this way must be invariant under the magnetic symmetry operations of the crystal at the impurity site, that is H_{eff} must transform like the Γ_1 or A_1 (identity) representation of the *magnetic* point group at the impurity site. The number of possible coefficients α_c is thus drastically limited by the site symmetry. As we shall illustrate in Sec. III, some significant additional reductions in the number of allowed coefficients α_c may occur when the matrix elements of Eq. (7) are evaluated for a specific system. It thus becomes feasible to determine the parameters α_c experimentally.

2. *Contributions of the individual interactions*

When interactions are considered between a pair of ions, one or both of which may be in an excited state, it is desirable to describe the interionic pair interactions in terms of the more fundamental interactions between pairs of electrons on the two centers. A particular set of interaction constants should then be applicable to any ionic excited states arising from the ground electronic configurations of the individual ions. This allows experimental data from a number of states to be used to empirically determine the interaction constants and allows the exchange effects for different states to be related.

a. Electronic exchange and the exchange potential. The exchange interaction[8] between two ions labeled a and b may be written[25,35,36]

$$H_{\text{exch}}(a,b)=\sum_{i,j}-\left[\sum_{\substack{k,k'\\q,q'}}\Gamma_{qq'}^{kk'}(ab)\,u_q^{(k)}(i)\,u_{q'}^{(k')}(j)\right](\tfrac{1}{2}+2\vec{s}_i\cdot\vec{s}_j)\ , \tag{8}$$

where the summations over i and j are over the electrons on ion a and ion b, respectively. The $u_q^{(k)}(i)$ and $u_q^{(k')}(j)$ are unit spherical tensor operators which act on the orbital angular momenta of the individual electrons,[52] while the $\vec{s}_i$ and $\vec{s}_j$ are the spin angular momentum operators for the individual electrons. The $\Gamma_{qq'}^{kk'}(ab)$ contain the radial dependence of the exchange integrals and are treated as parameters. The relationship of the $\Gamma_{qq'}^{kk'}(ab)$ to the equal number of independent exchange integrals for pairs of electrons on the two ions has been discussed earlier.[35,36,40,53] The Γ_{00}^{00} term represents the isotopic exchange, while terms with either k or k' nonzero represent the orbital anisotropy present in the exchange interaction.

For the operator of Eq. (8) to be Hermitian,

$$[\Gamma_{qq'}^{kk'}(ab)]^*=(-1)^{q+q'}\Gamma_{-q\,-q'}^{kk'}(ab)\ . \tag{9}$$

The requirement of invariance under time reversal gives

$$[\Gamma_{qq'}^{kk'}(ab)]^*=(-1)^{k+k'+q+q'}\Gamma_{-q\,-q'}^{kk'}(ab)\ . \tag{10}$$

This implies that $k+k'$ must be even.

The orbital operators $u_q^{(k)}$ have nonzero matrix elements only for $k\leqslant 2l$. These conditions limit the total number of terms required in Eq. (8), but for the general case of an ion with f electrons this number still turns out to be rather large,[35] namely, 1225. The symmetry of the pairs of ions under consideration generally limits the values of q and q' and hence the number of independent parameters, but large numbers of potentially nonzero contributions usually remain.[35] One of the main purposes of the present paper is to demonstrate that the number of parameters required to describe the highly localized impurity excitations is significantly less than that for the ion-pair interactions.

When the operator of Eq. (8) is summed over the magnetic neighbors and the host matrix elements are evaluated, the result is

$$H_{\text{exch}}=\sum_{kqm}\alpha_{kqm}\left[\sum_i u_q^{(k)}(i)\,s_m^{(1)}(i)\right]+\sum_{kq}\beta_{kq}\left[\sum_i u_q^{(k)}(i)\right]\ , \tag{11}$$

where[54]

$$\alpha_{kqm}=\sum_b\sum_{k'q'}-2(-1)^m\Gamma_{qq'}^{kk'}(ab)\times\langle g|\sum_j u_{q'}^{(k')}(j)\,s_{-m}^{(1)}(j)|g\rangle \tag{12}$$

and

$$\beta_{kq}=\sum_b\sum_{k'q'}-\frac{1}{2}\Gamma_{qq'}^{kk'}(ab)\langle g|\sum u_{q'}^{(k')}(j)|g\rangle\ . \tag{13}$$

Using Eqs. (9) and (10) and the properties of the spherical tensor operators, it may readily be shown that

$$(\alpha_{kqm})^*=(-1)^{q+m}(\alpha_{k\,-q\,-m}) \tag{14}$$

and

$$(\beta_{kq})^*=(-1)^q(\beta_{k\,-q})\ . \tag{15}$$

The values of k, q, and m for which the parameters α_{kqm} and β_{kq} may be nonzero are determined by the magnetic symmetry at the impurity site and the transformation properties of the operators $u_q^{(k)}$ and $s_m^{(1)}$. For proper rotations, the transformation properties are determined by the representations $\mathfrak{D}^{(k)}$ of the full rotation group, while under inversion, both the operators $u_q^{(k)}$ and $s_m^{(1)}$ are even. The reflection $\sigma_h=IC_2$ thus reduces to C_2, and improper rotations $S_n=\sigma_hC_n$ reduce to C_2C_n.[55] We note, in particular, that if there is an n-fold axis, allowed values of $q+m$ are $0,\pm n,\pm 2n,\pm 3n,\ldots$, and that if there is a horizontal reflection plane, odd values of $q+m$ are not allowed. These symmetry considerations provide no restrictions on the allowed values of k. Detailed results for C_{3h} symmetry are given in Sec. III.

For f electrons the spin and orbital operators in Eq. (11) may be coupled to give operators of rank $r\leqslant 7$ acting on the total angular momentum J. In Sec. II D it will be shown that only terms with odd r contribute to the splitting of Kramers doublets in first order. Those with even r are "crystal-field-like," in that they shift both components of a Kramers doublet equally. Such shifts are generally not observable since they tend to be small and difficult to separate from the true crystal-field shifts of energy levels.

b. Magnetic dipole-dipole interaction. The general form of the magnetic dipole-dipole interaction is well known

$$H_{\text{mdd}}(a,b)=\frac{1}{|r_{ab}|^3}\left[\vec{\mu}_a\cdot\vec{\mu}_b-3\frac{(\vec{\mu}_a\cdot\vec{r}_{ab})(\vec{\mu}_b\cdot\vec{r}_{ab})}{|r_{ab}|^2}\right]\ , \tag{16}$$

where

$$\vec{\mu}_a=\sum_i\mu_B(\vec{l}_i+g_s\vec{s}_i)$$

and

$$\vec{\mu}_b=\sum_j\mu_B(\vec{l}_j+g_s\vec{s}_j)\ , \tag{17}$$

and the vector $\vec{r}_{ab}$ relates the b lattice site to the impurity site a. This interaction is the best understood of the four interactions, and it can generally be evaluated explicitly and quite accurately. For rare-earth ions, it is of the same order of magnitude as the exchange interaction and must be considered carefully in the analysis of splittings. For transition metal ions, the exchange interactions tend to be larger and the magnetic-dipole coupling is often, therefore, relatively less important.

Using Eq. (6), we obtain an effective Hamiltonian for the magnetic dipole coupling to a particular impurity site a:

$$H_{\mathrm{mdd}} = -\vec{\mu}_a \cdot \vec{\mathrm{H}}_{\mathrm{dip}} \ , \tag{18}$$

which has the form of a simple effective field $\vec{\mathrm{H}}_{\mathrm{dip}}$ acting on the magnetic moment $\vec{\mu}_a$, where

$$\vec{\mathrm{H}}_{\mathrm{dip}} = -\sum_b \frac{1}{|r_{ab}|^3} \left(\langle g | \vec{\mu}_b | g \rangle - 3 \frac{\vec{\mathrm{r}}_{ab} (\langle g | \vec{\mu}_b | g \rangle \cdot \vec{\mathrm{r}}_{ab})}{|r_{ab}|^2} \right) \ . \tag{19}$$

The summation over b is here again over the magnetic host ions. The sum in Eq. (19) is conditionally convergent and depends on the shape of the sample, so demagnetizing effects must be considered. Matrix elements of the magnetic moment operators $\vec{\mu}_a$ and $\vec{\mu}_b$ can be determined experimentally from the Zeeman effect.

c. Electric multipole-multipole interaction. The electric multipole interaction has been considered by Wolf and Birgeneau[56] who also give references to earlier work. Following their notation it may be written

$$V_{\mathrm{emi}}(a,b) = \sum_{i,j} \sum_{\substack{kk' \\ qq'}} A_{qq'}^{kk'}(ab)\, y_q^{(k)}(i)\, y_{q'}^{(k')}(j) \ , \tag{20}$$

where the $y_q^{(k)}$ are spherical harmonics for the individual electron coordinates. Due to the complexities of the crystalline environment, as well as shielding and covalency effects, the $A_{qq'}^{kk'}$ must be regarded as essentially free parameters, with no *a priori* reason for assuming the higher-rank terms to be negligible relative to the $k=2$ quadrupole-quadrupole interaction. This has also been illustrated by the results of recent *ab initio* crystal-field calculations by Newman *et al.*,[57] which indicate that quite complex overlap and covalency effects can be significant.

The number of terms can be limited by the ion pair symmetry and by the angular momentum of the electrons under consideration, as in the case of the exchange coupling. Within a configuration, the $y_q^{(k)}$ have nonzero matrix elements only for k even and $k \leq 2l$. Representative sizes of matrix elements are given by Baker.[32]

Summing over the host-lattice neighbors we obtain an effective single-ion operator of the form

$$H_{\mathrm{emi}} = \sum_{kq} \gamma_{kq} \left(\sum_i y_q^{(k)}(i) \right) \ , \tag{21}$$

where

$$\gamma_{kq} = \sum_b \sum_{k'q'} A_{qq'}^{kk'}(ab) \langle g | \sum_j y_{q'}^{(k')}(j) | g \rangle \ . \tag{22}$$

For an ion with Kramers degeneracy, the electric multipole interaction will therefore not produce any additional splittings to this order and, as we discussed in connection with the derivation of Eq. (6), we may expect second-order effects to be generally small. However, we must note one possible complication, even within the first-order approximation, in that the expectation value in Eq. (22) should really be written as a sum over all thermally populated states of the host, so that Eq. (22) applies only if $kT \ll \Delta$. The contribution of the electric multipole interaction to the effective crystal field is therefore really temperature dependent, so that a consistent analysis can be made only if both the crystal field and the interactions are determined at temperatures satisfying condition (3).

d. Virtual phonon exchange. The fourth interaction mechanism which must be considered is the electric multipole coupling between moments *induced* at the ion sites by the exchange of virtual phonons.[31,32] This interaction has proved important in the ground terms of $\mathrm{UO_2}$,[58] the rare-earth ethyl sulfates,[59] $\mathrm{Pr^{3+}}$ pairs[60] and $\mathrm{Ce^{3+}}$ pairs[61] in $\mathrm{LaCl_3}$, in $\mathrm{PrAlO_3}$,[62] and in $\mathrm{Tb(OH)_3}$,[63] but for our present purposes it is simply another mechanism which can give rise to the terms discussed for the electric multipole interaction. Moreover, the energy denominator should suppress even these effects in optically excited states, so that this mechanism should be essentially negligible in the experiments we wish to analyze.

D. Matrix elements of the spherical tensor operators

Evaluation of the matrix elements for the spherical tensor operators involved in the exchange and other interactions is straightforward and well suited to computer calculations. In some cases, where the states are very nearly pure Russell-Saunders states, matrix elements may be evaluated directly in the $|SLM_SM_L\rangle$ representation.[53] In general, however, it is useful to couple the spin and orbital operators to act on the total angular momentum J, a process analogous to the coupling of angular momenta[64]

$$s_m^{(\kappa)}(i)\, u_q^{(k)}(i) = \sum_{r,t} (-1)^{-\kappa+k-t} (2r+1)^{1/2} \times \begin{pmatrix} \kappa & k & r \\ m & q & -t \end{pmatrix} [s^{(\kappa)}(i) \times u^{(k)}(i)]_t^{(r)} \tag{23}$$

If the operator $s_0^{(0)}$ is *defined* to be the identity operator in the spin space, and $s_m^{(1)}$ is the usual single-electron "real" spin operator, this expression may be used for all of the interactions discussed in Sec. II C. Equation (23) with $\kappa=0$ is then used for the electric multipole-multipole interaction, which is independent of spin [Eq. (21)] or for exchange terms of the second type in Eq. (11). The case with $\kappa=1$ corresponds to terms of the first type in Eq. (11). As in the more familiar case of addition of angular momenta, allowed values of r range from $|k-\kappa|$ to $|k+\kappa|$. Since $k\leq 6$ for f electrons and $\kappa\leq 1$, $r\leq 7$ for f electrons.

Reduced matrix elements of the coupled operators are given by[65]

$$(\alpha SLJ\| \sum_{i=1}^{N}[s^{(\kappa)}(i)\times u^{(k)}(i)]^{(r)}\|\alpha' S'L'J')=[(2J+1)(2J'+1)(2r+1)]^{1/2}$$

$$\times\begin{Bmatrix} S & S' & \kappa\\ L & L' & k\\ J & J' & r\end{Bmatrix}(\alpha SL\| \sum_{i=1}^{N} s^{(\kappa)}(i)u^{(k)}(i)\|\alpha' S'L')\ , \tag{24}$$

where the quantity in large curly brackets is the usual 9-J symbol.[66] The doubly reduced matrix elements

$$(\alpha SL\| \sum_{i=1}^{N} s^{(\kappa)}(i)u^{(k)}(i)\|\alpha' S'L')$$

for terms with $\kappa=0$ have been tabulated,[67] but those for $\kappa=1$ must be calculated using the coefficients of fractional parentage of Racah[68,69]:

$$(\alpha SL\| \sum_{i=1}^{N} s^{(\kappa)}(i)u^{(k)}(i)\|\alpha' S'L')=(-1)^{S+L+1/2+l+\kappa+k}[(2S+1)(2S'+1)(2L+1)(2L'+1)]^{1/2}$$

$$\times N\sum_{\bar\theta}(-1)^{\bar S+\bar L}(\theta\{|\bar\theta)(\bar\theta|\}\theta')\begin{Bmatrix} S & S' & \kappa\\ \frac{1}{2} & \frac{1}{2} & \bar S\end{Bmatrix}\begin{Bmatrix} L & L' & k\\ l & l & \bar L\end{Bmatrix}(\tfrac{1}{2}\|s^{(\kappa)}\|\tfrac{1}{2})(l\|u^{(k)}\|l)\ , \tag{25}$$

where $\theta=\alpha SL$, $\theta'=\alpha' S'L'$, and $\bar\theta=\bar\alpha\,\bar S\,\bar L$. (The barred states are the parent states for the configuration l^N.) The symbol $(\theta\{|\bar\theta)$ represents a fractional-parentage coefficient[68,69] and the quantities in large curly brackets are six-J symbols.[64] The single-electron reduced matrix elements in Eq. (25) are given by[70]

$$(l\|u^{(k)}\|l)=1\ , \tag{26}$$

$$(\tfrac{1}{2}\|s^{(0)}\|\tfrac{1}{2})=\sqrt{2}, \tag{27}$$

$$(\tfrac{1}{2}\|s^{(1)}\|\tfrac{1}{2})=\sqrt{3/2}\ . \tag{28}$$

Doubly reduced matrix elements for ions with more-than-half-filled shells such as Er^{3+} ($4f^{11}$) can be calculated from those with less-than-half-filled shells using the relation[68]

$$(\alpha SL\| \sum_{i=1}^{N} s^{(\kappa)}(i)u^{(k)}(i)\|\alpha' S'L')=(-1)^{\kappa+k+1}(\alpha SL\| \sum_{i=1}^{4l+2-N} s^{(\kappa)}(i)u^{(k)}(i)\|\alpha' S'L')\ . \tag{29}$$

In the case of intermediate coupling, which is required for an adequate description of most manifolds and particularly the excited ones, the reduced matrix elements are linear combinations

$$(\gamma J\| \sum_{i=1}^{N}[s^{(\kappa)}(i)\times u^{(k)}(i)]^{(r)}\|\gamma' J')=\sum_{\alpha SL}\sum_{\alpha' S'L'}a(\gamma J;\alpha SL)a(\gamma' J';\alpha' S'L')$$

$$\times(\alpha SLJ\| \sum_{i=1}^{N}[s^{(\kappa)}(i)\times u^{(k)}(i)]^{(r)}\|\alpha' S'L'J')\ , \tag{30}$$

where the $a(\gamma J;\alpha SL)$ are the components of the intermediate coupling states $|\gamma J\rangle$.

Using these expressions for the reduced matrix elements, we finally obtain the actual matrix elements required for the calculations using the Wigner-Eckart theorem[64,69]

$$\langle \gamma J J_z | \sum_{i=1}^{N} [s^{(\kappa)}(i) \times u^{(k)}(i)]_t^{(r)} | \gamma' J' J_z' \rangle = (-1)^{J-J_z} \begin{pmatrix} J & r & J' \\ -J_z & t & J_z' \end{pmatrix} (\gamma J \| \sum_{i=1}^{N} [s^{(\kappa)}(i) \times u^{(k)}(i)]^{(r)} \| \gamma' J') \quad , \tag{31}$$

where the quantity in large parentheses is a 3-J symbol. If we wish to analyze energy-level splittings in cases in which J mixing is not important, we need only consider matrix elements diagonal in J. In order for a particular term in the interaction to give rise to a splitting, the signs of the matrix elements for the two components of a doublet must be opposite, and examination of Eq. (31) shows that this occurs only for tensors of *odd rank r*.

Using Eq. (30), together with the property of the doubly reduced matrix elements

$$(\alpha SL \| \sum_{i=1}^{N} s^{(\kappa)}(i) u^{(k)}(i) \| \alpha' S' L') = (-1)^{S-S'+L-L'} (\alpha' S' L' \| \sum_{i=1}^{N} s^{(\kappa)}(i) u^{(k)}(i) \| \alpha SL) \quad , \tag{32}$$

and the property of the 9-J symbol that interchanging columns introduces a factor of $(-1)^x$ where x is the sum of the arguments,[71] it may be readily shown that $\kappa + k + r$ must be *even* for the diagonal reduced matrix element

$$(\gamma J \| \sum_{i=1}^{N} [s^{(\kappa)}(i) \times u^{(k)}(i)]^{(r)} \| \gamma J)$$

to be nonzero. Since r must be odd, we can therefore restrict our attention to operators for which $\kappa + k$ is odd. The electric multipole interaction with $\kappa = 0$ and k even thus cannot contribute to splittings in first order. On the other hand, both the exchange interaction and the magnetic dipole-dipole interaction do contain terms for which $\kappa + k$ is odd which will contribute to such splittings. As mentioned in Sec. II C, the exchange interaction can also give terms with r even, which are similar to crystal-field terms in that they will not split the Kramers degenerate states, although they will generally have quite different reduced-matrix elements.

III. APPLICATION OF THE THEORY TO Er^{3+} IN FERROMAGNETIC $Tb(OH)_3$

While a variety of real systems are appropriate for an analysis of the type described above, a particularly ideal choice is that of the Ising-like ferromagnet $Tb(OH)_3$ doped with a small percentage of Er^{3+} ions which occupy Tb^{3+} sites. In Sec. III A we shall relate the properties of this system to the requirements for a simple analysis discussed in Sec. II B, and we shall then consider in some detail the possible influences of the Er^{3+} impurities on the states of the neighboring Tb^{3+} ions. We shall show that changes of the Tb^{3+} states should be negligible in this system. Both the Er^{3+} crystal-field analysis and experimental values of the spontaneous magnetic splittings for Er^{3+} impurities in $Tb(OH)_3$ have been reported in an earlier paper.[72] In Sec. III B we shall describe the analysis of these splittings using the effective single-ion Hamiltonian method developed in Sec. II C. The results will illustrate unambiguously the relative importance of *anisotropic-versus-isotropic* exchange in this system, and by inference for all other systems with nonzero orbital angular momentum. Possible extensions of our results and recommendations for other kinds of systems are discussed in Sec. III C.

A. Reasons for choosing Er^{3+} in $Tb(OH)_3$

1. Properties of $Tb(OH)_3$

Previous work on $Tb(OH)_3$ has shown that it fulfills the requirements for a host discussed in Sec. II B to an unusually high degree. Optical studies[73,74] in the ordered state at 1.3 K ($T_c = 3.72$ K) have shown the ground state to be very well described by a doublet $|^7F_6, J_z = \pm 6\rangle$, which is split by dipolar and exchange interactions by 6.4 ± 0.2 cm^{-1}. The first-excited crystal-field level, a $\mu = \pm 1$ doublet (nearly pure $J_z = \pm 5$), is at 118 cm^{-1}, while all other crystal-field levels of the ground $^7F_6$ manifold are above 200 cm^{-1}.[74,75] (Extensive measurements of magnetothermal bulk properties also agree quite well with this picture.[50]) The excited crystal-field energies are thus more than an order of magnitude larger than the interionic interactions ($V_{int} \lesssim 10\,cm^{-1}$), and condition (2) of Sec. II B is therefore well satisfied for these states.

We now consider possible coupling terms between the two components of the ground doublet. The crystal-field analysis for $Tb(OH)_3$ of Scott *et al.*[74,75] has shown that the components of this doublet are *very nearly pure* $|J = -6\rangle$ and $|J = +6\rangle$, with only a small admixture of $|J = 0\rangle$, calculated to be about 0.04. Other J_z values are ruled out by the C_{3h} site symmetry. Coupling between pure $|J_z = -6\rangle$ and $|J_z = +6\rangle$ states for the interactions discussed in Sec. II C is *identically zero,* since it would require a q value of 12 for the effective operator, while the f character of the wave functions limits $q \leq 7$. Coupling between the two components arising from the small $|J_z = 0\rangle$ admixture or from second-order effects can be estimated to be of the order of 0.1 cm^{-1} which is negligible compared with the first-order effect on the ground state. [This point has also received careful consideration in the recent analysis of the bulk properties of $Tb(OH)_3$, mentioned earlier.[50]] It is reasonable to conclude, therefore, that condition (2) of Sec. II B should be well satisfied for $Tb(OH)_3$ in its ground state. Moreover, this conclusion should be valid not only for the case of two interacting Tb^{3+} neighbors, but also for one Tb^{3+} ion and any other rare-earth ion.

The dipole field for $Tb(OH)_3$ has been calculated by Skjeltorp[50, 76] and may be used together with the appropriate experimentally determined Er^{3+} moment[72] to separate the dipolar contribution [Eq. (18)] to the Er^{3+} splittings from the exchange contribution. The value of H_{dip} obtained from the lattice sum given in Eq. (19) is

$$H_{\text{dip}} = (9.45 \pm 0.2 \text{ kG}) - N(5.67 \pm 0.11 \text{ kG}) \ ,$$

where N is the demagnetizing factor[77] and the error limits represent the uncertainties due to the ground-state magnetic moment and the lattice parameters.[50, 76] The relatively accurate values available for $Tb(OH)_3$ permit rather good estimates of the dipolar contributions and corresponding good determinations of the exchange effects.

Another significant advantage of $Tb(OH)_3$ is the rather high rare-earth site symmetry (C_{3h}). This serves very effectively in limiting the number of parameters in the exchange potential, as we shall see in Sec. III B. It also gives rise to very desirable linear polarization selection rules, which enable the signs of the experimental splittings to be determined.

2. *Use of Er^{3+} as the impurity probe*

The probe ion to be used in conjunction with a $Tb(OH)_3$ host should clearly be a trivalent rare earth with an ionic radius near to that of Tb^{3+} to ensure minimum distortion of the crystal lattice when it is substituted for one of the Tb^{3+} ions. In addition, when the ion is in the crystal, it is necessary for it to have energy levels which are not nearly degenerate with those of the host, so that condition (2) can be met by the kind of interactions typically found in this sort of material ($\leq 10 \text{ cm}^{-1}$). It is also desirable (but not necessary) for the impurity ion to have an odd number of electrons, so that its crystal field levels all have Kramers degeneracy in the absence of the magnetic or exchange interactions.

The Er^{3+} ion satisfies all these conditions. The large number of energy levels resulting from the $4f^{11}$ configuration are well understood and many fall in a region of the optical spectrum which is accessible to highly accurate photographic techniques.

The crystal-field analysis for Er^{3+} at the C_{3h} sites in $Tb(OH)_3$ is straightforward, requiring only four parameters, and previous studies have shown that it can give a very good account of the observed levels.[72]

It turns out that the spontaneous magnetic ground-state splitting of the Er^{3+} impurity levels in $Tb(OH)_3$ is small enough to allow appreciable population of both components even at 1.3 K. This doubles the number of transitions observable in the temperature region defined by condition (3) of Sec. II B and thus makes available a substantial amount of additional experimental information. [Condition (3) was necessary to ensure that we are observing transitions involving highly localized modes.] Another more minor convenience associated with Er^{3+} is that the f^{11} configuration (conjugate to f^3) has only seven parent states[67]; this simplifies calculation of the reduced matrix elements of the exchange operators from Eq. (25).

Of the other possible choices for the probe ion, Dy^{3+} and Ho^{3+} may be expected to have large magnetic dipole-dipole contributions to their ground state splittings, which would reduce the number of observable transitions and which might make the determination of the exchange contribution somewhat more uncertain. Also the free-ion states are not quite as well known and simple as those of Er^{3+}, and in the case of Ho^{3+} there is also the disadvantage that the crystal-field states are not Kramers doublets. Even so, both these ions do present reasonable possibilities for the impurity probes, and experiments using these ions in $Tb(OH)_3$ may well be interesting. Another possible ion is Nd^{3+}, but for this ion J-mixing effects are larger and this will complicate the analysis. Yb^{3+} and Ce^{3+} have too few $4f$ levels to provide the amount of data to determine all of the exchange parameters, while the levels of Tm^{3+} and Sm^{3+} occur mostly in the infrared region where high-resolution experiments are more difficult. For Gd^{3+} the number of readily accessible states is limited to a small number of ^6P_J states, but the small orbital angular momentum of these states reduces the number of terms required in Eq. (11) to $k \leq 2$. For C_{3h} symmetry, only three parameters α_{00}, β_{10}, and α_{20} should be sufficient, and a simple and unambiguous analysis should again be possible. Experiments on Gd^{3+} in $Tb(OH)_3$ would be of considerable interest.

3. *Crystal-field perturbation for Tb^{3+} ions near an Er^{3+} impurity*

The purpose of the present section is to demonstrate that the Tb^{3+} ground state in $Tb(OH)_3$ is exceptionally *insensitive* to perturbations in its environment resulting from substitution of an Er^{3+} impurity for a Tb^{3+} neighbor. Two types of changes in the crystal-field levels of Tb^{3+} could effect our analysis—other values of J_z could be admixed into the ground levels $|J_z = \pm 6\rangle$, thus affecting their Ising-like nature (which was discussed in Sec. III A 1 above) or other crystal-field levels could be shifted to lower energy giving rise to measureable second-order contributions to the splittings.

Effects of both types could, in general, arise when an Er^{3+} ion replaces a Tb^{3+} ion, since this "destroys" the symmetry of the crystal field at the neighboring Tb^{3+} ion sites. *In principle,* this allows new terms in the crystal field, and it might also result in changes in the magnitudes of the usual C_{3h} terms. We should note, however, that there are a number of reasons to believe that in practice such changes in the crystal field will be small. First, the variation of the crystal-field parameters throughout the rare-earth hydroxide series from Eu^{3+} to Er^{3+} has been examined in an earlier paper[78] and found to be smooth and gradual; changes in the parameters from $Tb(OH)_3$ to $Er(OH)_3$ are small ($\leqslant 10\%$). Second, the ligands which account for a major part of the crystal field in compounds of this type[57] are unchanged and would be affected in the present case only to the degree that Er^{3+} introduces a distortion. The ratio of the parameters B_{66}/B_{60}, which gives a measure of this distortion is very nearly the same for Tb^{3+} in pure $Tb(OH)_3$, Er^{3+} in $Tb(OH)_3$, and Er^{3+} in $Er(OH)_3$: -13.0 ± 0.5, -13.2 ± 0.7, and -13.5 ± 0.5, respectively,[78] thus indicating that the distortion around an Er^{3+} ion in $Tb(OH)_3$ is small. Er^{3+} and the Tb^{3+} ion it replaces, of course, have the same monopole moment (i.e., ionic charge) and they have similar radii: 0.96 Å for Er^{3+} and 1.00 Å for Tb^{3+}.[79]

It thus seems reasonable to consider the changes in the Tb^{3+} wave functions using perturbation theory, with the wave functions for the undistorted case serving as zeroth-order wave functions. Off-diagonal matrix elements of the new crystal-field terms between the states $|J_z = \pm 6\rangle$ and higher levels are presumably small, since the changes in the crystal field will only be a very small fraction of the unperturbed crystal field. Furthermore, the energy denominators for the particular case of the $Tb(OH)_3$ ground state will all be quite large, since the lowest of the excited levels is at 118 cm^{-1}, while all others are above 200 cm^{-1}.[74,75] Consequently we would expect only small admixtures of other J_z values into the ground state (of the order of a few percent or less), and we would not expect any of the excited states to be shifted significantly.

It seems safe to conclude, therefore, that even the Tb^{3+} ions very close to one of the Er^{3+} impurities will behave very much like those in pure $Tb(OH)_3$.

B. Analysis of the highly localized Er^{3+} modes

1. Effective exchange potential for Er^{3+} in $Tb(OH)_3$

Considerable simplification of the effective exchange potential of Eq. (11) results from both the nature of the Tb^{3+} states and the Er^{3+} C_{3h} site symmetry in $Tb(OH)_3$. Let us first consider the terms in Eq. (11), involving both spin and orbital operators. If, as we suppose, all the Tb^{3+} ions are in their ferromagnetically ordered ground state $|{}^7F_6, J_z = -6\rangle$, the diagonal matrix elements of the Tb^{3+} operators

$$\sum_j u_{q'}^{(k')}(j)\, s_{-m}^{(1)}(j)$$

in Eq. (12) will be nonzero only for $q' = m = 0$ and we see, therefore, that the only nonzero parameters α_{kqm} in Eq. (11) will be those with $m = 0$. (The subscript m on the α's will thus be dropped in the future.) This is particularly fortunate since it immediately limits the Er^{3+} spin operators in Eq. (11) to the one component $s_0^{(1)}$. Since this transforms like the Γ_1 (identity) representation of the magnetic point group this implies that only operators $u_q^{(k)}$ which also transform like Γ_1 can occur in the product $u_q^{(k)} s_0^{(1)}$ for the Er^{3+} operator. From the previous general discussion in Sec. II C, this requires that $q = 0, \pm 6$. In Sec. II D, it was shown that for the analysis of first order splittings, we only need to consider *even* values of k with $k \leqslant 6$ for f electrons, so that $k = 0$, 2, 4, or 6.

Similar considerations apply to the second types of terms in Eq. (11), which contain only orbital operators. Again $u_q^{(k)}$ must transform like Γ_1, and this requires $q = 0, \pm 6$. In this case, however, as was shown in Sec. II D, only *odd* values of k must be considered in the analysis of first-order splittings, so that now $k = 1$, 3, and 5 will be allowed.

Combining these various restrictions, we finally derive the most general exchange potential allowed by symmetry in this case

$$H_{\text{exch}} = \sum_{i=1}^{11} \{\alpha_{00} u_0^{(0)}(i) s_0^{(1)}(i) + \alpha_{20} u_0^{(2)}(i) s_0^{(1)}(i) + \alpha_{40} u_0^{(4)}(i) s_0^{(1)}(i) + \alpha_{60} u_0^{(6)}(i) s_0^{(1)}(i) + \alpha_{66}[u_6^{(6)}(i) + u_{-6}^{(6)}(i)] s_0^{(1)}(i) + i\alpha'_{66}[u_6^{(6)}(i) - u_{-6}^{(6)}(i)] s_0^{(1)}(i) + \beta_{10} u_0^{(1)}(i) + \beta_{30} u_0^{(3)}(i) + \beta_{50} u_0^{(5)}(i)\} , \tag{33}$$

where the summation over i is over the individual electrons on the Er^{3+} ion, and all parameters are real. The operator following the coefficient $i\alpha'_{66}$ has zero *diagonal* elements; thus, for the purposes of the present analysis such terms may be dropped, leaving eight real parameters α_{kq} and β_{k0} to be determined by experiment.

2. Experimental results

Experimental results of the high-resolution optical-absorption experiments on Er^{3+} in $Tb(OH)_3$ have been discussed fully in an earlier paper.[72] Almost all of the lines were quite sharp at 1.3 K and could be measured with an accuracy of 0.01 cm^{-1}; furthermore, by using both line intensities and polarization selection rules, both the magnitudes and signs of the splittings could be determined. The observed levels and their spontaneous magnetic splittings at 1.3 K are listed in Table I. From 1.3 to 3.7 K, the splittings were found to be independent of temperature to within experimental error (0.01 cm^{-1}), and we may therefore take these values to correspond to the $T = 0$ K splittings given by the theory (Table I).

Some additional lines appeared in the vicinity of T_c, and these may be attributed to the expected shell modes involving "spin" flips on Tb^{3+} neighbors. The number and intensity of these additional lines increased as the temperature was increased, as would be expected on the basis of thermal population of higher-energy modes. Such lines could presumably be explained using statistical methods similar to those used by Prinz[80] for $NdCl_3$ and Wright[81] for $DyPO_4$; however, in the present case, the additional transitions were strongly observable for only one Er^{3+} level.[82] While it would be interesting to investigate this phenomenon further, using photoelectric techniques or pulsed dye laser absorption to get accurate intensity data, it is not directly relevant to a determination of the effective exchange-potential parameters and will thus not be considered further here.

3. *Analysis of the observed splittings*

Since crystal-field effects for systems such as Er^{3+} in $Tb(OH)_3$ are much larger than those of the interionic interactions, crystal-field wave functions provide the basis for evaluating the exchange-matrix elements. These wave functions were obtained by a diagonalization of the combined free-ion and crystal-field Hamiltonian, including the effects of intermediate coupling and J mixing, as discussed in a previous paper.[72] Comparison of experimental values of the Er^{3+} magnetic moments obtained from the Zeeman effect with corresponding values calculated using these wave functions was chosen as an appropriate test of their accuracy. If wave functions cannot reproduce matrix elements of the simpler magnetic moment operator, they certainly cannot be expected to give accurate values for the complicated exchange operators.

For 11 of the observed states belonging to the ${}^4I_{15/2}$, ${}^4I_{11/2}$, ${}^4I_{9/2}$, ${}^4F_{9/2}$, and ${}^4S_{3/2}$ manifolds,[72] this criterion

TABLE I. Spontaneous magnetic splittings of Er^{3+} in ferromagnetic $Tb(OH)_3$ at 1.3 K, with dipolar and exchange contributions. All energies are in cm^{-1}.

Level[a]		E_{av}[b]	Splitting ΔE[c]	ΔE_d[d]	ΔE_{exch}[e]
${}^4I_{15/2}$	$\frac{5}{2}$	0.00	−0.87 ± 0.01	−0.78 ± 0.02	−0.09 ± 0.03
${}^4I_{11/2}$	$\frac{3}{2}$	10275.14	0.92 ± 0.01	1.08 ± 0.04	−0.16 ± 0.05
	$\frac{1}{2}$	10279.22	0.05 ± 0.01	0.22 ± 0.02	−0.17 ± 0.03
	$\frac{1}{2}'$	10322.80	−4.71 ± 0.01	−4.45 ± 0.10	−0.26 ± 0.11
	$\frac{3}{2}'$	10341.11	−3.47 ± 0.01	−3.62 ± 0.10	0.15 ± 0.11
${}^4I_{9/2}$	$\frac{3}{2}$	12434.06	−0.61 ± 0.01	−0.70 ± 0.07	0.09 ± 0.08
	$\frac{1}{2}$	12581.25	0.49 ± 0.01	0.46 ± 0.04	0.03 ± 0.05
${}^4F_{9/2}$	$\frac{3}{2}$	15294.42	−4.01 ± 0.01	−4.37 ± 0.12	0.36 ± 0.13
	$\frac{1}{2}$	15362.01	0.66 ± 0.01	0.52 ± 0.03	0.14 ± 0.04
${}^4S_{3/2}$	$\frac{3}{2}$	18445.89	2.33 ± 0.01	2.13 ± 0.07	0.20 ± 0.08
	$\frac{1}{2}$	18497.78	0.50 ± 0.01	0.84 ± 0.04	−0.34 ± 0.05

[a] J manifold and μ quantum number.

[b] $E_{av} = \frac{1}{2}[E(\mu) + E(-\mu)]$, where $E(\mu)$ and $E(-\mu)$ indicate the energies of the two components of a doublet level.

[c] $\Delta E = E(\mu) - E(-\mu)$.

[d] Calculated magnetic dipole-dipole contribution to the splitting; $\Delta E_d = -2\mu_z H_{dip}$, where $H_{dip} = 9.45$ kG.

[e] $\Delta E_{exch} = \Delta E - \Delta E_d$.

was satisfactorily met. Agreement between theory and experiment for the Zeeman effect was better than 5% for all but four of the observed levels, with errors for those four falling in the range of 10%−20%. In contrast, errors as large as 100% were found to occur for some levels in the $^2H_{11/2}$ and higher manifolds and none of these were therefore used in the determination of the exchange effects. As our analysis included intermediate coupling and J-mixing effects, these discrepancies are presumably due to either inadequate intermediate coupling wave functions or inherent shortcomings of the "single-particle" crystal-field model.[72,78] Further discussion of these effects, which are clearly much smaller for the manifolds included in the analysis of the exchange splittings, is given in Sec. III C.

TABLE II. Diagonal reduced matrix elements of the double tensor operator

$$\sum_{i=1}^{11} [s^{(\kappa)}(i) \times u^{(k)}(i)]^{(r)}$$

for Er^3

Manifold	κ	k	r	Reduced matrix element
	1	0	1	2.366
	1	2	1	−0.2988
	1	2	3	0.03409
$^4I_{15/2}$	1	4	3	0.1739
	1	4	5	−0.2560
	1	6	5	−0.2399
	1	6	7	0.9899
	1	0	1	−0.08605
	1	2	1	−0.2221
	1	2	3	0.1135
$^4I_{11/2}$	1	4	3	−0.001862
	1	4	5	−0.1097
	1	6	5	−0.1250
	1	6	7	−0.5992
	1	0	1	−0.6303
	1	2	1	−0.2967
	1	2	3	−0.4139
$^4I_{9/2}$	1	4	3	0.03927
	1	4	5	0.09081
	1	6	5	0.1285
	1	6	7	−0.4504
	1	0	1	0.8349
	1	2	1	−0.0001614
	1	2	3	−0.3655
$^4F_{9/2}$	1	4	3	0.03304
	1	4	5	−0.05401
	1	6	5	0.1657
	1	6	7	−0.2502
	1	0	1	1.037
	1	2	1	0.02845
$^4S_{3/2}$	1	2	3	0.2791
	1	4	3	−0.05668

Matrix elements of the exchange operators were calculated using the methods of Sec. II D. The intermediate-coupling free-ion wave functions for Er^{3+} calculated by Rajnak,[83] which gave a good description of the crystal-field effects for the manifolds listed above, were used for the coefficients $a(\gamma J;\alpha SL)$ in Eq. (30). Calculated values for the reduced matrix elements are given in Tables II and III. The computer program used in this calculation is given in Ref. 84 and was checked by using the free-ion wave functions of Kahle[85] and comparing the results with those reported by Orlich and Hüfner.[17]

As we pointed out in Sec. II B, the splittings of the highly localized modes arising from the Er^{3+} Kramers-doublet crystal-field levels should be essentially a simple first-order effect in a system such as $Tb(OH)_3$. The exchange and magnetic dipole-dipole contributions are thus given by twice the diagonal matrix elements of the odd rank interactions for the levels involved and are simply additive. The dipole-dipole contribution to the splittings ΔE_d was calculated using the dipolar field determined by Skjeltorp[50,76] as

TABLE III. Diagonal reduced matrix elements of the double tensor operator.

$$\sum_{i=1}^{11} [s^{(\kappa)}(i) \times u^{(k)}(i)]^{(r)}$$

for Er^{3+}.

Manifold	κ	k	r	Reduced matrix element
	0	1	1	2.801
$^4I_{15/2}$	0	3	3	−0.8818
	0	5	5	0.6441
	0	1	1	2.285
$^4I_{11/2}$	0	3	3	−0.6418
	0	5	5	0.4834
	0	1	1	1.899
$^4I_{1/2}$	0	3	3	−0.6164
	0	5	5	0.3572
	0	1	1	1.476
$^4F_{9/2}$	0	3	3	−0.6858
	0	5	5	0.5254
$^4S_{3/2}$	0	1	1	0.1232
	0	3	3	0.4373

given in Sec. III A 1 and the values of the Er^{3+} magnetic moments determined spectroscopically.[72] The exchange contributions to the splittings ΔE_{exch} could then be determined directly by subtracting the dipolar contributions ΔE_d from the total observed splittings ΔE. The calculated quantities ΔE_d and ΔE_{exch} are given in Table I, along with the experimental errors which arise from uncertainties in the magnetic moments for the individual levels, the dipole field, and the measurement of the splittings ΔE. It is clearly evident from Table I that dipolar interations alone do not provide a complete explanation of the observed splittings.

Once the experimental values of ΔE_{exch} and the diagonal matrix elements of the exchange operators were determined, the fit of the exchange parameters to the data was straightforward. The calculated splittings are linear in the parameters as a consequence of the first-order nature of the splittings. Hence a normal least-squares method could be used, as opposed to a more complicated iterative procedure such as that required for a crystal-field analysis. In the least-squares fit, each level was assigned a weight of $1/\sigma^2$ where σ represents the experimental uncertainty of the exchange splitting for the level.

As a first step, a fit was made using only the α_{00} term in Eq. (33) which represents the isotropic exchange. This fit was quite unsuccessful since there was little correspondence between the signs of the matrix elements and those of the exchange splittings. The unweighted rms error was 0.20 cm^{-1}, and neither the signs nor the magnitudes of the splittings could be reproduced. Varying the dipole field produced no improvement. *Isotropic Heisenberg-type exchange alone thus appears to be completely incapable of explaining the observed splittings.*

When all eight terms in Eq. (33) were included, an excellent fit was obtained with an unweighted rms deviation of only 0.08 cm^{-1}, a value comparable to the experimental uncertainties of the splittings. The results of this fit are compared with the experimental splittings in Table IV which shows that the fit indeed gives both the correct sign and general magnitude for every observed level. Table V gives the individual contributions of the eight terms to each calculated splitting, while the fitted parameters are given in Table VI. The quoted error limits on the parameters reflect only the experimental uncertainties arising from the measurement of the total splittings and the separation of the dipolar contributions. Additional systematic errors, which are difficult to estimate, are expected to arise from the wave functions used in calculating the matrix elements of the exchange operator. Possible refinement of the wave functions will be discussed in Sec. III C 2, along with other possible sources of systematic error. It should also be noted that the fitted values of the parameters are somewhat sensitive to the relative weights assigned to the experimental levels.

C. Discussion of the results

1. Interpretation of the fit to the data

The seven anisotropic exchange terms together with a small isotropic term in α_{00} are really quite successful in reproducing the eleven observed splittings, especially when one considers that energy levels from a number of different J manifolds with dramatically different spin and orbital angular momentum components are involved. The general magnitude and sign are correct in every case; furthermore, within a given manifold the relative magnitudes of the calculated splittings for different levels correspond well to the relative magnitudes of the observed splittings.

The inadequacy of the isotropic exchange alone to describe the splittings is dramatically emphasized by an examination of Table V where it may be seen that the contributions of the anisotropic terms to the various splittings are generally an order of magnitude larger than those of the isotropic term. *This indicates that any realistic analysis of ion-ion interactions involving ions with large orbital admixtures must take into account the orbital dependence and the resulting anisotropy of the exchange interaction.* This result which was reported earlier[43] is supported by the more recent results of Cone and Meltzer[53] for $\mathrm{Gd}^{3+}-\mathrm{Gd}^{3+}$ exchange and by calculations of $4f-5d$ direct exchange in rare-earth metals by Yang, Huang Liu, and Orbach[86] and Huang Liu, Ling, and Orbach.[87]

Finally, we note from Table VI that α_{66}, β_{10}, and

TABLE IV. Comparison of theory and experiment for eight-parameter fit to exchange splittings of Er^{3+} doublet levels in $\mathrm{Tb(OH)}_3$ at 1.3 K. All energies are in cm^{-1}.

Level		Expt.	Calc.	Error
$^4I_{15/2}$	$\frac{5}{2}$	-0.09 ± 0.03	-0.10	-0.01
$^4I_{11/2}$	$\frac{3}{2}$	-0.16 ± 0.05	-0.17	-0.01
	$\frac{1}{2}$	-0.17 ± 0.03	-0.14	0.03
	$\frac{1}{2}$	-0.26 ± 0.11	-0.32	-0.06
	$\frac{3}{2}$	0.15 ± 0.11	0.09	-0.06
$^4I_{9/2}$	$\frac{3}{2}$	0.09 ± 0.08	0.17	0.08
	$\frac{1}{2}$	0.03 ± 0.05	0.07	0.04
$^4F_{9/2}$	$\frac{3}{2}$	0.36 ± 0.13	0.57	0.21
	$\frac{1}{2}$	0.14 ± 0.04	0.12	-0.02
$^4S_{3/2}$	$\frac{3}{2}$	0.20 ± 0.08	0.18	-0.02
	$\frac{1}{2}$	-0.35 ± 0.05	-0.27	0.07

TABLE V. Contributions of the separate terms in the effective exchange potential to the eleven observed exchange splittings of Er^{3+} doublet levels in $Tb(OH)_3$ at 1.3 K which result from a least-squares analysis with eight parameters. All energy contributions are in cm^{-1}.

Level		Term							
		$k=0,q=0$	$k=1,q=0$	$k=2,q=0$	$k=3,q=0$	$k=4,q=0$	$k=5,q=0$	$k=6,q=0$	$k=6,q=\pm 6$
		$\kappa=1,m=0$	$\kappa=0,m=0$	$\kappa=1,m=0$	$\kappa=0,m=0$	$\kappa=1,m=0$	$\kappa=0,m=0$	$\kappa=1,m=0$	$\kappa=1,m=0$
$^4I_{15/2}$	$\frac{5}{2}$	−0.019	0.013	−0.034	−0.012	0.142	−0.039	−0.185	0.028
$^4I_{11/2}$	$\frac{3}{2}$	−0.002	−0.030	0.001	0.063	0.299	−0.225	−0.301	0.028
	$\frac{1}{2}$	0.000	−0.005	−0.022	0.029	0.117	−0.088	−0.198	0.028
	$\frac{1}{2}'$	0.008	0.125	−0.463	0.110	−0.195	0.154	−0.033	−0.028
	$\frac{3}{2}'$	0.007	0.102	−0.258	−0.007	0.374	−0.285	0.187	−0.028
$^4I_{9/2}$	$\frac{3}{2}$	0.016	0.027	0.317	0.092	−0.224	−0.064	0.071	−0.066
	$\frac{1}{2}$	−0.008	−0.013	0.201	0.031	−0.192	−0.101	0.153	0.000
$^4F_{9/2}$	$\frac{3}{2}$	−0.088	0.089	0.446	0.120	−0.210	0.139	0.065	0.011
	$\frac{1}{2}$	0.010	−0.010	0.128	0.034	0.052	−0.149	0.057	0.000
$^4S_{3/2}$	$\frac{3}{2}$	0.152	−0.010	0.104	0.038	−0.108	0.000	0.000	0.000
	$\frac{1}{2}$	0.051	−0.003	−0.528	−0.113	0.324	0.000	0.000	0.000

β_{30} are not well determined by the fit to the experimental data. This is particularly true for α_{66}, the only term which is not axially symmetric. A search for further physical arguments to eliminate these terms in Eq. (33) has been unsuccessful; however, since the α's and β's each represent sums of contributions from nearest and next-nearest neighbors, it is possible that accidental near cancellations could make some of the terms quite small. In this connection we may note the competition between the various ground-state interactions found recently for both $Tb(OH)_3$ (Ref. 50) and $Gd(OH)_3$ (Ref. 88). As there are no detailed theoretical model calculations for the individual exchange mechanisms, it is not possible at this time to account for any such cancellations, but it is not unreasonable to relate them to competing overlap contributions.[89] (One could eliminate α_{66} if the interaction between Er^{3+} and the surrounding Tb^{3+} ions involved only the two nearest Tb^{3+} neighbors through simple two center processes. Such interactions would have axial symmetry and α_{66} would automatically be zero. However, such a specific interpretation is not necessary, and any model which required $q+q'=0$ would also give the same result.)

2. Possible refinements in the analysis

For several of the levels studied, the calculated splittings are outside the experimental uncertainties. This could be due to inadequacies of the wave functions, higher-order effects, or additional terms in the exchange potential.

As we have mentioned in Sec. III B 3, comparison of theory and experiment for the Zeeman effect indicates serious problems with the Er^{3+} wave functions in the $^2H_{11/2}$ manifold which we excluded from this study. It

TABLE VI. Comparison of the exchange parameters determined from a least-squares analysis of the experimental exchange splittings of Er^{3+} doublet levels in $Tb(OH)_3$ at 1.3 K. All values are in units of cm^{-1}.

Parameters	Eight-parameter fit
α_{00}	0.20 ± 0.10
β_{10}	−0.11 ± 0.08
α_{20}	4.64 ± 0.79
β_{30}	0.51 ± 0.40
α_{40}	−17.0 ± 5.2
β_{50}	−2.19 ± 0.76
α_{60}	3.43 ± 0.88
α_{66}	1.21 ± 1.51
Unweighted rms error	0.08

is also found that among the levels included in our analysis, the most serious errors for both the Zeeman effect and the exchange splittings occur in the $^4I_{9/2}$ manifold. Inadequacies of the wave functions thus appear to be a likely explanation for the lack of perfect agreement. Such problems could arise from inadequacies in the intermediate coupling wave functions which formed the basis for both the crystal-field calculation and evaluation of the reduced matrix elements for the exchange operators [Eq. (30)], or from shortcomings of the "single-particle" crystal-field model. Since the $^2H_{11/2}$ manifold in Er^{3+} is the first to have a major $S=\frac{1}{2}$ component, the problem may be a result of improper proportions of $S=\frac{3}{2}$ components in the intermediate-coupling wave functions. The spin-other-orbit interactions[90] which were not included in Rajnak's analysis[83] could affect this mixture. The use of effective operators to describe the configuration interaction effects may also affect the wave functions.[72,78] Crystal-field-induced configuration interaction effects and the more-general "correlation-crystal-field" terms of Newman and Bishton[91] have also not been included in our analysis, due to the intractable number of parameters involved. These effects may result in a term (L,S) dependence of crystal-field or exchange parameters. Hopefully, increasing interest in excited state interaction phenomena, energy transfer, and exciton effects will provide motivation for further investigation of these complex single-ion and "crystal-field" problems.

Contributions to the exchange splittings from second- and higher-order perturbation effects have been considered carefully in Secs. II B and III A and seem unlikely. However, there is also a possibility of second-order contributions from virtual-phonon exchange, and in this connection we may note that strong evidence has recently been found[63] for a major contribution from this mechanism to the energy dispersion of the $|^7F_6J_z=-5\rangle$ exciton band located at 118 cm^{-1} in pure $Tb(OH)_3$. In our case we would expect higher-order effects due to this interaction to be largest for the Er^{3+} ground doublet and negligibly small for the optically excited states, due to its energy denominator dependence. In fact, however, the larger discrepancies in the fit occurred for some of the optically excited levels, so that it would appear that second-order virtual phonon effects are probably not principally responsible for the residual differences.

Another possibility are additional terms in the exchange potential arising from the fact that superexchange interactions involving a ligand or the closed $5s^25p^6$ shells are not described completely by the expression given in Eq. (8). For such mechanisms[92] one may have, in addition to the scalar products of the spins, higher rank products such as $[s^{(1)}(i)\times s^{(1)}(j)]^{(1)}$ and $[s^{(1)}(i)\times s^{(1)}(j)]^{(2)}$. For C_{3h} symmetry, this could then result in terms of the form

$$\alpha_{kq-1}u_q^{(k)}(i)s_{-1}^{(1)}(i)+\alpha^*{}_{kq-1}u_{-q}^{(k)}(i)s_1^{(1)}(i) \;,$$

with α_{21-1}, α_{41-1}, α_{61-1}, and α_{6-5-1} nonzero. For a first-order analysis these coefficients may be regarded as real. Terms of the same form may arise from Eq. (8) if the host-ion ground state has nonzero matrix elements for $q'=\pm1$ or ±5. Explicit expressions for the coefficients based on Eq. (8) and contributions by nearest and next-nearest neighbors only are

$$\alpha_{kqm}=\sum_{k',q'}-2(-1)^m[2\Gamma_{qq'}^{kk'}(\mathrm{nn})+6\Gamma_{qq'}^{kk'}(\mathrm{nnn})] \times\langle g|\sum_j s_{-m}^{(1)}(j)\,u_{q'}^{(k')}(j)|g\rangle \tag{34}$$

and

$$\beta_{kq}=\sum_{k',q'}-\tfrac{1}{2}[2\Gamma_{qq'}^{kk'}(\mathrm{nnn})+6\Gamma_{qq'}^{kk'}(\mathrm{nnn})] \times\langle g|\sum_j u_{q'}^{(k')}(j)|g\rangle \;, \tag{35}$$

where the sums are restricted by $k+k'$ even and $q+q'=0,\pm6,\pm12$ for C_{3h} symmetry.

Such terms are clearly too complicated to include in the present analysis. One may hope that future experiments will be performed in which many more than 11 level splittings will be observed, so that a more extensive analysis becomes meaningful. Also, it may one day become possible to carry out microscopic calculations of the different exchange processes with sufficient accuracy to decide which of the possible mechanisms are in fact important. For the present, we can only speculate that the higher order effects which we have considered could indeed remove the residual discrepancies.

3. *Other possible systems*

While the system Er^{3+} in $Tb(OH)_3$ was ideal for the present analysis for a number of reasons, the magnitude of the exchange contributions to the splittings was not as large as those for which we hoped. It is interesting, therefore, to consider other systems for which these effects might be larger. Exchange interactions are generally larger for transition metal ions, but for such systems one would need to be careful to find states arising from the same electronic configuration. Interesting systems might also be found among the actinide compounds. UCl_3 for example appears to have large $U^{3+}-U^{3+}$ interactions since it orders at about 20 K.[93] Since the magnetic dipole-dipole interactions in such materials are comparable to those in $Tb(OH)_3$, it is clear that there must be a major contribution from nondipolar mechanisms, and these should show many of the features of our present system.

Other lanthanide materials are good candidates also.

GdCl$_3$:Er^{3+},[94] and GdCl$_3$:Dy^{3+},[95] have been studied but the experimental conditions for the reported measurements do not appear to satisfy the requirements for a simple analysis given in Sec. II. However, this difficulty may be overcome by using strong magnetic fields, which will generally provide a convenient means for simplifying and studying the complexities of anisotropic exchange effects.[40,51]

IV. CONCLUSION

We have shown that spontaneous splittings of highly localized impurity levels in ordered magnetic insulators are, under appropriate conditions, ammenable to a simple first-order analysis with negligible effects from higher-order terms. As a result, the exchange contribution to the splittings can be isolated experimentally and a detailed analysis of the effects of orbital anisotropy can be made. It can be shown that all the observable effects can be described quite generally by an effective Hamiltonian containing a reasonable number of empirical parameters.

This analysis has been applied to eleven optically observed exchange splittings in five manifolds of Er^{3+} in ferromagnetically ordered Tb(OH)$_3$, and it turns out that all the effects can be described by a spherical tensor operator involving only eight parameters. The contributions of the anisotropic terms are found to be about one order of magnitude *larger* than those of the isotropic term, dramatically illustrating the importance of anisotropic exchange in a case such as this and the complete inadequacy of the usual isotropic (Heisenberg) form. The parametrization used here has also been quite successful in *relating* exchange effects in several J manifolds involving *different* L and S components.

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$$\vec{s}_i\cdot\vec{s}_j=\sum_m(-1)^m s_m^{(1)}(i)\,s_{-m}^{(1)}(j)\quad .$$

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