Brief Reports

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Higher-order terms in the magnetic interaction of an ion in a solid

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We give a phenomenological Hamiltonian containing a sum over irreducible tensors that describes optical experiments showing energy-level splittings in rare-earth salts induced by magnetic ordering. The Hamiltonian encompasses anisotropic exchange mechanisms proposed by previous workers as well as a new magnetostatic mechanism (magnetic dipole-multipole coupling) described in this work.

Splittings of Stark levels induced by magnetic ordering have been observed in a number of optical experiments on rare-earth impurities in magnetically ordered rare-earth salts.[1-4] In these experiments, it was hoped that the splitting of the ith Stark level of the rare-earth impurity, ΔE_i, would be related to the expectation value of the magnetic dipole operator $\vec{\mu}$ in the ith level of the impurity by

$$\Delta E_i = -\langle i \mid \vec{\mu} \mid i \rangle \cdot \vec{H}_{\text{eff}} , \tag{1}$$

where $\vec{\mu} = -\mu_B(\vec{L}+2\vec{S})$, μ_B is the Bohr magneton, and $\vec{L}$ and $\vec{S}$ are the total orbital and spin angular-momentum operators. Equation (1) is valid provided that the magnetic interaction can be described in terms of a uniform, effective, internal magnetic field, $\vec{H}_{\text{eff}}$. In some of the experiments referred to above, the quantities $\langle i \mid \vec{\mu} \mid i \rangle$ were measured independently of the ΔE_i for several Stark levels, and Eq. (1) was found to be inadequate.

The purpose of the present Report is twofold. First, we present a phenomenological magnetic interaction Hamiltonian that describes the magnetically induced splittings in the same manner as the usual crystal-field Hamiltonian[5] describes Stark splittings. This magnetic interaction Hamiltonian encompasses the exchange mechanism proposed by Cone and Wolf[6] to explain splittings observed[4] for Er^{3+}:$Tb(OH)_3$. Second, we examine an alternative microscopic mechanism involving magnetic dipole-multipole interactions that also gives rise to a Hamiltonian of the correct form, but which (by itself) falls short of giving correct values for the magnetically induced splittings. We argue that both exchange and magnetostatic mechanisms should be considered in fitting experimentally observed splittings.

We consider the most general one-electron Hamiltonian that is invariant under the operations of the appropriate magnetic color group.[7] The effective Hamiltonian is of the form

$$H_M = \sum_k \left[a^{(k)} \cdot U^{(k)} + \sum_K b^{(k)}(K) \cdot \{V^{(1K)}\}^{(k)} \right] , \tag{2}$$

where $U^{(k)}$ is the usual unit irreducible tensor operating in orbital space and $\{V^{(1K)}\}^{(k)}$ is a unit double tensor of rank 1 in spin space and K in orbital space, coupled by means of a Clebsch-Gordan coefficient[8] to form a tensor of rank k in the total space. Our normalization of the $U^{(k)}$ and $V^{(1k)}$ is that of Nielson and Koster.[9] The sum on k covers the values $k = 1,3,\ldots,2l-1$ ($l=3$ for f electrons), with $K = k-1$, k, and $k+1$. The values $k = 2l+1$ and $K = 2l$ are also allowed in the second (spin-dependent) term in Eq. (2). Even-k terms can also appear in the Hamiltonian, but these contribute to the effective crystal-field interaction and cannot yield magnetically induced splittings (by virtue of time-reversal symmetry). The quantities $a^{(k)}$ and $b^{(k)}(K)$ are tensors of rank k (in the "external" space) whose nonvanishing components $a_q^{(k)}$ and $b_q^{(k)}(K)$ are determined by the magnetic color group of the rare-earth ion site.

Since the Hamiltonian, Eq. (2), is Hermitian, we must have

$$a_q^{(k)\dagger}=(-1)^q a_{-q}^{(k)} , \tag{3a}$$

$$b_q^{(k)}(K)^\dagger=(-1)^{k+K+q+1} b_{-q}^{(k)}(K) . \tag{3b}$$

Cone and Wolf[6] have derived a Hamiltonian of the form of Eq. (2) by considering anisotropic exchange interactions between the rare-earth impurity ion and the magnetic constituents of the host lattice based on the theoretical formalism developed by Levy.[10] Their results are expressed in terms of a set of constants $\alpha_{Km\nu}$ and β_{kq}, which are related to the coefficients of Eq. (2) by

$$a_q^{(k)}=\beta_{kq}^\dagger , \tag{4a}$$

$$b_q^{(k)}(K)=\sum_{\nu m} C(1Kk;\nu m)\alpha_{Km\nu}^\dagger , \tag{4b}$$

where $C(\ )$ is a Clebsch-Gordan coefficient.[11] By invoking the exchange mechanism, Ref. 6 obtains selection rules on ν and m separately rather than on the sum $\nu+m$, and thereby reduces the number of independent parameters of the form $b_q^{(k)}(K)$. Reference 6 also suggests that this further restriction be dropped in a more complete analysis.

A similar (but distinct) reduction of the number of parameters occurs if we consider magnetostatic contributions to Eq. (2). Consider a distribution of current (or equivalently, a distribution of magnetization density) that does not overlap the rare-earth ion. In the Coulomb gauge, the magnetic interaction Hamiltonian of an electron on the rare-earth ion with the vector potential $\vec{A}(\vec{r})$ due to this distribution is[12]

$$H_M=\mu_B\left[\frac{1}{\hbar}\vec{A}\cdot\vec{p}+\vec{s}\cdot(\vec{\nabla}\times\vec{A})\right] , \tag{5}$$

where $\vec{p}$ and $\vec{s}$ are the momentum and spin operators of the electron. We neglect terms quadratic in $\vec{A}$.[12] For simplicity, we consider the lattice as being composed of point magnetic dipoles $\vec{\mu}_j$ located at positions $\vec{R}_j$. We have in this case

$$\vec{A}(\vec{r})=-\sum_j \vec{\mu}_j\times\vec{\nabla}\frac{1}{|\vec{R}_j-\vec{r}|} . \tag{6}$$

Equation (5) can be cast into irreducible tensor form. Details of the straightforward but tedious derivation are given elsewhere[13]; we simply present the results here. We define the magnetic lattice sums

$$M^{(k)}=\sum_j\{\mu_j C^{(k+1)}(\hat{R}_j)\}^{(k)}/R_j^{k+2} , \tag{7}$$

where $C_Q^{(K)}\equiv[4\pi/(2K+1)]^{1/2}Y_{KQ}$, and where Y_{KQ} is an ordinary spherical harmonic.[14] The nonvanishing components $M_q^{(k)}$ of Eq. (7) are determined by the magnetic color group. In terms of the $M^{(k)}$, our result can be expressed as follows:

$$b^{(k)}(k-1)=-2\mu_B[k(k+1)(2k-1)(2k+3)]^{1/2}(l||C^{(k-1)}||l)\langle r^{k-1}\rangle M^{(k)} , \tag{8a}$$

$$a^{(k)}=\frac{1}{2(k+1)}\left[\frac{k(2l+k+1)(2l-k+1)}{(2k-1)}\right]^{1/2} b^{(k)}(k-1) , \tag{8b}$$

where $(l||C^{(K)}||l)=(2l+1)C(lKl;00)$ is the reduced matrix element of $C^{(K)}$ and where $\langle r^{k-1}\rangle$ is the expectation value of r^{k-1} in the electronic configuration under consideration. From Eq. (8b), the ratio $a_m^{(k)}/b_m^{(k)}(k-1)$ is independent of m. Further, we have $b^{(k)}(k)=b^{(k)}(k+1)=0$. The lowest term ($k=1$) in Eq. (2) can be shown to reduce to $-\vec{\mu}\cdot\vec{H}_{\rm eff}$, provided we take $\vec{H}_{\rm eff}=-\sqrt{10}M^{(1)}$. (This is the usual sum over point dipoles used to calculate the effective magnetic field.)

We have performed an *a priori* calculation of the magnetostatic contributions to the magnetically induced splittings of Er^{3+}:$Tb(OH)_3$. Since all Tb sites in this salt are magnetically equivalent (with a dipole moment[15] of $\sim 9\mu_B$ along $\hat{z}$), the magnetic lattice sums $M^{(k)}$ are simply proportional to lattice sums of the electrostatic type over the Tb ions. The resulting nonvanishing $M_q^{(k)}$ for $k\geq 3$ are $M_0^{(3)}$, $M_0^{(5)}$, $M_0^{(7)}$, and $M_6^{(7)}$, owing to the C_{3h} point symmetry, with $M_6^{(7)}$ complex and the other $M_q^{(k)}$ real.[16] These were used in conjunction with renormalized radial expectation values[17] of r^{k-1} and intermediate-coupling reduced matrix elements[18] of $U^{(k)}$ and $V^{(1K)}$ in Eqs. (2) and (8). Contributions to the splittings were determined for the Stark levels reported in Ref. 4 using Stark wave functions deduced from the reported[4,6] theoretical values of $\langle i|\mu_z|i\rangle$.

The calculated values of $\Delta E_{\rm exch}$, defined in Ref. 6 as the difference between the left- and right-hand sides of Eq. (1), are, in general, an order of magnitude smaller than those observed in Ref. 6. This

TABLE I. Comparison of calculated[a] and observed[b] $a_q^{(k)}$ and $b_q^{(k)}(K)$ (all in cm^{-1}) for Er^{3+}:$Tb(OH)_3$.

k	q	$a_q^{(k)}$ Calc.	$a_q^{(k)}$ Obs.	$b_q^{(k)}(k-1)$ Calc.	$b_q^{(k)}(k-1)$ Obs.	$b_q^{(k)}(k+1)$ Obs.[c]
1	0[d]		−0.11		0.20	−2.94
3	0	−0.109	0.51	−0.178	3.59	11.3
5	0	0.018	−2.19	0.060	−12.7	−2.33
7	0			−0.013	2.52	
7	6			0.003	0.46	

[a]Calculated by assuming magnetostatic interactions, Eq. (8). Values of the $M_q^{(k)}$ obtained from Eq. (7) are $M_0^{(3)}=-0.01576$, $M_0^{(5)}=-0.00240$, $M_0^{(7)}=-0.00011$, and $M_6^{(7)}=0.00003$, all in units of μ_B Å^{-k-2}. Values of $\langle r^k\rangle$ are from Ref. 16. The magnetic moment of a Tb^{3+} ion in the lattice is taken as $9\mu_B$.

[b]Obtained in Ref. 6 by fitting observed magnetically induced splittings, assuming exchange interactions. The $a_q^{(k)}$ and $b_q^{(k)}(K)$ given here are related to the β_{kq} and α_{Kmv} of Ref. 6 via Eq. (4). Note that the observed $b_0^{(k)}(k-1)$ and $b_0^{(k)}(k+1)$ are not independent but are related by Eq. (9).

[c]Calculated values are zero if we assume magnetostatic interactions.

[d]Calculated $a_0^{(1)}$ and $b_0^{(1)}(0)$ simply give the dipolar splittings of Eq. (1), which were subtracted from the observed splittings in Ref. 6 before fitting.

discrepancy is most easily seen in Table I, where we compare calculated and observed values of the $a_q^{(k)}$ and $b_q^{(k)}(K)$. However, the calculated contribution to the splittings from the magnetostatic interaction is of the same order of magnitude as the difference between calculated and observed splittings presented in Ref. 6.

It is clear that the assumption of point magnetic dipoles for the neighboring magnetic ions is a major restriction on our development. By analogy with the crystal-field case,[19] we would expect important contributions from higher-order magnetic multipoles of the Tb^{3+} ions. If these are included, we can still use Eq. (2) [with Eq. (8b) still valid with $b^{(k)}(k)=b^{(k)}(k+1)=0$, provided the magnetization distribution of the lattice does not overlap that of the rare-earth impurity ion]. The multipolar calculation is so complex, however, that we should treat the $b_m^{(k)}(k-1)$ as adjustable parameters. Nevertheless, the exchange terms considered in Ref. 6 should be somewhat larger than these magnetostatic terms.

The relative contributions of magnetostatic and exchange effects in magnetically induced splittings can be determined unambiguously from experiment, provided a sufficiently large number of splittings have been measured accurately. The procedure would be to treat each coefficient in Eq. (2) that is allowed by symmetry as an independent parameter; for reasons discussed in Ref. 6, we do not consider the $b^{(k)}(k)$ terms. In Er^{3+}:$Tb(OH)_3$, for example, we would have the following nonvanishing parameters: $a_0^{(1)}$, $a_0^{(3)}$, $a_0^{(5)}$, $b_0^{(1)}(0)$, $b_0^{(1)}(2)$, $b_0^{(3)}(2)$, $b_0^{(3)}(4)$, $b_0^{(5)}(4)$ $b_0^{(5)}(6)$, $b_0^{(7)}(6)$, and $b_6^{(7)}(6)$; thus, we would require well in excess of eleven experimental splittings. In the magnetostatic model, only four of these parameters are independent. In the exchange model, we have [$m=\nu=0$ in Eq. (4)]

$$\frac{b_0^{(K+1)}(K)}{b_0^{(K-1)}(K)}=-\left[\frac{K+1}{K}\right]^{1/2}, \tag{9}$$

and so only eight of the parameters are independent for the exchange interaction. Thus, by fitting the observed splittings and examining the resulting constants in Eq. (2), we can perhaps determine the relative importance of magnetostatic and exchange effects. It may turn out that additional interactions need to be considered to explain all the data.

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[7]The conditions under which the one-electron magnetic Hamiltonian is valid have been discussed in some detail in Ref. 6; however, it is possible that some of the conditions in Ref. 6 are too stringent, and that the phenomenological Hamiltonian presented here in Eq. (2) can encompass a wide variety of local and nonlocal magnetic effects, by analogy with the crystal-field Hamiltonian [see, for example, D. J. Newman, Adv. Phys. 20, 197 (1971)].

[8]Our notation for tensor couplings is that of B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).

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[11]M. E. Rose, *Elementary Theory of Angular Momentum* (McGraw-Hill, New York, 1963).

[12]L. I. Schiff, *Quantum Mechanics,* 3rd ed. (McGraw-Hill, New York, 1968). In Eqs. (5) and (6), the $\vec{\nabla}$ operator is considered to act only on the function directly to its right (not on the wave function).

[13]R. P. Leavitt and C. A. Morrison, Harry Diamond Laboratories Report No. TR-1852 (unpublished), available from U. S. National Technical Information Service, Springfield, VA, Report No. 054 747.

[14]Because the sum in Eq. (7) for $k=1$ is not absolutely convergent, $M^{(1)}$ is dependent upon sample shape. On the other hand, the $M^{(k)}$ for $k>1$ are not shape dependent.

[15]C. A. Catanese, A. T. Skjeltorp, H. E. Meissner, and W. P. Wolf, Phys. Rev. B 8, 4223 (1973).

[16]As indicated in Ref. 6, however, the imaginary part of $M_6^{(7)}$ does not contribute in a first-order calculation. The coordinate system for our calculation is chosen so that the crystal-field parameter B_{66} is real and positive.

[17]C. A. Morrison, N. Karayianis, and D. E. Wortman, Harry Diamond Laboratories Report No. TR-1816 (unpublished), available from U. S. National Technical Information Service, Springfield, VA, Report No. 042 447. The electrostatic shielding factors σ_k used in calculating $\langle r^k \rangle$ for crystal-field interactions in this reference are, of course, not included for the present purposes.

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