Mean g Values of Rare-Earth Ions in Crystals

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The mean g value of a Kramers's doublet in a lattice with a symmetry axis is shown to have extrema of magnitude $\frac{2}{3}\Lambda(J+1)$ and $\frac{2}{3}\Lambda J$, where Λ is the Landé splitting factor and only the lowest free-ion J state is considered. The extrema are associated, respectively, with positive and negative values of the product $g_xg_yg_z$. The mathematical properties of the extrema are used to derive simple relationships between the parameters of a general wave function, and the results are applied to the anisotropic paramagnetic-resonance spectra of LaF_3:Yb^{3+} and CaO:Er^{3+}.

THE paramagnetic resonance of a Kramers's doublet may be described in an effective $S'=\frac{1}{2}$ notation by the magnitudes of the principal components g_x, g_y, g_z of the g tensor.[1] It has been noted[2] that, in noncubic symmetries, doublet ground states of odd-electron rare-earth ions often have mean g values which are similar to isotropic g values observed from a Γ_6 or Γ_7 level of the same ion in cubic symmetry.[3] This agreement has sometimes been used to infer that the symmetry of the noncubic system is approximately cubic. Although this assumption is often valid, examples may be found in which the symmetry does not appear to be near to cubic. In this paper, we show that a mean g value equal to an isotropic Γ_6 or Γ_7 g value is not necessarily related to a system with cubic symmetry, but rather to a theoretical extremum of the mean g value if there is at least one axis of twofold or higher symmetry. The isotropic Γ_6 or Γ_7 g value is just one example of an extremum mean g value. In addition, we find that the sign of the product $g_xg_yg_z$, on which the sense of the Larmor precession depends,[4] is associated with the magnitude of the mean g value at the extremum. For systems in which the mean g value is close to an extremum, the mathematical properties of the extremum may be used to derive simple relationships between the parameters of a trial wave function, thus allowing the problem of fitting such a function to a set of experimental g values to be greatly simplified. Two examples are considered: the rhombic spectrum of LaF_3:Yb^{3+} [5] and the axial spectrum of CaO:Er^{3+}.[6]

The components of a Kramers's doublet may be represented in an $S'=\frac{1}{2}$ notation as

$$|\alpha\rangle\equiv|+\tfrac{1}{2}\rangle,\quad |\beta\rangle\equiv|-\tfrac{1}{2}\rangle. \tag{1}$$

If the mixing of free-ion J manifolds by the crystal field is neglected, then the doublet wave functions may be expressed as linear combinations of states of different magnetic quantum number M associated with a single value of J,[1] i.e.,

$$\begin{aligned}|\alpha\rangle&=\sum_M a_M|J,M\rangle,\\ |\beta\rangle&=\sum_M(-1)^{(J-M)}a_M{}^*|J,-M\rangle,\end{aligned} \tag{2}$$

where $a_M{}^*$ is the complex conjugate of a_M and the values of M in the summation are determined by the symmetry. The form of the component $|\beta\rangle$ is derived from that of $|\alpha\rangle$ by a time-inversion operation.[7] If the wave functions are normalized, then

$$\sum_M|a_M|^2=1. \tag{3}$$

The principal components of the g tensor are defined as follows:

$$\begin{aligned}g_z(=g_{\parallel})&=2\Lambda\langle\alpha|J_z|\alpha\rangle,\\ g_x+g_y(=2g_{\perp})&=2\Lambda\langle\alpha|J_+|\beta\rangle,\\ g_x-g_y(=0)&=2\Lambda\langle\alpha|J_-|\beta\rangle,\end{aligned} \tag{4}$$

where $J_\pm=J_x\pm iJ_y$, Λ is the Landé splitting factor, and the values in parentheses refer to a spectrum with axial symmetry. There is still some ambiguity, since the signs of g_x and g_z depend upon which component of the doublet is chosen to be $|\alpha\rangle$ in Eq. (2).[8] This ambiguity is eliminated by means of the following convention: if the z axis has threefold or higher symmetry, $|\alpha\rangle$ is chosen so that g_x and g_y are of the same sign[4,8]; if the z axis has twofold symmetry, $|\alpha\rangle$ is chosen to contain the component $|J,\frac{1}{2}\rangle$. Applying the definitions of Eq. (4) to the wave functions of Eq. (2),

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[2] U. Ranon (private communication); examples may be seen in Ref. 13.

[3] Isotropic g-values are observed from Γ_6 and Γ_7 levels which occur only once in the decomposition of the J manifold by the cubic field; see, for example, K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

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with a_M chosen to be real, we obtain

$$g_z = 2\Lambda \sum_M a_M{}^2 M\,, \tag{5a}$$

$$g_x + g_y = 2\Lambda \sum_M (-1)^{(J-M)} a_M a_{M'} \times [(J+M)(J+M')]^{1/2} + \Lambda(-1)^{(J-1/2)}(2J+1)a_{1/2}{}^2\,, \tag{5b}$$

$$g_x - g_y = 2\Lambda \sum_M (-1)^{(J-M)} a_M a_{M''} \times [(J-M)(J-M'')]^{1/2}\,, \tag{5c}$$

where

$$M' = -(M-1)\,, \quad M'' = -(M+1)\,. \tag{6}$$

Since the signs of the components of the g tensor cannot be determined by paramagnetic resonance, and are to some extent a matter of definition, we define an experimental mean g value as follows:

$$3\bar{g}(\text{expt}) = |g_z| + |g_x| + |g_y|\,. \tag{7}$$

The components g_x, g_y, g_z can have either sign, so that there are several combinations that can lead to a given value of $\bar{g}$(expt). Accordingly, we look for the maxima and minima of the four following expressions:

$$3\bar{g} = g_z \pm (g_x + g_y)\,, \tag{8a}$$

$$3\bar{g} = g_z \pm (g_x - g_y)\,. \tag{8b}$$

To begin with, we consider the function of Eq. (8a) in the case that the component $|\alpha\rangle$ of Eq. (2) has, for each value of M, an associated M' given by Eq. (6). (In this case, the coefficient $a_{1/2}$ must be zero.) Maxima and minima are found by applying the Lagrange method of undetermined multipliers to the function obtained by inserting Eqs. (5a) and (5b) into Eq. (8a), with Eq. (3) providing the restrictive condition. In this way, the conditions for the extrema are found to be

$$a_{M'} = \pm(-1)^{(J-M)}[(J-M+1)/(J+M)]^{1/2} a_M \tag{9a}$$

for the maximum

$$\bar{g}_{\max} = \tfrac{2}{3}\Lambda(J+1) \tag{9b}$$

and

$$a_{M'} = \mp(-1)^{(J-M)}[(J+M)/(J-M+1)]^{1/2} a_M \tag{10a}$$

for the minimum

$$\bar{g}_{\min} = -\tfrac{2}{3}\Lambda J\,. \tag{10b}$$

The upper and lower signs in Eqs. (9a) and (10a) correspond to those in Eq. (8a). If $|\alpha\rangle$ contains a value of M without an associated M', then the parameter a_M appears only as the square in Eq. (8a). A different procedure is then adopted, in which the isolated a_M is eliminated initially from $\bar{g}$ by means of Eq. (3), the normalization condition, and the remaining parameters are treated as independent variables. In particular, if the parameter $a_{1/2}$ is nonzero, only one of the signs appears in Eqs. (9a) and (10a), since the terms of Eq. (5b) containing the products $a_M a_{M'}$ must have the same sign at an extremum as the term in $a_{1/2}{}^2$.

If g_x and g_y are nonzero, then Eq. (8b) can lead to an extremum only if the z axis has twofold symmetry. In calculating the extrema, the same procedures are adopted as above, this time using Eqs. (3), (5a), (5c), and (8b). We obtain

$$a_{M''} = \pm(-1)^{(J-M)}[(J-M)/(J+M+1)]^{1/2} a_M \tag{11a}$$

for the maximum

$$\bar{g}_{\max} = \tfrac{2}{3}\Lambda J \tag{11b}$$

and

$$a_{M''} = \mp(-1)^{(J-M)}[(J+M+1)/(J-M)]^{1/2} a_M \tag{12a}$$

for the minimum

$$\bar{g}_{\min} = -\tfrac{2}{3}\Lambda(J+1)\,. \tag{12b}$$

The upper and lower signs in Eqs. (11a) and (12a) correspond to those in Eq. (8b).

It may be seen from Eqs. (8a) and (9b) that, at $\bar{g}_{\max} = \frac{2}{3}\Lambda(J+1)$, g_z is positive and g_x and g_y have the same sign; therefore the product $g_x g_y g_z$ is positive. Likewise, Eqs. (8b) and (12b) show that, at $\bar{g}_{\min} = -\frac{2}{3}\Lambda(J+1)$, g_z is negative and g_x and g_y have opposite signs; therefore, the product $g_x g_y g_z$ is again positive. Thus, the solution of magnitude $\frac{2}{3}\Lambda(J+1)$ is always associated with a positive product. Similarly, the solution of magnitude $\frac{2}{3}\Lambda J$ is in each case associated with a negative product.[9] These conclusions may be checked in a simple manner for the special case of cubic wave functions.[3,8] From the above, it may be deduced that in all cases in which $\bar{g}$(expt) is greater than $\frac{2}{3}\Lambda J$, the sign of the product is positive. It should be noted that the value $\bar{g}(\text{expt}) = \frac{2}{3}\Lambda J$ need not be associated with an extremum. However, the two cases could be distinguished by experiment, since the nonextremum value is associated with the positive sign of the product.

In practice, some of these conclusions may have to be modified slightly, since the measured g values do not correspond exactly to the formulas of Eq. (5). This is because of such effects as the coupling of different J manifolds by the crystal field,[1] the covalent reduction of the orbital moment,[10,11] and the dynamical lowering of the symmetry through lattice vibrations.[12] These effects are observed in cubic fields through the deviation of the isotropic g value of a Krammers's doublet from one of the values $\frac{2}{3}\text{H}(J+1)$ or $\frac{2}{3}\text{H}J$. In the case of the Γ_7 state lying lowest in the configuration $4f^{13}$ ($J=\frac{7}{2}$), the theoretical value of $\frac{2}{3}\Lambda(J+1)$ is 3.43, while experimental values range from 3.45 for $CaF_2{:}Tm^{2+}$ [10] to 3.12 for

[9] Both positive and negative values of g_z (as well as the value $g_z=0$) occur in the solutions of Eqs. (10) and (11). However, positive values of g_z in the solution of Eq. (10) and negative values of g_z in the solution of Eq. (11) do not correspond to $|\bar{g}| = \bar{g}$(expt), and such solutions should be rejected.

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CdTe:Yb^{3+}.[13] In a noncubic field, it is not possible to know for certain if a value of $\bar{g}$(expt) in this range corresponds to an extremum. However, in dealing with values of $\bar{g}$(expt) near the extremum $\frac{2}{3}\Lambda(J+1)$, we have assumed that the errors are small in treating them as extrema, and we have defined an effective Landé factor by the equation

$$\bar{g}(\text{expt})=\tfrac{2}{3}\Lambda'(J+1). \tag{13}$$

For a highly anisotropic spectrum, it would be more realistic to use a nonisotropic effective Landé factor, but we have not attempted to do this. Values of $\bar{g}$(expt) near $\frac{2}{3}\Lambda J$, as mentioned earlier, are not necessarily near an extremum. Since the signs of the products $g_xg_yg_z$ have not been measured in such cases, we have chosen not to consider them. Two examples in which $\bar{g}$(expt) is near $\frac{1}{2}\text{H}(J+1)$ are treated below:

(i) *LaF_3:Yb^{3+}* $(4f^{13}, J=\frac{7}{2})$. The experimental g values at 14°K are[5]

$$|g_z|=5.20\pm0.01\,,\quad |g_x|=1.210\pm0.005\,,\quad |g_y|=3.76\pm0.03\,, \tag{14}$$

where the z axis has twofold symmetry and the x and y axes are interchangeable. The magnitude of $\bar{g}$(expt) is 3.39, so that Eq. (13) gives $\Lambda'=1.13$. Since the z axis has twofold symmetry, $|\alpha\rangle$ of Eq. (2) has the form

$$|\alpha\rangle=a|\tfrac{5}{2}\rangle+b|\tfrac{1}{2}\rangle+c|-\tfrac{3}{2}\rangle+d|-\tfrac{7}{2}\rangle, \tag{15}$$

where the quantum number $J=\frac{7}{2}$ has been omitted. Equation (3) gives

$$a^2+b^2+c^2+d^2=1. \tag{16}$$

Equations (5a)–(5c) give

$$g_z\ =\Lambda'(5a^2+b^2-3c^2-7d^2)\,, \tag{17a}$$

$$g_x+g_y=-8\Lambda'(\sqrt{3}ac+b^2)\,, \tag{17b}$$

$$g_x-g_y=-4\Lambda'[(\sqrt{7})ad+(\sqrt{15})bc]. \tag{17c}$$

The only physically acceptable solution is found to occur for the $\bar{g}_{\min}$ of Eq. (12b), for which the following additional relationships are obtained:

$$c=\pm(5/3)^{1/2}b\,,\quad d=\pm(\sqrt{7})a. \tag{18}$$

The magnitudes of the parameters a, b, c, and d may be calculated from Eqs. (16), (18), and either (17a) or (17c), the extra relation being redundant. Equation (17b), which has not yet been used, provides a test of the theory. There are two distinct solutions for Eq. (17b), which depend on the sign of the factor ac. With ac positive, the theoretical magnitude of 2.59 for g_x+g_y is in good agreement with the experimental magnitude of 2.55±0.04. [The difference in experimental values is taken because Eq. (12b) requires g_x and g_y to be of opposite sign.] Choosing the parameter a to be positive, we obtain

$$a=0.311\,,\quad b=\pm0.290\,,\quad c=0.375\,,\quad d=\pm0.824 \tag{19}$$

leading to the theoretical g factors

$$g_z=-5.20\,,\quad g_x=\pm1.19\,,\quad g_y=\mp3.78. \tag{20}$$

(ii) *CaO:Er^{3+}* $(4f^{11}, J=\frac{15}{2})$. The experimental g values for the axial spectrum at 4.2°K are[6]

$$|g_{\parallel}|=4.730\pm0.005\,,\quad |g_{\perp}|=7.86\pm0.01. \tag{21}$$

The value $\bar{g}$(expt)$=6.82$ is close to the theoretical value $2\Lambda(J+1)/3=6.80$, so that the real Landé factor $\Lambda=1.2$ is used. The z axis has fourfold symmetry, and there are two possible functions for $|\alpha\rangle$, i.e.,

$$|\alpha\rangle=a|\tfrac{13}{2}\rangle+b|\tfrac{5}{2}\rangle+c|-\tfrac{3}{2}\rangle+d|-\tfrac{11}{2}\rangle, \tag{22a}$$

$$|\alpha\rangle=p|\tfrac{9}{2}\rangle+q|\tfrac{1}{2}\rangle+r|-\tfrac{7}{2}\rangle+s|-\tfrac{15}{2}\rangle. \tag{22b}$$

In either case, three independent parameters remain after normalization. Since there are only two g factors, the problem would have been previously considered underdetermined. However, in place of the theoretical expression for one of the g factors, we can now use the two additional relations obtained for each function from Eq. (9a), i.e.,

$$c=\mp(\tfrac{3}{5})^{1/2}b\,,\quad d=\mp(1/7)^{1/2}a\,, \tag{23a}$$

$$r=(\tfrac{1}{3})^{1/2}p\,,\qquad s=0. \tag{23b}$$

The following solutions are obtained in a straightforward manner:

$$|a|=0.458\,,\quad |c|=0.534\,,\quad |b|=0.689\,,\quad |d|=0.173\,, \tag{24a}$$

where the products ad and bc have the same sign, and

$$|p|=0.739\,,\quad |r|=0.426\,,\quad |q|=0.522\,,\quad |s|=0.000\,, \tag{24b}$$

where the product pr is positive. The calculated g values corresponding to these functions are

$$g_{\parallel}=+4.70\,,\quad g_{\perp}=\pm7.85. \tag{25}$$

We conclude by noting that although a useful mathematical aid has been found for fitting wave functions to the measured g values when the mean g value corresponds to an extremum; the more fundamental problem of understanding why these special values occur so often[14] remains unsolved.

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[14] For example, about 60% of all measured noncubic spectra of Yb^{3+} have mean g values which could correspond to $\frac{2}{3}\Lambda'J$ or $\frac{2}{3}\Lambda\ (J+1)$. However, the percentages are much lower for other rare-earth configurations.