EPR in the 21st Century
A Kawamori, J Yamauchi and H Ohta (Editors)
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g Tensor of Er^{3+} centers in axial symmetry

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A scheme for the numerical calculation of Zeeman splitting factors for erbium ions in a crystalline environment is described. The examples of crystal fields of trigonal or tetragonal symmetry are presented in some detail. From the results it is concluded that the trace of the g tensors can be remarkably constant upon distortion from an initially cubic symmetry to a lower axial symmetry.

1. INTRODUCTION

Over the past forty years an impressive data base on the Zeeman effect of erbium ions in crystals has been brought about. For more than 70 such centers the g tensors for splitting of energy levels in a magnetic field have been reported. This paper discusses analysis of these data of which a summary with references is given in Ref. 1.

The ion Er^{3+} has electronic configuration $4f^{11}$ and possesses orbital momentum L = 6 and spin S = 3/2, resulting in a 52-fold degeneracy. By spin-orbit interaction moments couple to form levels characterized by quantum number J, which can take the values 15/2, 13/2, 11/2 and 9/2. For erbium, the J = 15/2 level is the ground state. In a crystal the still 16-fold degeneracy of the ground state is further reduced by formation of doublet and quartet levels and spin resonance is observed in these states. In cubic symmetry the resonance in states of Γ_6 symmetry type has isotropic g value g = 6.8; for the resonance in the Γ_7 doublets the g tensor is an isotropic g = 6.0. These theoretical predictions have been abundantly confirmed by experimental observations. In axial symmetry the Zeeman splitting becomes anisotropic and will be described by a tensor interaction with the principal values $g_{//}$ and $g_{\perp}$. Some fifty spectra of axial centers have been described [1]. Applying perturbation theory, it was shown already in an early paper [2] that for small axial distortion the trace $g_{//} + 2g_{\perp}$ of the g tensors remains constant. Also for a purely axial field the g tensors can be derived by analytical means. In an axial field the states quantize as $|15/2,m_J\rangle$ with $m_J = \pm1/2,.....,\pm15/2$. For instance, for the transition between states in the doublet $|15/2,\pm1/2\rangle$ the g tensor is normally quoted as $g_{//} = 1.2$ and $g_{\perp} = 9.6$. Its trace $g_{//} + 2g_{\perp} = 20.4$ equals the trace of a Γ_6 state in the cubic symmetry, establishing an apparent relation between the two cases. In interpreting experimental data caution is in order, as both in theory and experiment the sign of a g value is not easily determined. In the theoretical calculation upper parallel spin state and lower anti-parallel state should be identifiable. This is straightforward in few cases only, such as, for instance, a magnetic field parallel to the axis of crystal field with axial symmetry. Also, in experiment normally only the energy difference between Zeeman split levels is measured and is taken as positive. To establish the relation to spin quantization requires a dedicated set up [3]. If the principal g values of the doublet |15/2,±1/2> have opposite signs the calculated trace becomes ±18.0, equal to the value of a Γ_7 doublet in cubic symmetry. Numerical calculations as presented in this paper allow the variation of g values continuously to be followed as a function of axial field between the extreme limits of pure cubic and pure axial field. This allows to follow the variation of the trace and to detect possible changes of sign. Analytical treatments which are restricted to the limiting cases do not have this feasibility.

2. OUTLINE OF COMPUTATIONAL METHOD

Energy levels in zero magnetic field are obtained by solving the eigenvalue equation for the crystal field potentials in the basis set of the 16 states for the J = 15/2 spin-orbit ground state. A cubic field, valid for T_d symmetry, has the forth- and sixth-order contributions

$$V_{cu4} = 35(x^4 + y^4 + z^4) - 21r^4 \quad (1)$$

and

$$V_{cu6} = 231(x^6 + y^6 + z^6) - 315(x^4 + y^4 + z^4)r^2 + 90r^6. \quad (2)$$

Representative expressions for axial trigonal and tetragonal potentials are, respectively,

$$V_{tr} = xy + yz + zx \quad (3)$$

and

$$V_{te} = z^2. \quad (4)$$

Equivalent crystal-field operators H_{cf} acting on spin the states $|J,m_J>$ are derived from the potentials. A general expression will have the form

$$H_{cf} = V_{cf}[\cos\beta(\sin\alpha.H_{cu4} + \cos\alpha.H_{cu6}) + \sin\beta.H_{tr/te}], \quad (5)$$

Parameters α and β, with $-90^\circ \le \alpha,\beta \le +90^\circ$, describe the relative strengths of various contributions to the potential and V_{cf} the total strength.

To obtain the Zeeman effect, the energy due to a magnetic field is added to the crystal field Hamiltonian. This energy is given, directly in operator form, by

$$H_{mf} = g_J\mu_B(B_xJ_x + B_yJ_y + B_zJ_z). \quad (6)$$

For the $^4I_{15/2}$ ground state of Er^{3+} the Landé factor has value $g_J = 6/5$, which is experimentally well confirmed to be the applicable value in the cubic Γ_6 and Γ_7 states. By this feature of not adding new freely adjustable parameters, the Zeeman effect is a valuable tool in spectroscopy.

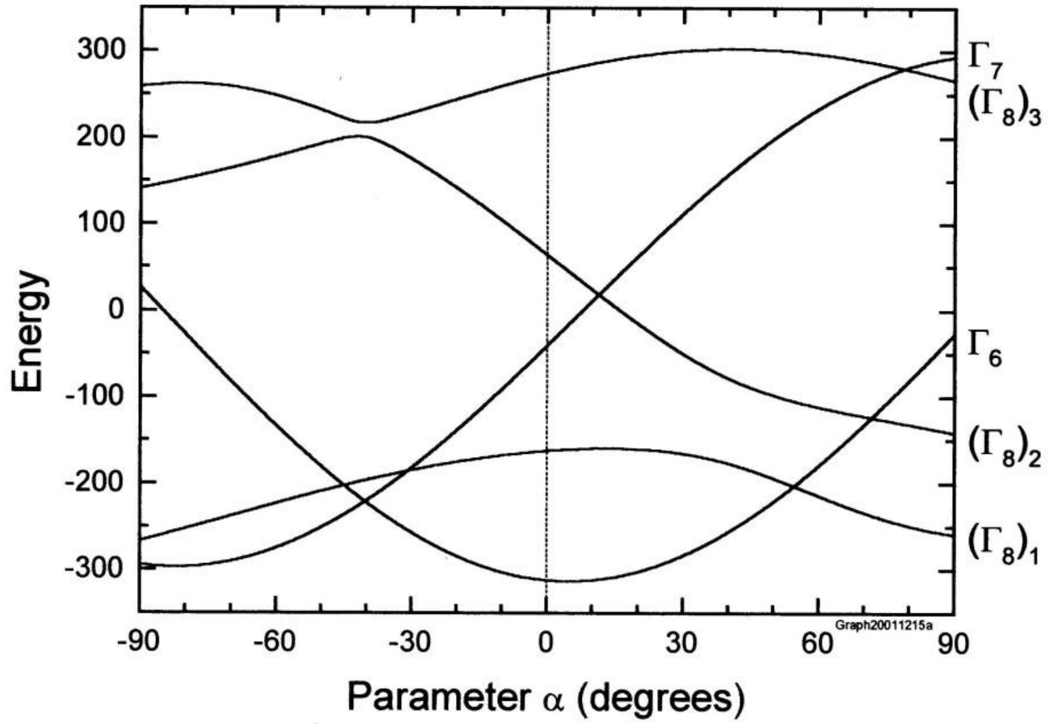

Figure 1. Crystal-field energies in cubic symmetry of the spin-orbit ground state J = 15/2 of the Er^{3+} ion. States are labeled with their symmetry type Γ_6 or Γ_7 for the doublets and $(\Gamma_8)_i$, i = 1, 2 and 3, for the quartets. Parameter α in the range $-90^o < \alpha < +90^o$ controls the mixing of fourth- and sixth-order contributions to the cubic crystal field. Parameter $V_{cf} > 0$.

3. ENERGIES AND g VALUES

In the absence of axial fields, the calculated energy level diagram for cubic symmetry is given in Figure 1. The results are equivalent to the classical data of Lea, Leask and Wolf [4], but are presented in a form matching the parameters V_{cf} and α as introduced in Equation (5). The calculations predict a ground state of Γ_7 symmetry for $-90 \leq \alpha \leq -40.4^o$, for instance, therefore, for the case of pure 4th-order cubic field ($\alpha = -90^o$), with corresponding g value g = 6.0. In the range $-40.4^o \leq \alpha \leq +54.5^o$ there will be a Γ_6 type ground state, with g value g = 6.8. This includes the case of pure 6th-order cubic crystal field ($\alpha = 0^o$). In the remaining range $+54.5^o \leq \alpha \leq +90^o$ the ground state is a Γ_8 quartet, to be described by an effective spin J = 3/2 with a Hamiltonian including cubic terms and with an anisotropic spectrum.

With an axial field present energy diagrams are given in Figures 2(a) to 2(d), for two selected cases of cubic potential, $\alpha = -90^o$ and $\alpha = 0^o$, and including trigonal and tetragonal cases. In the lower axial symmetry all degeneracy is lifted and the energy spectrum consists of eight doublets. Crossings of levels as a function of the relative strength of the axial field, specified by parameter β, frequently occur. Figures 3(a) to 3(d) present the calculated principal g values $g_{//}$ and $g_{\perp}$ for the ground states of the considered cases, as well as tensor trace $g_{//} + 2g_{\perp}$. The sudden changes in ground state properties are related to level crossings at particular values of β. Figures 3 indicate that for small values of β the trace remains constant at the value 18.0 for states around the Γ_7 state and at 20.4 near the Γ_6 state. The numerical

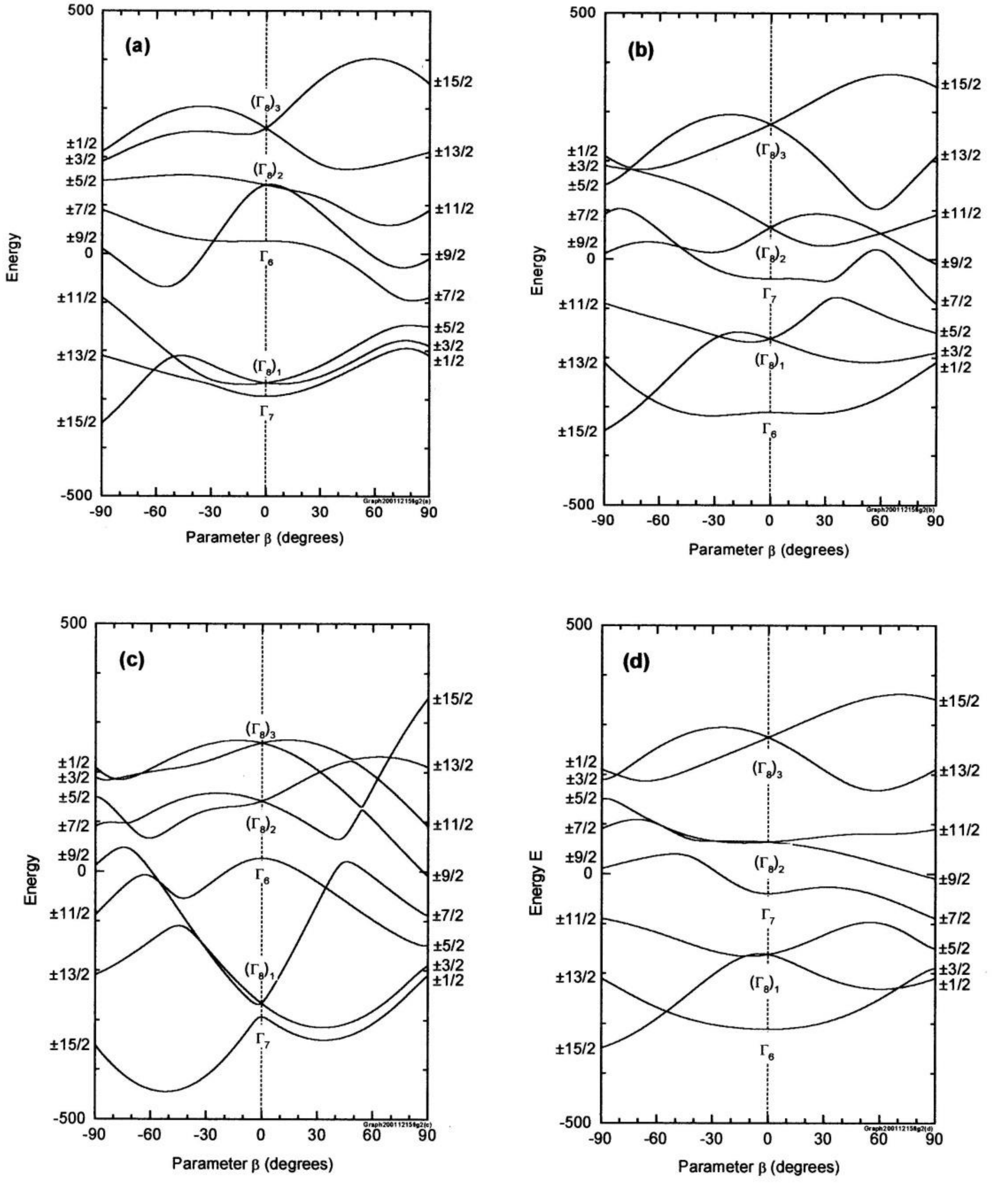

Figure 2. Energies of the eight doublet levels for fourth- or sixth-order cubic crystal field together with a second-order trigonal or tetragonal crystal field calculated from Equation (5) for (a) $\alpha = -90^{o}$, trigonal, (b) $\alpha = 0^{o}$, trigonal, (c) $\alpha = -90^{o}$, tetragonal and (d) $\alpha = 0^{o}$, tetragonal and positive V_{cf}. Parameter β in the range $-90^{o} < \beta < +90^{o}$ controls the mixing of the cubic and the axial crystal fields.

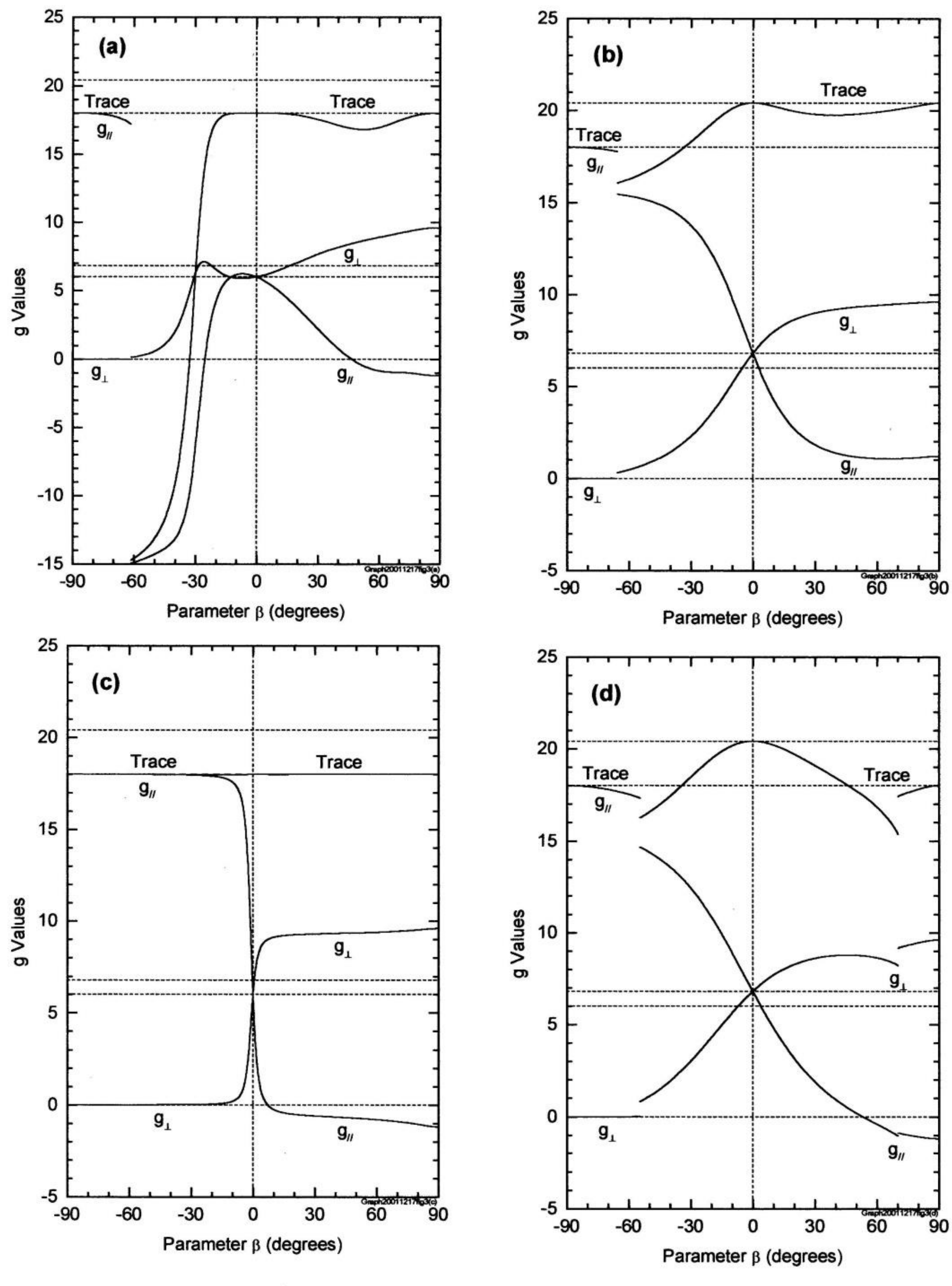

Figure 3. Principal g values $g_{//}$ and $g_{\perp}$ and trace $g_{//} + 2g_{\perp}$ for transitions in the lowest-energy doublets. Illustrated cases, (a) $\alpha = -90^{o}$, trigonal, (b) $\alpha = 0^{o}$, trigonal, (c) $\alpha = -90^{o}$, tetragonal and (d) $\alpha = 0^{o}$, tetragonal, correspond to the energy diagrams shown in Figure 2. Parameter β in the range $-90^{o} < \beta < +90^{o}$ controls the mixing of the cubic and the axial crystal fields.

calculations provide a full confirmation of the early result based on perturbation theory [2], for both trigonal and tetragonal axial fields, both for states derived from Γ_6 or Γ_7 states in the cubic symmetry, and for ground or excited states. Positive values of the parameter β correspond, according to Equation (5), to equal signs of the cubic and axial potentials. In the range $0^\circ \leq \beta \leq +90^\circ$ energy curves of the ground state do not tend to cross the first excited state in the crystal field. If so, then at $\beta = +90^\circ$ the doublet state |15/2,±1/2> is reached. Transitions within this doublet in the axial field have the g values $g_{//} = 1.2$ and $g_\perp = 9.6$. Inspection of Figure 3(b) for $\alpha = 0^\circ$ shows that positive values are to be taken for both $g_{//}$ and $g_\perp$ resulting in the trace 20.4, equal to the trace 3g of the isotropic Γ_6 state. For $\alpha = -90^\circ$ the Figures 3(a) and 3(c) show that upon mixing axial field into the cubic field the principal value $g_{//}$ changes sign in the interval $0 \leq \beta \leq +90^\circ$. At $\beta = +90^\circ$ the better choice for $g_{//}$ is therefore $g_{//} = -1.2$. The trace $g_{//} + 2g_\perp = 18.0$ at this point is equal again to the trace 3g of the cubic symmetry state from which the axial state can be considered to be derived. For negative values of β, on increasing the axial potential, the doublet |15/2,±15/2> will be reached, or, in case a level crossing occurs, the doublet |15/2,±13/2>. The g tensors for transitions within these doublets have components $g_{//} = 18.0$, $g_\perp = 0$ and $g_{//} = 15.6$, $g_\perp = 0$, respectively. It is then immediately clear that for states derived from Γ_6 in cubic symmetry, with trace 20.4, the trace cannot be a constant. In contrast, for the doublet related to the Γ_7 state, with trace 18.0 this might well be the case. Indeed, as Figure 3(c) shows, the case of tetragonal distortion for $\alpha = -90^\circ$, reveals a remarkably constant value of its trace also for negative values of β. For this particular case, over the whole range of β, the trace can decrease a bit below its limiting value of 18.0, but never falls below 17.95. The more substantial reductions of trace occur in the region of β adjoining $\beta = -90^\circ$. It will be noted, however, that for the corresponding tensors $g_\perp = 0$. This implies that the states are EPR silent; these resonances with the reduced trace are not observable. It adds support to the empirical fact that observed resonances for the erbium ion its threefold ionized state are characterized by traces in the range from 18.0 to 20.4.

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