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Correlation between superhyperfine constants and $4f$ crystal-field parameters of Tm^{2+} in CaF_2, SrF_2, and BaF_2

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The $4f$ crystal-field parameters of Tm^{2+} in CaF_2, SrF_2, and BaF_2, after subtracting a calculated point-charge contribution, are shown to be linearly related to the scalar hyperfine constant of the first-shell fluorine ions. This provides direct experimental proof that admixture of the ligand wave functions with the metal-ion wave function plays a dominant role in determining the splitting of the $4f$ electronic levels in these highly ionic hosts. The electron-nuclear-double-resonance values for Tm^{2+} in BaF_2 are reported here for the first time.

I. INTRODUCTION

The crystal-field parameters of rare-earth ions have generally been interpreted in terms of the electrostatic point-charge model, but recently it has been shown that overlap and covalency effects have a more dominant role.[1-8] Divalent thulium in the alkaline-earth fluorides plays an important part in these discussions because it is the simplest rare-earth-ion–host system known for which there exists a large number of excellent data. In this paper we show that the $4f$-electron crystal-field parameters of Tm^{2+} in CaF_2, SrF_2, and BaF_2 obtained from optical measurements are strongly correlated with the scalar hyperfine constant of the first-shell fluorine ions as measured using electron-nuclear double resonance (ENDOR). This provides a direct experimental proof that the admixture of the ligand wave functions with the metal-ion wave function plays a dominant role in determining the splitting of the $4f$ electronic levels in these highly ionic hosts.

Jorgenson[1] made a very early attempt to fit the CaF_2:Tm^{2+} crystal-field parameters as measured by Kiss[2] using a one-parameter weak antibonding model which gave rather inconclusive results in this case, but quite good qualitative results for a variety of other systems. Axe and Burns[3] have carried out a more detailed calculation and found that rough estimates of the admixture parameters gave much better agreement with the data than the best point-ion electrostatic calculations given by Bleaney.[4] Watson and Freeman[5] suggested that it was the admixture due to overlap of the $4f$-electron wave function to the F^--ion wave function which makes the major contribution in this case, and this has been confirmed by detailed calculations by Anisomov and Dagys.[6]

Baker[7] has handled the Axe and Burns (AB) calculation in a phenomenological fashion to fit the first-shell fluorine hyperfine constants in CaF_2:Tm^{2+} and to fit all the data on the isoelectronic system CaF_2:Yb^{3+}. He also found a numerical error which AB made and showed that their model explains a substantial fraction of the orbital reduction factor obtained from measuring the g value of the ground state in CaF_2, a point which AB felt was a major defect of their calculation. Axe and Burns also predicted that one orbital reduction factor would apply to both the ground state $^2F_{7/2}(\Gamma_7)$ and excited state $^2F_{5/2}(\Gamma_7)$, and this has been confirmed by Hayes and Smith[8] in both CaF_2:Tm^{2+} and SrF_2:Tm^{2+}. Basically this paper builds on and extends Baker's approach to the series CaF_2:Tm^{2+}, SrF_2:Tm^{2+}, and BaF_2:Tm^{2+}.

A complete set of experimental parameters is given in Table I. Reported here for the first time are the first-shell fluorine scalar and tensor superhyperfine constants A_s and A_p in BaF_2:Tm^{2+}, which we measured using standard ENDOR techniques. These parameters complete the table and make possible the analysis given in this paper.

II. THEORETICAL BACKGROUND

The ground configuration of divalent thulium is $4f^{13}$, a single hole in the $4f$ shell, which is split by about 9000 cm^{-1} into two spin-orbit J multiplets $^2F_{5/2}$ and $^2F_{7/2}$, the latter lying lowest in energy. In the hosts CaF_2, SrF_2, and BaF_2 the Tm^{2+} ion sits on the alkaline-earth metal-ion site which has cubic symmetry. No charge compensation is required although the eight nearest-neighbor fluorine ions, located at the points of a cube centered on the metal ion, do expand or contract slightly from their normal host lattice position to accommodate the ion. The ground $^2F_{7/2}$ state is

TABLE I. Experimental crystal-field parameters (b_4 and b_6), first-shell fluorine superhyperfine constants (A_s and A_p), and orbital reduction factor $(1-k)$ for Tm^{2+} in CaF_2, SrF_2, and BaF_2.

Host	b_4 (cm^{-1})	b_6 (cm^{-1})	A_s (MHz)	A_p (MHz)	$1-k$
CaF_2	45.8 [a]	5.16 [a]	2.584 (10) [b]	12.283 (10) [b]	0.0115 (3) [c]
SrF_2	40.0 [d]	4.23 [d]	2.023 (20) [c]	11.112 (20) [c]	0.0114 (3) [c]
BaF_2	33.6 [d]	3.50 [d]	1.56 (2) [e]	10.02 (2) [e]	0.0124 (3) [c]

[a] Data from Kiss (Ref. 2) modified by Bleaney (Ref. 4).

[b] R. G. Bessent and W. Hayes, Proc. R. Soc. A 235, 430 (1965).

[c] Reference 8.

[d] H. A. Weakliem (private communication).

[e] This work.

split into three crystal-field levels of Γ_6, Γ_8, and Γ_7 symmetry, the Γ_7 forming the ground state.

In the absence of spin-orbit coupling the $4f$ hole splits in a cubic field into three levels of symmetry a_{2u}, t_{1u}, and t_{2g}. This leads to two crystal-field energy parameters which AB have defined

$$\Theta = E(t_{1u}) - E(t_{2g}), \quad \Delta = E(t_{2g}) - E(a_{2u}). \tag{1}$$

These parameters have a similar meaning to that which $10Dq$ has in the more familiar d-orbital case. These parameters are directly related to the standard crystal-field parameters through the expressions

$$b_4 = (2\Delta + 3\Theta)/44, \quad b_6 = (4\Delta - 5\Theta)/616. \tag{2}$$

The wave function for the antibonding hole, which determines the optical and magnetic properties of the $Tm^{2+}F_8^-$ complex, has the form

$$\psi(\Gamma) = \varphi_m(\Gamma) - \sum_\nu \lambda_{\Gamma\nu}\chi(\Gamma, \nu). \tag{3}$$

The parameter Γ designates the symmetry of the metal-ion wave function $\varphi(\Gamma)$, i.e., $\Gamma = a_{2u}$, t_{1u}, and t_{2g}. The $\chi(\Gamma, \nu)$ are linear combinations of the ligand orbitals centered on the eight nearest fluorine ions, which transform with symmetry Γ and are composed of orbitals of type ν, where $\nu = 2s$, $2p\sigma$, and $2p\pi$. The admixture parameters $\lambda_{\Gamma\nu}$ are small; so the wave function need not be renormalized.

The admixture parameters are given by expressions of the type

$$\lambda_{\Gamma\nu} = \frac{\langle\varphi|H|\chi\rangle - S\langle\varphi|H|\varphi\rangle}{\langle\chi|H|\chi\rangle - \langle\varphi|H|\varphi\rangle}, \tag{4}$$

where the subscripts have been dropped to emphasize the essential form. The factor S represents the overlap parameters

$$S(\Gamma\nu) = \langle\varphi(\Gamma)|\chi(\Gamma, \nu)\rangle, \tag{5}$$

and H represents the one-electron Hamiltonian of the complex. Axe and Burns in their calculation forced the parameters $\lambda_{\Gamma\nu}$ to be proportional to the corresponding overlap factors $S(\Gamma, \nu)$, which the later calculations showed was reasonable. Although the results of this paper do not explicitly depend on this fact, we shall fit the dependence of the observed parameters on the radial position of the nearest fluorine ions, R, with the form R^{-n} and compare the values of n obtained with those given by AB.

Using perturbation theory the additional energy which comes from the admixture of the ligands can be written

$$E(\Gamma) = \sum_\nu \lambda^2_{\Gamma\nu}[\langle\varphi(\Gamma)|H|\varphi(\Gamma)\rangle - \langle\chi(\Gamma, \nu)|H|\chi(\Gamma, \nu)\rangle]. \tag{6}$$

The energy terms inside the brackets are to a very good approximation independent of Γ. AB estimate them to be approximately

$$\langle\varphi|H|\varphi\rangle - \langle 2p|H|2p\rangle \cong 10^5\ cm^{-1}$$

and (7)

$$\langle\varphi|H|\varphi\rangle - \langle 2s|H|2s\rangle \cong 3\times 10^5\ cm^{-1}.$$

Using these values we have from Baker the explicit expressions

$$\Delta \cong [3\lambda^2_{a_{2u}s} + (\lambda^2_{t_{2u}p\sigma} - \lambda^2_{t_{2p}p\pi})]\times 10^5\,cm^{-1}$$

and (8)

$$\Theta \cong (3\lambda^2_{t_{1u}s} + \lambda^2_{t_{1u}p\pi} + \lambda^2_{t_{1u}p\sigma} - \lambda^2_{t_{2u}p\pi})\times 10^5\,cm^{-1}.$$

Following Baker, we now note that all the other experimentally measured parameters depend only on the three admixture parameters which appear in the expression for Δ and hence shall relabel them λ_s, λ_σ, and λ_π for convenience [i.e., $\Delta = (3\lambda_s^2 + \lambda_\sigma^2 - \lambda_\pi^2)\times 10^5\ cm^{-1}$].

AB defined two orbital reduction factors

$$k = \langle a_{2u}|L_z|t_{2u}\rangle / \langle fa_{2u}|L_z|ft_{2u}\rangle$$

and

$$k' = \langle t_{2u} | L_z | t_{2u} \rangle / \langle f t_{2u} | L_z | f t_{2u} \rangle \,, \qquad (9)$$

which give unity in the limit of no ligand admixture. They found that the second factor k' is unity to first order and the other can be calculated from

$$1 - k = \lambda_s^2 + \lambda_\pi^2 + \lambda_\sigma^2 + \tfrac{2}{3}\lambda_\sigma\lambda_\pi \,. \qquad (10)$$

Baker[7] has given similar explicit expressions for the contributions to the tensor A_p and scalar A_s first-shell fluorine superhyperfine constants of

$$A_p = \tfrac{1}{140}P\left[(9 + 2.5\kappa)\lambda_\pi^2 + 4\lambda_\sigma^2 + 25\sqrt{\tfrac{2}{3}}\,\lambda_\sigma\lambda_\pi\right]$$

and (11)

$$A_s = -\tfrac{1}{140}P\left[-2.5\kappa\lambda_\pi^2 + 10\kappa\lambda_\sigma^2 + 20\lambda_\sigma\lambda_\pi\right] + \tfrac{1}{14}\lambda_s^2 A_{2s} \,,$$

where for the fluorine atom $\kappa \cong -0.1$, $P = 6.3$ GHz, and $A_{2s} = 46$ GHz. Baker also estimated, using the fluorine hyperfine data for CaF_2:Eu^{2+}, that the indirect coupling through the $5p$ shell of the Tm^{2+} ion would make an additional contribution to A_s and A_p of the order of -0.9 and -0.5 MHz, respectively.

Equations (8), (10), and (11) all contain quadratic functions of the admixture parameters $\lambda_{\Gamma\nu}$. The calculations of AB show that no single admixture parameter dominates the others. In analyzing the CaF_2:Yb^{3+} data Baker allowed the coefficients arising from the s and p orbitals of the F^- ion to vary independently, but forced those from the p orbital to have the same ratio found in CaF_2:Tm^{2+}. In analyzing the changes in these parameters over the limited range of the Tm^{2+}-F^- spacing in the host crystals CaF_2, SrF_2, and BaF_2 we shall assume that *all* the coefficients change proportionally to one another. This is the simplest procedure to use, and some justification for it is given later in the paper.

The measured scalar superhyperfine constant A_s is the experimental parameter most directly related to the admixture parameters. Therefore the contribution due to the admixture of the ligand wave functions to the tensor superhyperfine constant and crystal-field parameters will be assumed to be proportional to the A_s. There is an uncertainty in this procedure due to the contribution from the indirect coupling through the $5p$ shell ~ -0.9 MHz, and so comparisons will be made with and without this factor.

The tensor superhyperfine constant is then given by

$$A_p = \alpha_p A_s + g\mu_B g_F \mu_N / R^3 \,, \qquad (12)$$

where α_p is the constant of proportionality discussed above. The additional term is the contribution due to the magnetic dipole-dipole interaction between the Tm^{2+} spin and the first-shell fluorines at a distance R ($g\mu_B g_F g_N = 129$ MHz Å^3). There is the addition factor of -0.5 MHz which Baker estimates for the indirect $5p$ contribution. The crystal-field parameters[9] become approximately

$$\begin{aligned} b_4 &= \alpha_4 A_s + 136\langle r^4\rangle\,(2.36/R)^5 \,, \\ b_6 &= \alpha_6 A_s + 6.42\langle r^6\rangle\,(2.36/R)^7 \,, \end{aligned} \qquad (13)$$

where α_4 and α_6 are the proportionality constants. The second terms in these expressions are the point-charge contributions Bleaney[4] calculated for an undistorted lattice spacing of 2.36 Å. Written this way it becomes apparent that the A_s, A_p, b_4, and b_6 form a remarkably similar set of parameters.

III. ANALYSIS OF DATA

One of the most vexing questions in dealing with impurity ions is the location of the neighboring host lattice ions. The ENDOR measurements clearly show for all three hosts that the second and third shells of fluorine ions occupy normal lattice positions. Our measurements show no static nor dynamic distortion of the first-shell fluorine from cubic symmetry in BaF_2. This is also true in CaF_2, and we believe it to be true in SrF_2.[10] The radial position of the ions in this shell can be inferred from the measurements of A_s and A_p in the following procedure, which is similar to the one Baberschke[11] used for Eu^{2+} in the same set of crystals. The quantity $A_p - A_d$, where A_d is the calculated dipolar contribution, is plotted against A_s for several possibilities for the Tm^{2+}-F^- spacing R in Fig. 1. In curve (a) R is taken as the normal host lattice spacing. In curve (b) the spacing is fixed at a distance equal to the Tm^{2+} and F^- ionic radii ($R = 1.08 + 1.36 = 2.44$ Å).[12] The actual case presumably lies between these two extremes. Curve (c) is a straight line drawn through the origin and the intersection point of curves (a) and (b) and therefore satisfies the above limits as well as Eq. (12). From the values of A_d obtained from line (c) it is possible to calculate the ion spacings in all three hosts. The spacings obtained in this way are given in Table II along with the normal host lattice positions. When line (c) is extended through the origin it passes very close to the point ($A_s = -0.9$, $A_p = -0.5$); so, if Baker's estimates of the $5p$ contributions are correct and the values are assumed to be roughly the same in all three hosts, the same relaxed positions are found. This places the nearest-neighbor fluorines very close to the Tm^{2+}-F^- spacing in all three hosts, in agreement with what Baberschke[11] found for Eu^{2+} in these crystals. There is a slight dilation from the normal host lattice position in CaF_2, a slight contrac-

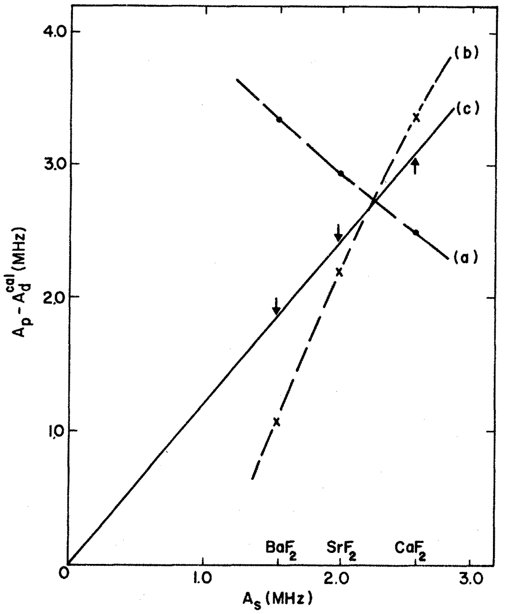

FIG. 1. Observed Tm^{2+}–nearest-neighbor-fluorine tensor hyperfine constant minus the direct magnetic dipole interaction calculated for several possible ion spacings (see text) plotted against the corresponding scalar hyperfine constant.

tion in SrF_2, and a rather large contraction in BaF_2.

The point-charge contributions to the crystal-field parameters have been calculated using the nearest-neighboring fluorine positions given in Table II and the rest of the shells in their normal lattice sites. This is somewhat more complex than implied by Eq. (13). These are given in Table III using calculated values for the electron radial moments $\langle r^4 \rangle$ and $\langle r^6 \rangle$.[13] The values of b_4 and b_6 minus their point-charge contribution are plotted in Fig. 2 as a function of A_s. For comparison the uncorrected value of b_4 is also plotted in the same figure. The linearity of the points strongly supports the assumptions put forth in this paper.

Extrapolating the solid lines to the origin is questionable, but of interest. The intercepts on the ordinate axis occur at a value of b_4 which is roughly half the point-charge contribution, while that for b_6 is of the same magnitude as the point-charge contribution. These could be taken as the uncertainties in the separation of the measured crystal-field parameters into their two components. Alternatively, the intercept on the abscissa for both the b_4 and b_6 lines occurs at the same point where $A_s = -0.5$ MHz. This is remarkably close to the value of -0.9 MHz which Baker estimated for the indirect $5p$ contribution. When the energy parameters Δ and Θ are calculated from the crystal-field parameters minus their point-charge contribution it is found that Θ is very much smaller than Δ.[12] (See Table III.) Thus the simplest interpretation of the linearity of both solid lines in Fig. 2 is that Δ is directly proportional to A_s, and this fact also accounts for both lines having the same intercept on the abscissa. That Θ does not scale linearly with A_s is explained by noting its small value results from the fact that two large terms in Eq. (6) are opposite in sign and of almost the same magnitude. The calculations by AB and Baker show this explicitly. This makes Θ very sensitive to the different admixture coefficients's having slightly different de-

TABLE II. First-shell cation-anion spacings (Å).

Host	Undistorted lattice position[a]	Distorted position	Difference
CaF_2	2.36	2.42	+0.06
SrF_2	2.50	2.46	−0.04
BaF_2	2.68	2.51	−0.17

[a] R. G. Bessent and W. Hayes, Proc. R. Soc. A 235, 430 (1965).

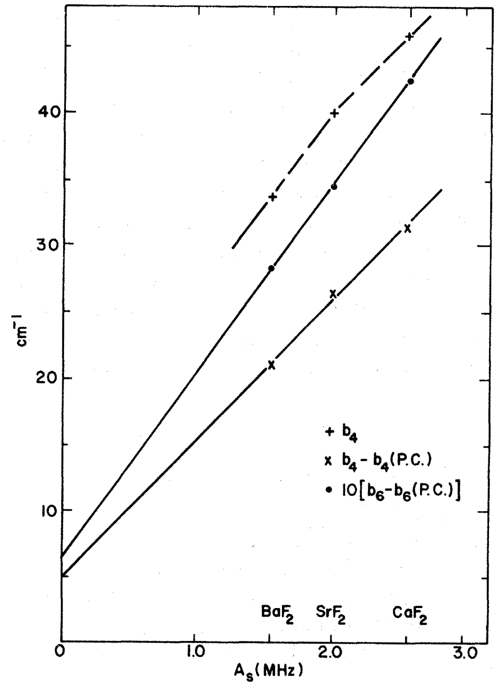

FIG. 2. $4f$ crystal-field parameter b_4 and b_6 with the point-charge (PC) contribution subtracted, plotted against the scalar hyperfine constant. For comparison b_4 is also plotted without the point-charge correction.

TABLE III. Calculated point-charge (PC) contributions to the crystal-field parameters. Data in cm^{-1}.

	$b_4(\mathrm{PC})$ [a]	$b_4-b_4(\mathrm{PC})$	$b_6(\mathrm{PC})$ [a]	$b_6-b_6(\mathrm{PC})$	Δ	Θ
CaF_2	14.4	31.4	0.846	4.31	676	10
SrF_2	13.5	26.5	0.785	3.44	554	19
BaF_2	12.5	21.1	0.669	2.83	449	10

[a] See Ref. 13.

pendences on the nearest-neighbor position R.

There is a serious question ignored so far as to why the orbital reduction factor increases slightly upon going from CaF_2 to BaF_2, where in the model presented here it should decrease linearly along with A_s. This increase is even difficult to explain if the factors $\lambda_{\Gamma\nu}$ are allowed to vary independently. The only explanation we have is that the contribution to this factor by dynamic coupling to the lattice, as calculated by Inoue,[14] increases upon going from CaF_2 to BaF_2. This is consistent with the result obtained from spin-lattice relaxation measurements that the dynamic coupling constants do increase in this direction.[15] This is the first evidence for the existence of this effect, and it would seem prudent to search for the predicted temperature dependence in BaF_2:Tm^{2+}

IV. CONCLUSIONS

It has been noted in this paper that the superhyperfine constants with the first-shell fluorines A_s and A_p along with the two crystal-field parameters b_4 and b_6 form a remarkably similar set of parameters. They all contain a contribution due to the interaction with the nearest-neighbor ligands which is a quadratic function of the admixture parameters and a second contribution which scales as an odd inverse power (i.e., 3, 5, or 7) of the ligand spacing R and is in principle fairly straightforward to calculate. A consistent picture of the data is obtained for a particular set of nearest-neighbor positions with the contributions from the interaction with the ligands being proportional to one another.

Using the relaxed lattice positions given in Table II we find ($A_s+0.5$ MHz) scales as R^{-n} with $n=11\pm1$, b_4 with $n=10.5\pm0.5$, b_6 with $n=11.5\pm1.5$, and Δ with $n=11.0\pm0.7$. These values for n are all reasonably close to the values AB gave for the overlap parameters with the $2s$ and $2p\pi$ orbitals of 12.1 and 10.4, respectively, but not with that for the $2p\sigma$ orbital of 6.5. These values of n are also consistent with the value of ~ 12 Newman[16] has obtained for a number of rare-earth oxides. Because we find the nearest fluorines to remain closer to the Tm^{2+}-F^- ionic spacing than their normal host positions in these crystals, it would seem that the local compressibility is less than the host lattice. This would make the value of n AB found in their stress measurements on CaF_2:Tm^{2+} larger and hence in better agreement with their calculation.

In conclusion, we do not claim our analysis of the data is precise, but that its simplicity and the results, especially those illustrated in Fig. 2, provide one of the clearest bits of evidence that the admixture of ligand wave functions with the $4f$ orbitals of rare-earth ions makes a major contribution to the crystal-field splittings. Allowing the admixture parameters to vary independently would certainly provide a better fit to the data and might result in slightly different positions of the neighboring fluorines, but would not change the general picture given here in any significant way.

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[*] This work was performed while on leave at the Clarendon Laboratory.

[1] C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, J. Chem. Phys. 39, 1422 (1963).

[2] Z. J. Kiss, Phys. Rev. 127, 718 (1962).

[3] J. D. Axe and G. Burns, Phys. Rev. 152, 331 (1966); *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience, New York, 1966).

[4] B. Bleaney, Proc. R. Soc. A 277, 289 (1964).

[5] R. E. Watson and A. J. Freeman, Phys. Rev. 156, 251 (1967).

[6] F. Anisimov, R. Rakauskas, and R. Dagys, Phys. Status Solidi 35, 75 (1969); F. Anisimov and R. Dagys, *ibid.* B 44, 821 (1971); F. Anisimov, A. Vala, and R. Dagys, *ibid.* A 6, 15 (1971).

[7] J. M. Baker, J. Phys. C 1, 1670 (1968). In a private communication the author has indicated that the term $20\lambda_\sigma\lambda_\pi$ in Eq. (11) was incorrectly published as $14\sqrt{\frac{2}{3}}\lambda_\sigma\lambda_\pi$ in Ref. 7.

[9] In most publications the crystal-field parameters for Tm^{2+} have been given in the form used in this paper. These are related to the more standard parameters obtained in the point-charge model as follows: $b_4=0.2424A_4\langle r^4\rangle$ and $b_6=0.1865A_6\langle r^6\rangle$.

[10] The nearest-neighbor fluorine ENDOR lines for Tm^{2+}

show structure in SrF_2 not found in CaF_2, and it was tentatively suggested by Hayes and Smith (Ref. 8) that off-center motion of the impurity ion might be responsible. We find structure of a similar sort in BaF_2, but it is dependent on experimental conditions in such a way as to indicate that it is not due to off-center motion. We do not, however, have a satisfactory explanation for the observations.

[11] K. Baberschke, Phys. Lett. A 34, 41 (1971).

[12] Axe and Burns (Ref. 3) point out that the very small value of Θ makes the ${}^2F_{7/2}(\Gamma_6)$ and ${}^2F_{7/2}(\Gamma_8)$ levels almost degenerate. Since the ratio of the crystal-field parameters of the other rare-earth ions in these hosts are similar to those of Tm^{2+}, it is tempting to speculate that the observed grouping of the crystal-field levels in the maximum J manifold into two sets in these systems reflects the fact that $\Theta \approx 0$ as a hidden symmetry. This explanation certainly works far better for Tm^{2+} than the semiclassical argument put forth by G. T. Tramell [Phys. Rev. 131, 932 (1963)].

[13] R. E. Watson and A. J. Freeman [Phys. Rev. 127, 2058 (1962)] give $\langle r^4 \rangle = 0.1212$ Å^4 and $\langle r \rangle = 0.1651$ Å^6. Using the more recent values given by F. G. Wakim, M. Synek, R. Grossgut, and A. DaMommio [Phys. Rev. A 5, 1121 (1971)] of $\langle r^4 \rangle = 0.1053$ Å^4 and $\langle r^6 \rangle = 0.1287$ Å^6 does not change the results of this paper in any significant way.

[14] M. Inoue, Phys. Rev. Lett. 11, 196 (1963).

[15] E. S. Sabisky and C. H. Anderson, Phys. Rev. B 1, 2028 (1970).

[16] D. J. Newman, Adv. Phys. 20, 197 (1971) and G. E. Stedman and P. J. Newman, J. Phys. Chem. Solids 32, 2001 (1971).