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EPR and ENDOR of BaF_2:Tm^{2+} under uniaxial stress

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Abstract. Spin–lattice Hamiltonian parameters have been derived from measurements of the effects of uniaxial stress upon the EPR of BaF_2:Tm^{2+}. Using these parameters, one may calculate spin–lattice relaxation rates for the direct process which are in excellent agreement with the measurements of Sabisky and Anderson.

ENDOR has been used to measure the change of the ligand hyperfine interaction $\partial(A_p - A_s)/\partial F$ for stress applied parallel to the bond axis, giving 12·5(2) kHz kg^{-1} mm^2. This value is nearly twice as large as that predicted by any model which has been previously discussed in the literature of the hyperfine interaction and local distortion of the lattice.

1. Introduction

Baker and van Ormondt (1974, hereafter called I) have measured the effect of uniaxial stress upon the EPR of Tm^{2+} in CaF_2 and SrF_2. They have found excellent correlation with the spin–lattice relaxation rates measured by Sabisky and Anderson (1970). In the first part of our work, described in § 2, we have performed the same sort of measurements on Tm^{2+} in BaF_2. The theoretical basis for this work has been discussed in I, so we shall not repeat that discussion.

The theoretical interpretation of these measurements in terms of the orbit–lattice interaction requires a knowledge of the displacements of ligand ions produced by applied stress. These may not be simply deduced from bulk elastic constants, because of the various effects discussed by Malkin and his co-workers (Malkin 1969, Ivanenko and Malkin 1970, Malkin *et al* 1971). In order to try to measure these displacements experimentally we have measured the stress dependence of some ligand ENDOR frequencies (§ 3). The interpretation of these measurements, discussed in § 4, is not straightforward because of the relatively large covalent contribution to the ligand hyperfine interaction.

Crystals of BaF_2 containing 0·02% and 0·05% Tm^{2+} were supplied by Dr C H Anderson of RCA Laboratories. The Tm^{3+} in the crystals had been reduced by baking in alkaline earth metal vapour.

The apparatus used for our EPR and ENDOR experiments was similar to that described by Fainstein and Oseroff (1971) operating at ~35 GHz, with 115 kHz modulation of the magnetic field. Uniaxial stress was applied vertically to a specimen of uniform cross

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section ~1 mm × 1 mm and about 3 mm length. The end faces of the specimen were carefully polished so that the applied stress was uniform throughout the sample. The magnetic field was rotated in a horizontal plane, and was therefore always perpendicular to the applied stress.

2. Electron paramagnetic resonance

The parameters of the spin–lattice Hamiltonian relating to Γ_3 strains may be measured by finding Δg_{100}, the change in the value of g induced by applying a stress $\boldsymbol{F}$ in the (100) direction, hereafter written $F(100)$, and those for Γ_5 strains by measuring Δg_{111} (Sroubek *et al* 1968, Baker and van Ormondt 1974). Calvo *et al* (1974) have shown that one may measure both of these parameters in one experiment by applying $F(110)$ and measuring the anisotropy of Δg as $\boldsymbol{H}$ is rotated in the $\{110\}$ plane. The values of Δg for $H(001)$ and $H(111)$ are the same as Δg_{100} and Δg_{111}, and the variation of $\Delta g/g$ with angle θ measured from (001) is

$$\Delta g/g = b + a \sin^2 \theta, \tag{1}$$

so that $\Delta g_{100}/g = b$ and $\Delta g_{111}/g = b + \frac{2}{3}a$.

We have used the technique of Calvo *et al*, making measurements on a pillar cleaved along $\{111\}$ faces with ends polished perpendicular to these faces, so that $\boldsymbol{F}$ is applied along (110). This has the advantage that only one specimen is required, but the disadvantage that one can have problems with crystal alignment. Misalignment can occur in two ways. Firstly, the stress may not be applied in the desired direction, either because of misalignment of the specimen cut from the solid material, or because of movement of the specimen when the stress is applied. Secondly, the stress may not be accurately applied perpendicular to the plane of rotation of the magnetic field.

Two samples were used in I, one cut for $F(100)$ and one for $F(111)$, which, although it is somewhat more difficult to prepare the specimens, has advantages in respect of both of these alignment difficulties. Firstly, for $F(100)$ and $F(111)$, misorientation by θ of the direction of $\boldsymbol{F}$ only produces changes in the desired strain by a factor of $\cos\theta$ and produces undesired strain of order $\sin\theta$; secondly, the accuracy of alignment of both $\boldsymbol{F}$ and $\boldsymbol{H}$ may be checked by the lack of angular variation as $\boldsymbol{H}$ is rotated in the plane perpendicular to $\boldsymbol{F}$.

For $F(110)$ both Γ_3 and Γ_5 strains occur in comparable magnitude, and the sensitivity of these to misorientation of $\boldsymbol{F}$ is greater; one also has no check on either orientational problem as one will always find an angular variation such as equation (1) for the rotation of $\boldsymbol{H}$ in any plane for any direction of $\boldsymbol{F}$.

Hence, in using the technique of Calvo *et al* it is necessary to take great care in preparing and mounting the specimens. As an indication that our crystals are well oriented, we have compared new measurements on two specimens of SrF_2:Tm^{2+} with the measurements of Baker and van Ormondt; see table 1.

Figure 1 shows the anisotropy of $\Delta g/g$ for Tm^{2+} in BaF_2, SrF_2 and CaF_2, and table 1 lists our new measurements of the parameters for BaF_2. These are in excellent agreement with the predictions in I (their table 1), which were calculated from the spin-lattice relaxation measurements of Sabisky and Anderson (1970), if allowance is made for an error of a factor of 2 in $\Delta g_{100}/g$. For direct comparison with the results of Sabisky and Anderson, we have calculated the B_n parameters introduced in I (see their table 3) obtaining $B_3 = 6{\cdot}5(2) \times 10^3\ \mathrm{s}^{-1}$ and $B_5 = 96(8) \times 10^3\ \mathrm{s}^{-1}$; a recalculation of B_4 gives

Table 1. Experimental values of $\Delta g/g$ in units of $10^{-4}\,\mathrm{kg\,mm^{-2}}$ for different crystals of SrF_2 and BaF_2 containing Tm^{2+}.

Crystal	⟨100⟩	⟨111⟩
SrF_2 (a)	−1·2(1)	+1·2(2)
SrF_2	−1·20(11)	+1·16(10)
SrF_2	−1·21	+1·05
BaF_2	−2·0(3)	+4·5(2)

(a) From Baker and van Ormondt (1974).

$B_4 = 12{\cdot}5 \times 10^3\,\mathrm{s^{-1}}$. The parameters which come directly from the relaxation data of Sabisky and Anderson are $(B_4 + 3B_3)$ and $(B_4 + B_5)$, which are listed in table 2. We have also listed in table 2 our new values for SrF_2 and those for CaF_2 obtained in I. There is clearly excellent accord for all of these materials. As noted in I, the data of Abragam *et al* (1972) is not in such good accord with the other data.

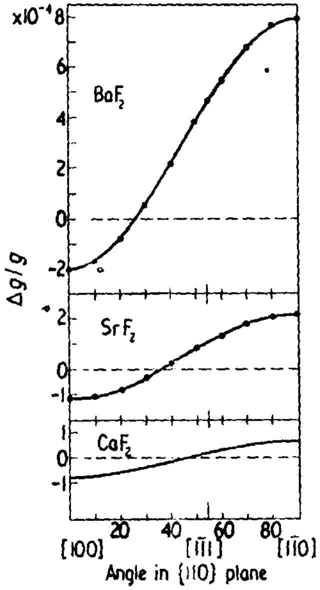

Figure 1. Angular variation of $\Delta g/g$ in the {110} plane for uniaxial stress applied along (110) and $F = 1\,\mathrm{kg\,mm^{-2}}$. The curve for CaF_2 is calculated from the data of I for comparison with our measurements.

Table 2. Comparison of the parameters $(B_4 + 3B_3)$ and $(B_4 + B_5)$ obtained from spin–lattice relaxation (Sabisky and Anderson 1970) and stress measurements (Baker and van Ormondt 1974 and this work). Parameters were calculated for 2·68T in units of $10^3\,\mathrm{s^{-1}}$.

Crystal	$(B_4 + 3B_3)$		$(B_4 + B_5)$	
	Relaxation	Stress	Relaxation	Stress
CaF_2	2·99(60)	3·46(30)	1·7(1)	1·95(3)
SrF_2	8·9(1·2)	8·6(9)	8·9(6)	7·9(7)
BaF_2	30(2)	32·0(6)	104(4)	109(8)

3. ENDOR

One of the problems encountered by Baker and van Ormondt in I when they attempted to interpret their measurements of spin–lattice Hamiltonian parameters was that of knowing the movement of the ligand ions produced by an external uniaxial stress. Estimation of the expected orbit–lattice parameters is made difficult by uncertainties in the local compressibility around an impurity ion, and unknown displacements of the F–Ca–F basis of the BCC crystal structure.

In order to discover something about the movement of the ligand ions, we have attempted to measure the change in ligand ENDOR frequencies under uniaxial stress. Measurements of this sort have previously been made for Eu^{2+} in alkaline earth fluorides by Zimmermann and Valentin (1975). Our measurements are essentially the same as theirs.

In the absence of stress, the ligand hyperfine structure has the form $\mathscr{H}_{hfs} = A_p(3S_zI_z - \boldsymbol{S}.\boldsymbol{I}) + A_s\boldsymbol{S}.\boldsymbol{I}$, where [illegible] lies along the ligand bond. For $\boldsymbol{H}$ applied at angle θ to this bond, the two ENDOR frequencies are given by

$$h\nu_{\pm} = [\![\{g_F\beta_nH \mp M[A_s + A_p(3\cos^2\theta - 1)]\}^2 + \tfrac{9}{4}A_p^2 \sin^2\theta \cos^2\theta]\!]^{1/2}, \tag{2}$$

where $M = \pm\frac{1}{2}$ corresponds to the two quantum states of the electronic fictitious spin.

Stress was applied along the [111] direction, and ENDOR was observed for $\boldsymbol{H}$ parallel to $[11\bar{2}]$ in which direction the ENDOR for ligands along [111] ($\cos\theta = 0$) is not degenerate with that for any other ligand. Hence, the shift of the ENDOR is more easily observed. The ENDOR for ligands along $[11\bar{1}]$ ($\cos\theta = \sqrt{8}/3$) is also non-degenerate. That for $[\bar{1}11]$ is degenerate with that for $[1\bar{1}1]$ ($\cos\theta = \sqrt{2}/3$) but, as these ligands are related by reflection in the plane containing $\boldsymbol{F}$ and $\boldsymbol{H}$, one expects them to remain degenerate unless there is a misorientation of $\boldsymbol{F}$ or $\boldsymbol{H}$. Like Zimmermann and Valentin, we found a measurable shift of the ENDOR frequency for ligands along [111] but not for any other ligand. For this direction equation (2) takes the simple form:

$$h\nu_{\pm} = g_F\beta_nH \mp M(A_s - A_p). \tag{3}$$

There is a difficulty in our measurements which is not present in those of Zimmermann and Valentin. They used an EPR line which was unaffected by the stress. Our EPR line is shifted by the stress (§ 2), so the ENDOR frequency is changed both because of a change of ligand hyperfine structure parameters (A_s, A_p and [illegible] in equation 2) and because of a change in the electronic g-factor, and hence of H in equation (2). As the shift of the EPR line produced by our stress is comparable with the linewidth, one may still observe ENDOR when stress is applied without altering the magnetic field for EPR. However, the spin packets which are saturated will then be different with and without stress. Alternatively, one may change the magnetic field when stress is applied so as to remain at the centre of the EPR line, and hence on the same spin packet.

As the changes in ENDOR frequency produced by the change in hyperfine parameter and by the change in magnetic field are comparable, it is essential to be able to compensate experimentally or theoretically for the latter in order to be able to measure the former. In order to estimate the uncertainties due to the shift of the EPR line, we have measured the dependence of ENDOR frequency upon magnetic field H as one sweeps through the EPR line, both with and without stress. This has been done for both values of M and for both ^{169}Tm hyperfine lines (both values of the quantum number m; ie for four different ENDOR lines.) This data is presented in figure 2.

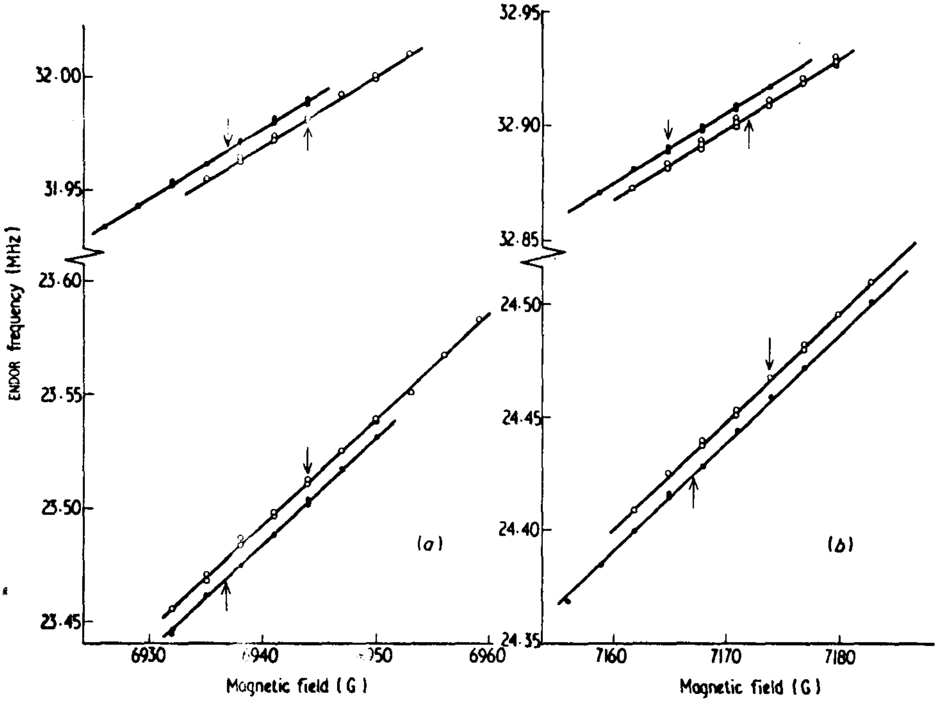

Figure 2. Variations of ENDOR frequency with field H. Points marked ○ correspond to a stress of 0·869 kg mm^{-2} and those marked ● to 3·155 kg mm^{-2}. (*a*) corresponds to the EPR of the low-field hyperfine line and (*b*) to that for the high-field hyperfine line. The position of the centre of the EPR line is indicated. The data derived from these curves are given below

M	F (kg mm^{-2})	H (G)	Slope (kHz G^{-1})	Frequency at centre of line (kHz)
$-\frac{1}{2}$	0·869	6944·0	4·648(38)	23521·09(27)
$-\frac{1}{2}$	3·155	6936·8	4·734(28)	23478·45(16)
$+\frac{1}{2}$	0·869	6944·0	3·026(31)	31980·87(19)
$+\frac{1}{2}$	3·155	6936·8	3·031(34)	31966·76(21)
$-\frac{1}{2}$	0·869	7174·0	4·695(34)	24465·29(22)
$-\frac{1}{2}$	3·155	7166·8	4·677(87)†	24421·38(66)†
$+\frac{1}{2}$	0·869	7172·2	3·032(46)	32904·29(25)
$+\frac{1}{2}$	3·155	7165·0	3·014(41)	32889·06(22)

† The relatively large uncertainty in these numbers is caused by three points at the extreme ranges of our values which lie off the straight line. If these points are disregarded, the slope becomes 4·781(40) and the frequency at the centre of the line 24422·15(26). This changes the quantity $\partial(A_s - A_p)/\partial F$ for the high-field line to 12·21(24) kHz kg^{-1} mm^2, and the mean value for both hyperfine lines to 12·34(22) kHz kg^{-1} mm^2.

Abragam and Bleaney (1970) have discussed the mechanism of inhomogeneous broadening of ENDOR lines and the change of ENDOR frequency produced by a change in external magnetic field δH. Adapting their formulae (4.64) and (4.65) to our system, the electron resonance energy may be written

$$\begin{aligned} h\nu_e = g\beta H &+ g\beta\Delta H_e + (h\nu_e)_{\mathrm{hfs}} + MA \\ &+ \delta g\beta H + \delta(h\nu_e)_{\mathrm{hfs}} + M\delta A. \end{aligned} \tag{4}$$

We have separated the effects of hyperfine interactions into two parts, one depending upon $A = (A_s - A_p)$, which is the contribution from the ligand along [111] whose ENDOR we have studied, and the other $(h\nu_e)_{\mathrm{hfs}}$ which represents the hyperfine interaction with all other nuclei. ΔH_e is the random variation of local field due to neighbouring dipoles, and δg, $\delta(h\nu_e)_{\mathrm{hfs}}$ and δA represent the effect upon g, $(h\nu_e)_{\mathrm{hfs}}$ and A of random variations in crystal fields. Writing $h\nu_e = g\beta H_0 + (h\nu_e)_{\mathrm{hfs}} + MA$ for the centre of the EPR line, a spin packet shifted by δH must correspond to an appropriate combination of the possible variations which satisfy equation (4). The frequency of the ENDOR line is given by

$$h\nu_n = g_n\beta_n H + g_n\beta_n\Delta H_n + MA + M\delta A. \tag{5}$$

Hence, the same two sources contribute to the inhomogeneous broadening of both the EPR and ENDOR lines.

If the broadening were due only to the effects of random crystal fields, which for Tm^{2+} leads to correlated g and A values such that $\delta A/A \simeq \delta g/g$ (see §4), the traversal of the EPR line selects spin packets corresponding to a specific δA:

$$\delta H = -\left(1 + \frac{MA}{g\beta H}\right)\frac{\delta g}{g}H \simeq -\frac{\delta A}{A}H \quad \text{as } MA/g\beta H \ll 1.$$

Hence, such a shift δH leads to a correlated shift of ENDOR frequency:

$$\delta\nu_n = [g_n\beta_n + MA/H]\delta H.$$

An effect of this sort has been observed by Locher and Geschwind (1963) for $^{61}\mathrm{Ni}^{3+}$ ENDOR in $\mathrm{Al_2O_3}$, where the inhomogeneous broadening was due to correlated zero-field electronic and nuclear quadrupole splittings. They found the slope $\delta\nu_n/\delta H$ for positive M to be smaller than $g_n\beta_n$ and for negative M to be greater than $g_n\beta_n$, the mean of the two slopes being equal to $g_n\beta_n$.

If, however, the inhomogeneous broadening of the EPR is dominated by magnetic fields from randomly oriented neighbouring magnetic moments, there is no direct correspondence between the field change δH for EPR and $\delta\nu_n$. Moving δH from the centre of the EPR line corresponds to selecting spin packets for which the local internal field $\Delta H_e = -\delta H$. However, the local fields set up at one of the ligand nuclei will not be the same as that set up at the paramagnetic ion, though one would expect it to have the same sign and comparable magnitude; ie $\Delta H_n \neq \Delta H_e$. Hence, the change in ENDOR frequency produced by the change δH is different from $g_n\beta_n\delta H$ and should not depend upon the value of M. Qualitative arguments suggest that $h\delta\nu_n$ should be of the same sign but smaller than $g_n\beta_n\delta H$.

Our data in figure 2 show that both effects contribute to the inhomogeneous broadening in our samples. This is really clear from EPR spectra as one knows from ligand ENDOR measurements that there is appreciable contribution to the EPR linewidth from ligand hyperfine structure, and the fact that it is not resolved indicates some other comparable source of line broadening. The slopes $\delta\nu_n/\delta H$ are clearly different for different M values, showing the presence of random crystal-field effects, and the difference is less than A/H, as one would expect for two competing mechanisms. The mean slope is less than $g_n\beta_n$.

showing the effect of the difference in local internal magnetic field, ie $\Delta H_n < \Delta H_e$. It is worth noting that the difference in ν_n between the two hyperfine components of the EPR line is equal to $g_F \beta_n DH/h$, because movement by DH from the centre of one of these lines to the centre of the other corresponds to remaining on the same spin packet, but reversing the direction of the ^{169}Tm nuclear spin.

These measurements show that theoretical compensation for the change of the g-value on application of stress would be impossible without making measurements of $\delta\nu_n$ as a function of δH. If one has to make such a measurement, one can just as accurately reset H to the centre of the EPR line after stress is applied. One still has to estimate the uncertainty produced by errors in setting on the centre of the EPR line†.

In order to find the hyperfine structure parameters, one needs to subtract the measured values of the two ENDOR frequencies corresponding to the two values of M in equation (3). For each line, one could estimate the uncertainty $\delta\nu_n$ which arises because of the uncertainty δH in setting H to the centre of the line. However, this would overestimate the uncertainty in $(A_s - A_p)$ because the shift of ENDOR frequencies for the two M values are correlated for a given δH:

$$h\nu_{\pm} = g_n\beta_n H \pm \tfrac{1}{2}(A_s - A_p) + [g_n\beta_n - h(\delta\nu_{\pm}/\delta H)]\delta H.$$

Hence

$$h(\nu_+ - \nu_-) = A_s - A_p - h\left(\frac{\delta\nu_+}{\delta H} - \frac{\delta\nu_-}{\delta H}\right)\delta H.$$

The quantity $\partial(A_s - A_p)/\partial F$ for both hyperfine lines give values 12·48(21) and 12·55(39)‡ kHz kg^{-1} mm^2, respectively.

As the uncertainties in δH for these two lines are uncorrelated, the compatibility of the uncertainty on each with the difference between them is satisfactory. Combining these two results leads to

$$\partial(A_s - A_p)/\partial F = 12{\cdot}5(2)\ddagger\ \text{kHz kg}^{-1}\ \text{mm}^2.$$

4. Ligand displacements

We are interested in finding the displacements u of the ligand ions produced by a stress F in the [111] direction, so like Zimmermann and Valentin (1975) we will express our results in terms of u_{zz}/F_{zz}, which for ligands at a distance R along [111] is equivalent to $\partial R/\partial F$.

Calculating this quantity from the bulk elastic constants leads to

$$\partial R/\partial F = \tfrac{1}{3}(s_{11} + 2s_{12} + s_{44})R.$$

Malkin *et al* (1971) introduce two modifications to this: (i) displacement of the basis which adds $-\frac{1}{6}\alpha_1 s_{44} R$, and (ii) replacement of the elastic constants by local values appropriate to the region around the impurity. For Tm^{2+} their calculations require $(s_{11} + 2s_{12})$ to be increased by 1·35 and s_{44} by 1·14. Both the calculations of Malkin *et al* and the admittedly rather model-dependent deductions from the experiments of Baker

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† It is worth noting that such errors should be allowed for in all ENDOR experiments, and also that this effect will produce systematic errors in ENDOR experiments where one works deliberately at the side of the EPR line.

‡ See the footnote in the caption to figure 2.

and van Ormondt (1974) give $\alpha_1 = 0{\cdot}5$. Table 3 gives the values of $\partial R/\partial F$, both uncorrected and corrected for these effects.

Table 3. Values of $\partial R/\partial F \times 10^5\,\mathrm{nm\,kg^{-1}\,mm^2}$.

Calculated from bulk elastic constants	3·92
Calculated from the elastic constants of Malkin *et al*	4·61
Calculated including α_1 displacements	3·75
Deduced from our data, assuming:	
(i) undistorted lattice and $n = 7$	7·1(3)
(ii) the model of Anderson *et al* and $n = 12$	7·5(3)
(iii) $(A_p - A_s) \propto R^{-3}$	9·3(4)
(iv) $(A_p - A_s) \propto R^{-7}$	3·9(2)

The parameter A_s arises solely from covalent bonding, but A_p has a contribution $A_d = g g_F \beta\beta_n / R^3$ from dipole–dipole interactions and a contributions $A_p - A_d$ from covalent bonding. When stress is applied, A_d changes because of changes both of g-value and of R; these two terms are written out explicitly in equation (6). These are also essentially the same two mechanisms which cause changes in the covalent contributions to A_p and A_s; the change of g-value occurs because the change of crystal field induced by the strain mixes in excited states of the metal ion and, as these have different covalent interactions with the ligand, there are consequent changes in A_s and A_p; there are also direct changes in the covalent overlap, which is a function of R. These terms are not easy to separate and require explicit calculation. The stress dependence of $(A_p - A_s)$ may may be written:

$$\frac{\partial(A_p - A_s)}{\partial F} = \frac{A_d}{g}\frac{\partial g}{\partial F} - \frac{3A_d}{R}\frac{\partial R}{\partial F} + \frac{\partial(A_p - A_d - A_s)}{\partial R}\frac{\partial R}{\partial F}. \tag{6}$$

For the undistorted $\mathrm{BaF_2}$ lattice, $R = 0{\cdot}2685$ nm and $A_d = 6{\cdot}58$ MHz. However, as $\mathrm{Tm^{2+}}$ is considerably smaller than $\mathrm{Ba^{2+}}$, one expects some local contraction of the lattice around the impurity ion. This has been estimated by Anderson *et al* (1975), using a technique similar to that used by Babershke (1971) for $\mathrm{Eu^{2+}}$ in the same lattices, by comparing the transferred hyperfine structure in $\mathrm{CaF_2}$, $\mathrm{SrF_2}$ and $\mathrm{BaF_2}$. The model assumes that the change in R between the different crystals causes both A_s and $(A_p - A_d)$ to change in the same way, which is equivalent to supposing that they vary as R^{-n}. This model leads to $R = 0{\cdot}251$ nm and $A_d = 8{\cdot}06$ MHz. The measured value of $(A_p - A_s) = 8{\cdot}46$ MHz, so that the model of Anderson *et al* indicates only a very small covalent contribution. The first term in equation (6) is then $2{\cdot}97(13)\,\mathrm{kHz\,kg^{-1}\,mm^2}$ using undistorted lattice parameters and $3{\cdot}63(16)\,\mathrm{kHz\,kg^{-1}\,mm^2}$ using the parameters of Anderson *et al*.

One may calculate the contribution to the last term of equation (6), due to the admixture of excited states, by perburation theory. The admixture of ligand wavefunctions into the $\mathrm{Tm^{2+}}$ wavefunctions is described by six covalency parameters, which may be estimated from calculated values of the overlap parameters (Axe and Burns 1966, Baker 1968). There is reasonable correspondence between this theory and the measured ligand hyperfine structure parameters for the ground state, Γ_7, so we may take these parameters as reasonably well established. The perturbation of the ground state produced by strain may be expressed in terms of matrix elements of the orbit–lattice interaction coupling the Γ_7 states to the excited Γ_8 and Γ_6 states. The matrix element with Γ_8 is that which produces the change $\partial g/\partial F$ of the g-value, and so is experimentally determined. That with Γ_6 does not contribute to $\partial g/\partial F$, and so it must be estimated using a model. Hence, there are some uncertainties in the calculation of this contribution to the last term in equation (6).

As, at least in the model of Anderson *et al*, the covalent contribution is so small, one could approximate by writing

$$\frac{\partial(A_p - A_d - A_s)}{\partial F} = \frac{(A_p - A_d - A_s)}{g}\frac{\partial g}{\partial F}.$$

This is the assumption we have made in § 3 leading to $\partial A/\partial F = (A/g)\partial g/\partial F$ (3·81(17) kHz kg^{-1} mm^2).

After allowing for these contributions to the last term in (6), we may write an expression for the explicit dependence of this term on the change of R, by assuming that the covalent contributions vary as R^{-n}, so that $\partial(A_p - A_d - A_s)/\partial R = -n(A_p - A_d - A_s)/R$. Hence, equation (6) reduces to an explicit equation which may be solved for $\partial R/\partial F$ if one knows the value of n.

The model of Anderson *et al* mentioned above leads to a value of $n = 12$. This contrasts with the value of $n = 7$ found by Babershke (and by Newman 1971) which was used by Zimmermann and Valentin (1975) to produce a successful correlation between their measured value of $\partial A/\partial F$ in Eu^{2+} and the values of $\partial R/\partial F$ deduced from bulk elastic constants. Table 3 gives the values of $\partial R/\partial F$ deduced from our data, making various assumptions about the value of n.

There is clearly no agreement with the calculated values. Inverting this calculation, one can obtain agreement only by assuming that the whole ligand hyperfine interaction scales as R^{-7}. As it seems impossible to find a model of the combined effects of covalency and dipole–dipole interaction which would give so large a dependence, one is forced to conclude that local displacements of the ligands are much greater than those indicated by the calculations of local elasticity.

If this conclusion is correct, the interpretation of Baker and van Ormondt of the EPR data is erroneous.

5. Conclusion

The positive conclusions of this work, apart from adding to the excellent correlation between calculated and measured relaxation rates, is to show that local elasticity when a crystal is strained is far from well known or simple. To understand this completely, one must measure A_p and A_s separately, and measure the parameters for other ligands. Also, similar measurements would have to be made for CaF_2 and SrF_2 if a complete understanding were to be obtained.

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