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Large-Magnitude High-Spin Nuclear Parameters in a Ti^{3+} Center from X-band EPR Measurements at 10 K

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Precise 10 K X-band EPR measurements and subsequent spin-Hamiltonian analysis by direct matrix diagonalization methods are reported for a Ti^{3+} ($S = 1/2$) center in tetragonal zircon (zirconium silicate, $ZrSiO_4$). A special, and previously unobserved, feature of the supposedly uniaxial spectrum is the marked angular dependence of the titanium hyperfine lines in the perpendicular, *ab* crystal plane. As discussed, this can only arise from the presence of high-spin nuclear terms of dimension BI^k, SI^k ($k = 3, 5$) in the spin Hamiltonian. Parameters arising from these terms were determined to have magnitudes very much larger than observed previously in first-row transition ions. The consequences of precise determination of these high-spin parameters are significant and several: a precise determination of the nuclear quadrupole tensor leading to a ratio $^{47}P/^{49}P$ in excellent agreement with the ratio derived from the corresponding nuclear quadrupole moments; an apparent anisotropy in the nuclear Zeeman interaction which can be identified with anisotropy in the chemical shielding "tensor"; a marked hyperfine anomaly. The origin and significance of these observations are discussed. © 1999 Academic Press

I. INTRODUCTION

Zircon (zirconium silicate) is a good representative of an interesting class of a mixed ionic–covalent crystal: covalent SiO_4^{4-} tetrahedral units ionically bound with Zr^{4+} ions. Such crystals provide the opportunity to study the interaction between molecular defects of the type produced in α-quartz and ionic defects of the type formed in alkali halides. We shall not discuss these aspects further in this paper except to note the importance of electron paramagnetic resonance (EPR) in studying the formation and structure of paramagnetic centers, often at the ppm level, which can strongly influence the electrical and electronic properties of the host crystal. From the EPR standpoint zircon is an ideal crystal for study since the crystal structure and morphology is known. Furthermore, the tetragonal structure (space group $I4_1/amd$) normally gives rise to paramagnetic species with tetragonal or monoclinic point group symmetries.

A recent paper (*1*) gave a detailed description of a 10 K X-band EPR study of a d^1 Ti^{3+} ($S = 1/2$) center in zircon (zirconium silicate) in which it was claimed that high-spin nuclear Zeeman (HSNZ) parameters of dimension BI^3 and BI^5 are present with sizes several orders of magnitude larger than had been observed

previously for first-row transition ions. As a result of including such terms in the spin-Hamiltonian (SH) analysis of the center, the ratio of the nuclear quadrupole moments, $^{47}Q/^{49}Q$, for the two Ti isotopes involved was determined in good agreement with, but apparently more precisely than by, direct nuclear methods (*2*). A further consequence was that an apparent anisotropy in the nuclear *g* parameter matrix ("tensor") could be detected, corresponding to uniaxial site symmetry, and measured with considerable precision.

That such precision and such unexpectedly large-magnitude HSNZ parameters resulted from a largely conventional EPR experiment elicited some skepticism from the referees of our earlier paper (*1*). It was conceded that the evidence is statistical and could not, at that time, be established unequivocally. The symmetry of the Ti^{3+} site in zircon is $\bar{4}2m$ (D_{2d}) tetragonal, and it was acknowledged (*1*) that presence of HSNZ terms in the SH should result in an angular dependence of lines in the perpendicular orientation of the crystal which would be absent in a system described by a conventional and uniaxial SH. The magnitude of this angular dependence was calculated to be small but, in principle, detectable within the quoted uncertainty in the measurements. Unfortunately attempted measurements in the *ab* plane of the crystal proved inconclusive because (i) there was low overall intensity in this plane, (ii) some of the lines had calculated transition probabilities close to zero, and (iii) there were many interferences from residual $Zr^{3+}(\alpha)$ lines (*3*) not removed in the annealing process.

In an attempt to resolve the above difficulties we have (i) made instrumental modifications resulting in an order-of-magnitude improvement in S/N, (ii) complemented this by a computer averaging data collection system, and (iii) experimented with annealing rates to obtain the best possible proportion of the wanted Ti^{3+} center at the expense of other interfering centers. These improvements resulted in satisfactory spectra being obtained in the *ab* plane and an unequivocal confirmation of the earlier results: large magnitude parameters of dimension BI^3 and BI^5 were obtained for both the $^{47,49}Ti$ isotopes ($I = 5/2$ and 7/2, respectively). Contrary to the earlier results, the parameters of dimension I^4, SI^3, and SI^5 are also found to be large and significant. The evidence is both statistical, i.e., a highly significant diminution in the fitting errors, and visual—a marked angular dependence of the lines in the crystal *ab* plane. The nuclear Zeeman interaction is shown to be a function of

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three sets of terms, those of dimension BI, BI^3, and BI^5. The nuclear electric quadrupole tensor is precisely determined, leading to a well-determined ratio for the nuclear quadrupole moments, $^{47}Q/^{49}Q$. The consequences of these results and their significance are discussed.

II. EXPERIMENTAL

The crystal, mounted on a copper holder, was irradiated with X-rays (W target, 45 mA and 45 kV) for 1 h at 77 K and then transferred cold to the goniometer system in the EPR cavity. The spectrum at 10 K was used to determine precisely the orientation of the crystal. The Displex cooler was then turned off and the cavity filled with helium gas for efficient heat transfer. The crystal warmed to room temperature within 1 h and was then cooled back to 10 K for EPR measurements.

After annealing as detailed above, all traces of the $Zr^{3+}(\alpha)$ center had been removed and there remained only the previously reported (1) $B(Ti^{3+})$, the C-center (4), and several hole centers (3). Three other weak sets of lines, which are believed also to arise from Ti^{3+} centers, were also observed. The relative positions of the various centers are shown in the c axis spectrum depicted in Fig. 1 of (3). One of the three additional Ti centers has been studied in detail and reported (5).

Earlier measurements (1) suggested that the (1 1 0) crystal plane is the most favorable plane from the point of view of obtaining a wide selection of both allowed and forbidden lines with reasonable intensities; this plane contains both the parallel (c axis) and perpendicular orientations of the uniaxial $B(Ti^{3+})$ center. Data were collected in this plane over a 180° angular range in 5° intervals and in the perpendicular, (0 0 1), plane over a 210° angular range in 10° intervals. Alignment of the crystal in the (1 1 0) plane was confirmed, prior to annealing, by observing the previously determined $Zr^{3+}(\alpha)$ and $[AlO_4]^0$ centers, each of which collapses from up to four symmetry-related species in planes containing the tetragonal axis to a single species for $\mathbf{B} \parallel \mathbf{c}$. The alignment in the (0 0 1) plane was confirmed by observing the nonangular dependence of the spinless isotope $^{46,48,50}Ti$ lines to within the inherent error in their measurement, ±0.0008 mT; the positions of the a and b axes in this plane were determined by observing the known angular dependence of a recently reported Y-compensated Ti^{3+} center for which the point-group symmetry of the site is $m(C_s)$ (5). Goniometer settings were determined to within 2 min of arc, the static magnetic field (with Bruker ER 033M NMR Gaussmeter) to ±0.002 mT, and the microwave frequency (with Systron Donner 6016 Counter) to ±1 kHz.

III. RESULTS

The main features of the $B(Ti^{3+})$ spectra have been detailed (1). The new results presented here are those obtained in the ab crystal plane: complex spectra of around 64 lines arising from $^{47,49}Ti$ lines of $B(Ti^{3+})$ and at least two other Ti^{3+} centers were observed (linewidths ranged from 0.02 mT for $\mathbf{B} \parallel \mathbf{c}$ to 0.08 mT

for $\mathbf{B} \perp \mathbf{c}$). The overall intensity of the spectra in this plane was markedly angular dependent, with 90° periodicity, being greatest in the [1 1 0] (and equivalent) direction and least along the a or b axes. There was a visual indication of angular dependence of line positions in the ab plane, but because of complicated overlapping of lines this could not be analyzed simply without the procedure outlined below. As pointed out in the previous section, any angular dependence observed is *not* a result of imperfect crystal alignment in the ab plane—the spinless isotope lines are, within error, isotropic in this plane. Figure 1 shows the observed spectrum in the [1 1 0] crystal orientation in the ab plane.

Initially four sets of data, those from the (1 0 0) and (1 1 0) planes used by Claridge et al. (1) and the current data from (1 1 0) and (0 0 1) planes, were refined simultaneously. All four sets could be fitted by a single parameter set which, within fitting errors, was close to that given in Ref. (1). The earlier data sets were then discarded and refinement continued with the current sets only; for these the S/N was at least an order of magnitude better than for the 1995 data.

The data were refined using program EPR-NMR developed by the University of Saskatchewan EPR Group (6). This program, which utilizes matrix diagonalization least-squares methods, contains, in addition to procedures for obtaining elements of the second-rank parameter matrices $\bar{g}$, $\bar{A}$, $\bar{P}$, $\overline{g_N}$ of the conventional SH, operator algebra (7) for obtaining coefficients (tensor elements) of terms of dimension I^4, I^6, BI^3, BI^5, SI^3, and SI^5. We shall now comment briefly on these terms and the choice of SH for the analysis of the current data.

The justification for including higher order spin terms in the SH when $S, I \geq 3/2$ is well established (see Ref. (7) for historical survey). The general term in the SH is $B^{l_B} S^{l_S} I^{l_I}$ where the actual terms allowed are restricted by (i) time reversal invariance and (ii) invariance under the symmetry operations of the point group of the site of the paramagnetic ion. The terms to be considered in this paper are formulated, initially, as two-vector spherical tensor operators which, to be experimentally useful, must be decomposed to single-vector operators. This imposes a further constraint, that of satisfying the triangle rule for addition of angular momenta.

McGavin et al. (7) detailed the decomposition of spherical tensor 2-vector operators $T_{l,m}(\mathbf{V}, \mathbf{W})$ of rank l to experimentally usable products of single-vector tensor operators and formulated a SH in terms of tesseral combinations, $\mathfrak{I}_{l,m}(\mathbf{J})$ ($\mathbf{J} = \mathbf{B}, \mathbf{S}, \mathbf{I}$), of these expressions. Terms of dimension $V^{l_V} W^{l_W}$ were considered, where V, W can represent any one of B, S, or I, l_V any one of l_B, l_S, or l_I ($l_B = 1, 2$; $l_S, l_I = 1$), and l_W one or other of l_S, l_I ($= 1, 2, 3, 4, 5$). Thus implicitly covered are all terms of the following types: BJ, BJ^3, BJ^5, $JJ(J^2)$, J^4 (J^2J^2), J^6 (J^2J^4), JJ^3, JJ^5 (where $J = S, I$), as well as terms quadratic in the magnetic field, here neglected. (See Ref. (7) for further discussion and relations between SHs expressed in conventional and tensorial forms.) For convenience of comparison of results as conventionally expressed, we shall formulate the SH for the present study in standard form but with
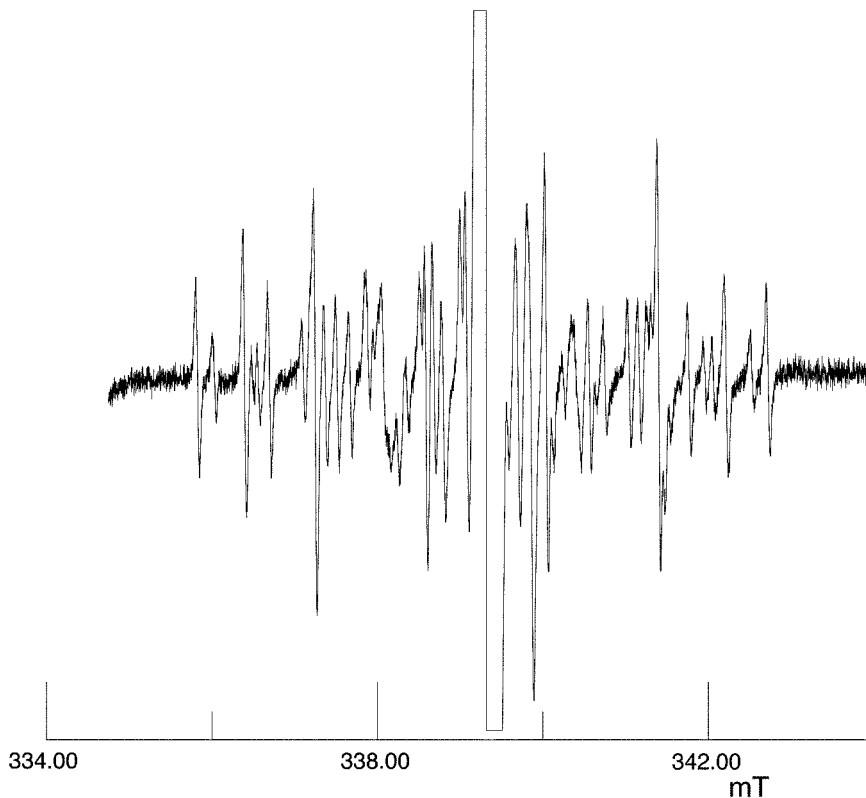
FIG. 1.   9.222 GHz EPR spectrum in the [1 1 0] direction at 10 K.

high-spin nuclear (HSN) terms necessarily in (tesseral) spherical tensor notation. Thus,

$$\aleph_S = \beta_e \mathbf{B} \cdot \bar{g} \cdot \mathbf{S} + \mathbf{S} \cdot \bar{A} \cdot \mathbf{I} + \mathbf{I} \cdot \bar{P} \cdot \mathbf{I}$$
$$- \beta_N \mathbf{B} \cdot \overline{g_N} \cdot \mathbf{I} + \aleph_{HSN}, \qquad [1]$$

where

$$\aleph_{HSN} = \sum_{l=4,6} \sum_{m=-l}^{l} B_{l,m}^{0,0,l} \mathfrak{S}_{l,m}(\mathbf{I})$$

$$+ G'\{ \sum_{m=-2}^{2} (B_{2,m}^{1,0,3} U'_{3,2,m}) + \sum_{m=-4}^{4} (B_{4,m}^{1,0,3} U'_{3,4,m})\}$$

$$+ G'\{ \sum_{m=-4}^{4} (B_{4,m}^{1,0,5} U'_{5,4,m}) + \sum_{m=-6}^{6} (B_{6,m}^{1,0,5} U'_{5,6,m})\}$$

$$+ \sum_{m=-2}^{2} (B_{2,m}^{0,1,3} U_{3,2,m}) + \sum_{m=-4}^{4} (B_{4,m}^{0,1,3} U_{3,4,m})$$

$$+ \sum_{m=-4}^{4} (B_{4,m}^{0,1,5} U_{5,4,m}) + \sum_{m=-6}^{6} (B_{6,m}^{0,1,5} U_{5,6,m}). \qquad [2]$$

For site symmetry $\bar{4}2m$ the parameter matrices in [1] are necessarily diagonal and uniaxial. In [2]: $G' = -g_N\beta_N B$ and the $U_{k,l,m}$ (obtained from Table 3 of Ref. (7)) are functions of $\mathfrak{S}_{l,m}(\mathbf{I})$ and $\mathfrak{S}_{l,m}(\mathbf{B})$ for the primed set, and $\mathfrak{S}_{l,m}(\mathbf{I})$ and $\mathfrak{S}_{l,m}(\mathbf{S})$ for the unprimed set. The coefficients (SH parameters) in [2], expressed in the notation $B_{l,m}^{l_B,l_S,l_I}$ with one of l_B, l_S, l_I necessarily zero, are components of irreducible tensors of rank l. For $\bar{4}2m$ site point group symmetry (Laue class $4/mmm$) the number of terms in [2] is restricted by symmetry considerations (7, 8) to those for which $l = 2, 4$; $m = 0, 4$. The number of parameters to be refined is then, for $I = 5/2$, $2(\bar{g}) + 2(\bar{A}) + 1(\bar{P}) + 2(\overline{g_N}) + 2(I^4) + 3(BI^3) + 4(BI^5) + 3(SI^3) + 4(SI^5) = 23$. For $I = 7/2$ (^{49}Ti isotope) terms in I^6, BI^7 and SI^7 are also allowed, increasing the number of parameters possible to 29. Of these latter terms only those in I^6 are currently available in program EPR-NMR.

With so many parameters to be refined it was necessary to ensure that all parameter sets were considerably overdetermined. This was achieved by setting criteria similar to that used in single-crystal X-ray crystallography, namely, number of data points $\geq 10 \times$ number of parameters to be iterated upon. The actual numbers used for the final data sets were as follows:

No. non-zero-weighted data points:	381	(^{47}Ti)	528	(^{49}Ti)
No. unit-weighted data points:	250	”	265	”
No. parameters to be iterated upon:	23	”	26	”

The weights were set taking into account linewidth, calcu-

TABLE 1
SH Parameters for the Ti^{3+} Center at 10 K; Error Estimates in Parentheses

Matrix $\bar{Y}$	^{47}Ti principal values		^{49}Ti principal values		^{46,48,50}Ti principal values	
	$Y_{\parallel}$	$Y_{\perp}$	$Y_{\parallel}$	$Y_{\perp}$	$Y_{\parallel}$	$Y_{\perp}$
$\bar{g}$	1.926873(6)	1.940835(3)	1.926893(9)	1.940800(4)	1.926885(6)	1.940861(3)
$\bar{A}/g_e\beta_e$ (mT)	2.9714(6)	0.8986(10)	2.9638(8)	0.8554(3)		
$\bar{P}/g_e\beta_e$ (mT)	0.16713(28)	$-0.08352(14)$	0.06288(17)	$-0.03144(8)$		
$\bar{g}_N$	$-0.542(40)$	$-0.213(5)$	$-0.532(110)$	$-0.205(5)$		
Data points	381		528		42	
Unit-weighted data points	250		265		35	
RMSD (mT)	0.0082		0.0137		0.0027	
Parameters	23		26		2	
Crystal orientations	35		39		39	

lated and observed intensity, and ease of measurement (freedom from interference and so on). It had been ascertained by measurement and calculation that the two planes of measurement used were more than adequate for complete determination of parameters for the center whose symmetry is uniaxial.

Results are summarized in Tables 1 and 2, and in Figs. 2, 3, and 4.

IV. DISCUSSION

From Tables 1 and 2 the data for both isotopes are fitted to within the inherent error in measurement of any one data point, i.e., to around ±linewidth/3. For ^{47}Ti the root-mean-squared-deviation (RMSD) was 0.0082 mT and for the ^{49}Ti 0.0137 mT. All parameters are statistically well determined as evidenced by the parenthesized errors in Tables 1 and 2. Of particular interest are the HSNZ parameters (associated with terms BI^3, BI^5) and the HSN parameters associated with terms I^4, SI^3, SI^5. The mean errors of determination for these terms are respectively ±20% and ±5% for the 47 and 49 isotopes. Contrary to the earlier work (1), where only the ^{47}Ti data was analyzed in detail, the latter group of terms is also shown now to be well determined and significant. It is possible that the

analysis of the ^{49}Ti data could be modified by the inclusion of terms in BI^7, SI^7 which are not currently available in program EPR-NMR. However, we note from Table 2 that parameters associated with I^6 are three orders of magnitude smaller than those associated with I^4.

Before commenting on the angular dependence of spectra in the ab plane of the crystal it is necessary to comment briefly on the energy-level assignments and the signs of $A_{\parallel}$, $A_{\perp}$, and $P_{\parallel}$. The energy level assignments are relatively simple for $\mathbf{B} \parallel \mathbf{c}$ but become increasingly difficult as the Zeeman field approaches the perpendicular crystal orientation. Level labels were established by a stepwise procedure in the (1 1 0) plane, starting at $\mathbf{c}$ and proceeding in 5° steps using successive cycles of refinement and simulation, including intensity computation. Labels were then assigned in the (0 0 1) (ab) plane by simulating positions and transition probabilities for all possible transitions. Final refinements were then made with both planes of data simultaneously while retaining these level assignments. We shall see that the signs of $A_{\parallel}$ and $A_{\perp}$ can be established as being both positive from a ligand-field analysis of the principal g and A values. In Ref. (1) the A values were taken as positive to agree with the theoretical analysis of Rinneberg and Weil

TABLE 2
Values of High-Spin Nuclear Parameters for ^{47,49}Ti at 10 K; Error Estimates in Parentheses

Term type	^{47}Ti($I = 5/2$)		^{49}Ti($I = 7/2$)	
$I^l/g_e\beta_e$ (mT)	$B_{l,0}^{0,0,l}$	$B_{l,4}^{0,0,l}$	$B_{l,0}^{0,0,l}$	$B_{l,4}^{0,0,l}$
$l = 4$	$-0.0185(13)$	$-0.0071(13)$	0.0219(5)	0.0216(6)
$l = 6$	—	—	0	$-0.0004(2)$
$SI^m/g_e\beta_e$ (mT)	$B_{l,0}^{0,l,m}$	$B_{l,4}^{0,l,m}$	$B_{l,0}^{0,l,m}$	$B_{l,4}^{0,l,m}$
$l = 2, m = 3$	0.0025(36)	—	$-0.0016(14)$	—
$l = 4, m = 3$	$-0.0075(14)$	0.0306(55)	$-0.0024(14)$	$-0.0718(19)$
$l = 4, m = 5$	0.0045(14)	0.0631(44)	0.0205(4)	0.0178(11)
$l = 6, m = 5$	0.0048(15)	0.0024(52)	0.0171(4)	$-0.0177(14)$
BI^m (unitless)	$B_{l,0}^{1,0,m}$	$B_{l,4}^{1,0,m}$	$B_{l,0}^{1,0,m}$	$B_{l,4}^{1,0,m}$
$l = 2, m = 3$	$-0.0039(26)$	—	$-0.0588(28)$	—
$l = 4, m = 3$	$-0.0288(31)$	0.0062(26)	$-0.0082(30)$	$-0.1017(6)$
$l = 4, m = 5$	$-0.0148(24)$	0.0290(9)	0.0180(4)	$-0.0147(2)$
$l = 6, m = 5$	0.0015(25)	$-0.0268(14)$	0.0099(4)	0.0239(2)

(9). Then the fittings apparently gave the sign of $P_\parallel$ as negative relative to $A_\parallel$. However, it has since become apparent that $P_\parallel$, for both ^{47,49}Ti, must take the same positive sign as the respective nuclear quadrupole moments, Q (see later discussion). In fact it was found that the data could be fitted equally well taking $A_\parallel$ and $P_\parallel$ both positive, but the labels of some energy levels swap. It follows that the signs of neither $A_\parallel$ nor $P_\parallel$ are established from the EPR measurements alone, and in addition the sign of $P_\parallel$ is not established generally relative to that of $A_\parallel$. A correct statement of the position seems to be: the sign of $P_\parallel$ is known relative to that of $A_\parallel$ *for a given choice of energy-level labels.*

For the ^{47}Ti ($I = 5/2$) isotope the angular dependence in the *ab* plane only just exceeds the errors in measurement. In fact it was necessary to correct data to constant frequency (Fig. 2)
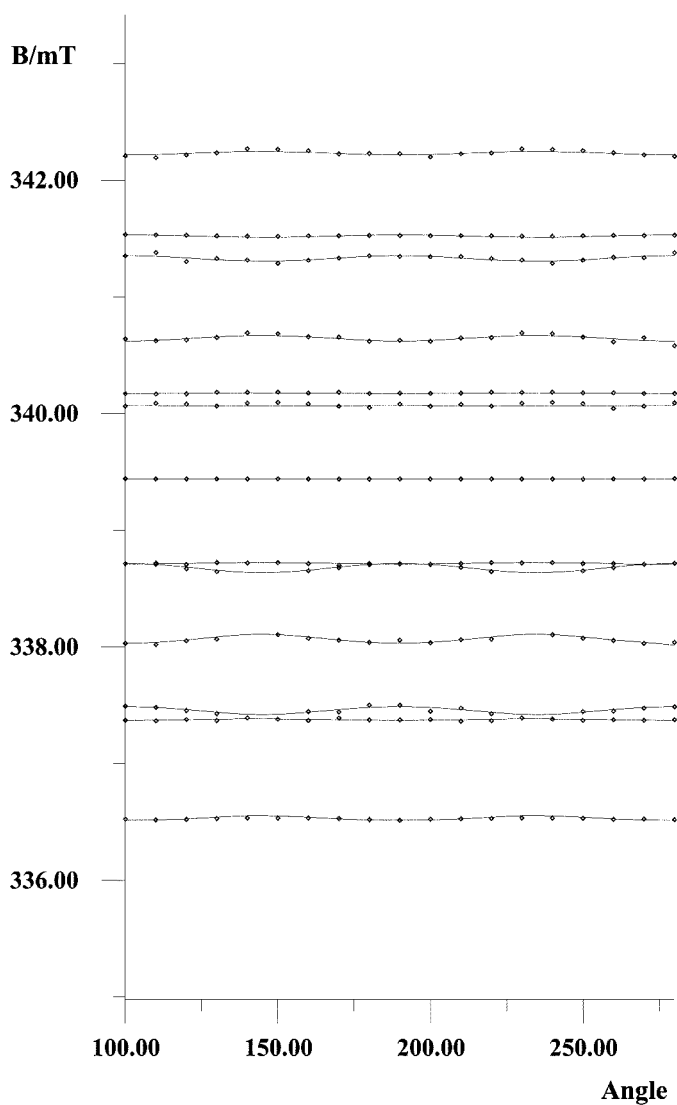

FIG. 2. Angular dependence of the ^{47}Ti ($I = 5/2$) lines in the *ab* crystal plane. Solid lines are calculated from Eqs. [1], [2] and the experimental points are indicated.
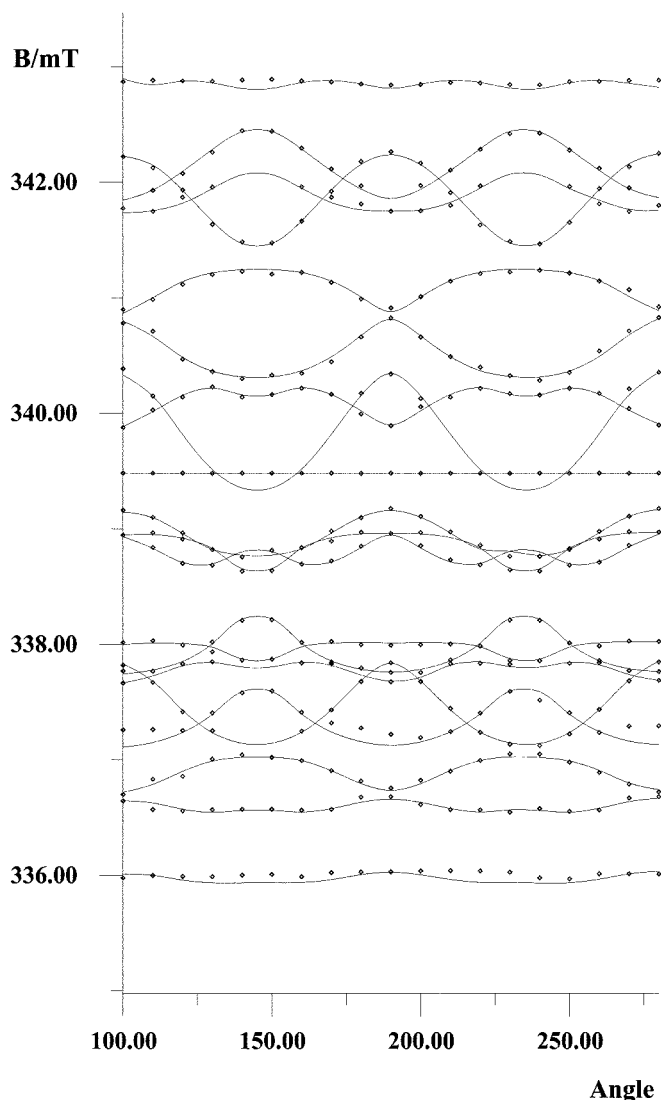

FIG. 3. Angular dependence of the ^{49}Ti ($I = 7/2$) lines in the *ab* crystal plane (see legend to Fig. 2).

in order to eliminate scatter from small variations in microwave frequency from one crystal orientation to the next, in order to obtain a reliable view of the angular variation of the line positions. Nevertheless the results depicted in Fig. 2 are convincing: there is a marked angular dependence of some of the lines in the plane which exceeds the error bars and which would not be present in the absence of HS interactions.

For the ^{49}Ti ($I = 7/2$) isotope the angular dependence (Fig. 3) is very marked and the results unequivocal. The observed angular dependence could not be explained in the absence of HS interactions and the degree of agreement between observed and calculated line positions could not be explained by any artifact of measurement or fitting procedure. Figure 4 illustrates, for two of the ^{49}Ti transitions, the angular variation of both line position and calculated line intensity. Generally calculated and observed intensities were in agreement across all
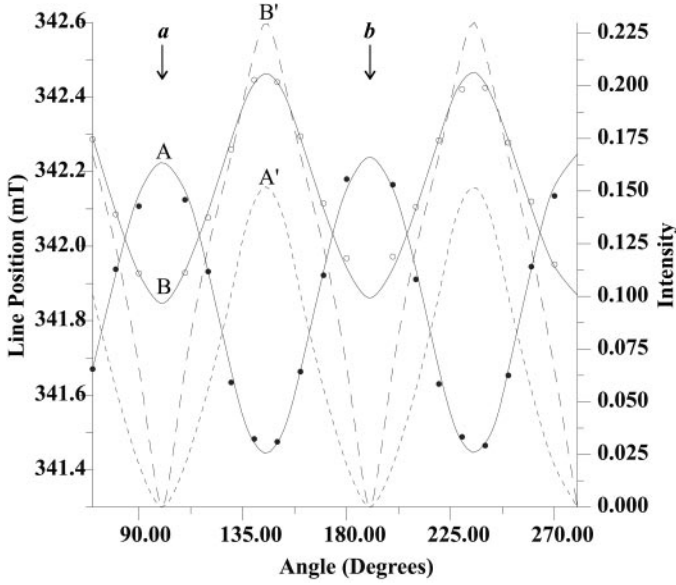
FIG. 4. Angular dependence of observed resonant fields (solid lines and left-hand abscissa) and intensities (dashed lines and right-hand abscissa) for two of the ^{49}Ti lines in the *ab* plane: *A*, *A'* transition 8–12; *B*, *B'* transition 7–9. Experimental points are indicated.

lines in the plane. There were some apparent anomalies which may be due to noninclusion of certain HS terms in the intensity computations.

In the following we discuss, in turn, analysis of the principal *g* and *A* values, the nuclear quadrupole interaction, and the nuclear Zeeman interaction, including where appropriate the effects of higher spin terms on these interactions.

A. The Electronic Zeeman and Nuclear Hyperfine Interactions

As discussed in Ref. (*1*), the ground state of the Ti^{3+} center under D_{2d} point group symmetry can be either $d_{x^2-y^2}$ (B_1 representation) or d_{xy} (B_2 representation) depending on the choice of *x* and *y* axes. Equations [2]–[4] of Ref. (*1*), approximated by neglecting all terms of order $(\zeta/\Delta_1)^2$, $(\zeta/\Delta_2)^2$ (see below for definitions of these terms), referred to the former choice and were used to analyze the *g* and *A* values. With all second-order terms included (*10*), the appropriate expressions are

$$g_\parallel = g_e(N^2 - 4yN - x^2 + y^2) \quad [3]$$

$$g_\perp = g_e(N^2 - xN + xy - y^2) \quad [4]$$

$$A_\parallel = -\wp(4N^2 + 56yN + 6xN$$
$$+ 8x^2 + 4y^2 + 6xy + 7\kappa)/7 \quad [5]$$

$$A_\perp = \wp(2N^2 - 11xN + 11xy - 2y^2 - 7\kappa)/7, \quad [6]$$

where (*10*) $N = (1 - \frac{1}{2}x^2 - y^2)^{1/2}$, $x = \zeta_2/\Delta E_2$, $y = \zeta_1/\Delta E_1$,

and $\wp\kappa$ is the isotropic contact interaction where $\wp_{3d} = \mu_0 g_e g_N \beta_e \beta_N \langle r^{-3}\rangle_{3d}/4\pi$ and $\kappa = -8\pi\overline{\delta(r_i)}/3 \langle r^{-3}\rangle_{3d}$ represents core polarization of the *s* electrons. $\Delta E_1 = E_{B_2} - E_{B_1}$ and $\Delta E_2 = E_e - E_{B_1}$. Furthermore, $\zeta_1 = k_1\zeta$, $\zeta_2 = k_2\zeta$, where k_1, k_2 are the orbital reduction factors and ζ is the free ion spin–orbit coupling constant. Since k_1 and k_2 are not known, and not obtainable from the present experiments, we shall be content to treat *x*, *y* as parameters to be obtained from the experimental *g* values and Eqs. [3] and [4]. A quantity closely related to $\wp_{3d}$ is the theoretical uniaxial parameter $b_{3d} = \alpha\wp_{3d}$ where α (= 2/7 in this instance) is the appropriate *d*-type spherical harmonic contribution to the *d*-orbital.

Using the experimental *g* values (Table 1), Eqs. [3] and [4] were solved iteratively for *x* and *y*, and then Eqs. [5] and [6] were solved for $\wp$ and κ using these *x* and *y* values and the experimental *A* values from Table 1. The derived values ΔE_1, ΔE_2 (using the free-ion value $\zeta = 154$ cm^{-1}), $\wp$, κ, and $\langle r^{-3}\rangle_{3d}$ are listed in Table 3 for both Ti isotopes. The values of $\wp$ and κ agree rather well in magnitude with the values given for tetragonal Ti^{3+} sites in MgO and CaO by Davies and Wertz (*11*) and also for the C_2 Ti^{3+} sites in α-quartz (*12, 13*), when $\wp$ was treated similarly as a variable parameter (the ground state in the α-quartz centers is predominantly A_1 (d_{z^2})). The value of the radial expectation value $\langle r^{-3}\rangle_{3d}$ is considerably lower than the Watson and Freeman (*14, 15*) free-ion value, 2.55 a.u., but is also in good agreement with that found by Davies and Wertz (*11*) and that derivable from the α-quartz results (*12, 13*). Recent theoretical calculations (R. G. A. R. McLagan, personal communication) based on Ti^{3+} in octahedral coordination with oxygens at varying distances suggest a value around 2.47 a.u. The apparently low "experimental" values of $\langle r^{-3}\rangle$ are at this time not explained, but may indicate simply that the ligand-field analysis is not a particularly good approximation. The core polarization fields resulting from the single unpaired *d* electron, given by $\wp\kappa/2g_N\beta_N$, are, respectively, 8.403 and 8.203 T for the 47 and 49 isotopes.

The isotropic and uniaxial components, *a* and *b*, respectively, of the hyperfine interactions given by $a = \text{Tr}(\mathbf{A})/3$ and $b = (A_\parallel - A_\perp)/3$, may be extracted from the data of Table 1.

TABLE 3
Electronic and Nuclear Quantities Derived from Eqs. [3]–[6] and the g and A Values of Table 1

Quantity	^{47}Ti isotope	^{49}Ti isotope
ζ_1/Δ_1	0.03036	0.03038
ζ_2/Δ_2	0.00908	0.00907
$\Delta_1{}^a$	16,967 cm^{-1}	16,972 cm^{-1}
$\Delta_2{}^a$	5072 cm^{-1}	5069 cm^{-1}
$\wp$	-21.3081×10^{-4}cm^{-1}	-21.6755×10^{-4}cm^{-1}
κ	0.6325	0.6072
$\langle r^{-3}\rangle_{3d}$	2.1227 a.u.	2.1563 a.u.
$\wp\kappa/2g_N\beta_N$	8.403 T	8.203 T

^{a} Based on $\zeta_1 = \zeta_2 = \zeta = 154$ cm^{-1}, the free-ion spin–orbit coupling constant.

These are clearly slightly different for the two isotopes, and from the relations (see and compare Ref. (*14*), p. 707)

$$|^{47}a/^{49}a| = (^{47}g_N/^{49}g_N)(1 + \Delta)$$

and

$$|^{47}b/^{49}b| = (^{47}g_N/^{49}g_N)(1 + \Delta')$$

one gets a measure of the so-called hyperfine anomaly Δ (or Δ'). The former relation gives $1.5895/1.5582 = 1.0201$ and $\Delta = 0.0204$ (2%) and the latter, $0.6909/0.7028 = 0.9831$ and $\Delta' = -0.0166$ (1.7%). The apparent hyperfine anomaly is an order of magnitude greater than that observed from ENDOR measurements of the 63, 65 isotopes of Cu^{2+} in Al_2O_3 (*16*). However, examination of Table 2 reveals that the derived quantities $\wp$, κ, and $\langle r^{-3} \rangle$ all differ for the two isotopes and one should compare rather the isotopic ratios of the products $a \sim g_N \langle r^{-3} \rangle \kappa$ and $b \sim g_N \langle r^{-3} \rangle$. The set of self-consistent "experimental" parameters $\langle r^{-3} \rangle$, κ and the accepted isotropic g_N values (*17*) give

$$|^{47}b/^{49}b| = {}^{47}g_N{}^{47}(\langle r^{-3} \rangle)/{}^{49}g_N{}^{49}(\langle r^{-3} \rangle) = 0.984$$
$$|^{47}a/^{49}a| = (^{47}b/^{49}b)(^{47}\kappa/^{49}\kappa) = 1.025.$$

It has been common to analyze the experimental isotropic and uniaxial components of the hyperfine interaction by the Morton and Preston procedure (*18*), where a, b are compared to the quantities A^C and P^d derived from Hartree–Fock–Slater atomic orbitals tabulated by Herman and Skillman (*19*). Such an analysis of the present data (*1*) showed that ~100% of the spin population lies on the Ti^{3+} ion with around 93.6% in the d-orbital.

We have not herein, or previously (*1*), considered Jahn–Teller distortions which, by reference to other d^1 ions in zircon (*20, 21*) and Ti^{3+} ions in other crystals (*22*), are presumably present. It was found that there are apparently no features in the present study which required such an analysis. As noted by Di Gregorio *et al.* (*20*), a static Jahn–Teller splitting of the degenerate E levels is not possible under D_{2d} symmetry, but there is a possibility of coupling of the degenerate E states to vibronic states of the same symmetry leading to dynamic Jahn–Teller distortion (DJTE). We have noted above what appears to be an anomalously low "experimental" value of $\langle r^{-3} \rangle$. Modification of Eqs. [3], [4]) to include a DJTE (see Ham (*23*) and Eqs. [9], [10] of Di Gregorio *et al.* (*20*)) involve the parameter q which takes values between 1 (no DJTE) and $\frac{1}{2}$ (maximum DJTE). From the present data, and modified Eqs. [3], [4], any value of q less than unity leads to an *even smaller* value of $\langle r^{-3} \rangle$.

B. The Nuclear Electric Quadrupole Interaction

$P_\parallel$ is related to the nuclear quadrupole moment, Q, by (see Ref. (*14*), p. 456)

$$P_\parallel = 3e^2Q\langle r_q^{-3} \rangle(1 - 3x^2/4)/7I(2I - 1), \quad [7]$$

where the factor $(1 - 3x^2/4)$ is a second-order correction and x is defined in Eqs. [3]–[6]. Experimentally, the second-order correction term is, in this instance, less than 0.01% $P_\parallel$ and is subsequently ignored. A closely similar equation to [7] in terms of the nuclear quadrupole coupling, e^2qQ, is (*14*)

$$P_\parallel = 3e^2qQ/4I(I - 1), \quad [8]$$

where eq $(=V_{zz})$ is the z-component of the electric field gradient (efg) at the nucleus. The nuclear moment Q is known experimentally (*2, 24, 25*) to be positive for both the 47 and the 49 Ti isotopes. The efg at the nucleus results from one or both of electronic (i.e., from the single unpaired d-electron) and lattice interactions. The quantity $\langle r_q^{-3} \rangle$ is normally expected to be different from $\langle r^{-3} \rangle$ in Eqs. [5] and [6] because of electrostatic shielding of the nucleus (*14*) described by shielding (or anti-shielding) factors $(1 - R)$ and $(1 - \gamma_\infty)$, respectively for the electronic and lattice (ionic) contributions. The factor R is usually small (*12*) ($\approx$10%) and may describe either shielding or antishielding while the Sternheimer factor γ_∞ is known (*26*) to be large and negative for all but light atoms.

From our present data it is possible, through Eq. [7], to calculate the quadrupole moment Q, using $\langle r^{-3} \rangle$ determined from Eqs. [5], [6], i.e., neglecting shielding, or, to calculate $\langle r_q^{-3} \rangle$ using values of Q determined from independent nuclear measurements. We follow this latter course. Channappa and Pendlebury (*2*) measured Q $^{47}Ti = 0.29b$ and Q $^{49}Ti = 0.24b$ without correction for shielding effects. From hyperfine-structure measurements, Q ^{47}Ti has been more recently determined (*24*) as $0.303b$ and predicted (*25*) as $0.346b$. Using the values $0.303b$, $0.24b$, respectively, for $^{47,49}Ti$ and the equation

$$\langle r_q^{-3} \rangle = (4\pi\epsilon_0/e^2)7P_\parallel(2I - 1)/3Q, \quad [9]$$

we find $\langle r_q^{-3} \rangle = 1.610$ and 1.534 a.u., respectively, for the $^{47,49}Ti$ isotopes. Alternatively, if we considered using the $\langle r^{-3} \rangle_{3d}$ value determined from Eqs. [5] and [6] together with appropriate shielding factors, then it is evident that the principal effect is that of a small electronic shielding, and writing $\langle r_q^{-3} \rangle = (1 - R) \langle r^{-3} \rangle_{3d}$ we find $R = 0.241$ and 0.287, respectively, for the $^{47,49}Ti$ isotopes (see and compare Ref. (*14*), p. 708).

Much the same result can be reached by a slightly different but roughly equivalent route. The theoretical valence contribution, q_{val}, to the efg for a single unpaired electron in the $d_{x^2-y^2}$ orbital is $q_{val} = V_{zz}/e = +4 \langle r^{-3} \rangle_{3d}/7$. The resulting contribution to $P_\parallel$ is, from Eq. [8], $3e^2qQ/40 = 0.2211$ mT (in

units $1/g_e\beta_e$). To obtain the experimentally observed $P_\parallel$, this result must be multiplied by a shielding factor $1 - R = 0.72$. A crude point-charge calculation indicates that the lattice contribution to the efg, from 8 surrounding O ions, is negative and negligibly small.

From Eq. [7] $^{47}P_\parallel/^{49}P_\parallel = 21(^{47}Q/^{49}Q)/10$. The experimental P ratio (Table 1) is 2.65 ± 0.05, which compares well with the ratio determined from quadrupole moments: $0.303/0.24 = 2.65$ (2, 24) or $0.346/0.24 = 3.03$ (2, 25). In the absence of high-spin terms, the P-ratio was found (1) to be 2.27. A similar magnitude was found earlier (12) for the ratio in the $[\mathrm{TiO_4/Li}]_A^0$ center in α-quartz, also in the absence of high-spin terms.

The presence of HS terms leads to a modification of the nuclear-quadrupole-interaction matrix because the operators from the HS and quadrupole interactions span the same ket vectors. These types of HS interactions could therefore be thought of as a pseudo-nuclear-quadrupole interaction. This must be distinguished from the so-called pseudo-nuclear-quadrupole interaction discussed by Abragam and Bleaney (Ref. (14), p. 37) which arises from mixing of low-lying electronic states by the hyperfine interaction. In the present instance the lowest orbital state is some 5000 cm⁻¹ above the ground state. It needs to be stressed that, although the nuclear quadrupole matrix is modified in the presence of HS interactions, the parameter matrices are observed to be numerically uncorrelated, as is required of orthogonal tensors.

C. The Nuclear Zeeman Interaction

From Table 1 an apparent anisotropy in the nuclear Zeeman tensor has been found. This anisotropy turns up only if all terms of dimension BI, BI^3, BI^5 are included in the analysis. However, again, it is important to note that these orthogonal tensors should not be correlated and indeed, as was shown by the covariances in the variance–covariance matrix of the EPR-NMR fitting procedure, they are numerically uncorrelated.

How does one interpret this apparent anisotropy? The nuclear Zeeman interaction can be written

$$\aleph = -\beta_N \mathbf{B} \cdot \mathbf{G} \cdot \mathbf{I} = -\beta_N \mathbf{B} \cdot \begin{pmatrix} G_\perp & 0 & 0 \\ 0 & G_\perp & 0 \\ 0 & 0 & G_\parallel \end{pmatrix} \cdot \mathbf{I}. \quad [10]$$

The elements of the nuclear Zeeman matrix can be expressed alternatively in the tensorial notation of Eq. [2] (7):

$$G_\perp = g_N \left(-\frac{1}{\sqrt{3}} B_{0,0}^{1,0,1} - \frac{1}{\sqrt{6}} B_{2,0}^{1,0,1} \right)$$

$$G_\parallel = g_N \left(-\frac{1}{\sqrt{3}} B_{0,0}^{1,0,1} + \frac{\sqrt{2}}{\sqrt{3}} B_{2,0}^{1,0,1} \right).$$

Then [10] can be written

$$\aleph = g_N \beta_N \mathbf{B} \cdot \left\{ \frac{1}{\sqrt{3}} B_{0,0}^{1,0,1} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right.$$
$$\left. + \frac{1}{\sqrt{6}} B_{2,0}^{1,0,1} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \right\} \cdot \mathbf{I}. \quad [11]$$

Equation [11] can be compared to the NMR expression

$$\aleph = -g_N \beta_N \mathbf{B} \cdot (\mathbf{1} - \boldsymbol{\sigma}) \cdot \mathbf{I}$$

where σ is the chemical shielding matrix ("tensor"). Therefore,

$$\sigma_{xx} = \sigma_{yy} = \sigma_\perp = -\frac{1}{\sqrt{6}} B_{2,0}^{1,0,1} \text{ and } \sigma_{zz} = \sigma_\parallel = \frac{\sqrt{2}}{\sqrt{3}} B_{2,0}^{1,0,1}.$$

From Table 1, $G_\parallel = -0.542$ and $G_\perp = -0.213$. Then:

$$B_{0,0}^{1,0,1} = -\frac{g_N}{\sqrt{3}} \mathrm{Tr}(\mathbf{G}) = 0.559 g_N = -0.176$$

$$B_{2,0}^{1,0,1} = \frac{\sqrt{2}}{\sqrt{3}} (G_\parallel - G_\perp) = -0.269 g_N = 0.085,$$

where the accepted isotropic g_N value (17) -0.31539 has been used. Experimentally we obtain $g_{N(exp)} = \mathrm{Tr}(\mathbf{G})/3 = -0.328$ in reasonable agreement with the accepted nuclear-determined value. Also, $\sigma_\parallel = 0.070$ and $\sigma_\perp = -0.035$. Similarly for the ⁴⁹Ti isotope, using the accepted value (17) -0.315477 for g_N, we obtain $B_{0,0}^{1,0,1} = 0.553 g_N = -0.174$, $B_{2,0}^{1,0,1} = -0.285 g_N = 0.090$, $\sigma_\parallel = 0.074$, $\sigma_\perp = -0.037$, and $g_{N(exp)} = -0.319$.

HSN terms of order BI^3, BI^5 produce effects, as discussed above for the nuclear quadrupole interaction, which might be considered as pseudo-nuclear-Zeeman interactions. Again, these must be distinguished from the pseudo interaction discussed in Abragam and Bleaney (14) which involves mixing of low-lying electronic levels in second order by the electronic Zeeman and hyperfine interactions.

V. CONCLUSIONS

We believe that we have demonstrated conclusively the necessity for the presence of HSNZ (terms of dimension BI^3, BI^5) and HSN (terms of dimension I^4, SI^3, SI^5) terms in the SH for the Ti³⁺ center. The parameters arising from these terms are several orders of magnitude larger than have been found previously for first-row transition ions. The effects of the terms on the observed EPR spectra are rather subtle but certainly not trivial: (i) a marked cos 4θ angular dependence of the spectra in the perpendicular crystal orientation which can only arise from operators $\widetilde{\mathfrak{I}}_{4,m}(\mathbf{J})(m = 0, 4;$

$\mathbf{J} = \mathbf{S}, \mathbf{I}$), and which would be absent in the conventional, uniaxial SH; (ii) apparent anisotropy in the nuclear Zeeman interaction which we have identified with anisotropy in the chemical shielding "tensor," $\boldsymbol{\sigma}$; (iii) an experimental ratio $^{47}P_{\parallel}/^{49}P_{\parallel}$ which is in good agreement with the derived ratio of the corresponding nuclear quadrupole moments; and (iv) observation of a marked "hyperfine anomaly."

It is clear from the results of Tables 1 and 2 that the electronic properties, g-values, and orbital splittings, are, as expected, independent of isotope. However, the nuclear parameters $\wp(\sim A)$, κ, and hyperfine fields are markedly different for the two isotopes. One can rationalize this in a hand-waving way by assuming that the two quadrupolar nuclei in question are of different sizes and distortions and are penetrated differently by the electronic orbitals (see discussion in Ref. (14), p. 706).

We have reported recently (27) 10 K EPR for an Fe^{3+} spectrum in tetragonal scheelite ($CaWO_4$) where terms of dimension BS^3, BS^5 were found necessary to explain the angular dependence of the spectra. Again the g and HS tensors were numerically uncorrelated, but inclusion of the latter produced a marked anisotropy in the former, unusual in high-spin Fe^{3+} EPR spectra. In this example the symmetry was only triclinic (Laue class $\bar{1}$) so that all operators $\tilde{\mathfrak{I}}_{l,m}(\mathbf{B}, \mathbf{S})$ ($l = 4, 6$; $-l \leq m \leq l$) need be included. The evidence in this case was mainly statistical—a marked diminution in the RMSD.

We shall not, at this stage, comment on the meaning of the HSN terms, but several queries need be posed. Are they real? Have we been lucky in observing two isolated cases where, for unknown reasons, the terms are apparently important, or is their occurrence more widespread, but the effects hidden because of the complexity of spectra and/or imprecision in the measurements?

In answer to the second query, we have, in the example reported herein, been fortunate in that the relative magnitudes of the nuclear hyperfine, nuclear electric quadrupole, and nuclear Zeeman interactions are such as to produce a large number of "forbidden" hyperfine transitions, most of which we were able to identify and utilize in our analysis. Precise fitting of these forbidden lines was crucial in obtaining well-determined HS parameters. Secondly, because the symmetry of the spectra is uniaxial, there were relatively few HS terms involved. Had the point-group symmetry of the site been triclinic, there would have been required 94 HS terms in the SH for an ion with $I = 5/2$, and one then has the valid criticism that anything could be fitted numerically to so many parameters. Of course there would have been more data: four-fold site splitting in a general crystal orientation which would be equivalent (28) generally to measurement in four distinct crystal planes.

Recently we have examined two other uniaxial systems in zircon: Ti^{3+} in the silicon site of the structure (as distinct from the zirconium site in the present instance) and Nb^{3+} ($S = 1/2$, $I = 9/2$). In both instances no forbidden hyperfine lines were identified and neither analysis required the presence of HS terms in the SH. In the former case the quadrupole interaction

is an order of magnitude smaller than for Ti in the Zr site of the crystal, and in the latter case the nuclear hyperfine interaction is an order of magnitude larger than for Ti/Zr. (These two systems will be reported elsewhere.) These observations raise the interesting possibility that HSN terms may be required to explain the mixing of levels by the magnetic field interaction when the magnitudes of the nuclear quadrupole and nuclear Zeeman interactions are significant fractions of the nuclear hyperfine energy. If one examines the $S + I = 7$, 9 zero-field hyperfine multiplets for the $I = 7/2$ ^{49}Ti nucleus, there is apparent a complicated mixing of states over the first 10 mT or so of field range as the magnetic-field interaction is applied.

We are pursuing currently further studies on synthetic Ti-doped zircon crystals to clarify some aspects of this work. One is the inclusion of terms in BI^7, SI^7 in the SH to make the ^{49}Ti study more complete. Doping the crystal with isotopically enriched ^{47}Ti or ^{49}Ti, as was done recently (29) for Ti in orthophosphate single crystals, would greatly simplify the spectra in the ab crystal plane and probably allow a more precise analysis with certainty of identification of lines.

Precise measurements such as outlined in this paper allow the determination of nuclear properties from essentially conventional EPR measurements. If good theoretical values of $\langle r^{-3} \rangle_{3d}$ and $\langle r_q^{-3} \rangle$ were available, then g_N and the quadrupole moment Q, particular to the crystalline environment of the nucleus, could be obtained.

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