NBS TECHNICAL NOTE

372

Mathematical Techniques for EPR Analysis of S=5/2 Ions in C_2 Symmetry. Application to FE^{3+} in Quartz.

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards [1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in four broad program areas. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Measurement Services and the following technical divisions:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic and Molecular Physics—Radio Physics [2]—Radio Engineering [2]—Time and Frequency [2]—Astrophysics [2]—Cryogenics.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

Analytical Chemistry—Polymers—Metallurgy—Inorganic Materials—Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

Engineering Standards—Weights and Measures — Invention and Innovation — Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center consists of the following divisions:

Reactor Radiation—Linac Radiation—Nuclear Radiation—Applied Radiation.

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

Information Processing Standards—Computer Information — Computer Services — Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information [3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Located at Boulder, Colorado 80302
[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

UNITED STATES DEPARTMENT OF COMMERCE
Maurice H. Stans, Secretary
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director

NBS TECHNICAL NOTE 372

ISSUED JUNE 1969

Nat. Bur. Stand. (U.S.), Tech. Note 372, 23 Pages (June 1969)
CODEN: NBTNA

MATHEMATICAL TECHNIQUES FOR EPR ANALYSIS OF S = 5/2 IONS IN C_2 SYMMETRY. APPLICATION TO FE^{3+} IN QUARTZ.

R. L. PETERSON, L. M. MATARRESE, AND J. S. WELLS

Radio Standards Physics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

NBS Technical Notes are designed to supplement the Bureau's regular publications program. They provide a means for making available scientific data that are of transient or limited interest. Technical Notes may be listed or referred to in the open literature.

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402
Price 35 cents.

Mathematical Techniques for EPR Analysis of S = 5/2 Ions in C_2 Symmetry. Application to Fe^{3+} in Quartz

Robert L. Peterson, L. M. Matarrese, and J. S. Wells

ABSTRACT

Various formulas and mathematical techniques useful for the analyses of the EPR spectra of ions of angular momentum 5/2 in sites of C_2 symmetry are presented. Special emphasis is given to the spectrum of Fe^{3+} in synthetic brown quartz. Included are: matrix elements of the Racah operators for arbitrary direction of the axis of quantization relative to the crystalline electric field axes, spectral line-position formulas based upon a usage of second-order perturbation theory which is somewhat different from the usual, and line-intensity formulas.

Key Words: electron paramagnetic resonance; ferric ion; synthetic quartz

The purpose of this paper is to present various mathematical formulas and techniques which are useful for the analysis of the EPR spectra of $S = 5/2$ ions in fields of C_2 symmetry. Special application is made to the spectrum of Fe^{3+} in synthetic brown quartz.[1,2]

Fe^{3+} is an S-state ion with spin $S = 5/2$. In quartz it apparently finds itself in a crystalline electric field environment of two-fold symmetry, C_2.[1] The crystalline potential may be developed in spherical harmonics $Y_{\ell m}$. Only $\ell = 2$ and 4 terms need be considered since the matrix elements of $Y_{\ell m}$ for other ℓ values vanish.[3,4] The C_2 symmetry eliminates odd m values. Since the crystal field potential must be real, it finally can be written as

$$V_{20} + V_{22} + V_{40} + V_{42} + V_{44}, \tag{1}$$

where

$$V_{\ell m} \equiv a_{\ell m} Y_{\ell m} + a_{\ell m}^{*} Y_{\ell, -m}. \tag{2}$$

We have here used spherical harmonics with the property

$$Y_{\ell, -m} = (-1)^{m} Y_{\ell m}^{*}. \tag{3}$$

In constructing the Hamiltonian it is convenient and conventional to use spin operators which have the same transformation properties as the $Y_{\ell m}$. Bleaney and Stevens[3] have discussed one such scheme, which has been reviewed by Hutchings.[4] Kikuchi and Matarrese[5] have used a more systematic prescription, based upon the Racah operators,[6] $T_m^{(\ell)}$. These were used in the analysis of Fe^{3+} in quartz,[1] and will be used here. The $T_m^{(\ell)}$ are generated by the process

$$T_{m-1}^{(\ell)} = [\ell(\ell + 1) - m(m - 1)]^{-\frac{1}{2}} [S_{-}, T_m^{(\ell)}]. \tag{4}$$

With the normalization of Kikuchi and Matarrese,[5] the $T_m^{(\ell)}$ necessary for the present purposes are

$$\begin{aligned}
T_0^{(2)} &= S_r^2 - X/3, \\
T_{\pm 2}^{(2)} &= S'^{2}_{\pm}/\sqrt{6}, \\
T_0^{(4)} &= [35S_r^4 - 30XS_r^2 + 25S_r^2 - 6X + 3X^2] \\
T_{\pm 2}^{(4)} &= -S'^{2}_{\pm} [X - 9 \mp 14S_r - 7S_r^2] \sqrt{10}/8, \\
T_{\pm 4}^{(4)} &= S'^{4}_{\pm} \sqrt{70}/16,
\end{aligned} \tag{5}$$

where

$$X \equiv S(S+1) \ . \tag{6}$$

In Eqs. (5), the subscript r refers to the two-fold axis of the crystalline electric field. The remaining two orthogonal axes will be denoted by p and q. The raising and lowering operators, $S'_{\pm}$, of Eqs. (5) are defined by

$$S'_{\pm} = S_p \pm i\, S_q . \tag{7}$$

The complete spin Hamiltonian for an S-state ion (excluding nuclear spin interactions) in an environment of C_2 symmetry, and an external magnetic field $\underset{\sim}{H}$ in an arbitrary direction, is

$$\begin{aligned} \mathcal{H} = {} & \beta_o \underset{\sim}{H} \cdot \tilde{g} \cdot \underset{\sim}{S} + C_{20}\, T_0^{(2)} + C_{22}\, (T_2^{(2)} e^{-2i\lambda_{22}} + T_{-2}^{(2)} e^{2i\lambda_{22}}) + C_{40} T_0^{(4)} \\ & + C_{42}\, (T_2^{(4)} e^{-2i\lambda_{42}} + T_{-2}^{(4)} e^{2i\lambda_{42}}) + C_{44}\, (T_4^{(4)}\, e^{-4i\lambda_{44}} + T_{-4}^{(4)}\, e^{4i\lambda_{44}}). \end{aligned} \tag{8}$$

Here β_o is the Bohr magneton (used here as positive) and $\tilde{g}$ is the g-tensor. The coefficients of the $T_m^{(\ell)}$ have been written as a real number, $C_{\ell m}$, multiplying a phase factor. The $C_{\ell m}$ clearly can be taken as positive without loss of generality, for $|m| > 0$. The C_{20} and C_{40} must be real but may be positive or negative.

To use perturbation theory at high fields, one diagonalizes the Zeeman term. If the g-tensor is isotropic, as is the usual case for S-state ions, and has been shown to be true for iron-doped quartz,[1] the axis of quantization is just the direction of $\underset{\sim}{H}$. Let this axis be the z-axis of any x, y, z orthogonal coordinate system. The direction of the z-axis relative to the p, q, r crystalline electric field axes is given by the Euler angles α, β, in the convention of Rose.[7] The axes and angles are illustrated in Figure 1.

The transformation equations from the S_r, $S'_{\pm}$ operators to the S_z, $S_{\pm}$ operators are

$$S'_{\pm} = \tfrac{1}{2}\, e^{\pm i\alpha}\, [S_{\pm}(\cos\beta + 1) + S_{\mp}(\cos\beta - 1)] + S_z e^{\pm i\alpha} \sin\beta,$$
$$S_r = -(S_+ + S_-)\tfrac{1}{2}\sin\beta + S_z \cos\beta, \tag{9}$$

where

$$S_{\pm} = S_x \pm iS_y. \tag{10}$$

The matrix elements of the $T_m^{(\ell)}$ in the representation of the eigenstates $|M\rangle$, $-S \leqslant M \leqslant S$, of S_z, are given in Tables I - V. Table VI lists, for the reader's convenience, the associated Legendre polynominals $P_{\ell m}$ for $0 \leqslant \ell \leqslant 4$ and $m \leqslant \ell$, which occur in Tables I and III. The diagonal elements of the Zeeman term are of course just $g\beta_0 HM$.

For reasons which will be discussed, we have used a perturbation analysis somewhat different from the usual one.[8] In the conventional perturbation theory, one develops the eigenstates and eigenvalues in perturbation series as

$$|E_M\rangle = |M\rangle + |M^{(1)}\rangle + |M^{(2)}\rangle + \ldots, \tag{11}$$

$$E_M = E_M^{(0)} + E_M^{(1)} + E_M^{(2)} + \ldots, \tag{12}$$

where

$$\mathcal{H} = \mathcal{H}_0 + V, \tag{13}$$
$$\mathcal{H}_0 |M\rangle = E_M^{(0)} |M\rangle, \tag{14}$$
$$\mathcal{H} |E_M\rangle = E_M |E_M\rangle, \tag{15}$$

and V is the perturbation. Substituting Eqs. (11) - (14) into (15), and performing the standard manipulations,[9] one obtains in the nondegenerate case,

$$E_M^{(1)} = \langle M | V | M \rangle | , \tag{16}$$

$$E_M^{(2)} = \sum_{M'}^{(M)} \frac{|\langle M | V | M' \rangle|^2}{E_M^{(0)} - E_{M'}^{(0)}} , \tag{17}$$

$$E_M^{(3)} = \sum_{M'}^{(M)} \sum_{M''}^{(M)} \frac{\langle M | V | M' \rangle \langle M' | V | M'' \rangle \langle M'' | V | M \rangle}{(E_M^{(0)} - E_{M'}^{(0)}) (E_M^{(0)} - E_{M''}^{(0)})} \tag{18}$$

$$- \sum_{M'}^{(M)} \frac{|\langle M | V | M' \rangle|^2 \langle M | V | M \rangle}{(E_M^{(0)} - E_{M'}^{(0)})^2} .$$

The notation $\sum_{M'}^{(M)}$, for example, means that $M' = M$ is excluded from the summation on M'. Now for Fe^{3+} in quartz, it turns out that C_{20} is numerically quite large: its correction to the line-position values is sometimes more than 30% of the free-ion value. Thus $\langle M | V | M \rangle$ is "large." It does not occur in the second-order term $E_M^{(2)}$, but does occur in the third order terms, with the result that for certain lines and certain orientations, the third-order terms should not be neglected. However, for $\beta = 0^\circ$ (H parallel to the two-fold axis), the $T_0^{(2)}$ term lies completely on the diagonal. Therefore by including it in $\mathcal{H}_0$, a vast improvement in accuracy in the second-order calculations is achieved. We systematically have put all diagonal elements of V in with $\mathcal{H}_0$. This renormalizes $E_M^{(0)}$, and gives the following perturbation corrections:

$$E_M^{(1)} = 0 , \tag{19}$$

$$E_M^{(2)} = \sum_{M'}^{(M)} \frac{|\langle M|V|M'\rangle|^2}{E_M^{(0)} - E_{M'}^{(0)}} , \tag{20}$$

$$E_M^{(3)} = \sum_{M'}^{(M)} \sum_{M''}^{(M)} \frac{\langle M|V|M'\rangle \langle M'|V|M''\rangle \langle M''|V|M\rangle}{(E_M^{(0)} - E_{M'}^{(0)}) (E_M^{(0)} - E_{M''}^{(0)})} . \tag{21}$$

At $\beta = 0^o$ the third-order terms in this reformulation are entirely negligible at K-band frequencies in iron-doped quartz. For $\beta = 90^o$, the $T_0^{(2)}$ term has off-diagonal elements, and the two perturbation treatments tend to be equivalent in their results. (These conclusions could be drawn as soon as rough estimates of the $C_{\ell m}$ were known).

The line-position formulas, through second order in the modified perturbation treatment, are given in Table VII. The definitions of the terms appearing in this Table are given in Table VIII. H_1 corresponds to the $(E_{5/2} - E_{3/2})$ transition, H_2 to the $(E_{3/2} - E_{1/2})$ transition and so on.

One other point may be discussed here. C_2 symmetry, by itself, does not define the orientations of the p and q crystalline field axes. For example, from a crystallographic analysis, one knows that the optic axis of quartz (Z) lies in the p, q plane, and that the X-axis of the quartz coincides with the two-fold axis of one of the sites at which the Fe^{3+} resides. (See Fig. 1). The angle α, defined as measured from the p-axis, is not immediately measurable. The measured angle is $\alpha - \Theta$, where Θ is the (arbitrary) angle from p to Z. For example, when $\underset{\sim}{H}$ is parallel to the optic axis, parameters such as $C_{22} \cos 2(\Theta - \lambda_{22})$ and $C_{44} \sin 4(\Theta - \lambda_{44})$ appear in the line position formulas. Thus the angles λ_{22} and λ_{44}, which locate the V_{22} and V_{44} lobes in the p, q plane, can be measured only relative to Θ, that is, relative to the optic axis. In reference 1, we arbitrarily set p to coincide with Z (i. e., $\Theta = 0$); this was purely for convenience.

We turn finally to the line-intensity formulas. We consider only the case for which $\underset{\sim}{H}$ is along the r-axis, and the microwave field H_1 lies in the p, q plane (Fig. 2). It was for this situation that an interesting effect was uncovered in iron-doped quartz: for H_1 nearly perpendicular to the optic axis, and for small values of H, several lines are readily observable. However, when $\underset{\sim}{H}_1$ is rotated into orientations near the Z-axis, all the lines disappear into the noise. Substitution of the parameter values, determined from the high-field data, into the line-intensity formulas shows that this effect is to be expected, and further confirms our choice of parameter values,[1] including the orientations of the crystalline field lobes. However, line intensities are difficult to measure accurately, and so the determination of the parameters from line-position analyses is still to be preferred.

The interaction between the ion and the microwave field is (see Fig. 2)

$$\begin{aligned} \mathcal{H}_1 &= \frac{1}{2} g\beta_o H_1 \left[S_p \cos \Phi + S_q \sin \Phi \right] \\ &= \frac{1}{2} g\beta_o H_1 \left[S_+ e^{-i\Phi} + S_- e^{i\Phi} \right] \quad . \end{aligned} \tag{22}$$

Here we have used Eqs. (7) and (9), setting both α and β equal to zero. (The value of α here is actually arbitrary, as it is in the spin-Hamiltonian matrix for $\underset{\sim}{H}$ parallel to the r-axis (Table IX). However, the same value of α must be used in both places for consistency; we use $\alpha = 0$.)

For $\underset{\sim}{H}$ parallel to the r-axis, the 6×6 matrix of the spin Hamiltonian separates into two independent 3×3 matrices. This case is given in Table IX. The $|5/2\rangle$, $|1/2\rangle$, and $|-3/2\rangle$ states couple together to form three exact eigenstates of the Hamiltonian, which we call $|E_k^+\rangle$, k = 0, 1, 2. Similarly, $|-5/2\rangle$, $|-1/2\rangle$, and $|3/2\rangle$ couple to form $|E_k^-\rangle$. The secular equations for determining the energies $E_k^\pm$ and eigenstates $|E_k^\pm\rangle$ are thus cubic and can be solved analytically.

Writing

$$|E_k^\pm\rangle = a_k^\pm\,|\pm 5/2\rangle + b_k^\pm\,|\pm 1/2\rangle + c_k^\mp\,|\mp 3/2\rangle, \tag{23}$$

one finds the nonvanishing matrix elements of $\mathcal{H}_1$ (Eq. (22)) in the $|E_k^\pm\rangle$ basis to be

$$\langle E_\ell^-|\mathcal{H}_1|E_k^+\rangle = \frac{1}{2} g\beta_o H_1 \left\{\sqrt{5}\, e^{i\Phi}(a_\ell^{-*} c_k^- + c_\ell^{+*} a_k^+) + 3e^{i\Phi} b_\ell^{-*} b_k^+ + \sqrt{8}\, e^{-i\Phi}(b_\ell^{-*} c_k^- + c_\ell^{+*} b_k^+)\right\}. \tag{24}$$

The line intensities are proportional to the absolute-value-squared of Eq. (24).

It is instructive first to consider two special cases. Assume that $C_{42} = C_{22} = 0$ and that $C_{44} \neq 0$. From Table IX one sees at once that the states $|\pm \frac{1}{2}\rangle$ are uncoupled from the remaining states, and hence are eigenstates of the spin Hamiltonian. Thus, for one value of k the coefficients $b_k^\pm$ of Eq. (23) are unity, and $a_k^\pm$ and $c_k^\mp$ are zero, while for the other two values of k, $b_k^\pm$ is zero, and $a_k^\pm$ and $c_k^\mp$ are not. By inspection of Eq. (24), one sees that $\langle E_\ell^-|\mathcal{H}_1|E_k^+\rangle$ then depends upon Φ only through $e^{i\Phi}$ or through $e^{-i\Phi}$, so that all line intensities are independent of Φ. That is, although there are lobes of V_{44} in the p, q plane, the line intensities are uniform for $\underset{\sim}{H}_1$ anywhere in that plane.

Next consider $C_{22} \neq 0$ and $C_{44} = C_{42} = 0$. This case is more complicated than the preceding, but still quite tractable. By expressing both $a_k^{\pm}$ and $c_k^{\mp}$ in terms of $b_k^{\pm}$ from the secular equations, one can draw the desired conclusion without further determining the coefficients or the energies. After a small amount of manipulation, one can write Eq. (24) as

$$\langle E_\ell^- | \mathcal{H}_1 | E_k^+ \rangle = g\beta_o H_1 b_\ell^{-*} b_k^+ \left\{ 10 C_{22}^{\,2} e^{i\Phi} \left(\frac{1}{(f_{-5} - E_\ell^-)(f_{-3} - E_k^+)} + \frac{1}{(f_3 - E_\ell^-)(f_5 - E_k^+)} \right) + \frac{3}{2} e^{i\Phi} - 2\sqrt{6}\, C_{22}\, e^{-i(\Phi - 2\lambda_{22})} \left(\frac{1}{f_{-3} - E_k^+} + \frac{1}{f_3 - E_\ell^-} \right) \right\}, \tag{25}$$

where $f_{-5} \equiv \langle -\frac{5}{2} | \mathcal{H} | -\frac{5}{2} \rangle$, $f_3 \equiv \langle \frac{3}{2} | \mathcal{H} | \frac{3}{2} \rangle$, etc. Squaring the absolute value, one has

$$|\langle E_\ell^- | \mathcal{H}_1 | E_k^+ \rangle|^2 = (g\beta_o H_1)^2 \, |b_\ell^-|^2 \, |b_k^+|^2 \left\{ (A_{k\ell} + B_{k\ell})^2 \cos^2(\Phi - \lambda_{22}) + (A_{k\ell} - B_{k\ell})^2 \sin^2(\Phi - \lambda_{22}) \right\}, \tag{26}$$

where $A_{k\ell}$ and $B_{k\ell}$ are the coefficients of $e^{i\Phi}$ and $e^{-i(\Phi - 2\lambda_{22})}$, respectively, within the braces of Eq. (25), and are real. In this case line-intensity extrema do exist, occurring at $\Phi = \lambda_{22}$ and every 90° therefrom.

When C_{22}, C_{42}, and C_{44} are all considered, the equations for the line-intensity extrema are quite complicated (transcendental) and we will not give them here. However, since C_{42}, $C_{44} \ll C_{22}$ for iron in quartz, we can expect that the line-intensity extrema will be shifted but slightly from the V_{22} lobes, and this is indeed the case experimentally.[1] The coefficients $a_k^{\pm}$, $b_k^{\pm}$, $c_k^{\mp}$ were determined by computer from the analytic solutions to the secular equations for many values of H, and the locations (Φ) of the maxima and minima in the line intensities were calculated. Agreement with these results is observed to within our ability to locate the intensity extrema experimentally.

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{10}{3} P_{20}$	$\frac{2\sqrt{5}}{3} P_{21}$	$\frac{\sqrt{10}}{6} P_{22}$	0	0	0
3/2	$\frac{2\sqrt{5}}{3} P_{21}$	$-\frac{2}{3} P_{20}$	$\frac{2\sqrt{2}}{3} P_{21}$	$\frac{1}{\sqrt{2}} P_{22}$	0	0
1/2	$\frac{\sqrt{10}}{6} P_{22}$	$\frac{2\sqrt{2}}{3} P_{21}$	$-\frac{8}{3} P_{20}$	0	$\frac{1}{\sqrt{2}} P_{22}$	0
-1/2	0	$\frac{1}{\sqrt{2}} P_{22}$	0	$-\frac{8}{3} P_{20}$	$\frac{-2\sqrt{2}}{3} P_{21}$	$\frac{\sqrt{10}}{6} P_{22}$
-3/2	0	0	$\frac{1}{\sqrt{2}} P_{22}$	$-\frac{2\sqrt{2}}{3} P_{21}$	$-\frac{2}{3} P_{20}$	$-\frac{2\sqrt{5}}{3} P_{21}$
-5/2	0	0	0	$\frac{\sqrt{10}}{6} P_{22}$	$\frac{-2\sqrt{5}}{3} P_{21}$	$\frac{10}{3} P_{20}$

Table I. Matrix of $T_0^{(2)} = S_r^2 - X/3$. The $P_{\ell m}$ are associated Legendre polynomials (see Table VI).

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{10}{3} Q_{20}$	$\frac{2\sqrt{5}}{3} Q_{21}^{+}$	$\frac{\sqrt{10}}{6} Q_{22}^{+}$	0	0	0
3/2	$\frac{2\sqrt{5}}{3} Q_{21}^{-}$	$-\frac{2}{3} Q_{20}$	$\frac{2\sqrt{2}}{3} Q_{21}^{+}$	$\frac{1}{\sqrt{2}} Q_{22}^{+}$	0	0
1/2	$\frac{\sqrt{10}}{6} Q_{22}^{-}$	$\frac{2\sqrt{2}}{3} Q_{21}^{-}$	$-\frac{8}{3} Q_{20}$	0	$\frac{1}{\sqrt{2}} Q_{22}^{+}$	0
-1/2	0	$\frac{1}{\sqrt{2}} Q_{22}^{-}$	0	$-\frac{8}{3} Q_{20}$	$-\frac{2\sqrt{2}}{3} Q_{21}^{+}$	$\frac{\sqrt{10}}{6} Q_{22}^{+}$
-3/2	0	0	$\frac{1}{\sqrt{2}} Q_{22}^{-}$	$-\frac{2\sqrt{2}}{3} Q_{21}^{-}$	$-\frac{2}{3} Q_{20}$	$-\frac{2\sqrt{5}}{3} Q_{21}^{+}$
-5/2	0	0	0	$\frac{\sqrt{10}}{6} Q_{22}^{-}$	$-\frac{2\sqrt{5}}{3} Q_{21}^{-}$	$\frac{10}{3} Q_{20}$

Table II. Matrix of $T_2^{(2)} = S_+^{\prime 2}/\sqrt{6}$. $\langle M \mid T_{-2}^{(2)} \mid M' \rangle = \langle M' \mid T_2^{(2)} \mid M \rangle^*$.

$$Q_{20} = \frac{\sqrt{6}}{4} \sin^2\beta \; e^{2i\alpha}; \quad Q_{21}^{\pm} = \sqrt{\frac{3}{2}} \sin\beta (\cos\beta \pm 1) e^{2i\alpha};$$

$$Q_{22}^{\pm} = \sqrt{\frac{3}{2}} (\cos\beta \pm 1)^2 e^{2i\alpha} .$$

M	5/2	3/2	1/2	-1/2	-3/2	-5/2
5/2	$\frac{15}{2} P_{40}$	$\frac{3\sqrt{5}}{2} P_{41}$	$\frac{3}{8}\sqrt{10}\, P_{42}$	$\frac{\sqrt{10}}{8} P_{43}$	$\frac{\sqrt{5}}{16} P_{44}$	0
3/2	$\frac{3\sqrt{5}}{2} P_{41}$	$\frac{-45}{2} P_{40}$	$\frac{-15}{\sqrt{8}} P_{41}$	$\frac{-5}{8}\sqrt{2}\, P_{42}$	0	$\frac{\sqrt{5}}{16} P_{44}$
1/2	$\frac{3}{8}\sqrt{10}\, P_{42}$	$\frac{-15}{\sqrt{8}} P_{41}$	$15 P_{40}$	0	$-\frac{5}{8}\sqrt{2}\, P_{42}$	$\frac{-\sqrt{10}}{8} P_{43}$
-1/2	$\frac{\sqrt{10}}{8} P_{43}$	$-\frac{5}{8}\sqrt{2}\, P_{42}$	0	$15 P_{40}$	$\frac{15}{\sqrt{8}} P_{41}$	$\frac{3}{8}\sqrt{10}\, P_{42}$
-3/2	$\frac{\sqrt{5}}{16} P_{44}$	0	$-\frac{5}{8}\sqrt{2}\, P_{42}$	$\frac{15}{\sqrt{8}} P_{41}$	$\frac{-45}{2} P_{40}$	$\frac{-3\sqrt{5}}{2} P_{41}$
-5/2	0	$\frac{\sqrt{5}}{16} P_{44}$	$\frac{-\sqrt{10}}{8} P_{43}$	$\frac{3}{8}\sqrt{10}\, P_{42}$	$\frac{-3\sqrt{5}}{2} P_{41}$	$\frac{15}{2} P_{40}$

Table III. Matrix of $T_0^{(4)} = \frac{1}{8}\, [\, 35S_r^4 - 30XS_r^2 + 25S_r^2 - 6X + 3X^2]$. The $P_{\ell m}$ are associated Legendre polynominals (see Table VI).

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{15}{2} R_{40}$	$\frac{3\sqrt{5}}{2} R_{41}^{+}$	$\frac{3}{8}\sqrt{10}\, R_{42}^{+}$	$\frac{\sqrt{10}}{8} R_{43}^{+}$	$\frac{\sqrt{5}}{16} R_{44}^{+}$	0
3/2	$\frac{3\sqrt{5}}{2} R_{41}^{-}$	$-\frac{45}{2} R_{40}$	$-\frac{15}{\sqrt{8}} R_{41}^{+}$	$-\frac{5}{8}\sqrt{2}\, R_{42}^{+}$	0	$\frac{\sqrt{5}}{16} R_{44}^{+}$
1/2	$\frac{3}{8}\sqrt{10}\, R_{42}^{-}$	$-\frac{15}{\sqrt{8}} R_{41}^{-}$	$15\, R_{40}$	0	$-\frac{5}{8}\sqrt{2}\, R_{42}^{+}$	$-\frac{\sqrt{10}}{8} R_{43}^{+}$
-1/2	$\frac{\sqrt{10}}{8} R_{43}^{-}$	$-\frac{5}{8}\sqrt{2}\, R_{42}^{-}$	0	$15\, R_{40}$	$\frac{15}{\sqrt{8}} R_{41}^{+}$	$\frac{3}{8}\sqrt{10}\, R_{42}^{+}$
-3/2	$\frac{\sqrt{5}}{16} R_{44}^{-}$	0	$-\frac{5}{8}\sqrt{2}\, R_{42}^{-}$	$\frac{15}{\sqrt{8}} R_{41}^{-}$	$-\frac{45}{2} R_{40}$	$-\frac{3\sqrt{5}}{2} R_{41}^{+}$
-5/2	0	$\frac{\sqrt{5}}{16} R_{44}^{-}$	$-\frac{\sqrt{10}}{8} R_{43}^{-}$	$\frac{3}{8}\sqrt{10}\, R_{42}^{-}$	$-\frac{3\sqrt{5}}{2} R_{41}^{-}$	$\frac{15}{2} R_{40}$

Table IV. Matrix of $T_2^{(4)} = \frac{-\sqrt{10}}{8} S_+'^{\,2}(X - 9 - 14S_r - 7S_r^2)$.

$\langle M \mid T_{-2}^{(4)} \mid M' \rangle = \langle M' \mid T_2^{(4)} \mid M \rangle^*$. $R_{40} = \frac{\sqrt{10}}{8} s^2(7c^2 - 1)\, e^{2i\alpha}$;

$R_{41}^{\pm} = \frac{-\sqrt{10}}{4} s(c \pm 1)(1 \pm 7c - 14c^2)e^{2i\alpha}$; $R_{42}^{\pm} = 3\sqrt{\frac{5}{2}}(c \pm 1)^2(1 \mp 7c + 7c^2)e^{2i\alpha}$;

$R_{43}^{\pm} = -21\sqrt{\frac{5}{2}}\, s(c \pm 1)^2(2c \mp 1)e^{2i\alpha}$; $R_{44}^{\pm} = -21\sqrt{10}\, s^2(c \pm 1)^2 e^{2i\alpha}$;

$s = \sin\beta$, $c = \cos\beta$.

M	5/2	3/2	1/2	- 1/2	- 3/2	- 5/2
5/2	$\frac{15}{2} S_{40}$	$\frac{3}{2}\sqrt{5}\, S^{+}_{41}$	$\frac{3}{8}\sqrt{10}\, S^{+}_{42}$	$\frac{\sqrt{10}}{8} S^{+}_{43}$	$\frac{\sqrt{5}}{16} S^{+}_{44}$	0
3/2	$\frac{3\sqrt{5}}{2} S^{-}_{41}$	$\frac{-45}{2} S_{40}$	$\frac{-15}{\sqrt{8}} S^{+}_{41}$	$-\frac{5}{8}\sqrt{2}\, S^{+}_{42}$	0	$\frac{\sqrt{5}}{16} S^{+}_{44}$
1/2	$\frac{3}{8}\sqrt{10}\, S^{-}_{42}$	$\frac{-15}{\sqrt{8}} S^{-}_{41}$	$15\, S_{40}$	0	$-\frac{5}{8}\sqrt{2}\, S^{+}_{42}$	$\frac{-\sqrt{10}}{8} S^{+}_{43}$
-1/2	$\frac{\sqrt{10}}{8} S^{-}_{43}$	$-\frac{5}{8}\sqrt{2}\, S^{-}_{42}$	0	$15\, S_{40}$	$\frac{15}{\sqrt{8}} S^{+}_{41}$	$\frac{3}{8}\sqrt{10}\, S^{+}_{42}$
-3/2	$\frac{\sqrt{5}}{16} S^{-}_{44}$	0	$-\frac{5}{8}\sqrt{2}\, S^{-}_{42}$	$\frac{15}{\sqrt{8}} S^{-}_{41}$	$\frac{-45}{2} S_{40}$	$\frac{-3\sqrt{5}}{2} S^{+}_{41}$
-5/2	0	$\frac{\sqrt{5}}{16} S^{-}_{44}$	$\frac{-\sqrt{10}}{8} S^{-}_{43}$	$\frac{3}{8}\sqrt{10}\, S^{-}_{42}$	$\frac{-3\sqrt{5}}{2} S^{-}_{41}$	$\frac{15}{2} S_{40}$

Table V. Matrix of $T^{(4)}_4 = \frac{\sqrt{70}}{16} S'^{\,4}_{+}$. $\langle M \mid T^{(4)}_{-4} \mid M' \rangle = \langle M' \mid T^{(4)}_4 \mid M \rangle^*$.

$$S_{40} = \frac{\sqrt{70}}{16} s^4 e^{4i\alpha}; \quad S^{\pm}_{41} = \frac{\sqrt{70}}{4} s^3 (c \pm 1)\, e^{4i\alpha}; \quad S^{\pm}_{42} = \frac{3}{4}\sqrt{70}\, s^2 (c \pm 1)^2 e^{4i\alpha};$$

$$S^{\pm}_{43} = \frac{3}{2}\sqrt{70}\, s (c \pm 1)^3 e^{4i\alpha}; \quad S^{\pm}_{44} = \frac{3}{2}\sqrt{70}\, (c \pm 1)^4 e^{4i\alpha};$$

$s = \sin\beta$; $c = \cos\beta$.

$\ell \backslash m$	0	1	2	3	4
0	1				
1	c	$-s$			
2	$\frac{1}{2}(3c^2-1)$	$-3sc$	$3s^2$		
3	$\frac{1}{2}c(5c^2-3)$	$-\frac{3}{2}s(5c^2-1)$	$15s^2c$	$-15s^3$	
4	$\frac{1}{8}(35c^4-30c^2+3)$	$-\frac{5}{2}sc(7c^2-3)$	$\frac{15}{2}s^2(7c^2-1)$	$-105s^3c$	$105s^4$

Table VI. Associated Legendre Polynominals, $P_{\ell m}$.

($s = \sin\beta$, $c = \cos\beta$)

$$H_1 = H_o + \Delta_2 - \frac{2V_{53}}{H_1 - \Delta_2} + \frac{V_{31}}{H_1 - \Delta_1} - \frac{V_{51}}{2H_1 - \Delta_{12}} + \frac{V_{3,-1}}{2H_1 - \Delta_1} - \frac{V_{5,-1}}{3H_1 - \Delta_{12}} - \frac{2\Delta_2 V_{5,-3}}{16H_1^2 - \Delta_2^2}$$

$$H_2 = H_o + \Delta_1 + \frac{V_{53}}{H_2 - \Delta_2} - \frac{2V_{31}}{H_2 - \Delta_1} - \frac{V_{51}}{2H_2 - \Delta_{12}} - \frac{2\Delta_1 V_{3,-1}}{4H_2^2 - \Delta_1^2} + \frac{V_{5,-1}}{3H_2 + \Delta_{12}} - \frac{V_{5,-3}}{4H_2 + \Delta_2}$$

$$H_3 = H_0 + \frac{2H_3 V_{31}}{H_3^2 - \Delta_1^2} + \frac{4H_3 V_{51}}{4H_3^2 - \Delta_{12}^2} - \frac{4H_3 V_{3,-1}}{4H_3^2 - \Delta_1^2} - \frac{6H_3 V_{5,-1}}{9H_3^2 - \Delta_{12}^2}$$

$$H_4 = H_o - \Delta_1 + \frac{V_{53}}{H_4 + \Delta_2} - \frac{2V_{31}}{H_4 + \Delta_1} - \frac{V_{51}}{2H_4 + \Delta_{12}} + \frac{2\Delta_1 V_{3,-1}}{4H_4^2 - \Delta_1^2} + \frac{V_{5,-1}}{3H_4 - \Delta_{12}} - \frac{V_{5,-2}}{4H_4 - \Delta_2}$$

$$H_5 = H_o - \Delta_2 - \frac{2V_{53}}{H_5 + \Delta_2} + \frac{V_{31}}{H_5 + \Delta_1} - \frac{V_{51}}{2H_5 + \Delta_{12}} + \frac{V_{3,-1}}{2H_5 + \Delta_1} - \frac{V_{5,-1}}{3H_5 + \Delta_{12}} + \frac{2\Delta_2 V_{5,-3}}{16H_5^2 - \Delta_2^2}$$

Table VII. Line Position Formulas. $H_o = \hbar\omega/g\beta_o$. H_1 corresponds to the $(E_{5/2} - E_{3/2})$ transition, etc.

$$g\beta_o\Delta_1 = (1 - 3c^2)\, C_{20} - \sqrt{6}\; s^2 c_{22} C_{22} + \frac{75}{16} (3 - 30c^2 + 35c^4)\, C_{40}$$

$$+ \frac{75}{16} \sqrt{70}\; s^4 c_{44} C_{44} - \frac{75}{8} \sqrt{10}\; s^2 (1 - 7c^2)\, c_{42} C_{42}$$

$$g\beta_o\Delta_2 = 2(1 - 3c^2)\, C_{20} - 2\sqrt{6}\; s^2 c_{22} C_{22} - \frac{15}{4} (3 - 30c^2 + 35c^4)\, C_{40}$$

$$- \frac{15}{4} \sqrt{70}\; s^4 c_{44} C_{44} + \frac{15}{2} \sqrt{10}\; s^2 (1 - 7c^2)\, c_{42} C_{42}$$

$$g^2\beta_o^2\, V_{5,3} = 20s^2 \left[\frac{2}{\sqrt{6}}\, s_{22} C_{22} - \frac{3}{8} \sqrt{10}\, (1 - 7c^2)\, s_{42} C_{42} + \frac{3}{8} \sqrt{70}\, s^2 s_{44} C_{44}\right]^2$$

$$+ 20s^2c^2 \left[C_{20} - \frac{2}{\sqrt{6}}\, c_{22} C_{22} - \frac{15}{8} (3 - 7c^2) C_{40}\right.$$

$$\left. + \frac{3}{4} \sqrt{10}\, (4 - 7c^2)\, c_{42} C_{42} - \frac{3}{8} \sqrt{70}\; s^2 c_{44} C_{44}\right]^2$$

$$g^2\beta_o^2 V_{3,1} = 8s^2 \left[\frac{2}{\sqrt{6}}\, s_{22} C_{22} + \frac{15}{16} \sqrt{10}\, (1 - 7c^2)\, s_{42} C_{42} - \frac{15}{16} \sqrt{70}\; s^2 s_{44} C_{44}\right]^2$$

$$+ 8s^2c^2 \left[C_{20} - \frac{2}{\sqrt{6}}\, c_{22} C_{22} + \frac{75}{16} (3 - 7c^2)\, C_{40}\right.$$

$$\left. - \frac{15}{8} \sqrt{10}\, (4 - 7c^2)\, c_{42} C_{42} + \frac{15}{16} \sqrt{70}\; s^2 c_{44} C_{44}\right]^2$$

$$g^2\beta_o^2 V_{5,1} = \frac{5}{2} \left[s^2 C_{20} + \frac{2}{\sqrt{6}} (1 + c^2)\, c_{22} C_{22} - \frac{45}{8}\, s^2 (1 - 7c^2)\, C_{40}\right.$$

$$\left. + \frac{9}{4} \sqrt{10}\, (1 - 6c^2 + 7c^4)\; c_{42} C_{42} + \frac{9}{8} \sqrt{70}\; s^2 (1 + c^2)\, c_{44} C_{44}\right]^2$$

$$+ 10\, c^2 \left[\frac{2}{\sqrt{6}}\; s_{22} C_{22} - \frac{9}{8} \sqrt{10}\, (5 - 7c^2)\, s_{42} C_{42} + \frac{9}{8} \sqrt{70}\; s^2 s_{44} C_{44}\right]^2$$

Table VIII. Formulas supplementary to Table VII. (Continued on next page)

$$g^2\beta_o^2 V_{3,-1} = \frac{9}{2}\Big[s^2 C_{20} + \frac{2}{\sqrt{6}}(1 + c^2)\, c_{22}C_{22} + \frac{25}{8}s^2 (1 - 7c^2)\, C_{40}$$

$$- \frac{5}{4}\sqrt{10}\,(1 - 6c^2 + 7c^4)\, c_{42}C_{42} - \frac{5}{8}\sqrt{70}\, s^2 (1 + c^2)\, c_{44}C_{44}\Big]^2$$

$$+ 18c^2\Big[\frac{2}{\sqrt{6}}\, s_{22}C_{22} + \frac{5}{8}\sqrt{10}\,(5 - 7c^2)\, s_{42}C_{42} - \frac{5}{8}\sqrt{70}\, s^2 s_{44}C_{44}\Big]^2$$

$$g^2\beta_o^2 V_{5,-1} = \frac{3^2 \cdot 5^2 \cdot 7}{4^2}\, s^2 \Big\{c^2\Big[\frac{\sqrt{70}}{2}\, s^2 C_{40} + 2\sqrt{7}\, c^2 c_{42}C_{42}$$

$$- (3 + c^2)\, c_{44}C_{44}\Big]^2 + \Big[\sqrt{7}\,(1 - 3c^2)\, s_{42}C_{42} + (1 + 3c^2) s_{44}C_{44}\Big]^2\Big\}$$

$$g^2\beta_o^2 V_{5,-3} = \frac{3^2 \cdot 5^2 \cdot 7}{8^3}\Big[\sqrt{70}\, s^4 C_{40} - 4\sqrt{7}\, s^2 (1 + c^2)\, c_{42}C_{42}$$

$$+ 2(1 + 6c^2 + c^4)\, c_{44}C_{44}\Big]^2$$

$$+ \frac{3^2 \cdot 5^2 \cdot 7c^2}{8}\Big[\sqrt{7}\, s^2 s_{42}C_{42} - (1 + c^2)\, s_{44}C_{44}\Big]^2$$

$$\Delta_{12} \equiv \Delta_1 + \Delta_2$$

$s = \sin\beta$	$c = \cos\beta$
$s_{22} = \sin 2(\alpha - \lambda_{22})$	$c_{22} = \cos 2(\alpha - \lambda_{22})$
$s_{44} = \sin 4(\alpha - \lambda_{44})$	$c_{44} = \cos 4(\alpha - \lambda_{44})$
$s_{42} = \sin 2(\alpha - \lambda_{42})$	$c_{42} = \cos 2(\alpha - \lambda_{42})$

Table VIII. Formulas supplementary to Table VII.

M	5/2	1/2	- 3/2	- 5/2	- 1/2	3/2
5/2	$\frac{5}{2} G + \frac{10}{3} C_{20} + \frac{15}{2} C_{40}$	$2\sqrt{\frac{5}{3}} C_{22} e^{-2i\lambda_{22}} + \frac{45}{2} C_{42} e^{-2i\lambda_{42}}$	$\frac{15}{2}\sqrt{14} C_{44} e^{-4i\lambda_{44}}$			
1/2	$2\sqrt{\frac{5}{3}} C_{22} e^{2i\lambda_{22}} + \frac{45}{2} C_{42} e^{2i\lambda_{42}}$	$\frac{1}{2} G - \frac{8}{3} C_{20} + 15 C_{40}$	$2\sqrt{3} C_{22} e^{-2i\lambda_{22}} - \frac{15}{2}\sqrt{5} C_{42} e^{-2i\lambda_{42}}$			
-3/2	$\frac{15}{2}\sqrt{14} C_{44} e^{4i\lambda_{44}}$	$-\frac{15}{2}\sqrt{5} C_{42} e^{2i\lambda_{42}} + 2\sqrt{3} C_{22} e^{2i\lambda_{22}}$	$-\frac{3}{2} G - \frac{2}{3} C_{20} - \frac{45}{2} C_{40}$			
-5/2				$-\frac{5}{2} G + \frac{10}{3} C_{20} + \frac{15}{2} C_{40}$	$2\sqrt{\frac{5}{3}} C_{22} e^{2i\lambda_{22}} + \frac{45}{2} C_{42} e^{-2i\lambda_{42}}$	$\frac{15}{2}\sqrt{14} C_{44} e^{4i\lambda_{44}}$
-1/2				$2\sqrt{\frac{5}{3}} C_{22} e^{-2i\lambda_{22}} + \frac{45}{2} C_{42} e^{-2i\lambda_{42}}$	$-\frac{1}{2} G - \frac{8}{3} C_{20} + 15 C_{40}$	$-\frac{15}{2}\sqrt{5} C_{42} e^{+2i\lambda_{42}} + 2\sqrt{3} C_{22} e^{2i\lambda_{22}}$
3/2				$\frac{15}{2}\sqrt{14} C_{44} e^{-4i\lambda_{44}}$	$-\frac{15}{2}\sqrt{5} C_{42} e^{-2i\lambda_{42}} + 2\sqrt{3} C_{22} e^{-2i\lambda_{22}}$	$\frac{3}{2} G - \frac{2}{3} C_{20} - \frac{45}{2} C_{40}$

Table IX. Spin-Hamiltonian matrix for C_2 symmetry, for $\underset{\sim}{H}$ parallel to the two-fold axis. $G \equiv g\beta_o H$.

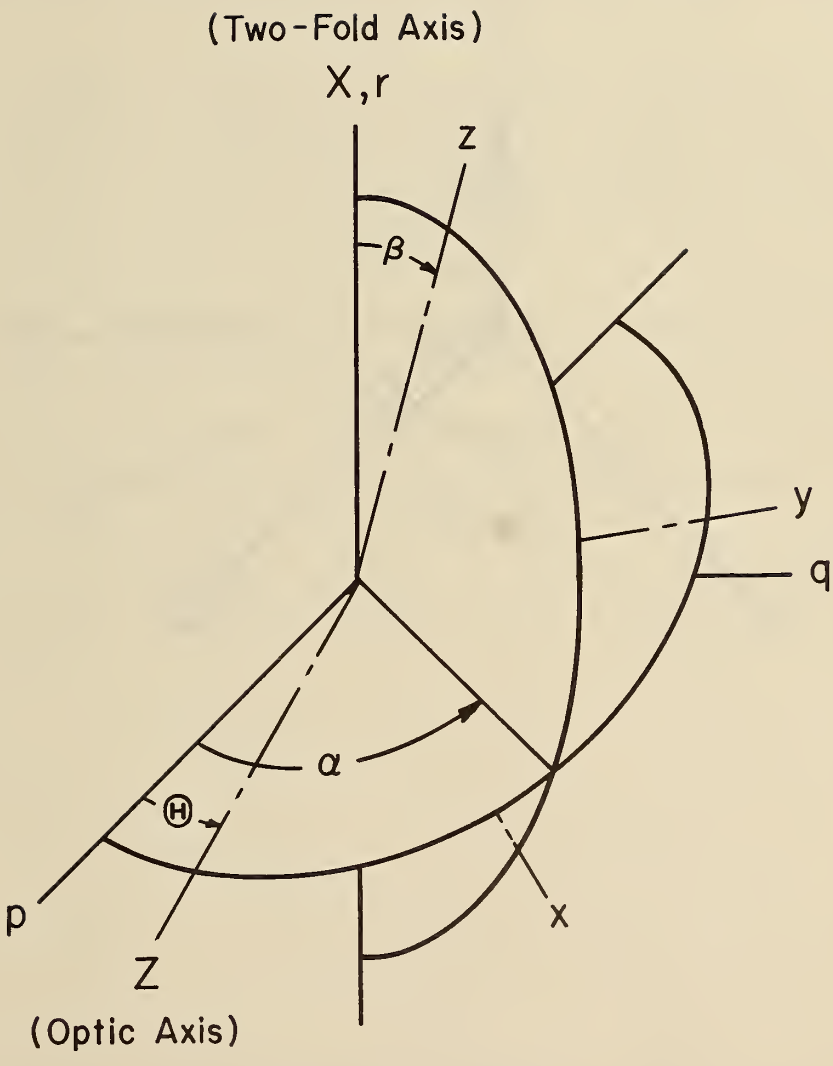

Figure 1. Relation between the p, q, r crystalline electric field axes and the x, y, z quantization axes. The optic axis (Z) of the quartz crystal is also shown.

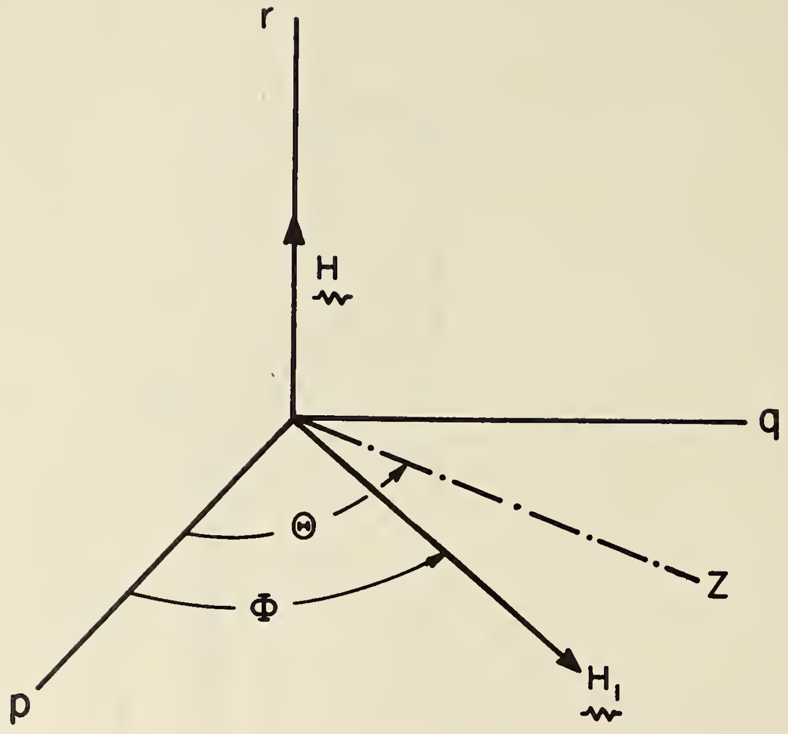

Figure 2. The orientation of the microwave field H_1 in the p, q plane, used in the line-intensity analysis. The optic axis (Z) is also shown.

REFERENCES

1. L. M. Matarrese, J. S. Wells, and R. L. Peterson, J. Chem. Phys., 50, 2350-2360 (1968).
2. A. R. Cook and L. M. Matarrese, J. Chem. Phys., 50, 2361-2364 (1968).
3. B. Bleaney and K. W. H. Stevens, Repts. Progr. Phys. 16, 108 (1953).
4. M. T. Hutchings, in Solid State Physics (Academic Press, New York, 1964), edited by F. Seitz and D. Turnbull, Vol. 16, p. 227.
5. C. Kikuchi and L. M. Matarrese, J. Chem. Phys., 33, 601 (1960).
6. G. Racah, Phys. Rev., 62, 438 (1942).
7. M. E. Rose, Elementary Theory of Angular Momentum (John Wiley & Sons, Inc., London, 1957), p. 50.
8. This procedure is discussed briefly by E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, (Cambridge Univ. Press, Cambridge, 1951), pp. 35-36.
9. E. Merzbacher, Quantum Mechanics (John Wiley & Sons, New York, 1961), Chap. 16.

GPO 851-765

U.S. DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20230

OFFICIAL BUSINESS

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE