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ELECTRIC QUADRUPOLE INTERACTION IN THE
NUCLEAR MAGNETIC RESONANCE

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ABSTRACT

The general case of the dependence on crystal orientation of the frequency splitting of the nuclear magnetic resonance absorption line in a single crystal sample into 2I components due to the coupling between the nuclear electric quadrupole moment and the electric field gradient in the crystal at the site of the nuclei in question is examined both theoretically and experimentally.

The theoretical part of this thesis consists of a detailed exposition of the first order perturbation theory applicable to crystals with axially symmetric fields which was outlined in condensed form by Prof. R. V. Pound, and of the extension of this first order theory to non-axially symmetric cases suggested by Prof. G. M. Volkoff.

The experimental part of this thesis consists of the description of an exploratory experiment proposed by the author, and performed by him, with some assistance from Mr. H. E. Petch, for the purpose of obtaining a preliminary check on the theory, and of demonstrating the feasibility of a later more carefully performed experiment. Such an experiment with an improved crystal mount has since then been performed by Mr. Petch.

A single crystal of spodumene was used, and the angular dependence of the frequency splitting^{for Li^{7}} was measured

as the crystal was rotated about the C-axis of its monoclinic structure. The apparatus used was an oscillating detector type of nuclear magnetic resonance spectrometer previously designed and built by Dr. T. L. Collins. The axis of rotation of the crystal was kept perpendicular to the uniform magnetic field of the spectrometer. The direction of the b-axis of the crystal inferred from this rotation was found to coincide within experimental error with its orientation as obtained later by standard optical methods.

An experiment was designed to indicate the relative magnitudes of the spin-lattice relaxation by magnetic dipole and electric quadrupole coupling is proposed.

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ELECTRIC QUADRUPOLE INTERACTION IN THE NUCLEAR MAGNETIC RESONANCE

INTRODUCTION

Nuclear paramagnetic resonances absorption (PTP) or nuclear induction (BHP) provides a means of observing the interaction between atomic nuclei and their surroundings. These interactions may be either of a magnetic or electric type. For nuclei of spin $1/2$, the interactions are of necessity magnetic only. Nuclei of spin I greater than $1/2$ may possess an electric quadrupole moment which will interact with the gradient of an electric field at the nucleus. In liquids, where the electric field at the nucleus is oscillating rapidly due to random motions of neighbouring ions, this electric quadrupole interaction may well be the dominating mechanism for the thermal or spin-lattice relaxation process (P50). In ionic crystals, the oscillating electric fields due to lattice vibrations also give rise to an electric quadrupole interaction which will be the dominating relaxation mechanism if paramagnetic impurities

are absent (B48, P51). In some crystals, there will be a steady component of the electric field gradient at the site of the nucleus under study, and the nuclear magnetic resonance absorption line will be broken up into $2I$ components due to a perturbation of the normal Zeeman levels of the nuclear spin system.

The frequency separation between components depends on crystal orientation, since the latter determines the relation between the external magnetic field and the principal axes with respect to which the 3×3 matrix representing the rectangular components of the electric field gradient tensor is diagonalized. The angular dependence of the frequency splitting of the satellite absorption lines for the Li^{7} resonance in crystalline $\text{LiAl}(\text{SiO}_3)_2$ serves as an illustration of the general case of the electric quadrupole interaction in a crystal with non-axial symmetry.

R. V. Pound, in the pioneering work in this subject (P50) has examined the electric quadrupole interaction in crystals possessing an axis of symmetry. The present work investigates the more general case of crystals with non-axially symmetric fields. It is found that the analysis of the angular dependence for three rotations about mutually perpendicular axes yields the coupling energy for the crystal, the electric field gradient asymmetry, and the orientation of the principal axes of the electric field gradient tensor.

CHAPTER I

THE PHENOMENON OF NUCLEAR PARAMAGNETIC RESONANCE

Since its conception in 1946 by the groups at Stanford (BHP) and Harvard (PTP) the phenomenon of nuclear paramagnetic resonance absorption or nuclear induction has received much attention both theoretically and experimentally. Several excellent review articles have been written, to which the reader is referred (Pu48, R48, Pa50). In view of the large volume of existing literature, only a brief discussion will be given.

If a ^{spinning} magnetic dipole is placed in a magnetic field H_0 it will precess about the field direction with a frequency called the Larmor precession frequency which is independent of the angle between H_0 and μ , the magnetic dipole moment. A nucleus of spin I , magnetic moment μ may exist in a magnetic field in one of a discrete set of energy levels called the Zeeman levels. These levels correspond to different values of M , the projection of the nuclear angular momentum or spin vector I on the field direction. The energy levels are such that a transition between adjacent levels involves the emission or absorption of a quantum of energy of frequency equal to the Larmor precession frequency. One experimental technique involves placing a

small coil excited by an r-f. voltage with its axis at right angles to the steady magnetic field H_0 and detecting the absorption of r-f. energy by a sample placed within the coil when the Larmor precession frequency is reached. Since the probability for absorption of a photon by the nuclear spin system is the same as the probability for induced emission, there will be a net absorption in the sample only if the number of nuclei in lower energy states is greater than the number in higher energy states. This is realized because of the Boltzmann factor.

If a sample containing nuclear magnetic moments is suddenly thrust into the gap of an electromagnet producing a high field, the excess number of nuclei in lower energy states will initially be zero and will approach the equilibrium value defined by the Boltzmann distribution according to the relation

$$n = n_0 \left\{ 1 - \exp (-t/T_1) \right\}$$

where T_1 is called the spin-lattice or thermal relaxation time. T_1 is determined by the interaction between the nuclear spin system and fields of frequency at or very near the Larmor precession frequency caused by random motions in the surrounding lattice. It is a measure of the time required for thermal equilibrium to be established in the sample. T_1 also determines the rate at which the spin system "relaxes" after it has absorbed r-f. energy, in other words, transmits energy to the

lattice and returns to its original energy state. For a given r-f. level in the driving coil, T_1 must be sufficiently short or the sample will saturate.

The relative phases of precessing nuclear spins will be destroyed in a time of the order of T_2 , the spin-spin relaxation time. T_2 is a measure of the reciprocal of the line width of the nuclear magnetic resonance absorption line. This line has a finite width because of the variation in local field at different positions within the sample, giving rise to a slight spread in the Larmor precession frequencies.

A nucleus may interact so strongly with its surroundings that, in the absence of strong fluctuations in fields set up by the surrounding medium, an otherwise single absorption line may be broken up into several component lines. There are two sources of this "fine structure". Firstly, neighbouring magnetic dipoles may be sufficiently close that their mutual magnetic interaction perturbs the normal Zeeman levels in a manner depending on the relative orientations of the two dipoles (Pa48, GKPP). Thus transitions will occur at frequencies slightly different from the normal Larmor precession frequency. Secondly, an electric quadrupole interaction may perturb the normal Zeeman levels in such a way that the 2I possible transitions between adjacent levels occur at slightly different frequencies.

Other sources of line structure and line broadening will not be discussed. They are useful for determining structure and internal motion in solids (GP).

CHAPTER II

THE APPARATUS

The apparatus used for the present research was the nuclear magnetic resonance spectrometer built by Collins (C50). It consists of a stabilized electromagnet to provide the steady magnetic field H_0 , together with an oscillating detector, used to detect the nuclear magnetic resonance absorption. Only a brief description of the apparatus will be given. The reader is referred to the thesis of its originator for details.

The magnet current is controlled by a bank of 19 twin triode 6AS7 tubes. D-c. stabilization is obtained by comparing the voltage across part of a 1 ohm potentiometer with 3 volts from a pair of dry cells. The difference voltage is amplified and applied to the grids of the 6AS7's. A-c. voltages appearing across the magnet coil are fed into the third stage of this d-c. amplifier and also cause a compensating voltage to appear on the grids of the 6AS7's. The magnetic field is also stabilized by means of a proton resonance signal to better than 1 part in 100,000. An oscillating detector of a design similar to the one used for signal detection is in use.

The sample being investigated is placed in the

oscillating detector's tank coil which is mounted in the magnetic field. The oscillating detector is a weakly oscillating oscillator whose amplitude is very sensitive to the absorption of energy from the tank coil. As the frequency of the oscillator is varied, the amplitude drops sharply when appreciable absorption of r-f. energy by the sample takes place. The field H_0 is modulated at an audio frequency by means of small "sweep coils" mounted on either side of the tank coil with axes in the H_0 direction. Thus when the oscillator frequency is near resonance, the total field ($H_0 + \text{audio}$) sweeps over part of the absorption line. We then have a modulated r-f. output from the oscillator which is amplified and then detected. The resulting audio wave is amplified by several stages. A phase-sensitive or "lock-in" detector rectifies signals in a narrow frequency band about, and nearly in phase with, an applied audio signal. This signal is obtained from the same audio oscillator which supplies the coils for magnetic field modulation, but it passes through an adjustable phase shifting network before reaching the phase-sensitive detector. The rectified audio wave is smoothed using an adjustable time constant, passes into a vacuum-tube voltmeter (VW) and the output is recorded on an Esterline-Angus Recording Milliammeter.

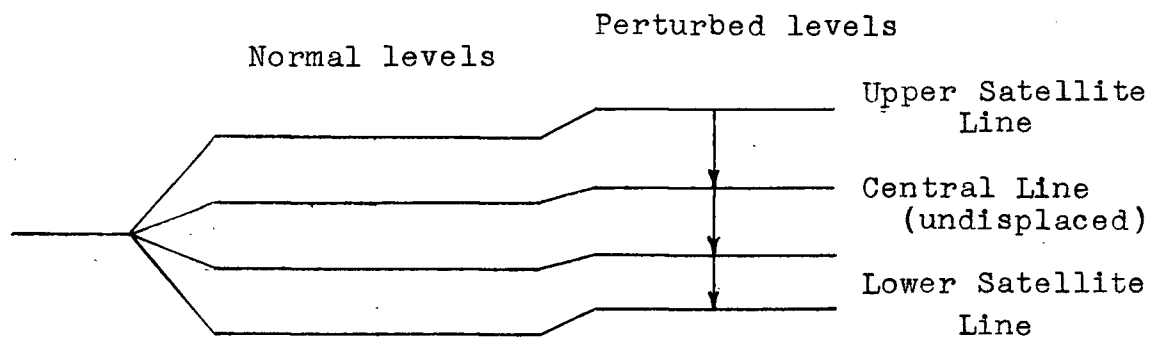
The exploratory work on the nuclear electric quadrupole interaction described in this thesis was performed using a single crystal of spodumene mounted in a slot on the

end of a bakelite rod and inserted in the tank coil of the oscillating detector. The method of measuring angles of rotation of the crystal was rather crude and will not be described. An improved mount has been constructed by Mr. H. E. Petch and will be described in a forthcoming paper (VPS).

CHAPTER III

THE NUCLEAR ELECTRIC QUADRUPOLE INTERACTION IN CRYSTALS

In a crystal in which the symmetry is such that the electric field gradient does not vanish at the site of a nucleus under study, the nuclear magnetic resonance absorption line is split up into $2I$ components. If the interaction is not too strong, so that first order perturbation theory is adequate, it is found that the separation in frequency between the components is proportional to the electric field gradient in the H_0 direction and to the electric quadrupole moment of the nucleus under study. $2I$ components occur because the electric quadrupole interaction perturbs the normal Zeeman levels of the nuclear spin system in such a way that the $2I$ allowed transitions between adjacent levels occur at slightly different frequencies. For example, for $I = 3/2$,



The above diagram is for a positive coupling

energy. For small interactions, such as the Li^7 interaction in spodumene, the central resonance line is undisplaced, the phenomenon being described using first order perturbation theory.

Theory

The theory presented below is a more detailed exposition of the brief sketch given by Pound (P50) for axially symmetric fields, and an extension of Pound's work to non-axially symmetric crystals suggested by Prof. Volkoff.

The electrostatic energy of interaction between a system of nuclear charges i and an external charge distribution j is given by

$$V = \sum_{i,j} \frac{e_i e_j}{r_{ij}} \quad (1)$$

Expanding $\frac{1}{r_{ij}}$ in Legendre polynomials this may be written

$$V = \sum_{i,j} \frac{e_i e_j}{r_j} \sum_{k=0}^{\infty} \left(\frac{r_i}{r_j} \right)^k P_k(\cos \theta_{ij}) \quad (2)$$

The term corresponding to $k = 0$ represents the energy of the total nuclear charge concentrated at the origin of coordinates in a potential determined by the external charge distribution. The $k = 1$ term represents the energy of an electric dipole in the electric field of the external charge distribution. However, since nuclei do not possess

electric dipole moments, this term will be non-existent in the nuclear case. The $k = 2$ term represents the energy of the nuclear electric quadrupole in the electric field gradient at the origin of coordinates.

By using certain theorems pertaining to spherical harmonics, we may express V as

$$V = \sum_{i,j} \frac{e_i e_j}{r_j} \sum_{k=0}^{\infty} \left(\frac{r_i}{r_j} \right)^k \sum_{q=-k}^k (-)^q C_q^k(i) C_{-q}^k(j) \quad (3)$$

i always refers to the nuclear charge configuration, j to the external charge configuration. Following Racah (R42),

$$C_q^k = \left[\frac{4\pi}{2k+1} \right]^{\frac{1}{2}} Y_k^q(\cos \theta, \phi),$$

$$Y_k^q(\cos \theta, \phi) = \frac{1}{(2\pi)^{\frac{1}{2}}} \Theta_k^q(\cos \theta) e^{iq\phi},$$

and Condon and Shortley's definition (CS) for the normalized Associated Legendre Polynomials is used, viz.

$$\Theta_k^q(\cos \theta) = (-)^q \left[\frac{(2k+1)(k-q)!}{2(k+q)!} \right]^{\frac{1}{2}} \sin^q \theta \frac{d^q}{(d \cos \theta)^q} P_k(\cos \theta).$$

The electric quadrupole interaction is expressed by the $k = 2$ term in (3),

$$\sum_{i,j} \frac{e_i e_j}{r_j} \left(\frac{r_i}{r_j} \right)^2 \sum_{q=-2}^2 (-)^q C_q^2(i) C_{-q}^2(j) \quad (4)$$

We may also express the electric quadrupole interaction

as the dyadic (second rank tensor) scalar product

$$F = \bar{Q} \cdot \nabla \vec{E} = \sum_{q=-2}^2 (-)^q Q_q (\nabla E)_{-q} \quad (5)$$

where
$$\bar{Q}_q = \sum_i e_i r_i^2 C_q^2(i) \quad (6)$$

$$(\nabla E)_{-q} = \sum_j \frac{e_j}{r_j^3} C_{-q}^2(j) \quad (7)$$

To obtain \bar{Q} and $\nabla \vec{E}$ in the above form, we may first of all consider the rectangular components of $\nabla \vec{E}$ and show how to transform these components into the form (7). The components of the electric quadrupole moment operator transform in an analogous fashion.

The 3X3 matrix representing the rectangular components of $\nabla \vec{E}$, viz.

$$\begin{pmatrix} \frac{\partial E_x}{\partial x} & \frac{\partial E_x}{\partial y} & \frac{\partial E_x}{\partial z} \\ \frac{\partial E_y}{\partial x} & \frac{\partial E_y}{\partial y} & \frac{\partial E_y}{\partial z} \\ \frac{\partial E_z}{\partial x} & \frac{\partial E_z}{\partial y} & \frac{\partial E_z}{\partial z} \end{pmatrix}$$

may be simplified when it is considered that $E = -\nabla V$, hence $\nabla \times E = 0$, i.e. the tensor is symmetric, reducing it to six independent components. The requirement that $\text{div } \vec{E} = 0$ reduces it to five independent components.

From the definition
$$\vec{E} = - \sum_j \frac{e_j}{r_j^3} \vec{r}_j, \quad ,$$

$$\frac{\partial \vec{E}}{\partial x} = - \sum_j \frac{3e_j x_j}{r_j^5} \vec{r}_j + \sum_j \frac{e_j}{r_j^3} \vec{r}_j, \quad \text{etc. and}$$

$$\nabla E = \sum_j e_j \begin{pmatrix} \frac{1}{r_j^3} - \frac{3x_j^2}{r_j^5} & -\frac{3x_j y_j}{r_j^5} & -\frac{3x_j z_j}{r_j^5} \\ -\frac{3x_j y_j}{r_j^5} & \frac{1}{r_j^3} - \frac{3y_j^2}{r_j^5} & -\frac{3y_j z_j}{r_j^5} \\ -\frac{3x_j z_j}{r_j^5} & -\frac{3y_j z_j}{r_j^5} & \frac{1}{r_j^3} - \frac{3z_j^2}{r_j^5} \end{pmatrix} \quad (9)$$

The C 's may be written in the form

$$\begin{aligned} C_0^2 &= \frac{1}{r^2} \left(\frac{3}{2} z^2 - \frac{1}{2} r^2 \right) \\ C_{\pm 1}^2 &= \pm \sqrt{\frac{3}{2}} \frac{xz \pm i yz}{r^2} \\ C_{\pm 2}^2 &= \sqrt{\frac{3}{8}} \frac{(x^2 - y^2) \pm 2i xy}{r^2} \end{aligned} \quad (10)$$

It may be shown that $(\nabla E)_0$, $(\nabla E)_{\pm 1}$, $(\nabla E)_{\pm 2}$ bear the same relation to the rectangular tensor components (9) as the above C 's (10) do to the spherical harmonics defined in Racah's notation (3). In fact,

$$\begin{aligned} (\nabla E)_0 &= -\frac{1}{3} \left(\frac{3}{2} \frac{\partial E_z}{\partial z} - \frac{1}{2} \nabla \cdot \vec{E} \right) = -\frac{1}{2} \frac{\partial E_z}{\partial z} \\ (\nabla E)_{\pm 1} &= \pm \frac{1}{\sqrt{6}} \left(\frac{\partial E_x}{\partial z} \pm i \frac{\partial E_y}{\partial z} \right) \\ (\nabla E)_{\pm 2} &= -\frac{1}{2\sqrt{6}} \left(\frac{\partial E_x}{\partial x} - \frac{\partial E_y}{\partial y} \pm 2i \frac{\partial E_x}{\partial y} \right) \quad * \end{aligned} \quad (11)$$

By analogy, the electric quadrupole moment operator

$$Q_q(i) = \sum_i e_i r_i^2 C_q^2(i)$$

* Factor of 1/2 in this expression is missing in Pound (p50)

is expressible in components

$$Q_0 = \frac{eQ}{2I(2I-1)} [3I_z^2 - I(I+1)]$$

$$Q_{\pm 1} = \mp \frac{\sqrt{6}}{2} \frac{eQ}{2I(2I-1)} [(I_x \pm iI_y)I_z + I_z(I_x \pm iI_y)] \quad (12)$$

$$Q_{\pm 2} = \frac{\sqrt{6}}{2} \frac{eQ}{2I(2I-1)} [(I_x \pm iI_y)^2]$$

where Q is the scalar nuclear electric quadrupole moment defined in the usual manner (C36,FL).

The first order energy perturbation on the normal Zeeman levels of the nuclear spin system is given by the matrix element of the quadrupole interaction term F defined by (5)

$$(m|F|m) = \frac{eQ}{2I(2I-1)} [3m^2 - I(I+1)] (\nabla E)_0. \quad (13)$$

Thus in the first order theory only the component $(\nabla E)_0$ occurs. The other four components of ∇E need not be known unless second order calculations are contemplated. The remainder of our problem is now the determination of $(\nabla E)_0$ for the general case of no axial symmetry. The electric field gradient tensor may be transformed to a coordinate system in which the 3X3 matrix representing its rectangular components is diagonalized. When this is done, we may choose our z -axis along the principal axis having largest component, and $\frac{\partial E_{z''}}{\partial z''} = -eq$,

where $eq = \sum_j \frac{e_i(3\cos^2\theta_i'' - 1)}{r_j''^3},$

$$(\nabla E)_0'' = \frac{eq}{2}$$

$$(\nabla E)_{\pm 1}'' = 0$$

$$(\nabla E)_{\pm 2}'' = \frac{1}{2\sqrt{6}} neq \quad (14)$$

$$\text{where } \eta = \frac{\frac{\partial E_x''}{\partial x''} - \frac{\partial E_y''}{\partial y''}}{\frac{\partial E_z''}{\partial z''}}$$

Here, the (double primes) refer to the coordinate system in which (∇E) is diagonalized. The (unprimed) axes will continue to refer to a laboratory coordinate system in which z is in the H_0 direction and x, y, z form a right-handed orthogonal set. Let the transformation matrix between the $x y z$ system and the $x'' y'' z''$ system be:

	x	y	z	
x''	P_{11}	P_{12}	P_{13}	
y''	P_{21}	P_{22}	P_{23}	(15)
z''	P_{31}	P_{32}	P_{33}	

The tensor (∇E) transforms in exactly the same way as the tensor C ?

$$\begin{aligned} r^2 C_0^2 &= \frac{3}{2} z^2 - \frac{1}{2} r^2 \\ &= \frac{3}{2} (P_{13}^2 x''^2 + P_{23}^2 y''^2 + P_{33}^2 z''^2 + 2P_{13}P_{23}x''y'' + \end{aligned}$$

$$+ 2 p_{13} p_{33} x'' z'' + 2 p_{23} p_{33} y'' z'' \Big) - \frac{1}{2} r^2$$

Substituting for x''^2 , y''^2 , z''^2 , $x''y''$, $x''z''$, $y''z''$, ^{and} using relations (10) and the fact that $\frac{\partial}{\partial t} = 0$,

we obtain a relation for C_0^2 in terms of the C^2 's.

Then, by analogy, and making use of the fact that $(\nabla E)''_{\pm 1} = 0$,

$$\begin{aligned} (\nabla E)_0 = & \frac{3}{2} p_{13}^2 \left[\sqrt{\frac{2}{3}} (\nabla E)''_{\pm 2} - \frac{1}{3} (\nabla E)_0'' \right] \\ & + \frac{3}{2} p_{23}^2 \left[-\sqrt{\frac{2}{3}} (\nabla E)_2'' - \frac{1}{3} (\nabla E)_0'' \right] + p_{33}^2 \frac{2}{3} (\nabla E)_0'' \end{aligned}$$

Substituting relations (14),

$$(\nabla E)_0 = \frac{e q}{4} \left[3 p_{33}^2 - 1 + n (p_{13}^2 - p_{23}^2) \right] \quad (16)$$

It remains now to obtain explicit expressions for p_{i3} ($i = 1, 2, 3$) in terms of crystal orientation. Let us introduce a set of any three mutually perpendicular axes fixed with respect to the crystal which are easily recognizable externally, to be referred to as the (single primed) set. We may choose, if we wish (though it is not essential) some of these single primed axes to coincide with some of the crystallographic axes of the crystal.

Let the transformation from the (primed) to the (double-primed) systems of axes be defined by the nine direction cosines: λ_i ($i = 1, 2, 3$), which define the

orientation of the x' axis with respect to the (double-primed) set, and μ_i and ν_i (for the y' and z' axes respectively). Further, let the (primed) system be rotated about an axis fixed with respect to both the x', y', z' and the x, y, z (lab) systems. We have chosen z to coincide with H_0 . We choose an axis of rotation perpendicular to H_0 , designating it y . We now consider rotating the crystal in turn about its x', y', z' axes, making the axis of rotation in each case coincide with the y -axis in the lab system. If we label the three rotations respectively X, Y, Z and choose the initial positions of the crystal so that x', y', z' , initially coincide with y, z, x (for the X rotation); x, y, z (for the Y); z, x, y (for the Z), then the three transformation matrices are defined by the following Table:

	X		
	x	y	z
x'	0	1	0
y'	$\sin \theta_x$	0	$\cos \theta_x$
z'	$\cos \theta_x$	0	$-\sin \theta_x$

Y

	x	y	z
x'	$\cos \theta_y$	0	$-\sin \theta_y$
y'	0	1	0
z'	$\sin \theta_y$	0	$\cos \theta_y$

Z

	x	y	z
x'	$\sin \theta_z$	0	$\cos \theta_z$
y'	$\cos \theta_z$	0	$-\sin \theta_z$
z'	0	1	0

The product of the transformation from x'', y'', z'' to x', y', z' , and the transformation from x', y', z' to x, y, z then gives:

$$\begin{aligned}
 (P_{13})_x &= \mu_1 \cos \theta_x - \nu_1 \sin \theta_x \\
 (P_{13})_y &= \nu_1 \cos \theta_y - \lambda_1 \sin \theta_y \\
 (P_{13})_z &= \lambda_1 \cos \theta_z - \mu_1 \sin \theta_z
 \end{aligned}
 \quad (i=1,2,3) \quad (17)$$

where the cyclic permutation is evident.

Substitution of these into eq. (16) then yields:

$$(\nabla E)_0 = \frac{eq}{4} (a_x + b_x \cos 2\theta_x + c_x \sin 2\theta_x) \quad (18)$$

$$\begin{aligned} a_x &= \frac{3}{2} (\mu_3^2 + \nu_3^2) - 1 + \frac{n}{2} (\mu_1^2 + \nu_1^2 - \mu_2^2 - \nu_2^2) \\ &= \left(\frac{1}{2} - \frac{3}{2} \lambda_3^2 \right) + \frac{n}{2} (\lambda_2^2 - \lambda_1^2) \end{aligned} \quad (I)$$

$$b_x = \frac{3}{2} (\mu_3^2 - \nu_3^2) + \frac{n}{2} (\mu_1^2 - \nu_1^2 - \mu_2^2 + \nu_2^2)$$

$$c_x = -3\mu_3\nu_3 + n(\mu_2\nu_2 - \mu_1\nu_1)$$

Two similar sets for Y and Z rotations are obtained by cyclic permutation.

From eq. (13) it follows that the frequency splitting between lines corresponding to transitions $m \leftrightarrow m-1$ and $-(m-1) \leftrightarrow -m$ is given by:

$$2\Delta\nu = 2 \frac{eq}{2I(2I-1)h} 3(2m-1)(\nabla E)_0 \quad (19)$$

$$= A + B \cos 2\theta + C \sin 2\theta \quad (20)$$

where $A = 2ka$, $B = 2kb$, $C = 2kc$,

$$k = \frac{e^2 q Q}{h} \frac{3(2m-1)}{8I(2I-1)} \quad (II)$$

Performing the three rotations X,Y,Z it appears that one obtains nine relations of the form (I, II) involving nine experimentally determined A B C's.

However, these are not all independent. Thus $(\nabla E)_0$

$$= -\frac{1}{2} \frac{\partial E_z}{\partial z} \text{ is the same for } \theta_x = 0 \text{ and } \theta_z = -90^\circ$$

and in both cases equal to $-\frac{1}{2} \frac{\partial E_y'}{\partial y'} = \frac{eq}{4} (a_x + b_x) = \frac{eq}{4} (a_z - b_z)$

Similar expressions hold for Y and Z axes, and Laplace's equation then guarantees that $a_x + a_y + a_z = 0$ (also $b_x + b_y + b_z = 0$). Thus only any one pair AB is an independent pair, the others being related to it. Thus, experimentally we obtain from three rotations only five independent constants: the three C's and any two of the following three:

$$\alpha = A_y - B_y = A_z + B_z = -2A_x$$

$$\beta = A_z - B_z = A_x + B_x = -2A_y$$

$$\gamma = A_x - B_x = A_y + B_y = -2A_z \quad (\text{III})$$

$$(\alpha + \beta + \gamma = 0)$$

Since experimentally we cannot determine which of the two lines is $m \leftrightarrow m - 1$ and which $-(m - 1) \leftrightarrow -m$, we obtain only the relative signs of $C_x, C_y, C_z, \alpha, \beta, \gamma$ but not the absolute sign.

Of the nine direction cosines only three are independent (by virtue of six orthonormality relations), since only three parameters are required to describe the orientation of one set of axes with respect to the other. These three direction cosines plus the values of η and k form a set of five unknowns determined by our set of five independent constants.

The Spodumene Crystal

A single crystal of spodumene, dimensions about 37 mm. x 8 mm. x 3 mm. was used in the experimental work. It originated in the Minas Geraes region of Brazil and was purchased from Minerals Unlimited by Dr. R. M. Thompson of the Department of Geology and Geography. The orientation of the crystallographic C-axis was determined by Dr. L.D. Mantuani, using a polarising microscope. The orientation of the b-axis was described by the supplier.

The unit cell of monoclinic spodumene (WB) contains four Li atoms, but these atoms have similar electrical surroundings. This equivalence of the arrangement of neighbouring atoms is due to the existence of two-fold rotation axes and screw axes in the b-direction within the structure. The symmetry is such that the electric field at two of the Li nuclei is equal in magnitude but opposite in direction to that at the other two Li nuclei. The electric field gradient (∇E), being of the second rank, will have the same sign at all four sites. In other words, the orientation of the coordinate system in which ∇E is diagonalized is the same at all Li nuclei, thus giving rise to a unique set of experimental results. If this condition did not hold, there would be a superposition of two or more different frequency splitting patterns at each crystal orientation.

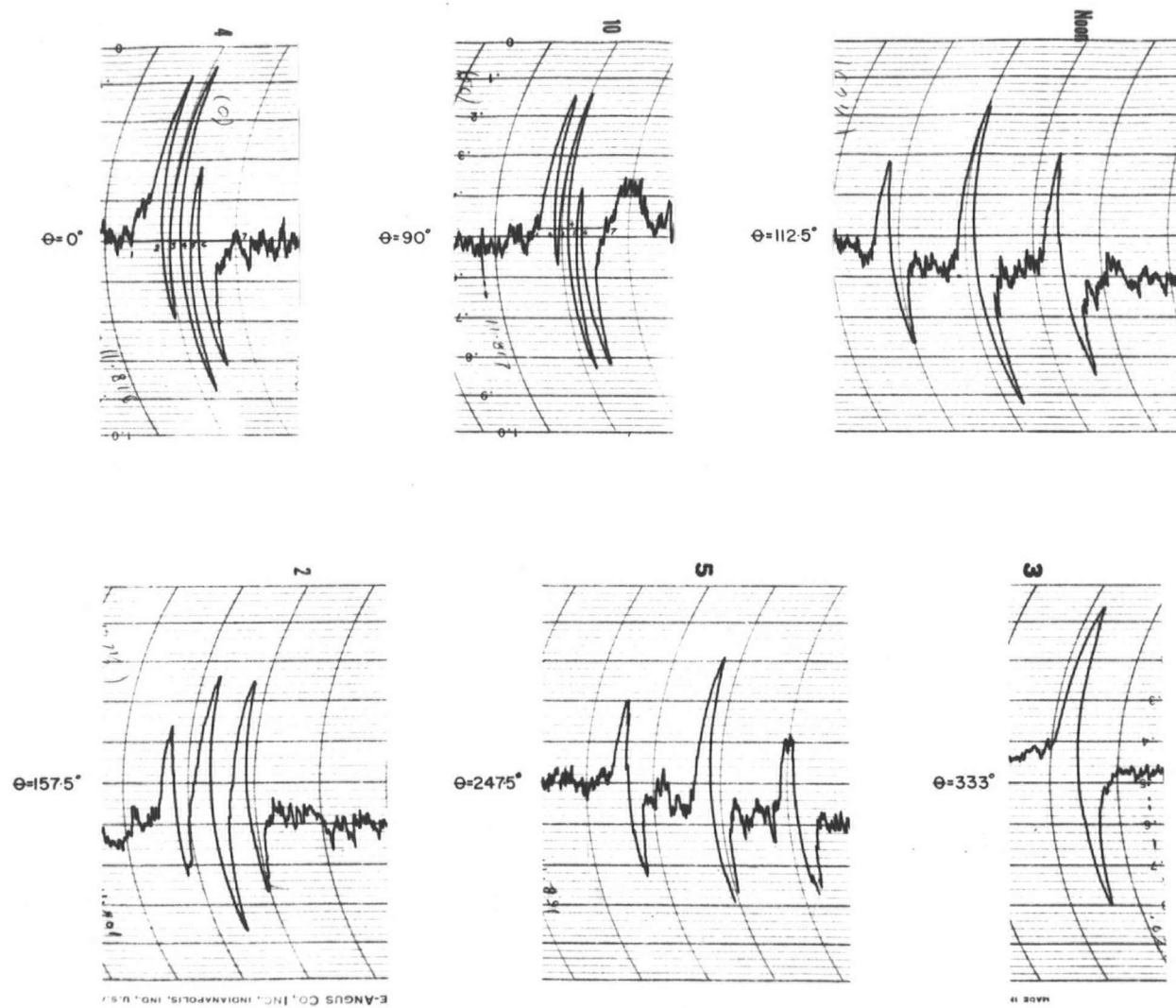


FIG.1: RECORDED ABSORPTION LINE DERIVATIVES

The symmetry properties of spodumene are also such that the b-axis coincides with one of the principal axes of the electric field gradient tensor.

Experimental

The Li^7 resonance was located at about 11.84 Mc. in a field of about 8000 gauss. The crystal was rotated about the C-axis into positions where the direction which was believed to be the crystalline b - axis made various angles with the direction of the magnetic field H_0 . Traces of the three - line nuclear magnetic resonance absorption line spectrum for the Li^7 resonance were obtained at angles differing by 22.5° . A few intermediate readings were taken as checks. Typical traces of the absorption line derivative as a function of frequency as recorded by the Esterline-Angus recording milliammeter are shown in fig. 1. Frequency readings were taken at various points along the trace while the frequency was varying slowly through the region of the three resonances. For the well-resolved resonances, the frequency difference between the two satellite absorption lines was measured directly from the chart. For unresolved resonances, the recorded derivative curves were integrated using a planimeter and the separation of the satellites estimated from the integrated absorption curves. The angular variation of the splitting

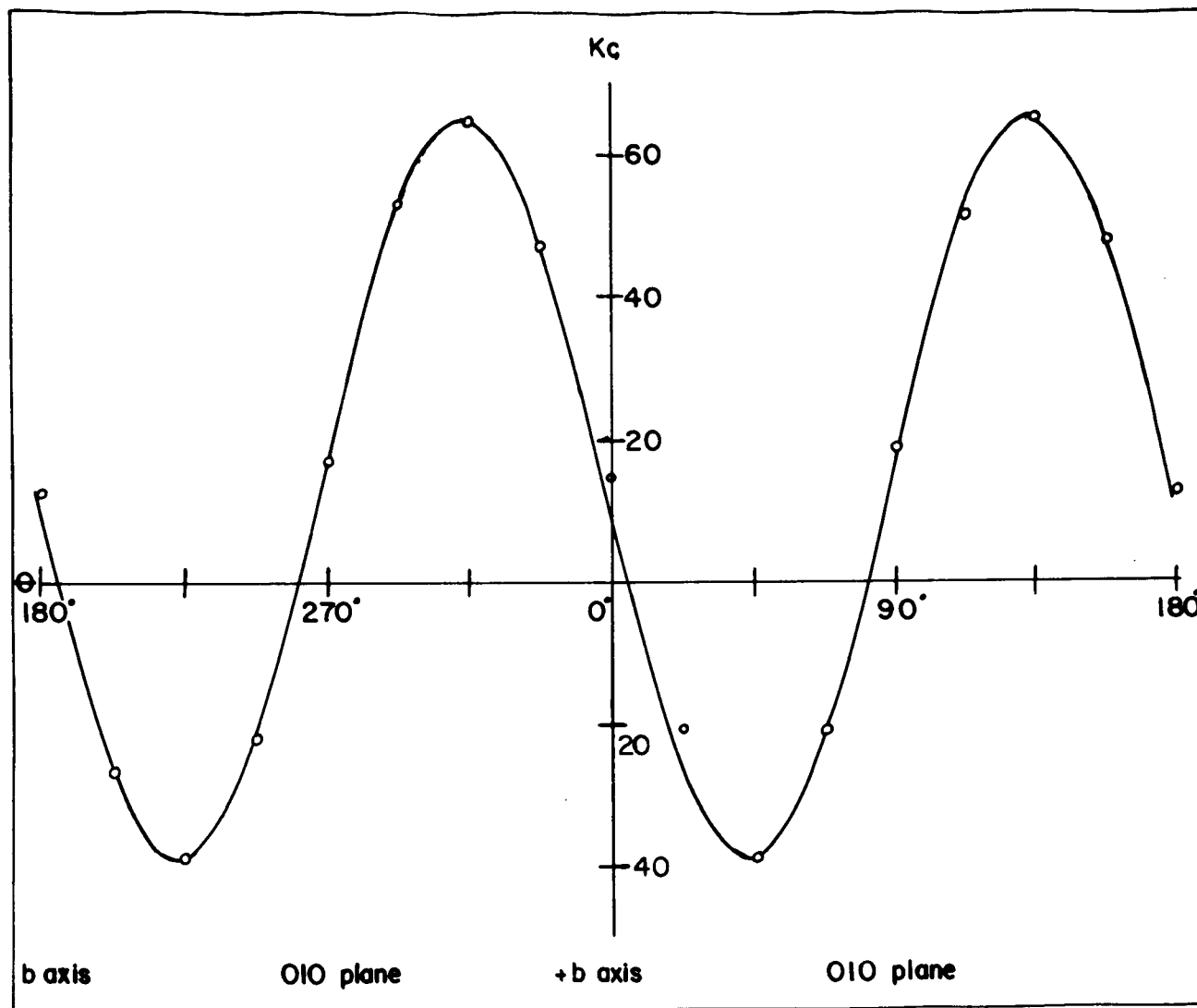


Fig. 2 -- Frequency splitting in kilocycles of satellite absorption lines as a function of angle between +b axis and H_0 , for the three-line $Li7$ nuclear magnetic resonance absorption spectrum in spodumene. Circles represent experimental points. The solid curve is $2\Delta\nu = 13.1 + 51.9 \cos 2(\theta + 47^\circ)$. The c-axis of the crystal is vertical, i.e. perpendicular to H_0 .

of the satellite lines is shown in fig. 2. Circles represent experimental points; the solid curve is

$$2\Delta\nu = 13.1 + 51.9 \cos 2(\theta + 47^\circ)$$

which is of the form (20).

This relationship, using the originally - specified axes, does not agree with the known fact that one of the principal axes of ∇E coincides with the b-axis of the crystal. This implies that the curve be symmetric about the b-axis. Thus, an error in the original assignment of axes as shown in fig. 2 was suspected, and it appeared that the b-axis should be shifted either to $\theta = 43^\circ$ or $\theta = -47^\circ$. Very recently, Dr. K. C. MacTaggart examined a thin section of the crystal optically and found that the b-axis should be in a position given approximately by $\theta = 45^\circ$ (see fig. 2). Allowing for an error of about 2° in measurements, the curve is symmetric about the true b-axis and in terms of this correct designation,

$$2\Delta\nu = 13.1 - 51.9 \cos 2\phi,$$

where ϕ is the angle between the b-axis and H_0 . Or, since only relative signs for the splitting are discernible,

$$2\Delta\nu = -13.1 + 51.9 \cos 2\phi.$$

This agrees within a few percent with subsequent measurements made for the same rotation by Petch (PSV) and also by Pake (Pa51).

Conclusions

The angular dependence obtained above is consistent with the theory of the general case of the angular dependence of the nuclear electric quadrupole interaction in crystals with asymmetric fields and is the first experimental treatment of it. Previous work (P50) has been concerned with the angular dependence about an axis of symmetry. From subsequent results (PSV) obtained for this and two other rotations by H. E. Petch,

$$\left| \frac{e^2 q Q}{h} \right| = 75.6 \text{ kc./sec.}, \quad \eta = 0.793$$

for ^{Li7} in _Aspodumene. Other results, such as the orientation of the principal axes of the field gradient tensor, are quoted in the reference. In order to deduce a value of the magnitude of the nuclear electric quadrupole moment of Li⁷ from these results, it is still necessary to know eq, for this crystal.

CHAPTER IV

SUGGESTIONS FOR FURTHER WORK

An experiment similar to the one described in this thesis might well be performed with a single crystal of jadeite, $\text{NaAl}(\text{SiO}_3)_2$, using the Na^{23} resonance. The crystal structure of jadeite is almost identical with that of spodumene. An estimate of the quadrupole moment ratios $Q_{\text{Na}^{23}} / Q_{\text{Li}^7}$ might be obtained.

Work on the splitting of the nuclear magnetic resonance absorption line due to magnetic dipole-dipole interactions between neighbouring nuclei (Pa48) might be carried out using the proton resonance in various hydrated crystals, such as the minerals analcite, $\text{NaAl}(\text{SiO}_3)_2 \cdot \text{H}_2\text{O}$, goethite, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and diaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. In cryolite, Na_3AlF_6 , the Al^{27} resonance should show a fine structure due to magnetic interaction with the large magnetic moments of neighbouring F^{19} nuclei, which are located a mere 1.8\AA away (NS). If the gradient of the electric field at the Al sites in the crystal is non-zero, an electric quadrupole interaction would also take place, since Al^{27} has a large quadrupole moment (L49). This would provide a striking illustration of both effects.

The present apparatus is particularly adapted to

the search for unknown resonances and the measurement of line splitting due to electric quadrupole coupling. For more accurate work on line structures and relaxation times, a bridge type circuit with variable r-f. input would be invaluable. The method of progressive saturation (BPP) could then be used for the determination of the spin-lattice relaxation time T_1 . The following proposed experiment might shed some light on the relative magnitudes of the relaxation by magnetic dipole as compared to electric quadrupole interaction. The relaxation time T_1 for a series of nuclei which are roughly known to have progressively larger electric quadrupole moments could be measured. For example, one might compare the Li^7 , Na^{23} and Al^{27} resonances in solutions of the sulphates of lithium, sodium and aluminum, all at the same concentrations. Of course, the strength of the interaction would also depend on the ionic radii of the atoms whose nuclei are being compared, and this would have to be allowed for. T_1 could also be measured for several nuclei of spin $1/2$ under conditions similar to the above, and the results compared with the results for Li, Na and Al, where the relaxation is supposedly through the electric quadrupole mechanism. In this way, one might discern whether or not the electric quadrupole interaction is actually the dominating mechanism for thermal relaxation for nuclei of spin $I > 1/2$.

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