NUCLEAR MAGNETIC RESONANCE STUDIES OF CRYSTAL STRUCTURE

Thesis for the Degree of Ph. D.

MICHIGAN STATE UNIVERSITY

John Hubert Muller

1958

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NUCLEAR MAGNETIC RESONANCE STUDIES
of
CRYSTAL STRUCTURES

by

JOHN ROBERT TULLER

AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and
Applied Science in partial fulfillment of
the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics

1953

APPROVED: R. D. Spence

JOHN HUBERT MILLER

AN ABSTRACT

This thesis is a demonstration of the usefulness of nuclear magnetic resonance (n m r) as a tool for the study of crystal and liquid crystal structure.

The method is illustrated by application to six compounds. The magnetic dipole-dipole interaction is the only structure sensitive perturbation considered. This is useful because of its dependence upon separation and relative orientation of the perturbing and resonant nuclei. The data is presented as angular dependant splittings and broadenings of the nuclear resonance spectrum. Stereochemical arguments connect the conclusions about magnetic ingredients to the rest of the structure.

In barium chlorate monohydrate, the water protons are located by splitting due to nearest neighbor protons, and the more remote neighbors broaden the split lines in agreement with theory.

The water molecules are located in dioptase (copper silicate hydrate) and the effect of the electron paramagnetism of the coppers is discussed. A magnetic transition is found near 20 degrees kelvin, below which the proton spectrum vanishes.

The structure of guanidine aluminum sulfate hexahydrate is outlined solely on the basis of nuclear resonance data, the space group, and the number of molecules in the unit cell.

The x-ray derived structure of euclase (beryllium aluminum silicate hydroxide) is rejected on the basis of the nuclear resonance spectrum.

In the final chapter the magnetic ordering in the liquid crystals p-azoxyanisole and p-azoxyphenetole is destroyed mechanically, and the nmr spectrum narrows strongly, in agreement with theory.

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It is indeed a pleasure to thank Professor Robert D. Spence not only for suggesting the problems studied in this thesis, but also for his all-inclusive help. He has given more than generously of his time in helping with a-thousand-and-one pedestrian details, and has at the same time aided and advised on every general aspect of the subject. Perhaps my greatest debt to Professor Spence is the constant single-minded pursuit of the problem from a practical standpoint that he has taught and in so many ways exemplified.

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INTRODUCTION

Nuclear resonance has been successfully studied in bulk matter since late 1945 when Purcell, Torrey, and Pound (1946) first found the resonance of protons in paraffin. Almost simultaneously, and independantly, Bloch, Hansen, and Packard (1946) found the proton resonance in water by a slightly different technique. Shortly thereafter Bloch (1946) gave a classical macroscopic theory of nuclear resonance which discussed the subject from a purely phenomenological standpoint.

This field has now become one of the very active branches of physics. Although there has been application both to nuclear theory and to technical developments such as the accurate measurement of magnetic fields; the most extensive application of the method has been to the study of the structure of matter.

Solids, liquids, and gases have been studied, though the low density of gases tends to confine the use of nuclear resonance to the other two states of matter. The first observation of nuclear resonance in gases was made by Purcell, Pound, and Bloembergen (1946) in hydrogen gas. Though there have been a number of experiments in gases they are, in the main, of rather special interest, and will not be discussed here.

Nuclear resonance was first found in a liquid or quasi-liquid (paraffin); and one of the earliest discussions of the effect of molecular environment upon nuclear resonance was the paper on the relaxation of nuclear magnetic moments in liquids by Bloembergen, Purcell, and Pound (1947). This was followed by an extensive general article on nuclear resonance by Bloembergen, Purcell, and Pound (1948) which also gave more detailed consideration to spin-lattice relaxation in liquids.

In solids an early paper of importance by Pake (1948) discussed the magnetic dipole-dipole interaction and its effect upon the nuclear resonance spectrum. Another major contribution was the theoretical calculation by Van Vleck (1948) of the magnetic dipole-dipole broadening of lines in solids; and the accompanying experimental paper by Pake and Purcell (1948). The relaxation mechanism that is most important in solids has been shown by Rollin and Hatton (1948) and Bloembergen (1949) to be due to minute amounts of paramagnetic impurities.

Knight (1949) extended the study of environmental effects upon nuclear resonance by finding a minute shift in the resonance frequencies of nuclei from compound to compound, and especially between metals and salts. This effect has been ascribed to the paramagnetism and orbital diamagnetism of environmental electrons by a number of authors notably: Townes, Herring, and Knight (1950), Ramsey (1950 a and b), and Proctor and Yu (1950). Further studies resulting in a very extensive literature on fine structure especially in liquids and gases have been initiated by Gutowsky, McCall, Slichter, and McNeil (1951).

Nuclei having spins greater than one-half also possess quadrupole electric moments. The first study of this property in solids was by Pound (1947). Nearly pure quadrupole electric resonance was studied in individual molecules by molecular beam methods by Nierenberg, Ramsey, and Brody (1947). It was therefore a natural development by Dehmelt and Kruger (1950) to find pure electric quadrupole resonance in solids.

The numerous advances in technique since the first demonstration of nuclear resonance, though of great interest and consequence, will not be treated here. That is because this thesis is not concerned with methods.

The purpose of this thesis is to extend the study of magnetic dipole-dipole interactions as a tool for the investigation of crystal structure. We will include liquid crystals in our designation of crystals, despite the usual connotation of solid with the word crystal.

It so happens that all the substances will be studied by means of the magnetic resonance spectrum of protons. This is accidental except in so far as protons form a very common constituent of matter and possess a large magnetic moment. No general conclusions will be reached that could not be adapted to other nuclei possessing magnetic moments.

We will not consider electric quadrupole interactions between nuclei and their crystalline environment. Some of the constituents of the substances studied will possess quadrupole moments; but since we will not study their resonance spectra, the only effect we need consider will be due to their magnetic dipole moment.

To exemplify our thesis that nuclear resonance is a tool of considerable value in the study of crystal structure, we will examine: two hydrates whose structure has previously been determined by x-ray analysis except for the protons in the waters of hydration; next a hydrated crystal of previously unknown structure; a hydroxide mineral whose structure has been suggested by x-ray technique; and finally two organic liquid crystals.

Throughout our work we will use the magnetic dipole-dipole interaction as a probe for the presence of other magnetic constituents in the materials examined. We will therefore consider that interaction in some detail before proceeding to the individual cases.

The phrase, "dipole-dipole interaction" refers to the perturbing effect of one magnetic dipole upon the nuclear resonance spectrum of another. The change in the spectrum of the perturbed nucleus depends both upon the separation of the dipoles and on the orientation of the magnetic field with respect to the line joining the two magnetic dipoles. As a result, measurement of this perturbation yields structural information of considerable value.

In most cases here considered, the perturbing dipole is another nucleus. Only a small proportion of the nuclei are in transition at any given time from one spin orientation to another. Therefore in calculating the perturbation upon a nucleus which is undergoing transition, it is a safe assumption to consider that the perturbing nucleus remains in the same state for the period occupied by the transition.

In one case, dioptase, one of the perturbing dipoles is the magnetic moment of an unpaired electron associated with the copper ion in the lattice. At room temperatures however, the electrons pass so rapidly from one state to another, that in spite of their large magnetic moment, the time average effect upon the nuclei is only a little different from zero.

The change in the magnetic field due to a nearby magnetic dipole is classically calculated to be (μ/r^3) $(3 \operatorname{Cos}^2\theta - 1)$. Where μ is the magnetic moment of the perturbing dipole, r is the length of the line joining the dipoles, and θ is the angle between that line and the ambient magnetic field. This yields an experimentally correct effect for dissimilar nuclei of spin 1/2; but for the case of identical nuclei it is necessary to consider one additional factor.

In this last instance one has to allow for the quantum-mechanical phenomenon of "spin exchange". Because the perturbing and the perturbed nuclei are of the same variety, an interchange of their spin orientations, when they are lying in the same magnetic field, will not change the total energy of the system. And because they are identical, the coupling through precessional dipole magnetic radiation will be large. As a result, the splitting of the levels due to classically calculated fields of a magnetic dipole located in the position and orientation of the perturbing nucleus has to be augmented.

Pake (1948) has shown by rigorous quantum-mechanical calculation that the total splitting then becomes $3/2(\mu/r^3)(3\text{Cos}^2\theta - 1)$ where μ, r, and θ are defined as before. This formula is that of a surface of revolution whose distance from the origin is proportional to the magnitude of the splitting, and whose long axis, which is the axis of revolution, is parallel to the line joining the nuclei. The median section of this is illustrated in Figure 1. This type of dependance will be considered so often in this thesis that it will simply be referred to as "$(3\text{Cos}^2\theta - 1)$ dependance".

Usually the data leading to the perception of these interactions is taken as a series of line splittings measured as a function of rotation angle about an axis perpendicular to the external magnetic field. This will produce a graph of splitting versus angle that will correspond to a planar section through this three-dimensional surface of revolution. The resulting data may be presented in polar form, or more commonly, as splitting magnitude the ordinate against an abscissa of angle. As can be seen at once from the formula

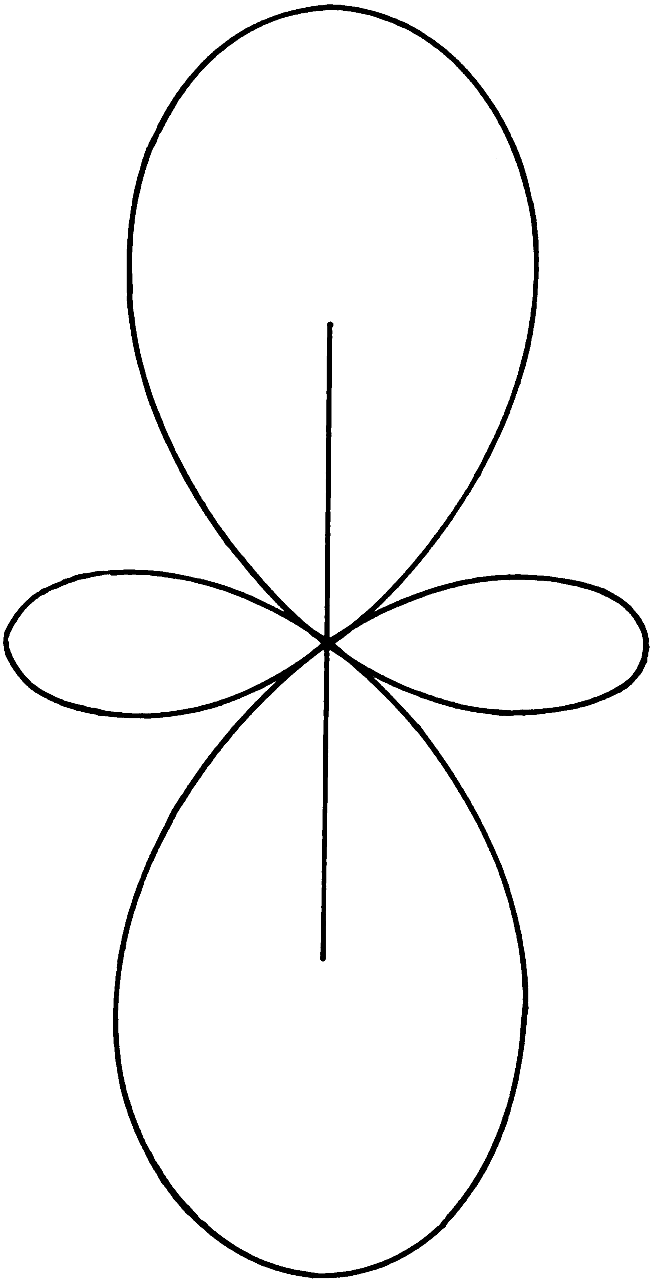

Figure 1. The function $R = 3\cos^2\theta - 1$ plotted in polar coordinates. θ is measured from the long axis of the figure. An isolated magnetic dipole-dipole interaction causes a splitting proportional to R if θ is the angle between the dipole-dipole axis and the applied magnetic field. One should think of this pattern as a section of a solid of revolution about the long axis of the figure.

and Figure 1, this dependance is repeated every 180 degrees. Therefore only data for a half circle will be presented.

Because the nuclear spin levels are so close together at the magnetic fields usually used, there is at room temperature only a small excess of nuclei in the ground state over the upper state. The proportion is about one in ten to the fifth. This means that the signals in even the best-relaxed substances are going to be small and not easy to detect.

Furthermore, in most solids the relaxation mechanisms are perhaps an order of magnitude less effective than in liquids. In some solids such as barium chlorate the relaxation time will be even longer, amounting to more than one second. Extreme cases not studied here can only be detected by methods using pulses separated by minutes.

Long relaxation times, besides being an experimental nuisance, also give information; since they depend upon the presence of certain factors. Close coupling to paramagnetic electrons, for instance, or to nuclei with electric quadrupole moments may give strong spin-lattice coupling or short relaxation times; while the isolation of nuclei from these factors, or the location of nuclei with electric quadrupole moments in a lattice having a high degree of symmetry and therefore a low electric field derivative, would tend towards long relaxation times.

In this study, we have used both the rf bridge method of detection and the sensitive oscillator. The work has been carried out in a temperature range from 4.2 to 423 degrees kelvin. Because of the dependance upon temperature of the relative population of the ground state to the upper levels very low temperatures have been used in some cases.

BARIUM CHLORATE MONOHYDRATE

BARIUM CHLORATE MONOHYDRATE

This substance was studied in the form of single crystals grown from an evaporating supersaturated water solution. Crystals about 25 by 7 by 7 millimeters were formed in about a month. The chemical was obtained in c.p. form, but no particular precautions were taken to insure that the material remained absolutely pure.

Crystals were grown both from distilled water solutions, and from tap water solutions. No significant differences were ever noticed nor should they be expected, since the nuclear resonance is an effect depending on the gross number of nuclei of a partiular species and the relaxation mechanism. Crystallization is a purifying process that tends to limit the quantity of impurities. The only possible effect of such impurities as would escape this selective process would be to alter the relaxation time and hence the signal amplitude. It would not affect the observed spectrum or its angular variation.

The crystals grew in two habits. Those grown at large supersaturations and high rates of growth were relatively needlelike with the long axis being the <u>c</u> axis. Others grown more slowly tended to be more tabular, <u>c</u> remaining the long axis though relatively shorter. In the first case the dominant faces were the (110), $(1\bar{1}0)$ and (101) but not $(10\bar{1})$ faces. In the second case the dominant

faces were (110) and $(1\bar{1}0)$ as before but the remaining face was replaced by (011) and $(0\bar{1}1)$ faces. It can be seen then, that these crystals possess a distinct enantiomorphism in the first modification; and indeed in all modifications there are vestiges of this in the emphasis upon certain small faces. No crystals were observed with opposite handedness.

The structure of barium chlorate has been studied by means of x-ray diffraction by Kartha (1952); and has been specified except as to the location of the protons in the waters of hydration as in Figure 2. The crystal is monoclinic of space group C_{2h}^{6}. The nuclear resonance spectrum has been studied already by Spence (1955).

He found three lines, a doublet showing $3\text{Cos}^2\theta - 1$ dependance of splitting upon orientation and a weak sharp central line. The maxima in the splitting of the doublet occurred in the ac plane 30.5° from the positive a axis towards the negative c axis. See Figures 3 and 4. This spectrum indicates that most of the waters in the crystal have their proton-proton axes aligned in one direction only. The spacing of the protons was determined from the magnitude of the splitting to be 1.56 angstroms. Spence also noticed that the widths of the lines in the doublet varied in such a manner as to seem due to the next nearest neighbor protons. The central line was ascribed to minute amounts of water trapped in the crystal during growth.

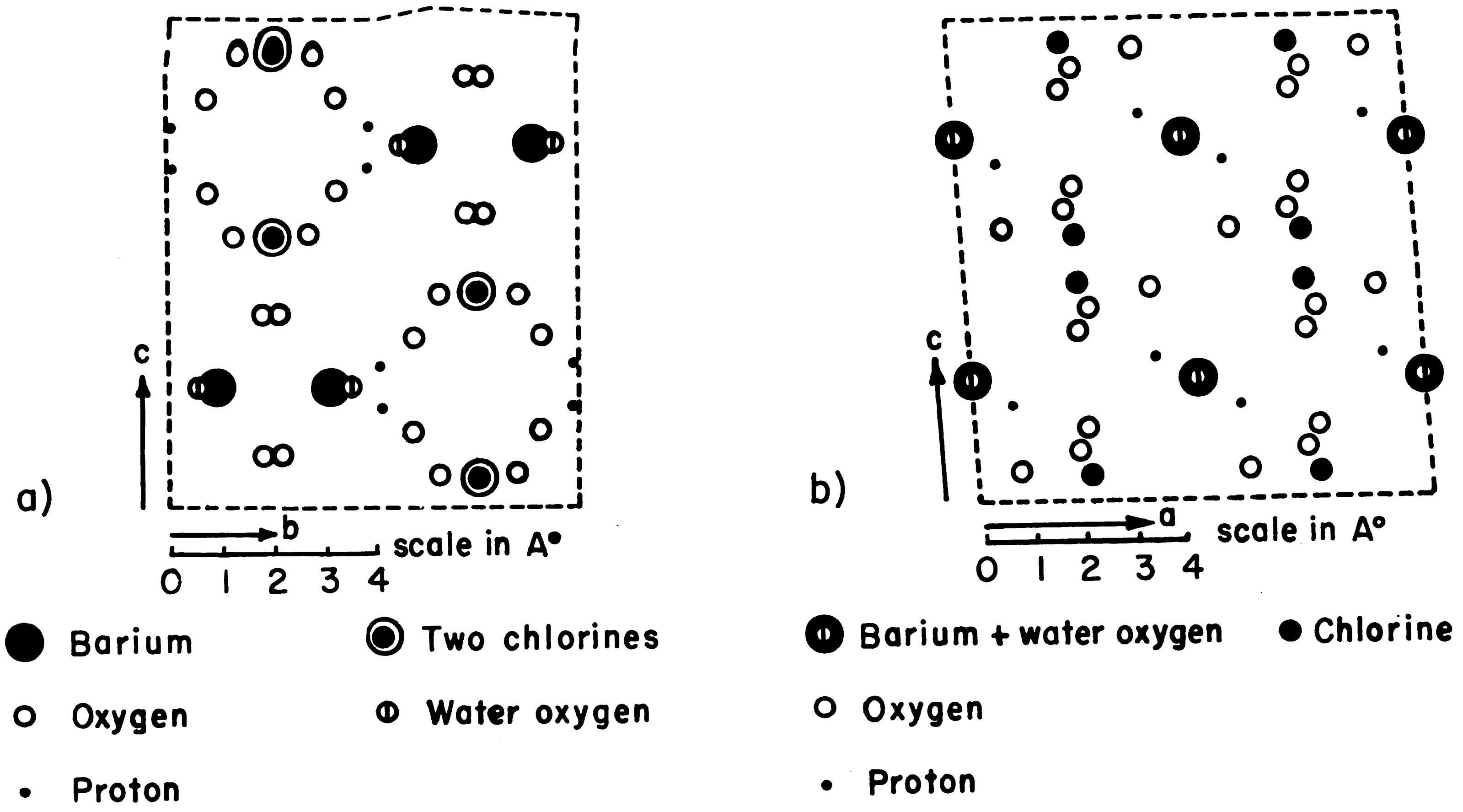

Figure 2. Projections of the structure of barium chlorate monohydrate according to Kartha, with the addition of the hydrogen atoms located by nuclear resonance. a) Projection on the <u>bc</u> plane. b) Projection on the <u>ac</u> plane.

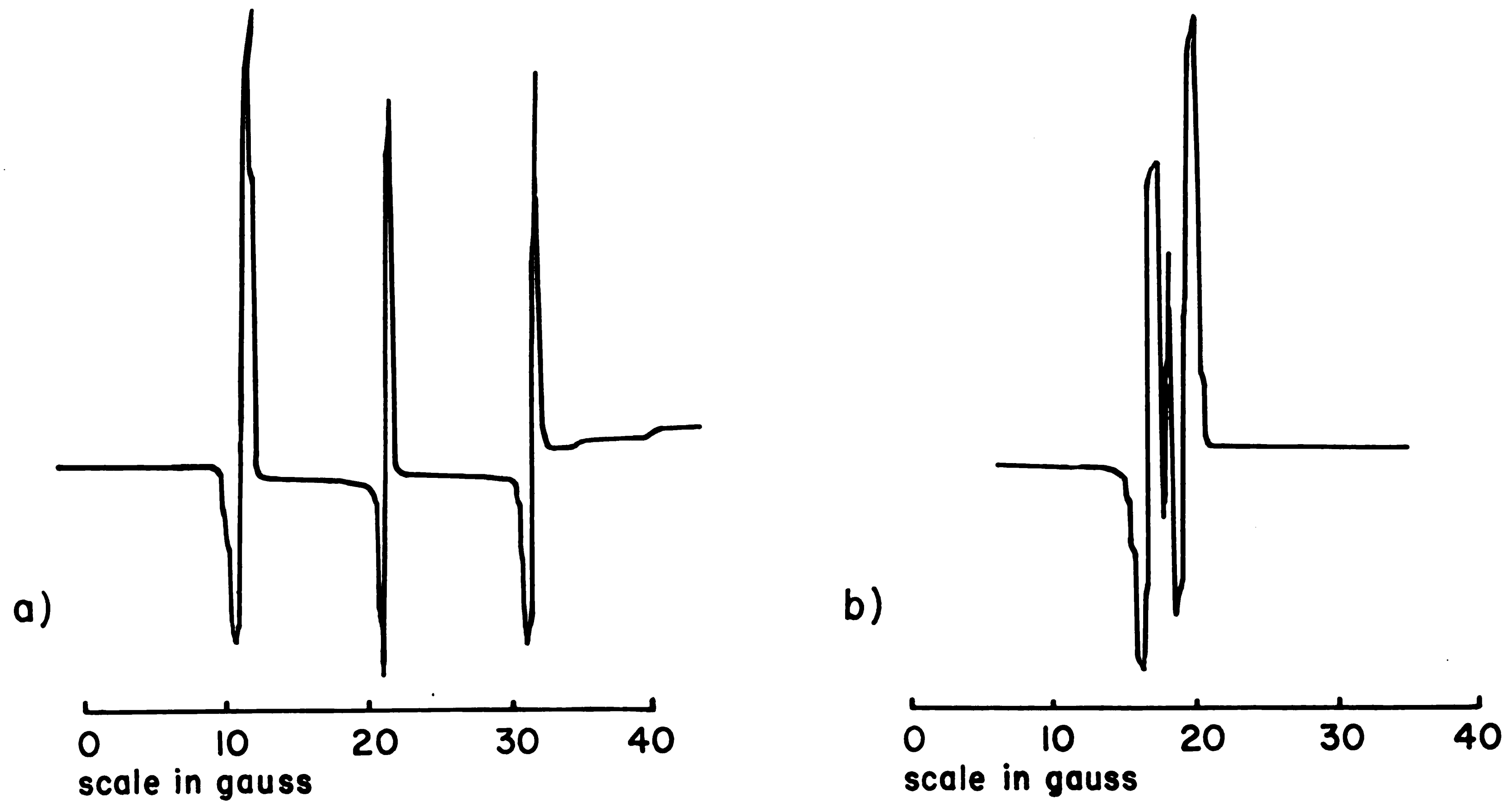

Figure 3. Lock-in derivatives of proton resonance of barium chlorate monohydrate. a) 124 degrees, b) 72 degrees, from the positive c axis in the ac plane. The lines merge near the c axis.

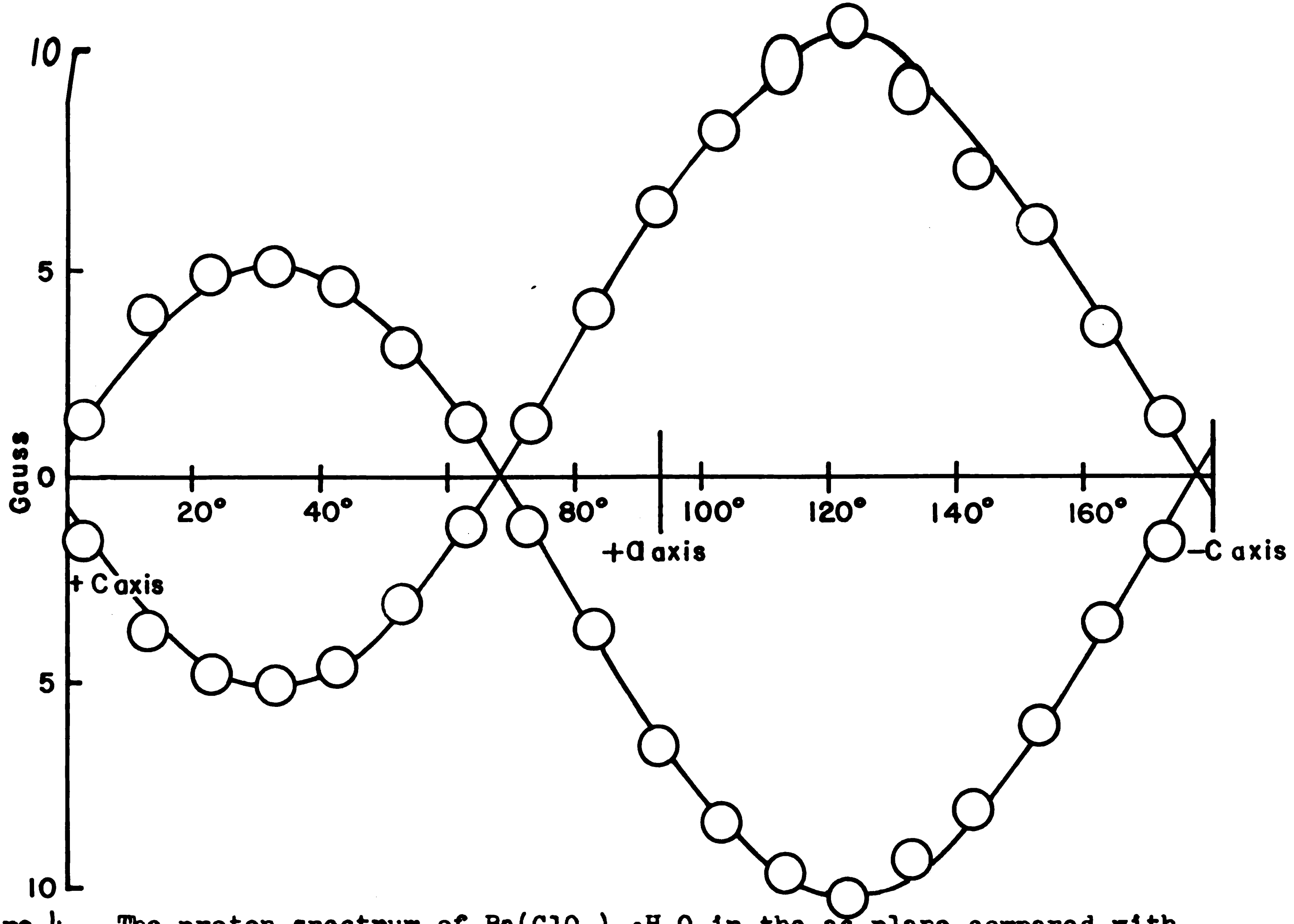

Figure 4. The proton spectrum of $Ba(ClO_3)_2 \cdot H_2O$ in the ac plane compared with $3\cos^2\theta - 1$ versus angle.

Assuming that the protons are located approximately along the lines joining the water oxygens to the chlorate oxygens as in Figure 5, one gets a sublattice of protons as indicated in Figure 6. One should note that adjacent sublattice layers are translated not only one-half unit cell distance in the b direction from each other, but also one-half unit cell distance in the a direction too. The location of water oxygens is determined by x-ray analysis and their specification as belonging to the water molecules is made by valence and stereo-chemical arguments. The choice is completely unique in this case.

In the present work we have re-examined the structure of barium chlorate with a view to determining whether the original hypothesis as to the source of the line width is correct. And in particular, whether it is possible to infer the positions of the next nearest neighbors from the line width data, rather than from the actual spectrum. The present experiment has been accomplished with considerably more resolution then that reported by Spence. See Figure 3.

Measurements of line width were made from such recordings. In this case, line width means the separation between points of steepest slope of the absorption line. Since these recordings are derivative curves, line width is measured by the lateral separation between adjacent peaks of opposite sign.

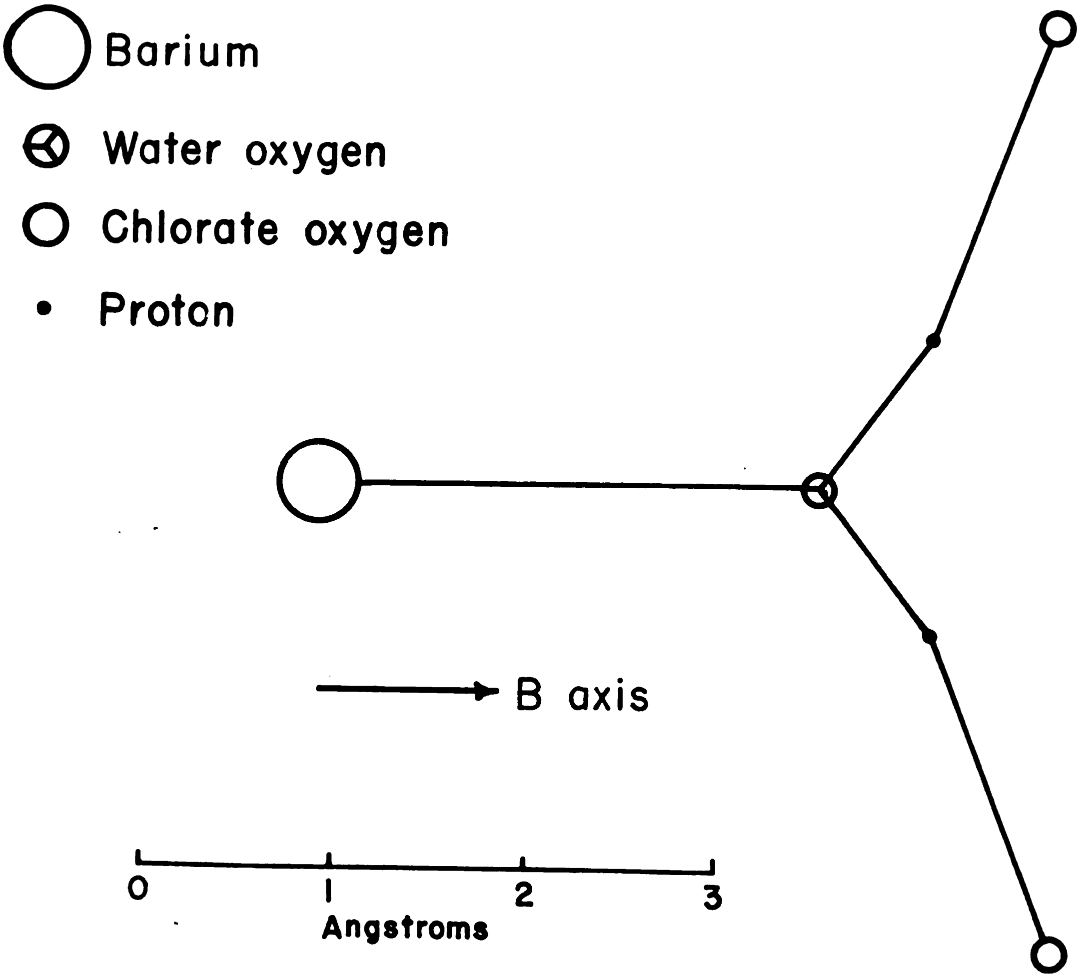

Figure 5. The arrangement of atoms in the plane containing the water of hydration. This plane contains the b axis and is inclined 30.5 degrees below the positive a axis. The chlorate oxygens are not quite in the plane.

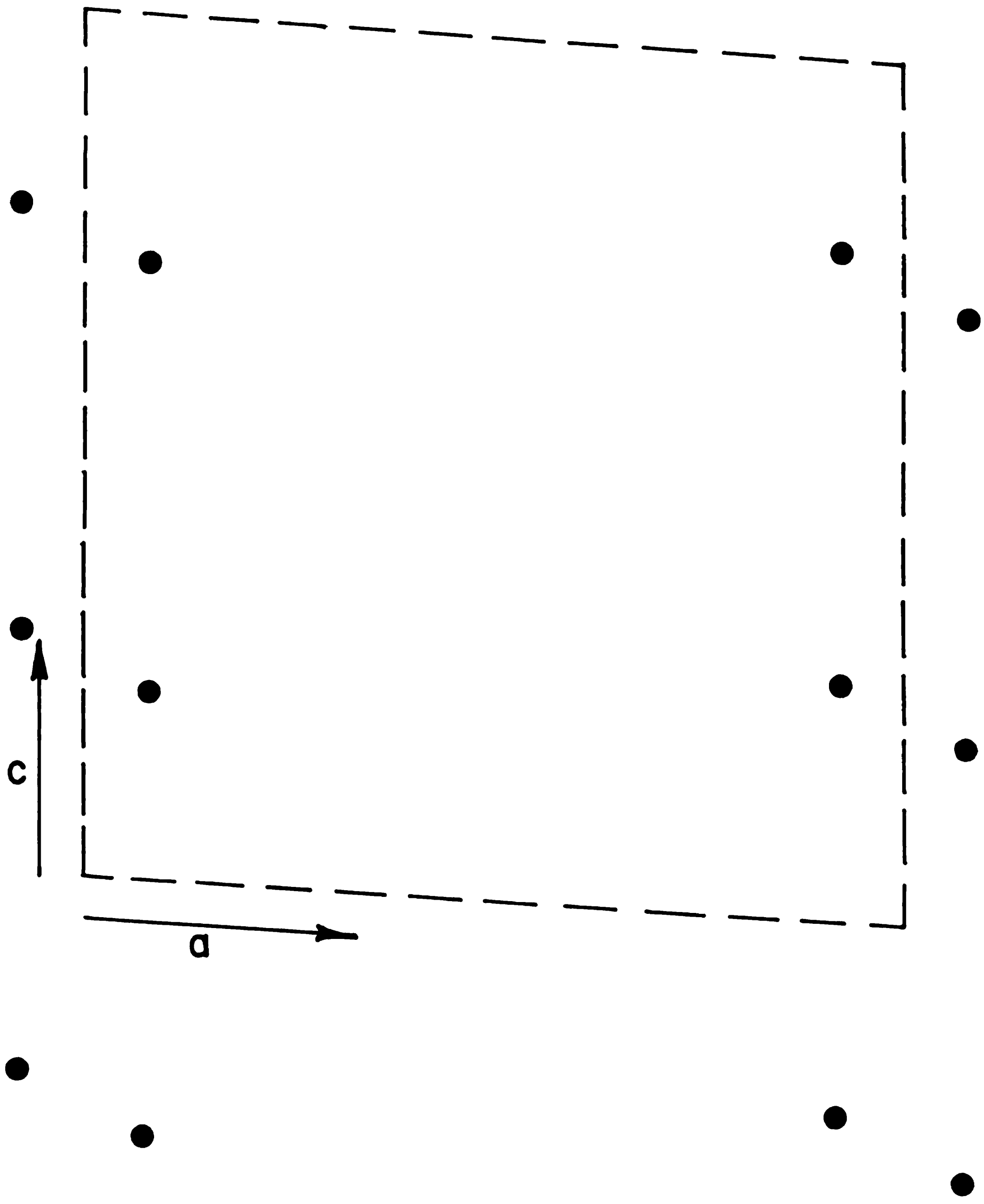

Figure 6. The proton sublattice planes in barium chlorate monohydrate. These layers of protons are located at y/b = 0 and y/b = 1/2; and are laterally displaced by an amount a/2. The separation between the planes is 3.90 angstroms.

If one assumes that these curves are gaussian in shape, this distance is just twice the second moment of the line. Such an assumption is not so arbitrary as it might seem. The shape of the line can be seen on the oscilliscope to be not very different from a gaussian and the error introduced by small departures from this shape will be small compared to line width.

The measured line width has been corrected for modulation broadening by the following formula: $\sigma^2 = \sigma'^2 - H_m^2/4$. Where σ is the true second moment; σ' is the observed second moment; and H_m is the peak-to-peak modulation amplitude. This correction has been shown to be theoretically correct by Andrew (1953).

We have calculated the second moment of the lines using the results given by Van Vleck (1948). Our calculation is carried out to three degrees of approximation. See Figure 7. The first includes only the four protons in the waters of hydration immediately above and below the protons of the water molecule under consideration. The second refinement includes a considerably larger number of protons and accounts for all those up to a lattice distance in every direction. In addition this refinement includes a factor of 1.02 to account for all similar nuclei in an infinite linear lattice in the same direction as the nucleus considered in the first lattice distance. This does not include those nuclei occurring at new directions from the

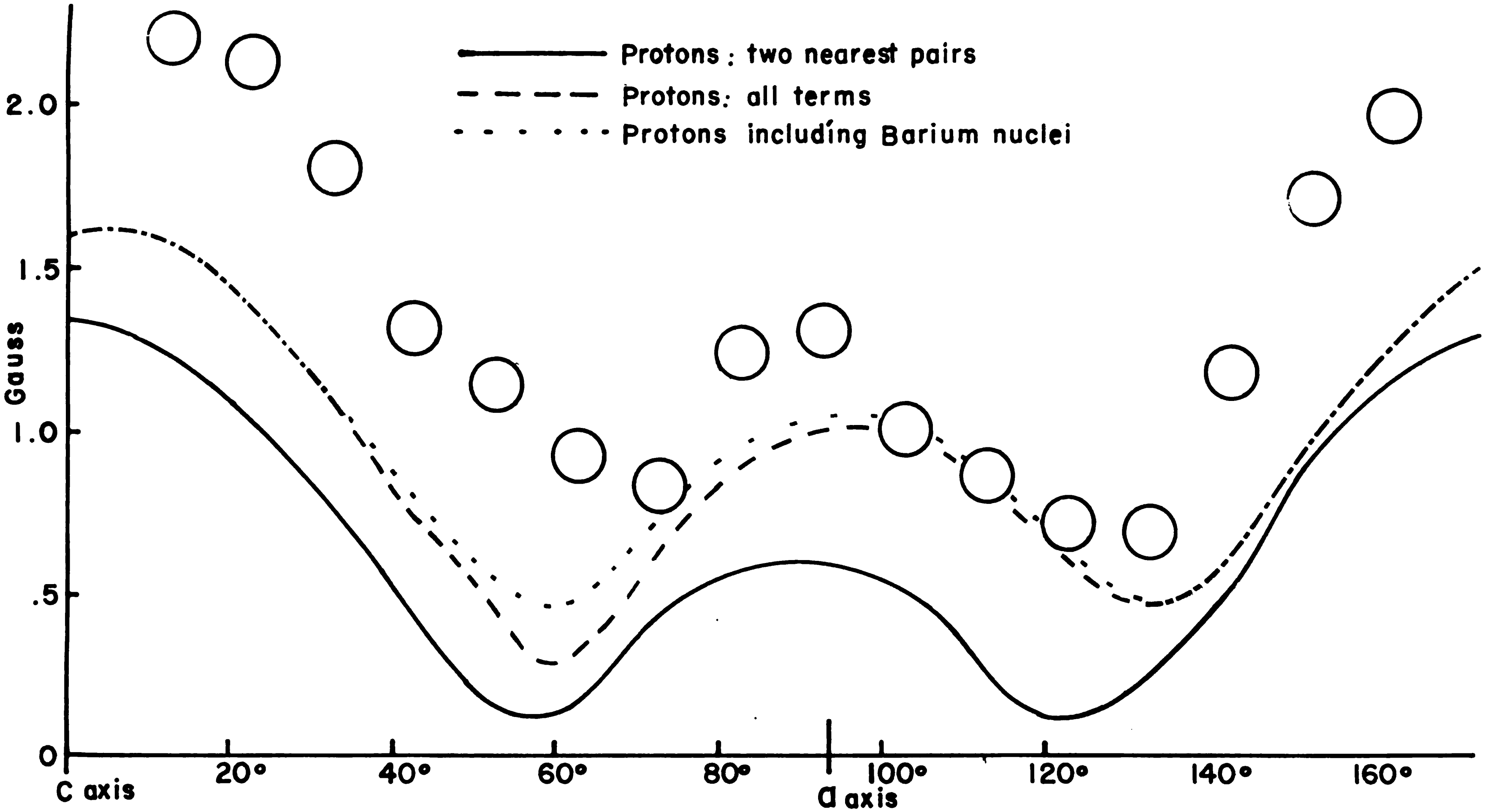

Figure 7. Line width of satellite lines in proton resonance spectrum of barium chlorate as a function of orientation in the ac plane. The data (circles) has been corrected for modulation broadening by the method of Andrew (1953). The heavy line represents the first approximation calculated for the width of the lines. Successively higher lines show the effect of including additional small terms.

perturbed nucleus and so accounts for only an indefinitely small proportion of the more distant nuclei. However, further corrections must be relatively small since the dipole field falls off as $1/r^3$. The last refinement includes the magnetic moments of the barium muclei, of which isotopic fractions (amounting to eighteen percent) have small magnetic moments.

The magnetic moment of the barium nuclei might be thought to be too small, or the isotopic percentage of magnetic nuclei among the non-magnetic might be considered negligible to contribute to the line width in comparison with the contribution of the protons. But, at the orientation in the magnetic field where the line width due to the protons alone is at a minimum, the contribution of the barium nuclei is at its maximum. This is because of the great proximity of the nearest barium nuclei as compared to the second nearest proton neighbors; and due to the particular relative orientation of the barium nuclei which causes this contribution to be near a maximum at just this point. See Figure 7. It is interesting to note that the result of Van Vleck (1948) includes the case of isotopic percentages directly without modification.

In using this formula for the calculation of split line widths, we have neglected the fact that it is meant to apply to the line width of single unsplit lines. However, these lines are so completely separated over most of the orientations of the sample in the magnetic field, that it was thought a good approximation to do so. But we do not expect this to be valid at small splittings. Here we are omitting the first term in the formula and are considering it to apply to the splitting separately.

This may be justified as follows: Consider the second moment of the entire pattern

$$S = \frac{\int_{-\infty}^{+\infty} h^2 \, P(h) \, dh}{\int_{-\infty}^{+\infty} P(h) \, dh}$$

where h is the magnetic field measured from the center of the resonance pattern and P(h) is the spectrum as an even function of h. Let $P(h) = W(h+\delta h) + W(h-\delta h)$ That is, P is composed of two identical lines whose spectral functions are W and which are centered at $-\delta h$ and $+\delta h$ respectively. Assuming that $\int_{-\infty}^{+\infty} hW(h) \, dh = 0$ and $\int_{-\infty}^{+\infty} W(h) \, dh = 1$

then $S = \dfrac{\int_{-\infty}^{+\infty} h^2 (W(h+\delta h) + W(h-\delta h)) \, dh}{\int_{-\infty}^{+\infty} W(h+\delta h) + W(h-\delta h) \, dh} =$

$$\tfrac{1}{2} \int_{-\infty}^{+\infty} h^2 W(h+\delta h) \, dh + \tfrac{1}{2} \int_{-\infty}^{+\infty} h^2 W(h-\delta h) \, dh$$

Substituting $h = h' - \delta h$ and $h = h'' + \delta h$ in the two integrals respectively one gets the result

$S = \int_{-\infty}^{+\infty} h^2 W(h) \, dh + \delta h^2$. This says that the second moment, S, of the entire pattern is equal to the second moment of one satellite line about its center, plus δh^2, the square of the separation of the satellite from the center of the entire pattern. This is analogous to Steiner's theorem in mechanics.

From Van Vleck's result one can get

$$S = \sum_{1}^{n} h_i^{2}$$

where $h_i = B_{jk} \sqrt{s(s+1)/3}$

and $B_{jk} = -\left[g\beta(3\mathrm{Cos}^2\theta_{jk}-1)\,/r_{jk}^{3}\right]\left[1+\frac{\delta^*_{jk}}{2}\right]$

In these formulas s is the spin of the perturbing dipole; g is its splitting factor; β is the magneton (such that $g\beta s$ is the magnetic moment of the perturbing dipole); r_{jk} is the length of the line joining the perturbed nucleus to the perturbing dipole; and θ_{jk} is the angle between that line and the external magnetic field; δ^*_{jk} is a specialized kronecker symbol which is zero except when the perturbing dipole, k, is the same variety as the perturbed nucleus, j. h_i is the same as the splitting that one would get from calculating a single isolated dipole-dipole interaction separately. See Pake (1948). Separating off the largest term which we will call h_1^2 we get $S = h_1^{2} + \sum_{2}^{n} h_i^{2}$. We assume that for large splitting of narrow lines we can identify h_1^{2} with δh^2.

This may be rationalized by noting that for a nearly isolated pair of nuclei the first term h_1^{2} is 1/3 of the square of that calculated by Pake for a completely isolated pair. This pair by itself would give two sharp lines. As perturbing nuclei are brought nearer to the pair we can see that the first effect must be a broadening caused by a spread in magnetic field about the sharp value. This is due to the permuted orientations of the perturbing nuclei. When the perturbing nuclei come so close that the broadening is of the order of the splitting, it is clear that we cannot allow the approximation. The region in which the assumption starts to fail is very narrow since the dipole magnetic fields fall off as $1/r^3$.

In $Ba(ClO_3)_2.H_2O$ this condition of widely split narrow lines is generously satisfied as the line shape shows. If we can identify h_1 with δh then $S = \delta h^2 + \sum_2^n h_i^2$. As a result, it is possible to assign the broadening of the lines to the remaining terms $\sum_2^n h_i^2$. Our calculation of these terms depends upon Kartha's structure and on the single fixed orientation of the waters. It is found to agree very well with the variation in the experimental line width.

The most significantly incorrect feature in this calculation is that the protons have been assumed to lie in the <u>ac</u> plane at $y/b=0$ and $y/b=\frac{1}{2}$. The protons in fact do not quite lie in these planes. Both members of any pair of protons are on the same side of the plane. But nearest neighbor pairs near any given plane are alternately on opposite sides of the plane. The distance from the plane to the protons is plus or minus .11 angstroms. However,

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neglecting this feature changes the largest three terms in the broadening only slightly.

Thus the second order interactions that we have measured form an integrated picture in relation to the structure of the proton sublattice and the remaining magnetic ingredient, the barium nuclei. Though we have not carried out a calculation of such structure from the data, but rather have worked in the reverse direction; the confirmation shows the possibility of locating next nearest neighbors by line width measurements.

DIOPTASE

DIOPTASE

Dioptase is a handsome green mineral possessing iridescent reflecting planes in the interior of the slightly translucent crystal. It is comparatively rare, and single crystals large enough for nuclear resonance study are extremely rare. The lack of perfection in large specimens accounts for the fact that dioptase is not ordinarily more than semi-precious.

The formula is $CuSiO_3 \cdot H_2O$. There are eighteen molecules to the unit cell and the space group is $R\bar{3}$. The mineral has been examined by x-ray diffraction by Heide and Boll-Dornberger (1955) who give a complete structure except for the location of the hydrogen atoms.

The crystal consists of hexagonal rings of six silicate tetrahedra in the *xu* plane while copper ions are disposed around the rings. The water oxygens lie in puckered rings of six between and coaxial with the silicate rings. All oxygen atoms except those chosen for the waters of hydration are in tetrahedral inter-relationship about the silicon atoms, as centers. See Figure 8. Heide and Boll-Dornberger speculated that the hydrogens are somehow located in the interior of the oxygen rings where there is certainly considerable space otherwise vacant.

Our problem in this section of the thesis is to show: a) how nuclear magnetic resonance can locate the

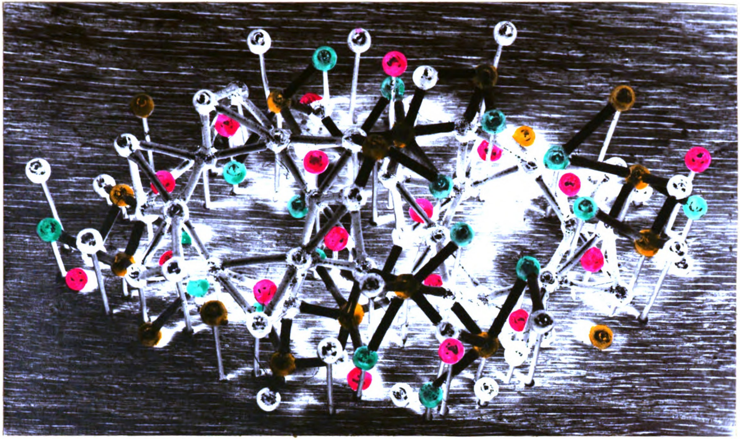

Figure 8. The structure of dioptase. The different colors represent different species or functions of atoms as follows: Orange: copper, Red: silicon, Green: oxygen which is part of a water molecule, Gray: oxygen belonging to silicon tetrahedra.

protons in the waters of hydration in a more complicated crystal than barium chlorate monohydrate; and b) the effect of the paramagnetic copper ions upon the proton resonance as a function of temperature. This will further demonstrate the utility of nuclear resonance in structural analysis, and its application to the gross magnetic properties of a strongly paramagnetic crystal.

This work has been made possible by the extensive x-ray analysis. Not only have the locations of all the atoms heavier than hydrogen been determined, but also the selection of those oxygens belonging to the waters of hydration has been set by valence bond saturation arguments. These oxygens are the only ones with bonds unsaturated by attachment to other atoms. Each one is part of the sixfold coordination of oxygen atoms around two copper atoms, but is not otherwise attached to any of the atoms besides hydrogen.

Furthermore, we know that the waters of hydration are difficult to remove from the lattice by heating.* Therefore the bonds holding the waters in the crystal cannot be extremely weak, as they are in the case of barium chlorate monohydrate.

The nuclear resonance data was readily obtained with the strong signals that might be expected in a crystal

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*Heide and Boll-Dornberger, (1955).

containing a large number of paramagnetic ions. Figure 9 shows some typical data. Both the apparent number and splitting of the lines varies with orientation of the sample in the magnetic field. At some orientations there is so much overlapping that only one broad line showing little detail is seen.

Figures 10 and 11 show the resonance spectrum as a function of angle about two mutually perpendicular axes. These are the $\underline{z}$ or trigonal axis, and the $\underline{x}$ axis perpendicular to it.

Rotation about the $\underline{z}$ axis shows hexagonal symmetry which is the result of the inherent 180 degree symmetry of nuclear resonance dipole-dipole interactions superimposed upon the trigonal symmetry of the crystal.

An instructive detail of the angular splitting dependance is the maximum splitting of 10 gauss. Knowing that waters of hydration reside in the crystal; and knowing that the smallest maximum splitting so far reported for firmly bound waters of hydration is about 19 gauss; we can be assured that the proton-proton axes are not in a plane perpendicular to the $\underline{z}$ axis. If such a plane were perpendicular to the $\underline{z}$ axis we would observe a much greater splitting of the resonance pattern at some angle in this rotation.

Furthermore, the maxima of the splitting occur approximately at an angle of thirty degrees from the $\underline{x}$ axes or parallel to the $\underline{u}$ axes. This is also perpendicular to the $\underline{x}$ axes.

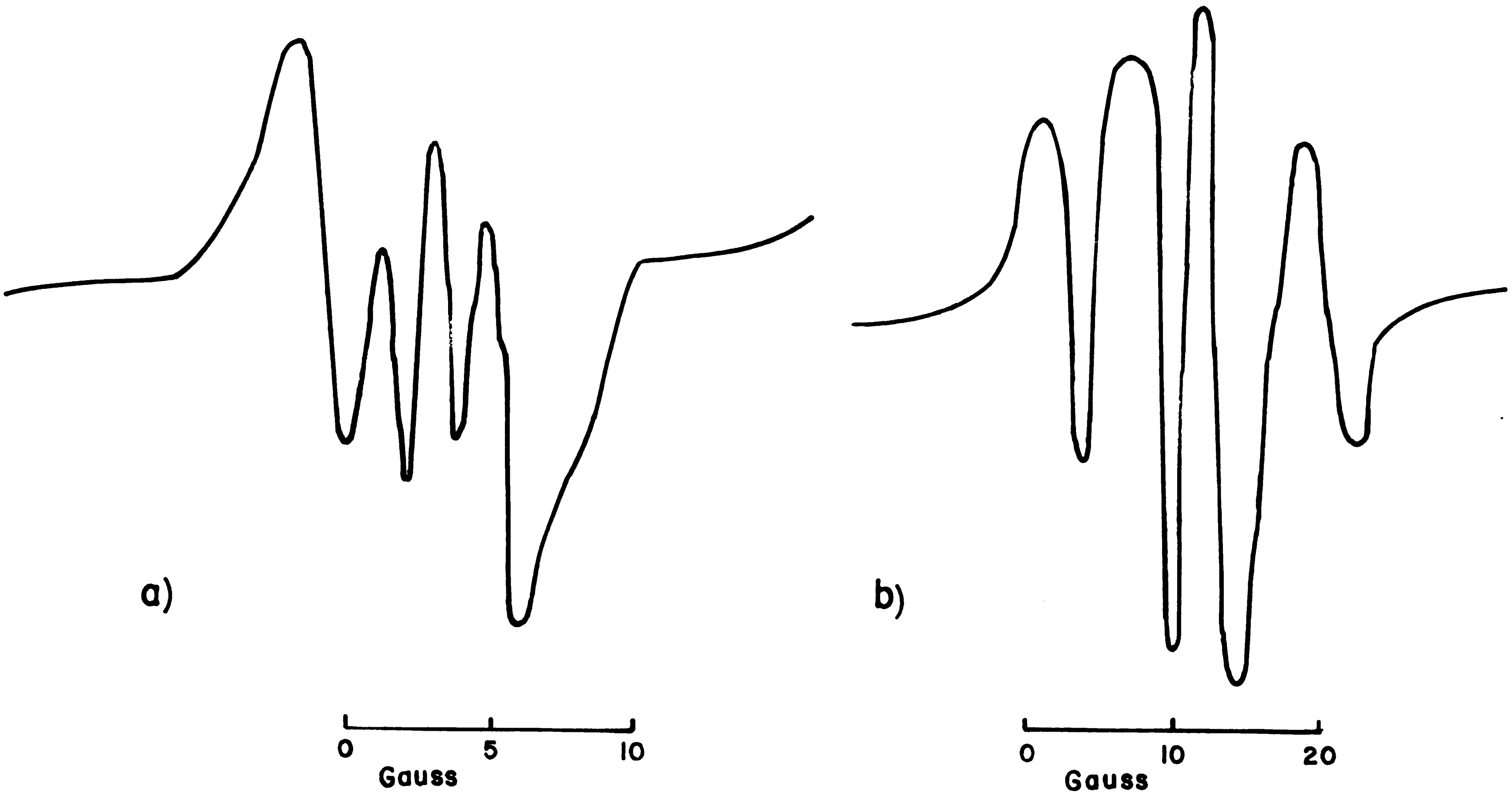

Figure 9. The lock-in derivative of the proton spectrum of dioptase at two orientations of little overlap. a) The spectrum 40 degrees from the u axis in the rotation about z. b) The spectrum 28.5 degrees from the z axis in the rotation about x. Note the different scales of magnetic field.

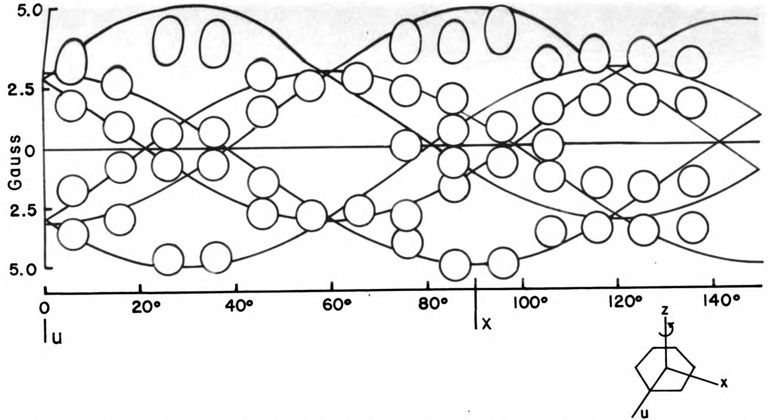

Figure 10. Proton magnetic resonance spectrum of dioptase as a function of angle about the z axis. Only 130 degrees are plotted since the hexagonal symmetry of the spectrum dependance yields no new information for the remainder of the half-circle. The poor quality of the data is due to overlapping of the lines rather than to any lack of signal strength.

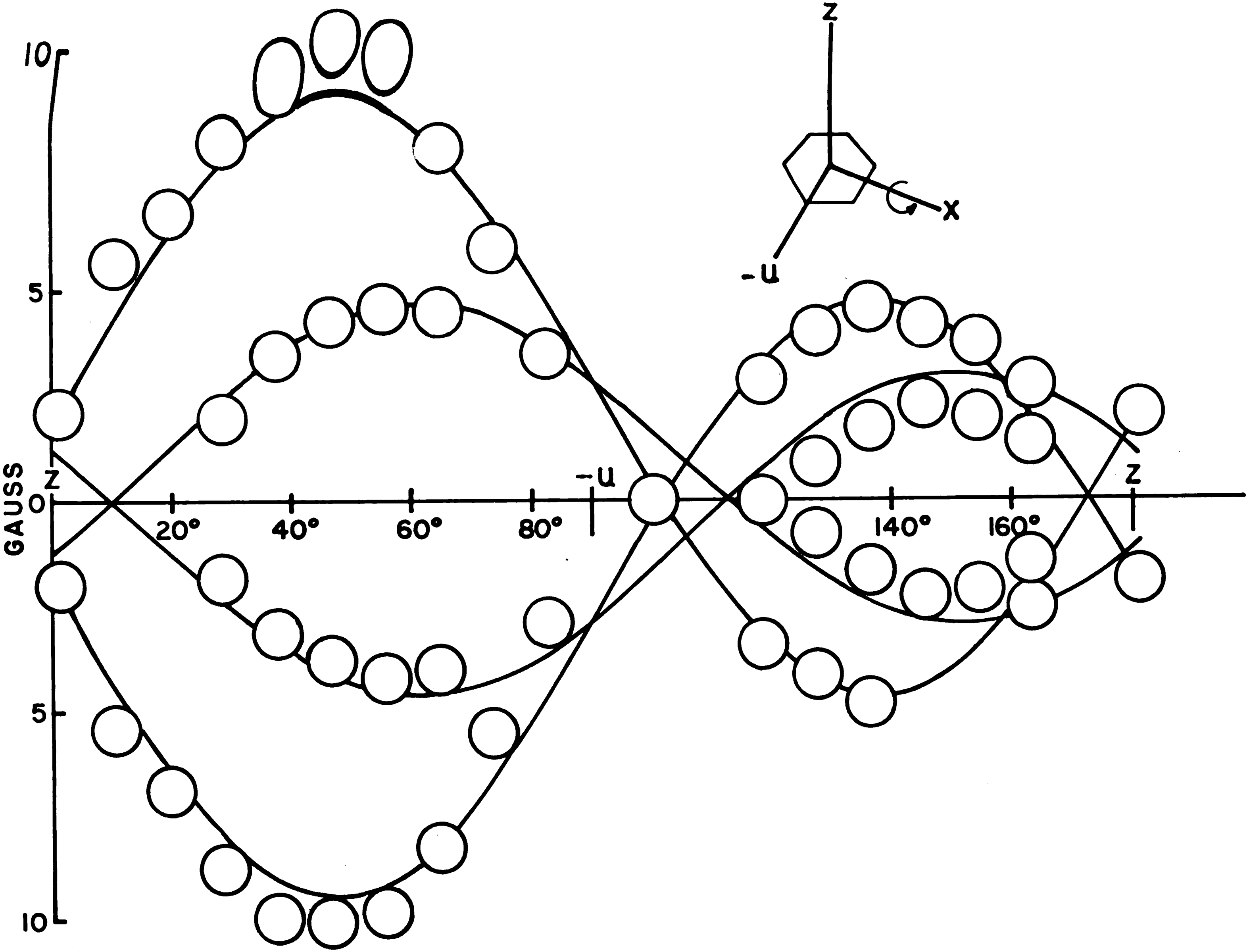

Figure 11. Proton resonance of dioptase versus angle of rotation about the x axis.

Figure 11 showing the splitting of the proton resonance pattern as a function of orientations in the magnetic field perpendicular to the x axis, shows the broadest splitting observed in the proton resonance spectrum of dioptase. The proton-proton axis is evidently perpendicular to the x axis and tipped about 47.5 degrees from the z axis. There is a great deal of additional evidence for such a conclusion in this figure.

To appreciate this evidence properly we must consider both the symmetry operations for the space group of the crystal and the effect of the geometric detail upon the nuclear resonance pattern. Now all the waters of hydration located regularly in the crystal must be subject to the symmetry operations of the space group $R\bar{3}$. All possible permutations of the proton-proton axes in a unit cell can be generated from the orientation of only one water molecule. This is because there is only one water molecule in the chemical formula; and there are eighteen molecules in the unit cell; and eighteen different equivalent locations are generated in the unit cell by the symmetry operations.

A set of symmetry operations sufficient to generate all eighteen are: one threefold rotation axis, a glide plane with three equivalent positions, and one space inversion. The translation along the glide plane cannot be detected by first order measurements of nuclear resonance splittings. Furthermore, a space inversion leaves orientations altered by exactly 180 degrees which cannot affect the nuclear resonance angular dependance which already has this two fold symmetry. As a result one is able to detect three, and only three, dipole-dipole axes by first order nuclear resonance measurements.

Let us visualize the pertinent angular relationships by considering the dipole-dipole axes to lie along the inclined edges of a three sided pyramid as in Figure 12. The base of the pyramid is equilateral. The angle of the inclined edges to the altitude of the pyramid is equal to the angle between the dipole-dipole axes and the $\underline{z}$ axis in the crystal. Call that angle A_o. In this case it will be 47.5 degrees. The axis about which our particular rotation is taking place is parallel to one edge of the base of the pyramid.

We will get two splittings. One will be from the proton-proton axis perpendicular to the axis of rotation and the other resonance pattern will be due to the other two hydrogen-hydrogen axes which will have identical resonance patterns. The identity of the last two resonance patterns arises because the dipole-dipole axes are coplanar with, and inclined symmetrically to, the axis of rotation. The angle of these axes to the plane of rotation is $C_o = \mathrm{Sin}^{-1}(\sqrt{3}/2 \ \mathrm{Sin}\ A_o)$.

The angle between the $\underline{z}$ axis and the side of the pyramid containing these two dipole-dipole axes and the

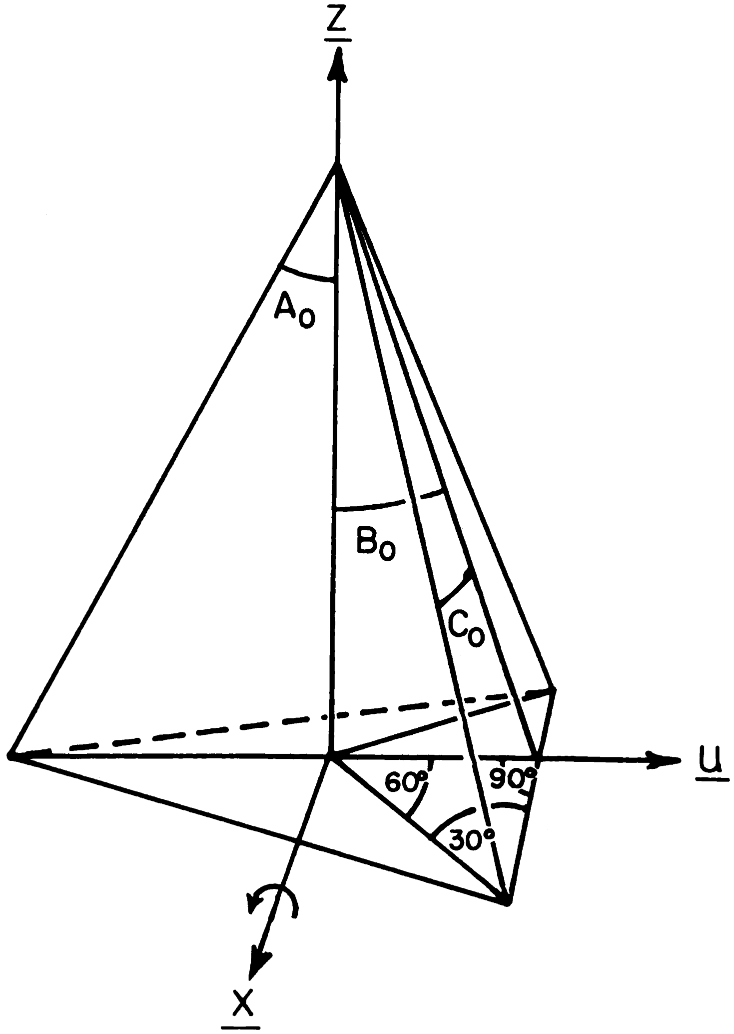

Figure 12. Angular relationship of dipole-dipole axes in dioptase.

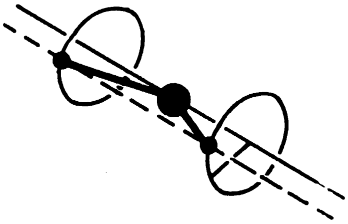

Figure 13. Possible locations of protons with respect to water oxygens.

axis of rotation will be $B_o = \text{Tan}^{-1}(1/2 \text{ Tan } A_o)$. The sum $A_o + B_o$ has to be the separation between the maxima of the two angular dependance curves in Figure 11. The z axis has to lie between these two maxima so that we must measure this sum in Figure 11 backwards from the largest maximum to the near z axis and continuing in the same sense from the z axis at the other end of the diagram to the smallest maximum. This comes out to be 76.5 degeees as can be seen in the figure. The curves are drawn according to the values calculated for the geometric situation outlined above, while the data are shown by the circles.

We thus confirm by nuclear resonance methods our selection of the z axis by external morphology. Consequently we assure ourselves of the correct choice of the xu plane. Our data in Figure 11 indicates a slightly incorrect selection since the errors are systematic in their angular dependance, but not merely shifted in angle. What we had chosen as the x axis is therefore a little out of the true xu plane.

We will now consider what the proton-proton axes that we have found mean in terms of the structure of the mineral. As noted before, the water oxygens lie in puckered rings of six between and coaxial with the silicate rings. Attached to each oxygen within a radius of approximately .98 angstroms must lie two hydrogen nuclei. Approximately this distance has always been found for the O-H bond length when measured by neutron diffraction or infra-red absorption spectra in a great variety of compounds.

By specifying the orientation of the proton-proton axes, and the radii of the protons about the oxygen atoms we restrict the spatial location of the protons to opposite ends of lines parallel to the specified direction and lying on a paraxial circular cylinder as in Figure 13. The only atoms near enough to share these protons with the water oxygens are other water oxygens or certain oxygens in the silicate rings. The particular inclination of the proton-proton axes suggests a unique assignment of the locations of the protons.

To consider possible locations for the protons we may imagine a circular cylinder coaxial with the $\underline{z}$ axis (and the silicate rings and the water oxygen rings) and passing through the water oxygen atoms. Such a cylinder will have a radius of 2.41 angstroms. We may then unwrap that cylinder and spread it out in a plane as in Figure 14.

We can now see that the only rational location for the protons is approximately in the surface of this cylinder and with locations specified by the proton-proton axis orientation and the standard separation from the oxygen atoms.

This picture explains why the waters are so firmly bound in the mineral. The waters are tied to each other in a two-dimensional ice structure and the alternate waters

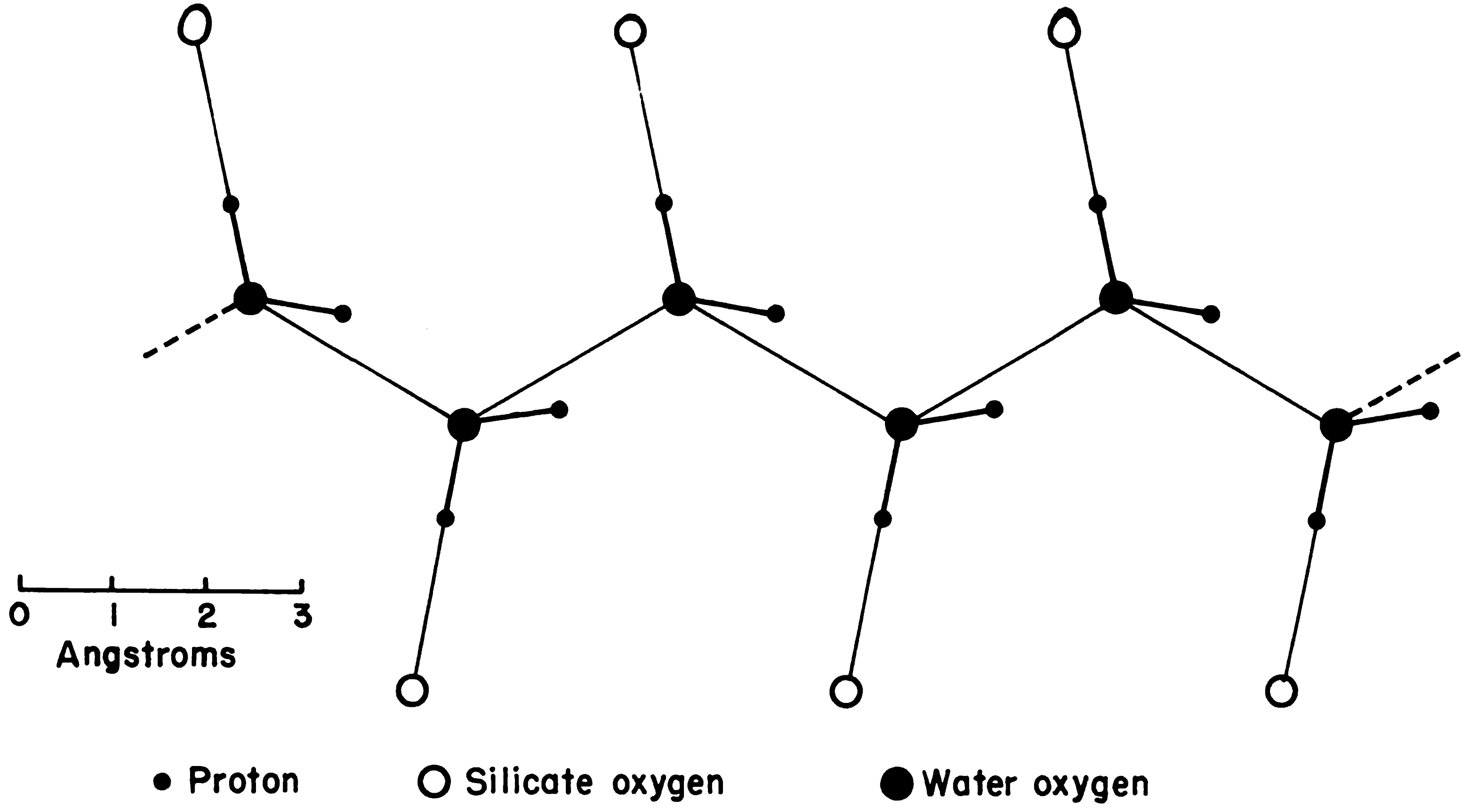

Figure 14. The arrangement of the water molecules in dioptase. The atoms have been projected upon a cylinder whose axis is parallel to the c axis, and coaxial with the silicate rings. The cylinder has been unwrapped to form a flat surface with the c axis vertical.

are attached to silicate oxygens in the silicate rings above and below the waters of hydration. As a result each water molecule is tied to the rest of the structure by three hydrogen bonds as well as being part of the coordinations about the copper atoms.

The O-H-O bonds within the ring itself are probably bent somewhat with the proton slightly shared with the second nearest neighbor oxygen atom. Therefore these protons probably lie slightly towards the inside of the cylinder.

Considering all these factors, we assign the following relative coordinates to the protons.

	x/a	y/a	z/c
P_1	.174	.067	.294
P_2	.124	.966	.414

Where a = 14.61 angstroms and c = 7.80 angstroms. These values are operated upon by the symmetry operations of the space group $R\bar{3}$ to produce all eighteen sets of two protons each in the unit cell of dioptase.

We will now discuss the magnetic moment of the unpaired valence electron on the copper ions. Because nuclear resonance is the matter under discussion we will consider only the effect of this component upon the proton resonance and the uses of the proton resonance in studying the electronic paramagnetism.

The first matter to be considered is the effect of the electrons upon the proton resonance spectrum at room temperature. To do this, we must estimate the magnetic moment associated with each copper ion. This will be done in two ways. In the first the magnetic moment of the copper ion is calculated assuming a magnetic moment equal to that from exactly one electron spin per ion. In the second we make an estimate of the magnetic moment of each copper ion, starting only from the bulk paramagnetic susceptibility of the crystal. The net effect of such a moment upon the spectrum is then calculated.

The susceptibility of a single unpaired electron is given by $g^2b^2\ S(S+1)/3kT$ where g is the Lande splitting factor of the electron, b is the Bohr magneton, S is the spin quantum number, k is Boltzmann's constant, and T is the absolute temperature. If this is multiplied by the magnetic field, 7000 gauss, that we have used throughout our experiments one gets the average magnetic moment of a single electron in this field.

This average moment is what has to be used in computing the effect of the electronic paramagnetism upon the nuclear resonance because the electronic relaxation time is short compared to the nuclear resonance period. As a result, the nucleus sees a field which fluctuates so rapidly that the only effect of the electronic moment is an average one.

Inserting the values of 2.00 for g; .927 x 10^{-20} erg/gauss for b; 1/2 for S; 1.38 x 10^{-16} erg/degree for k; and 289 degrees for T; one gets 2.33 x 10^{-27} erg/gauss^2 for the susceptibility. Multiplying this by the magnetic field of 7000 gauss yields a moment of 16.25 x 10^{-24} erg/gauss for the average magnetic moment of the electron.

We can arrive at a value for this from bulk measurements upon the crystal. Foex (1921) gives the specific susceptibility of powdered dioptase at this temperature as 8.8 x 10^{-6} erg/gauss^2 gm. This is an average over the various orientations of the powder particles so that we can only consider the isotropic average paramagnetism. The specific susceptibility χ_s is simply converted to the atomic susceptibility χ_a by the following formula: $M\chi_s/L = \chi_a$ Where L is Avogadro's number, 6.03 x 10^{23}, and M, the molecular weight, is 157 grams, for dioptase. χ_a comes out to be 2.30 x 10^{-27} erg/gauss^2. The resulting value for the magnetic moment of the copper ion will be 16.1 x 10^{-24} erg/gauss. Thus at room temperature the gross paramagnetism of the material is in excellent agreement with the supposition of one unpaired electron per copper ion.

Let us calculate the effect of this moment upon the proton resonance. There are two copper ions near each proton pair. More remote coppers may be neglected due to the rapid falling off of the field of magnetic dipoles with distance. The distances of the near copper ions from one proton of the pair are 3.0 angstroms and 3.2 angstroms. The distances of the coppers from the other proton in the pair are 2.9 and 3.2 angstroms. Both coppers are almost in the same direction from the proton pair.

For simplicity let us assume that both coppers are as close as 2.9 angstroms and in the same direction from the protons. To begin with we will treat the case of one copper ion only.

We are here considering the magnetic effect of an electron which passes so rapidly from one state to the other that the only net effect is due to a slight preponderance of time spent in one state. Thus we will use the average magnetic moment instead of the total magnetic moment of the electron. Let us call this $\bar{\mu}$. Then $(\bar{\mu}/r^3)$ $(3\mathrm{Cos}^2\theta - 1)$ is equal to the magnetic field at the proton due to the electron. Here r is the length of the line from the ion to the proton, and θ is the angle between this line and the external magnetic field. We can find the upper limit of the field due to the electron by picking the maximum value for $(3\mathrm{Cos}^2\theta - 1)$ which is 2; and simply multiplying the magnetic moment divided by the cube of the distance by this same factor of two. $2\times 16.13 \times 10^{-24}/24.4 \times 10^{-24} = 1.32$ gauss at room temperature. Now because this is due to an average moment we will not see both a plus and minus effect upon the resonance, but rather a shift of the resonance line of approximately one-and-one-third gauss. This will be anisotropic for a particular pair of protons. However, the lines are so broad that the observation of merely the presence or absence of such a shift is uncertain.

At 87 degrees kelvin the susceptibility and the average magnetic moment get be calculated in the same way as at room temperature. We can an atomic susceptibility of 7.18×10^{-27} erg/gauss^2 and a magnetic moment at a field of seven thousand gauss of 50.3×10^{-24} erg/gauss. From the specific paramagnetic susceptibility of 21.1×10^{-6} erg/gauss^2 gm measured at this temperature by Foex (1921) we calculate an atomic susceptibility of 5.53×10^{-27} erg/gauss^2 and a resulting magnetic moment per electron of 38.7×10^{-24} erg/gauss. Using the experimental value for the calculation of the maximum possible shifting of the resonance lines as before, one arrives at 3.2 gauss. Since the lines are considerably broader at liquid air temperatures than at room temperatures we cannot report observing this anisotropic shift. No attempt was made to observe the static shift due to the bulk paramagnetism of the sample. Actually this is much less than the anisotropic component at the protons, amounting only to .147 gauss at 87 degrees kelvin.

So far we have ignored the fact that there are actually two copper ions instead of one as near neighbors to the protons. We can justify this as follows: Consider the effect of the addition of a second unpaired electron to the first. We assume that each electron produces the same effect at the location of a particular proton. This assumption is very nearly fulfilled in practice, because of the proximity of the coppers to each other and the same general direction between the proton pair and each copper.

Furthermore we assume that the orientations of the electrons fluctuate in an uncorrelated fashion from alignment with the field to alignment against the field. The first electron spends only a little more than half of its time oriented with the applied magnetic field, and only a little less time aligned oppositely. Accordingly, the two electrons considered together spend only about one quarter of the time both aligned against the field and one quarter of the time aligned cooperatively with the magnetic field. They are aligned antiparallel to each other for half the time.

The only contribution to the net magnetic moment will be the surplus of time spent cooperatively parallel with the field over the time spent both parallel to each other but against the field. Although the magnetic moment of these states is twice as great as in the case of the single electron, the surplus time spent in one over the other, is only half as great. As a result the average magnetic moment is unchanged.

Exchange coupling between the electrons can destroy the assumption that the electrons fluctuate independantly. However so long as the substance remains paramagnetic as opposed to ferromagnetic or antiferromagnetic this assumption will probably hold.

When dioptase was cooled further the proton resonance suddenly disappeared in the neighborhood of 20 degrees absolute. It was not observed below this temperature.

In a purely paramagnetic substance one would still expect to see nuclear resonance at such temperatures since the relaxation mechanism through the spin-lattice interaction should not be quenched yet.

As a result we have concluded that the material has undergone a magnetic transition which has two effects. The first is that the spread in the values of the magnetic field at the protons has been greatly increased by the strong alignment of the electrons by cooperative interaction.

The second is that a definite alignment may effectively diminish the spin-lattice interaction of the electrons. The consequence of this is the reduction of the spin-flipping frequency of the electrons to the point where the spin-lattice mechanism for the relaxation of the proton spins may be interfered with.

We have sought to distinguish whether this transition is to a ferromagnetic or antiferromagnetic state. It is possible that the transition is to some intermediate state, such as ferrimagnetic. In order to make such a distinction we have measured the location of the resonance line as a function of temperature just above the transition point. This would furnish an estimate of the bulk susceptibility of the material.

The suceptibility of ferromagnets in the region above the curie temperature is a monotonically decreasing function of temperature. The susceptibility of antiferromagnets tends to have a knee in the dependance on temperature such that there is either a maximum in the susceptibility above the Curie temperature or at least a point where the slope of the paramagnetism with temperature suddenly becomes more greatly negative.

We have not been able to measure any such change in the susceptibility by comparing the proton resonance against a reference sample. However, the very lack of slope to the paramagnetic susceptibility curve near the transition is an indication against ferromagnetism. Thus there is a strong likelihood that what is observed in dioptase at 20 degrees is an antiferromagnetic, or at most a ferrimagnetic transition.

The accuracy of measurement of temperature in this region is unfortunately not very great as we had only an erratic carbon resistance thermometer available. We therefore set limits of plus or minus six degrees on the temperature measurement.

The conclusion that is to be drawn from this study in the proton resonance of dioptase is that nuclear resonance has proven to be not only useful in locating the protons in the waters of hydration; but also has demonstrated for the first time in this material the existence of a magnetic transition. Something about the nature of that transition has also been shown, and it is perfectly possible that further resonance experiments would show conclusively the nature of this transition. The effect of the electron paramagnetism above the transition has been estimated, but because of its relatively small size has not been definitely detected.

We believe therefore that the utility of nuclear resonance as a tool for the study of matter has been forcefully demonstrated once more.

GUANIDINE ALUMINUM SULFATE

GUANIDINE ALUMINUM SULFATE

We next come to a material whose structure was unknown prior to our nuclear resonance observation. It represents perhaps the first compound whose main structural features have been deduced from nuclear resonance data and stereo-chemical arguments. As such, it is a very favorable case for the application of nuclear resonance to structure determination.

Guanidine aluminum sulfate hexahydrate, or as is usually abbreviated GASH, is a ferroelectric trigonal crystal of space group C_{3v}^2 according to Wood (1956). It is grown from a water solution of guanidine sulfate and aluminum sulfate as apparently perfect clear crystals. The formula is $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$.

There are three types of ferroelectric regions, each of which can have two opposite orientations in a single crystal. The type of region depends upon the direction of growth in the original crystal. These properties are a permanent part of the crystal, since the Curie temperature is above the melting point. See Holden, Merz, Remeika and Matthias (1956).

The three regions differ from each other in the amount of bias that the ferroelectric hysteresis loops of the regions exhibit. Growth along the z or trigonal axis produces the greatest bias, while there are two types of region with lesser bias produced by lateral growth. Preferred growth is in only one direction along the z axis.

Since a complete structure analysis has not been made separately for the three ferroelectric regions of GASH, it is not certain that the three regions are of identical structure. The permanent nature of the different regions in the crystal suggests that there may actually be a structural difference between them.

Etch pits made in the (0001) planes of the crystal with water are triangular pryamids. The pyramids are symmetric if growth in that region has taken place along that axis. Where the crystal has grown laterally the etch pits are tilted. See Wood (1956).

Our study has been made upon two crystals which have been very kindly supplied by the Bell Telephone laboratories. The samples were cylinders of rotation about the z and x axes. The crystal cylinder concentric with the z axis showed both symmetric and tilted etch pits. We therefore cannot be sure whether we have studied a crystal that was "single", or twinned, or even more radically different, from portion to portion. Rotations of these crystals in the magnetic field were made, and the nuclear resonance derivative curves were recorded for every ten degrees.

The nuclear resonance data as a function of orientations of the crystal in the magnetic field perpendicular to the z axis showed hexagonal symmetry. See Figure 15. This is to be expected from a trigonal crystal. The large major splitting of 20 gauss is characteristic of the maximum splitting of waters of hydration. It therefore seemed evident from the first that three sets of proton-proton axes belonging to the waters of hydration lie in the (0001) plane. The relative orientation of the maxima about the z axis showed that the p-p' axes were perpendicular to the x axes or parallel to the u axes.

The orientation of the crystals was marked on them at the Bell Laboratories. The choice of axes was checked and confirmed by the alignment of the sides of the etch pits in the cleavage planes at the ends of the crystal.

The supposition that the most widely split lines were due to the waters of hydration was strengthened by measurement of the relative area under these lines. On photographs of the absorption spectrum these seemed to have one-ninth of the total area. See Figure 16. As there are two such lines symmetrically displaced about the center of the pattern, the combined area of the two is two-ninths of the total area under the absorption spectrum.

Since there are three such sets of maxima, the total area of absorption belonging to the most widely split lines must be three, times two-ninths. This is just two-thirds. That is the stoichometric proportion of protons associated with the water of hydration in $C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$. There

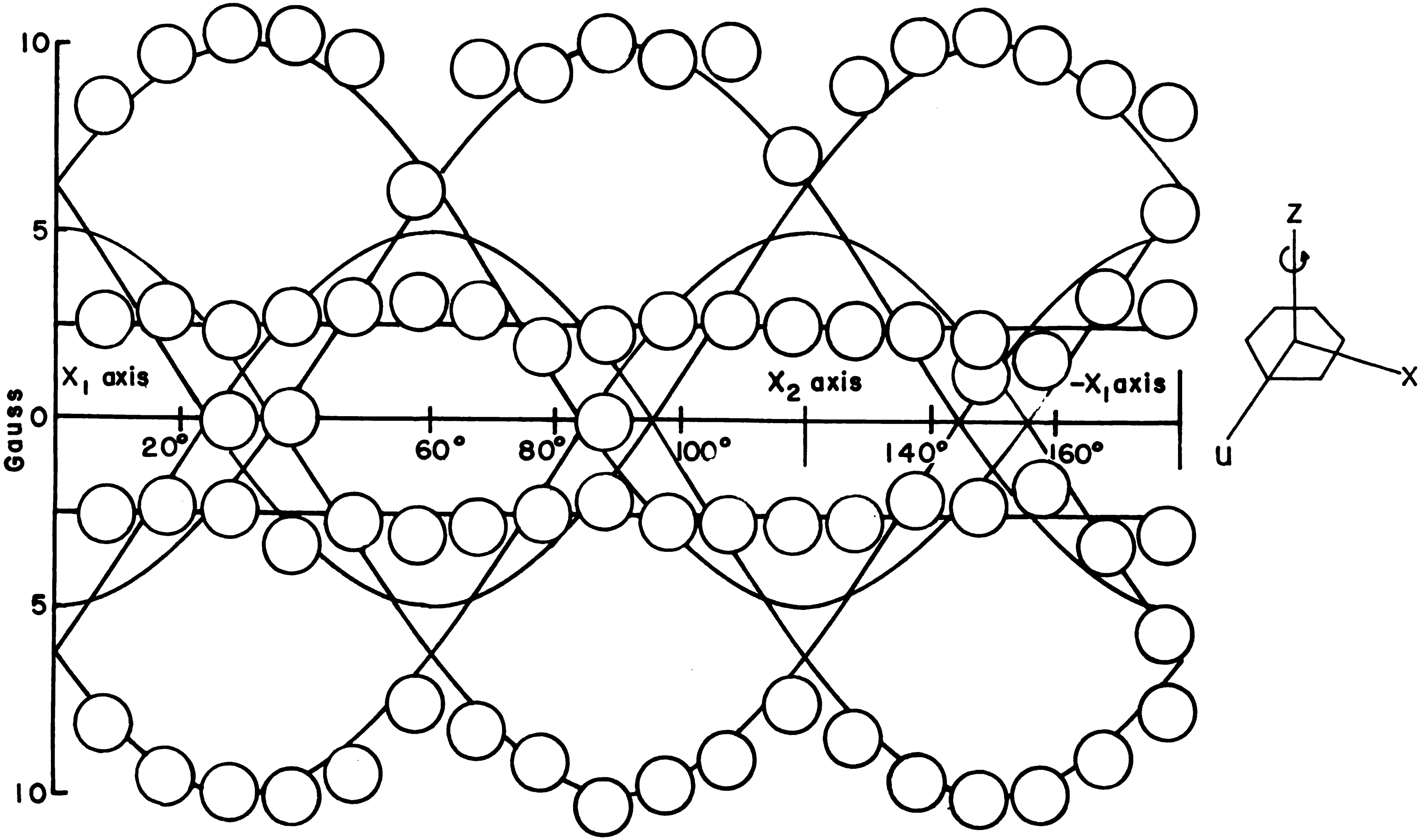

Figure 15. The dependance of the splitting of the nuclear resonance spectrum of GASH upon angle of the magnetic field H_0 in the plane perpendicular to the z axis. The u axis is parallel to the magnetic field at thirty, ninety, and one hundred and fifty degrees.

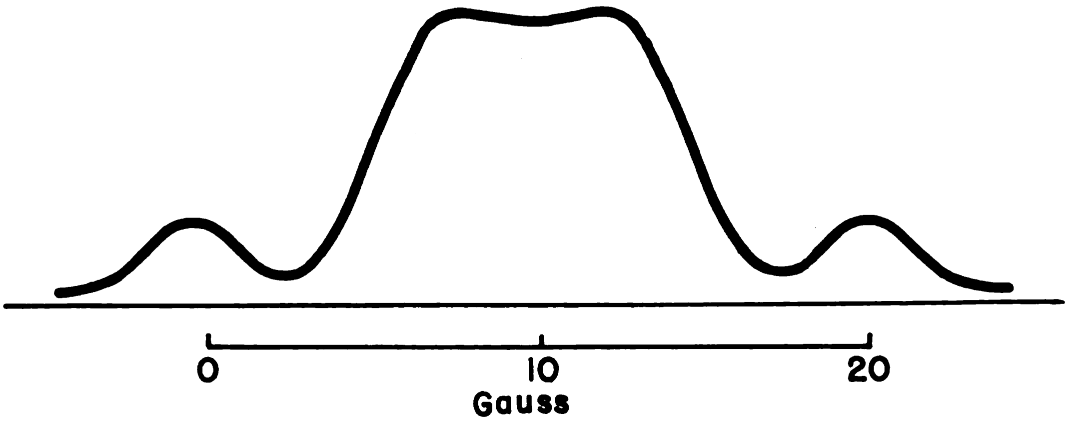

Figure 16a. A schematic representation of the proton resonance absorption in GASH. This is taken from photographs of an oscilloscope trace of the absorption at the angle of maximum splitting. This occurs for H_0 parallel to the u axis. The area under the two humps is approximately one-ninth of the total.

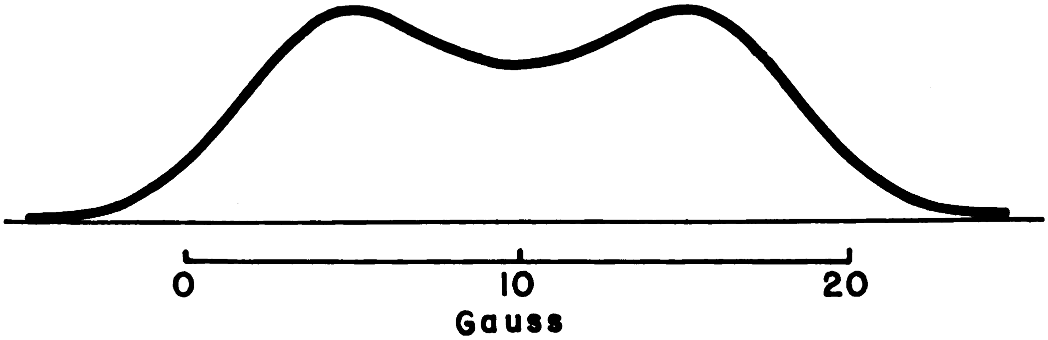

Figure 16b. The absorption spectrum of GASH for H_0 parallel to the z axis. This pattern is one found in the rotation of the crystal about the x axis.

is no guarantee that this reasoning is correct, but it does lend an air of probability to the conclusion that the most widely split lines belong to the waters of hydration.

For such reasoning, a necessary condition is that the protons should all contribute equally to the total absorption in this region. This condition was insured by the following. The lines were very difficult to saturate; the signal-to-noise ratio of the absorption spectrum was high; and the area measurements were made with the applied radio-frequency power sufficiently low to ensure no saturation of the resonance absorption.

The central portion of the spectrum contains not only a large number of lines which are widely split at some orientations as we have just discussed, but also additional absorption lines which are not distinguishable in this rotation of the crystal.

A rotation about the $\underline{x}$ axis was therefore also made yielding the data shown as circles in Figure 17. Based on the conclusions from the previous rotation, both the position and the relative area under two sets of lines could be predicted. The most widely split line shows just one ninth of the total area and as before is due to a proton pair in the (0001) plane perpendicular to the $\underline{x}$ axis which is the axis of rotation for the crystal. In addition, there is one pair of lines which is due to the two proton pairs which are perpendicular to the other $\underline{x}$ axes. These are at 120 degrees to the axis of rotation.

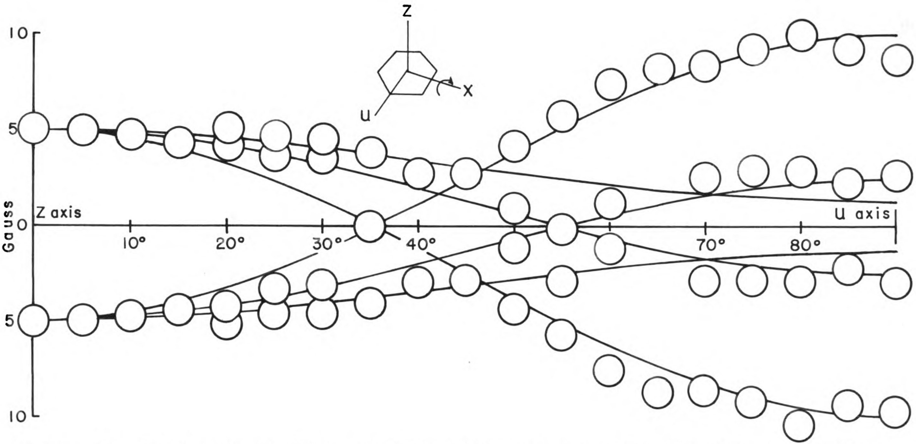

Figure 17. The dependance of the splitting of the proton resonance spectrum upon angle of rotation about the x axis. The magnetic field assumes the various orientations in the plane perpendicular to the x axis. Only data for ninety degrees of rotation is shown for clarity of detail. The angular dependance reflects at the x and u axes so that it is symmetric with respect to those axes.

The remaining data suggests a set of proton pairs which are parallel to the z axis. The splitting of this pair of lines is less than what one would expect if it were due to the interproton distance in the hydrogen pairs in guanidine. Furthermore it would seem from the data that all of the guanidine proton-proton axes are parallel to each other. The guanidine radical is usually supposed to be planar in structure and trigonal in symmetry. The carbon is supposedly surrounded by three nitrogen atoms and to each of these are attached two hydrogen atoms. If the proton-proton axes are parallel to each other in such a model, either the trigonal symmetry or the planar structure would have to be violated.

Furthermore, the wide spacing of the hydrogen atoms is contrary to previous knowledge of the structure.

These difficulties can be simultaneously resolved by the supposition that the guanidine radical is in rotation about its axis of symmetry. This axis is assumed to coincide with the z or trigonal axis in the crystal. The rotation is supposed to take place with a frequency that is of the order of the nuclear resonance frequency. The effect of such rotation upon the spectrum is to yield a pattern equivalent to a pair of resonant dipoles whose connecting axis is parallel to the axis of rotation. See Gutowsky and Pake (1950). The line splitting of such a case is just half of what it would be for the same separation of similar static non-rotating dipoles.

The actual dipoles could then lie at angles of 120 degrees to each other in the plane of the radical as is commonly supposed to be the case. Each dipole-dipole axis would then be rotating about the carbon at the center of the molecule and there would be no distinction between them in the spectrum.

Support for such a view of the structure of guanidine aluminum sulfate hexahydrate is to be found in the classic demonstration by Andrew and Eades (1953 a and b). They showed that some entire benzene molecules rotate about their axes of symmetry in solid benzene at temperatures above 90 degrees kelvin. Above 120 degrees kelvin almost all the benzene molecules are in rotation about their hexagonal axes. The melting point of benzene is 278.5 degrees kelvin. It is not surprising therefore if a radical of smaller moment of inertia and similar size should be in rotation at temperatures of the order of 293 degrees kelvin.

An attempt was made to study the resonance at low temperatures by cooling a sample of GASH to liquid air temperatures. The large internal stresses induced by the temperature change however destroyed the crystal. At some sufficiently low temperature the rotation of the radical should cease, and a corresponding broadening of the resonance should be observed.

Finally, the second moment of the line shape of a powdered sample has been observed by McCall (1957) at low temperatures. The second moment increased from 21.7 gauss at 296 degrees kelvin to 26.9 gauss at 77 degrees kelvin. He concluded that some of the proton groups in the material were in motion at room temperatures, and hypothesized that these were in fact, in the guanidine radical, which rotated about its trigonal axis.

Knowing the orientation of the proton-proton axes in GASH, and assuming that we can assign the different resonances to the different constituents of the crystal, it is possible solely through the addition of stereo-chemical arguments to suggest an approximate atomic structure for the crystal.

Let us first note some pertinent matters. The formula of GASH is very similar to the formula of the alums. The only change is the substitution of the guanidine radical for a cation such as sodium or potassium. Waters of hydration in most hydrates generally tend to cluster around the highest valence cations. This suggests that the waters might be clustered around the aluminum. Aluminum has a valence of three, and in the alums has a coordination of six oxygen atoms around it. These are arranged like the corners of a regular octahedron. Such coordination has an axis of three-fold symmetry. The nuclear resonance patterns imply that the dipole-dipole axes associated with the waters are arranged in three pairs. All this suggests that the aluminum is surrounded by six waters of hydration in trigonal symmetry with respect to the $\underline{z}$ axis.

Let us consider how an alum structure which is cubic could be distorted into trigonal form. The trigonal axis associated with a cube is along the body diagonal. In an alum the cations are located at the corners of the unit cube. The two species of cation alternate along all three axes. The unit cell has twice the dimension of the unit cube and contains four of each cation, and eight anion complexes such as sulfate radicals.

Along the body diagonal therefore, the cations alternate also. Thus distortion of this structure into a trigonal form must have both the aluminum and the guanidine lying on trigonal axes and alternating with each other. From valence considerations sulfate radicals have to be interspersed between the aluminums and the guanidines. The waters of hydration must lie around the aluminums with their axes of symmetry along what would otherwise be the cubic axes but now are diagonals in the trigonal crystal.

This is as far as one can go in the structure without x-ray data. If one adds the additional information from x-rays that there are three molecules in the unit cell, one can tell that the three aluminums have to be coplanar (in the (0001) plane) because the space group allows only coplanar locations to have a multiplicity of three. Likewise the six sulfate radicals have to lie in general positions in the molecule in order to allow for their number.

A complete structure will require a thorough x-ray analysis. Our tentative arrangement has been supported in part by Geller (1957) who stated that a partial x-ray analysis showed that the aluminums were indeed on the three-fold axes of symmetry. Because of the number of possible arrangements of the atoms in the unit cell included in our general arrangement of the structure, and because of the unresolved question of whether we are dealing with one or with several structures we offer no definite structure. Any possible structure however, must agree in major features with our conclusions.

We believe that this example is outstanding as a demonstration of the power of nuclear resonance as a crystal structure tool. It is accidentally very much more fortunate than most cases, but it is not by any means negligible or trivially simple.

EUCLASE

EUCLASE

We have attempted to extend the analysis of hydrogen compounds by proton resonance to a hydroxide, as well as to the more favorable cases usually presented by the hydrates. Other workers have also studied hydroxides. For example see Elleman and Williams (1956) for a study of brucite. The substance chosen for this study is the mineral euclase. The nuclear resonance spectrum of aluminum in euclase has already been carried out by Eades (1955), but no study of the proton resonance spectrum has appeared.

Euclase is a basic orthosilicate of aluminum and beryllium, occurring as prismatic crystals. The (010) plane shows perfect cleavage. It is an attractive transparent vitreous mineral that varies from colorless to pale green or blue.* Our specimen came from Minas Geraes in Brazil, and exhibited only small imperfections.

Rotations of the crystal in the magnetic field about the c axis and the b axis were made. Only one proton resonance line was found, which varied in width as a function of orientation. See Figures 18, 19 and 20.

The lock-in amplifier records of the line at orientations near the greatest width of the line suggested that the line was made up of two overlapping components.

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*See Dana (1932). pp. 618, 619.

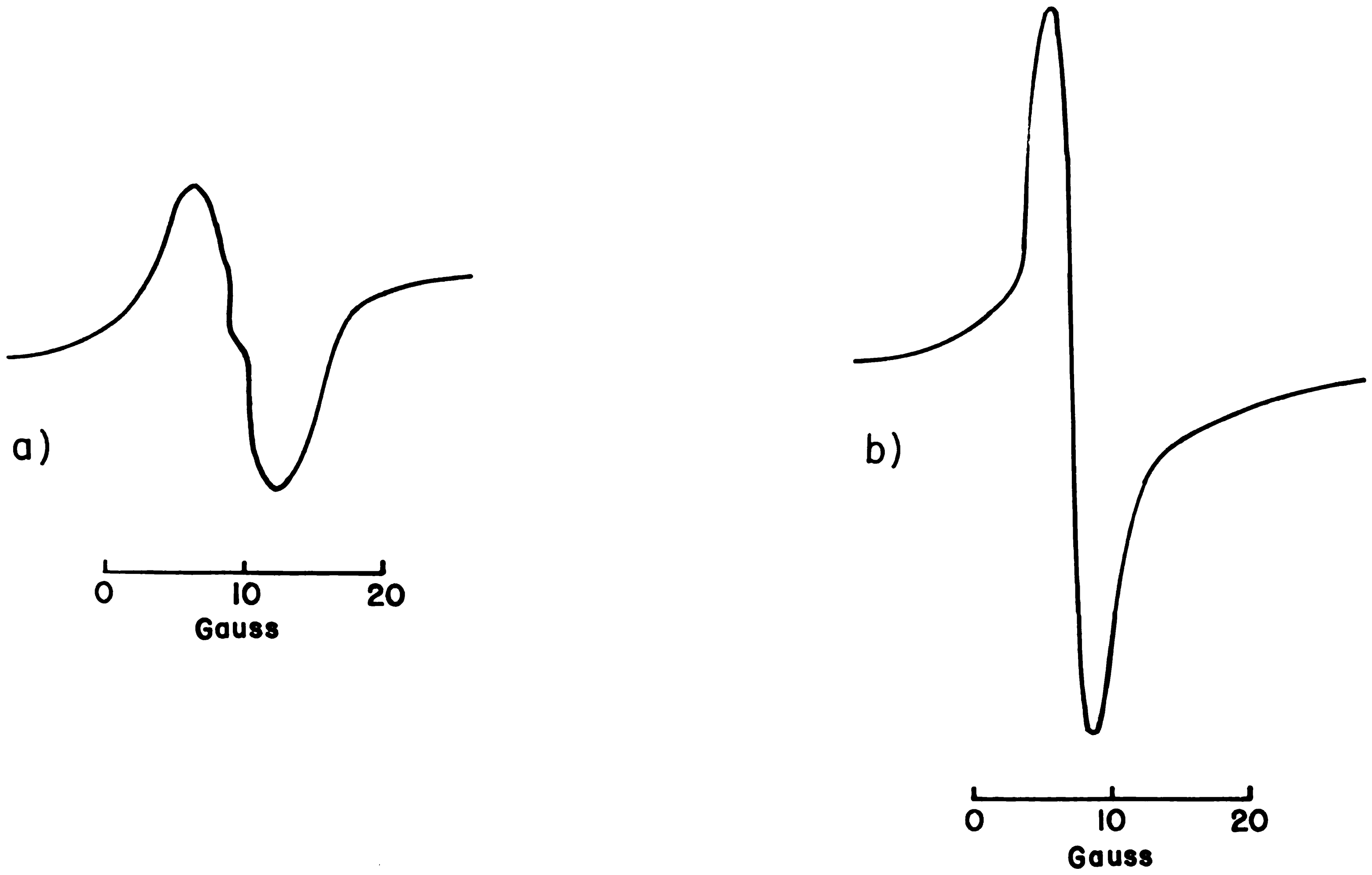

Figure 18. Some typical data for Euclase. a) Near the maximum line width at 176 degrees on the rotation about the z axis. Note the decrease in slope of the derivative of the absorption near the center of the pattern. b) At 56 degrees on the rotation about the z axis. Here the various components have effectively coalesced. All data taken is a lock-in amplifier derivative of the absorption.

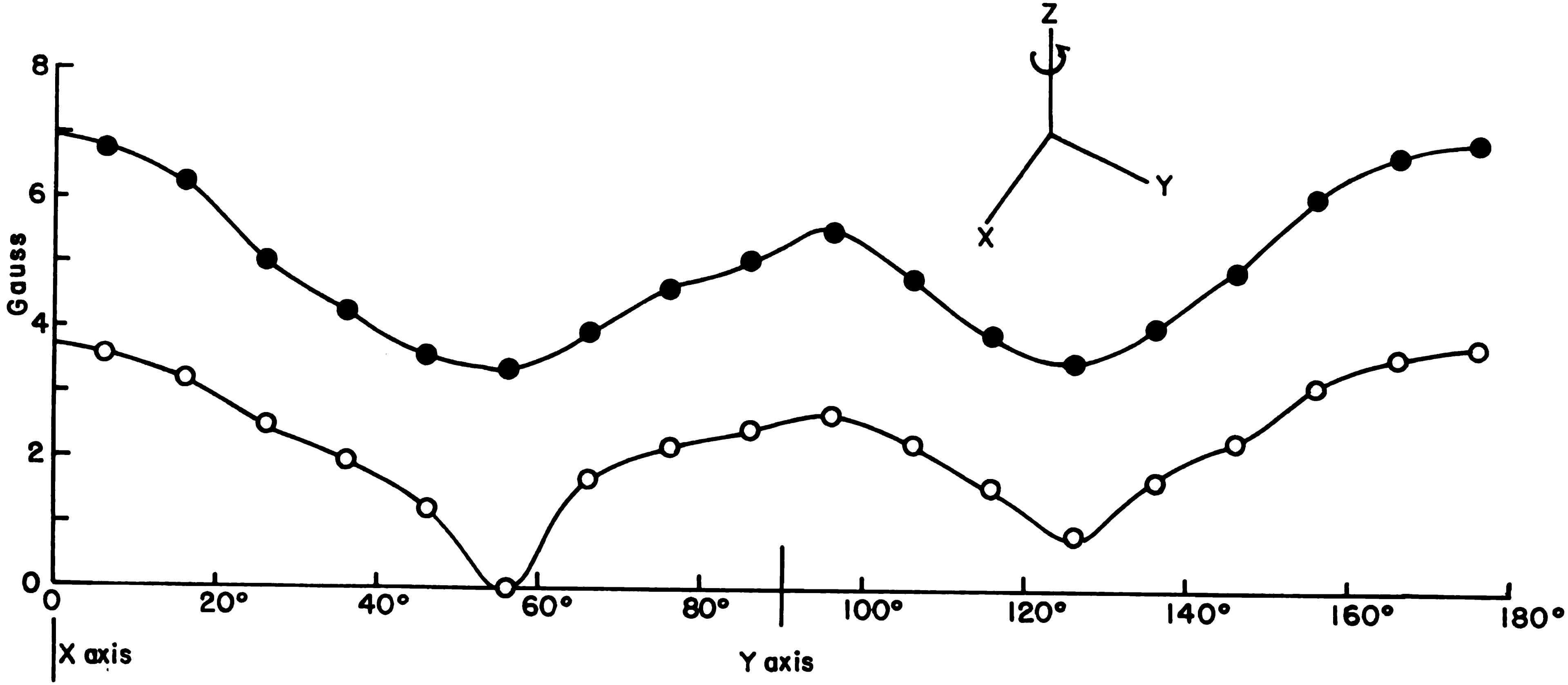

Figure 19. The proton magnetic resonance line width as a function of angle in the plane perpendicular to the z axis. The solid dots are the raw data, while the circles show the separation of two gaussian curves whose relative position could be considered the cause of the angular variation in line width.

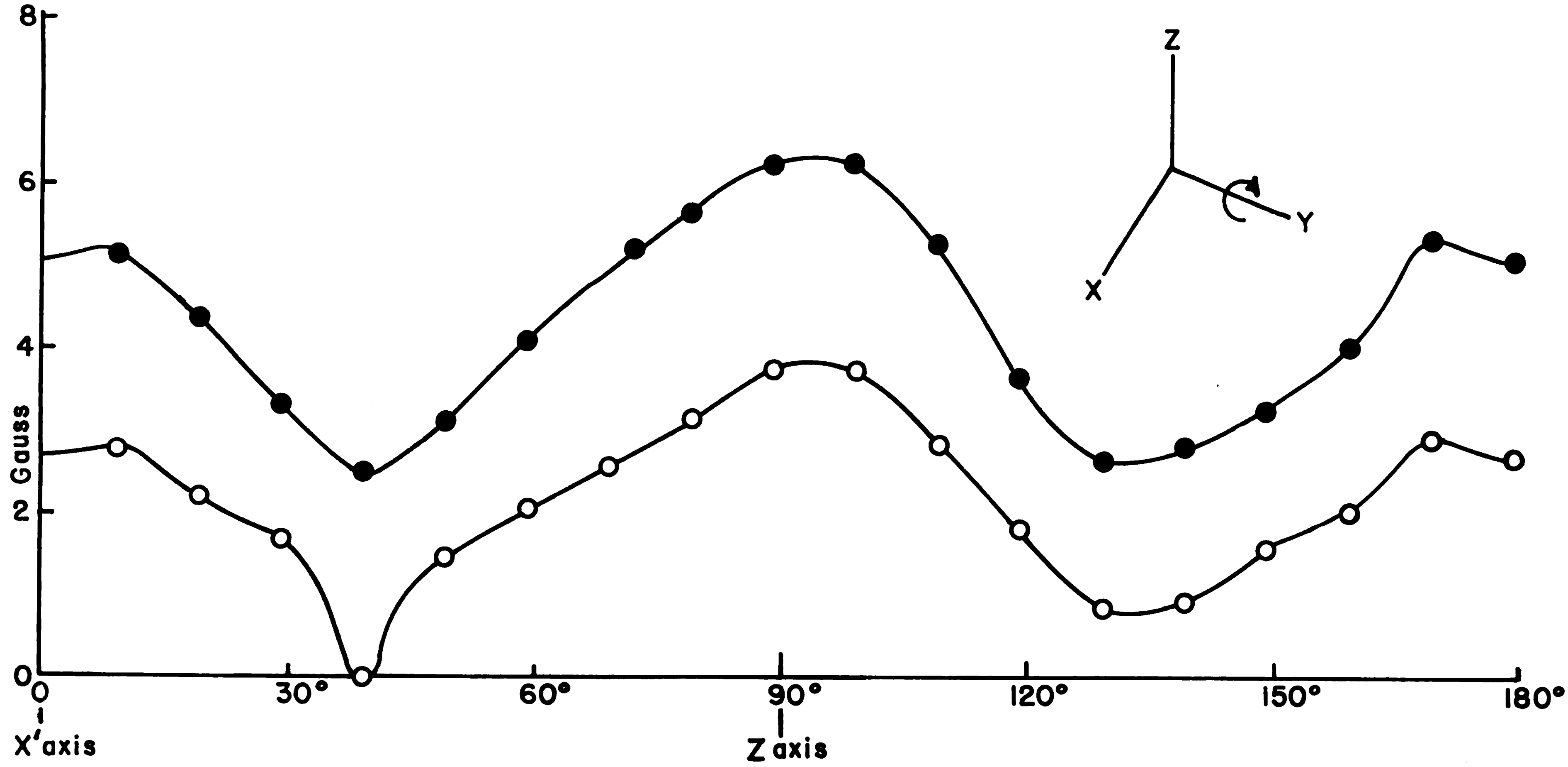

Figure 20. The angular dependance of the line width in Euclase about the y axis. The solid dots represent raw data. The circles are the result of treating the data as if it was due to the superposition of two gaussian curves as in Appendix II.

This is shown by the decrease of the slope of the derivative curve near the very center of the line in Figure 18 a).

If one assumes that the overlapping components are identical and are gaussian in shape, one can derive a relation between the separation of the centers of the individual lines and the separation between the maximum and minimum derivative points obtained from the lock-in amplifier records. See Appendix II.

The use of such a relation implies that one knows the width of the individual components. To avoid this difficulty, one may assume that at the point of narrowest line width the components have coalesced, and hence the observed line width at that point is the width of the components. This is a rather dangerous assumption since there is no reason to assume that the line widths of the components are independant of orientation. Nevertheless we have deduced component separation by this method. The general conclusions that we reach are not dependant upon any assumption of the width of the components, or, in fact, upon the number of components. The justification for such treatment of the data is rather in the form of the experimental curves themselves.

Our nuclear resonance data show maxima in the width of the line approximately along the a, b, and c axes of the crystal. Since one observes only a single broad line one can identify only the main sources of broadening. As the greatest width of line occurs for H_o parallel to the c axis, one must suppose either a magnetic dipole along the c axis or a confluence of magnetic dipoles in the ab plane about the protons in the compound.

The variation in the ab plane requires that the broadening cannot be solely due to magnetic dipoles displaced in the c direction from the protons. Furthermore the broadening is larger in the a orientation of the crystal in the magnetic field than in the b. As a result, one would suppose that any predominent magnetic dipoles in the ab plane about the protons must lie in the a direction.

The space group for euclase according to Biscoe and Warren (1933) is C^5_{2h}- $P2_1$ /c. There are four non-equivalent molecules in the unit cell. In this space group any one molecule can be transformed into any other by glide planes and twofold screw axes. It is impossible to distinguish among molecules related by these symmetry operations by means of nuclear resonance. The reason for this is that nuclear resonance patterns arising out of magnetic dipole-dipole interactions have 180 degree symmetry. We can therefore consider the orientation dependance of the resonance spectrum of only one proton and can be assured that any result will apply to the others as well.

Biscoe and Warren (ibid.) have made a selection of the oxygens associated with the hydrogens. This selection is made upon the basis of the location of all the atoms in the crystal, and upon valence grounds. If one accepts the rest of the structure, one has to accept the selection of the hydroxyl oxygens since valence arguments leave only one oxygen unsaturated.

We are therefore obliged to consider where the protons could be located within about one angstrom radius from the oxygen atoms. This is about the upper limit on O-H bonds. Within this radius there is no feasible location that can satisfy the requirements of the nuclear resonance spectrum. It is easy to satisfy the requirement that there be minimal splitting due to dipoles in the b direction. However as one can see from Figure 21 it is hard to satisfy the requirement for a largest splitting in the c direction.

We cannot achieve even a fraction of the necessary broadening from the interaction with magnetic moments of other protons. See Appendix I. These are too far away. It is not possible under the symmetry operations allowed to bring the protons sufficiently close to each other to provide the necessary broadening.

If we examine possible splitting from other nuclei we come to the conclusion that only the aluminum has sufficient magnetic moment that a reasonably large separation between it and the proton would not rule out the observed broadening. However, even in this case such a location of the proton in relation to the hydroxyl oxygen

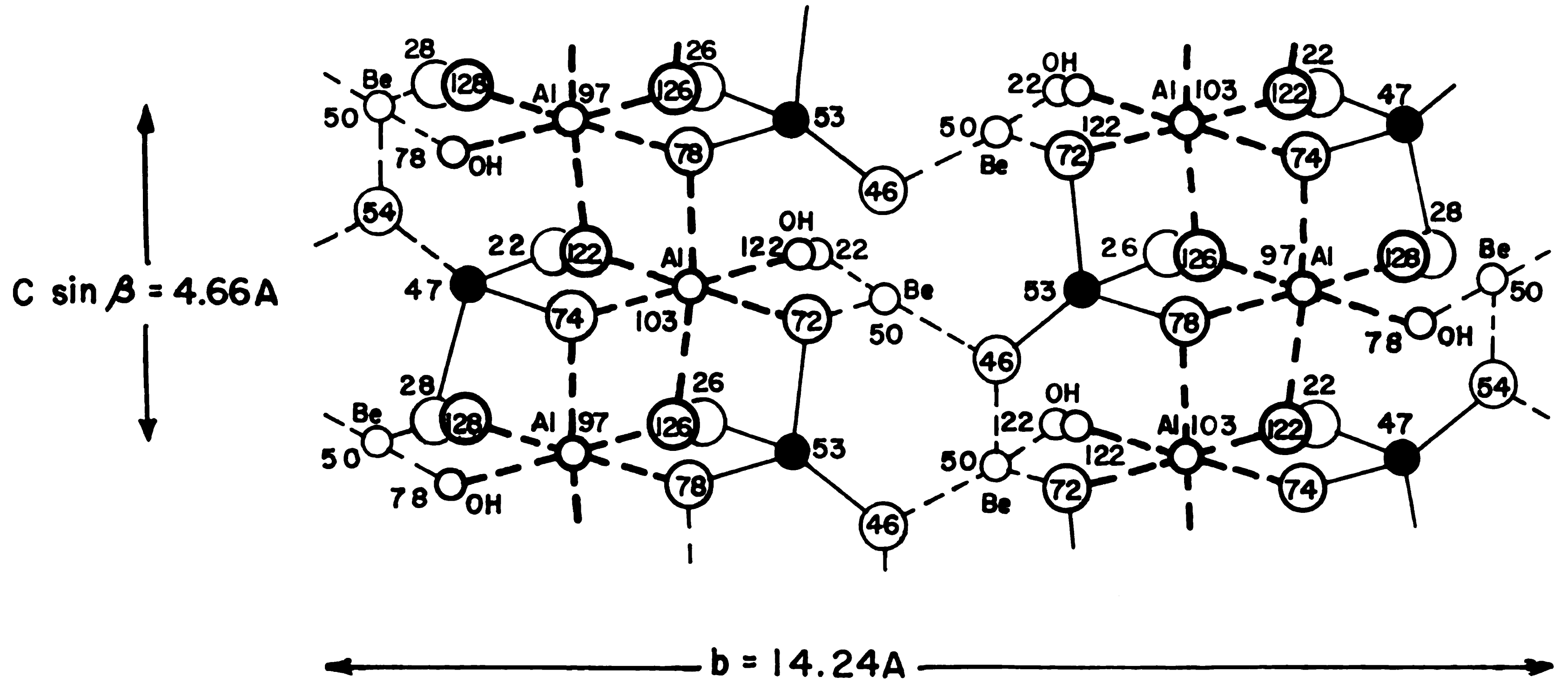

Figure 21. The structure of euclase according to Biscoe and Warren (1933). Projection is normal to the a axis. Heights in percent of the unit cell dimension, 4.62 angstroms, are measured from the (100) face of the unit cell. Oxygen atoms are shown symmetrically displaced where they should be superposed. Slightly more than one unit cell is drawn to facilitate visualizing the entire neighborhood of the OH oxygens.

seems extremely unlikely. This is because this oxygen is a part of the sixfold octahedral coordination of oxygen atoms about the aluminum. Since the proton and the aluminum and the beryllium are all cations, it would be strange if any two of these were closer together than their common anion. This reasoning leads to an upper limit for the broadening due to the aluminum of 4.8 gauss. This is too small since there is no other interaction sufficiently large to warrent consideration in such a location. Furthermore the only possible location so near to the aluminum would give the wrong angle dependance of line width. Therefore we must reject the tentative structure proposed by Biscoe and Warren.

Eades' study of the aluminum resonance agreed with the symmetry of the crystal as proposed by Biscoe and Warren. The proton resonance results also agree with the symmetry of the crystal. This is not surprising since the space group of crystals is generally known with greater certainty than their structure. The aluminum resonance, however did not yield any specific disagreement with the complete structure according to Eades.

In their paper on euclase, Biscoe and Warren stated that there were other possible structures. Had all the alternatives been published, one of the structures might have fitted our results. We were not able to supply an alternative structures on the basis of the nuclear resonance data alone. This shows the interdependance of the two methods of structure study.

We conclude that nuclear resonance has shown itself to be a useful tool in this case not only by rejecting a tentative x-ray derived structure, but also by furnishing a basis for choice among other possible structures.

LIQUID CRYSTALS

LIQUID CRYSTALS

In this last section we demonstrate a useful application of nuclear magnetic resonance to the study of the structure of liquid crystals. Liquid crystals are materials possessing a separate phase between the solid and liquid states. This is a true phase separated from the neighboring states of the substances by heats of transition. The macroscopic appearance and behaviour of liquid crystals is that of a cloudy liquid, which clears completely when the temperature rises above the transition to the liquid state.

It appears that there are at least three distinguishable types of liquid crystals, nematic, cholesterine, and smectic.* We will not discuss the particular features of the last two types, as the liquid crystals under discussion here are nematic.

Nematic liquid crystals are to be found only among compounds whose molecules are long and rod-like in general shape. We will be concerned with just two: p-azoxyanisole and p-azoxyphenetole whose chemical structures are shown in Figures 22 and 23.

It has been established that the molecules in liquid crystals are oriented parallel to each other over regions

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*Friedel (1922). Annales de Physique.

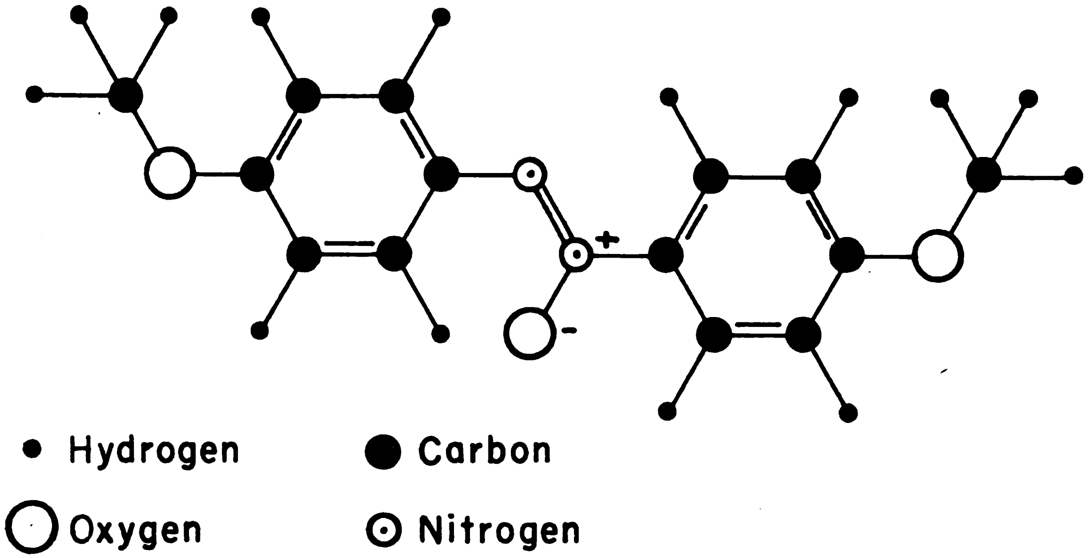

Figure 22. The structure of p-azoxyanisole. The methoxy groups at each end are thought free to rotate about both oxygen-carbon bonds.

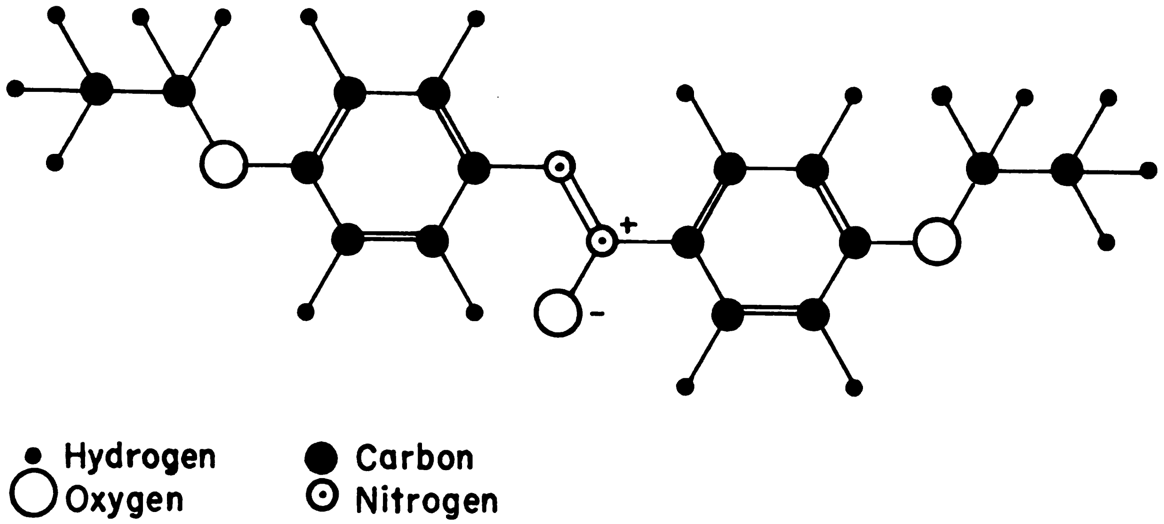

Figure 23. The structure of the molecule of p-azoxyphenetole. The ethoxy groups are thought free to reorient about both oxygen-carbon bonds on the end oxygens.

large in comparison with molecular dimensions. See Friedel (1922). On the average these regions contain approximately 10^5 to 10^6 molecules. Perfect alignment within these regions has not been demonstrated, but the average alignment of the molecules cannot be disputed. The boundaries of these regions are probably extremely vague and change rapidly in response to electric, magnetic, or mechanical forces.

The effect of magnetic fields upon liquid crystals is to introduce a common alignment to the various regions and hence provide a general ordering throughout the liquid. This has been discussed by Chatelaine in an extensive review (1954). Without the local self-orientation, the diamagnetic anisotropy of the molecules would be insufficient to cause alignment against the disordering effect of thermal vibration.

The nuclear magnetic resonance spectrum of p-azoxyanisole has been reported by Spence, Moses and Jain (1953); and the spectrum of p-azoxyphenetole has been reported by Jain, Moses, Lee, and Spence (1953). These spectra are shown as lock-in derivative curves in Figures 24 and 25.

These are the broadest nuclear resonance spectra to be found in fluids. The explanation for this splitting and broadening has been given by Spence, Gutowsky, and Holm (1953) and Jain, Lee, and Spence (1955).

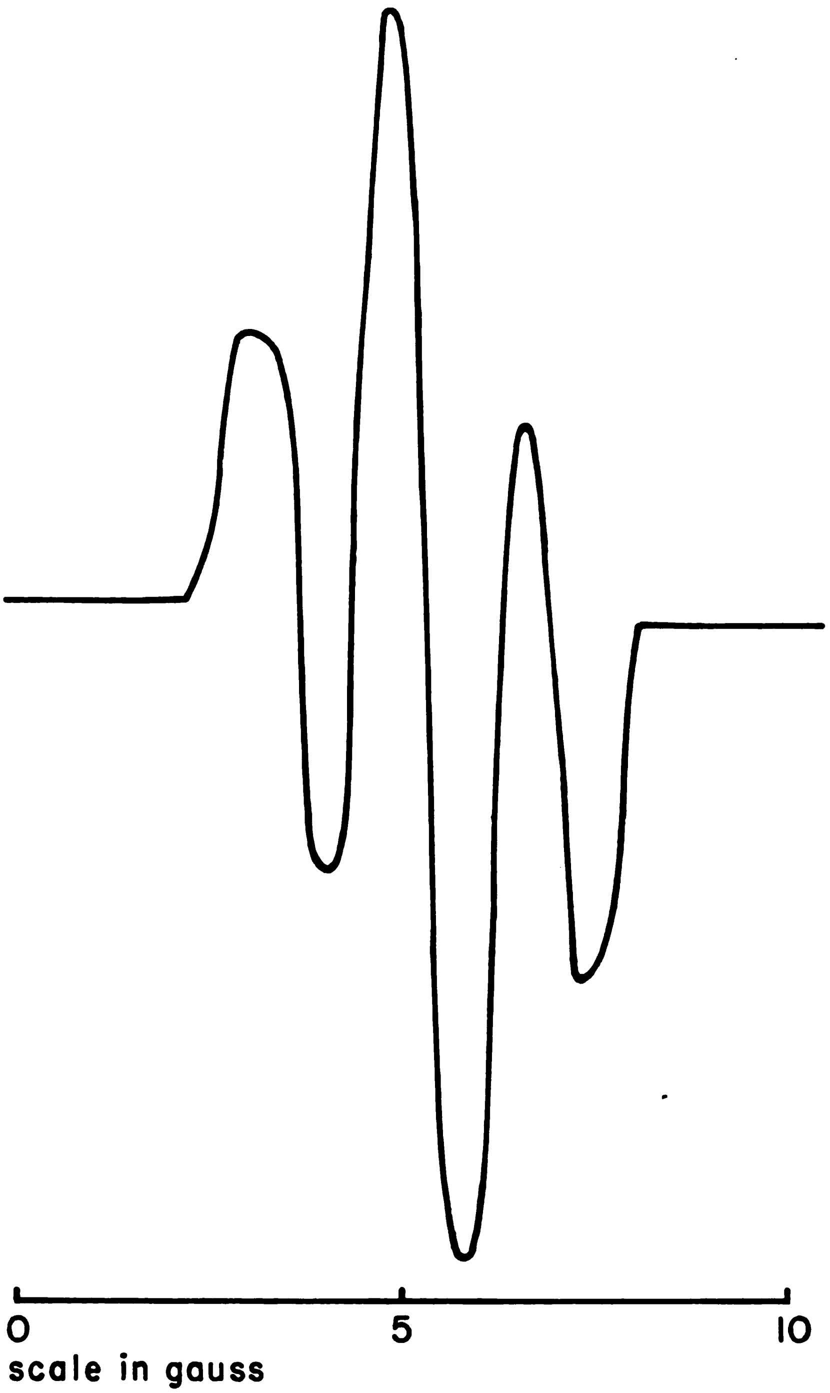

Figure 24. The lock-in derivative curve of the proton magnetic resonance absorption in p-azoxyanisole.

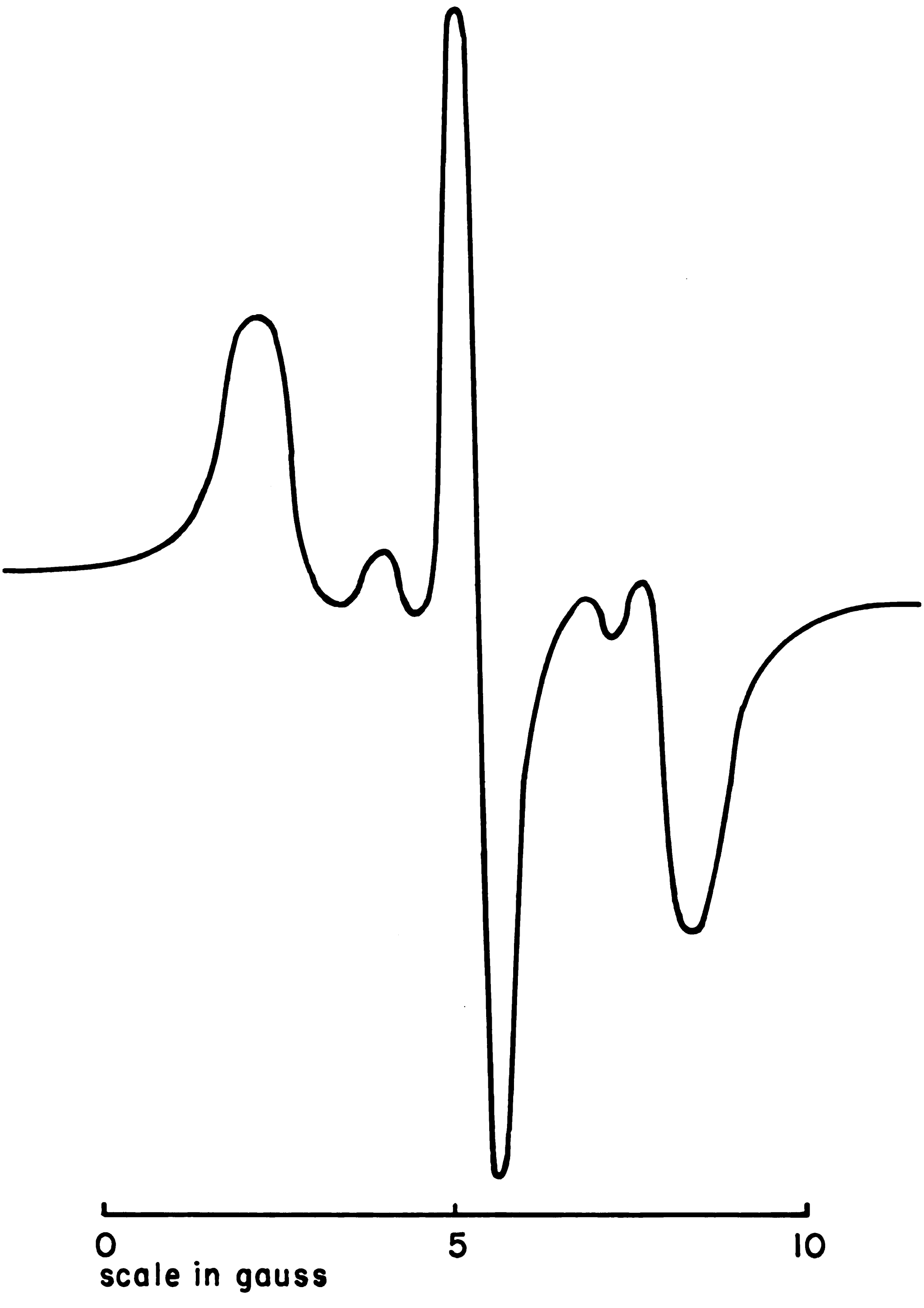

Figure 25. The lock-in derivative of the proton magnetic resonance absorption in p-azoxyphenetole.

According to these authors, the molecules of both compounds are aligned approximately along the magnetic field. p-azoxyanisole is aligned not nearly so parallel to the magnetic field as p-azoxyphenetole. The former is strongly oriented approximately 40 degrees away from the magnetic field direction. This alignment causes adjacent protons on the benzene rings to be similarly oriented. The magnetic dipole-dipole interaction between these protons results in a pattern consisting of two split lines. Due to the angle between the average orientation of the molecular axes of p-azoxyanisole and the applied magnetic field, that compound has a smaller splitting than p-azoxyphenetole has.

The end methyl or ethyl groups in the two compounds are relatively free to reorient about the molecular axis, and so provide a central broad line. This was confirmed by using deuterated methyl groups in the case of p-azoxyanisole. The central line was nearly absent from the spectrum of the deuterated compound as shown by Jain, Lee, and Spence (1955).

In this research we have sought to reinforce that conclusion by destroying the ordering of the liquid crystal by mechanical means while simultaneously observing the nuclear magnetic resonance signal. In order to destroy the magnetic ordering it was thought sufficient to stir the liquid on a macroscopic scale. The ordering in a magnetic field is due only to the fact that the molecules are already in cooperative local alignment. As a result, the only restraint that the magnetic field ordinarily has to overcome is that of the gross viscosity of the material against the rotation of the oriented liquid crystal. Without the local self-alignment, the magnetic field would be powerless to maintain orientation against thermal disordering. The effect of stirring upon the liquid crystal should be to destroy the over-all alignment of the fluid.

In order to avoid large microphonically induced voltages in the nuclear resonance sample coil that would prevent observation of the resonance signal, some method was sought to provide smooth and continuous stirring of the sample.

The first method tried was bubbling gas through the liquid. Helium was used because of its chemical inertness. The gas was preheated by passage through a glass loop which was immersed in the same air bath used to maintain the sample at the high temperature at which it is a liquid crystal. A glass nozzle projecting into the test tube containing the sample was an integral part of the loop. Remarkably, this arrangement worked on the first try.

Though microphonics occurred, they were of entirely tolerable magnitude. Both photographic records and lock-in derivative curves of the spectrum were obtained. See Figures 26 and 27 for lock-in curves. A powerful narrowing of the lines is immediately evident.

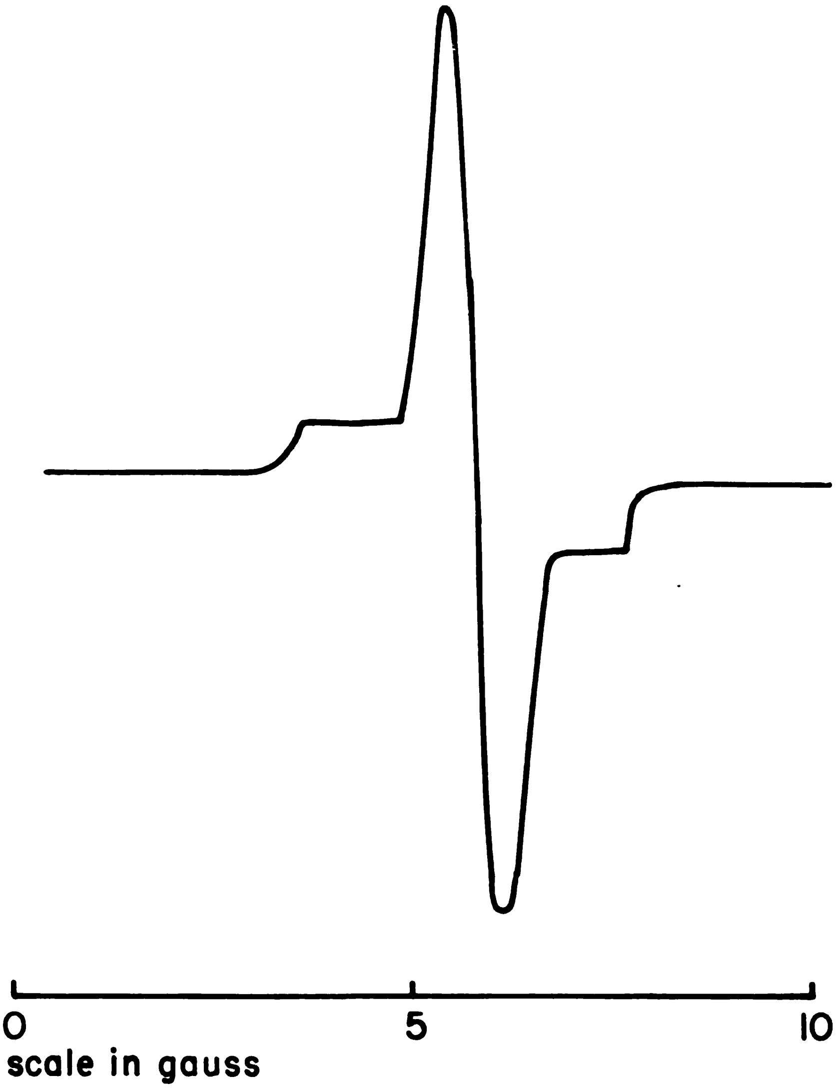

Figure 26. The lock-in derivative curve of the proton magnetic resonance absorption in bubbled p-azoxyanisole.

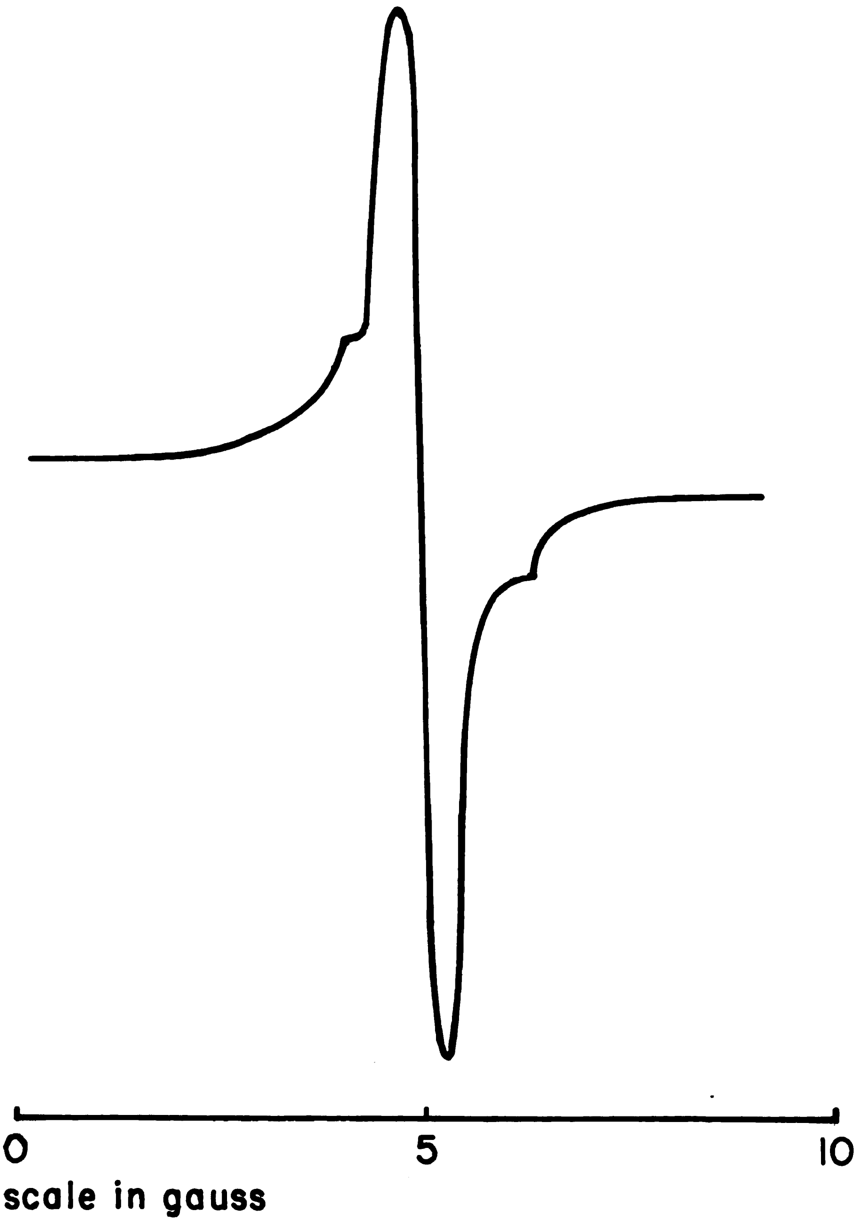

Figure 27. The lock-in derivative curve for the proton magnetic resonance absorption of bubbled p-azoxyphenetole.

Though perfect alignment in the undisturbed state is not to be expected, the great difference in the spectra between the stirred and undisturbed samples is convincing proof of a high degree of ordering in the undisturbed samples. The effect is found in both liquid crystals. Curiously, both have about the same line width in the stirred state, whereas they have very different splittings in the quiescent condition. This greatly strengthens the supposition previously postulated by Jain, Lee, and Spence (1955) that the narrower splitting in p-azoxyanisole is due to a definite orientation of the proton-proton axis at an angle to the magnetic field.

The spectrum remaining during stirring is to be interpreted as a random orientation pattern. Near equality of width of the spectra of the two compounds when stirred shows that the interproton distance causing the major splitting is the same for the two compounds.

One feature of interest is the time required after stirring stops for the liquid crystal to return to its ordered condition in the magnetic field. We have determined this time by using a moving film oscillograph to measure the rate at which the resonance spectrum returns to that found for the undisturbed state of the liquid crystal. It turns out to be approximately .03 second for p-azoxyanisole.

This can be compared with the time constant required for the reorientation of a diamagnetically anisotropic rigid sphere immersed in a viscous liquid. It is acted upon by a magnetic field and by the viscous drag of the liquid. The differential equation for this situation is:

$$I \frac{d^2\theta}{dt^2} + 8\pi r_o^3 \eta \frac{d\theta}{dt} + H_o^2 \chi_s \frac{4}{3}\pi r_o^3 \rho \,\mathrm{Sin}\theta \,\mathrm{Cos}\theta = 0$$

Where I is the moment of inertia of the sphere; θ is the angle of the sphere with respect to its equilibrium orientation; t is the time; r_o is the radius of the sphere; η is the viscosity of the liquid; H_o is the applied magnetic field; χ_s is the surplus diamagnetic moment per unit mass of the sphere; and ρ is the density of the sphere.

Assuming that we can neglect acceleration torques in comparison with viscous and magnetic torques, we drop the first term of this equation. The resulting equation integrates directly to

$$\mathrm{Tan}\,\theta = e^{-t/T}\,\mathrm{Tan}\theta_o \quad \text{where } T = 6\eta / H_o^2 \chi_s \rho$$

and $\mathrm{Tan}\theta_o$ is the tangent of the angle of orientation of the sphere at time $t=0$ with respect to the orientation of the sphere in equilibrium.

Inserting the values of η , χ, and ρ for para-azoxyanisole and 7000 gauss for the value of H_o, the magnetic field that we have been using, into the expression for T; one arrives at a range for T of .03 to .1 seconds. This range occurs principally because of the spread in the value for the viscosity of the liquid crystal. This depends not only on temperature; but more importantly on whether the shear in the fluid crystal is parallel or perpendicular to the magnetic field. According to Miesowicz (1936) the viscosity parallel to the magnetic field is about 250 x 10^{-4}; while the viscosity perpendicular to the magnetic field ranges from 550 x 10^{-4} at 135 degrees centigrade to 950 x 10^{-4} at 120 degrees centigrade which is nearly the liquid crystalline range of the compound.

The agreement between such a very crude model and the measured value is probably accidental. It does suggest some additional justification for supposing the existence of some sort of swarms. Furthermore the work of Kast (1931) on the dependance of the x-ray diffraction pattern of liquid crystalline p-azoxyanisole upon the frequency of an applied electric field suggests that the assumption of negligible acceleration forces is valid. Kast found that up to a frequency of 25,000 cycles there was no change in the diffraction pattern indicating that the permanent electric moments of the molecules and hence the molecules themselves, were following the field up to that frequency. Significant inertial forces could be expected to have altered the pattern by preventing the following of the field by the permanent dipole moments of the molecules. We can therefore be confident that there will be no inertial effects worth consideration at frequencies as low as 33 cycles per second.

Finally we may compare our measurement of the reorientation period in a magnetic field with that of Carr and Spence (1954). They found that a period of the order of one minute was necessary for realignment at the field of 200 gauss that they employed. In this case alignment was studied by microwave dielectric measurements. According to our model T depends inversely on H_o^2. Therefore their value reduces to .05 seconds at our magnitude of the magnetic field. Considering the crudity of our measurement which depended upon subjective estimation of the relative appearance of the nuclear resonance pattern, this is good agreement. We thus may be confident not only of the order of magnitude of this measurement, but also of the general picture of the reorientation of local swarms.

We believe that this study of liquid crystals has demonstrated the ability of nuclear magnetic resonance to show the state of a material undergoing changes between an ordered state and a disordered state. Furthermore, it has been able to measure roughly the rate of change of the state. This method is moreover capable of considerable refinement. Thus the utility of nuclear resonance for structure study even in such a borderline case as liquid crystals has been demonstrated.

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APPENDIX I

THE MAGNETIC PROPERTIES OF ELECTRONS AND NUCLEI CONSIDERED IN THIS THESIS

Particle [*]	Isotopic Abundance	Spin	Magnetic Moment in Nuclear Magnetons[+]	Maximum Field in Gauss One Angstrom Away [*]
${}_{-1}e$	100.0	1/2	-1837.1	$\frac{9.39 \times 10^3}{T}$
${}_{1}H^{1}$	100.0	1/2	+2.7925	42.3#
${}_{4}Be^{9}$	100.0	3/2	-1.1774	8.86
${}_{6}C^{13}$	1.1	1/2	+0.7023	7.09
${}_{7}N^{14}$	99.6	1	+0.4037	3.32
${}_{7}N^{15}$	0.4	1/2	-0.2830	2.86
${}_{13}AL^{27}$	100.0	5/2	+3.6408	25.1
${}_{14}Si^{29}$	4.7	1/2	-0.5549	5.60
${}_{16}S^{33}$	0.7	3/2	+0.6429	4.84

THE MAGNETIC PROPERTIES OF ELECTRONS AND NUCLEI
CONSIDERED IN THIS THESIS (Continued)

Particle	Isotopic Abundance	Spin	Magnetic Moment in Nuclear Magnetons+	Maximum Field in Gauss One Angstrom Away
$_{17}CL^{35}$	75.4	3/2	+0.8219	6.19
$_{17}CL^{37}$	24.6	3/2	+0.6841	5.15
$_{29}Cu^{63}$	69.1	3/2	+2.2262	17.0
$_{56}Ba^{135}$	6.6	3/2	+0.8346	6.28
$_{56}Ba^{137}$	11.3	3/2	+0.9351	7.04

+The nuclear magneton is equal to $5.0493 \pm .0002 \times 10^{-24}$ erg/gauss.

*The electron is considered to change so rapidly from state to state that only the time average field as a function of absolute temperature, T, is tabulated. The magnetic field due to the electron can be thought to be caused by the surplus fraction of time spent in one orientation over the other in an externally applied field of 7,000 gauss.

#This is not the classical value as for the other items in this column; but has been augmented by the factor 3/2 to account for the spin exchange between protons. As the only resonant nucleus considered in the thesis is the proton, no other value in this column has been so treated.

APPENDIX II

APPENDIX II

In this appendix we calculate the apparent width of a line composed of two overlapping gaussian curves. Width of line is taken to mean the separation between peaks of opposite sign on a lock-in amplifier record. Such a record is a graph of the derivative of the absorption spectrum. Consequently this width is the separation between the point of maximum positive slope and the point of maximum negative slope of the spectrum.

In order to calculate this width for two overlapping gaussian functions we must add them together, and find the points of steepest slope of the sum.

A gaussian absorption curve can be expressed as $G = e^{-h^2/2\sigma^2}$ where G(h) is the absorption; h is the magnetic field measured from the center of the resonance line such that $\int_{-\infty}^{+\infty} hG\,dh = 0$; and σ is the second moment of G such that

$$\frac{\int_{-\infty}^{+\infty} h^2 G\,dh}{\int_{-\infty}^{+\infty} G\,dh} = \sigma$$

It so happens in the case of a gaussian function that σ is also a measure of the distance from the center of the gaussian to the point of steepest slope. It is therefore the half-width of the gaussian function itself by our criterion for line width. That is, $\pm\sigma$ are the roots of $\frac{d^2G}{dh^2} = 0$. This last may be more fully expressed, by saying that the equation $(x^2/\sigma^4 - 1/\sigma^2)\, e^{-h^2/2\sigma^2} = 0$ has the root $h = \pm\sigma$. The second moment generally does not equal the line width for other functions.

Let us designate the separation of the two gaussian absorption curves center-to-center by δh. We will suppose that they are symmetrically displaced from $h=0$ by an amount $\delta h/2$. The total absorption will then be proportional to $F(h) = e^{-(h + \delta h/2)/2\sigma^2} + e^{-(h - \delta h/2)/2\sigma^2}$. The situation is illustrated in Figure 28. Calculating the second derivative, d^2F/dh^2, and setting it equal to zero yields the equation:

$$2(h/\sigma)(\delta h/2\sigma) \text{ Hyperbolic Tangent } ((h/\sigma)(\delta h/2\sigma)) = (h/\sigma)^2 + (\delta h/2\sigma)^2 - 1 \quad .$$

This transcendental equation can be solved numerically for $\zeta = h/\sigma$ as a function of $\alpha = \delta h/2\sigma$. The solution is displayed in Figure 29. The points of steepest slope occur at those values of h satisfying this graph for particular values of δh and σ.

Given δh and σ we can find h directly in units of σ. We can then find 2h, the width of the combined gaussian absorption curves in terms of: δh, the separation center-to-center, and σ, the half-width of the components.

Experimentally, we measure 2h, make some assumption about the value of σ, (for instance we may let σ be the

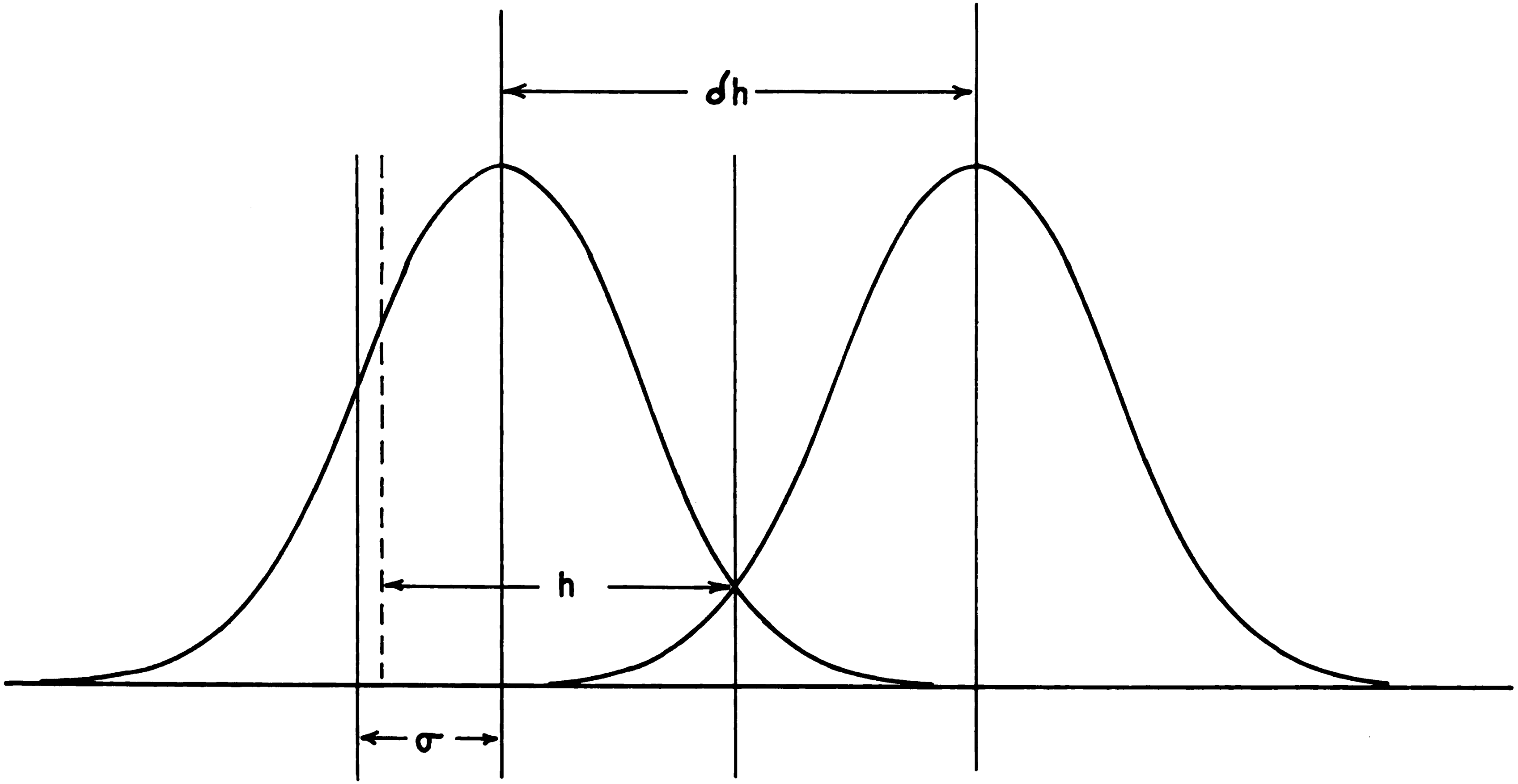

Figure 28. Two overlapping gaussian distribution functions.

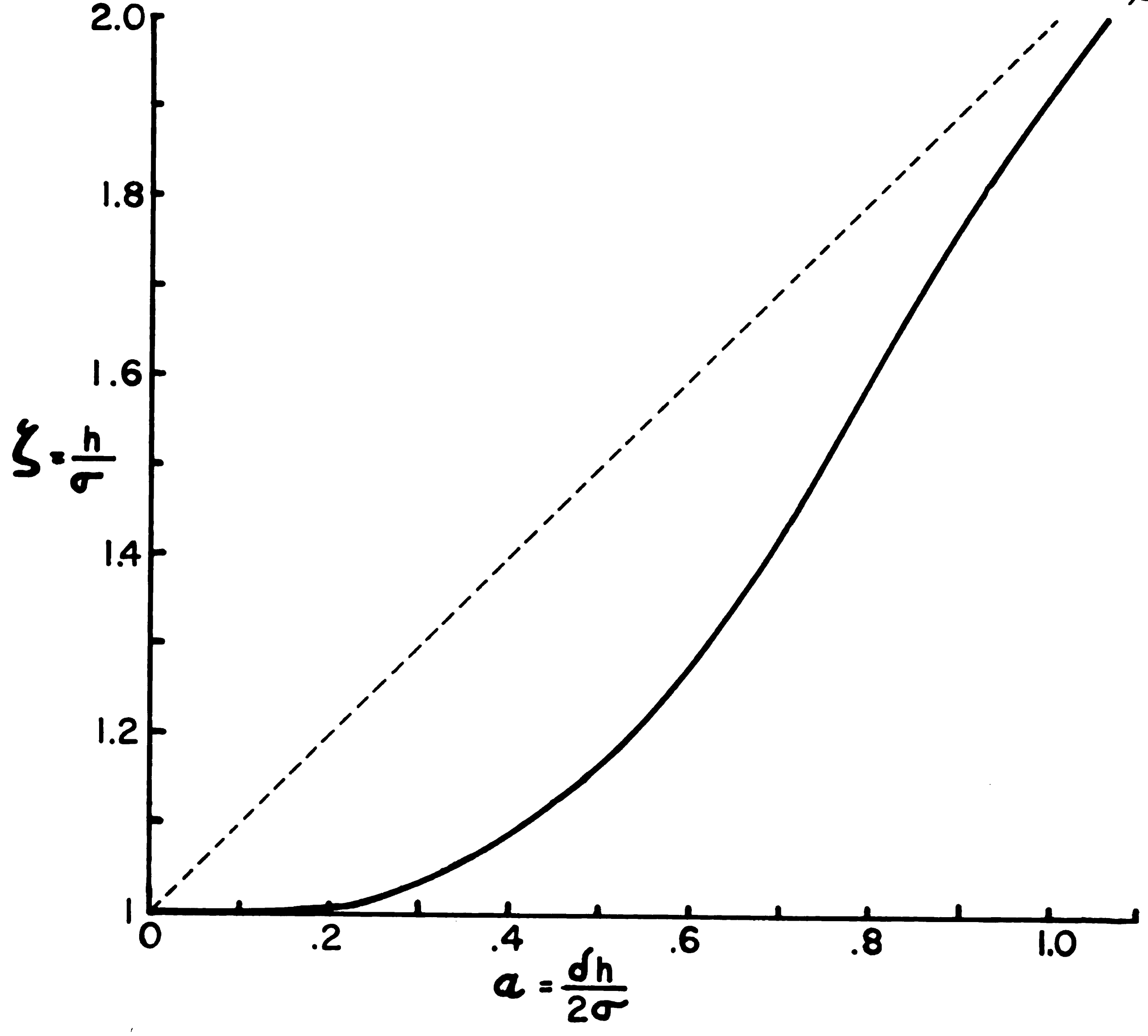

Figure 29. The apparent half width of two overlapping gaussian curves. This shows the apparent half-width, h, of two overlapping identical gaussian curves as a function of their half-separation, h/2, in units of their individual half-width, .

minimum value of the orientation dependant line width) and then δh can be found with the aid of the graph.

APPENDIX III

APPENDIX III

The purpose of this appendix is the calculation of the total number of unadjustable constants that can be obtained from measurements of the second moment of a line in the most general case.

We will assume that the second moment of a line will be generated entirely by magnetic dipole-dipole interactions.

The square root of the sum of the squares of such interactions was shown by Van Vleck (1948) to be equal to the second moment.

Van Vleck's results can be cast into the form

$$\sigma^2 = \sum_{i=1}^{n} k_i^2 (P_2 \mathrm{Cos}\ \Theta_i)^2$$ where σ is the second moment of a line; k_i is a constant for each particular dipole-dipole interaction perturbing the resonant species of nucleus; and Θ_i is the angle between the dipole-dipole axis and the magnetic field. k_i depends upon the kinds of perturbing and perturbed dipoles and their separation. P_2 is the legendre function of the first kind, $(1/2)(3\mathrm{Cos}^2\Theta_i - 1)$.

We are going to show the number of constants required to express the square of such an interaction at an arbitrary angle in an arbitrarily oriented coordinate system. The sum of such interactions will then simply result in separate sums of these constants.

Because these constants will be multipliers of functions chosen so as to be linearly independant in the arbitrary coordinate system, addition of the squares of interactions can only result in sums of coefficients of the orthogonal functions. Consequently no new kinds of functions will be generated by the addition, and a smaller number of functions can arise only in special cases. Usually all constants will be non-zero.

Consider then $(P_2(\mathrm{Cos}\gamma))^2$ where γ is some particular Θ_1 . Expressing this as first powers of legendre functions of the first kind, one gets:

$(P_2\mathrm{Cos}\gamma)^2 - (18/35)\,P_4(\mathrm{Cos}\gamma) - (5/7)P_2(\mathrm{Cos}\gamma) + 9/20$

Now consider this in an arbitrarily oriented spherical coordinate system such that γ is a great circle arc from the point $(1,\Theta_0,\phi_0)$ to the point $(1,\Theta,\phi)$; where Θ_0 and ϕ_0 represent the angular orientation coordinates of a dipole-dipole axis in the Θ_1 direction; and Θ and ϕ are the angular coordinates of the magnetic field direction.

In such a coordinate system

$$\mathrm{Cos}\,\gamma = \mathrm{Cos}\Theta_0\ \mathrm{Cos}\Theta + \mathrm{Sin}\Theta_0\mathrm{Sin}\Theta\mathrm{Cos}\ (\phi - \phi_0)\ ;\ \text{and}\ P_n(\mathrm{Cos}\gamma)$$

$$= P_n(\mathrm{Cos}\Theta_0)(P_n\mathrm{Cos}\Theta) + 2\sum_{m=1}^{n}((n-m)!/(n+m)!)$$

$P_n^m(\mathrm{Cos}\Theta_0)\ P_n^m(\mathrm{Cos}\Theta)\ \mathrm{Cos}\ m(\phi_0 - \phi)$ where P_n are legendre functions of the first kind and P_n^m are associated legendre functions of the first kind.

Making use of these relations we can now transform $(P_2(\mathrm{Cos}\gamma))^2$ into:

$$
\begin{aligned}
&(18/35)\Big[P_4(\mathrm{Cos}\theta_o)\ P_4(\mathrm{Cos}\theta) \\
&\quad + (1/10)\mathrm{Cos}\ (\phi - \phi_o)P_4^1(\mathrm{Cos}\theta_o)P_4^1(\mathrm{Cos}\theta) \\
&\quad + (1/180)\mathrm{Cos}2(\phi - \phi_o)P_4^2(\mathrm{Cos}\theta_o)P_4^2(\mathrm{Cos}\theta) \\
&\quad + (1/2520)\mathrm{Cos}3(\phi - \phi_o)P_4^3(\mathrm{Cos}\theta_o)P_4^3(\mathrm{Cos}\theta) \\
&\quad + (1/20160)\mathrm{Cos}4(\phi - \phi_o)P_4^4(\mathrm{Cos}\theta_o)P_4^4(\mathrm{Cos}\theta)\Big] \\
&-(5/7)\Big[P_2(\mathrm{Cos}\theta_o)P_2(\mathrm{Cos}\theta) \\
&\quad + (1/3)\mathrm{Cos}(\phi - \phi_o)P_2^1(\mathrm{Cos}\theta_o)P_2^1(\mathrm{Cos}\theta) \\
&\quad + (1/12)\mathrm{Cos}2(\phi - \phi_o)P_2^2(\mathrm{Cos}\theta_o)P_2^2(\mathrm{Cos}\theta)\Big] \\
&+ 9/20
\end{aligned}
$$

The legendre functions in this expression may be defined as follows:

$$P_2(\mathrm{Cos}\theta) = (1/4)(3\mathrm{Cos}2\theta + 1)$$

$$P_2^1(\mathrm{Cos}\theta) = (3/2)(\mathrm{Sin}2\theta)$$

$$P_2^2(\mathrm{Cos}\theta) = (3/2)(1 - \mathrm{Cos}2\theta)$$

$$P_4(\mathrm{Cos}\theta) = (1/64)(35\mathrm{Cos}4\theta + 20\mathrm{Cos}2\theta + 9)$$

$$P_4^1(\mathrm{Cos}\Theta) = (5/16)(2\mathrm{Sin}2\Theta + 7\mathrm{Sin}4\Theta)$$

$$P_4^2(\mathrm{Cos}\Theta) = (15/16)(3 + 4\mathrm{Cos}2\Theta - 7\mathrm{Cos}4\Theta)$$

$$P_4^3(\mathrm{Cos}\Theta) = (105/8)(2\mathrm{Sin}2\Theta - \mathrm{Sin}4\Theta)$$

$$P_4^4(\mathrm{Cos}\Theta) = (105/8)(3 - 4\mathrm{Cos}2\Theta + \mathrm{Cos}4\Theta)$$

We have now expressed in an arbitrarily oriented spherical coordinate system a single dipole-dipole interaction contribution to the square of the second moment. Not all these terms are linearly independant in Θ and ϕ over the unit sphere, so we must regroup them accordingly.

$$\begin{aligned}
&(18/35)\Big[P_4(\mathrm{Cos}\Theta_0)P_4(\mathrm{Cos}\Theta) \\
&\qquad + (1/180)\mathrm{Cos}2(\phi - \phi_0)P_4^2(\mathrm{Cos}\Theta_0)P_4^2\mathrm{Cos}\Theta) \\
&\qquad + (1/20160)\mathrm{Cos}4(\phi - \phi_0)P_4^4(\mathrm{Cos}\Theta_0)P_4^4(\mathrm{Cos}\Theta)\Big] \\
&+ (18/35)\Big[(1/10)\mathrm{Cos}(\phi - \phi_0)P_4^1(\mathrm{Cos}\Theta) \\
&\qquad + (1/2520)\mathrm{Cos}(\phi - \phi_0)P_4^3(\mathrm{Cos}\Theta_0)P_4^3(\mathrm{Cos}\Theta)\Big] \\
&+ (5/7)\Big[\;P_2(\mathrm{Cos}\Theta_0)\;P_2(\mathrm{Cos}\Theta) \\
&\qquad + (1/12)\mathrm{Cos}2(\phi - \phi_0)P_2^2(\mathrm{Cos}\Theta_0)\;P_2^2(\mathrm{Cos}\Theta)\Big] \\
&+ (5/7)\Big[(1/3)\;\mathrm{Cos}(\phi - \phi_0)\;P_2^1(\mathrm{Cos}\Theta_0)\;P_2^1(\mathrm{Cos}\Theta)\Big] \\
&+ 9/20
\end{aligned}$$

Each square bracket is linearly independant in Θ from the others. Within each bracket there are a number of terms which are independant in ϕ. In the first bracket there are five; in the second, four; in the third, three; in the fourth, two; and in the fifth is the remaining linearly independant term.

Thus there are exactly fifteen constants generated by $(P_2(\text{Cos })\gamma)^2$ which are orthogonal over the entire range of orientations that can be assumed by the magnetic field. Therefore from second moment measurements alone, one can determine fifteen independant constants.