NUCLEAR QUADRUPOLE COUPLING IN EPR

SPECTRA OF CUPRIC ION IN MgSO₄·7H₂O

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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Cupric Ion in MgSO₄·7H₂O

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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Nuclear Quadrupole Coupling in EPR Spectra of Cupric Ion in MgCl$_2$·7H$_2$O

I. Introduction

A. INTRODUCTORY REMARKS

Magnetic resonance is one of the principal structural tools available to the chemist. Studies of the effect of a magnetic field on matter by Stern and Gerlach in 1922, and Phipps and Taylor in 1927, inspired the theory of electron spin, a fundamental concept of modern chemistry.

Advances in equipment, especially electronics, and further sophistication of experiment have revealed increasingly subtle features of spin energy level quantisation. These features can be used as structural probes in paramagnetic species.

Thus, the basic EPR phenomenon—electron spin quantization in a magnetic field—is now acknowledged to be affected by the interaction of the electron with the nuclear spin (hyperfine splitting), of the nuclear spin with the magnetic field (nuclear Zeeman shift), and, of interest here, the nuclear quadrupole moment with the electron (quadrupole coupling). These are represented by the Hamiltonian:

$$ H = h \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - B_N \mathbf{B} \cdot \mathbf{I} + h \mathbf{I} \cdot \mathbf{P} \cdot \mathbf{I} \quad (1) $$

where $\mathbf{I}$ is the nuclear spin, $\mathbf{A}$ is the hyperfine tensor, $\mathbf{S}$ is the electron spin operator, $\mathbf{B}$ is the magnetic field vector,
Figure 1. a) Schematic energy level diagram for $S=\frac{1}{2}$, $I=3/2$, showing nuclear hyperfine, nuclear quadrupole, and nuclear Zeeman shifting.

b) Spectral line positions corresponding to transitions shown in 1(a).

Both drawings from reference 5.
$\xi_{ij}$ is the nuclear $g$ tensor, and $Q$ is the nuclear quadrupole tensor. An energy level diagram and line spectrum is shown in figure 1.

B. WHAT IS A QUADRUPOLE MOMENT?

A quadrupole moment is part of the most common systematic description of a charge density. It is the third term in the multipole expansion of a field due to a localized charge distribution:

$$U(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|} \, dv'$$

The potential is given by:

$$U(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \int \frac{\rho(r')}{|\mathbf{r}-\mathbf{r}'|} \, dv'$$

The denominator of the integral can be expanded in a Taylor series that is good for $\mathbf{r} \gg \mathbf{r}'$:

$$|\mathbf{r}-\mathbf{r}'| = \left( r^2 - 2 \mathbf{r} \cdot \mathbf{r}' + r'^2 \right)^{-\frac{1}{2}}$$

$$= \frac{1}{r} \left[ 1 - \frac{2 \mathbf{r} \cdot \mathbf{r}'}{r^2} + \frac{r'^2}{r^2} \right]^{-\frac{1}{2}}$$

$$= \frac{1}{r} \left[ 1 - \frac{1}{2} \left( \frac{-2 \mathbf{r} \cdot \mathbf{r}'}{r^2} + \frac{r'^2}{r^2} \right) + \frac{1}{4} \left( \frac{3}{2} \right) \frac{1}{2} \left( \frac{-2 \mathbf{r} \cdot \mathbf{r}'}{r^2} + \frac{r'^2}{r^2} \right)^2 + \ldots \right]$$

Using this expansion in our integral above:

$$U(\mathbf{r}) = \frac{1}{4\pi\varepsilon_0} \int \left[ \frac{1}{r} + \frac{\mathbf{r} \cdot \mathbf{r}'}{r^3} + \frac{3}{2} \left( \frac{3 \mathbf{r} \cdot \mathbf{r}'}{r^3} - \frac{r'^2}{r^3} \right) \right] \rho(\mathbf{r}') \, dv'$$
Breaking up the integral:

\[
U(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \int \rho(\mathbf{r}') d\mathbf{v}'
+ \frac{\mathbf{r}' \cdot \mathbf{E}}{r^3} \int \rho(\mathbf{r}') d\mathbf{v}'
+ \sum \frac{3x'_ix'_j}{r^5} (3x'_i x'_j - \delta_{ij} r'^2) \rho(\mathbf{r}') d\mathbf{v}'
\]

The energy of a monopole in a potential field is given by:

\[ W = qU \]

and the energy of a dipole is given by the vector product:

\[ W = \mathbf{p} \cdot \mathbf{E} \]

and the energy of the quadrupole moment is given by a tensor product with the second derivative of the potential (first derivative of the electric field, hence, "efg" or electric field gradient).

Nuclear quadrupole interaction with potential fields created by surrounding charge (electrons, ligands, solvent molecules) can result in quadrupole coupling. The quadrupole interaction Hamiltonian is:

\[
H = \frac{e_0 e Q}{4I(2I-1)} (3I_z^2 - I(I+1)) + \eta (I_+^2 + I_-^2)
\]

where: \(I\) = nuclear angular momentum (nuclear spin)

\[ \eta = \frac{U_{xx} - U_{yy}}{U_{zz}} \quad U_{xx} \text{ and the others are second partials with respect to the subscript coordinate} \]

\([U = \text{potential created by surrounding charge.}]

\text{Quadrupole coupling has three principal effects on EPR spectra: 1) enhancement of intensity of forbidden } (\Delta m_I \neq 0) \text{ trans-}
sitions: 1) change of line positions of forbidden transitions with magnetic field direction; and 2) change of line positions of the allowed \((m_z=0)\) lines. For single crystals, these effects can all be used to determine quadrupole coupling constants.\(^{3,4,5}\)

C. THEORY OF POWDER SPECTRA

The effect of quadrupole coupling on powder spectra is less obvious than described above, since the powder spectrum represents an average of spatially random crystal configurations. The basic lineshape is commonly derived for an axially symmetric system \((g_x=g_y=g_\perp, g_z=g_\parallel)\), for which:

\[
g^2 = g_\parallel^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta
\]

This is equivalent to

\[
\cos \theta = \left( \frac{g_\parallel^2 - g_\perp^2}{g_\parallel^2 - g_\perp^2} \right)^{\frac{1}{2}}
\]

Since \(\hbar = g_\parallel h\),

\[
\cos \theta = \left( \frac{H_\parallel^2 - H_\perp^2}{H_\parallel^2 - H_\perp^2} \right)^{\frac{1}{2}}
\]

The solid angle subtended by a range of axes dictates the probability of the resonant field lying between \(H\) and \(dH\) (see figure 2). Thus geometry gives us

\[
P(H) dH = \frac{\sin \theta}{dH} d\theta
\]

\[
P(H) \frac{\sin \theta}{dH} d\theta = \frac{H^{-3}}{((H^{-2} - H_\perp^{-2})(H_\parallel^{-2} - H_\perp^{-2}))^{\frac{1}{2}}}
\]
Figure 2. Geometry involved in calculating angular distribution of randomly aligned axes.
Continuing the derivation:

\[ P(H) \propto \frac{H^2_i dH}{H^2((H^2 - H^2_1)(H^2 - H^2_2))^{\frac{3}{2}}} \]

The transition probability also depends on the crystallite angle; this gives the multiplicative factor:

\[ \frac{g_1^2 + g_2^2}{g_2^2} \]

\[ = \frac{H^2_i + H^2_2}{H^2_2} \]

Combining these two factors to find the intensity distribution:

\[ I_x \frac{H^2_i (H^2_i + H^2_2) dH}{H^2_i H^2((H^2 - H^2_1)(H^2 - H^2_2))^{\frac{3}{2}}} \quad (6) \]

This function and its derivative are shown in figures 3a and 3b. A finite value at \( H = H_1 \) can be accommodated by inclusion of some line shape function.

Quadrupole coupling effects on this spectrum may include line shifts, intensity changes, line shape changes, and/or the appearance of new peaks. Assignment of features to specific, quantitative molecular parameters by inspection is nearly impossible for even very simple spectra. Computer simulations have been proven to be a method of readily obtaining those parameters, or at least verifying suggested quantities.7,8,9

D. COMPUTER SIMULATION

Considerable effort by Nilges and his predecessors has produced computer programs capable of simulating spectra for
Figure 3. Idealized powder spectrum (axial symmetry).

a) Absorption vs. field strength.

b) Derivative of absorption with respect to field vs. field strength.
spin = $\frac{1}{2}$ systems, with consideration of nuclear hyperfine, nuclear quadrupole, and superhyperfine, with the possibility of non-alignment of the principal axes of the hyperfine, quadrupole, and $g$ matrices. The calculation is done via two-dimensional 4-point gauss-point integration. It is described in Hilges' thesis (reference 8), where the programs themselves may also be found.

II. CuSO$_4$ Doped MgSO$_4$·7H$_2$O

A. IMPETUS TO INVESTIGATE SYSTEM

Some of the early work by Bleaney was done on copper (II) octahedrally coordinated to water;\textsuperscript{4,5} generally it was doped into Tutton salts (K$_2$M(II)SO$_4$)$_n$H$_2$O. Single crystal EPR and some analysis of the system, Cu$^{2+}$ doped MgSO$_4$·7H$_2$O, has been reported recently.\textsuperscript{10} This analysis did not mention quadrupole coupling, and it has been shown that this effect can be quite significant in correctly simulating systems with large coupling constants. Belford and Duan (reference 11) have shown that octahedrally coordinated copper(II) does exhibit large quadrupole coupling constants.

Quadrupole coupling constants have been determined by simulation of square-planar Cu-O$_4$ systems,\textsuperscript{11} and by single crystal studies of Cu doped Tutton salts.\textsuperscript{5} This suggested a determination and/or verification of quadrupole coupling in the Cu(H$_2$O)$_6^{2+}$/MgSO$_4$·7H$_2$O system.
B. HOST UNIT CELL AND CRYSTAL STRUCTURE

The predominant crystal structure of MgSO$_4$·7H$_2$O at normal conditions is rhombic, with space group P2$_1$2$_1$2$_1$. There are four molecules per unit cell, described by the positions:

\[ x, y, z; x, y, z+\frac{1}{2}; x+\frac{1}{2}, y, z; \frac{1}{2} - x, y+\frac{1}{2}, z \]  

A projection of a unit cell is shown in figure 4.

The X-ray determined crystal structure is shown in figure five.\textsuperscript{14} Each Mg$^{2+}$ ion is octahedrally coordinated to six water oxygens, with the seventh water in a non-coordinating, "interstitial" position. The molecular symmetry is nearly tetrahedral, with the Mg-O axis most nearly parallel to the crystallographic axis, having slightly longer Mg-O distances.

Thus, there are four unique metal sites from the point of view of impinging radiation. In any crystal plane, however, the projection of each molecular principal axis is parallel to one of its unit cell neighbors, so two unique magnetic sites are possible with a magnetic field perpendicular to any crystal axis (i.e., parallel to any crystal plane). Along any crystal axis, the four projections are at the same angle with the magnetic field, and are equivalent. This is illustrated in figure 6.

The crystal morphology relates in a straightforward way to the crystal axes, as shown in figure 7.\textsuperscript{15}
Figure 4. Representations of a MgSO₄·7H₂O unit cell.

a) The Mg²⁺ ions are darkened.

b) Packing model; most of the atoms visible are oxygens from SO₄²⁻ or H₂O.

Both from reference 13.
Figure 5. X-ray determined structure of MgSO$_4$·7H$_2$O. From reference 14.
Figure 6. MgSO$_4$·7H$_2$O unit cell. Spheres and segments are projections of Mg$^{++}$ and its "long" (z) axis onto the ab crystal plane.

a) With the magnetic field perpendicular to the c axis, each ion is equivalent to one of its neighbors: $\theta_1=\theta_2$ and $\theta_3=\theta_4$.

b) and c) With the magnetic field perpendicular to the c axis and parallel to either the a or b axis, all sites are magnetically equivalent: $\theta_1=\theta_2=\theta_3=\theta_4$. 
Figure 7. MgSO₄·7H₂O crystal morphology; a, b, and c are crystallographic axes.

From reference 15.
III. Experimental

A. PREPARATION OF CRYSTALS AND POWDERS

Both natural abundance and isotopically pure ($^{63}\text{Cu}$) were used. $^{63}\text{CuSO}_4\cdot5\text{H}_2\text{O}$ was made by addition of sulfuric acid to an aqueous suspension of $^{63}\text{CuO}$ obtained from Oak Ridge National Laboratories. The resulting blue solution was poured into a large quantity of acetone; the blue precipitate was washed with acetone and air dried. Anal. Calculated for $^{63}\text{CuSO}_4\cdot4\text{H}_2\text{O}$: Cu, 26.40; S, 13.32; H, 3.76. Found: Cu, 26.34; S, 13.41; H, 3.59.

Reagent grade natural abundance ($69.1\%^{63}\text{Cu}, 30.9\%^{65}\text{Cu}$) $\text{CuSO}_4\cdot5\text{H}_2\text{O}$ was used.

$\text{Cu}^{24}$ doped $\text{CuSO}_4\cdot7\text{H}_2\text{O}$ was prepared by evaporation of a mixture of saturated (aqueous) $\text{CuSO}_4$ and $\text{MgSO}_4$. When the evaporation was done quickly, under vacuum, the resulting crystals showed no incorporated copper (titration with EDTA; PAN indicator). Copper was incorporated when the solutions were left at room pressure; crystals formed after approximately 36 hours. Varying amounts of copper in solution led to varying amounts of copper in the crystals; some of those analyzed are shown below:

<table>
<thead>
<tr>
<th>sat’d sat’d %v/v CuSO$_4$/MgSO$_4$</th>
<th>%w/w, Cu in crystals</th>
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<tr>
<td>0.5</td>
<td>0.083</td>
</tr>
<tr>
<td>2.0</td>
<td>0.0086</td>
</tr>
<tr>
<td>2.5</td>
<td>0.169</td>
</tr>
<tr>
<td>2.5</td>
<td>0.016</td>
</tr>
<tr>
<td>4.0</td>
<td>0.017</td>
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Even though the solubilities of CuSO$_4$ and MgSO$_4$ are fairly near each other at room temperature (18.0, 27.6 g/100g soln, respectively, at 25 C), copper was incorporated in very small amounts. Variations in room temperature may be a factor, but no obvious correlation was observed. There was some indication of greater copper doping with slower crystal growth. Crystal growth remains an art.

Typically, many hundreds of small crystals appeared nearly simultaneously; a few of these were moved with the supernatant to another container. Crystals with nearly perfect morphology could be grown to any size (the only limiting factors were the size of the container and the distance to the nearest neighbor).

Powders were created by extensive grinding, with mortar and pestle, of crystals.

3. SPECTRA: EQUIPMENT AND TECHNIQUE

Spectra were recorded at X-band with a Varian E9 EPR equipped with an E101 microwave bridge and a Hewlett-Packard 5240A digital frequency meter. Temperatures between -40 and -150 C were maintained with a Varian V-540 temperature controller (nitrogen blowing mechanism); the cavity temperature was monitored independently with an Assembly Products Sim-Ply-Trol inserted occasionally into the sample space.

Spectra were recorded at Q-band on another Varian instrument, equipped with an E110 bridge. Temperatures were assumed to be near 77K, since the sample-holding part of the cavity was inside a dewar with the cavity bottom turning rod immersed
in liquid nitrogen. Modulation coils were attached to the exterior of the dewar.

For both X- and Q-band measurements the magnetic field was calibrated with a Bruker B-NM20 NMR oscillator, which is able to track and digitally display (to .01 Gauss) the field as it is swept. Since no frequency meter was attached to the Q-band waveguide, DPPH was used as a standard to determine the frequency at a known field position.

Some work was done at X-band with an Oxford ESR-10 liquid helium system using a GFS 300 transfer tube and DTC-2 temperature controller. However, before good spectra were obtained, other users severely contaminated the internal glassware; the contaminant g-value was very near the region of interest here, and completely obscured attempted spectra. As of this writing, it is still contaminated. It was hoped that Jahn-Teller effects such as seen for the Cu$^{2+}$ doped Tutton salts$^{17}$ might be observed (see future studies, part V). No evidence was seen at liquid nitrogen temperatures.

IV. Results

A. SINGLE (?) CRYSTALS

Radhakrishna and Rao$^{10}$ reported spectra showing two sets of four hyperfine (I=3/2) lines with the magnetic field in any of the three crystallographic planes. This would be the expected result if Cu$^{2+}$ entered Mg$^{2+}$ sites, retaining the host's symmetry (see IIB; figure 6).
That was not the typical result observed here. In fact, it was observed for only one mounted crystal (figure 8). It was hoped to analyze the spectra after So and Belford, using the spacing between the forbidden lines to determine the quadrupole coupling constant (see figure 1 for an idea of how the quadrupole coupling affects the positions of forbidden lines). However, the spectral lines of the one "good" spectrum were so broad as to obscure any existent forbidden lines. The broadness is explainable as Cu-Cu dipolar broadening, since subsequent more dilute crystals were significantly narrower (figure 9). These spectra did exhibit what appear to be forbidden transitions.

Unfortunately, for all the dilute crystals studied, "extra" sets of lines obscured the forbidden lines so that their positions could not be followed as the magnet was moved. The appearance, with consistency, of multiple sets of hyperfine indicates a discrepancy in one or more of the three basic crystal symmetry assumptions:

1. **Crystal Alignment.** Radhakrihna and Rao imply that their alignment was done by morphology, as was done here, suggesting that the method is valid. The alignment and transfer device has been used routinely with success; it is pictured and described in Simpson's thesis. A cursory examination of this device showed no flaws, and it was used, successfully, in the same time span by another group member (although his lines were much broader and less revealing of slight misalignment).
Figure 8. Q-band spectra: variation with magnetic field direction. Single crystal, natural abundance Cu.
Figure 9. Typical Q-band spectra. Arrows indicate suspected forbidden transitions.

a) Natural abundance Cu.

b) More dilute natural abundance Cu.

c) $^{63}$Cu; also fairly dilute.
The splitting between the twin sets was not constant, nor a simple function of field angle, as would be expected from a constant, systematic misalignment.

2. Metal Ion Substitution. The site symmetry described in IIB is for pure orthorhombic MgSO₄·7H₂O. Cu²⁺ may not retain the symmetry of the Mg²⁺ site, or may completely disrupt the lattice. The retention of the described morphology and the success of the powder spectra suggest, however, that Cu²⁺ has retained the same crystal structure.

It was suggested by Professor Belford that a phase transition may be occurring between room temperature (preparation and known structure temperature) and spectral temperatures. Such a phase change was suggested for Cu²⁺ doped Tutton salts to explain anomalous changes in apparent site symmetry at low temperatures (LHe),²⁰ but this was later shown rather convincingly to be due to a dynamic Jahn-Teller effect.¹⁷ It is possible that differential thermal gradients in the crystal could result in different phases for different portions of the sample. An attempt was made to anneal the crystal by repeated cooling and slight warm-up, thus taking the entire crystal to its equilibrium phase at the spectral temperature. Resulting spectra were exactly the same as that observed for non-annealed crystals. The experiment was far from rigorous, however, as the epoxy used to cement the crystal to the quartz mounting rod would only withstand six or seven cool/warm cycles before relinquishing its grip.
Also, as in the first suggested explanation, this would be a more systematic effect (assuming a small number of phases involved), whereas the spacing between the multiple sets varied by almost the hyperfine splitting from crystal to crystal.

3. "Married" Crystals. The allegedly single crystals could be twinned. Indeed, although all but two of the crystals showed one extra set of lines (sixteen rather than eight, in a crystal plane), one of the others showed what may be three sets (24 lines), although overlapping makes assessment of number of lines difficult. This is the acknowledged scourge of crystal growth because it is difficult to diagnose by independent (non-spectral) means.

A plot of line position vs. magnet angle, in the ab plane, is shown in figure 10. Line assignments were based on intensities, predicted position due to constants hyperfine splitting in a given spectrum for a given set of four lines, and trends seen in the function(s) plotted (i.e., assumed continuity).

B. POWDER

Isotopically pure $^{63}\text{CuSO}_4$ doped MgSO$_4$·7H$_2$O spectra are shown in figures 11 and 12, respectively.

The X-band spectrum was simulated. A simulation using BFCW and the parameters suggested by Radhakrishna and Rao is shown in figure 13. Since the $g$ and hyperfine values in the parallel (low field) region are significantly off, and they reported difficulty in determining the complete hyperfine ten-
Figure 10. Spectral line position vs. magnetic field direction, in the ab plane. $^{63}$Cu, Q-band, single crystal.
Figure 11. $^{63}\text{Cu}$, powder, X-band, near -150 C.
Figure 12. $^{63}$Cu, powder, Q-band, near 77K.
Figure 13. a) X-band powder simulation, using the parameters of reference 10:

\[ g_x = 2.098, \quad g_y = 2.089, \quad g_z = 2.441 \]

\[ A_x = -22E-4 \text{ cm}^{-1}, \quad A_y = -18E-4 \text{ cm}^{-1}, \quad A_z = -116E-4 \text{ cm}^{-1} \]

b) Experimentally observed spectrum.
\( v = 9.1049 \text{ GHz} \)
sor, an attempt was made to fit the spectrum by varying the principal values of the $g$ and $A$ tensors, using BPOW.

That attempt was fruitless. Some of the poorly fit features could be improved, but only at significant expense to another part of the spectrum.

Use of QPOW, with inclusion of quadrupole coupling, proved quite successful. A value of 1.482 for the $^{63}$Cu nuclear $g$-factor was reported to the computer. Figure 14 shows how the features change dramatically as the principal quadrupole coupling term, $QD (=3P_{zz}/2c)$, is increased from zero to 30 MHz (10E-4 cm$^{-1}$).

An analysis near this value showed that a much better fit could be obtained if some corrections to the values of Radhakrishna and Rao were made. Most notably, the hyperfine tensor is found to be more nearly axial than suggested. These studies were done with well known field and frequency values (see description of equipment in experimental section), so they are reported with some confidence:

$g_x=2.0995, g_y=2.0897, g_z=2.4480$

$A_x=-55$ MHz, $A_y=-54$ MHz, $A_z=-362$ MHz

The quadrupole coupling constant $QD$ is suggested to be $32\pm4$ MHz (11±2E-4 cm$^{-1}$); figure 15 shows variation in the simulations in this range. The fit could perhaps be improved (see Future Studies); the justification of the upper limit of $QD$ is a rather subtle feature (figure 15) which could be sig-
Figure 14. Variation of X-band simulation with QD.

a) \( QD = 0 \).
b) \( QD = 10 \) Mhz.
c) \( QD = 20 \) MHz.
d) \( QD = 31 \) MHz.
e) Experimentally observed spectrum.
Figure 15. Variation in X-band simulation with QD. Colinear arrows show changing position of the shoulder.

a) QD=26 MHz.

b) Experimentally observed spectrum.

c) QD=32 MHz.
Figure 16. Variation in X-band simulation with QD. Arrows show the feature mentioned in the text.

a) QD=25 MHz.

b) QD=35 MHz.

c) Experimentally observed spectrum.

d) QD=40 MHz.
nificantly affected by slight changes in other (non-quadrupole) parameters, or even by slight quadrupole coupling x-y anisotropy (QE≠0).

V. Future Studies

This is a somewhat embarrassingly important part of this paper. There is much that could be done on this system. Some suggested avenues of approach:

A. SIMULATION OF THE Q-BAND SPECTRUM

This was feebly attempted, and the fit was not very good; this means the Q-band spectrum contains more restraints on the simulation, which is very valuable information in our type of analysis. The fit with QPOW was dramatically better than just POW, as with the X-band simulation.

B. SINGLE CRYSTAL STUDIES

If good single crystal obtained, there is good evidence that forbidden transitions could verify or suggest an alternative value for the quadrupole coupling constant. I suggest slower crystal growth, perhaps at reduced temperatures.

C. SEARCH FOR JAHN-TELLER EFFECT

This system is a prime candidate for Jahn-Teller splitting, by analogy to the Tutton salts.17 The crystal structure shows the Mg$^{2+}$ center in an axially elongated octahedron; putting a potentially degenerate d$^9$ ion (Cu$^{2+}$) in an already axially asymmetric site may have interesting results.
D. INVESTIGATION OF ONE ANOMALOUS SPECTRUM

The X-band spectrum of one of the natural abundance copper samples showed some additional peaks superimposed on the "normal" spectrum (figure 17). Slight traces of these peaks were seen on other spectra, but never with this order of magnitude of intensity. A temperature dependence study (on another sample) was done to see if this was possibly a phase effect; no such effect was evidenced. It is possible that some of the crystals in that batch chose to grow monoclinic. Although no specific information was found for MgSO₄, FeSO₄ is known to be monoclinic at near-room temperatures.²²

VI. Conclusion

The quadrupole coupling constant QD of $^{63}$Cu²⁺ doped MgSO₄·7H₂O is approximated from X-band simulation as 11±2 E-4 cm⁻¹. This is in good agreement with values compiled by Belford and Duan¹¹ for Cu²⁺ in an octahedral environment.
Figure 17. Anomalous observation, and temperature series (of a different sample) mentioned in the text.
REFERENCES

(1) Any good ESR text, such as A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York (1967).


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