Most of the report is well written. You should have more and better results though.

B+

ELECTRON SPIN RESONANCE

Rodney V. McCormick

Physics 303

May 1970

The electron spin resonance experiment is essentially an attempt to "see" the energy it takes to "flip" an electron oriented in a magnetic field. The energy of an electron in a magnetic field is described by the relation

$$E = -\vec{\mu}\cdot\vec{B}$$

where $\vec{\mu}$ is the magnetic moment vector of the electron and $\vec{B}$ is the magnetic flux density vector. The magnetic moment $\vec{\mu}$ is simply the sum of the orbital and spin magnetic moments of the electrons:

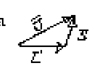
$$\vec{\mu} = -\sum_{i=1}^{n}\left[\frac{1}{2}\frac{e}{m}\vec{l}_i + \frac{e}{m}\vec{\sigma}_i\right],$$

where $\vec{l}$ and $\vec{\sigma}$ are the orbital and spin angular momentum vectors.

In other terms; $\vec{\mu} = -\frac{1}{2}\frac{e}{m}(\vec{L} + 2\vec{S})$

where $\vec{L}$ and $\vec{S}$ define the obvious.

Defining $\vec{J} = \vec{L} + \vec{S}$, then $\vec{\mu} = -\frac{1}{2}\frac{e}{m}(\vec{J} + \vec{S})$

Using the vector diagram 

and $|\vec{\mu}| = \frac{1}{2}\frac{e}{m}\left(|L|\cos(\vec{L},\vec{J}) + 2|S|\cos(\vec{S},\vec{J})\right)$

and by the law of cosines

$$\cos(\vec{L},\vec{J}) = \frac{|J|^2+|L|^2-|S|^2}{2|L||J|}, \quad \cos(\vec{S},\vec{J}) = \frac{|J|^2+|S|^2-|L|^2}{2|S||J|}$$

and substitution gives

$$|\vec{\mu}| = \frac{1}{2}\frac{e}{m}\left[1 + \frac{|J|^2+|S|^2-|L|^2}{2|J|^2}\right]|J|$$

$$\Rightarrow \quad W = E = \frac{1}{2}\,\frac{eB\hbar m_J}{m}\,g_L \quad , \text{where}$$

$$\hbar m_J = |\vec{J}| \quad \text{and} \quad g_L = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Using the relations $\mu_0 = \frac{e\hbar}{2mc}$ and Bc = H = the magnetic field, So $W = \mu_0 g_L H M_J$.

For a spectral transition $J_1 \to J_2$ the change in energy appears as a Photon (which is to be detected).

$$\Delta E = W_1 - W_2 = \mu_0 H (g_{L1} M_{J1} - g_{L2} M_{J2})$$

This quantum has a frequency $\nu = \Delta E / h$

The selection rule for such transitions is $\Delta M_J = 0, \pm 1$. This means, if $g_{L1} = g_{L2}$, (1) $\nu = \frac{\mu_0}{h} g_{L1} H$. This is true for an S state electron (with L=0), where $g_{L1} = g_{L2} = 2$.

If the electron produces a sufficient magnetic field $H_e(0)$ at the nucleus of the atom, then it is possible for the magnetic moments of both the nucleus and the electron to interact making the so-called hyperfine structure in the ESR spectrograph. As before the energy of such an interaction can be given by the relation

$$W = - \bar{\mu} \cdot \overline{H_e(0)}$$

where $\bar{\mu} = g_I \frac{e}{2m_p c} \bar{I}$ is the nuclear magnetic moment, with g_I as a constant related to the nucleus, m_p is the proton mass and $\bar{I}$ is the angular momentum vector for the nucleus.

$\overline{H_e(0)}$ is related to $\bar{J}$, the total angular momentum vector of the electron, reducing the relation above to

$$W = \frac{\mu}{|I|} \frac{H_e(0)}{|J|} \bar{I} \cdot \bar{J}$$

$$= \frac{\mu \, H_e(0)}{|I| \, |J|} I J \cos(\bar{I}, \bar{J})$$

But if one defines $\vec{F} = \vec{I} + \vec{J}$, then the law of cosines gives

$$\cos(\bar{I},\bar{J}) = \frac{|F|^2 - |I|^2 - |J|^2}{2|I|} \qquad 2$$

Putting this back into the equation

$$W = \frac{A}{2}\left[F(F+1) - I(I+1) - J(J+1) \right] \qquad 2a$$

where $A = \frac{\mu}{|I|} \; \frac{\langle H_e(0) \rangle}{|J|}$

So, the total energy of transition for spin resonance, including the hyperfine structure caused by magnetic dipole interaction is

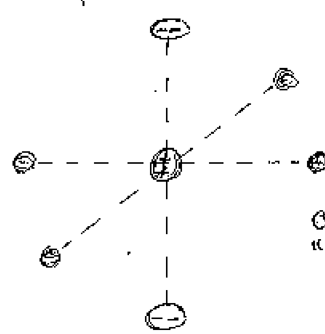
$$\Delta E_{TOTAL} = \mu_0 g_e H + \frac{A}{2}\left[(F,I,J)_1 - (F,I,J)_2 \right] \qquad 3$$

where $g_e = (g_{L1} m_{J1} - g_{L2} m_{J2})$,

and the term in brackets will be explicit later.

If the paramagnetic ion is settled in an asymmetric crystal structure, the electronic wave function loses its invariance with respect to rotation of axes. That is, $\psi(\phi,\theta) \neq \psi(\phi+\phi_0, \theta+\theta_0)$

As an illustration, consider a doubly positive charged ion surrounded by two strong doubly negative charged ions and four weakly negative ions:

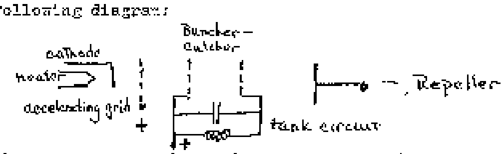


$CuSO_4 \cdot 4H_2O$
"Crystal Structure"

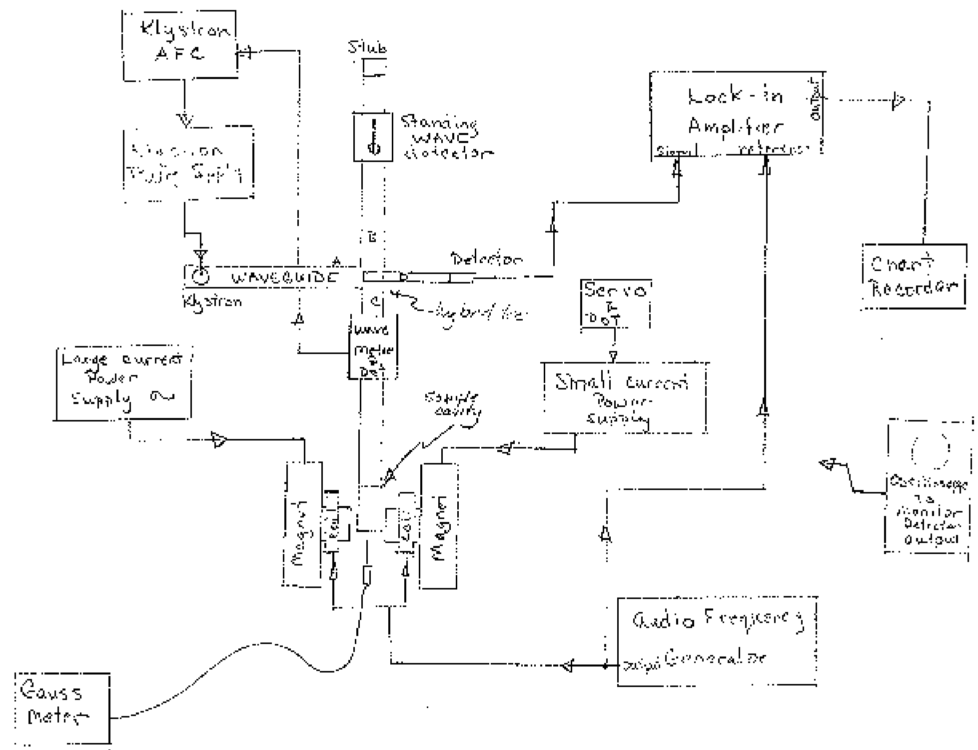
The electric field potential then is not isotropic. Consequently, applying an external magnetic field would give a different wave function according to the direction at which the external field is applied. So, g_e becomes a function of direction in the crystal, since it is a function of the quantum numbers describing the wavefunctions, which, in turn, is a function of the direction of the applied external magnetic field.

THE EXPERIMENTAL APPARATUS

<u>The klystron</u> is the source of electromagnetic radiation used in this system. The reflex klystron produces microwaves; that is, radiation near ten gigahertz. The klystron operates on the principle that accelerated electrons give up energy in the form of electromagnetic radiation. The equivalent circuit is like the following diagram:



Electrons are accelerated much as in an electron gun, then are "bunched" into packets according to the frequency of the tank circuit (in this case, just a resonant cavity). After being bunched, they are turned around and sent back by the repeller voltage. They are slowed down by the buncher-catcher and give up their energy; an energy having a frequency of the tank circuit. By adjusting the



ESR APPARATUS

PAR lock-in amplifier

515A oscilloscope

Klystron power supply #510

Klystron AFC circuit

Bell 600 Gaussmeter

Lab R3 Magnet

Perkin Elect. Power supply

R3 magnet power supply

Heath Servorecorder

Lab power servo

2K25 Klystron tube

size of the cavity, one may change the output frequency of the klystron. This may be done to some extent by changing the repeller voltage, but this is by less than one part in a thousand, whereas, the cavity method can change it by about one part in ten.

Waveguide. It is known that electromagnetic radiation may propagate along a hollow rectangular pipe, made of some conducting material, over a certain range of frequencies. The so-called cut-off frequency for a long rectangular waveguide of width a and height b,

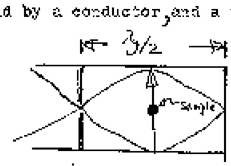
$$f_c = c\left[\left(\frac{m\pi}{a}\right)^2 + \left(\frac{n\pi}{b}\right)^2\right]^{1/2}$$

is the frequency below which electromagnetic propagation down the waveguide is imaginary. The wavelength of the radiation in the waveguide, λ_g, is related to the wavelength, λ_o, of the radiation of frequency f in air by,

$$\lambda_g = \frac{\lambda_o}{\sqrt{1-(f_c/f)}}$$

This is important in determining the size of the sample cavity.

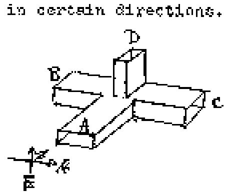
Sample cavity is just a small bit of waveguide blocked at one end by a conductor, and a wall with a hole in it at the other:



Sketch the E& B field in the cavity.

The sample is placed at maximum amplitude ($\frac{\lambda_g}{4}$) of the standing wave pattern.

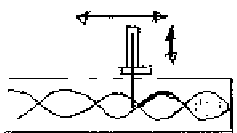
The hybrid tee is a device to selectively channel microwave power in certain directions.



Power coming into the tee from A divides and goes into B and C but not into D. Power from B or C goes into both A and D if B and C are not properly terminated. But if the amplitudes of the radiation from B and C are equal, no power is transmitted to d while twice amplitude is delivered to A.

The wavemeter is a frequency variable resonant cavity that absorbs from the waveguide microwave energy having the frequency of the resonant cavity. It has a microwave detector on it so that as the cavity size is changed to match the frequency of the microwave radiation, there is a "dip" in the power out of the detector

The standing wave detector is a small metal probe that extends down into the waveguide and can be moved up and down the length of a slotted piece of waveguide. The amount of microwave power taken out

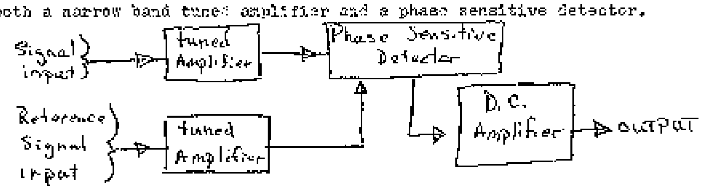


of the waveguide depends on how far down into the waveguide the probe is adjusted and where along the standing wave pattern the probe is set. This is used to obtain a null at arm "D" of the hybrid tee.

Magnetic field source. As can be seen in figure 1,, there are thre components of the magnetic field. 1) Constant magnetic field, 2) slowly decreasing magnetic field, and 3) an oscillating magnetic field. The constant magnetic field source produced a large flux and was necessary because a servo driven power supply did not produce a flux large enough. The power source that had a servo driven sweep capability was used to sweep through about 1000gauss of the ESR spectrum.

The smal. oscillating magnetic field was intended to modulate resonance at a certain frequency so that the lock-in amplifier could lock in on that frequency.

<u>The lock-in amplifier</u> is a device used to reduce the noise that is a gremlin for regular power amplifiers. It does this by both a narrow band tuned amplifier and a phase sensitive detector.



It acts like a switch that is driven off and on by a reference oscillating signal. If the reference frequency is w and the signal frequency is w', then the power received out of the lock in is P cos(w't + d) cos (wt); which equals (P/2)(cos(w't + wt +d)+ cos(wt+d - w't)). The tuned amplifier would get rid of the first cosine term, and the second term would have a maximum when

tuned amplifier is an input in your circuit?

$$w't = wt + d.$$

So, if one can adjust the phase term to zero the lock-in amplifier will give maximum output power to freqencies w = w'. This frequency is set for the modulating magnetic field and the reference input of the lock-in.

OBSERVATIONS

To see what kind of of output signal should be expected, one should consider what he is observing. Say that the electrons acts like a simple harmonic, damped and forced oscillator, where the ~~microwave~~ electric field supplies the forced oscillations, then the differential equation for such an oscillator is

a) $\ddot{x} + \frac{R}{m}\dot{x} + \omega_0^2 x = \frac{F}{m} e^{j\omega t}$

assume $x = Ae^{j\omega t} + Be^{-j\omega t}$

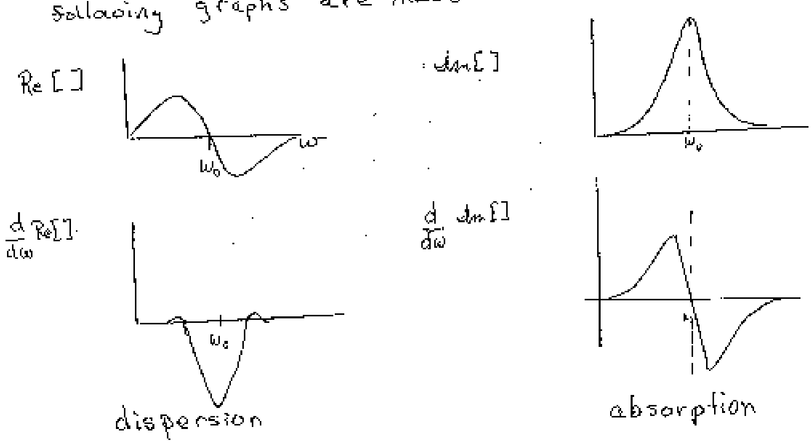
substitution into a) and equating $e^{j\omega t}$ coefficients gives

$$-A\omega^2 + \frac{R}{m}A\omega j + \omega_0^2 A = \frac{F}{m}$$

$$\Rightarrow A = \frac{F}{m(\omega_0^2-\omega^2)+R\omega j}$$

$$\Rightarrow x = Fe^{j\omega t}\left[\frac{m(\omega_0^2-\omega^2)}{m^2(\omega_0^2-\omega^2)^2+R^2\omega^2} - \frac{Rj\omega}{m^2(\omega_0^2-\omega^2)^2+R^2\omega^2}\right]$$

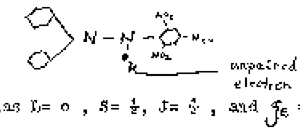
Considering just the bracketed term (called [ ]), the following graphs are made



Only the frequency derivatives of amplitude function can be observed because it is the change in frequency of oscillation of the electron that produces the quanta. ~~now~~

By adjusting the phase you can observe get either ~~the~~ absorption or the dispersion type of signal

The samples I used were to be representative of a resonance electron in an isotropic g-space and a non- isotropic space. I used DPPH (better known as diphenyl- picryl -hydrazil) which has an unpaired electron. The following illustration will clarify :



DPPH Molecule.

It has $L = 0$, $S = \frac{1}{2}$, $J = \frac{1}{2}$, and $g_e = 2$; if there is no nuclear magnetic dipole interaction. Using equation 3

$$\Delta E = \mu_0 \, g_e \, H + A/2 \left[(F,I,J)_1 - (F,I,J)_2 \right]$$

According to Melissinos, $A \propto Z^3$; and since Z is small (= 7) the hyperfine structure is too small to notice except for a possible broadening of spin resonance line.

$$\text{So,} \quad \Delta E = hf = \mu \, g_e \, H$$

$$\Rightarrow g_e = \frac{hf}{\mu H} = \frac{f}{H} \cdot \frac{1}{1.401 \times 10^6 \frac{\text{hz}}{\text{gauss}}}$$

For Chart #3 $f_0 = 4060.5$ mhz , $H_0 = 3065$ $\Rightarrow g = 2.110$

For Chart #1, which is apparently a dispersion curve, $f_0 = 4060.5$ mhz $H_0 = 3046$ gauss $\Rightarrow g_e = 2.122$. These values of g are within 6% of the accepted value of g for DPPH.

Charts #2 and #3 are two separate runs of the same sample of DPPH, with the only difference being the phase setting on the lock-in amplifier.

As a second sample I used a special crystal of $CuSO_4 \cdot 4H_2O$ paramagnetic salt in a lattice of a diamagnetic salt to reduce the spin- spin interaction of the unpaired electron of the copper ion. Copper has a ground state electron configuration of $[A]\,3d^{10}4s^1$; but the doubly ionized copper has $[A]\,3d^9$, or a hole in the 3d subshell. Thus $L = 2$, $S = \frac{1}{2}$.

This copper sample is an example of an electron being in an anisotropic electron potential, thus~~ly~~, as I have have said before, making ~~the effect of~~ an external magnetic field's effect dependent on the angle through the crystal. I was unable to observe this dependence, but was able to get one chart made of the copper sample. This is Chart #4. It shows the hyperfine structure.

Copper has a nuclear spin $I = \frac{3}{2}$ for virtually 100% of its isotopes by abundance.

Note that there are 2 stable isotopes of comparable abundance with slightly different nuclear magnetic moments

$$J = L+S = 2 \pm \tfrac{1}{2} = \tfrac{5}{2} \text{ or } \tfrac{3}{2}$$

$$F = I+J = \tfrac{3}{2}+\tfrac{5}{2}, \ldots, \tfrac{3}{2}-\tfrac{5}{2} = 4, 3, 2, 1, 0, -1 \quad \text{for } S = \tfrac{1}{2}$$

OR

$$F = I+J = \tfrac{3}{2}+\tfrac{3}{2}, \ldots, \tfrac{3}{2}-\tfrac{3}{2} = 3, 2, 1, 0 \quad \text{for } S = -\tfrac{1}{2}$$

Using equation 2a , I can find the relative energy shifts due to magnetic dipole interaction.

For $J = \frac{5}{2}$, $W = \frac{A}{2}\left[F(F+1) - \frac{15}{4} - \frac{35}{4}\right] = \frac{A}{2}\left[F(F+1) - \frac{25}{2}\right]$

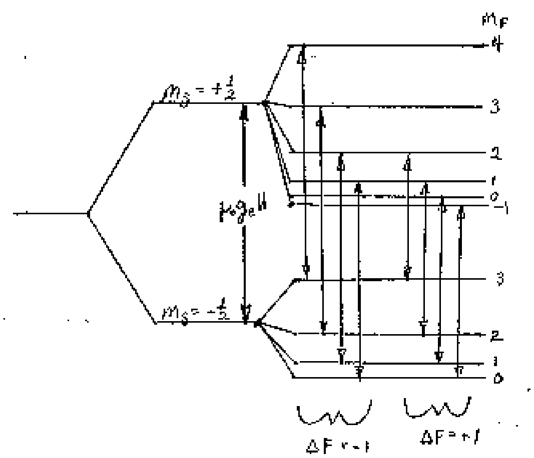
For $J = \frac{3}{2}$, $W = \frac{A}{2}\left[F(F+1) - \frac{15}{2}\right]$

Tabulation of these gives the following:

The orbital angular momentum L is not a good quantum number because of the anisotropic potential. In fact the transition elements Ti – Cu show "spin only" paramagnetism in a first approximation, in other words, the orbital angular momentum is quenched. F is therefore

	M_F	W
$J = 5/2$	4	+3.75A
	3	−0.25A
	2	−3.25A
	1	−5.25A
	0	−6.25A
	−1	−6.75A
$J = 3/2$	3	+2.25A
	2	−0.75A
	1	−2.75A
	0	−3.75A

Making an energy level diagram one can readily see the $\Delta F = \pm 1$ transitions:



not to scale

So the hyperfine structure should have eight lines. The amount of energy added to or taken from the $\mu g_J H$ energy is found by algebraically subtracting the ($J = \frac{5}{2}$)'s W from the ($J = \frac{5}{2}$)'s W for the lines:

$4 \to 3$	$\Delta E_{Hyperfine}$	$= +1.5A$	dispersion
$3 \to 2$		$= +0.5A$	
$2 \to 1$		$= -0.5A$	
$1 \to 0$		$= -1.5A$	
$2 \to 3$		$= -5.5A$	absorption
$1 \to 2$		$= -4.5A$	
$0 \to 1$		$= -3.5A$	
$-1 \to 0$		$= -3.0A$	

This would have a spectum li*e :

Chart #4 shows the first four peaks completely, but the last part of the fifth peak shows what happened to my experiment --- it met with a disaster which set me back three weeks at two weeks before the end of the term. These peaks are at 4550, 4350, 4150, 4000 and 3700 gauss with a frequency of microwave radiation of 9196.5 Mhz. Going by figure 20, the $\mu g_e H$ level would fall at 4250 gauss, making the effective g-factor

$$g_e = \frac{h}{\mu_0}\frac{f}{H} = \frac{1}{1.401\times10^6_{\frac{\mathrm{c}}{\mathrm{g}}}}\cdot\frac{9196.5\times10^6\,\mathrm{c}}{4250\,\mathrm{g}} = 1.544$$

This could have been predicted, since the transition is from L=2, S=$\frac{1}{2}$, J=$\frac{5}{2}$, to L=2, S=-$\frac{1}{2}$, J= $\frac{3}{2}$.

$$g_{L1} = 1+\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} = 1+\frac{\frac{35}{2}+\frac{3}{2}-6}{70/2} = 1.3715$$

$$g_{L2} = 1+\frac{15/2+3/2-6}{30/2} = 1.200$$

$$m_{J1} = 5/2 \quad ; \quad m_{J2} = 3/2$$

$$g_e = [g_{L1}m_{J1} - g_{L2}m_{J2}] = \left[1.3715\left(\tfrac{5}{2}\right)-1.200\left(\tfrac{3}{2}\right)\right]$$

$$= 1.630$$

The error in this part of the experiment then is

$$\frac{1.630-1.544}{1.630}\times100\% \doteq 5.3\%$$

which is about the same as the DPPH spectrum.

I am disappointed that I was unable to continue the experiment long enough to see the effect of rotating the crystal, but I feel that I still learned much from this "undertaking".

You don't mention your experimental difficulties in great detail. What was the problem? It is really a pity you didn't measure and analyze the Tutton salt in more detail.

PARTIAL LIST OF SOURCES

Principles of Modern Physics   Leighton

Introduction to Theoretical Mechanics   Becker

Modern Physics   Kelissinos

Electronics   H. Jacobowitz

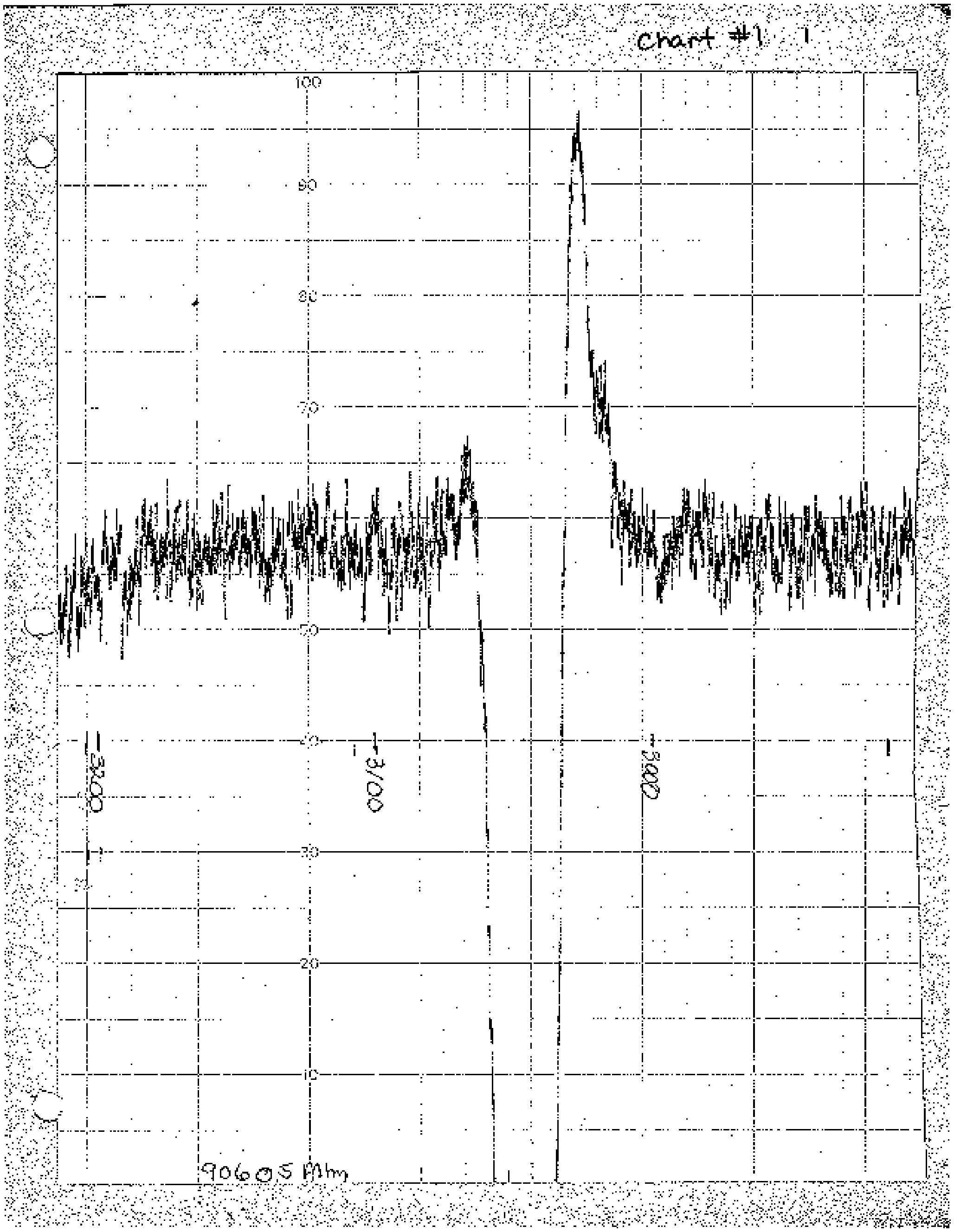


Chart #1
100
90
80
70
50
40
30
20
10
3200
3100
3000
90605 Mhm

chart #2 2

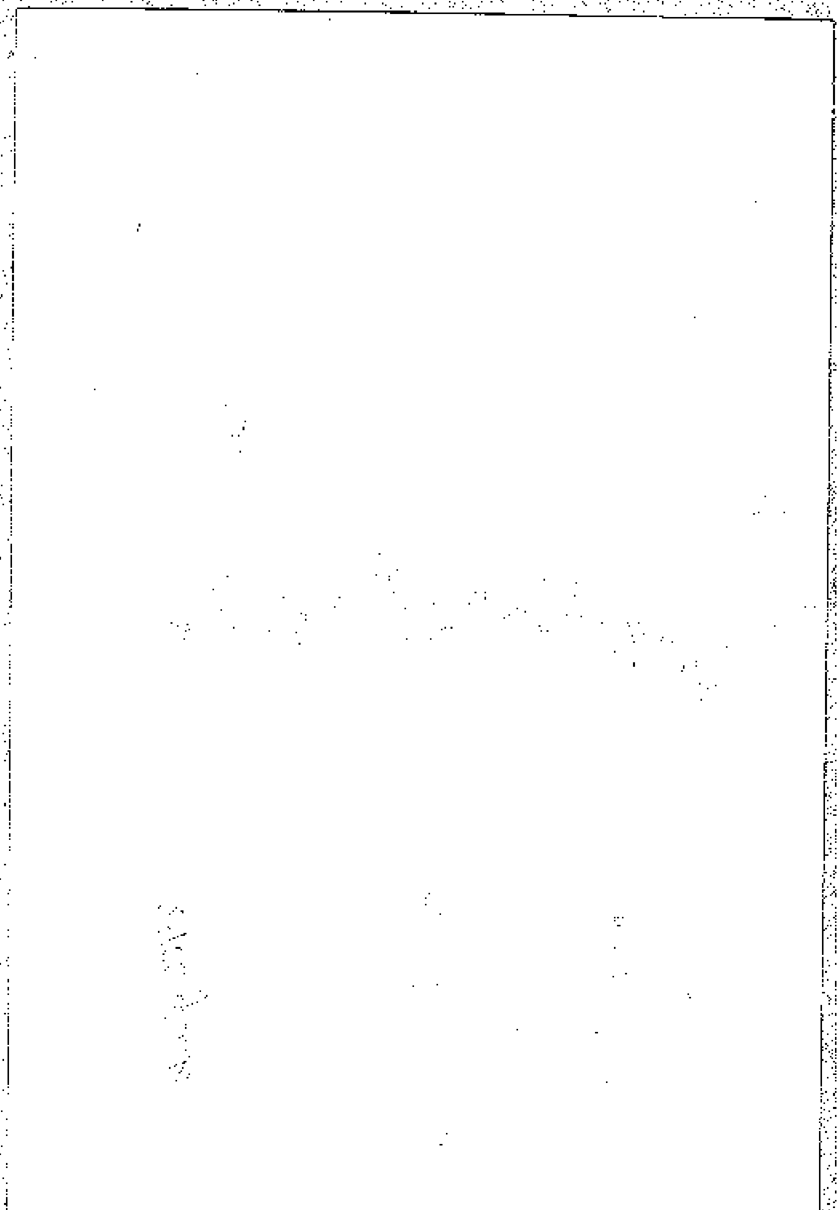


Chart # 3

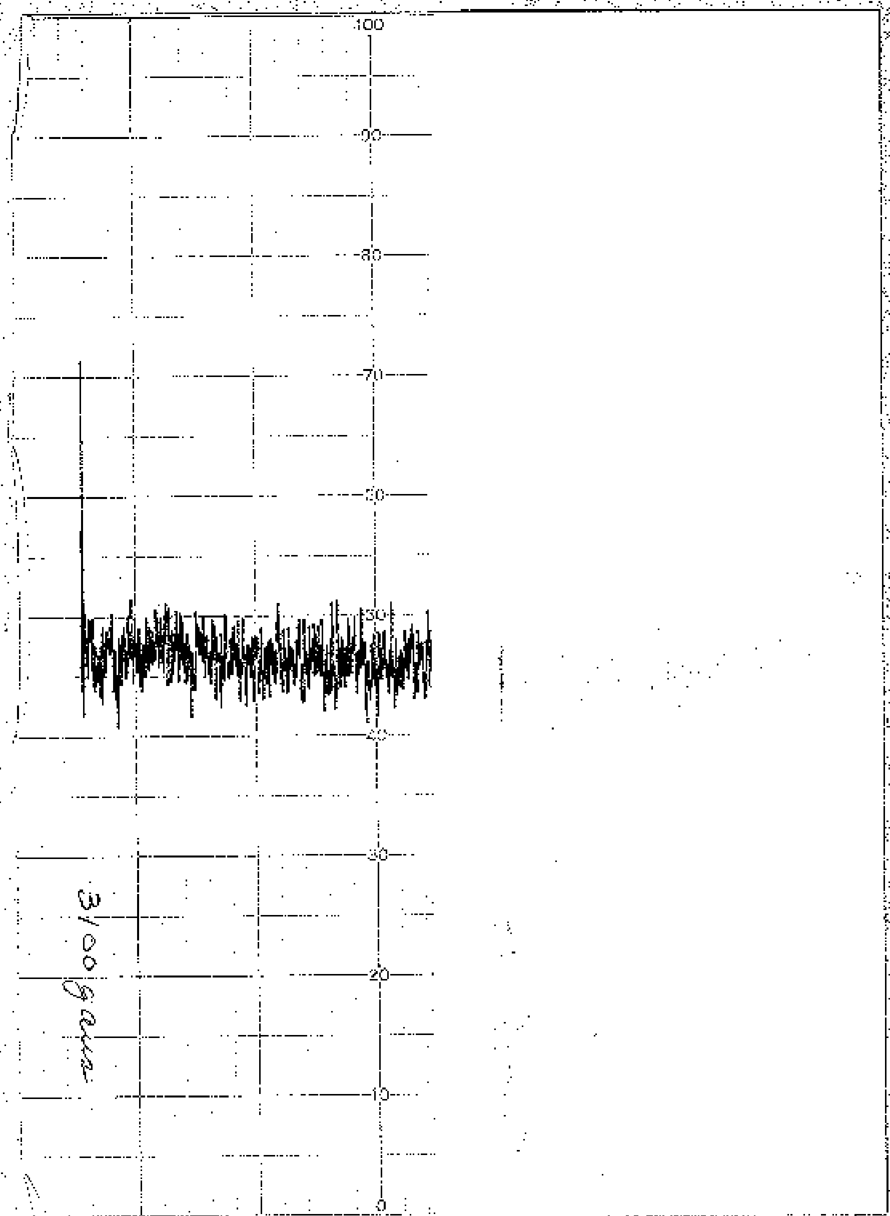


Chart # 4