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PARAMAGNETIC RESONANCE IN COPPER  
TETRAMMINE NITRATE

Thesis for the Degree of M. S.  
MICHIGAN STATE UNIVERSITY  
Edward Hill Carlson  
1955

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PARAMAGNETIC RESONANCE  
IN  
COPPER TETRAMINE NITRATE

by

Edward Hill Carlson

A Thesis

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

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Department of Physics

1955

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I wish to thank Dr. R. D. Spence for suggesting this problem and for his help and encouragement toward its completion. I also wish to thank Mr. Olen Kraus for translating papers from Russian, Mr. M. A. Breazeale for helping with the photography and my many friends in the department for their helpful suggestions.

*Edward H. Carlson*

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AN ABSTRACT

The construction of apparatus to detect paramagnetic resonance at 9332 Mc. and room temperature is described. The slope detection method used provides an output relatively low in noise and gives a large amount of information about any structure present in the absorption line.

Rather interesting structure was observed in signals obtained from some powdered copper ammine salts. The analysis of signals from single crystals of copper tetramine nitrate explained the origin of the structure in the signals from the powdered sample as due to a variation in the derivative amplitude and g factor with orientation of the single crystals in the magnetic field.

R. F. Jensen

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## INTRODUCTION

The method of electron spin resonance has become well established as a means of investigating the energy levels in paramagnetic salts.<sup>1</sup> This thesis discusses the assembly of apparatus for detecting paramagnetic resonance, and the preliminary results of an investigation of a salt, Copper Tetrammine Nitrate.

The method of paramagnetic resonance consists of splitting a degenerate ground level with a steady magnetic field and inducing transitions between the resulting levels with microwave radiation.<sup>2</sup> The condition for absorption is that the energy of the microwave photons  $h\nu$  is equal to the splitting of the ground energy level  $g\beta h$ , where  $\beta$  is the Bohr magneton,  $H$  is the magnetic field, and  $g$  is the spectroscopic splitting factor. For free electron spins,  $g$  is 2.00. The absorption of microwaves is plotted as a function of the magnetic field.

In the iron group transition elements, the ground level of the free ion is first split by the action of the local crystalline electric field.<sup>3</sup> The new energy levels have no orbital magnetic moment, since the electric field exerts a torque on the orbits, causing them to precess. Thus the orbital angular momentum is not constant, but is "quenched." The crystalline electric field cannot act similarly on the resultant electron spin since this is a quantum mechanical

property of the ion. Finally, a residual spin-orbit coupling takes place, introducing anisotropy in the g factor.

The width of the absorption line is due to two predominant effects. The lattice vibrations introduce a varying component to the crystalline electric field acting on the orbit, which then interacts with the spin through the spin-orbit coupling. This spin-lattice interaction decreases greatly at low temperatures. The line widths thus introduced at room temperature vary greatly from one substance to another. In some it broadens the line out so as to be undetectable. In others it is negligible compared to the other broadening effect, the spin-spin interaction.

The spin-spin interaction is really two effects, the dipole-dipole interaction, in which the magnetic fields of neighboring paramagnetic ions interact, broadening the line, and the exchange interaction which sometimes broadens and sometimes narrows the line. Neither of these effects is temperature dependent, and both may be decreased by diluting the magnetic ion content of the salt.

## APPARATUS

Figure 1 is a block diagram of the apparatus. A 723 A/B klystron is connected to a transmission cavity through an isolating flap attenuator. The cavity is constructed by inserting diaphragms  $3/2$  wavelengths apart in the rectangular wave guide. It resonates at 9332 Mc, in the  $TE_{10}$  mode. The sample is placed on the end of a conical brass plug flush with the wall on the narrow side of the wave guide. Here the microwave magnetic field is maximum and the electric field is near zero. The cavity is placed between the poles of an electromagnet such that the microwave magnetic field  $H_{rf}$  is perpendicular to the steady magnetic field  $H_0$ , Figure 2. The microwaves are coupled out of the bottom iris of the cavity and are detected by the 1N23B crystal. The crystal impedance is matched to the wave guide by the E-H tuner. The power supply amplitude modulates the klystron with square waves of about 1000 cycles. Thus the detected output of the crystal is an audio square wave of amplitude proportional to the power in the cavity. This output may be monitored on the oscilloscope.

When the steady magnetic field is varied so as to produce resonance absorption by the sample, the microwave power in the cavity drops. This can be detected directly on the SWR meter. However, this proved to be a rather insensitive method of detection and was limited by a high noise content.

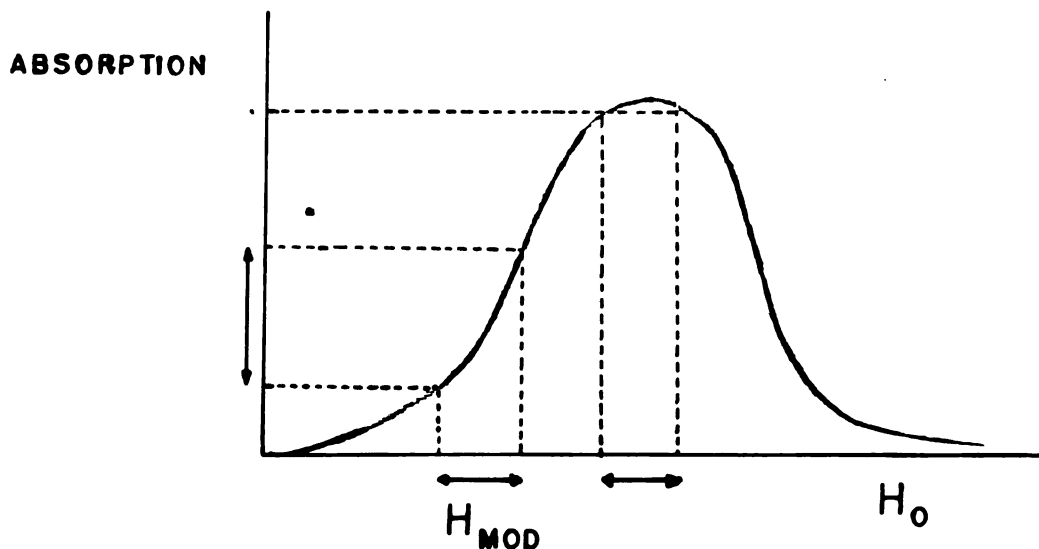


Figure 5

The principle of derivative detection which was used to improve the sensitivity is shown in Figure 5. A varying component  $H_{mod}$  is added to the steady magnetic field. It is seen that the output will now contain a component varying at the same frequency as  $H_{mod}$  and of an amplitude proportional to the slope of the absorption curve. This signal is amplified by the narrow band amplifier and is detected by the lock-in detector which is sensitive only to signals of the same frequency and phase as a reference signal.

Figure 6 is the schematic of the narrow band amplifier. The triode stages are tuned by United Transformer Company variable inductors. The total  $Q$  of these stages is about 9, however the top of the resonance curve is flattened.

Figure 7 is the schematic of the lock-in detector, which uses a Saunders Associates phase comparator. A phase

shifter is built in for adjusting the phase of the reference voltage equal to that of the signal.

The principle of the lock-in detector is to rectify the signal if and only if it has the same phase and frequency as the reference voltage. If the frequency of the signal is a few cycles different from the reference voltage, the output will vary at a few cycles per second. The detectors sensitivity to phase difference varies as the cosine of the phase angle between the reference voltage and the signal. Since any noise in the signal comes from the detector as a varying output, it may be removed if the output is filtered. This is the purpose of the capacitors that may be selected by the switch. Several time constants from .01 to 1 seconds can be used. Thus the lock-in detector gives a low noise output only by requiring that a relatively long time be spent in the measurement, i.e. until the capacitor has charged up to the new d.c. signal output level. The last stage of the detector is a d.c. cathode follower. Figure 4 is a photograph of the lock-in detector.

A 96 cycle generator was used to supply voltage to modulation coils on the magnet, and to supply the reference voltage to the detector. A 60 cycle modulation frequency was first attempted but stray pick-up proved bothersome.

The output is displayed on a Moseley Autograph X-Y recorder. The drum is driven by the voltage drop across a .01 ohm standard resistor which carries all the current for

the steady field  $H_0$ . The drum input is biased by a steady voltage so that the  $H_0$  scale could be expanded. The magnet was calibrated using a Sensitive Research Instrument Corp. model FM flux meter. The pen is driven by the signal from the lock-in detector. Figure 2 is a photograph of the apparatus.

The operation of the equipment is as follows:

- 1) Turn on the power to the electronic components.
- 2) Move the pick-up cable from the crystal to the probe on the slotted section and adjust the K-H tuner until the SWR amplifier indicates the line is flat. This needs to be done only infrequently, or after reassembling the wave guide components.
- 3) Turn on the cooling water and power to the magnet and modulating coils.
- 4) Turn on the bias to the recorder drum (if the recorder is to be used on the expanded scale).
- 5) Adjust the phase shifter to give the maximum signal. This will usually be near its extremes of travel.
- 6) Adjust the gain of the narrow band amplifier.
- 7) Measure the frequency of resonance on the wavemeter.
- 8) During the run, keep the klystron in resonance, using the fine adjustment, by watching the oscilloscope. A 60 cycle frequency modulation of the klystron is present. When it drifts off the peak of the cavity resonance, the frequency modulation is converted to an amplitude modulation which is very troublesome. A pound frequency stabilizer or a better filtered power supply would probably help this.

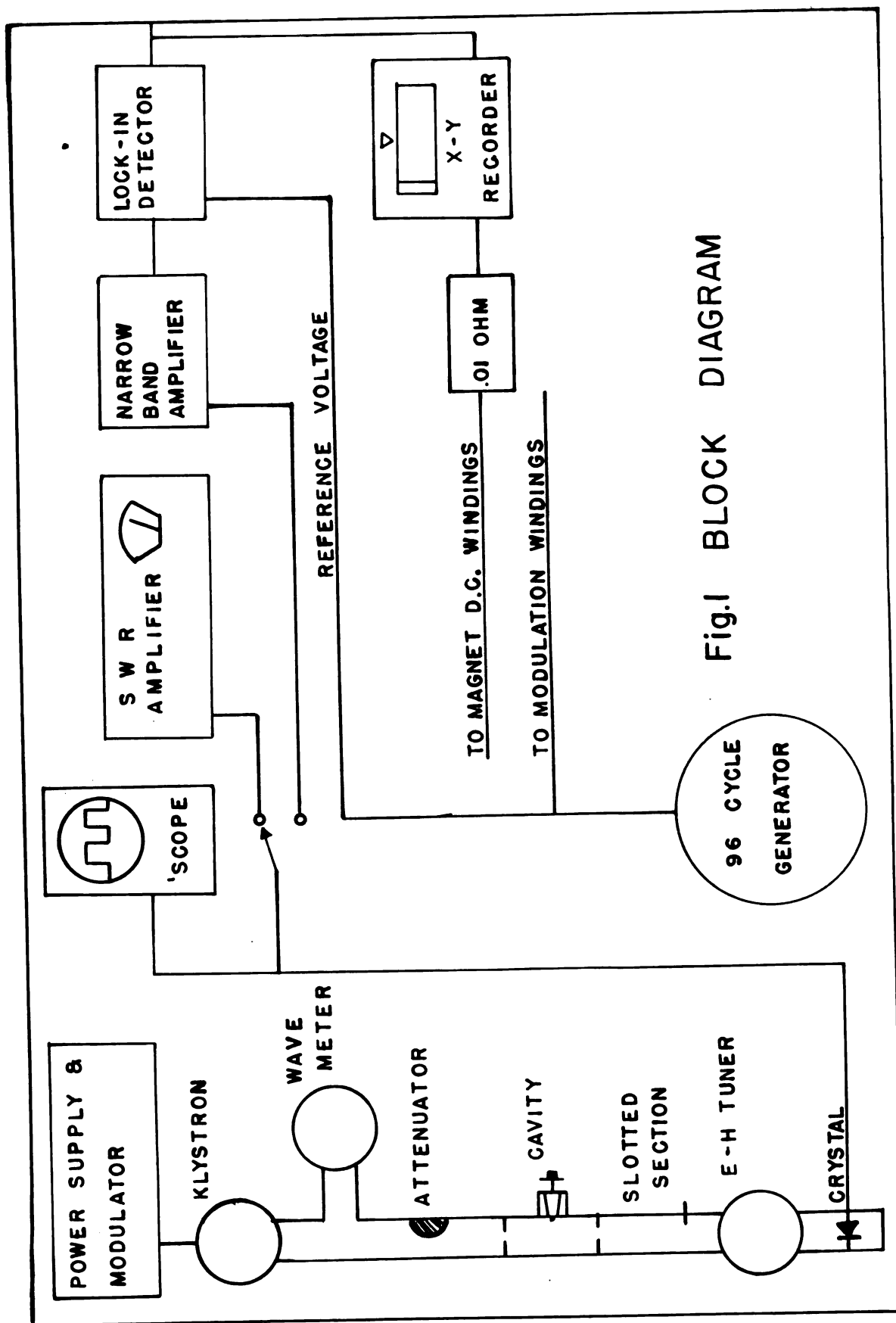


Fig.1 BLOCK DIAGRAM

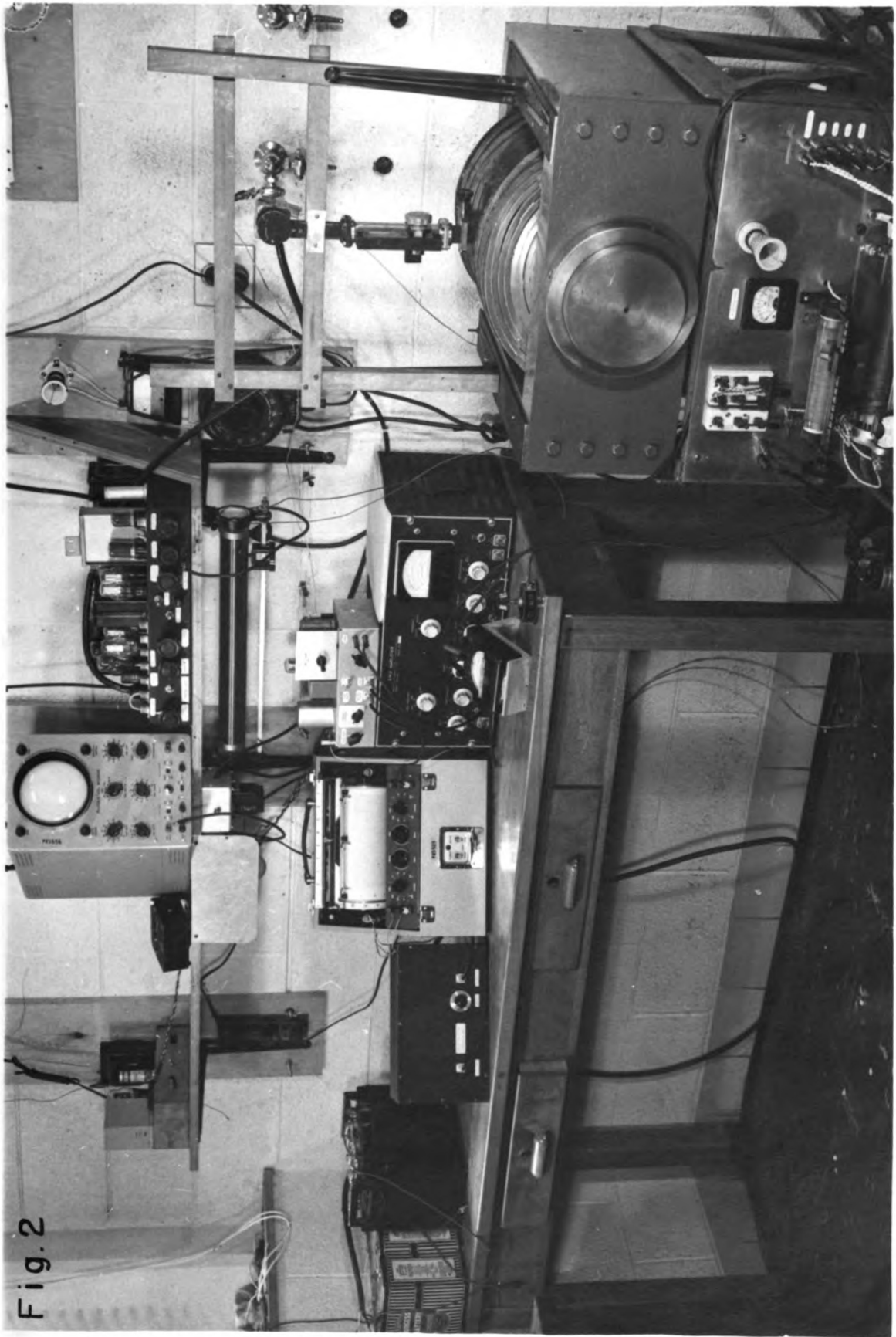


Fig. 2

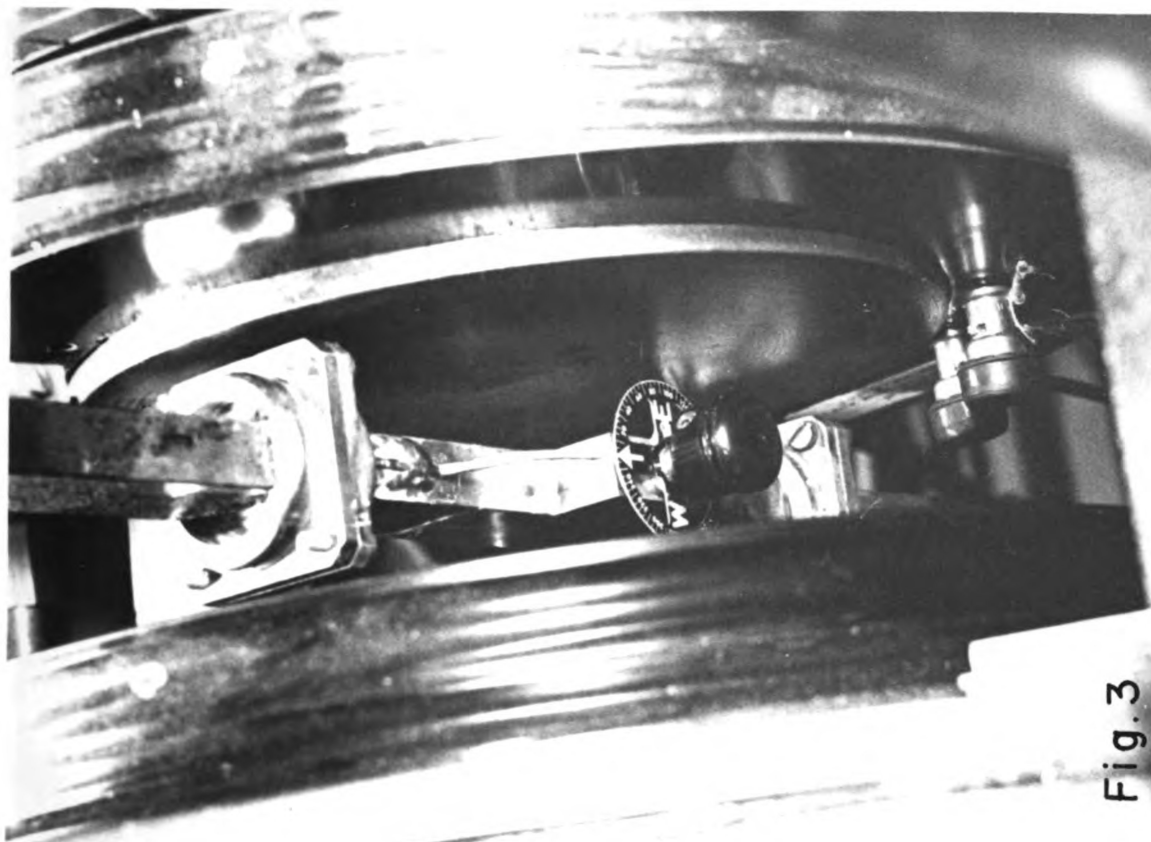


Fig.3



Fig.4

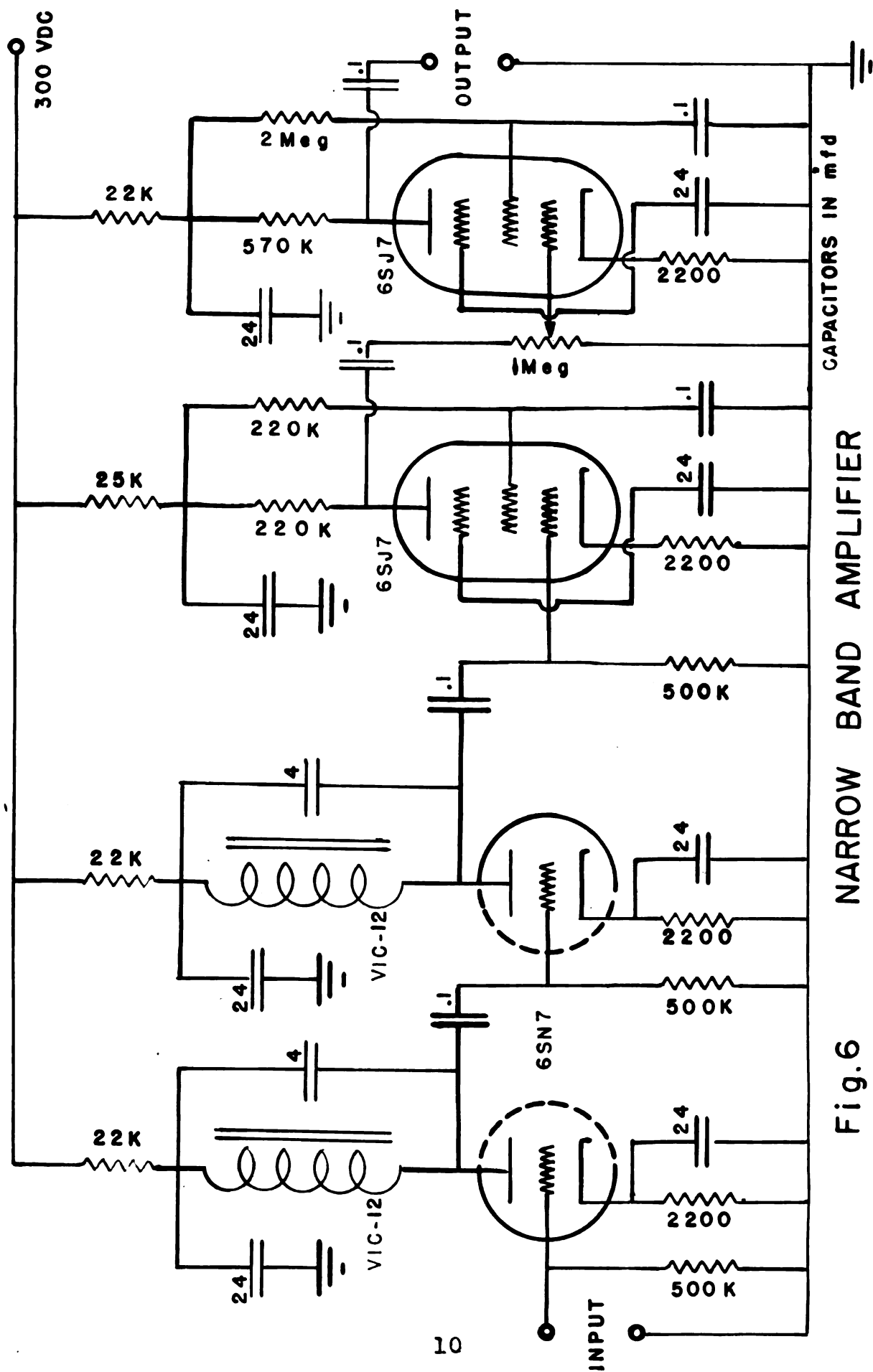


Fig. 6



## RESULTS

After the completion of the apparatus, many substances were examined for paramagnetic resonance, and gave quite normal results. However a powdered sample of Copper Tetrammine Sulphate Monohydrate gave the unexpected pattern shown in Figure 8. It was then discovered that Copper Tetrammine Nitrate gives a similar pattern, Figure 9, and since the latter compound was more easily grown in large crystals, we decided to work with it.

At first we thought that the peaks in the powdered sample signals were due to an impure sample, i.e. the existence of  $\text{Cu}^{++}$  ions with various numbers of waters of hydration replaced with ammonia molecules as coordinating groups. However the same crystals of Copper Tetrammine Nitrate which gave quite narrow single lines, Figure 10, gave the characteristic powder pattern when ground up. It was also noticed that the amplitude of the derivative signal from a single crystal is highly dependent on orientation in the  $H_0$  field, and an attempt to explain the powder patterns on this basis was undertaken.

Copper Tetrammine Nitrate crystallizes in the orthorhombic system, Figure 12. Axes were identified by measurement of the interface angles on a goniometer and the resulting axial ratios were compared with those given in Mellior.<sup>4</sup>



The amplitude of the derivative signal was plotted as a function of angle in the planes perpendicular to the a, b, and c axes, Figures 13, 14, and 15. The ordinate is in arbitrary units different for each figure. This amplitude change is due partly to a line width change. Assuming a Gaussian shape, the line width is the distance between maximum slopes, or peaks in the derivative curve. This is plotted in Figures 16, 17 and 18. The amplitude has three directions in which it is a maximum, and possesses a minimum in the ab plane. This is shown schematically in Figure 19, in which the distance from the origin to the surface of the solid represents the amplitude.

The variation of  $g$  in the planes perpendicular to the a, b, and c axes is plotted in Figures 20, 21, and 22.

The values of  $g$  along the axes are:

$$a \quad 2.08 \pm .02$$

$$b \quad 2.15 \pm .02$$

$$c \quad 2.02 \pm .02$$

which agree well with those published by Okamura and Date.<sup>5</sup>

Figure 11 was made by drawing lines at the positions corresponding to the  $g$  values along the a, b, and c axes, where the line length is proportional to the derivative amplitude in the given direction. Note how well this explains the positions of the two positive peaks, the minimum and the negative peak (but does not explain their relative heights quite so well). Since this does not explain the little jog in the negative peak, it was believed that



possibly there was an amplitude peak in some other direction. A rotation made in the (110) plane failed however to show this, Figures 23 and 24.

Finally an attempt to derive this jog was made by integration. The variation of  $g$  with orientation was fitted with the function  $g(\theta, \phi) = 2.02 + \sin^2 \theta (.05 + .07 \cos^2 \phi)$  and this was plotted as a lattice on a large graph paper with each area increment on the graph  $d(\cos \theta) d\phi$  equal to an area increment  $\sin \theta d\theta d\phi$  on the surface of the sphere. Lines of constant  $g$  were then drawn in, Figure 25 (solid lines).

The derivative amplitude variation was fitted with  $A(\theta, \phi) = 1 + \sin^2 \theta (-.994 + .444 \bar{A}(\phi))$ .  $\bar{A}(\phi)$  is defined by Figure 26, derived from the data, since an attempt to fit it with  $\sin^2 \phi$  and  $\cos^2 \phi$  failed. This function was similarly plotted, Figure 25 (dashed lines).

The paper was divided into strips along constant  $g$  lines and each strip was divided into small areas by amplitude lines. Integration was performed with a planimeter. The results, expressed as an amplitude vs.  $H_0$  field is shown in Figure 27. The agreement with experiment is poor. However all the gross features are present, including the jog, however distorted in magnitude. The method of integration was crude, and the method of obtaining Figure 27 from the integrated results was quite sensitive to errors in the integration, since it depends on the slope of the integrated amplitude vs.  $g$ .

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Even if the jog in the negative slope of Figure 27 is spurious, the process of integration convinced me that the powder pattern is quite sensitive to the variation in  $g$  and amplitude and that such a jog could be produced without additional directions of maximum amplitude being present. This is borne out by noting that the position, shape and size of the jog is the structure of the powder pattern most sensitive to residual anisotropies in the powdered sample due to incomplete grinding and mixing. This residual anisotropy can be detected by noting changes in the pattern as the sample is rotated by  $45^\circ$  and  $90^\circ$ .

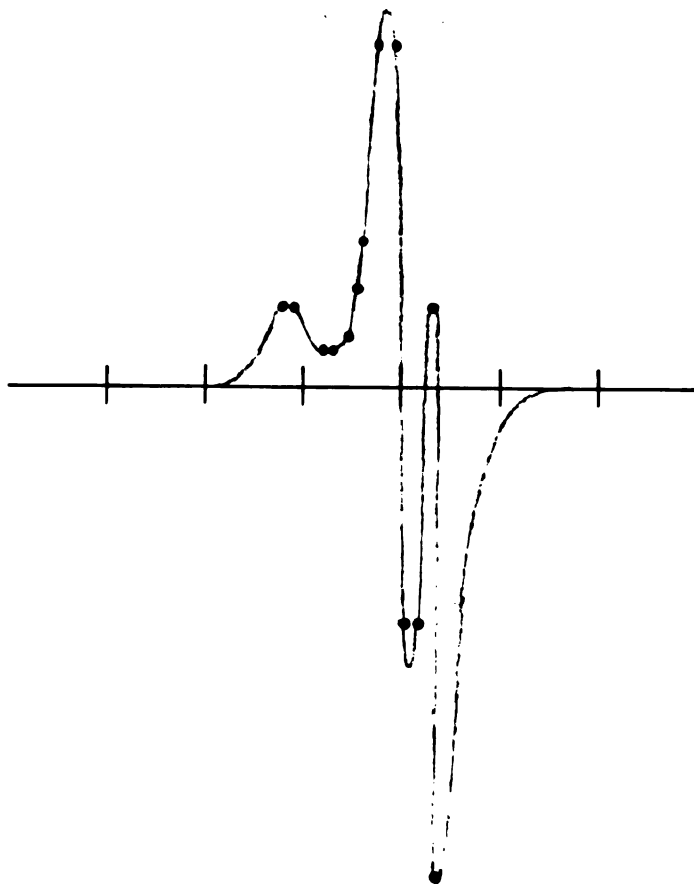
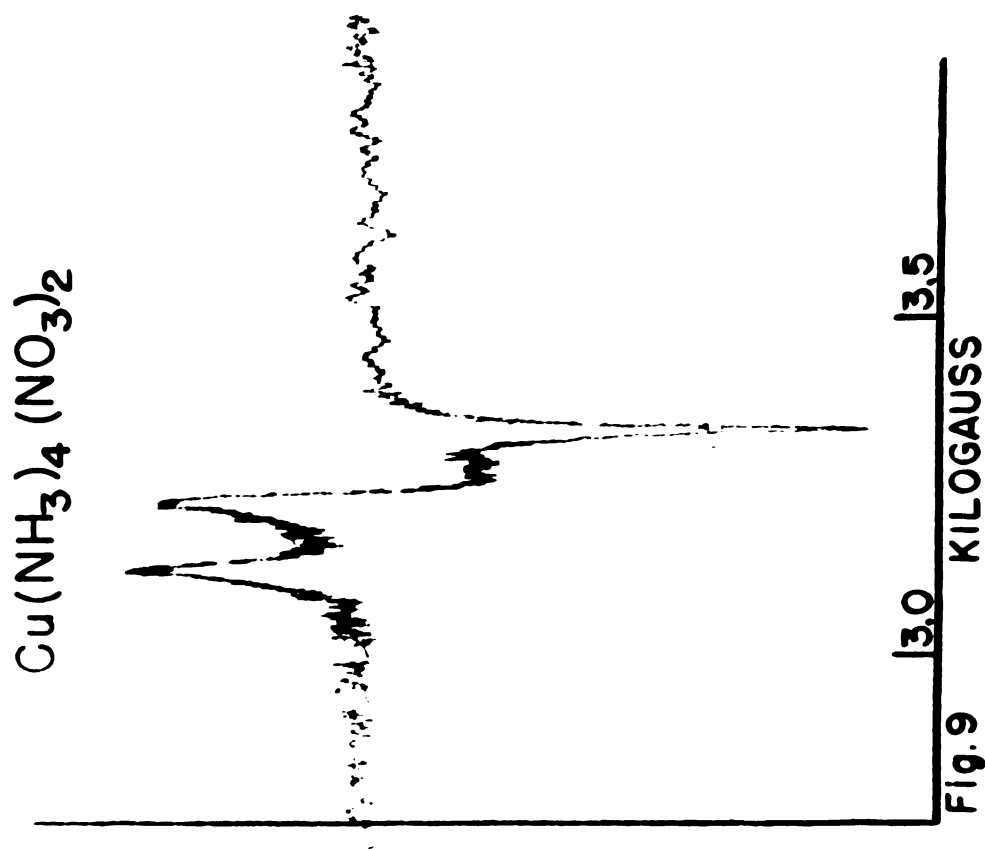
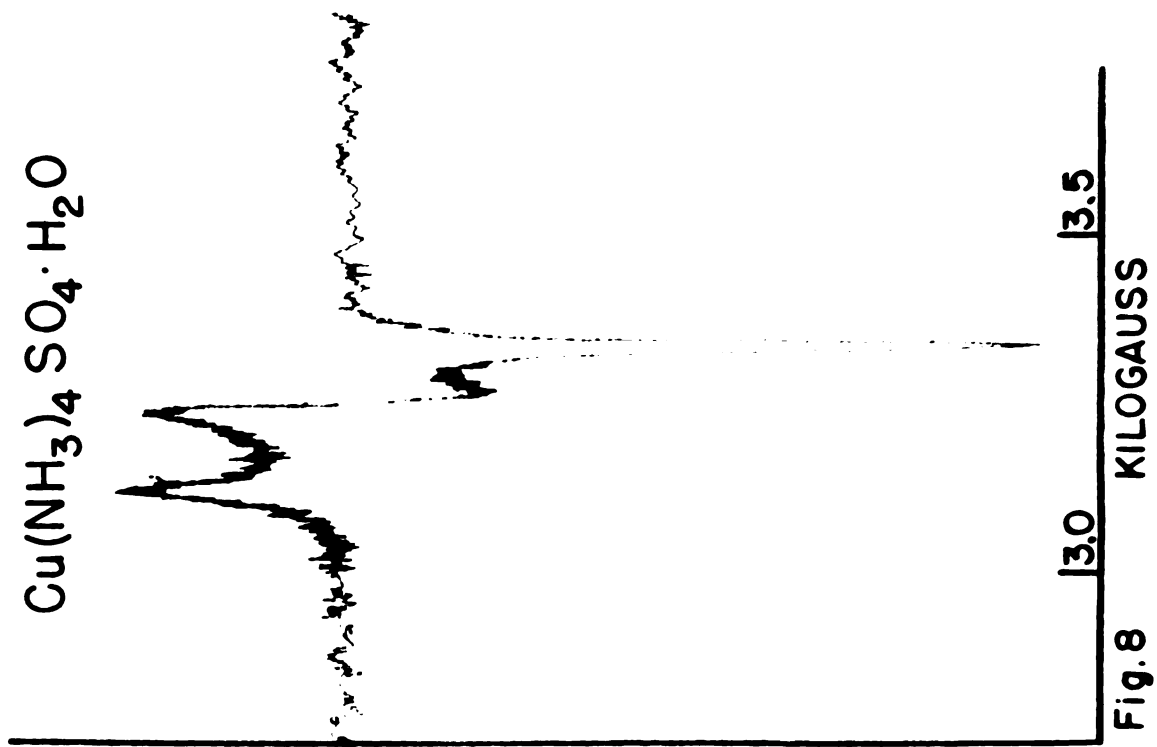
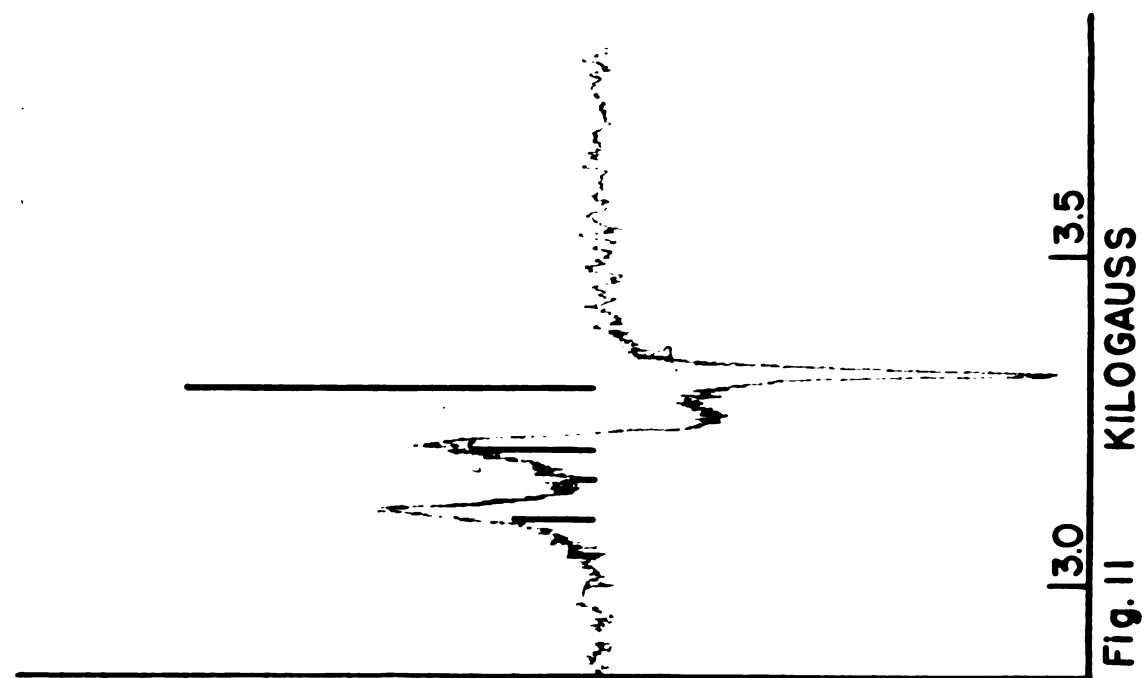
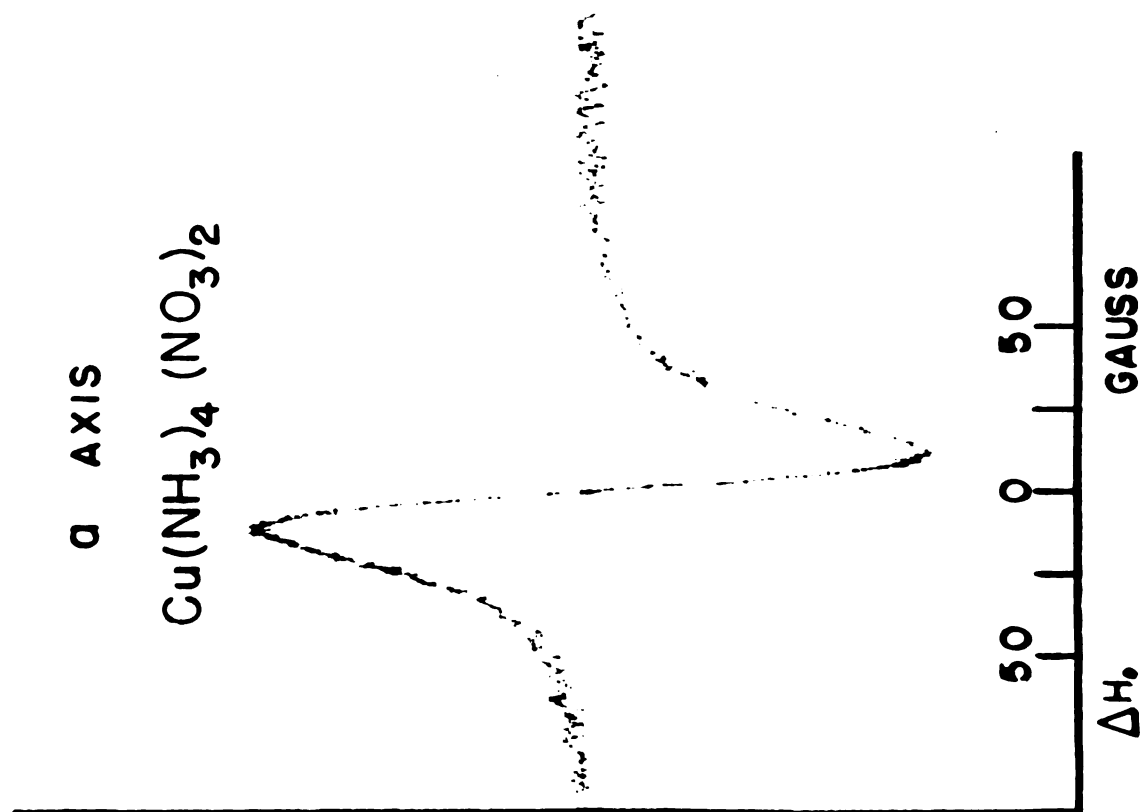


Figure 27





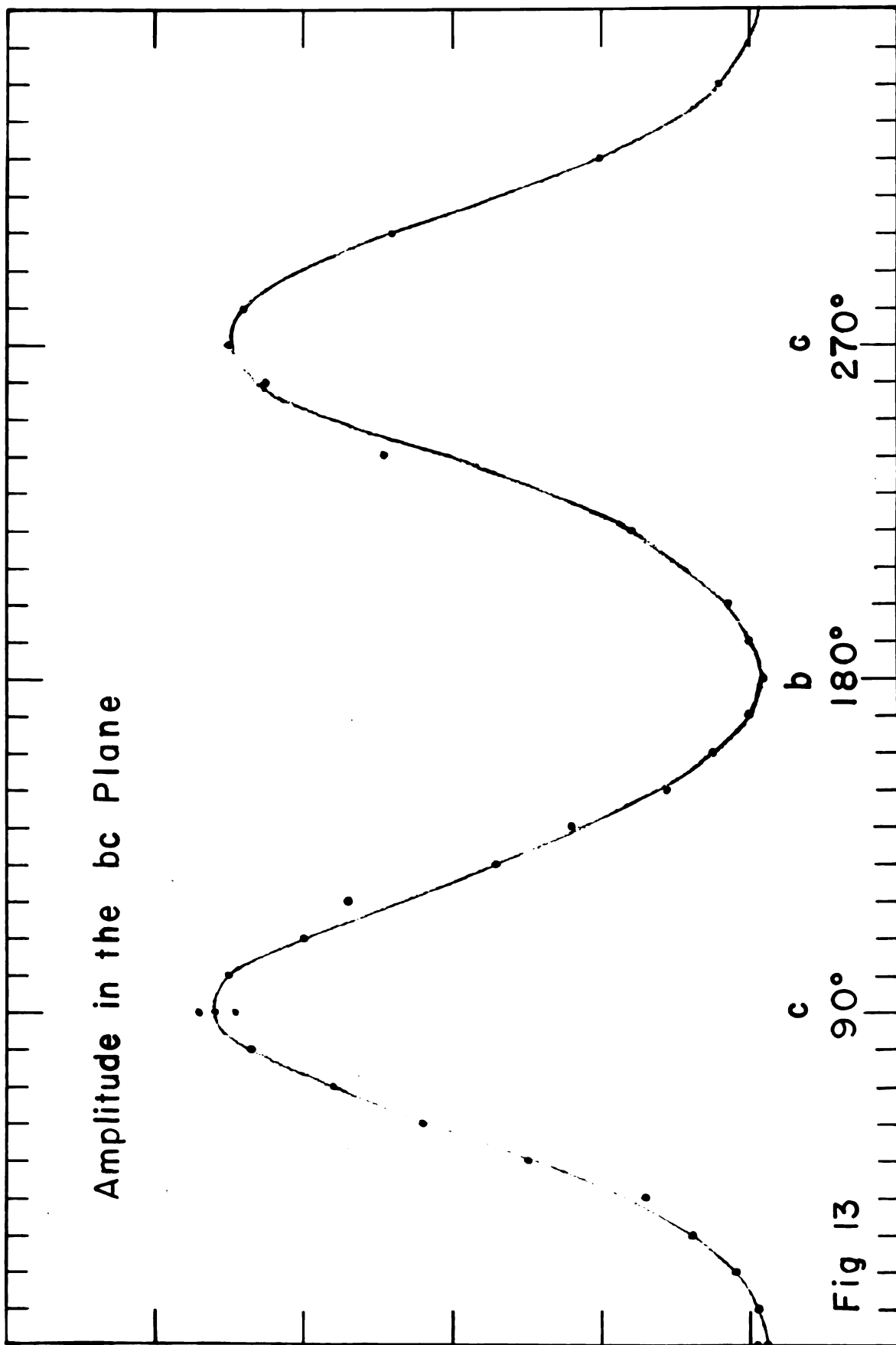


Fig 13

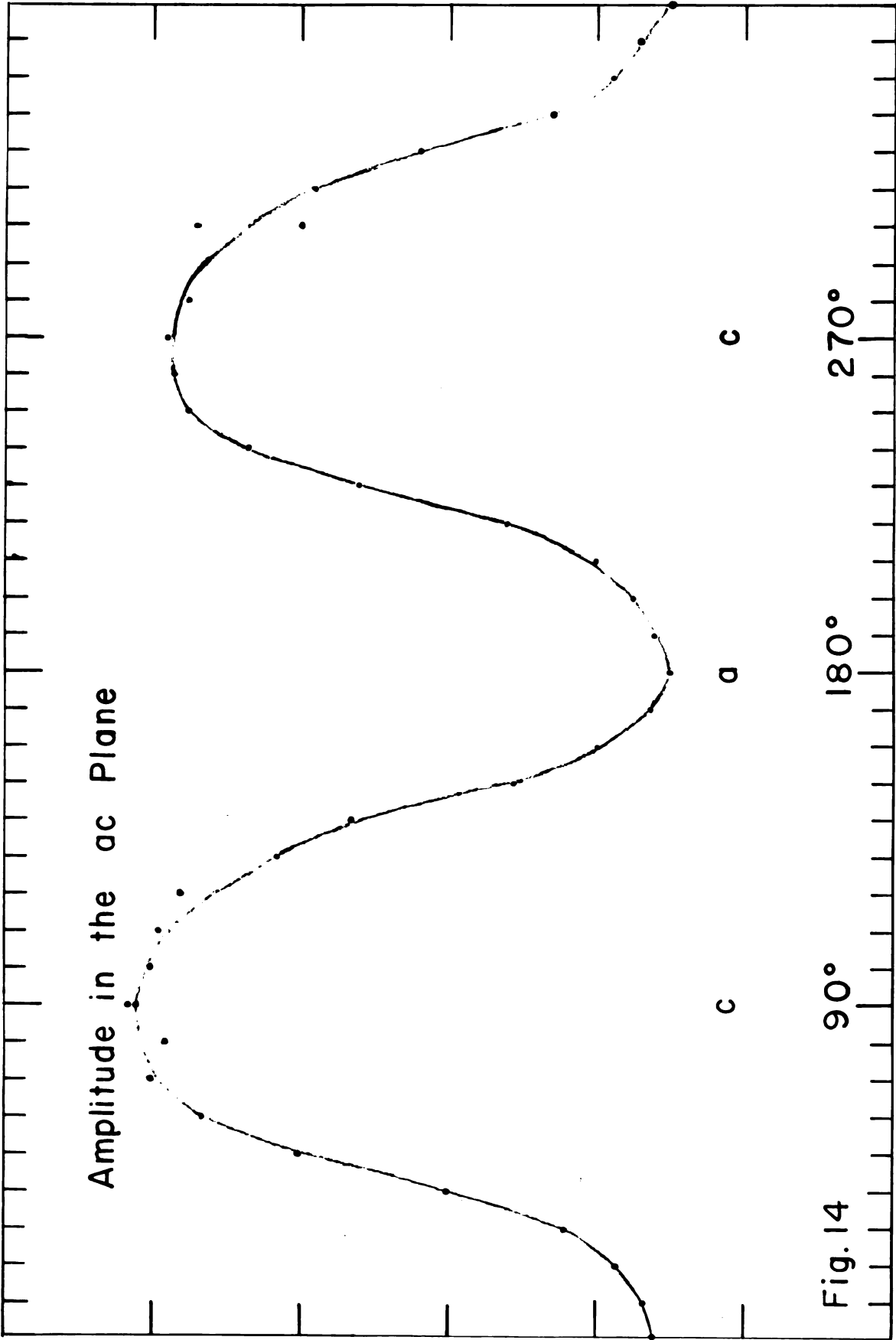


Fig. 14

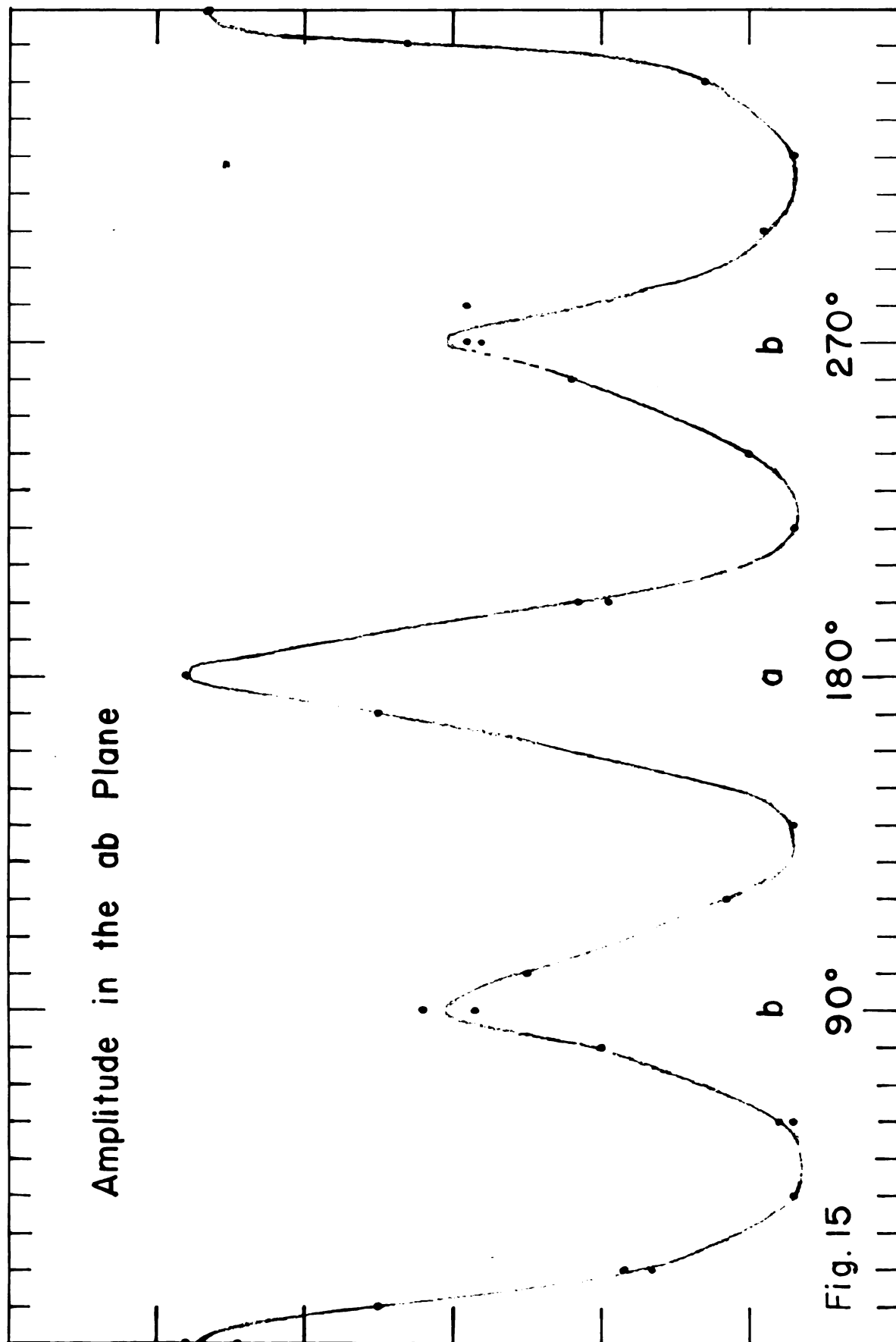
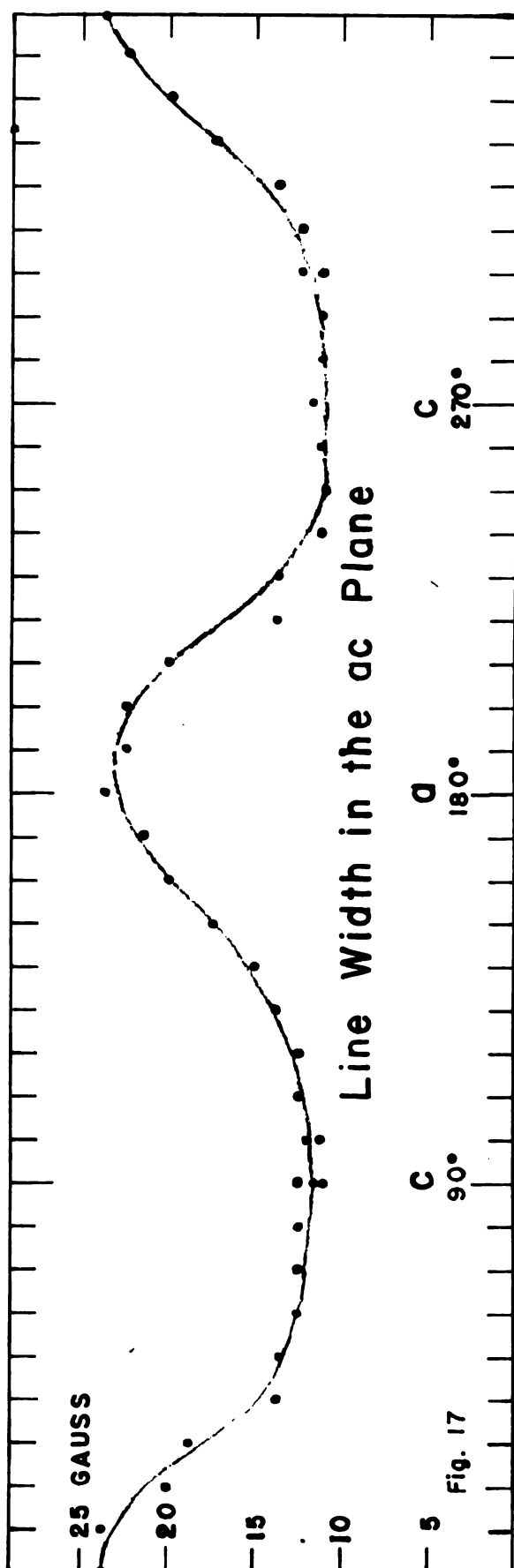
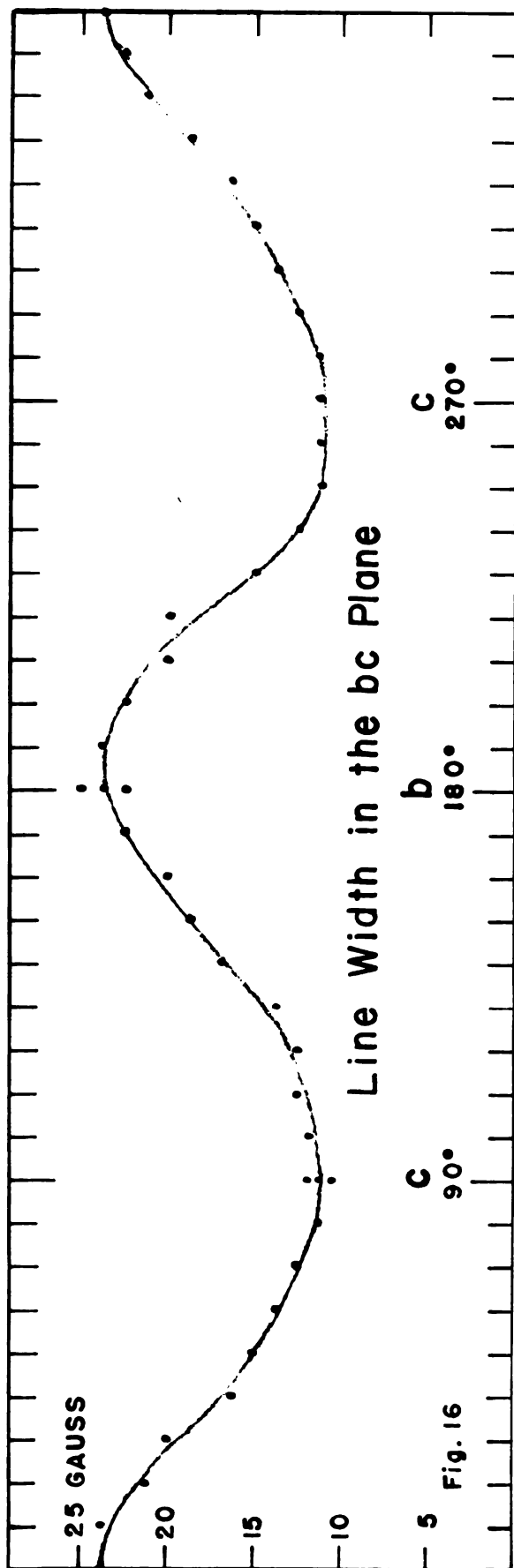


Fig. 15



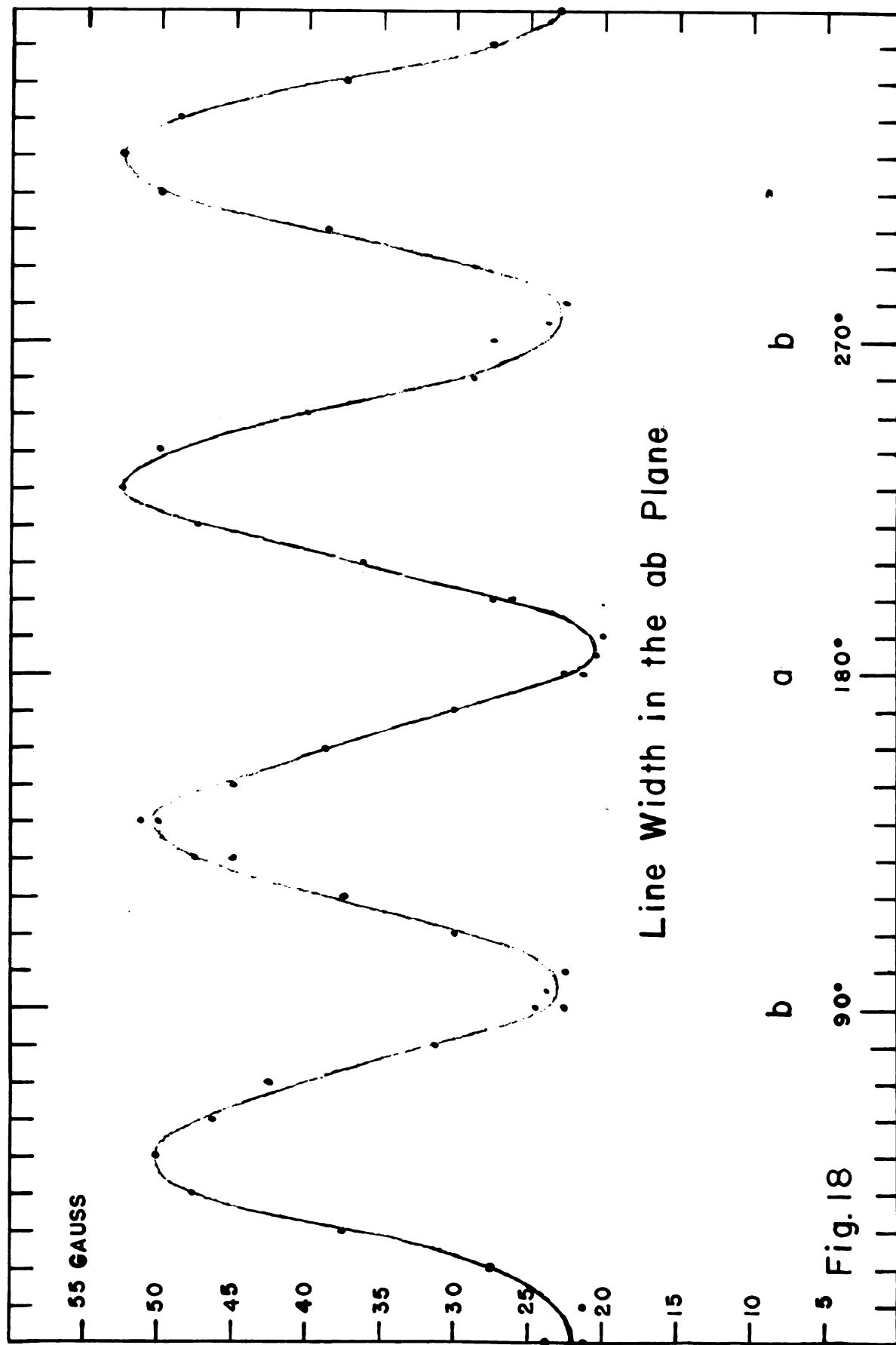


Fig. 18

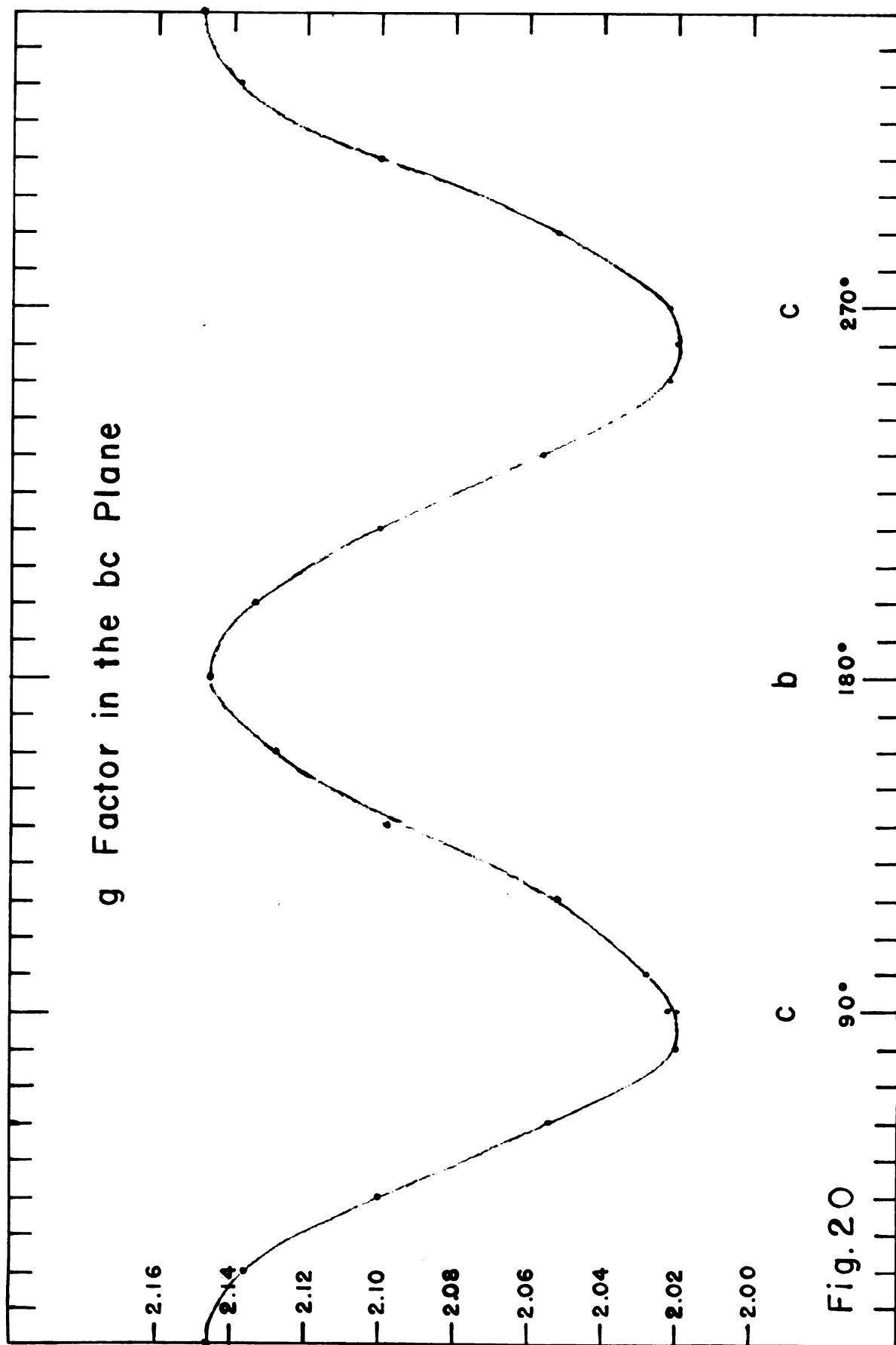
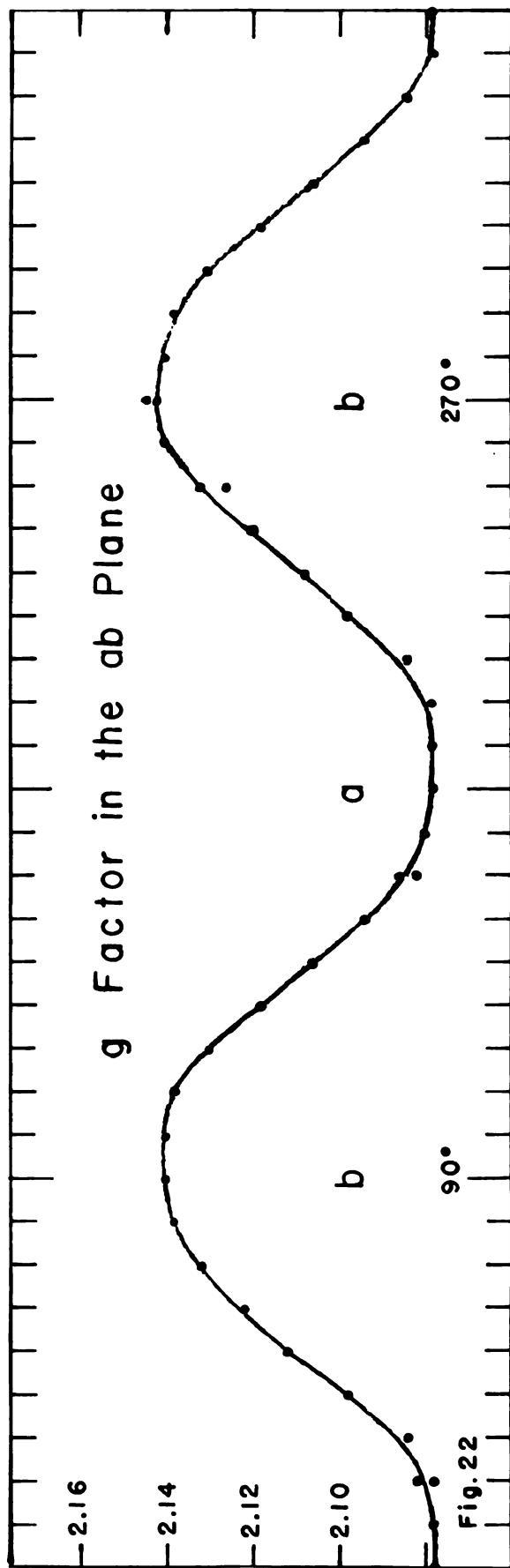
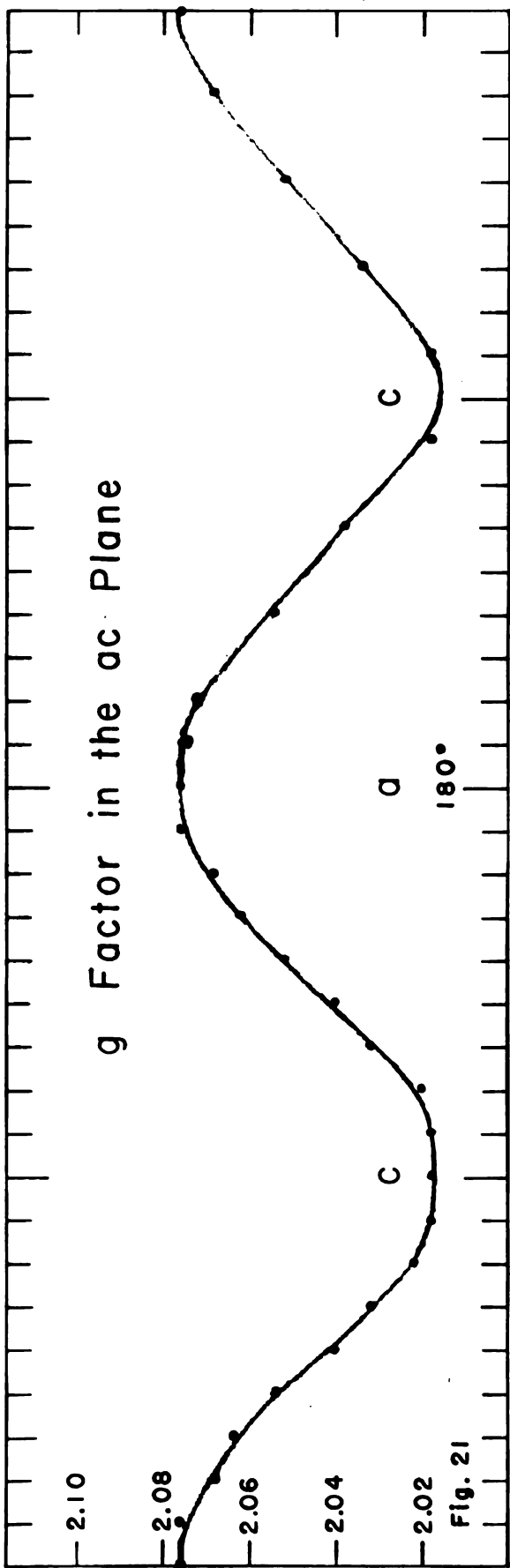
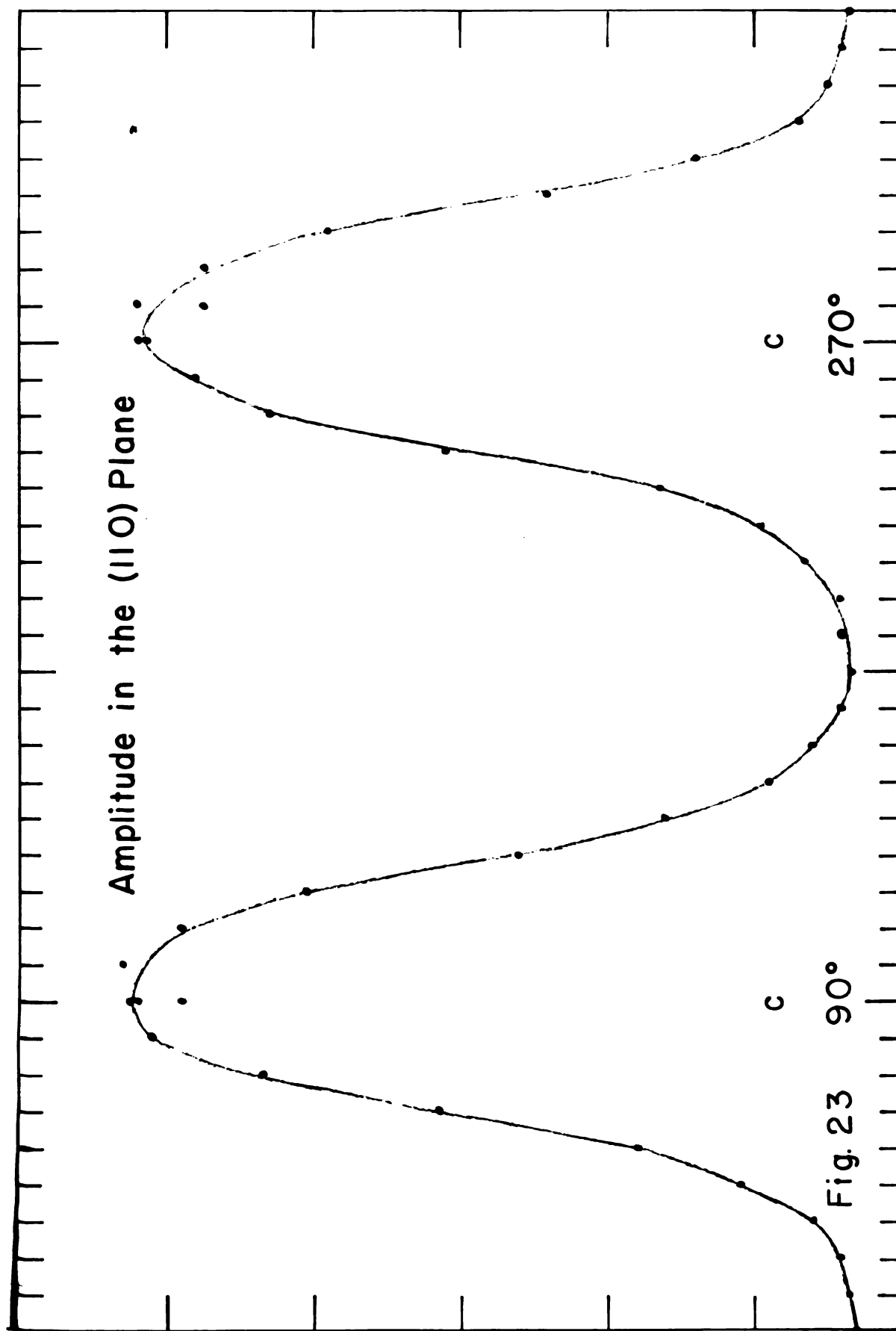


Fig. 20





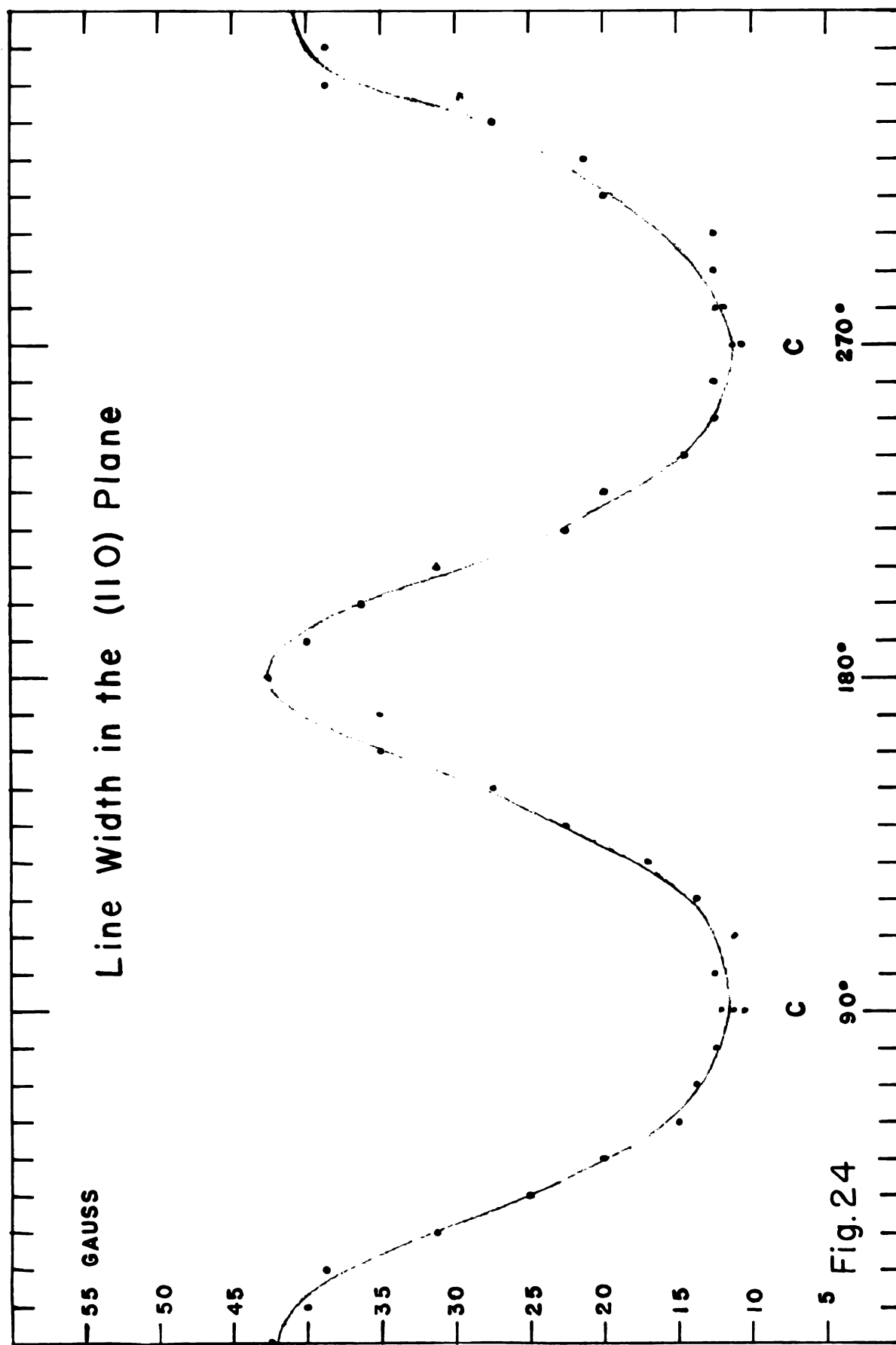


Fig. 24

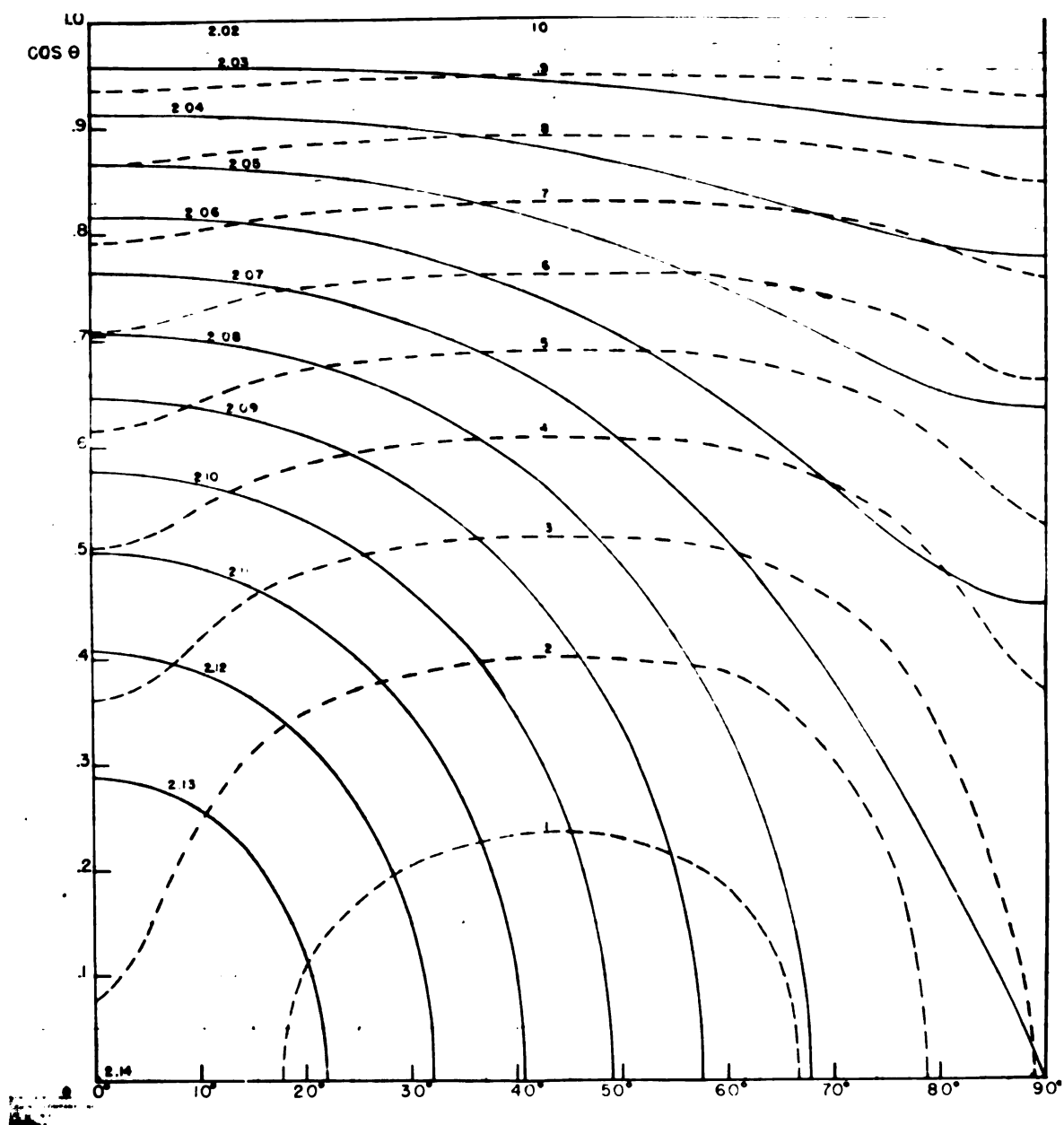


Fig. 25

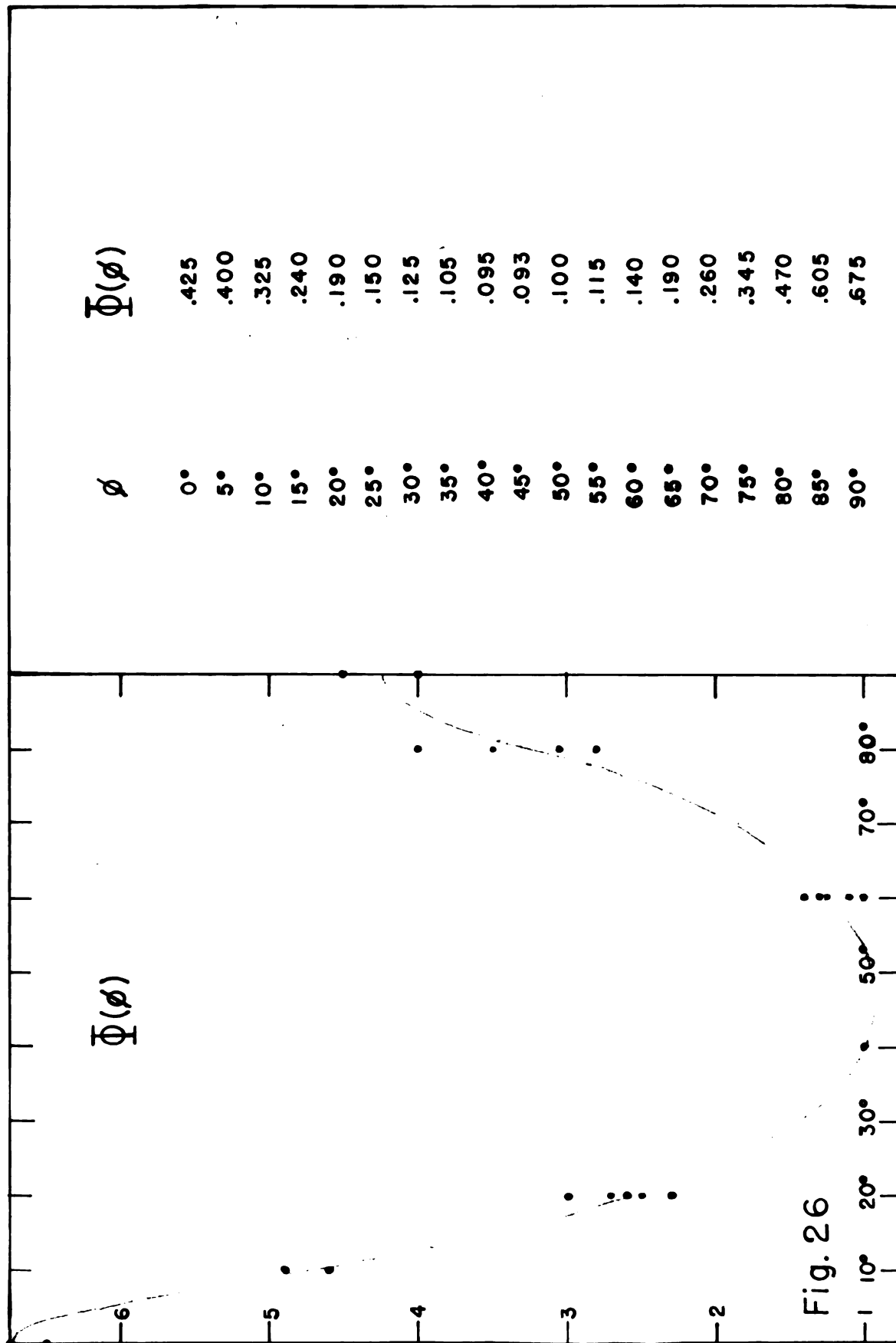


Fig. 26

## CONCLUSIONS

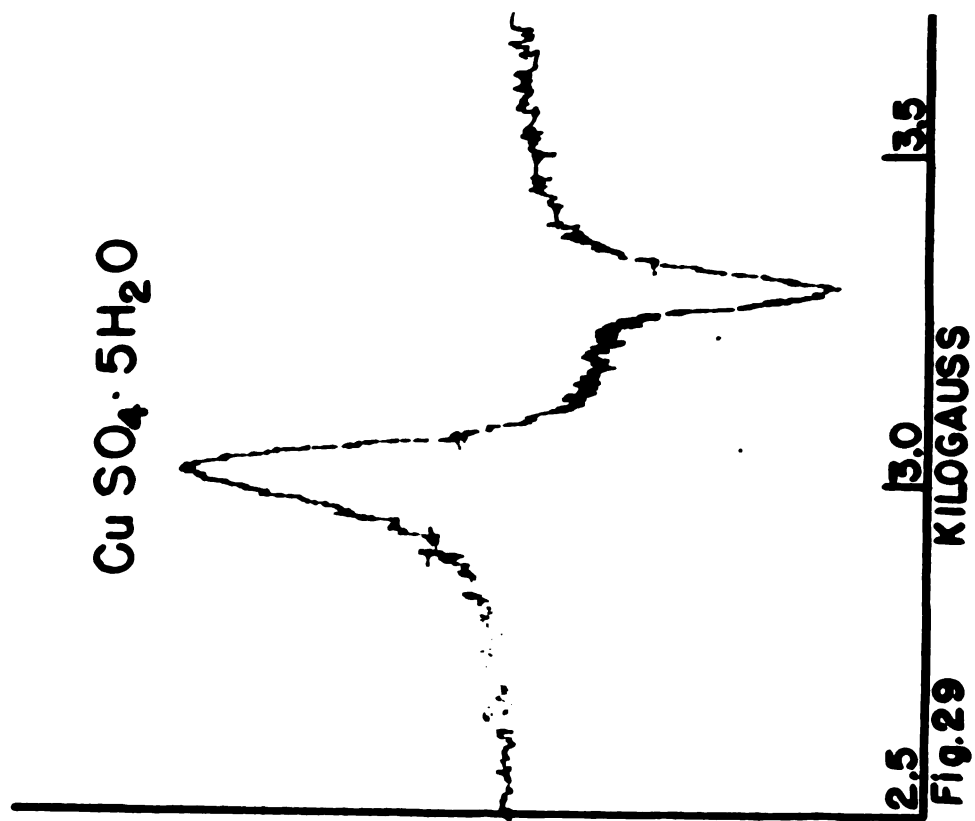
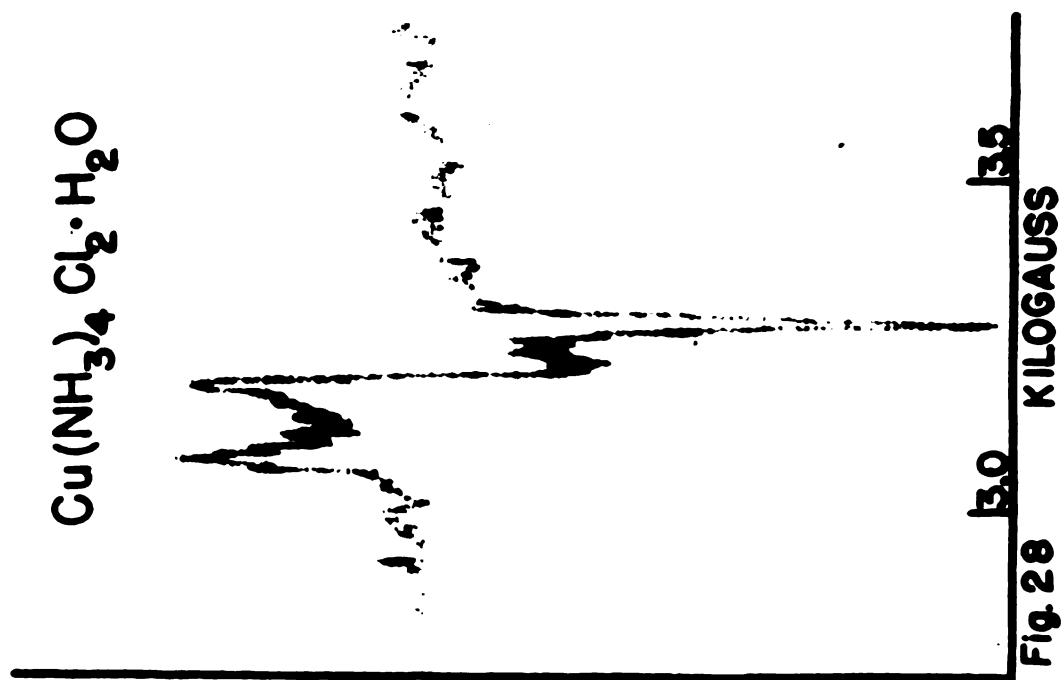
The above discussion of the signal produced by powdered Copper Tetrammine Nitrate is incidental to the real interest in the paramagnetic resonance in that compound. Unfortunately, the internal structure of the crystal has not been obtained from X-ray data. It is thus impossible to compare the experimental results with those calculated from theory. However, a few remarks can be made.

Note the similarity between the powdered patterns for Copper Tetrammine Sulphate Monohydrate, Copper Tetrammine Nitrate and Copper Tetrammine Chloride Monohydrate, Figures 8, 9, and 28, and their difference from the patterns for Copper Sulphate Pentahydrate, Copper Diammine Carbonate and Copper Hydrazine Sulphate, Figures 29, 30, and 31. This indicates, as one would expect, that the resonance depends almost entirely on the nature of the nearest neighbors, the coordinating groups. In the ammine coordinated ions we have a different effect from the water coordinated ions in that in the latter the waters are held to the ion by electrostatic effects while in the former it is believed that covalent bonds are present.<sup>6</sup>

The small line width has significance. Kozyrev and Salikhov worked with powdered Copper Tetrammine Sulphate Monohydrate at 207 and 68.8 Mc. and reported a line width of 40 gauss.<sup>7</sup> This was not done with a cavity resonance method.

Using a cavity at  $9.62 \times 10^3$  Mc., Kozyrev, Salikhov and Shamonin report a line width of 60 gauss and a g value of 2.11 for the same material.<sup>8</sup> (It is interesting to note that they observed an asymmetry in the absorption curve of powdered Copper Sulphate Pentahydrate, which would give a derivative similar to Figure 29.) I regret that I have been unable as yet to procure the paper by Ramaseshan and Suryan on Copper Tetrammine Nitrate.<sup>9</sup> The rather complete analysis of the above compound by Okamura and Date gives half widths of slightly larger than 30-50 gauss by direct absorption while my derivative data gives 12-50 gauss.<sup>10</sup> Since Okamura and Date estimated the contribution to the line width from dipole-dipole interaction would be about 400 gauss, their conclusion that strong exchange interactions are present to narrow the line is probably well founded. Thus the gaussian line shape approximation would be rather poor. The absorption curves given by Okamura and Date for the powdered Copper Tetrammine Sulphate and Nitrate show no sign of an asymmetry that would give derivatives similar to those that I observed.

It is hoped that crystal structure data will soon become available since a valuable insight into the nature of the ion-ammonia covalent bond may be obtained using the paramagnetic resonance in Copper Tetrammine Nitrate.



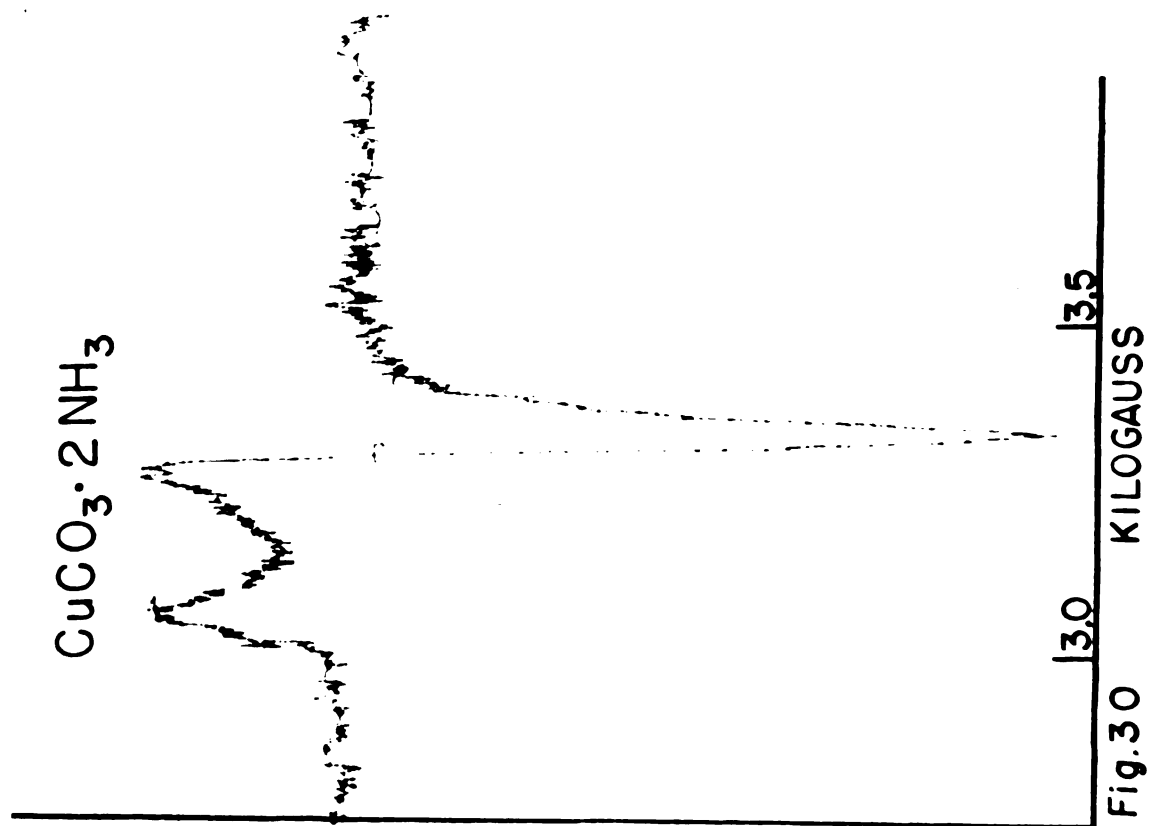


Fig.30

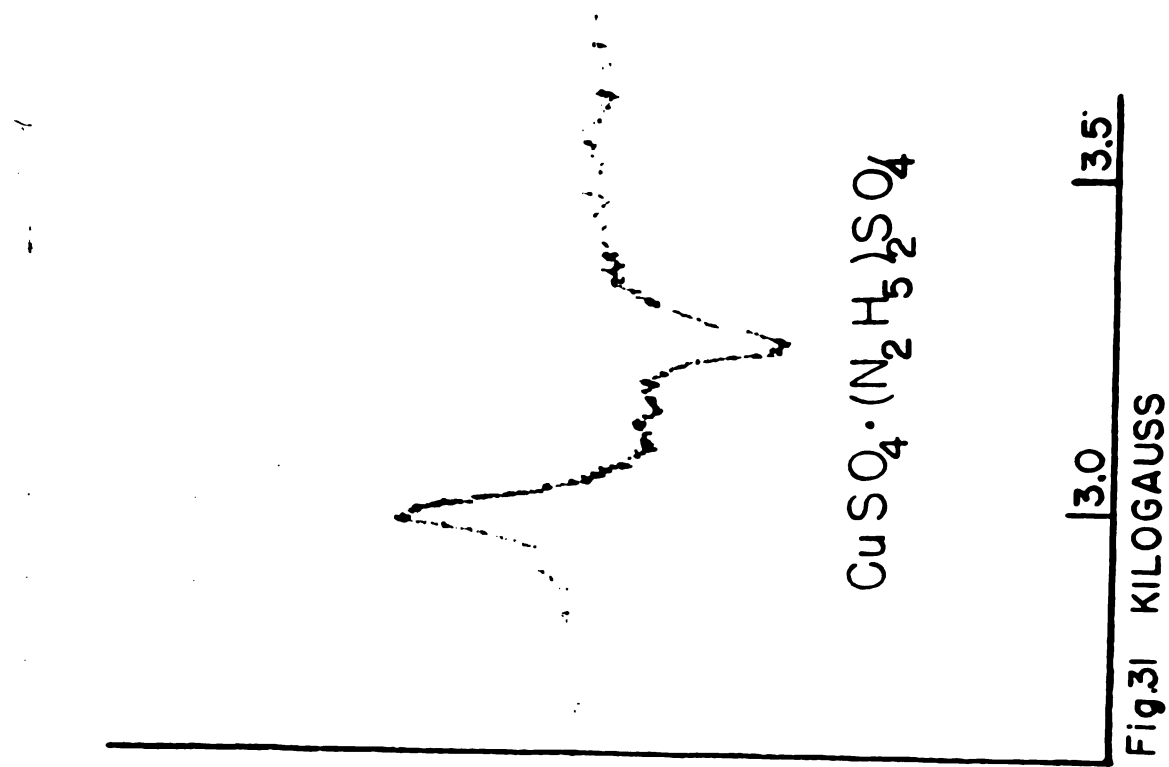


Fig.31

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