HYPERFINE SPLITTING IN ELECTRON PARAMAGNETIC RESONANCE STUDIES OF METAL-AMINE SOLUTIONS

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ABSTRACT

HYPERFINE SPLITTING IN ELECTRON PARAMAGNETIC RESONANCE STUDIES OF METAL-AMINE SOLUTIONS

by John E. Wreede

Solutions of lithium in ethylamine, cesium in ethylamine, and rubidium in methylamine were studied by means of electron paramagnetic absorption using a Varian Model 4500 Spectrometer with 100 KC field modulation. The primary purpose was the observation of hyperfine splitting but only rubidium in methylamine solution exhibited hyperfine structure under the conditions used.

This solution gave an eight-line spectrum at room temperature but another line in the center became apparent at low temperatures. The total hyperfine separation was plotted as a function of temperature giving an essentially linear relationship in the range studied (-40°C to +60°C). Below the freezing point of the solution, the splitting reverted to nearly its room temperature value.

A decomposed sample of Li-ethylamine solution had a broad line which may have been due to hyperfine interactions, since hyperfine splitting has been reported for this solution.

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By

John E. Wreede

A THESIS

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To my wife Trudi

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I. INTRODUCTION

Hyperfine splitting in epr is important because of the large amount of data readily obtainable by simple measurement. In simple cases the nuclear spin quantum number is determined merely by counting the number of peaks (given by 2I + 1). If one knows the nuclear magnetic moment (obtainable for most nuclei from Varian's NMR table)[2], the electron density at the nucleus can be calculated from a simple formula (see section on theory) using the total splitting. Of course, the data obtainable from just a single peak are also obtained when hyperfine splitting is observed. Magnetic susceptibility, gyromagnetic ratio, and an estimation of relaxation times can be obtained just as when no splitting is present.

The present study gives us the electron density at the metal nucleus as a function of temperature. We can use the data to demonstrate the presence of certain species in the solution and to test the various models for metal-amine solutions. By measuring the spin concentration as a function of temperature, it might be possible to estimate the equilibrium constants for the conversion of paramagnetic species to diamagnetic ones.

Other experimental procedures available for these determinations are not so specific. Absorption spectra, conductivity and static susceptibility, for example, involve assignment of properties to certain species by inference or comparison with other systems such as metal-ammonia solutions. Epr gives a less ambiguous measure of the electron density at particular nuclei than do Knight shift measurements or proton magnetic resonance studies.

The primary purpose of this research was to study the hyperfine splitting of solutions of Rb in methylamine. These data combined with optical and electrochemical data should help us deduce the species present in metal-amine solutions.

II. HISTORICAL

The first hyperfine structure experiments using epr techniques were reported by Penrose[1], who diluted $Cu(NH_4)_2(SO_4)_2 \cdot 6H_2O$ by substitution in an isomorphic crystal of diamagnetic $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$. By thus reducing the electron spin-spin interaction between copper ions, the line width was reduced so that a quartet, characteristic of the nuclear spin of Cu ($I = 3/2$), was resolved from the broad line previously described for this complex. Since Penrose's experiments in 1949 much work has been done with epr hyperfine splitting because of the vast amount of information obtainable from such studies.

Although much work has been done on the esr spectra of metal-ammonia and metal-amine solutions, as outlined in the review article of Symons[3], the first reports of hyperfine interaction in solutions of alkali metals in amine solvents were those of Vos and Dye[4] and Bar-Eli and Tuttle[5] in 1963. Vos and Dye reported hyperfine splitting of cesium and rubidium in methylamine, while Bar-Eli and Tuttle showed that solutions of lithium in ethylamine[6], potassium in ethylamine[6], and cesium in ethylamine[7] exhibit hyperfine splitting. The hyperfine splitting in lithium solutions was attributed by these authors to nitrogen nuclei rather than lithium.

III. THEORY

When the nucleus of a paramagnetic species has a magnetic moment, hyperfine interaction may be observed. If the magnetic field is large relative to the field contributed by the nucleus at the electron, the first order solution of the Hamiltonian becomes[8]:

$$h\nu = g\mu_B H + J_{13} M_I$$

where:

J_{13} = total angular momentum

g = spectroscopic splitting factor

μ_B = electron magnetic moment

H = magnetic field

M_I = nuclear magnetic quantum number

and each magnetic energy level will be split into 2I + 1 components (where I is the value of the nuclear spin in multiples of $h/2\pi$) with equal spacing J_{13}. At least four conditions must be satisfied for the observation of hyperfine structure[9]. These are:

1. The system must be sufficiently dilute so that the hyperfine interaction (electron-nucleus magnetic interactions) is larger than either the exchange interaction or the dipole-dipole interaction.
2. If $\Delta\omega$ represents the splitting interval in frequency units, the species' lifetime and the thermal relaxation time T_1 must be greater than $1/\Delta\omega$.
3. The microwave field amplitude must be small compared to the splitting interval when both are expressed in gauss.

4. The field inhomogeneity over the sample should be smaller than the splitting interval. Splitting intervals of less than 100 milligauss have been observed in compounds containing many protons while for free hydrogen atoms, the splitting would be in the neighborhood of 500 gauss. Since a phase detector is used for observation of the absorption's derivative, the field modulation amplitude must be much less than the splitting interval.

The (2I + 1) hyperfine lines will be of nearly equal intensity since the possible orientations of the nuclear spin vector are almost equally probable. However, when the electron moves in a delocalized orbital and comes under the influence of several nuclear magnetic moments, there are at least two possibilities for the structure. When two non-equivalent nuclei exhibit interaction with the unpaired electron and one has a much stronger interaction, then the stronger interaction produces $(2I_1 + 1)$ well spaced lines, while the other nucleus splits each of these lines into $2I_2 + 1)$ components. When two equivalent nuclei interact equally with the electron, the effective nuclear spin is 2I and thus (4I + 1) equally spaced lines occur. Similarly for any n equivalent nuclei (2nI + 1) lines occur. However, these lines are not equally intense, the intensity being directly proportional to the number of different combinations of the M_I values which result in the electron spin magnetic moment receiving an identical field.

This situation would arise if, as proposed by Dye and Dewald[10], an M_2^+ ion were one of the paramagnetic species in metal-amine solutions. For example, the Li_2^+ ion should give $(4 \cdot 3/2 + 1 = 7)$ lines with relative intensities 1-2-3-4-3-2-1 assuming just the Li^7 isotope

(92% abundance). Four nitrogen nuclei, to which Bar-Eli and Tuttle attribute their observed hyperfine splitting in lithium-ethylamine solutions, would give $(8 \cdot 1 + 1) = 9$ lines with relative intensities 1-4-10-16-19-16-10-4-1.

Figure 1 is a diagram of the hyperfine splitting of energy levels at constant magnetic field for a single nucleus with a spin of 1. However, because it is difficult to obtain a linearly variable frequency source in the microwave region, it is the usual practice in epr work to use constant frequency and vary the magnetic field. With this in mind, we may illustrate the formation of hyperfine lines as in Figure 2. One observes the expected number of lines in succession during an increase or decrease in magnetic field as the separation of the two levels becomes equal to h . Also, as can be seen from the diagram, the separation in gauss must be the same for the various levels because the separation of the energy of the various levels is the same.

In contrast to the simple picture given above, hyperfine lines are sometimes found to have unequal splitting. There are at least three possible explanations of this behavior:

1. If the external magnetic field is comparable to the magnetic field of the nucleus and not much larger as assumed above, the components of the nuclear angular moment in the direction of the field are no longer perfectly defined and an unequal splitting of the levels results.

2. There may be an electrostatic interaction between the gradient of the crystalline electric field at the nucleus and the nuclear quadrapole. Nuclear quadrapole moments exist when the spin quantum

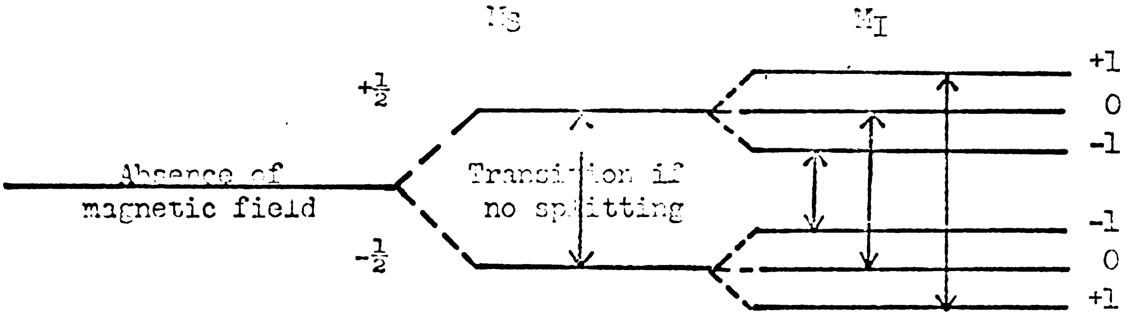

Fig. 1. Hyperfine Splitting

at Constant Magnetic Field

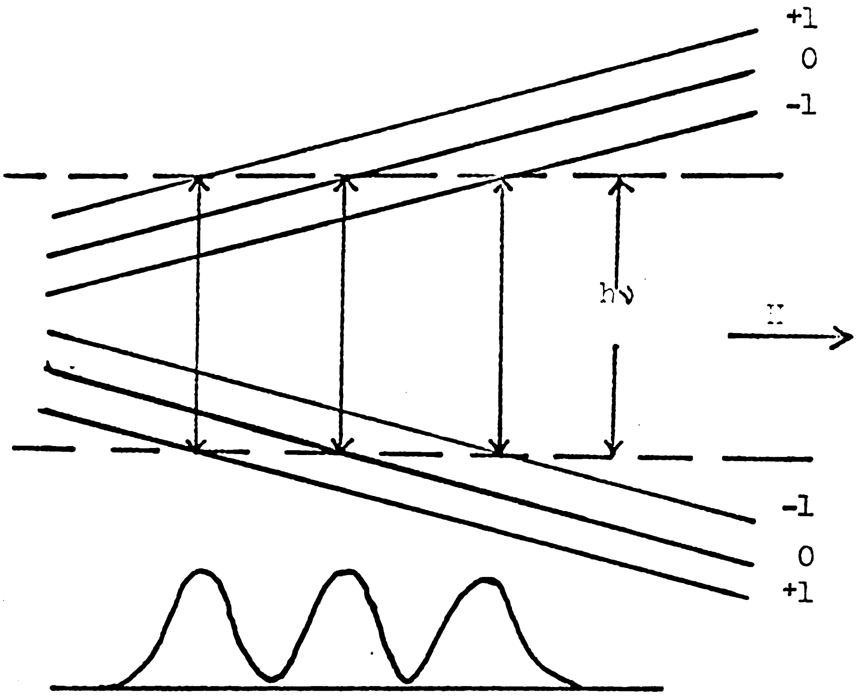

Fig. 2. Hyperfine Splitting

at Constant Frequency

number is greater than 1/2. Such a nucleus has an asymmetry of electric charge. From observation of this unequal hyperfine splitting, the quadrapole interaction can be determined. This effect may also result in variation of line-width for the individual hyperfine components.

3. Non-equidistant lines may also appear if two isotopes are present in comparable amounts, as the case of rubidium. In this case there are two spectra superimposed and the resulting lines need not be equally spaced.

The shape of lines resulting from exchange interaction depends upon whether the exchange is between similar or dissimilar ions. With similar ions, the exchange effect narrows the lines at the center and broadens them in the wings. With dissimilar ions, that is, ions having different Larmor frequencies, the line will broaden provided the component lines are sufficiently close. Exchange effects with dissimilar ions are most commonly observed where the same ion occurs in different magnetic sites in the same unit cell.

The width of a resonance line can give fundamental information about the various interactions. The spin-spin relaxation time, T_2, may be calculated from the line width if the curve is Lorentzian. The spin-spin interaction depends on the reciprocal of the cube of the distance between individual paramagnetic species. Diamagnetic dilution of the sample is useful in increasing T_2, thus reducing line width. This might also be accomplished by increasing the spin-lattice relaxation time, T_1, by lowering the temperature.

The width of the resonance line is influenced not only by relaxation times but also by unresolved hyperfine splittings and by local fields from other species if they are sufficiently close. The lifetime of the paramagnetic species if sufficiently short, can broaden the resonance through the operation of the Heisenberg Uncertainty Principle. Resonance line widths are very sensitive to viscosity[11] and Hausser[12] reports that there is an optimum viscosity for the observation of hyperfine structure.

Where hyperfine structure occurs, the shape of the observed spectra is determined by the degree of resolution which, in turn, is governed by the ratio of the width of the hyperfine components to the hyperfine separation. The two extreme cases would be distinct separate lines and a single broad line.

The only term in the Hamiltonian for the interaction of the nucleus with an electron to give hyperfine splitting which is of importance in our solutions is the Fermi contact term. The others are anisotropic and are averaged out in solutions.[13]

$$\mathcal{H}_{hfs} = -\frac{8\pi}{3} g_s \beta_s g_I \beta_I \, \delta(\vec{r}) \vec{I} \cdot \vec{S} = A \, \vec{I} \cdot \vec{S}$$

where:

g_s = electronic spectroscopic splitting factor

β_s = Bohr magneton

g_I = nuclear spectroscopic splitting factor

β_I = nuclear magneton

$\delta(\vec{r})$ = Kronecker delta

$$\vec{F} = \vec{I} + \vec{S}$$

$$\vec{I} \cdot \vec{S} = 1/2[F(F+1) - I(I+1) - S(S+1)]$$

Where:

$S = +1/2$ or $-1/2$

In the presence of a large external magnetic field there is no I-S coupling. The selection rules are $\Delta M_I = 0$, $\Delta M_S = +1$ for absorption; Thus: $\Delta E = g_s \beta_s H_0 + M_I A$ for transition $M_s = -1/2$ to $M_s = +1/2$ since the nuclear resonance frequency < < electron resonance frequency

$$\Delta E = M_I A$$

where:

$$M_I = -I,\ -I+1,\ -I+2,\ \text{to}\ +I$$

$$\Delta E = M_I\left(-\frac{8\pi}{3}\, g_s g_I \beta_s \beta_I\, \Psi_{(0)}^{2}\right)$$

$$g_I \beta_I = \frac{\mu_I}{I}$$

$$\Delta E = M_I\left(-\frac{8\pi}{3} \cdot \frac{\mu_I g_s}{I}\, \beta_s\, \Psi_{(0)}^{2}\right)$$

total separation between $M_I = -I$ to $M_I = +I$ is

$$\Delta(\Delta E) = 2I\left(-\frac{8\pi}{3} \cdot \frac{\mu_I}{I}\, g_s \beta_s\, \Psi_{(0)}^{2}\right)$$

total separation is then

$$\Delta(\Delta E) = -\frac{16\pi}{3}\, \mu_I g_s \beta_s\, \Psi_{(0)}^{2}$$

since

$$\Delta H_{\text{gauss}} = \frac{\Delta(\Delta E)}{g_s \beta_s}\text{ergs}$$

$$(\Delta H)_{\text{total}} = -\frac{16\pi}{3}\, \mu_I\, \Psi_{(0)}^{2}$$

The derivation followed is that suggested by Rogers.[14]

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IV. EXPERIMENTAL

A. Glassware Cleaning

The solvent purification train and the sample make-up vessel were cleaned with a hydrofluoric acid cleaner prepared according to the following formula:

2% acid stable detergent (Tide or equivalent)
33% concentrated nitric acid
5% hydrofluoric acid
60% distilled water.

The glassware was soaked in this solution for a few minutes, then rinsed in distilled water three or four times. The solvent purification apparatus was then washed with aqua regia, rinsed with distilled water about six times, demineralized water which had been redistilled in Pyrex, an additional three times, and dried in an oven at 140°C.

This procedure was considered inadequate for the sample make-up vessel because of the difficulty in filling the 3 mm tubes. These tubes had to be alternately heated and cooled to be filled with liquid and emptied. After soaking in the HF cleaner for a few minutes, the vessel was rinsed three times with distilled water, then filled with hot aqua regia to soak for at least four hours. It was rinsed three times more with distilled water and soaked in the demineralized water for at least four hours. After this it was rinsed at least six times with demineralized water and four times with the redistilled water. Finally the vessel was dried in an 140°C oven.

Without the aqua regia soaking the samples decomposed rapidly. Possibly some catalytic material had been precipitated when the HF cleaner was heated to drive the liquid from the tubes. This may not have dissolved in the ensuing water rinses but probably dissolved in the hot aqua regia.

Tap water was never used in the washing procedure and only reagent grade acids were used to make up the cleaning solutions.

B. Amine Purification

The mono-ethylamine was Eastman 506-X grade in 100 gm break-tip bottles. It was purified in an apparatus as illustrated in Figure 3. Powdered BaO and cut pieces of sodium were put into the pot to dry the amine. The bottle of ethylamine was cooled to 0°C, the tip broken, and the contents of the bottle poured into the still-pot which was at dry-ice-alcohol temperature. Nitrogen, which was purified by passing over Cu and CuO at 400°C and through silica gel at dry-ice-alcohol temperatures, was bubbled through the cold liquid (at dry-ice temperature) and the sample was refluxed. A polyethylene cup filled with powdered dry-ice was fitted around the column to aid the cold finger (filled with a dry-ice-alcohol mixture) during refluxing. Nitrogen was bubbled through the sample placed in a dry-ice bath for 15 minutes, in a 0°C bath for 1/2 hour and exposed to room temperatures for four hours. In all, about 30 ml was distilled into the trap during reflux. When the refluxing was completed, the sample was warmed, frozen, and degassed repeatedly until the pressure above the frozen sample stabilized at less than 1×10^{-4} torr. At this pressure the sample was distilled. The first 15 mls were condensed in the waste vessel and the remaining was distilled onto a potassium film in the sample flask. The sample was kept cold enough to distill at the rate of about one drop per second from the cold finger. The distilled sample was then warmed, frozen, and degassed until the pressure stabilized at 1 x 10^{-6} torr above the frozen sample. It was then distilled <u>in vacuo</u> onto another potassium film in a storage flask. Formation of the potassium solution in the ethylamine was very slow. At first only a slight blue coloration was visible but after two or three days at dry-ice temperatures a dark blue stable solution formed.

The mono-methylamine was obtained in a bomb from Mathieson Company, Inc. The purification in this case was similar to that of ethylamine. After about 150 mls had been condensed in the pot at dry-ice temperature, nitrogen was bubbled through the system for five hours. The methylamine, over Na metal, was then refluxed in an atmosphere of nitrogen at near atmospheric pressure for four hours. In these steps about 75 mls of the liquid was lost. The amine was then frozen and degassed and distilled <u>in vacuo</u> onto a potassium film. After standing in this vessel for 24 hours, the amine was warmed, frozen and degassed repeatedly until the pressure stabilized at 2 x 10^{-6} torr. It was then distilled onto another potassium film in the storage vessel.

As with ethylamine, potassium was very slow to dissolve in the purified methylamine. After much agitation a stable dark blue solution formed which had a more intense coloration than saturated solutions in ethylamine.

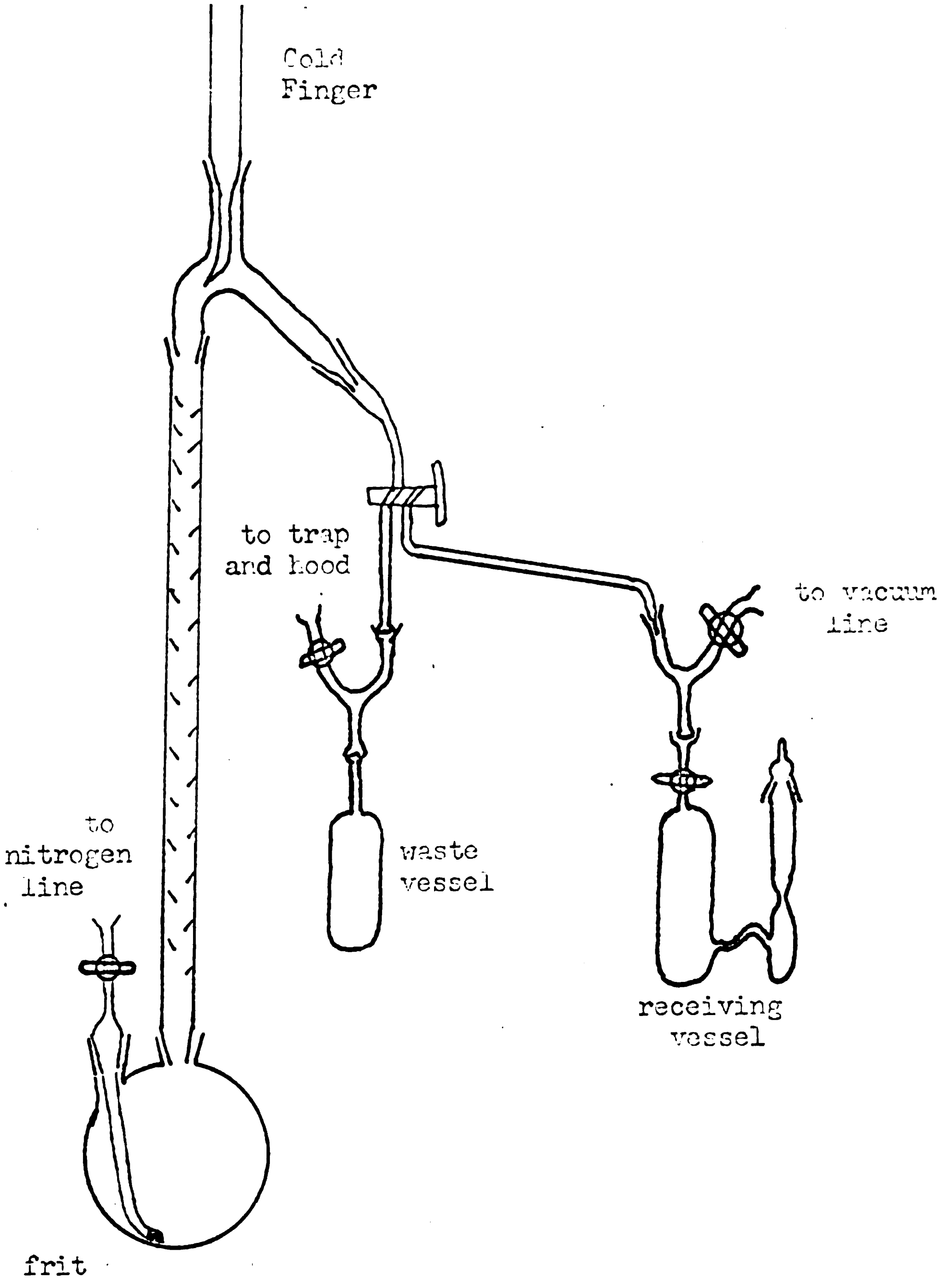


Fig. 3. Amine Purification Train

C. Sample Preparation

The sample make-up vessel used for lithium solutions is shown in Figure 4. Lithium was obtained from the Lithium Corporation of America in the form of half inch rods stored under mineral oil. After cleaning in purified benzene, a small piece was cut from the center of a rod using a dry-box filled with argon. The small piece was put into the sample vessel while still in the dry-box, and capped with a 24/40 standard joint using Apiezon T as lubricant. The vessel was then taken out, attached to the high-vacuum line <u>via</u> the 12/5 ball joint using Apiezon W wax, so that it could be evacuated immediately. Using this method, a bright piece of lithium could be obtained in the evacuated flask which showed no noticeable surface discoloration. The amine was then distilled onto the lithium by cooling the flask with liquid nitrogen. The stopcock was closed and the vessel was removed from the vacuum line and agitated to facilitate solution and the solution was poured into the sample tubes. The tubes had to be cooled slightly so that the vapor pressure of the amine would push the solution into the tubes. The height of liquid in each tube was measured and more amine was then distilled into the tubes from the other part of the flask. The amine was frozen and the tubes were sealed and pulled off. By this procedure a different concentration could be obtained in each tube and, while the absolute concentration was unknown, relative concentrations were known by the amount of dilution in each tube.

For cesium and rubidium, which could be distilled in Pyrex, the sample make-up vessel was as shown in Figure 5. A tube of purified metal (taken from stock prepared as described by Vos[14]) was placed in

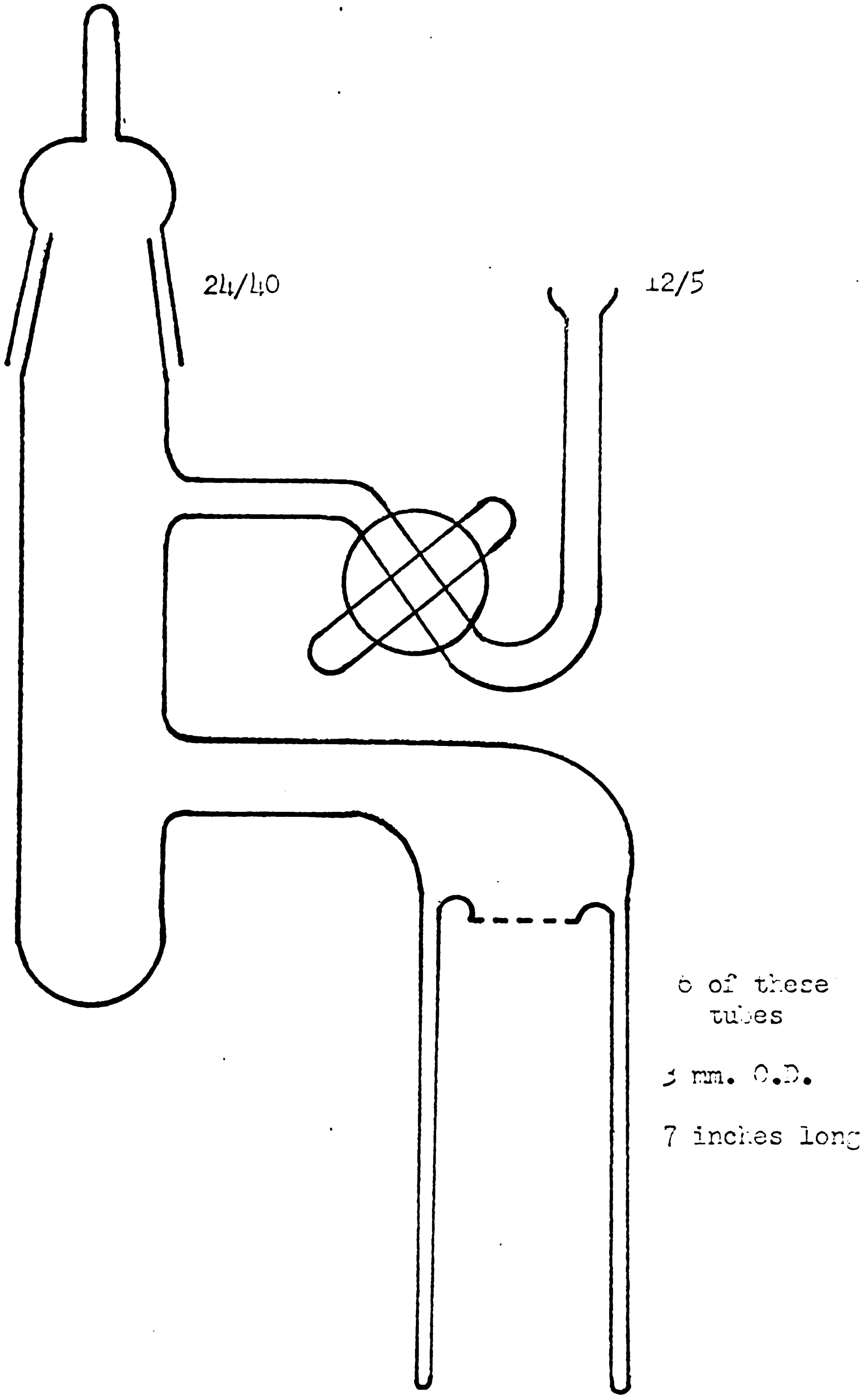


Fig. 4. Lithium Sample Makeup Vessel

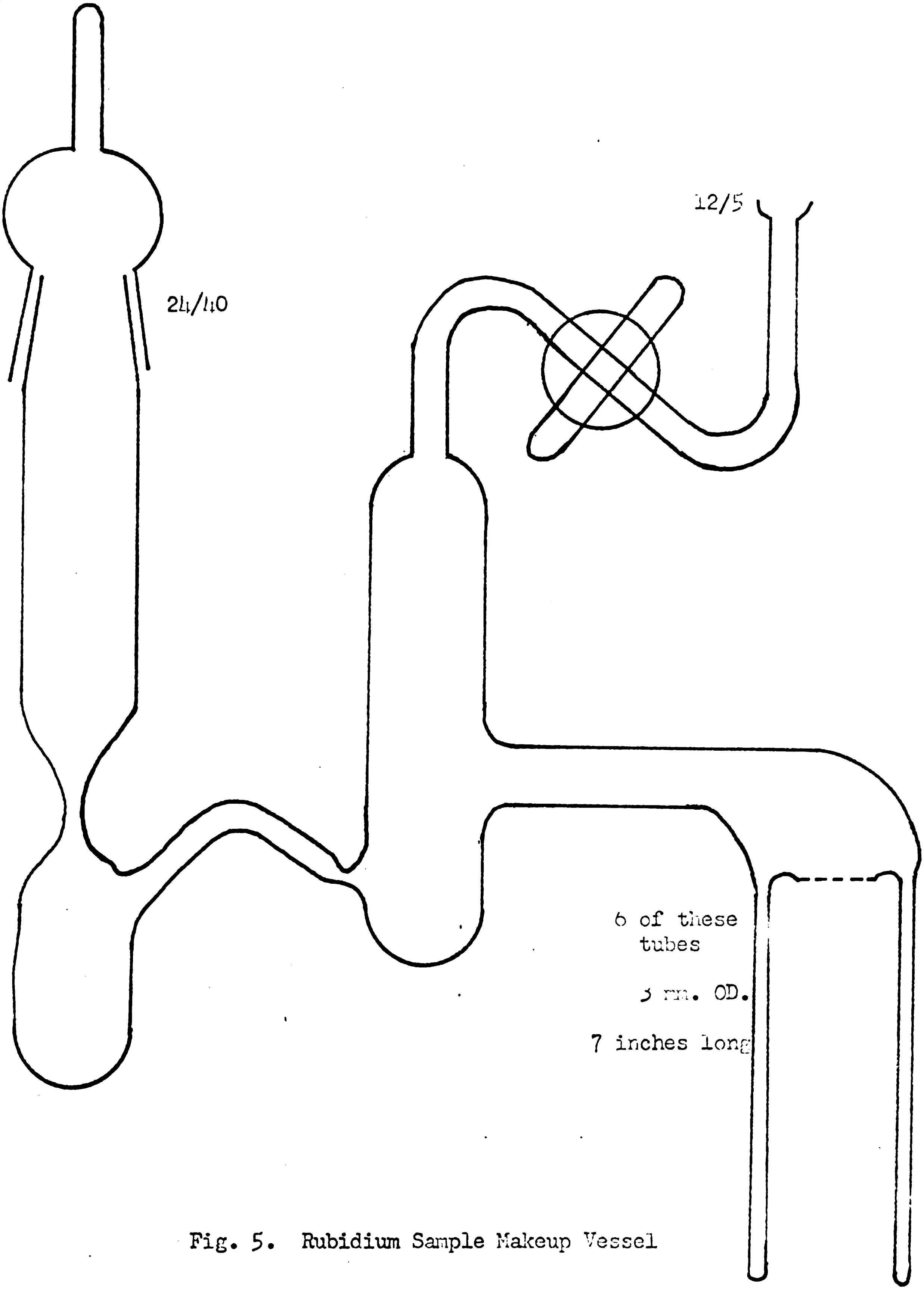


Fig. 5. Rubidium Sample Makeup Vessel

dry-ice to cool the metal. The top was broken off and the tube put into the side-arm on the sample make-up vessel. The side-arm was capped and the vessel immediately evacuated. After warming and degassing until pressures of less than 1×10^{-5} torr were reached, the metal was melted and allowed to flow through the constriction, the metal oxide remaining on the walls. The tube was then sealed off at the constriction and the top part pulled off. It was then necessary to warm and degas the metal again until a pressure of less than 2×10^{-6} torr was reached. The metal was then distilled in vacuo to form a mirror in the main part of the make-up vessel. The side-arm was sealed and pulled off so that this part of the flask could be immersed in liquid nitrogen to enable the amine to be distilled onto the metal mirror. The following steps were as described for lithium except that more agitation was required for cesium and rubidium than with lithium, in order to effect solution of these two metals by the amines. Also a solution concentrated enough for our work was easily obtained without saturation with lithium but even the essentially saturated solutions for the other metals lacked the desired signal strength but were apparently still concentrated enough to wash out the hyperfine splitting. An attempt to remedy this was made using sample tubes of 5 mm outside diameter with a less concentrated solution. However, this was unsuccessful because the dielectric losses of the extra glass and amine proved great enough to prevent the tuning of the klystron to the cavity.

In some cases it was necessary to dilute the solutions in the epr sample tubes to obtain the splitting. As these tubes were sealed under vacuum and the contents would decompose very rapidly if opened to the air, dilution could not be accomplished by the usual means. Instead, since the tubes were usually less than half full, it was possible to distill the solvent from one end of the tube to the other leaving some of the metal deposited on the walls and giving a less concentrated solution.

D. EPR Spectra

The epr spectrometer used was a Varian Model 4500 x-Band Spectrometer with 100 K. C. field modulation. The measurement of the magnetic field strength was done as described by Vos[14], by counting the frequency at which proton absorption occurs using a Hewlett-Packard Model 524C Electronic Frequency Counter. This makes use of the relationship between frequency and magnetic field at resonance:

$$2\pi \nu_p = \gamma_p H$$

where:

ν_p = frequency in cycles/sec

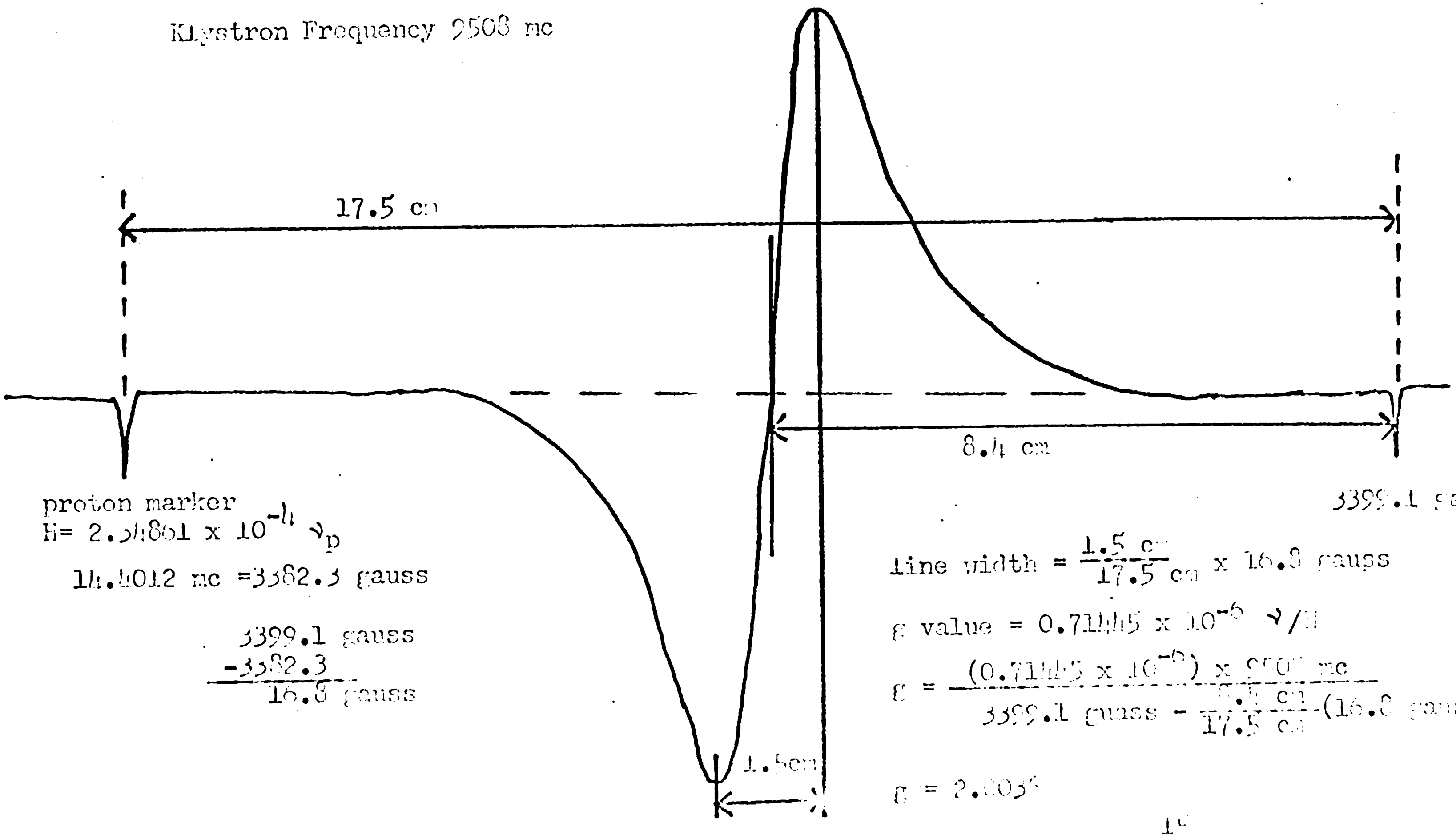
$\gamma_p = (2.67528 \pm 0.00006) \times 10^4 \text{ sec}^{-1}\text{gauss}^{-1}$

H = magnetic field in gauss = $2.34861 \times 10^{-4} \gamma_p$

The nmr sample used was a 3 cm length of 10 mm Pyrex tubing filled with Shaeffer's #316 black ink. This sample was fastened between the magnet's poles faces to the outside of the cavity and parallel to the epr sample.

The magnetic field at the epr absorption maximum for a sample was then determined from two proton markers, one on each side of the epr absorption. The hyperfine splitting can also be determined in this way. The method used is illustrated in Figure 6.

Klystron Frequency 9508 mc



proton marker
$H = 2.34861 \times 10^{-4}\ \nu_p$

14.4012 mc = 3382.3 gauss

$$\begin{array}{r} 3399.1 \text{ gauss} \\ -3382.3 \phantom{\text{ gauss}} \\ \hline 16.8 \text{ gauss} \end{array}$$

$$\text{line width} = \frac{1.5 \text{ cm}}{17.5 \text{ cm}} \times 16.8 \text{ gauss}$$

$$g \text{ value} = 0.71445 \times 10^{-6}\ \nu/H$$

$$g = \frac{(0.71445 \times 10^{-6}) \times 9508 \text{ mc}}{3399.1 \text{ guass} - \frac{8.4 \text{ cm}}{17.5 \text{ cm}}(16.8 \text{ gauss})}$$

$$g = 2.0032$$

Method used by Vos[15].

Fig. 6. Determination of Line Width and g Value

To determine the g value we need to know the klystron frequency as well as the magnetic field. This frequency could be determined from the micrometer reading on a Waveline 608 wavemeter which had previously been calibrated in terms of frequency. The precision was limited by the reading of the micrometer. The accuracy in klystron frequency was at least ± 1 mc. Apparatus was also available for beating the frequency of the klystron against the standard frequency of a "Micro-now" Model 101 Microwave Frequency Calibrator and counting the frequency with the Hewlett-Packard counter after amplification. This procedure can give accuracy in determining the klystron frequency to ± 0.02 mc, but it was felt that the error in determining the center of the splitting was great enough to make this measurement unnecessary.

E. Temperature Determination

Low temperatures were obtained by passing a stream of dry nitrogen gas through a liquid nitrogen bath and into the dewar holding the sample tube in the cavity to get the desired temperature. With the proper flow rates, a reasonably steady temperature could be obtained. A stream of nitrogen at room temperature flowed between the outside of the dewar and the inside walls of the cavity to prevent water condensation. It was desired to maintain the temperature to within ± 1° of the starting temperature and temperature stabilities of this order were obtained. It is easier to obtain stability using a dry-ice-acetone bath in place of the liquid nitrogen, but of course the range of temperatures possible is much smaller. A heater was incorporated in the flow line of the cold nitrogen but this was only needed for temperatures above -10°C, lower temperatures being obtained merely by adjusting the flow rates of the two streams of nitrogen.

Temperatures were measured with a copper-constantan thermocouple and a Honeywell 2746 potentiometer. At first the thermocouple was placed near the bottom of the dewar holding the sample tube in the cavity so that it would not interfere with the microwave field; however this proved unsatisfactory because of a temperature differential between the thermocouple and the sample tube. Also, the thermocouple appeared to stabilize before the temperature at the sample became stable enough for operation.

There is a null plane in the cavity at which the field is so low that absorption by the thermocouple wire causes no difficulty. This plane is easily found by fastening the thermocouple to the sample tube, placing it in the cavity, and rotating the tube until the klystron can be easily tuned (tuning dip at a maximum). Placing the tip of the thermocouple next to the sample in the center of the cavity does not interfere then with the signal and gives better temperature values than are determined with the earlier procedure.

F. Optical Spectra

The optical absorption spectrum of one of the solutions of rubidium in methylamine was qualitatively measured using the 3 mm sample tubes instead of special cells. A piece of black cardboard held the sample in the cell holder of the Beckman DK-2 spectrophotometer with black tape covering the edges so that light passed only through the solution. No reference cell was used as none was readily available. As only a qualitative spectrum was desired, it was felt that this procedure was adequate. The solution was too concentrated to obtain the spectrum so that dilution by distillation as described under Sample Preparation was effected after which a fairly reproducible spectrum was obtained.

V. RESULTS

A. Lithium in Ethylamine

The lithium-ethylamine solution first prepared was impure as evidenced by the poor stability of the sample. It was only stable for 10-15 minutes at room temperature. Therefore, the epr spectrum of this solution could not be run at room temperature and was run only at -60°C, at which temperature it showed an intense narrow single peak with g value 2.0015 ± 0.0002 and line width 0.99 gauss superimposed on a broad peak which might well have been due to hyperfine interactions, poorly received because the solution was too concentrated.

The ethylamine was then redistilled and its greater purity was indicated by the low solubility of the potassium film over which it was stored, requiring much agitation before a dark blue solution formed. This solution, once formed, was quite stable. The new solution of lithium in ethylamine proved much more stable, showing no visible decrease in color intensity or epr absorption until it had remained for about two hours at room temperature. These samples were run at temperatures ranging from room temperature down to -80°C; but at no temperature did the broad line, visible in the impure samples, occur, but only a single narrow line. One of these samples lost its epr signal while still a dark blue color, while for the others the epr signal seemed to decay along with the blue color.

A third run was made using a solution of lithium in ethylamine which was purified only by drying over pieces of lithium, the procedure reported by Bar-Eli and Tuttle. Care was still taken not to admit air or other contaminants but the only distillations made were those into the storage flask and then into the sample flask, but without the use of a nitrogen stream. The solution was very unstable, decomposing within one minute if brought to room temperature. The sample before decomposition gave an epr signal which appeared to consist of more than one line, perhaps three or four. We were unable to resolve these before the sample decomposed. The sample after decomposition (in which a white precipitate formed) also gave an epr signal. This consisted of a broad line with a narrow line superimposed, both of which were similar in intensity and shape to the results obtained in the first run. After 24 hours at room temperature the narrow peak was still 75% of its initial value while the broad peak was only 20% as high. The line width did not change appreciably. After another 24 hours at room temperature (separated by several days at liquid nitrogen temperature) both peaks had disappeared. Attempts to separate the liquid and the precipitate inside the tube to determine which gave the resonance, were unsuccessful. This broad peak had some unevenness which seemed to suggest unresolved hyperfine splitting, but this was not well enough defined to determine either the positions or number of lines.

B. Cesium in Ethylamine

Solutions of cesium in ethylamine were prepared before improvements in technique brought increased stability to the samples. For this reason and the very low concentration, the solutions in the 3 mm sample tubes were stable for only about a half-hour at room temperature. Although a saturated solution was used, the color was only a very light blue. The epr absorption was also quite weak with only a narrow single peak being visible above the noise.

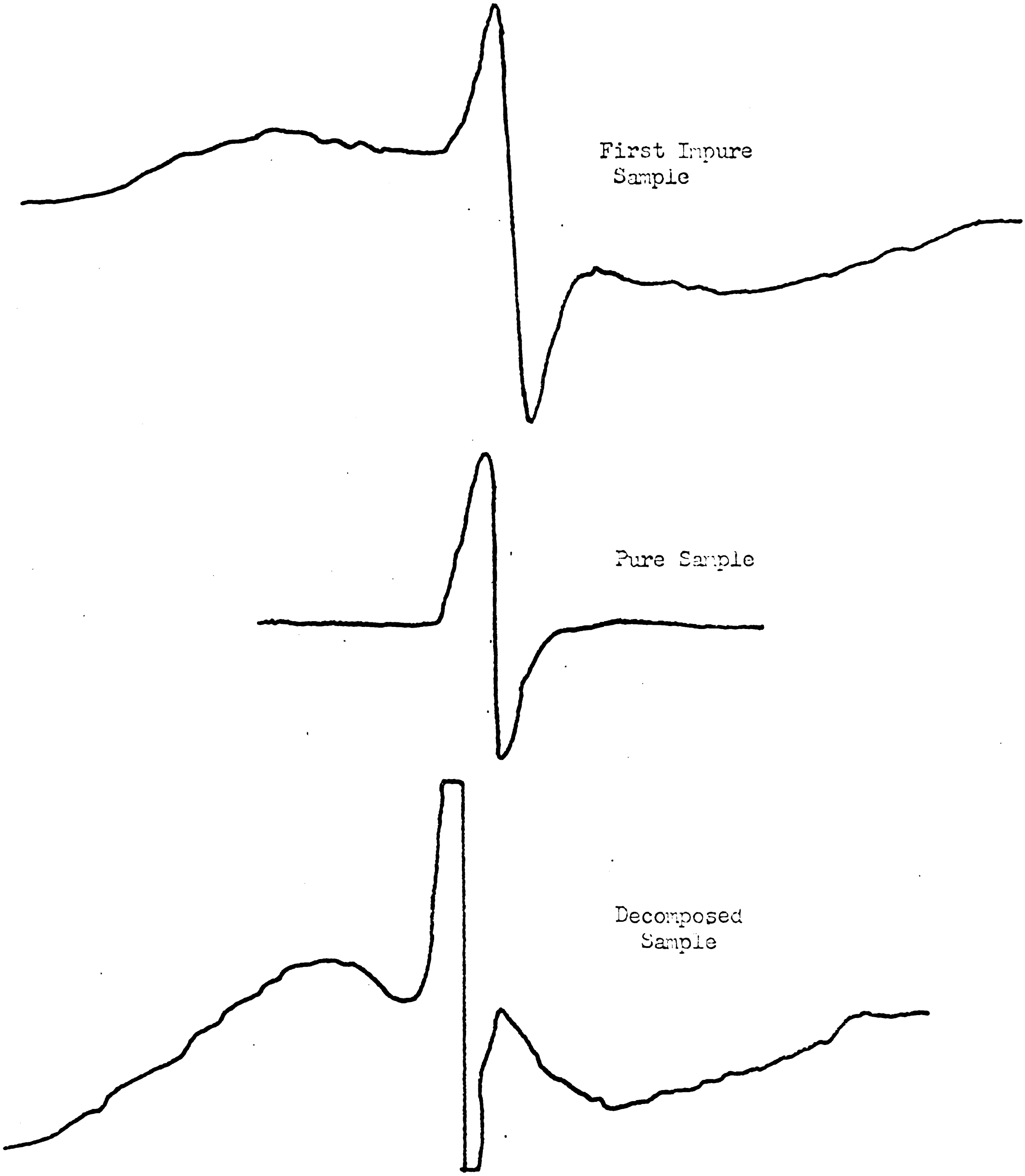


Fig. 7. Lithium-Ethylamine EPR Spectra

C. Rubidium in Methylamine

Samples of rubidium in methylamine in the 3 mm epr tubes proved to be quite stable, being visibly unchanged after at least four days at room temperature and still a light blue after six days. Both the color and the epr absorption disappeared after the seventh day. Eight peaks were apparent in the epr spectra: six narrow, intense lines and two broad lines of lower intensity having a total splitting of approximately twice the inner lines. Represeantative spacings of these lines are given in Figure 8 in order of increasing field strength.

Peak No.	1	2	3	4	5	6	7	8
Distance from center (in gauss)	-124	-62	-38	-11	11	38	62	124

Figure 8.

The temperature dependence of the total splitting of these lines is shown in Figure 9. The g value is 1.998 ± 0.003 at room temperature.

As the temperature is decreased, a single line superimposed upon the hyperfine spectrum appears. Below -40°C the hyperfine structure is completely masked by this center line. However, as Figure 11 shows, below the freezing point the hyperfine splitting reappears with a peak to peak separation near that for room temperature. The g value of the center line is 2.000 ± 0.003.

The two outside lines and the six inner lines appear to have the same temperature dependence, the ratio of total separations lying between 2.0 and 2.1 for all temperatures recorded. Rb^{87} should have a total separation 2.04 times that of Rb^{85} as calculated from the nuclear magnetic moments.

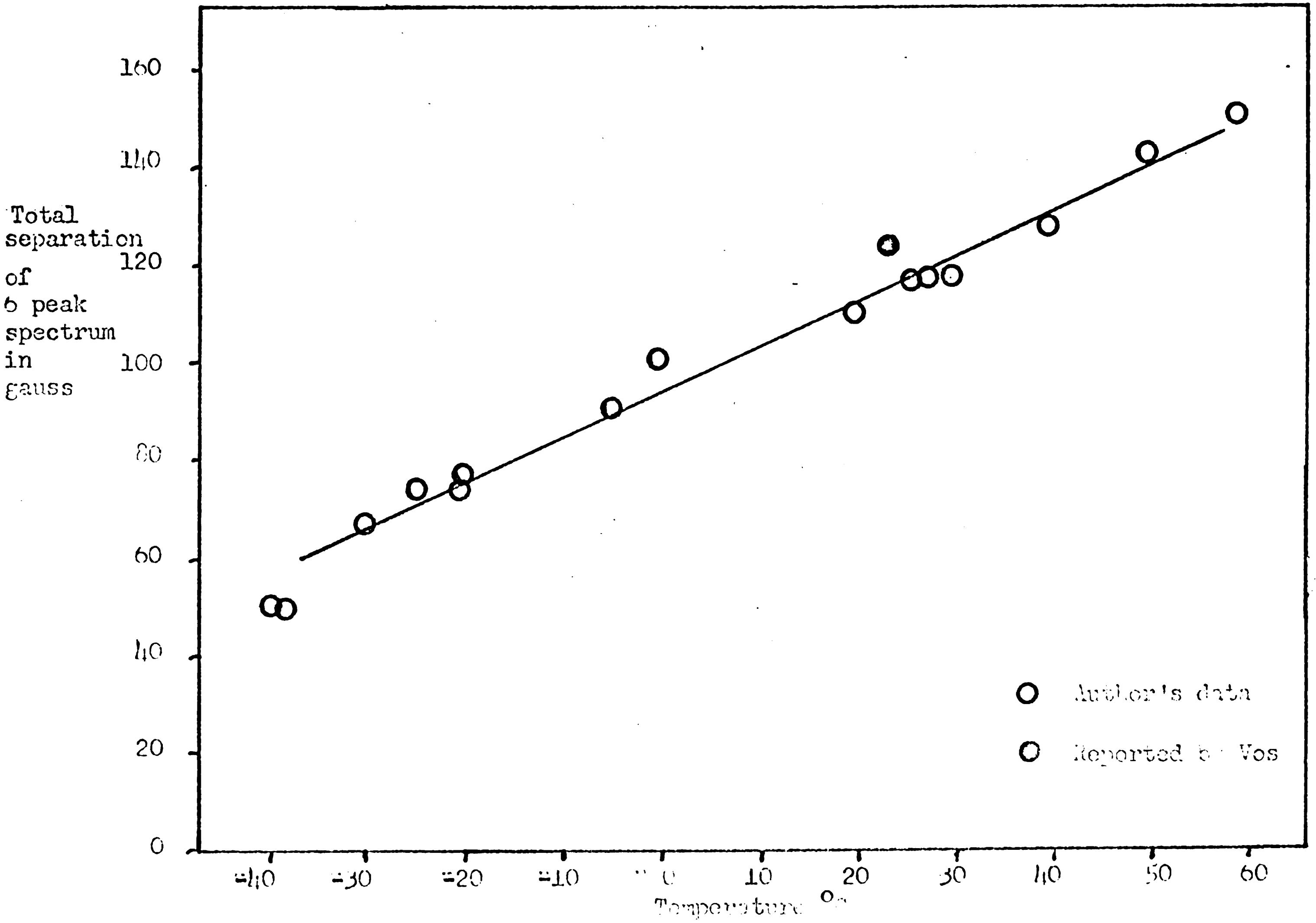


Fig. 9. Temperature Dependence of Splitting in Rubidium-methylamine epr spectra

Further runs were made using new samples of rubidium in methylamine to determine whether the two outside peaks could be due to impurities, but these were present in all samples. In certain spectra the lines were so broad as to be nearly unnoticeable. These further runs had stability equivalent to the first, a sample being visibly unchanged after two hours above 50°C.

An epr spectrum was run on sample #2 after five days at room temperature. The effect of decomposition on the shape of the spectrum is shown in Figure 11. The center line is predominant even at room temperature. Figures 10 through 12 show representative spectra. Shown are an experimental room temperature curve along with a calculated curve, a spectrum at -5°C showing the first signs of a central line, a curve at -90°C showing only the center line, and a curve at -125°C (below the freezing point) again showing the hyperfine splitting.

The optical spectra showed absorptions at 1230 mμ, 890 mμ, and in the vicinity of 650 mμ.

	Rb^{85}	Rb^{87}	extra
peak height (cm.)	3.3	0.8	5.0
line width (gauss)	17.8	25.4	~~25.0~~ 51.0
separation (gauss)	24.0	80.0	0

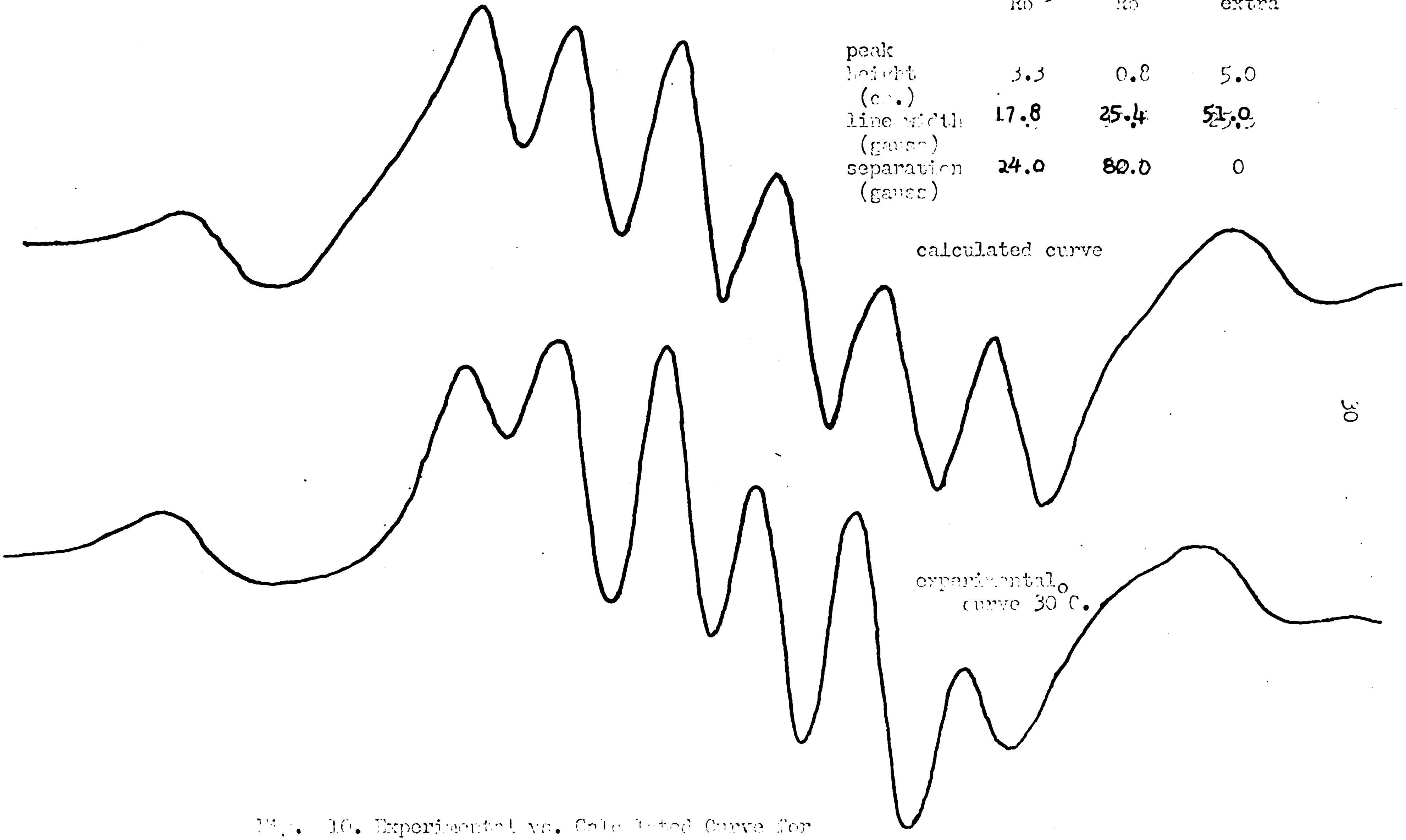


Fig. 10. Experimental vs. Calculated Curve for Rubidium- ethylamine Solutions

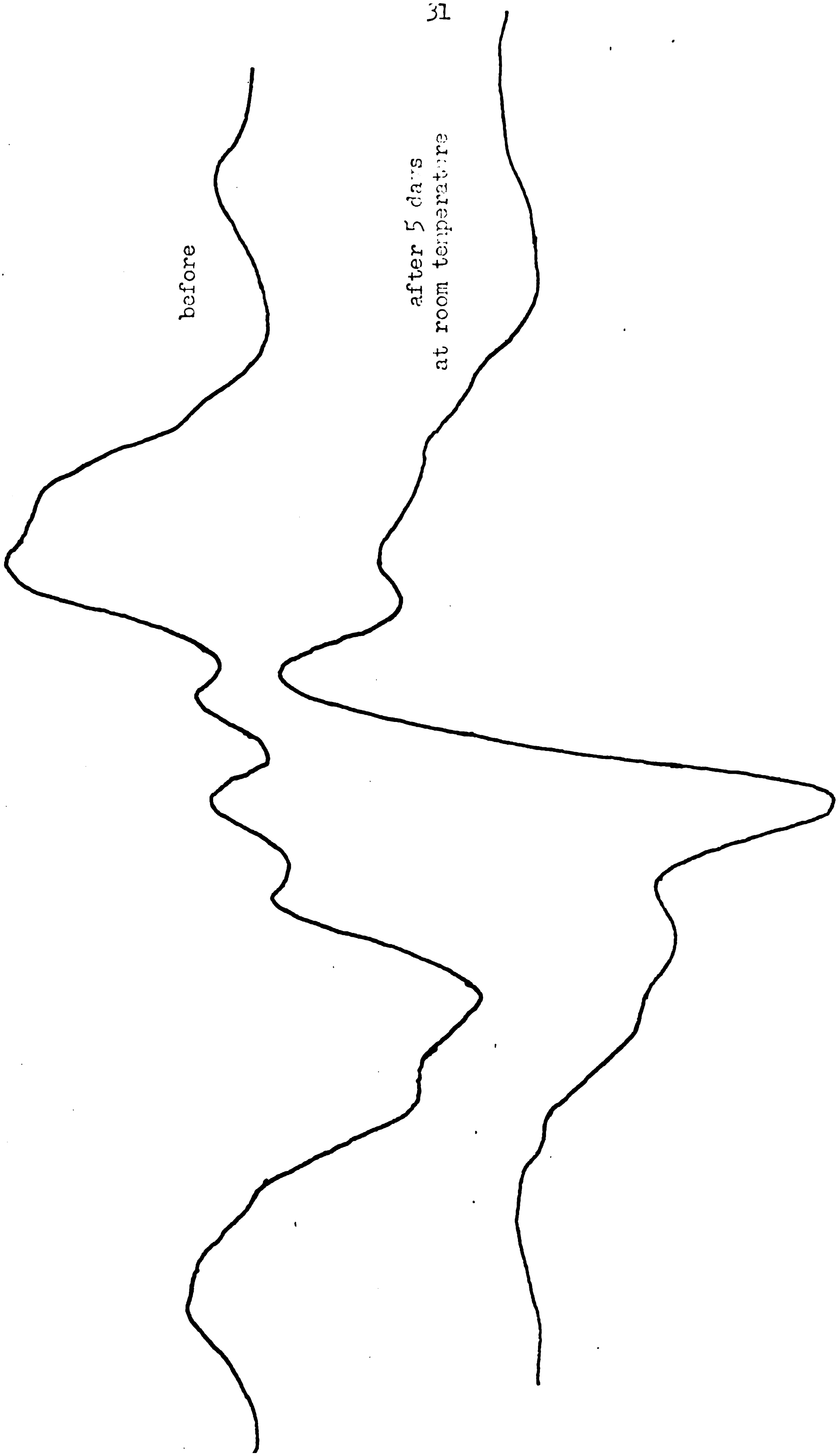


Fig. 11. Effect of Decomposition on Rubidium epr Spectra

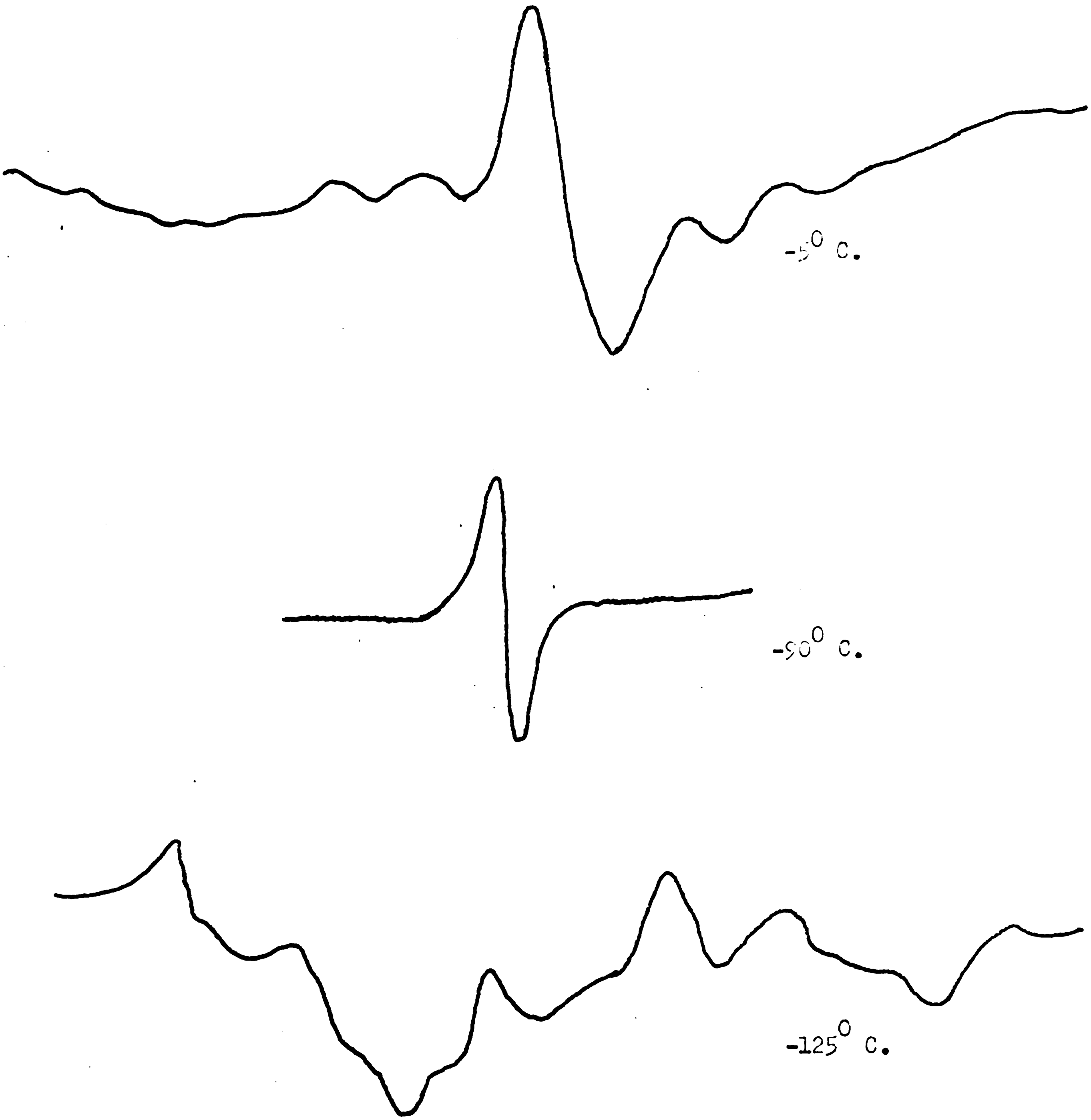


Fig. 12. Rubidium-Methylamine EPR Spectra

VI. DISCUSSION

A. Lithium in Ethylamine

Since the broad peak was not visible in the purer solutions of lithium in ethylamine, it was decided to determine whether this broad peak could be intensified relative to the narrow one and perhaps resolved into hyperfine structure by using impure ethylamine. It was believed that this absorption could be due to some minor species which obtained sufficient concentration relative to other paramagnetic species only in rapidly decomposing solutions. A possible species is the Li_2^+ ion, which if present should give seven hyperfine lines (neglecting the contribution of Li^6) with relative intensities 1-2-3-4-3-2-1. Bar-Eli and Tuttle report nine hyperfine lines which they believe to be due to splitting by four N^{14} nuclei using a modified form of the Becker-Lindquist-Alder monomer model for metal-amine solutions. That a rapidly decomposed sample still gave a resonance signal after complete disappearance of the blue color would indicate that the paramagnetic species responsible has been included in the precipitate, possibly as a salt of the ion. Since the narrow line and the broad line decay at different rates, at least two paramagnetic species are indicated. Bar-Eli and Tuttle also report the presence of two species and attribute the narrow line to the solvated electron.

B. Rubidium in Methylamine

Vos[15] did not detect the two outside peaks in the hyperfine structure of rubidium in methylamine which are clearly visible in our spectra. Since the Rb^{87} is split twice as much as the Rb^{85}, it is reasonable to assume that the outside peaks of the Rb^{87} should be separate from the six-line Rb^{85} spectrum and easily resolved from it if the six lines themselves are resolved. Indeed, in certain spectra, only the two outside lines (distinguishable by their greater width) are visible, the rest being masked out by the single center peak. Since the separation of the two outside peaks has the same temperature dependence as the total separation of the six inner peaks, the two sets of peaks appear to involve only an isotope effect.

Assuming these two outside peaks to be due to Rb^{87}, we can calculate from measurements on only these two the position of the Rb^{87} peaks, the position of the Rb^{85} peaks, the center of the spectrum, the line width of the Rb^{87} peaks, the relative intensity of the Rb^{87} absorption, and the total area under the Rb^{85} integrated peaks, since we know that the ratio of the total peak areas must be in the ratio of isotopic abundances, and that the ratio of the total separations is given by the ratio of the nuclear magnetic moments.

Using these calculated data, an attempt was made to reconstruct graphically, assuming Lorentzian line shape, the observed room temperature spectrum. It became apparent that at least one other line was also present. The peak positions were reproduced quite well, but the relative heights were not. We can assume that the broad single line is also present at room temperature and should be included as an extra line. With this extra line the relative heights are much better.

The data indicate that at low temperatures the line width of the center line in Rb-methylamine solutions follows the behavior of the center line in Cs-methylamine solutions as reported by Vos. If this

agreement extends to higher temperatures, the line width at the temperature of curve-fitting (30°C) should be too broad to detect with the other lines present. For this reason we believe that the line widths of the center lines for the two solutions are not the same at these higher temperatures. We cannot determine the line width in Rb solutions directly at these temperatures to see if this is correct.

Using the formula for the electron density as a function of the total splitting previously derived, we get a value for Ψ_0^2 of $0.165a_0^{-3}$ which is 7.0% of the value for the free atom at 25°C. This is twice the value obtained by Vos since he did not detect the two outer peaks, but rather attributed the two outer peaks of the six-line spectra to Rb^{87} rather than to Rb^{85}.

The hyperfine separation seems to be a linear function of temperature in the region investigated. However, it would probably not follow the linear relationship at lower temperatures since Vos's curve of cesium in methylamine also appears linear in this region but not at the lower temperatures.

The optical spectra obtained correspond fairly well with the absorptions reported by Dewald[16] for solutions of rubidium in ethylenediamine. Although the relative intensities of the various peaks are different in the two solvents, it indicates that the same types of absorbing species are present.

There are at least three possible explanations for the dependence of the hyperfine separation on temperature. Bar-Eli and Tuttle attribute this to an actual increase in the size of the framework over which the electron is spread as the temperature is decreased. This would result in a lower electron density at the nucleus at low temperatures.

This theory requires drastic changes in electron distribution with temperature. Perhaps a better explanation would involve the admixture of several s-type wave functions with the relative contributions varying with temperature. For example, the 2s wave function has a radial node which is not present in the 1s wave function. Therefore, for the wave functions to add constructively at large values of r, the 2s must have an opposite sign to the 1s at the nucleus, thereby decreasing the density at the nucleus without a large effect on the electron distribution. This explanation would be valid for higher s orbitals as well because each succeeding orbital has one more node than the previous one.

A third possible explanation would attribute the hyperfine splitting to dissolved atoms whose population relative to other paramagnetic centers would be strongly temperature dependent. To observe variation of the coupling constant with temperature rather than merely total collapse of the hyperfine structure would require that electron exchange be very rapid compared with the spin-spin relaxation time.

For each of these cases, possible explanations for only a very slight dependence on temperature of the splitting in the frozen sample might be either that the lattice binds the species more tightly in position, thus allowing little change in orbitals or that the relative concentration of the species giving hyperfine splitting is independent of temperature in the solid.

As was indicated, the splitting decreases as the temperature is lowered until the freezing point of the solution is reached. The separation then increases to approximately that at room temperature and remains nearly constant as the temperature is lowered. A similar type of phenomenon was observed by Bar-Eli and Tuttle[5] for lithium in ethylamine. In this case there was an increase in line width as the temperature decreased down to the freezing point of the ethylamine, when the line width suddenly decreased. They offer no explanation for this and at present we have no adequate explanation for the sudden change in electron density at the nucleus when the solution freezes.

VII. FUTURE WORK

If some Rb^{87} could be obtained and an epr spectrum in methylamine solution were determined, it could be proved conclusively that the two outside peaks were due to this isotope. However, due to the difficulty in separation of these isotopes, it is not anticipated that this will be done. This additional step is probably unnecessary since the spectrum can be so nearly duplicated by calculated values. In fact it is felt that the most desirable work for the rubidium-methylamine system would be to find the spin concentrations as a function of temperature which would give an estimate of the effect of temperature on the equilibrium between the species giving the hyperfine splitting and that giving the extra line.

Some work planned for the future involves trying to reproduce the spectra of lithium in ethylamine reported by Bar-Eli and Tuttle using Li^5 isotope. If the hyperfine lines reported were actually due to splitting by Li_2^+, only five lines would appear for Li^6 instead of seven for Li^7 (92% natural abundance). If Bar-Eli and Tuttle are correct in their report of nine lines and assignment of these nine lines to the four nitrogens, then substitution of the Li^5 isotope should produce no change in the pattern.

Attempts should also be made to study in more detail the esr spectrum of the decomposition products of a solution of lithium in ethylamine. The precipitate which forms in a very rapidly decomposing solution should be separated from the liquid to determine which phase is responsible for the epr signal.

New solvents could also be used in attempts to observe splitting due to the M_2^+ ion.

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