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RELAXATION TIME MEASUREMENTS IN ELECTRON PARAMAGNETIC RESONANCE

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ABSTRACT

We have measured the electron paramagnetic resonance (EPR) spectra of $VO(H_2O)_5^{2+}$, obtained from vanadyl perchlorate in solutions of both ordinary water and in heavy water, as a function of temperature. The linewidths in the vanadyl system are fit quite well by a combination of the relaxation theory for the tumbling of an anisotropic complex and the theory of spin-rotation interaction. The linewidths for the vanadyl ion in ordinary water solution are well fit with the glass spectrum values of $g_{\|} = 1.9311$, $g_{\perp} = 1.9785$, $A_{\|} = -203.3$ gauss, $A_{\perp} = -75.8$ gauss, and the average solution values of g = 1.9652, A = -115.9 gauss. The correlation time is consistent with a hydrodynamic radius of 3.67 A. In the deuterated system the radius is changed to 3.48 A, with the other parameters remaining the same. The small residual linewidths which have been observed for the vanadyl ion in ordinary water are also observed in the deuterated system. These residual linewidths cannot be due to hyperfine interaction with ligand protons, and must be due to terms neglected in the relaxation theory.

We have also measured the EPR spectra of $Cu(H_2O)_6^{2+}$ obtained from copper perchlorate in aqueous solution as a function of temperature. Isotopically pure (99.62%) copper-63 was used in order to remove uncertainties which could occur in the normal isotropic mixture. The EPR

spectrum of the hexaquocopper (II) ion consists of a broad, unresolvel line. The spectra obtained as a function of temperature were digitizel with a data acquisition system. A least squares fit of Lorentz line-shapes to the digitized spectra was used to obtain the spectral parameters and linewidths. The linewidths are found to depend upon hyperfine component and to increase with increasing temperature. We have attempted to fit the linewidths to a combination of the spin-rotation interaction theory and the theory of a tumbling anisotropic species. It is not possible to fit the linewidths with both of these theories consistenly. Hence, we propose that a third relation mechanism contributes to the linewidths in the copper system.

We have developed a system for the measurement of spin-lattice relaxation times consisting of a pulse-saturation spectrometer and a computer based data acquisition and analysis system. We have applied this system to the measurement of relaxation times for Ni^{2+} ions diluted in a host crystal of lanthanum magnesium nitrate. Relaxation times for the two strongest lines of the three line spectrum have been obtained. The data are well fit by $T_1^{-1} = .087\ T^2\ (msec^{-1})$. This relationship is consistent with a phonon bottleneck process. Measurements of a more dilute crystal support this theory since the relaxation times are slightly shorter.

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I. INTRODUCTION

Although magnetic resonance phenomena have been studied since 1946, magnetic relaxation phenomena have been studied for a much longer time. The early non-resonant experiments (Gorter, 1947) in magnetic phenomena served to establish many of the important ideas of magnetic relaxation. These experiments were usually interpreted in thermodynamic terms since many of the early experiments involved temperature measurements of magnetic systems. However, magnetic relaxation is usually more easily understood in terms of the resonance phenomenon.

According to the Bloch (1946) formalism a magnetic system may be characterized by two relaxation times which describe the return of a perturbed spin system to equilibrium. The spin-lattice relaxation time, T_1, is the characteristic time for spin populations in the available energy levels to return to a Boltzmann equilibrium. In terms of the phenomenological Bloch equations this is known as the longitudinal relaxation time, or the time constant for the z component of the magnetization to return to its equilibrium value. The spin-spin relaxation time, T_2, is a measure of the time for the spins to come to equilibrium among themselves or to dephase. T_2 is also known as the transverse relaxation time since it is the time constant for the x and y components of the magnetization to decay to zero.

The spin-spin relaxation time, T_2, is experimentally the easiest to determine and it is obtained from the widths of the measured magnetic resonance lines. For a Lorentz line, T_2 is related to the linewidth by

$$T_2^{-1} = \pi \sqrt{3}\, \Delta\nu \tag{1.1}$$

where $\Delta\nu$ is the peak-to-peak separation in Hz of the first derivative of the absorption line. The independent variable in magnetic resonance experiments is usually magnetic field rather than frequency, and T_2 is given by

$$T_2 = \frac{h}{g_\beta} \frac{1}{\pi\sqrt{3}} \frac{1}{\Delta H} \qquad (1.2)$$

where ΔH is the first derivative separation in gauss, h is Planck's constant, β, the Bohr magneton, and g, the "g" value or spectroscopic splitting constant for the absorption.

The spin lattice relaxation time, T_1, is usually determined by other methods such as c.w. saturation or pulse methods. However, the factors which influence T_1 also influence T_2. In many cases, especially in solution, T_1=T_2. In many cases when the value of T_1 is required, but is unknown, the equality is assumed. In any case, T_2 sets a lower limit for the value of T_1.

The relaxation effects characterized by T_1 and T_2 can be related to time dependent magnetic or electric fields which influence the spins. There has been much interest in magnetic relaxation because of the information which may be derived about the environment of the spins. The early theories of relaxation dealt mostly with the solid state. However, the liquid state has been of increasing interest since the original observation of magnetic resonance.

The original work on relaxation in solution was due to Bloembergen, Purcell and Pound (1948), hereinafter referred to as BPP. These workers computed relaxation times using time dependent perturbation theory and correlation functions. They utilized the methods of the theory of Brownian motion and related the relaxation times to the bulk viscosity of the solution. This has attracted much interest in the possibility of studying the structure of liquids by means of magnetic resonance linewidths in solution. Analysis of the linewidths could yield a correlation time which is characteristic of the solvent and of the complex being studied.

Indeed, nuclear magnetic resonance (NMR) linewidths have been extensively used to provide information about ion-solvent and ion-ion interactions (Burgess and Symons, 1968). The temperature dependence of ^{17}O NMR linewidths has been extensively used to study waters of hydration and their rates of exchange (Swift and Connick, 1962). However, in systems containing paramagnetic ions the nuclear magnetic moments are influenced by the magnetic moment of the paramagnetic species. The NMR linewidths may then have some dependence on the electron relaxation. An understanding of electron relaxation mechanisms is then useful in interpreting the data.

An understanding of electron paramagnetic resonance (EPR) linewidths is important both in understanding EPR itself, and in interpreting complicated EPR spectra. The EPR linewidths may also be used to study ligand exchange reactions, and to study exchange narrowing effects in concentrated solutions. The EPR linewidths of so-called spin-labels are proving to be important for the study of macromolecules.

The present study was undertaken to extend our knowledge of two important spin 1/2 systems: hexaquocopper (II), $Cu(H_2O)_6^{2+}$, and pentaquooxovanadium (IV), $VO(H_2O)_5^{2+}$. Past studies of these ions have provided some qualitative understanding of the relaxation effects. However, a complete quantitative interpretation was not possible with the available data. Only dilute solutions are studied so that exchange effects are unimportant.

Both ions are also rather stable in aqueous solution, and their perchlorate salts will give these ions in solution without further complications.

The measurement of the linewidths in these systems was greatly facilitated by the development and use of a digital data acquisition system. Indeed, the measurements of the hexaquocopper (II) complex would not have been feasible without this system. The data acquisition system operated in an "off-line" mode with the digitized spectra stored on the magnetic tape for later analysis by a digital computer. The successful operation of this system was conducive to the development of an "on line" digital computer system. An "on-line" digital computer system has been developed to measure spin-lattice relaxation times from pulse saturation experiments This laboratory has been interested in Ni^{+2} ions in various lattices for some time (Batchelder, 1970; and Jindo, 1971) and preliminary measurements of T_1 for Ni^{2+} in lanthanum magnesium nitrate single crystals have been performed.

II. THEORIES OF ELECTRON SPIN RELAXATION IN SOLUTION

In this section the results of the various relaxation theories for electron paramagnetic resonance (EPR) of spin 1/2 systems in dilute solution are presented. The theories which are specific to systems with spin greater than 1/2 or which apply to concentrated solutions are not presented. The results will not be derived in detail. The reader is referred to the original papers for detail or to the general discussions which are available. Two excellent reviews of relaxation in solution have appeared recently: Hudson and Luckhurst (1969) and Lewis and Morgan (1968). In addition a number of discussions of the general techniques have appeared: Fraenkel (1967); McClachlan (1964); Carrington and Luckhurst (1964).

The first treatment of magnetic resonance relaxation in liquids was due to Bloembergen, Purcell and Pound (1948). Although the original derivation was for nuclear magnetism, the method may also be used in electron paramagnetism. BPP considered the relaxation of protons in solution. The perturbation causing the relaxation was a magnetic dipole interaction which fluctuated in time due to random thermal motions in solution. BPP used time dependent perturbation theory to compute transition probabilities which could be directly related to the relaxation times. However, they were forced to use the correlation function methods of the theory of Brownian motions since the perturbation was random rather than periodic. The correlation functions were related to spectral densities which were then related to relaxation times. Yariv and Louisell (1962) have also applied perturbation theory to linewidths.

More elegant methods for computing relaxation times have since been developed. The best known methods are the linear response theory of Kubo and Tomita (1954), and the relaxation matrix theory of Redfield and of Wangsness and Bloch (Redfield, 1957, 1965; Wangsness and Bloch, 1953; Bloch, 1956, 1957). Both of these methods apply the technique of density matrices to the computation of relaxation times.

Although both methods involve the same assumptions and generally arrive at the same answers, the Kubo and Tomita method has not come into widespread use (Deutch and Oppenheim, 1968). The theory has mainly been applied by Kivelson (1957, 1960).

The relaxation matrix method has been widely used in relaxation theories. In this method the relaxation matrix is computed from the correlation functions derived from the perturbation Hamiltonian. The relaxation times are obtained from the components of the relaxation matrix. The method is discussed in detail in Abragam (1961) and in Slichter (1963). The method has been extended and applied by Feed and Fraenkel (1963).

The additional theories which have appeared, and which are extensions of the relaxation matrix theory, have not yet become popular: Fulton (1964); Argyres and Kelley (1964); Freed (1968); Sillescu and Kivelson (1968).

The procedure for the computation of a linewidth or a relaxation time begins with the assumption of a mechanism or time dependent interaction which could cause relaxation. The next step in the development of the theory is the formulation of a time dependent term (consistent with the mechanism) in the Hamiltonian for the system. The derivation of a mathematically tractable form is perhaps the most difficult part of the theory. The final, though by no means trivial, step is the application of one of general time dependent perturbation methods to compute the relaxation times.

A. Anisotropic g and A Tensors

The relaxation theory of anisotropic systems is probably the most important theory for transition metal complexes with spin 1/2. The essential ideas behind the anisotropic theory were first proposed by McConnell (1956). The basic idea was that the transition metal complex existed as a stable microcrystallite in solution. The complex therefore possessed the same anisotropic spin Hamiltonian which it would possess in the solid state. The microcrystalline complex could tumble in solution due to Brownian motion. The Zeeman interaction, which is orientation dependent for anisotropic systems, is modulated by the rotation of the complex as it undergoes random thermal motions.

This situation is very similar to the dipolar case treated by BPP. McConnell applied the BPP methods to a complex with axial symmetry and arrived at the following result:

$$\frac{1}{T_1} \approx (\Delta g_\beta \, Ho + b \, m_I)^2 \, h^{-2} \, \frac{\tau_c}{1 + 4\pi^2 \, \nu^2 \, \tau_c^{\,2}} \qquad (2.1)$$

where

$$\Delta g = g_\parallel - g_\perp \qquad (2.2)$$

$$b = A_\parallel - A_\perp$$

and $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ are the principal values of the g and A tensors, respectively, H_0, the resonance field corresponding to the microwave frequency, ν_o; m_I, the nuclear spin quantum number; and τ_c, the correlation time characteristic of tumbling in solution. The correlation time, τ_c, can be related to the hydrodynamic radius, r, of the complex and the viscosity, η, of the solution by the Stokes-Einstein equation

$$\tau_c = 4\pi \eta \frac{r^3}{3kT} \qquad (2.3)$$

where k is Boltzmann's constant, and T, the absolute temperature.

Equation 2.1 gives a linewidth with the following characteristics. The linewidths vary with m_I, the nuclear hyperfine quantum number. Secondly, the linewidths vary with the magnetic field. This is reasonable since the Zeeman interaction is proportional to magnetic field. Finally, the linewidths vary directly with the correlation time, or inversely with the temperature. This is opposite to the behavior usually observed in solid state where the temperature must be decreased to narrow the line.

Examination of Eq. 2.1 shows three kinds of terms: a term independent of m_I, a term linear in m_I, and a term quadratic in m_I. The m_I independent term is characteristic of the anisotropy on the g tensor; the quadratic term is related to the anisotropy of the A tensor; and the linear term is a cross term related to both anisotropies. Qualitatively a sample has a strong anisotropy in the A tensor if the spectrum shows a symmetric dependence on m_I, and a strong g tensor anisotropy if the spectrum is not symmetric in m_I.

Later, Kivelson (1960,1964) applied the Kubo and Tomita (1954) method and derived essentially the same result. However, he also showed that the linewidth could be expressed as a sum of secular and nonsecular parts. The secular parts do not contribute to T_1 processes, and T_1 may by estimated by using only the nonsecular parts of the theory.

Wilson and Kivelson (1966a) performed more extensive computations, retaining cross terms which had been neglected in the previous theory. They concluded that the linewidth must be expressed as a cubic polynomial in m_I rather than a quadratic:

$$\frac{1}{T_2} = \alpha' + \alpha'' + \beta m_I + \gamma m_I^2 + \delta m_I^3 \tag{2.4}$$

where α'', the residual width, accounts for contributions from effects not included in the tumbling theory. The coefficients of m_I are given by Eq. 2.5 - 2.8.

$$\begin{aligned}\frac{\alpha'}{\tau_R} = {} & \frac{4}{45}(\Delta\gamma B_o)^2 + \frac{3}{40} b^2 I(I+1) - \frac{1}{30} b \frac{a}{\omega_o} \Delta\gamma\, B_o I(I+1) \\ & + u\,\{\frac{1}{15}(\Delta\gamma B_o)^2 + \frac{7}{40} b^2 I(I+1) - \frac{1}{30} b \frac{a}{\omega_o} \Delta\gamma B_o I(I+1) \\ & - \frac{5}{40} b^2 \frac{a}{\omega_o} I(I+1)\, f\,\} \\ & + \frac{4}{15}(\delta\gamma B_o)^2 + \frac{2}{5} I(I+1)\, c^2 + u[\frac{1}{5}(\delta\gamma B_o)^2 + \frac{14}{15} I(I+1) c^2]\end{aligned} \tag{2.5}$$

$$\begin{aligned}\frac{\beta}{\tau_R} = {} & \frac{4}{15} b\, \Delta\gamma B_o - \frac{8}{45}(\Delta\gamma B_o)^2 \frac{a}{\omega_o} - b^2 \frac{a}{\omega_o}\,[-\frac{1}{20} I(I+1) + \frac{3}{40}] \\ & + u\,\{\frac{1}{5}[b\Delta\gamma B_o - \frac{2}{3}(\Delta\gamma B_o)^2 \frac{a}{\omega_o}(1+f)] - \frac{1}{20} b^2 \frac{a}{\omega_o} \\ & \times [I(I+1) + 1 + 7I(I+1)\, f]\} + \frac{16}{15} c\, \delta\gamma B_o + \frac{4}{5} c\, \delta\gamma B_o\, u\end{aligned} \tag{2.6}$$

$$\begin{aligned}\frac{\gamma}{\tau_R} = {} & \frac{1}{8} b^2 - \frac{7}{30} b \frac{a}{\omega_o} \Delta\gamma B_o \\ & - u\,\{\frac{1}{14} b^2 + \frac{1}{6} b \frac{a}{\omega_o} \Delta\gamma B_o + (\frac{2}{5} b \frac{a}{\omega_o} \Delta\gamma B_o - \frac{5}{40} b^2 \frac{a}{\omega_o}) f\} \\ & + \frac{2}{3} c^2 - \frac{2}{15} c^2 u\end{aligned} \tag{2.7}$$

$$\frac{\delta}{\tau_R} = \frac{1}{20}\, b^2 \,\frac{a}{\omega_o} + \frac{1}{20}\, b^2 \,\frac{a}{\omega_o}\, u\,(1+f) \tag{2.8}$$

where

$$b = \frac{2}{3}\left[A_z - \frac{1}{2}(A_x + A_y)\right] \qquad \Delta\gamma = \beta\Delta g/\hbar$$

$$\Delta g = g_z - \frac{1}{2}(g_x + g_y) \qquad \delta g = \frac{1}{2}(g_x - g_y)$$

$$c = \frac{1}{4}(A_x - A_y) \qquad B_o = \hbar\omega_o/g\beta$$

$$u = 1/(1+\omega_o^2\,\tau_R^2) \qquad \delta\gamma = \beta\delta g/\hbar$$

$$f = \omega_o^2\,\tau_R^2\,u$$

In the axial case all of the terms containing c, or $\delta\gamma$ vanish. Furthermore, we have

$$\begin{aligned} \Delta g &= g_{\parallel} - g_{\perp} \\ b &= A_{\parallel} - A_{\perp} \end{aligned} \tag{2.9}$$

Qualitatively, the linewidth has the same characteristics as the McConnell linewidth. However, the detailed behavior is much more complicated. The coefficients no longer have a simple interpretation in terms of a given anisotropy but include cross terms (however, the major contribution from a given anisotropy to a given coefficient is as discussed above). The temperature dependence of the linewidth is also slightly changed.

These results have also been derived by other workers using the relaxation matrix theory: Hudson and Luckhurst (1969); McClachlan (1964). Sames (1967) has also derived similar results.

B. Spin-Rotation Interactions

As a molecule tumbles in solution, the rotating electron cloud of the molecule produces a magnetic dipole moment. This moment can interact with the nuclear and the electronic spins in the molecule. This interaction can be considered as an interaction of the spin angular momenta with the rotational angular momentum of the molecule. The problem was treated for nuclear relaxation by a number of workers, notably Hubbard (1963).

Hubbard considered molecules with cylindrical symmetry and obtained

$$T_1^{-1} = T_2^{-1} = (2\mathcal{I}kT\ \tau_\omega/3\hbar^2)\ (2\ C_\perp^2 + C_\parallel^2) \tag{2.10}$$

where $C_\parallel$ and $C_\perp$ are the principal values of the spin-rotation interaction tensor; τ_ω, the correlation time characteristic of the spin-rotation interaction, and $\mathcal{I}$, the molecular moment of inertia. The correlation time τ_ω, is not the same as the correlation time for the tumbling process and is given by

$$\tau_\omega = \mathcal{I}/(8\pi r^3\eta) \tag{2.11}$$

where r is the hydrodynamic radius and η the viscosity. The spin-rotation linewidth is then independent of magnetic field and proportional to T/η. In contrast the anisotropic contribution of Eq. 2.1 is usually proportional to η/T.

The theory is difficult to apply in this form and was extended by Atkins and Kivelson (1966) for the problem in EPR. They related the electron spin-rotation tensor, C, to the g tensor and derived a linewidth

$$T_2^{-1} = (12\ \pi r^3)^{-1}\ (\Delta g_\parallel^2 + 2\Delta g_\perp^2)\ kT/\eta \tag{2.12}$$

where

$$\begin{aligned} \Delta g_\parallel &= g_\parallel - 2.0023 \\ \Delta g_\perp &= g_\perp - 2.0023 \end{aligned} \tag{2.13}$$

The linewidth is now independent of the moment of inertia of the molecule. The spin-rotation mechanism should be distinguished from the rotational-spin-orbit mechanism which will be discussed later.

Wilson and Kivelson (1966c) and McClung and Kivelson (1968) have shown that in many cases the hydrodynamic radius, r, must be replaced by

$$r = \kappa r_o \qquad (2.14)$$

where κ is a constant which depends upon the solvent and its interaction with the solute, and r_o is a radius determined by other measurements or by calculation of the molecular dimensions. The radius, r_o, is a constant characteristic of the molecule and may be determined from translational diffusion measurements. The parameter, κ, is related to the anisotropy of the intermolecular potential energy between the solvent and the solute, and is expected to be small for an isotropic interaction. It is expected to be large, i.e., $\kappa \sim 1$, for H_2O and hydrogen bonded solutes. The usual Stokes-Einstein equation should be adequate in aqueous solution with solutes(complexes) which are hydrogen bonded.

C. Al'tshuler and Valiev Mechanism

Al'tshuler and Valiev (1958) have proposed a relaxation mechanism for solutions which should be applicable to isotropic systems as well as to anisotropic systems. In contrast to the McConnell tumbling mechanism which is produced through rotational modulation of the spin Hamiltonian, the Al'tshuler and Valiev mechanism is produced by vibrational modulation.

In accord with the Van Vleck (1939) development for solid state, the complex is no longer regarded as a rigid molecule which can only rotate; the ligands around the central ion are permitted to vibrate. As a result the crystalline potential field of the complex, which is determined by the configuration of the ligands, is modulated. Spin relaxation may be produced through spin-orbit interaction.

The vibrational modulation is introduced into the spin Hamiltonian through the potential energy which is expressed as an expansion in the normal coordinates of an octahedral complex (Van Vleck, 1939)

$$\mathcal{H}' = \sum_{i=2}^{6} V^i Q_i \tag{2.15}$$

where Q_i is the ith symmetry coordinate of the octahedron, and $V^i = \partial V/\partial Q$. The perturbation is then independent of the anisotropy of the complex. The vibrations of the complex are stochastic since the ligands are influenced by the Brownian motions of the surrounding particles. Al'tshuler and Valiev assume an exponential form for the correlation function and derive a transition probability A_{lk} between energy levels l and k

$$A_{lk} = \frac{\overline{Q^2}}{\hbar^2} \sum_i |V^i_{lk}|^2 \frac{2\,\tau_c}{1 + \omega_{lk}^2 \tau_c^2} \tag{2.16}$$

$\overline{Q^2}$ is a kind of average measure for the amplitude of the normal vibrations. Al'tshuler and Valiev assume that the mean square amplitude of the oscillator is given by

$$\langle Q^2 \rangle = (\hbar/2m\,\omega_o) \coth (\hbar\omega_o/2kT) \tag{2.17}$$

where ω_o is an average frequency for the vibration and m is a mass close to the mass of the complex. To find the temperature dependence of A_{lk} they further assume that the correlation time, τ_c, is inversely proportional to the square root of the absolute temperature. Hence, they show the temperature dependence of the transition probability to be

$$A_{1k} \sim T^{-1/2} \coth (\hbar\omega_o/2kT) \quad (2.18)$$

for

$$\tau_c^2 \omega_{1k}^2 << 1$$

and

$$A_{1k} \sim T^{1/2} \coth (\hbar\omega_o/2kT) \quad (2.19)$$

for

$$\tau_c^2 \omega_{1k}^2 >> 1.$$

Hayes (1961) reconsidered the Al'tshuler and Valiev theory and indicates that two of the assumptions of the theory are incorrect. First, the spectral density for the random variable is not normalized, but should be since the total power in the system should not change with the correlation time. Furthermore, the mean square value of Q^2 is correct only at frequencies far removed from the resonant frequency.

In light of these criticisms Hayes rederived the result for the result for the transition probability with this mechanism. He concluded that the transition probability should be directly proportional to temperature. However, he comments that the proportionality constant would be very difficult to determine.

In a later work Valiev and Zaripov (1962) reconsidered the original theory. They indicate that a second term, quadratic in the normal coordinates, should be added to the perturbation. Furthermore, the quadratic term should be more effective than the linear term in producing relaxation. The original theory produced reasonable results because of the form assumed for the correlation functions. Valiev and Zaripov revise the correlation functions in accord with Hayes. Their result for the transition probability cannot be presented in a simple form. However, the temperature dependence can be shown to be

$$T_1^{-1} \approx \coth^2\left(\frac{\hbar\omega_o}{2kT}\right) \frac{\tau_c}{1 + \omega_{1k}^2 \ \tau_c^2} \tag{2.20}$$

The temperature dependence is similar to the McConnell temperature dependence until $T \approx \hbar\omega_o/2k$. For $T \gg \hbar\omega_o/2k, T_1^{-1}$ may in some cases increase with increasing temperature.

D. Inversion Mechanism

Spencer (1965) has considered a process which is applicable to complexes which have a number of equivalent ground state configurations, such as Jahn-Teller systems. In particular, an octahedral complex such as $Cu(H_2O)_6^{2+}$ may distort tetragonally along either of the equivalent x, y, and z axes. The result of passage from distortion along one axis to distortion along another axis is equivalent to a 90° rotation of the complex. However, unlike the tumbling mechanism, the complex does not pass continually through all possible orientations. The complex "inverts" or "jumps" from one orientation to another.

Spencer describes this process in the spin Hamiltonian by defining special delta functions. The delta functions are one or zero depending upon the orientation. Performing a McConnell type of derivation, Spencer shows that the linewidth contribution, $1/T_2'$, from this mechanism is

$$\frac{1}{T_2'} = \frac{32\pi}{9h^2} \left(\Delta g \ \beta H_o + b \ m_I\right)^2 \ \tau_i$$

where τ_i is the correlation time for inversion, and the other terms have their usual meanings. The contribution from this mechanism should be larger than the tumbling mechanism, but both mechanisms should have the same kind of dependence on field and m_I. However, this mechanism should have very little contribution to T_1 processes, unlike the tumbling process which has a strong contribution. Spencer does not discuss a temperature dependence for this mechanism. However, we expect $1/T_2'$ to be proportional to η/T.

E. Electric Field Fluctuation Mechanisms

Kivelson (1966) has considered a number of relaxation mechanisms which he calls electric field fluctuation (eff) mechanisms. In these mechanisms the crystal field of the complex is modulated by vibrations of collisions with surrounding molecules. Spin relaxation occurs through spin-orbit coupling. Among the eff mechanisms are the vibrational spin-orbit, the rotational spin-orbit, the Van Vleck Direct, the Van Vleck Raman, and the Orbach processes.

Kivelson and Collins (1962) originally considered the vibrational spin-orbit and the rotational spin-orbit processes. The rotational spin-orbit process which is an Orbach type of process is to be distinguished from the spin rotational interaction described above. Relaxation by the rotational spin-orbit process occurs through an excited electronic state in contrast to the spin rotation interaction which does not involve excited states. Kivelson and Collins show that the contribution to the linewidth from this mechanism is given by

$$T_2^{-1}\,(\mathrm{RSO}) = 4/3 \sum_n{}' \sum_\alpha |\langle 0|\, L_\alpha \,|\, n\rangle|^2 \,(\lambda/\Delta_{on})^2 \tau_r^{-1} \qquad (2.22)$$

where λ is the spin-orbit coupling constant, Δ_{on} the frequency of an electronic transition from the ground to the n^{th} state, τ_R the rotational correlation time, and $\langle 0|\, L_\alpha |n\rangle$ the matrix elements for the orbital angular momentum operator L_α. They compare this to the contribution from the tumbling mechanism and conclude that this is much smaller than the tumbing mechanism contribution. This mechanism can then be neglected.

The Van Vleck Direct, the Van Vleck Raman, and the Orbach processes are analogous to the solid state processes for which they were named. The direct process is a one phonon process and the Raman process is a two phonon process involving a virtual excited state. The Orbach process is a two phonon process involving an actual excited state.

The Orbach process, discussed by Kivelson (1966), was called the vibrational spin-orbit process by Kivelson and Collins (1962). The perturbation in the process is not due to the molecular normal coordinates, but rather to the lattice or liquid modes, that is, the fluctuations of the intermolecular coordinates in liquids. Kivelson considers the molecular normal coordinates only in a direct vibrational process. His results indicate that the contribution from the vibrational process is negligible. Atkins and Kivelson (1966) also consider the effect of molecular normal coordinates in direct, Orbach, and Raman types of processes. They indicate that the linewidth contribution is negligible.

Kivelson has computed the contribution of the Orbach process in the limit $\delta_{on}\ \tau_c >> 1$ to be

$$T_1^{-1} = T_2^{-1} = 16\,(\lambda/\Delta)^2 \left(\frac{\phi' g_o}{\Delta\, r_o}\right)^2 \left(\frac{\Delta}{\delta_{on}}\right)^2 \frac{\tau_c^{-1}}{[\exp(\hbar\,\delta_{on}/kT)-1]} \tag{2.23}$$

where Δ is the energy from the ground orbital state to the lowest excited orbital state (connected by spin-orbit coupling), τ_c the correlation time characteristic of the eff process, δ_{on} the energy of the lowest excited electronic state above the ground state. The term, $\phi' q_o / r_o$, is the measure of the time dependent electric field potential (Lewis and Morgan, 1968) with q_o a typical amplitude for a lattice (liquid) modes, r_o a characteristic intermolecular distance, and ϕ' a measure of the change in electric field with respect to the lattice mode. The Orbach linewidth contribution which depends on the phonon spectrum at a frequency not directly related to the EPR transition in independent of the applied field. Kivelson also indicates that the very similar process suggested by Al'tshuler and Valiev (1958) does not appear to give spin relaxation.

The contribution of the Van Vleck direct process to the linewidth is given by

$$T_1^{-1} = T_2^{-1} = 64\ (\lambda/\Delta)^2 \left(\frac{\phi' q_o}{\Delta r_o}\right)^2 \frac{(\omega_o \tau_c)^2\ \tau_c^{-1}}{1 + \omega_o^2\ \tau_c^2} \qquad (2.24)$$

where ω_o is the frequency of the spin transition. If $\omega_o^2\ \tau_c^2 << 1$ the the linewidth contribution is proportional to the applied field squared wh whereas if $\omega_o^2\ \tau_c^2 >> 1$, it is independent of the applied field.

Kivelson considered the linewidth contribution from both a first order Raman process and a second order Raman process. The first order process is less important than the second order process. The contribution from the second order process under the condition $\omega_o^2\ \tau_c^2 << 1$ is given by

$$T_1^{-1} = T_2^{-1} = 32\ (\lambda/\Delta)^2 \left(\frac{\phi' q_o}{\Delta r_o}\right)^4 \tau_c^{-1} \qquad (2.25)$$

This process is independent of the applied field.

However, in the case of a symmetric or nearly symmetric molecule the contribution from the Orbach process could be quite significant. The contributions from the direct and the Raman processes seem to be quite small.

III. VANADYL LINEWIDTHS

A. Introduction

The EPR spectrum of the oxovanadium (IV) ion (vanadyl ion)* in aqueous solution has been known for many years. It was first reported by Garif'yanov and Kozyrev (1954) in Russia and by Pake and Sands (1955) in this country. The spectrum exhibited eight hyperfine lines arising from an interaction with the nuclear spin I=7/2 of the vanadium-51 nucleus. The interesting feature of the spectrum was that the linewidths varied with the nuclear quantum number, m_I. The lines also narrowed as the temperature was increased.

The Kivelson (1957, 1960) extension of the McConnell (1956) theory was applied to explain the linewidths. The theory has been found to be quite successful in explaining the linewidths in spin 1/2 complexes and many complexes with vanadyl are well characterized by the Kivelson theory. However, although the vanadyl system is now used as a prime example of the success of the McConnell mechanism, the pentaquo-coordinated vanadyl ion itself has been very little studied (Lewis and Morgan, 1968).

The first confirmation of the Kivelson theory for the vanadyl system was reported by Rogers and Pake (1960). These workers measured the EPR spectra for aqueous solutions of the vanadyl ion at 9.25 GHz (X-band) and at 24.3 GHz (K-band). Using the X-band spectrum they determined the coefficients of the Kivelson linewidth polynomial which they wrote as

$$\frac{1}{T_2} = \pi \sqrt{3}\,(\alpha_1 + \alpha_2 m_I + \alpha_3\ m_I^2) \qquad (3.1)$$

*Strictly, vanadyl (IV)ion (Selbin, 1965). In this work the term vanadyl will be used to represent vanadyl (IV), VO^{2+}.

where the coefficients are given by

$$\begin{aligned} \alpha_1 &= \tau_c \{7/45\ (\Delta\gamma B_o)^2 + 63\ b^2/16\} + K \\ \alpha_2 &= -\tau_c \{7/15\ b\ \Delta\gamma B_o\} \\ \alpha_3 &= \tau_c \{b^2/10\} \end{aligned} \tag{3.2}$$

In these expressions K is a constant accounting for linewidth not explained by the theory. The other variables are as defined previously. From their X-band measurements Rogers and Pake predicted the K-band linewidths. The predicted widths were in relatively good agreement with the measured widths.

However, this work was unable to provide a quantitative check of the Kivelson theory. The authors lacked the anisotropic spin Hamiltonian parameters necessary to compute the Kivelson parameters. They also did not have a value for the correlation time, and neglected higher order terms in the Kivelson theory.

In a later work, McCain (1966, 1967) extended the study of the vanadyl system. He determined the anisotropic spin Hamiltonian parameters for the vanadyl ion from a glass spectrum. He also measured the solution EPR spectra at 3.12 GHz (S-band) as well as at 9.07 GHz. From the spectra he determined experimental values for the Kivelson coefficients in a polynomial which he wrote as*

$$\frac{1}{T_{2e}} = \alpha_2' + \alpha_2 + \beta_2 m + \gamma_2 m^2 + \delta_2 m^3 \tag{3.3}$$

He also computed theoretical values for these coefficients. However, he was forced to assume a correlation time for his computations. His comparisons indicated reasonable agreement between the theoretical and experimental terms for all the parameters except the alpha term. His

*The subscript e emphasizes that this is an electronic as opposed to the nuclear linewidth.

results indicated a 30% discrepancy at X-band and an even larger discrepancy at S-band. Some of this error could be attributed to the uncertainty in the correlation time and some to terms which were neglected in the theory. Another mechanism, the spin-rotation mechanism, could also account for part of the discrepancy.

Lewis and Morgan (1968) later reconsidered these results. They assumed a correlation time and computed both the tumbling and spin-rotation contributions to alpha. Their estimate of 9.4 gauss is 3.3 gauss less than the value of alpha which McCain observed. They suggested that the residual width was due to superhyperfine interaction with the protons of the water ligands. They predict a hyperfine coupling constant of about 2.2 G.

However, in another study Garif'yanov, et al. (Garif'yanov, Kozyrev, Timerov and Usacheva, 1962b) studied the EPR of dilute vanadyl chloride solutions at different temperatures and viscosities. They concluded from their data that, although the McConnell mechanism contributed to the linewidth of vanadyl solutions, it was not the dominant relaxation mechanism. Instead, they suggested that the Al'tshuler and Valiev (1958) mechanism was the most probable line broadening mechanism.

The present study was begun to clarify the situation in the vanadyl system. Moreover, McCain (1967) had also determined relative T_{1e} values for the S-band spectrum using an ingenious saturation method. Using the nonsecular parts of the Kivelson theory he also computed theoretical values for the relative T_{1e}'s. His comparisons indicated that the theory was not perfect. However, he did not have a good value for the correlation time. These results are reconsidered in this work.

B. Experimental Methods

1. Samples

All aqueous solution experiments were performed using samples of vanadyl perchlorate which were made in one of the following methods. In the first method, due to Selbin and Holmes (1962), a solution of vanadyl sulfate was treated with an equivalent amount of a solution of sodium hydroxide. The precipitate of vanadyl hydroxide was filtered and then dissolved in the necessary amount of perchloric acid. The solution of vanadyl perchlorate was then adjusted to the proper concentration.

In the second method vanadyl perchlorate was prepared by ion exchange using the following procedure (Lee et. al., 1968). An exchange column was loaded with a slurry of a cation exchange resin (AG50W-X2, 200-400 mesh, hydrogen form) in 2 M HCl. The column was then rinsed with distilled water to remove acid. A solution of vanadyl sulfate was then added to the column and the column was rinsed to remove sulfuric acid. A solution of barium perchlorate was used to elute the vanadyl perchlorate from the column. The separation is quite clean and may easily be followed by observing the blue color characteristic of the vanadyl ion move down the column.

In all cases the solutions were adjusted to a concentration between .01 and .02 F.* The solutions were made slightly acidic with perchloric acid to inhibit the decomposition of the vanadyl perchlorate. Both methods of preparation were found to be satisfactory for this work.

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*Formula weights per liter.

Solutions of vanadyl ion in D_2O were made by evaporating a stock solution of aqueous vanadyl ion almost to dryness and then dissolving the residue in heavy water. This process was repeated several times to insure a completely deuterated solution. The solutions were never evaporated completely to dryness in order to prevent decomposition from occurring. Deuterated perchloric acid, used in some of the experiments, was obtained in a similar manner.

2. Apparatus

EPR spectra were recorded using a standard Varian V-4502 homodyne EPR spectrometer operating at 9.2 GHz. Samples for linewidth studies were held in a V-4548 aqueous solution sample cell. This cell is specially designed to confine the sample to a thin plane, thus eliminating line distortion problems which could arise due to solution conductivity. The sample temperature was controlled with a V-4557 Variable Temperature Accessory which controlled the temperature of a stream of nitrogen gas. Temperature was measured with a copper-constantan thermocouple which was placed in the gas stream before or after each experiment in the same position as the sample.

The spectra were digitized using a Honeywell-EI Model S6114 Automatic Data Logging System (see Fig. 1). This system consists of a Hewlett-Packard Model 5245L electronic counter, a Honeywell-EI Model 630S multimeter, a Honeywell-EI Model 825 Output Control Unit, and a Kennedy Model 1400 incremental magnetic tape recorder.

The multimeter (digital voltmeter) measures the EPR signal from the 100 KHz phase detector. The electronic counter measures the magnetic field. In the Varian spectrometer a voltage proportional to the magnetic

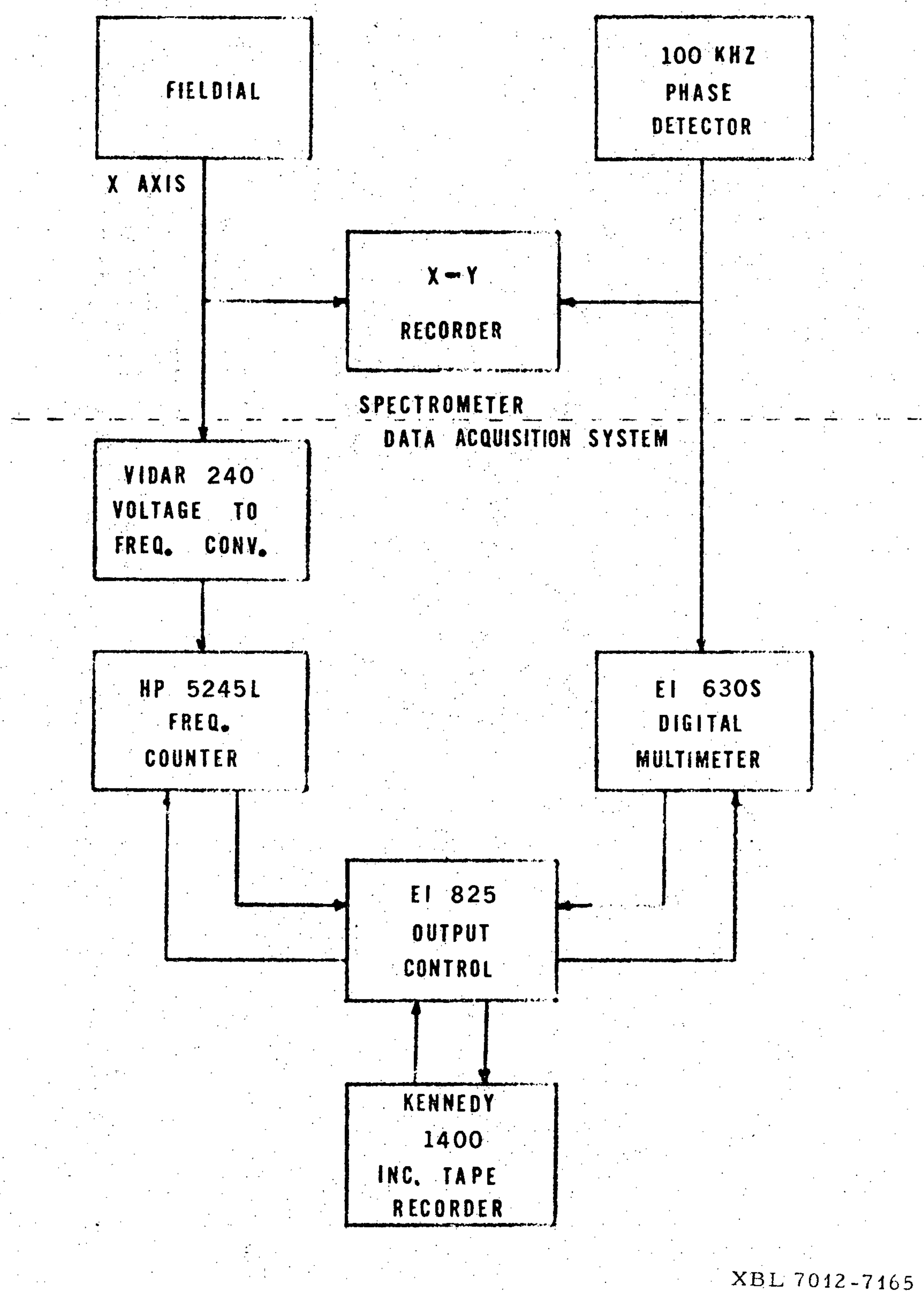


Fig. 1. Schematic of data acquisition system.

field is obtained from the x-axis retransmitting potentiometer of the Fieldial. This voltage, which originally varied from 0 to 15 volts in order to drive an x-y recorder, was changed to vary from 0 to 10 volts to drive a Vidar Model 240 voltage-to-frequency converter. The electronic counter measures the output from the Vidar and obtains a frequency measurement which can be related to the magnetic field.

The data logging system operates independently of the spectrometer and records the spectrum as a normal scan is in progress. The process of measurement involves simultaneously measuring the EPR signal and the magnetic field coordinates and then encoding and recording the measurement on magnetic tape. The system is capable of making measurements at the rate of 6 to 8 points per second. A digitized spectrum of 2400 points for a normal five minute scan can be routinely acquired with this system.

A measured point consists of seven digits from the frequency counter and five digits plus a sign from the digital voltmeter. The output control unit adds a "word mark" to form a 14 character word for the measurement. The output unit records the data in 80 word blocks separated by record gaps on the tape. This is, unfortunately, not compatible with the FORTRAN system on most computation centers. The data tape is preprocessed with a special program, SUMTAP (see appendix), before the actual analysis is performed. The SUMTAP program puts the data into a form compatible with the FORTRAN system, smooths the data to reduce noise, and reduces the number of data points in the spectrum for convenience in handling by the analysis programs. SUMTAP can also average several spectra to improve signal to noise.

The magnetic field is calibrated by measuring both the magnetic field and the Vidar frequency at several points in the sweep. The magnetic field was measured with a marginal oscillator (Harvey-Wells 0-502) equipped with a proton probe. The magnetic field may be computed at any point from the Vidar frequency by using a quadratic interpolation equation which is fit to the calibration points. The microwave frequency was measured with an HP 5245L frequency counter equipped with a HP 5255A 3-12.4 GHz frequency converter.

C. Discussion and Results

1. Spectra

Before a proper treatment of linewidths can be made, the anisotropic spin Hamiltonian parameters, which are utilized in the relaxation theories, must be known. Unfortunately, it is not possible to determine anisotropic parameters from solution (isotropic) spectra, and these parameters must be determined from solid state measurements. There is, however, no guarantee that the complex which exists in a crystal lattice is the same complex in solution. Distortions often occur in a crystal lattice which do not occur in solution. Hence, it is not clear that the anisotropic parameters determined from a crystal lattice bear a close relationship to those for a complex in solution, but these are the best parameters which are available.

Although solid state parameters are best determined from single crystal measurements, single crystals are not readily available for many transition metal complexes. Furthermore, it is usually necessary to obtain a crystal with the paramagnetic species diluted in a diamagnetic host lattice in order to avoid dipole-dipole broadening effects. In some cases, the parameters may be determined from polycrystalline or glass spectra. This method was originally used by Sands (1955).

The methods for analyzing polycrystalline spectra have been well developed (Blinder, 1960; Gersmann and Swalen, 1962; Ibers and Swalen, 1962; Johnston and Hecht, 1965; Kneubuhl, 1960; Neiman and Kivelson, 1961; Vanngard and Aasa, 1963). The spectrum of a polycrystalline sample consists of an envelope of absorption lines rather than distinct single lines. The anisotropic parameters, for example, $g_{\parallel}$ and $g_{\perp}$ in an axial case, are determined from the extrema of the absorption envelope.

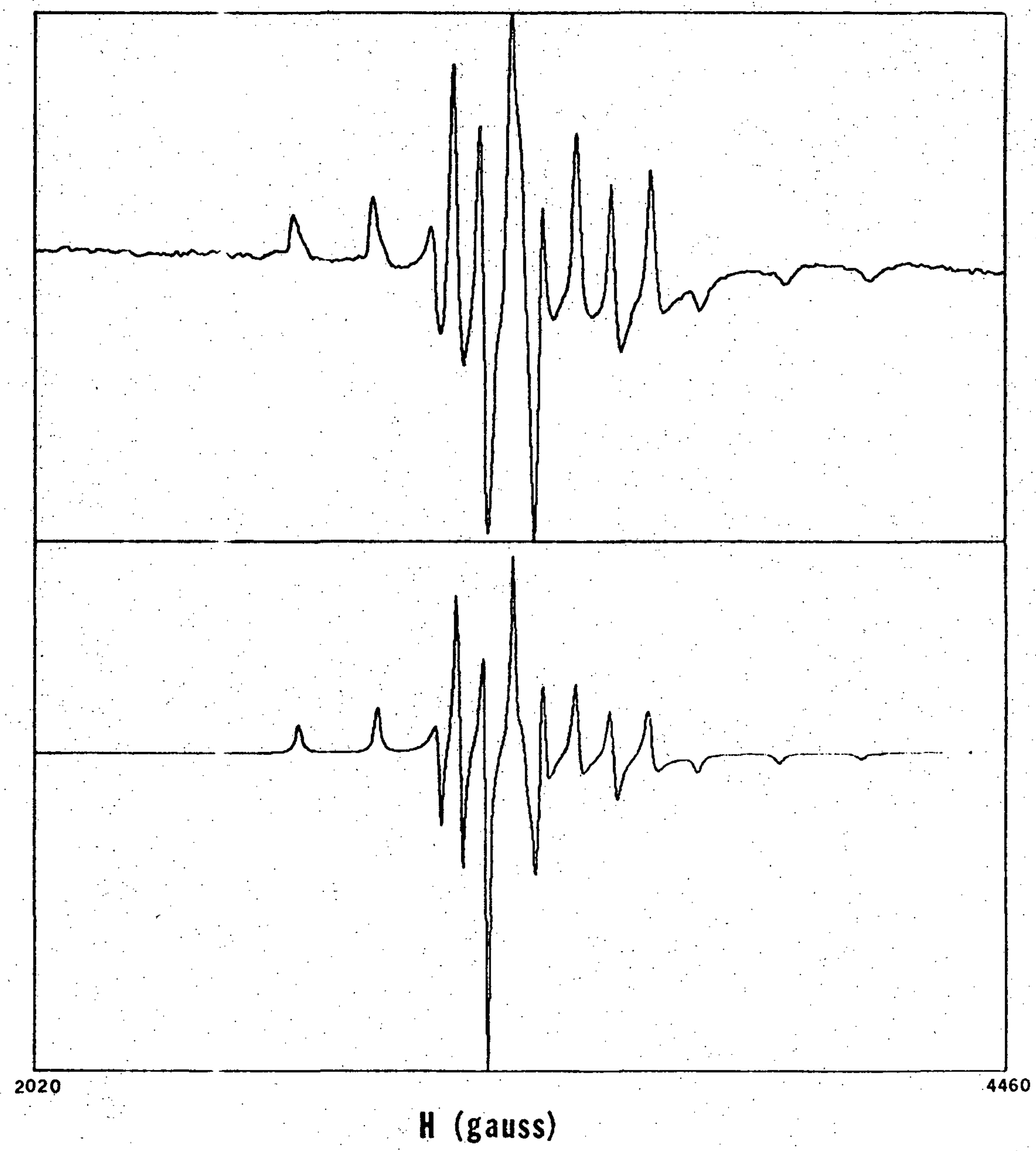
If hyperfine structure is present, the spectrum can be quite difficult to assign. This is especially true if the parameters are such that the spectral features are severely overlapped. In these cases a detailed study of the lineshape is useful. A digital computer can be used to simulate the theoretical absorption spectrum. The spectral parameters may be adjusted until satisfactory agreement between the theoretical and experimental spectrum is obtained. The parameters for quite complex spectra can be determined by this technique.

The major problem with polycrystalline spectra seems to be the production of a usable glass. Frozen aqueous solutions are not suitable due to aggregation of the solute and dipolar broadening (Ross, 1965). It is usually necessary to use solvent mixtures in order to obtain a useful glass medium and many such mixtures have been developed (Smith, et al., 1962). These media have an additional problem in that the solvent may complex with the solute. Spencer (1965) has developed a technique of using 5.26 F perchloric acid as a glass medium. A solution of the transition metal complex in perchloric acid can be quick frozen to near liquid nitrogen temperature to obtain an excellent glass. The advantage of the perchloric acid medium is that the perchlorate anion does not appear to form complexes with transition metals.

TABLE I Anisotropic Magnetic Parameters for Vanadyl

Solute/Solvent	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{*}$	$A_{\perp}^{*}$	Reference
$VOCl_2$/Methanol	1.92	1.98	190	82	Garif'yanov and Usacheva (1964)
$VOSO_4$/5.26F $HClO_4$	1.9312	1.9778	205.4	76.5	McCair (1967)
$VO(ClO_4)_2$/5.26F $HClO_4$	1.9311	1.9785	203.3	75.8	This work

*Coupling constants in gauss



XBL 7012-7167

Fig. 2. $VO(H_2O)_5^{2+}$ glass spectrum. Upper spectrum is experimental; lower spectrum is simulation.

The anisotropic parameters for $VO(H_2O)_5^{2+}$ have been determined from spectra of perchloric acid glasses. The glass spectra were analyzed by spectrum simulation with the method of Vanngard and Aasa (1963) (see Fig. 2). The vanadyl parameters are presented in Table I with those determined by other workers for comparison.

The EPR spectra for vanadyl ions in solution were measured at X band at temperatures between -15 and 100°C in order to determine the linewidths and the isotropic spin Hamiltonian parameters. The digitized spectra were analyzed by a least squares fitting procedure with the program FITESR which is described in the appendix (Bauder and Myers, 1968). The eight line vanadyl spectrum may be completely described with eleven parameters consisting of the spectrum center, the intensity, the coupling constant, and eight linewidths. Very good values for these parameters are obtained from the least squares fitting procedure. Two parameters to account for baseline offset and baseline drift are also used. An example of the fit to a vanadyl spectrum is shown in Fig. 3. The experimental data are plotted as the crosses and the fitted curve as a continuous line. The bottom curve (error curve) is the difference between the theoretical and experimental curves, and is useful for judging whether the fit has properly converged.

The vanadyl g and A value vary as a function of temperature as shown in Figs. 4 and 5. This variation, which is similar to that observed for vanadyl acetylacetonate, is thought to be due to changes in solvation and bonding (Wilson and Kivelson, 1966a). Indeed, the magnitudes of these parameters change in opposite directions as would be expected from bonding theories. Additional mechanisms are mentioned later in the discussion of

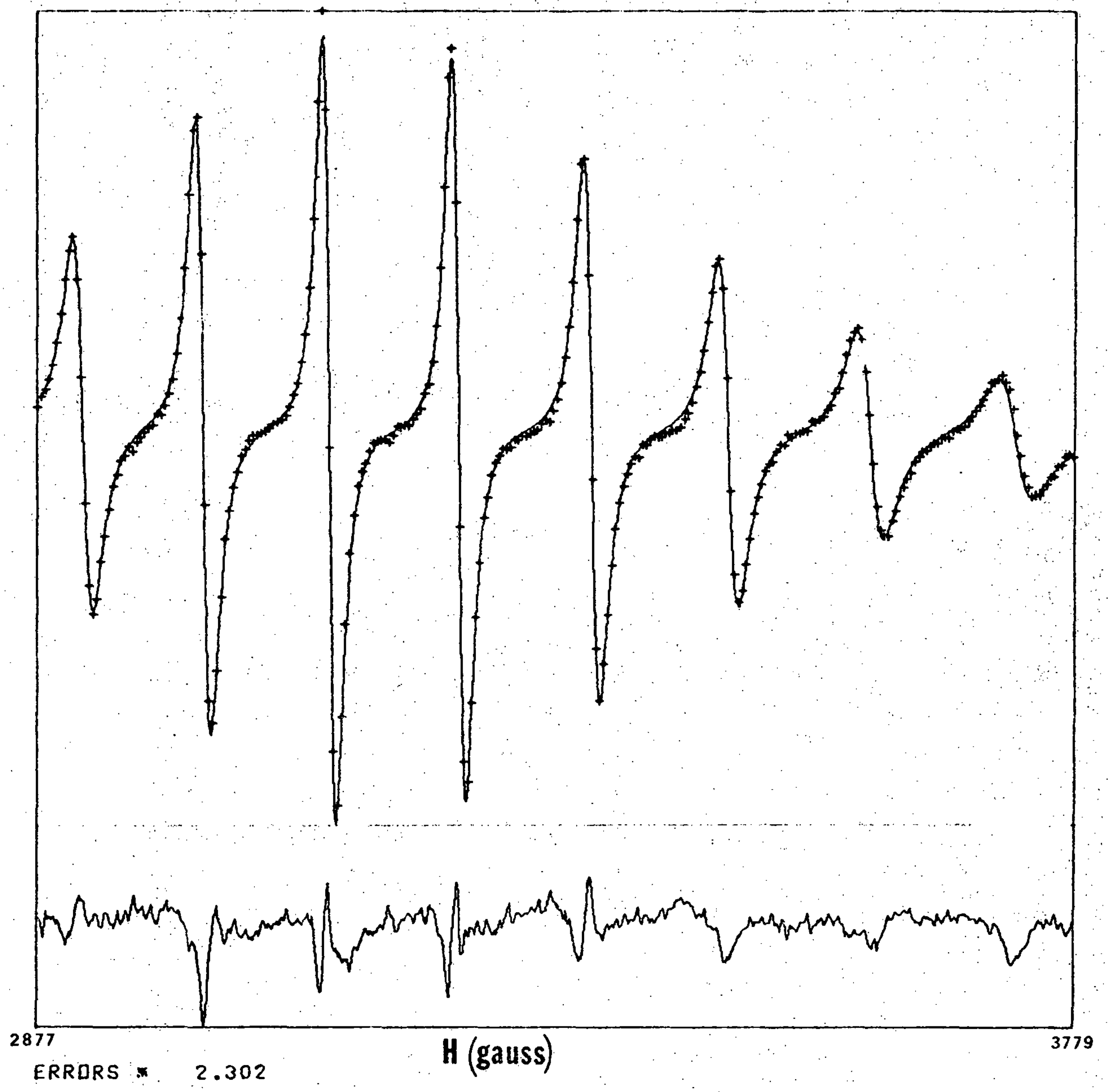


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Fig. 3. Example of fit to solution spectrum of $VO(H_2O)_5^{2+}$. The crosses are the experimental points. The continuous line is the theoretical fit to the data. The lower curve is the difference between the theoretical and experimental curves and has a scale expansion of 2.3.

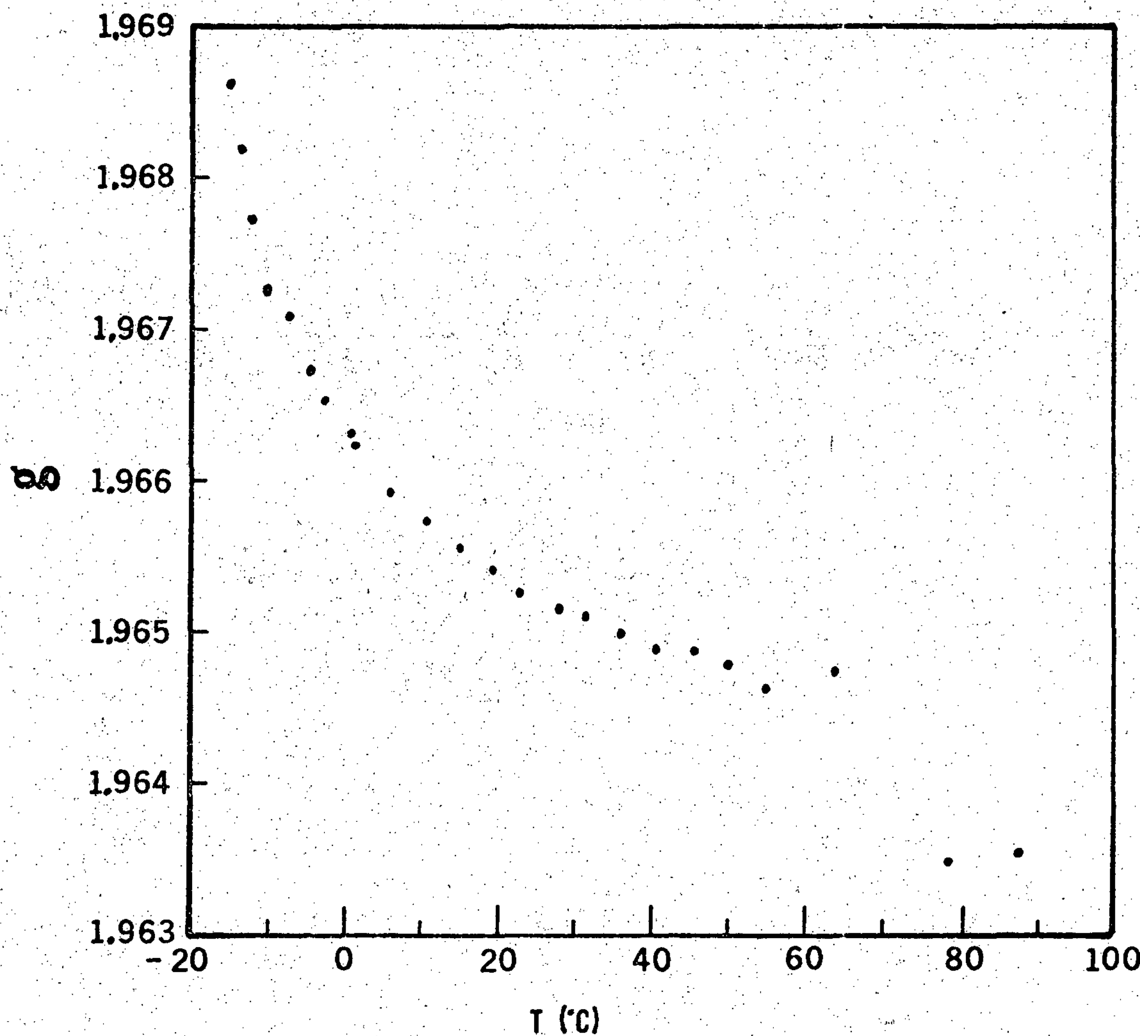

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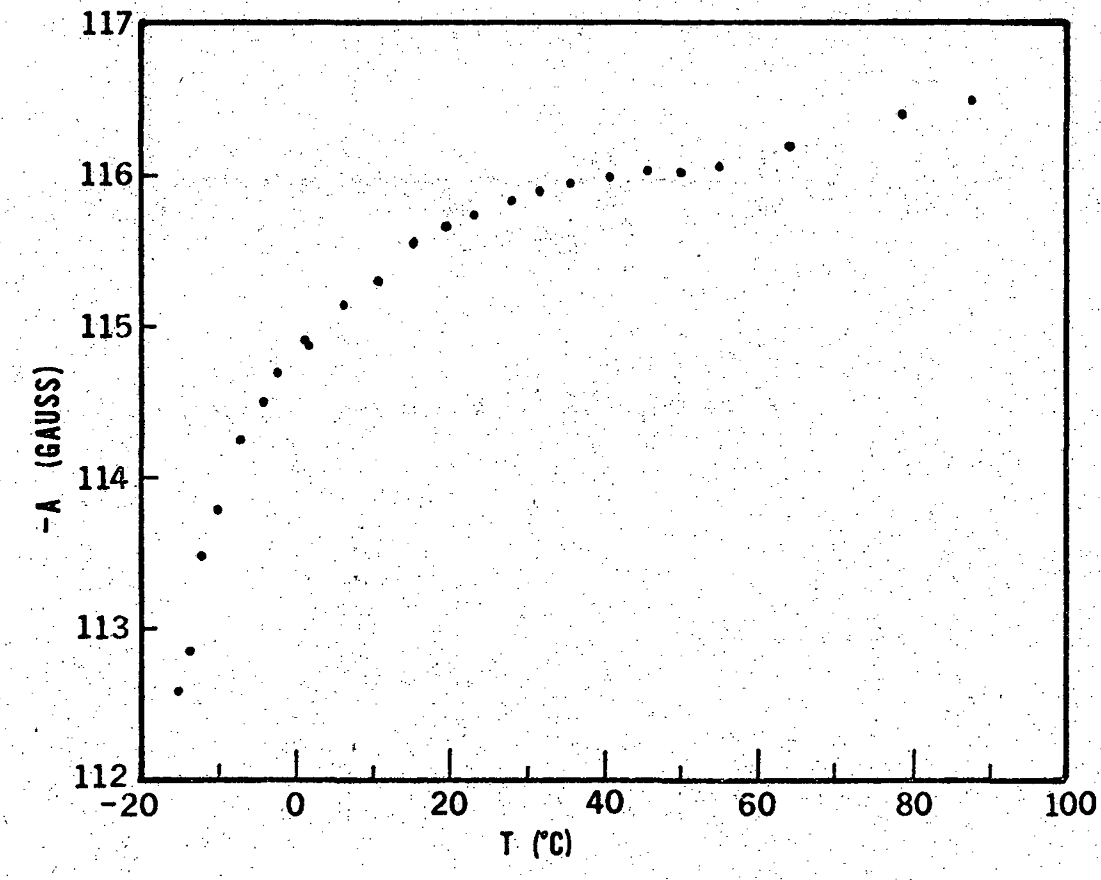
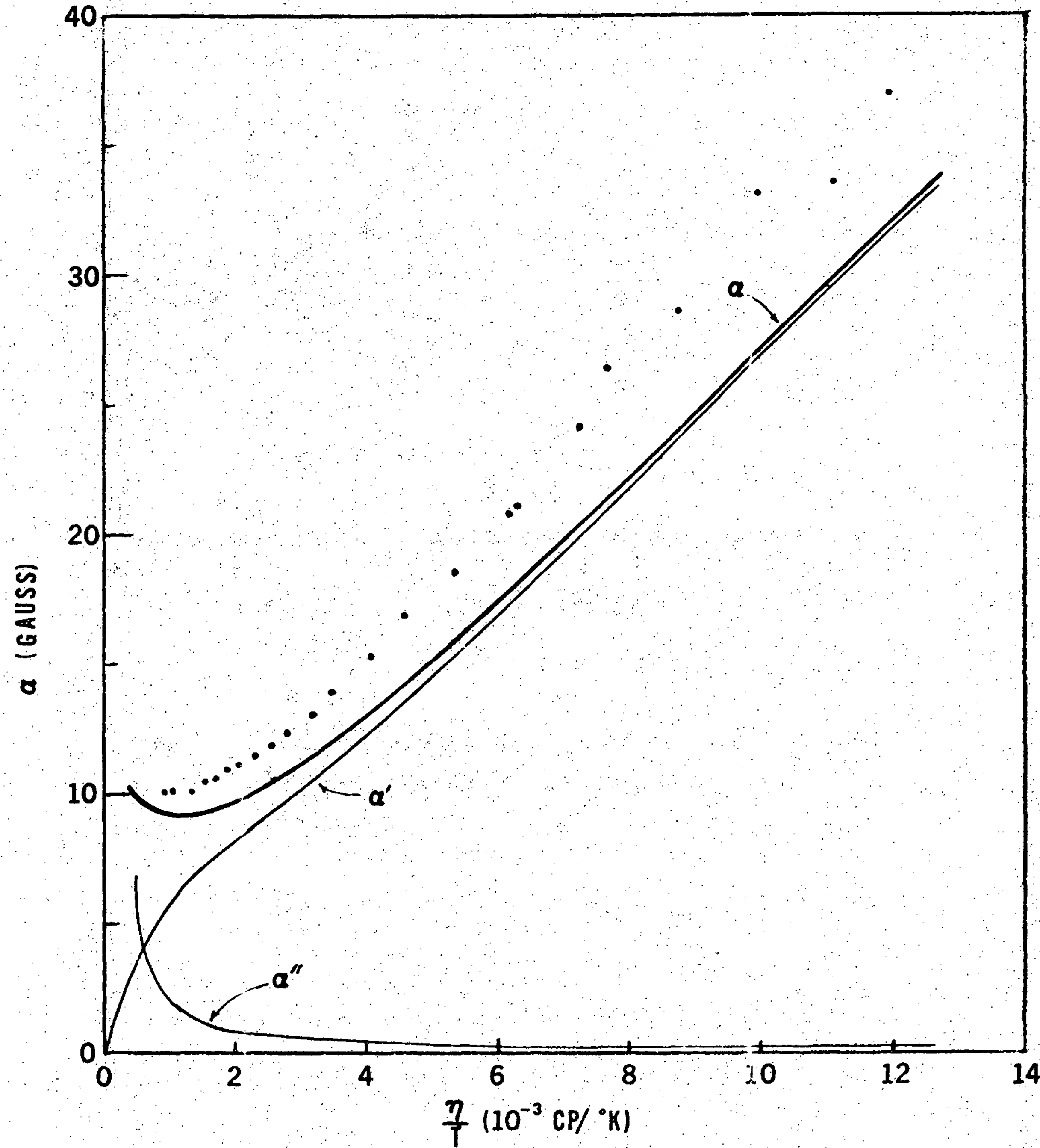
Fig. 4 g vs. T for $VO(H_2O)_5^{2+}$.



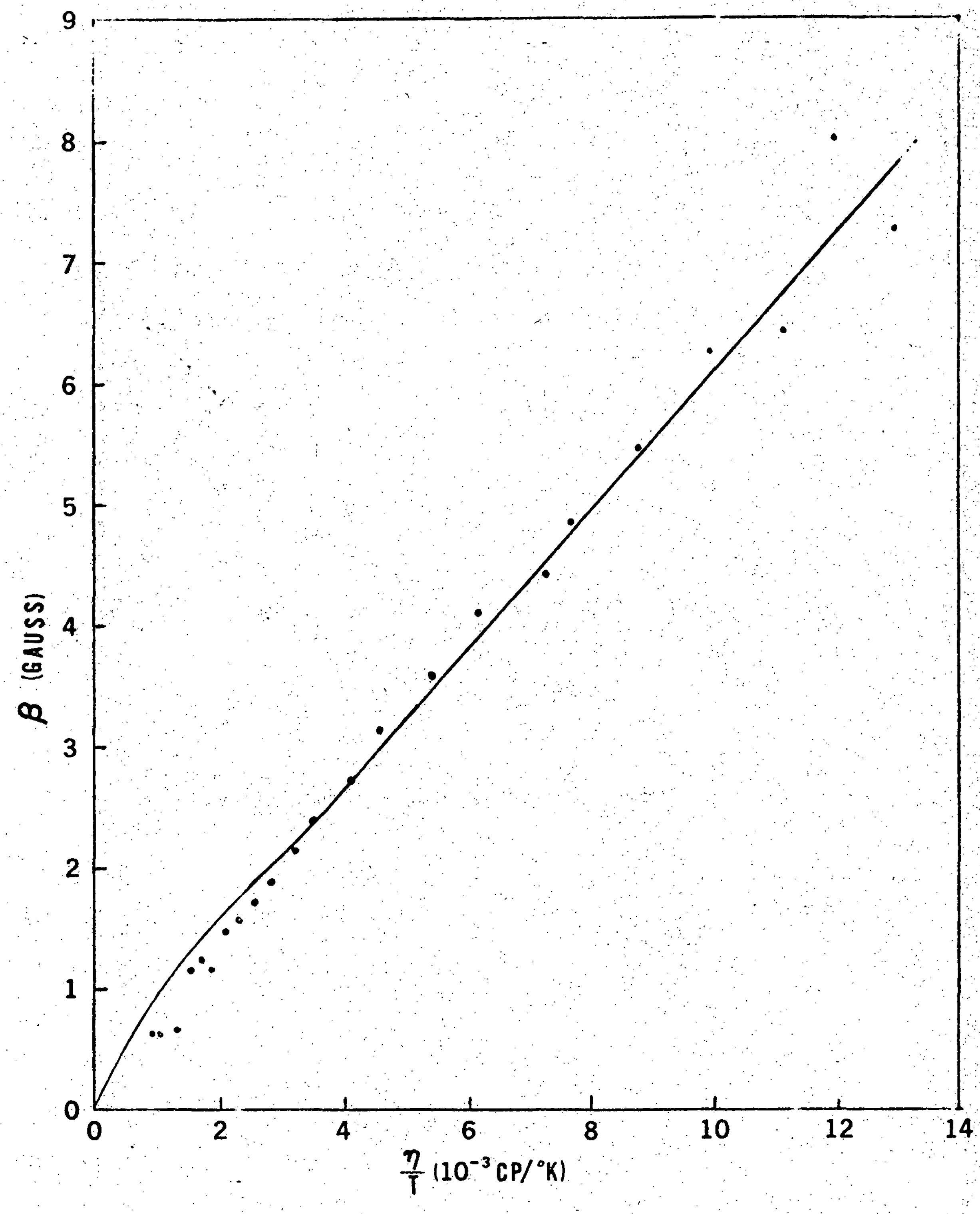
XBL 7012-7348

Fig. 5. -A vs. T for $VO(H_2O)_5^{2+}$.



XBL 7012-7342

Fig. 6. Alpha parameter vs η/T for $VO(H_2O)_5^{2+}$. Points are experimental data continuous; line is theoretical.



XBL 7012-7341

Fig. 7. Beta parameter vs. η/T for $VO(H_2O)_5^{2+}$.

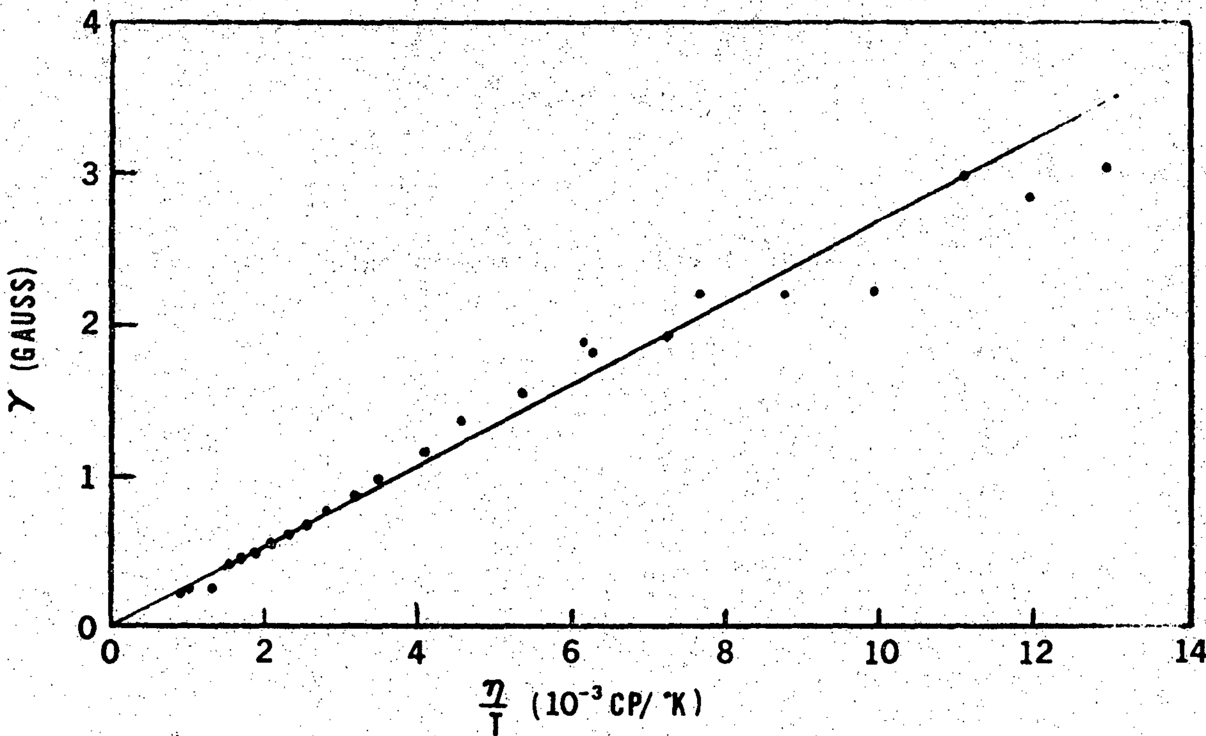


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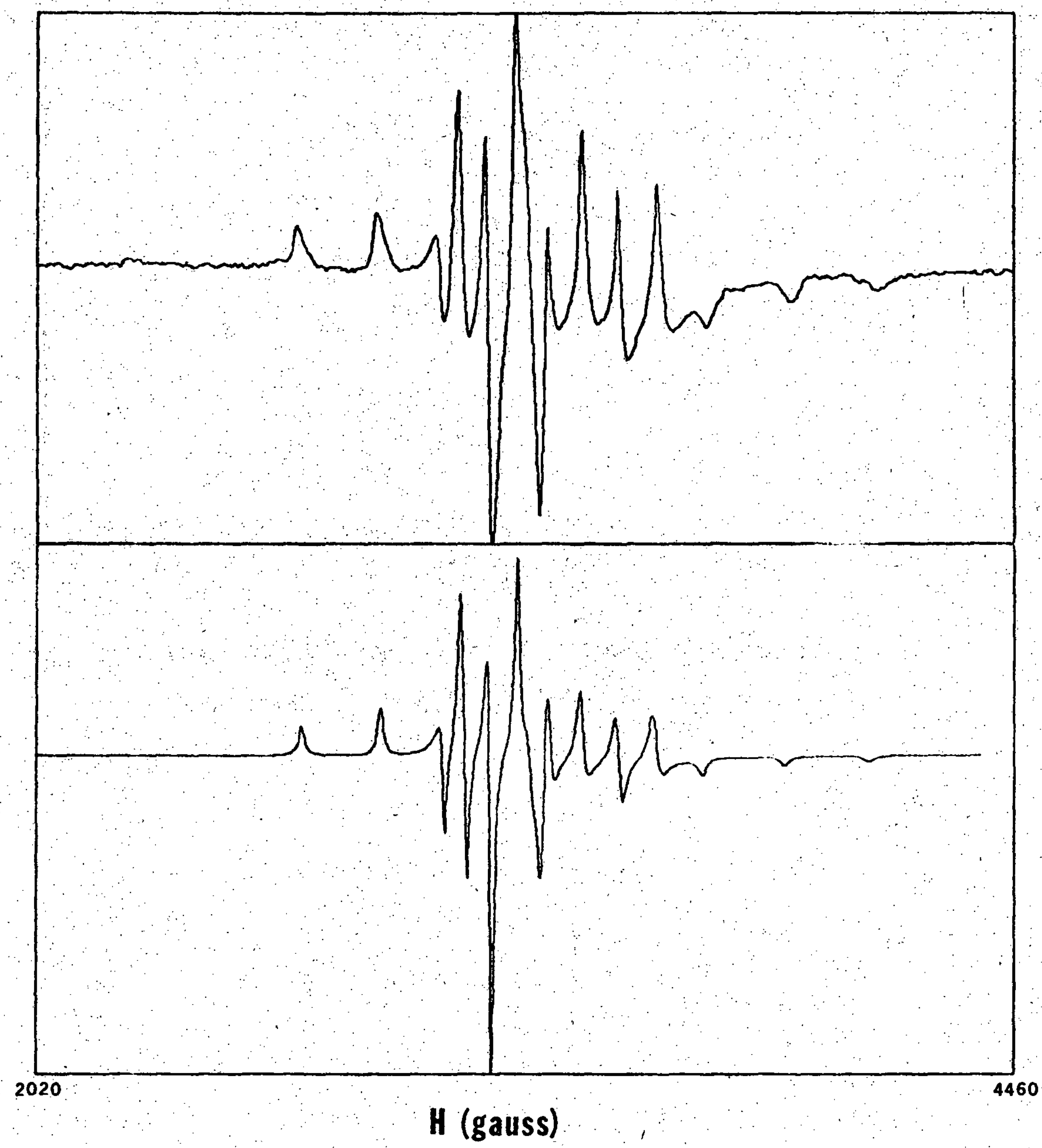
Fig. 8. Gamma parameter vs. η/T for $VO(H_2O)_5^{2+}$.



XBL 7012-7176

Fig. 9. $VO(D_2O)_5^{2+}$ glass spectrum. Upper spectrum is experimental; lower spectrum is simulation.

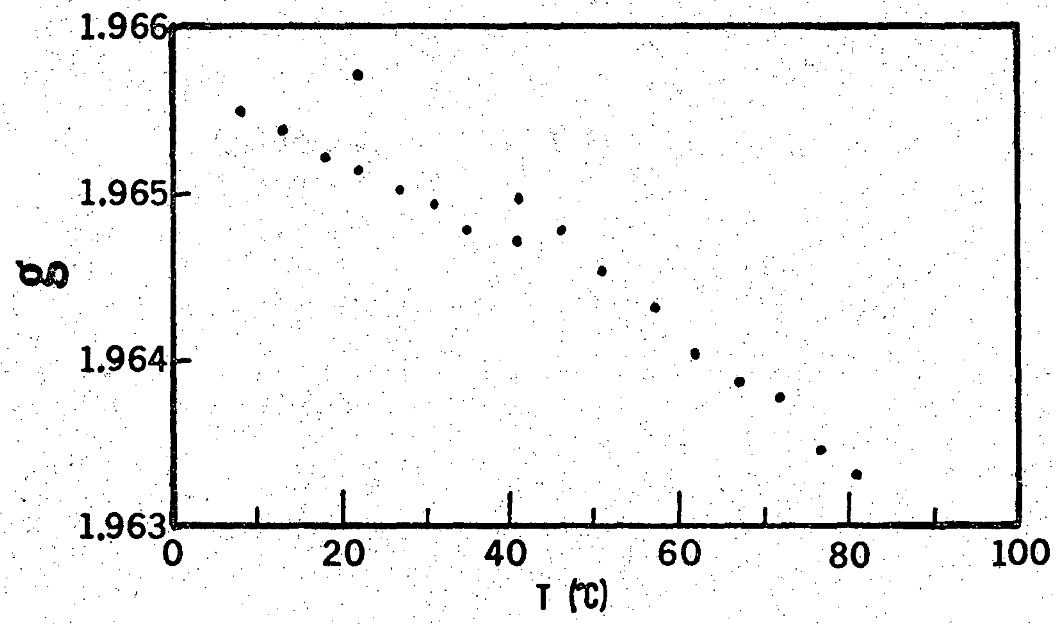


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Fig. 10. g vs. T for $VO(D_2O)_5^{2+}$.

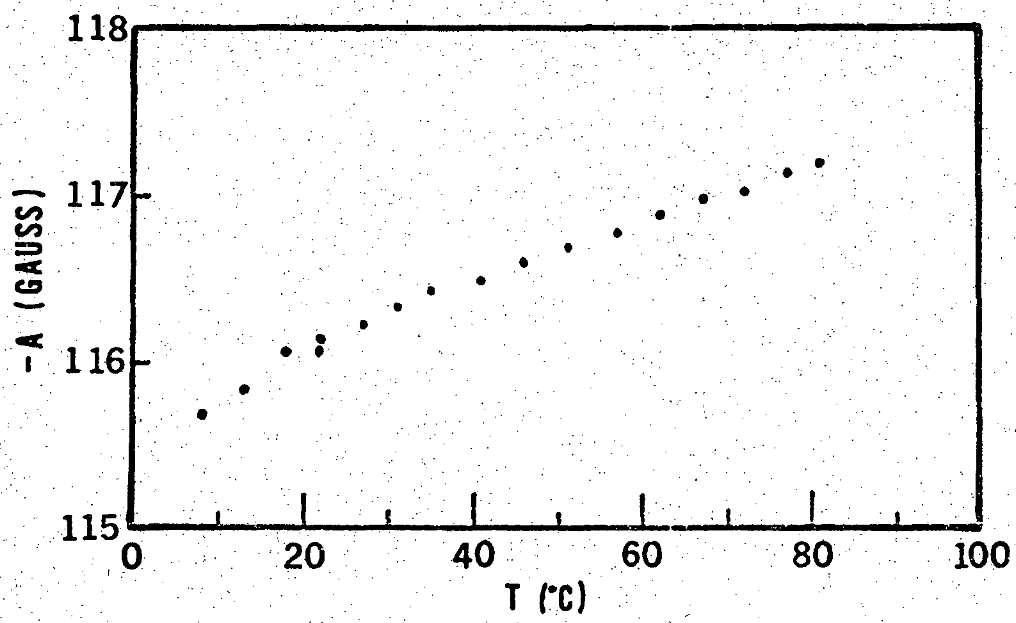

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Fig. 11. -A vs. T for $VO(D_2O)_5^{2+}$.

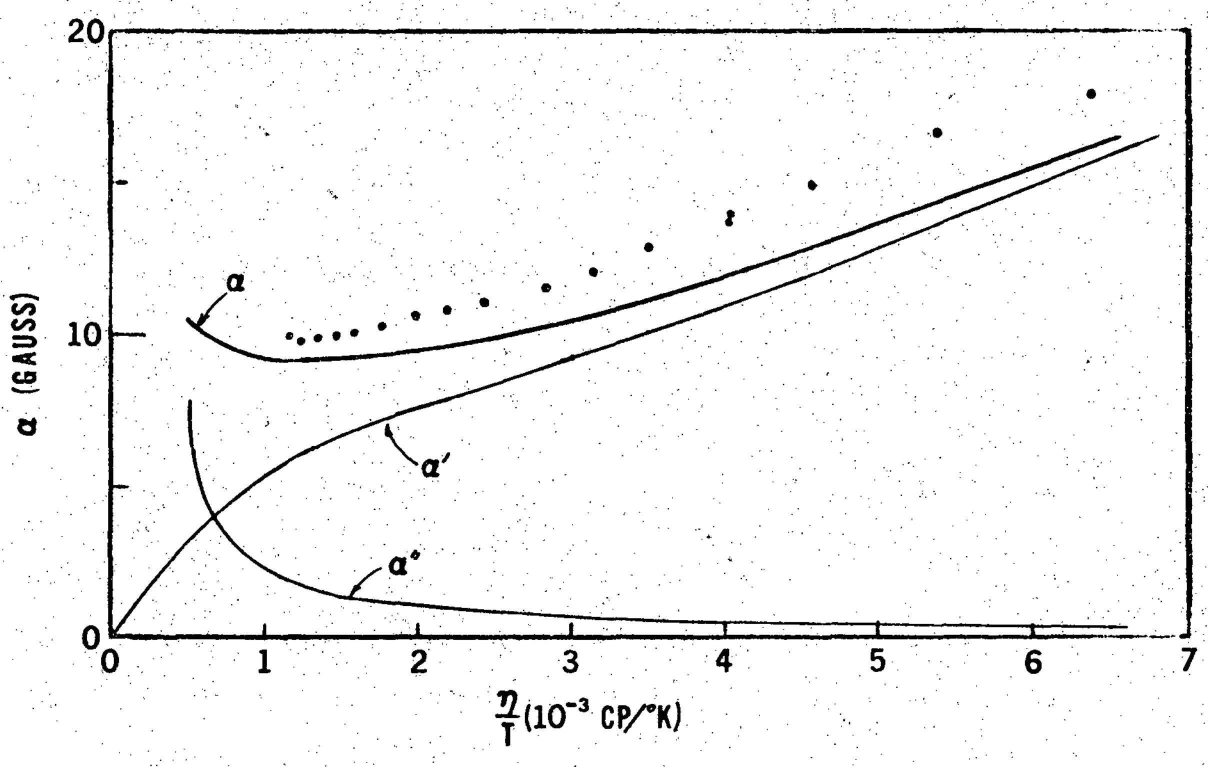

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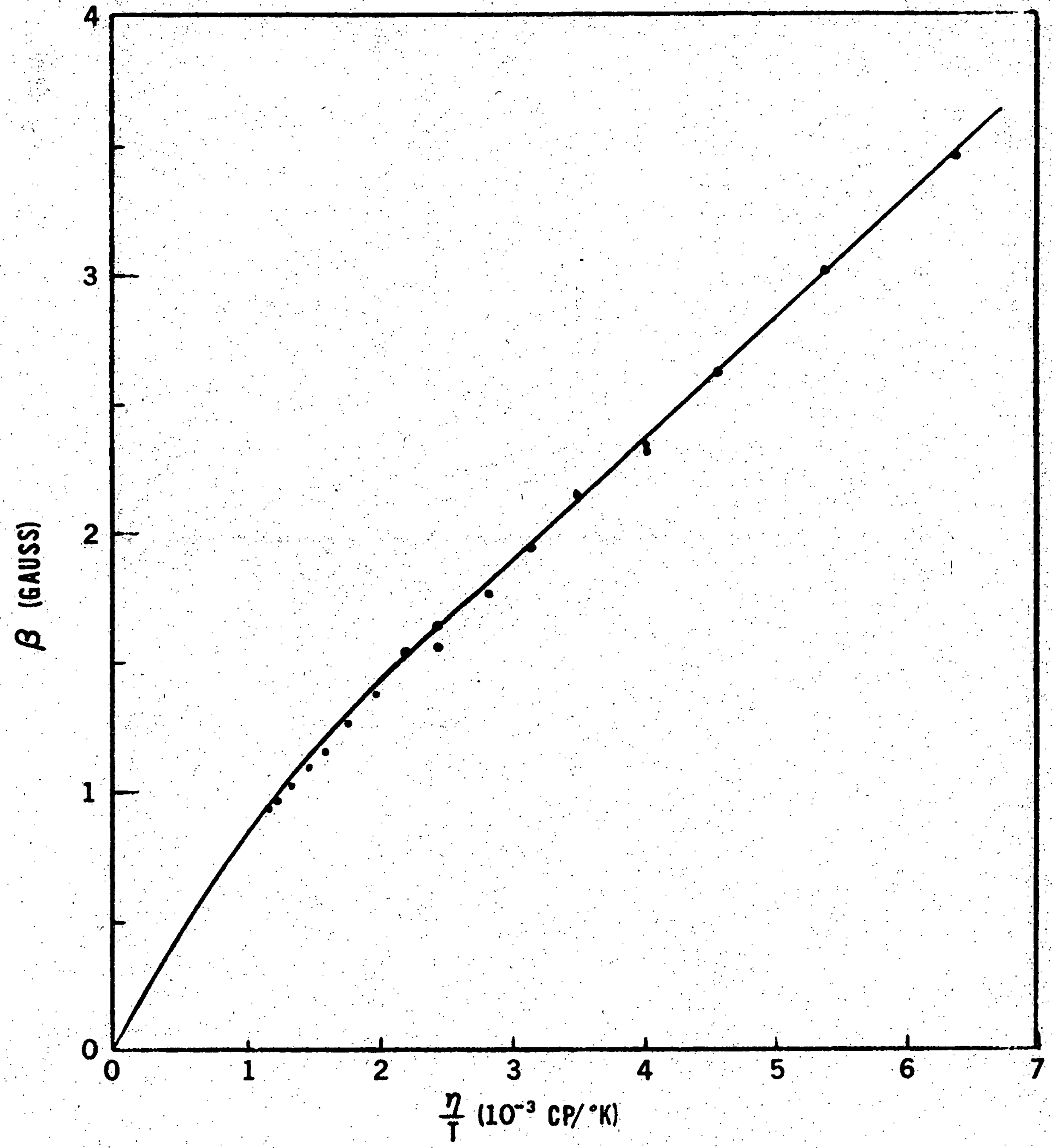
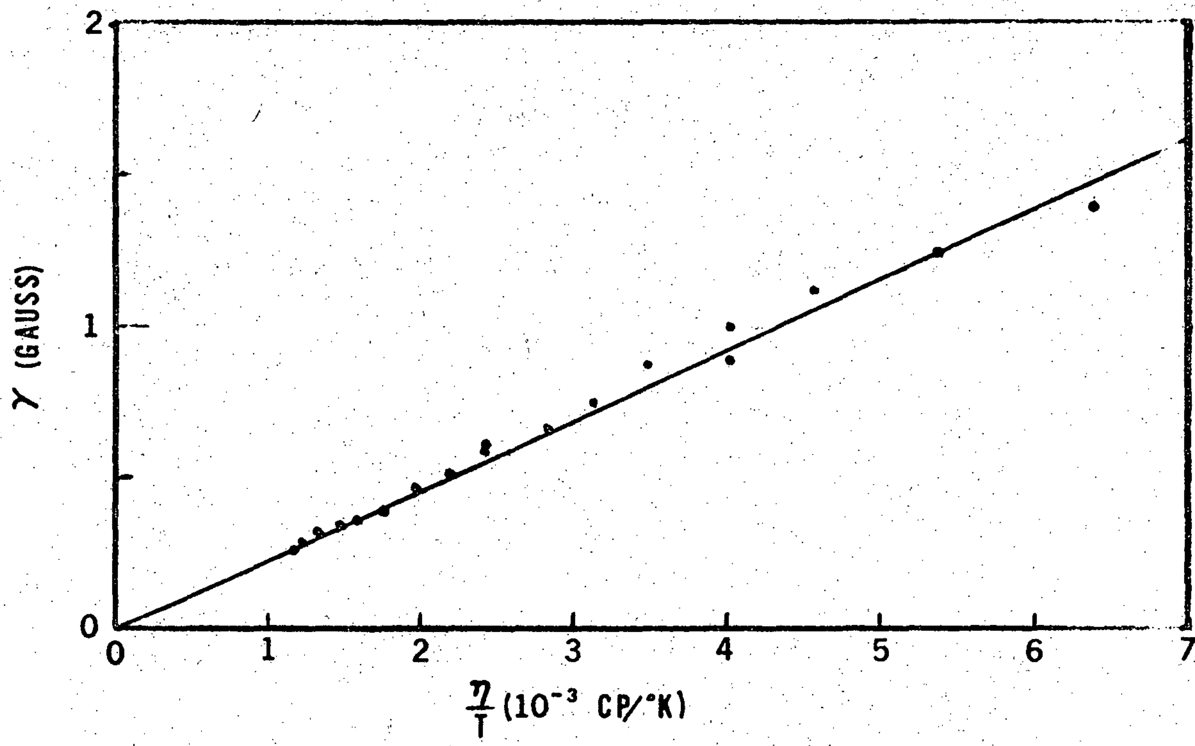
Fig. 12. Alpha parameter vs. η/T for $VO(D_2O)_5^{2+}$.



XBL 7012-7345

Fig. 13. Beta parameter vs. η/T for $VO(D_2O)_5^{2+}$.



XBL 7012-7350

Fig. 14. Gamma parameter vs. η/T for $VO(D_2O)_5^{2+}$.

TABLE II. Viscosities of H_2O and D_2O

T (°C)	H_2O η	H_2O η/T	D_2O η	D_2O η/T
-10	2.66	10.11		
0	1.7921	6.56		
10	1.3077	4.62	1.685	5.95
20	1.0050	3.43	1.2514	4.27
25	.8937	3.00	1.103	3.70
30	.8007	2.64	.972	3.21
40	.6560	2.09	.7872	2.51
50	.5494	1.70	.671	2.08
60	.4688	1.41	.5513	1.65
70	.4061	1.18	.488	1.42
80	.3565	1.01	.4141	1.17
90	.3165	.871	.3658	1.01
100	.2838	.760	.3265	.875

Note: Viscosities are in centipoises. Viscosities divided by temperature are in 10^{-3} cP/°K.

Viscosities for H_2O are from the Handbook of Chemistry and Physics, 43rd edition, CHemical Rubber Publishing Co.

Viscosities for D_2O are from R. C. Hardy and R. L. Cottington, J. Chem. Phys. 17, 509 (1949), and from the Landolt-Bornstein Tables, Vol. 5, Transport phenomena, Springer-Verlag (1969).

copper linewidths. The variation of these parameters with temperature forms a limitation on the interpretation of the linewidths. However, the variation is relatively small and does not seriously affect the theory. The values assumed for the linewidth treatment are g=1.9652 and A-115.9G. The values used by McCain (1967) were g=1.9623 and A=-119.5G. The values predicted from the anisotropic parameters (g=1.9627 and A=-117.62G) are slightly different, but the above values are thought to be better.

2. Relaxation

The vanadyl linewidths were least squares fit to a polynomial cubic in m_I in order to determine experimental values for the coefficients in Eq. 2.4. These values are plotted vs. viscosity divided by temperature as the points in Figs. 6-8. Selected values of the viscosity of water are presented in Table II to aid in the interpretation of the scales. The beta parameter was used to determine a value for the hydrodynamic radius of the complex from Eqs. 2.6 and 2.3. The radius, r=3.67 A, determined in this manner was used with Eqs. 2.5 and 2.7 to compute theoretical values for α' and γ. The value for α'' was computed using Eq. 2.12. The theoretical values are shown as the smooth curves in Figs. 6-8.

The theoretical and experimental values of the gamma parameter agree very well. This provides strong support for the Kivelson relaxation mechanism. Furthermore, the hydrodynamic radius determined from the theory is reasonable compared with the radius one would obtain from only structural considerations. The delta parameter is in relatively poor agreement with experiment, but terms of order $(a/\omega_o)^2$ have been neglected in the theory which contribute appreciably to the delta term

(Wilson and Kivelson, 1966a).

However, although the theoretical alpha parameter ($\alpha=\alpha'+\alpha''$) is in good qualitative agreement with the experimental values, the magnitudes are not in good agreement. Lewis and Morgan (1968) proposed that this discrepancy could be due to superhyperfine interaction with the protons of the complexed water molecules. To check this proposal we have made measurements of vanadyl ions dissolved in heavy water.

The anisotropic parameters for this system were determined from a deuterated perchloric acid glass. As expected (since the vanadium crystal field is determined mainly by the strongly bonded vanadyl oxygen), the parameters were the same as those for the aqueous system (in this section only, the term "aqueous" refers to ordinary water solutions as opposed to heavy water). The polycrystalline spectrum is shown in Fig. 9. The theoretical curve in Fig. 9 is the same as that in Fig. 2. The isotropic g and A values for the deuterated vanadyl system are shown in Figs. 10 and 11. The magnetic parameters used in the linewidth treatment were the same as those in the aqueous system.

The linewidth parameters are shown in Figs.12-14. As in the aqueous system, the beta parameter was used to determine a hydrodynamic radius from the theory. It is interesting that the radius, r=3.48 A, for the deuterated system is 0.19A smaller than the radius in the aqueous system. This may indicate an actual change in the effective size of the complex, or more likely, a change in the value of κ (see Eq. 2.14) for the deuterium oxide solvent from the hydrogen oxide solvent.

The agreement between the theoretical and experimental values for the gamma term is excellent. However, the alpha term shows a discrepancy similar to that in the aqueous system. If the residual linewidth is due to a superhyperfine interaction, it would decrease by close to a factor of three since the magnetic moment of the deuteron is that much smaller than that of the proton. A comparison of the two residual widths indicates that the deuterated complex does not have a smaller discrepancy.

Recently, however, the proton magnetic resonance work was reported for the vanadyl system (Reuben and Fiat, 1969a, b). These workers give a proton superhyperfine coupling constant of 3.2 MHz, or 1.2 G for g=1.97. Although this is sufficiently large to provide the residual linewidth in the aqueous vanadyl system, it does not explain the behavior of the deuterated complex.

It must be noted that the samples were not degassed so that the residual linewidth could be due to oxygen broadening. However, McCain (1967) indicates that the vanadyl widths did not narrow upon degassing. A preliminary investigation by the author also produced this result. The effect of dissolved oxygen is, therefore, expected to be quite small.

We are then led to somewhat of a dilemma for the vanadyl system. Since the residual width did not change upon deuteration, this width cannot be due to superhyperfine structure. However, if the residual width is ascribed to other causes, we must show why no hyperfine effect is shown. We must therefore reexamine the premises of the experiment.

A resonance line may be homogeneously or inhomogeneously broadened. A homogeneously broadened line is a single line which may be characterized by a "true" linewidth. An inhomogeneous line is a superposition of several homogeneous lines which have a "true" linewidth. The inhomogeneous line has an apparent width which is, in general, not the "true" width.

However, as the "true" width becomes larger and larger the apparent width of an inhomogeneously broaden line should be closer to the natural width. If the "true" width is very large compared to the separation of the components, the apparent width will become equal to the "true" width.

A proton hyperfine coupling constant of 1.2 G would surely produce a superhyperfine pattern in the vanadyl lines since proton exchange is slow. This should cause the vanadyl lines to be inhomogeneously broadened so that a least squares fit to determine the linewidth should produce an error in the linewidth. However, as the true linewidth becomes larger, the error in the linewidth is expected to become smaller. Since the linewidths in the vanadyl spectrum at low temperatures are quite large compared to the hyperfine splitting , the residual linewidth due to hyperfine structure should go to zero. We see from Figs. 6 and 12 that the residual width is either constant with temperature or increases as temperature is decreased. Hence, we must conclude that, because the residual width neither decreased with deuteration nor decreased with decreasing temperature, the main contribution to the residual width is not a superhyperfine interaction.

We would expect some contribution to the width from superhyperfine interaction. The residual width should have changed some upon changing to the heavy water solvent. The effect, however, is reduced because of the variation of linewidth with hyperfine component. The error of residual width in each hyperfine component due to superhyperfine interaction changes from component to component. The error in the alpha parameter would be a kind of average over the errors for all the components. For some of the lines the widths are large enough that the error is close to zero. Hence, the average contribution to the residual width is much smaller than the maximum possible contribution. Furthermore, the line-width variation is not symmetric with respect to the center of the spectrum. The narrowest line in the spectrum is to the low field side of the spectrum center. The result of this is that the beta and gamma parameters must also be affected by the superhyperfine interaction. The contribution of superhyperfine structure to the alpha parameter is much smaller than the possible contribution to a given line. The change in the residual width upon going to a deuterated solvent is smaller than the residual width due to superhyperfine interaction. It is not observed because it is so small.

We, therefore, have an unexplained residual width in the vanadyl system. The residual width cannot be due to the Al'tshuler and Valiev (1958) mechanism since this mechanism is temperature dependent. Furthermore, this mechanism would predict a linewidth increasing as temperature increases. The residual width on the other hand is constant or decreases with increasing temperature.

The linewidth in the vanadyl system is, nevertheless, almost completely explained by a combination of the spin-rotation and anisotropic g and A tensor mechanisms. We may test the field dependence of the mechanism by comparing theoretical predictions with the parameters measured by McCain (1967) and by Rogers and Pake (1960). These parameters are presented in Table III.

A comparison of the S band experimental and theoretical values shows a considerable disagreement. The alpha term is off by 5 gauss; the beta and gamma terms also disagree. McCain indicated that this disagreement

TABLE III. Comparison of Theoretical and Experimental Linewidth Parameters for $VO(H_2O)_5^{2+}$

S band (3.12 GHz) (McCain, 1967)		K band (24.3 GHz) (Rogers and Pake, 1960)	
Exp.	Th.	Exp.	Th.
21.9	17.	13.6	13.
1.333	2.15	2.8	4.5
.4977	.65	.47	.82
-.0544	-.05	***	-.004

was probably due to terms of order $(a/\omega_o)^2$ which were neglected in the theory. We feel that this is the most probable reason. Furthermore, this is probably also the reason for the residual width in the X band data. The neglected terms have relatively little effect on the beta and gamma parameters, but seriously affect the alpha parameter. This discrepancy is expected to be smaller at K band where the neglected terms would be quite small. A comparison of the K band experimental and theoretical data is somewhat disappointing. Although, the alpha term agrees well with theory, the beta and gamma terms are extremely wrong. We suspect that this is due to an error in the data rather than in the theory. Rogers and Pake indicate that the lines have some non-Lorentz character which we believe is an experimental problem which produced an error in the results. K bands experiments are quite difficult because the sample must be small to avoid distortion problems. The Kivelson theory is then expected to completely explain the linewidths. It would be interesting to obtain some additional K band data.

The theory may be used to compute theoretical estimates of the relative T_{1e} values for comparison with McCain's (1967) experimental values. However, the theory is only approximately correct for the S band data. McCain used a correlation time of $\tau=3\times10^{-11}$ sec in his work where the value determined in this work is $\tau=3.8\times10^{-11}$ sec. However, this change does not change the results enough. The agreement between theory and experiment is quite poor, but this is expected since the linewidth predictions are also poor.

IV. COPPER LINEWIDTHS

A. Introduction

The EPR spectrum of the hexaquocopper (II) complex in solution was certainly one of the first to be studied though it is difficult to say when it was first observed. Among the earliest studies of the system were those of Kozyrev (1955) and McGarvey (1956, 1957). These workers reported a spectrum consisting of a single line at ordinary temperatures with a g value of about 2.2 and a peak-to-peak linewidth of about 150 gauss. Although the copper nucleus has a nuclear spin I=3/2, no hyperfine structure was observed in the spectrum.

The intriguing characteristic of the spectrum was that the line width was observed to increase with increasing temperature (Kozyrev, 1957; Avvakumov,et al., 1960). At first glance the linewidth of this spin 1/2 complex would have been expected to decrease with increasing temperature on the basis of the McConnell theory (1956).

A number of explanations were proposed for the anomalous behavior of the copper system. Indeed, Kozyrev (1955) early proposed that the broadening and subsequent lack of hyperfine structure in the copper spectrum was due to the formation of copper dimers. This suggestion was based on an incomplete understanding of some of the early data, and is not tenable since the linewidth behavior persists in dilute solutions where copper dimers are quite unlikely. McGarvey (1957) proposed that the linewidth was due to a combination of tumbling and an interaction with a low lying excited state which was expected in the hexaquocopper (II) system as a result of the Jahn-Teller effect. Al'tshuler (Al'tshuler and Valiev, 1958; Al'tshuler and Kozyrev, 1964) proposed a theory involving vibrational modulation of the crystal field. He showed that this theory would fit their data quite well.

However, all the early theories suffered from incomplete information as to the true linewidth in the system. The linewidth was taken as the derivative peak-to-peak distance of the broad single line observed in the spectrum. But the EPR spectrum of hexaquocopper (II) must certainly consist of hyperfine structure. Hayes (1961) detected hyperfine structure in the spectrum by cooling to near 0°C. The coupling constant between 31 to 38 gauss, indicated that the linewidth was in a large part due to hyperfine structure.

Among other workers who have used the overall linewidth are Valiev and Zaripov (1966) and Fujiwara and Hayashi (1965). Valiev and Zaripov proposed a relaxation mechanism specific to the hexaquocopper (II) system. This mechanism, a modification of the Al'tshuler and Valiev (1958) mechanism, involved a vibrationally induced transition to the lowest orbital excited state with subsequent relaxation to the ground state. This is a kind of Orbach mechanism involving ligand vibrations rather than lattice modes. Valiev and Zaripov's work shows reasonable agreement with the overall linewidth if the hyperfine contributions are ignored.

Fujiwara and Hayashi studied the linewidth as a function of temperature, as a function of concentration, and as a function of the anion associated with the copper cation. These workers report no anion dependence in dilute solutions and also no concentration dependence for solutions less than .1 F. These results are qualitatively correct since although the true linewidth was not measured, a concentration effect would be observed in the overall line. Although these workers report measurements near 0°C, they report no hyperfine structure in the spectrum.

Spencer (1965) measured the EPR spectra of hexaquocopper (II) over a wide range of temperatures for both aqueous solutions and for perchloric acid solutions. He also measured the spectra of the hexamminecopper (II) system which was expected to be quite similar in behavior. Using the hyperfine coupling constant of .0053 cm^{-1} he was able to perform crude corrections to the linewidths. At low temperatures he observed the linewidth to decrease as the temperature increased. Spencer discusses two mechanisms to explain the linewidth: the anisotropic tumbling mechanism and an inversion mechanims. Although a definite conclusion was not reached, Spencer proposed that the linewidth could be explained by a combination of these mechanisms. Another explanation was that the linewidth was controlled by the rate of chemical exchange of the water molecules in the hydration sphere. Additional support for this proposal was obtained from the ^{17}O NMR data (Meredith, 1965). The ^{17}O linewidth was observed to vary with the same temperature dependence as the EPR linewidth.

Lewis, Alei, and Morgan (1966) also studied the copper system as a function of temperature. They study the copper system by means of a lineshape analysis using a simulation technique. At high temperatures (above room temperature) they assume that all the linewidths are equal. From their analysis they conclude that the linewidth should be due to a combination of the spin-rotational process and a second process which they describe as a Raman process. They propose the Raman process on the basis of extrapolation from reported solid state measurements. However, Kivelson (1966) indicates that Raman processes are not expected to be large in solution. Lewis, Alei and Morgan propose the following function for the linewidth

$$T_2^{-1} = 2.04 \times 10^4 \; [(T/\eta) + 0.23\, T^2] \qquad (4.1)$$

The main difficulty with the hexaquocopper (II) system, other than the actual interpretation of the linewidth behavior, is the measurement of the true linewidths for the hyperfine lines. The large linewidths leading to extreme overlap and lack of resolution in the spectrum produces an extremely frustrating problem. Simulation methods of analysis for lines as unresolved as the copper lines are very difficult. The present study was begun because it was felt that the use of a data acquisition system in connection with a least squares treatment would facilitate the treatment of the data and improve the results.

B. Experimental Methods

The apparatus and measurement procedures were the same as those described for the vanadyl experiments (see Sec. III-B). The initial experiments were performed with copper perchlorate obtained from the G. Frederick Smith Company. The final experiments were performed with isotopically enriched ^{63}Cu(99.62%) which was obtained from Oak Ridge National Laboratories in the form of the oxide. The oxide was dissolved in an equivalent amount of perchloric acid with gentle heating. The concentration of the resulting copper perchlorate solution was adjusted to .01-.02 F. Solutions in 5.26 F perchloric acid for glass spectra were obtained by evaporating the necessary amount of the copper perchlorate aqueous solutions and then redissolving the residue in perchloric acid.

C. Discussion and Results

1. Spectra

The anisotropic magnetic parameters for the hexaquocopper (II) system have proven to be quite elusive. A number of workers have determined these parameters in different glass systems, but have obtained varying results. These results are presented in Table III. In addition, we have repeated the measurements in the perchloric acid glass system.

Spencer (1965) originally measured the parameters for the perchloric acid glass system by measuring the line positions. The spectrum is quite simple and consists of a parallel band containing four resolved hyperfine components and a perpendicular band containing a doublet. The interpretation of this doublet is difficult without a simulation method to analyze the spectrum. We have redetermined the anisotropic magnetic parameters by using a simulation technique to analyze the spectrum.

Spencer suggests that the doublet could arise from either hyperfine structure or from two g values due to the complex having less than tetragonal symmetry in the glass, or from so-called "extra" absorptions. Hyperfine structure would produce four components and hence was expected to give four lines rather than two. However, the theoretical simulation in Fig. 15 shows that the spectrum can be fit quite well with an axial spin Hamiltonian. Only a doublet is observed because of a second order hyperfine effect which shifts two lines of the quartet further than the others. A variable linewidth further accentuates a doublet appearance over a quartet. The parameters determined from the analysis are presented in Table IV.

Table IV shows a large spread in the results of the various workers. Of the three systems utilized, the methanol results are probably the least correct for the hexaquo complex. These measurements were performed with

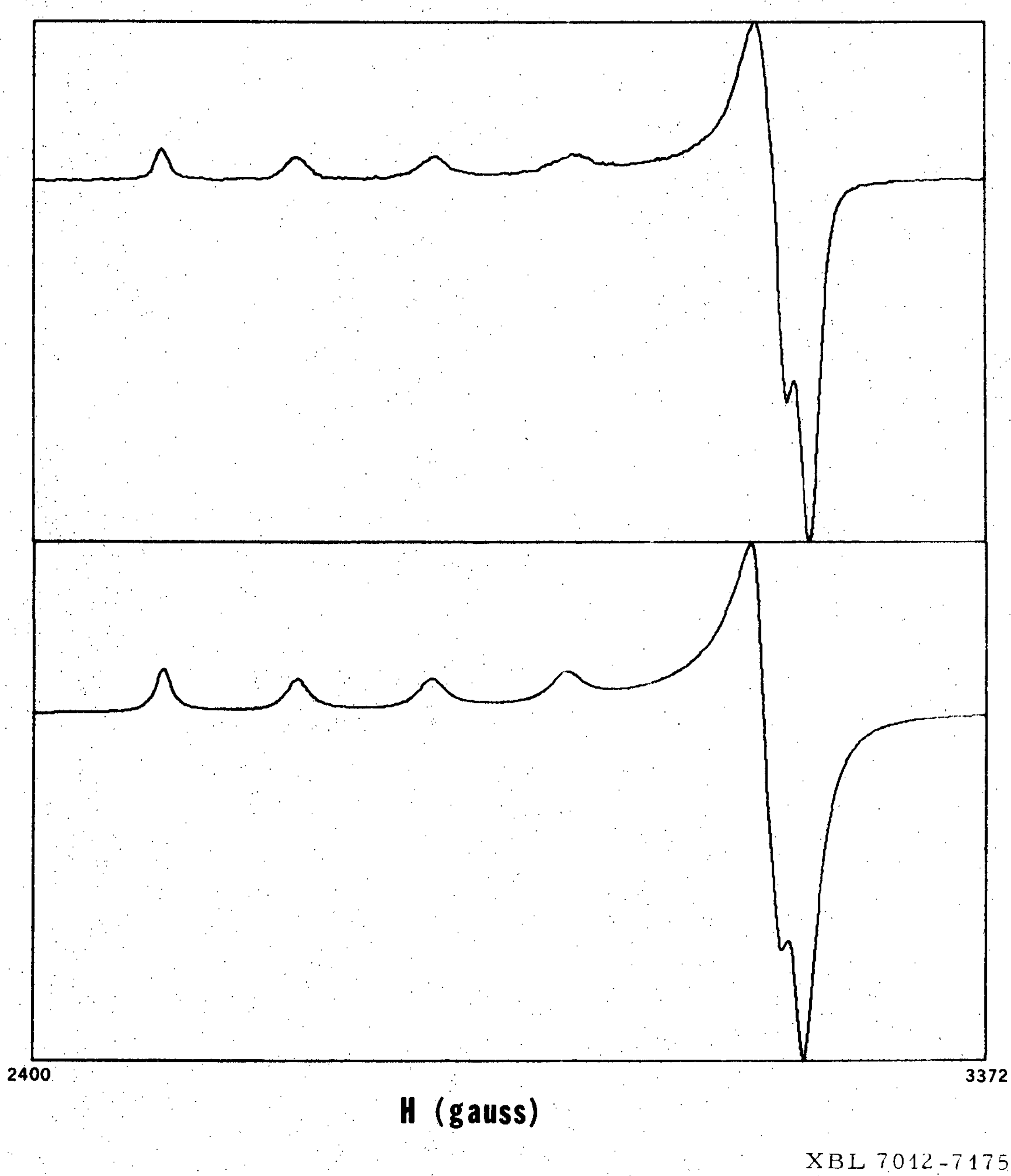


Fig. 15. Spectrum of $Cu(H_2O)_6^{2+}$ in perchloric acid glass. Upper spectrum is experimental; lower spectrum is simulation.

TABLE IV. Anisotropic Magnetic Parameters for $Cu(H_2O)_6^{2+}$

Solute/Solvent	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}^{a}$	$A_{\perp}^{a}$	g^{b}	$A^{a,b}$	Reference
$Cu(NO_3)_2$/methanol	2.39	2.07	106	70	2.1767	83.2	Garif'yanov and Usacheva (1964)
$Cu(ClO_4)_2$/5.3 $HClO_4$	2.379	2.066	139.6	7	2.1703	46.5	Spencer (1965)
$Cu(NO_3)_2$/glycerol	2.400	2.099	114.05	12.86	2.1993	33.3	Lewis, et al. (1966)
$^{63}Cu(ClO_4)_2$/5.3 $HClO_4$	2.387	2.072	137	5	2.177	46.9	This work

a. Coupling constants are in gauss

b. Average values computed from anisotropic values the hydrated salt in almost pure methanol. The results are probably incorrect due to the formation of copper-methanol complexes.

The results obtained for the 5.26 F perchloric acid and the 60% glycerol glasses are somewhat harder to reconcile. Initially, the perchloric acid system is expected to provide a better glass medium for the hexaquo complex since it is generally accepted that the perchlorate anion does not form complexes with transition metals although the same is not true for glycerol. Furthermore, there are more water molecules (40 F) available in 5.26 F perchloric acid that in 7.5 F glycerol (25 F in water).

However, the anisotropic parameters may be used to compute average g and A values which are expected to be close to the isotropic g and A values. The computed average values are also presented in Table IV. A comparison of these values with the experimental isotropic values which are presented later shows that the glycerol parameters agree quite well. But the perchloric acid parameters are very different from the experimental values. As mentioned in the vanadyl discussion, glass spectra need not necessarily produce correct values for the complex in solution. However, the measured difference is striking.

We may note that the g and A values are expected to be correlated due to bonding effects (Kivelson and Neiman, 1961). As the g value decreases, the A value should increase. This correlation seems to hold for the parallel parameters between the glycerol and the perchloric acid glass. However, the correlation breaks down in the perpendicular parameters. This might be a possible indication that different complexes are being observed. If both spectra were due to copper ions with octahedrally coordinated water molecules, the correlation would be expected to hold. The choice of which set of parameters to use is somewhat arbitrary. Fortunately, the parameters desired for a linewidth theory are the anisotropies, i.e., the differences between the parallel and perpendiuclar values, rather than the actual parameters. The anisotropies are in somewhat better agreement than the actual parameters. In fact, both sets of parameters were used for the linewidth study.

The EPR spectra for hexaquocopper (II) ions in solution have been messured between -15 and 100°C. The spectral parameters were obtained from the digitized spectra using the least squares fitting procedure described previously. The spectra could be fit very well using one intensity, one g value, one coupling constant, and four linewidths. Examples of the fits to the spectra at various temperatures are shown in Figs. 16-19. The crosses are the experimental points; the continuous lines are the theoretical fit. The lower curves in the figures are plots of the difference between the theoretical and experimental curves. We can see from the error curves that the fits are very good. The low temperature spectra (Figs. 16 and 17) exhibit the presence of four hyperfine lines quite clearly. However, the spectra at higher temperatures (Fig. 19) do not exhibit structure.

At room temperature and above the spectra consist of a single, broad, symmetric line. Much of the early work has considered the peak-to-peak width of the unresolved line to be the true width of the line. This would be true if the hyperfine coupling constant were small compared to the linewidth. The observed line would then be very nearly a Lorentz lineshape whose peak-to-peak width would be an excellent

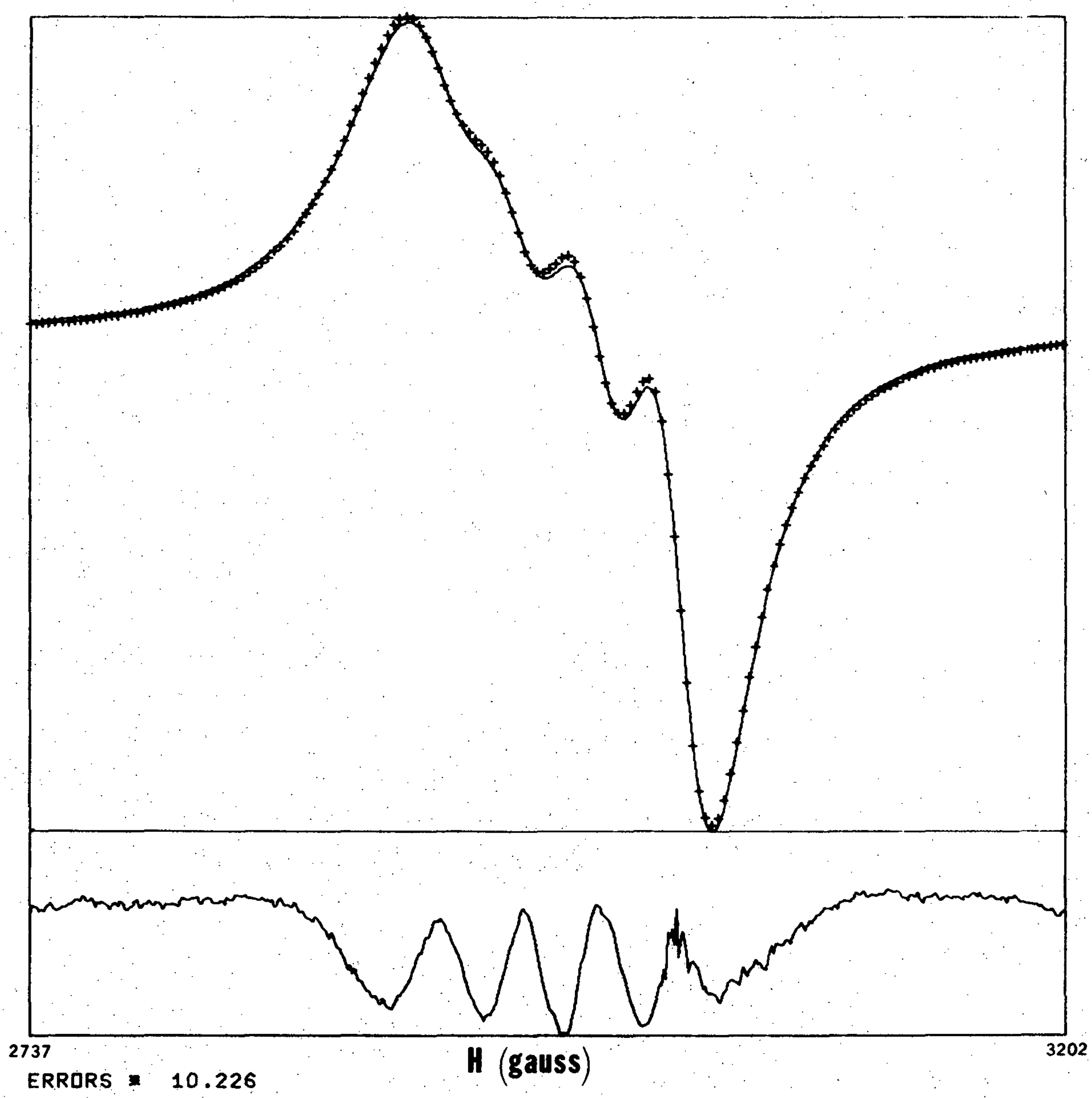


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Fig. 16. Example of fit to solution spectrum of $Cu(H_2O)_6^{2+}$ at -10°C. In this spectrum and in the following spectra the crosses are the experimental points; the continuous line is the theoretical fit to the data; and the lower curve is the difference between the theoretical and experimental spectra with a scale expansion given by the ERROR* number.

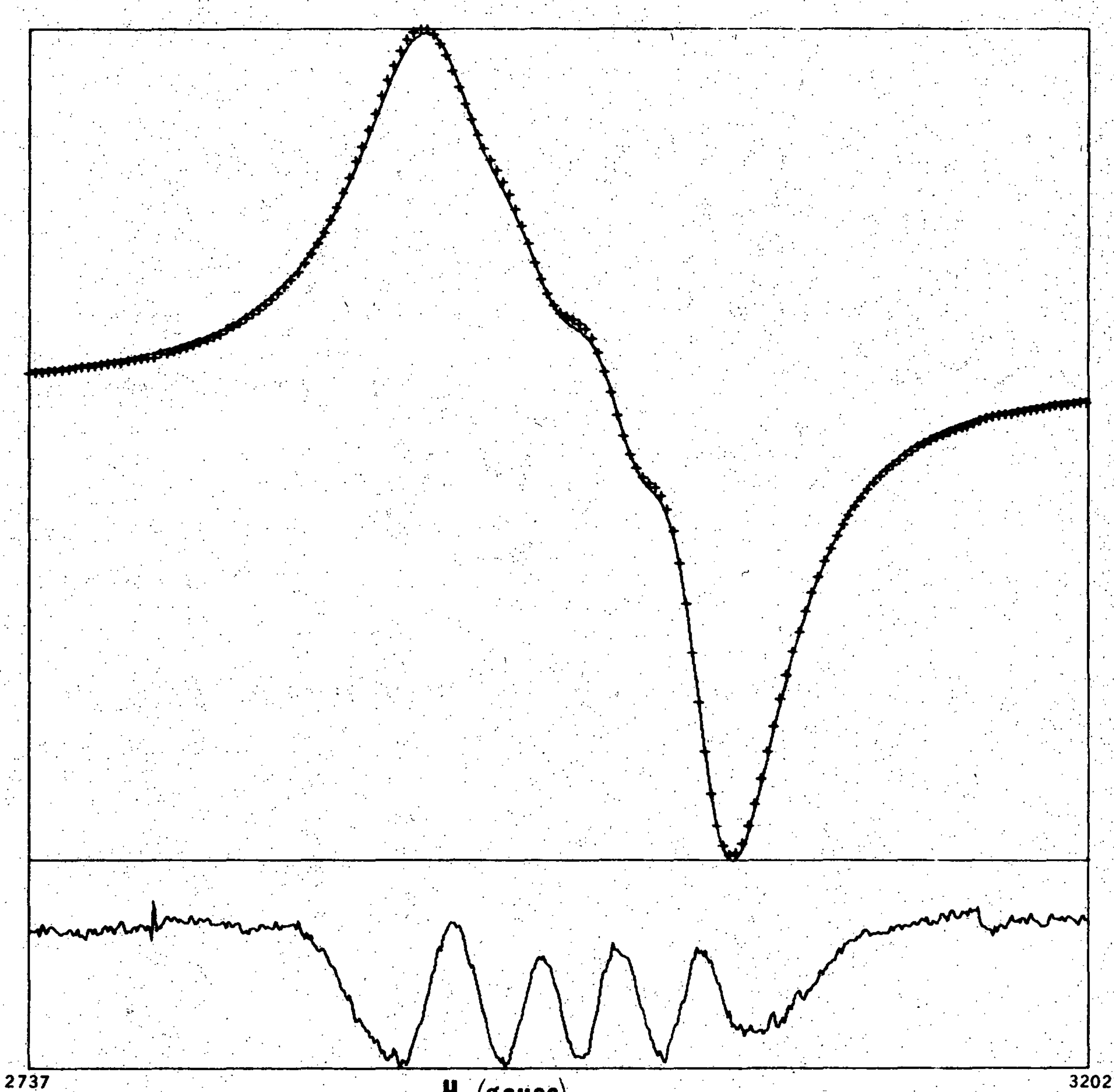

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Fig. 17. Example of fit to solution spectrum of $Cu(H_2O)_6^{2+}$ at 1°C.

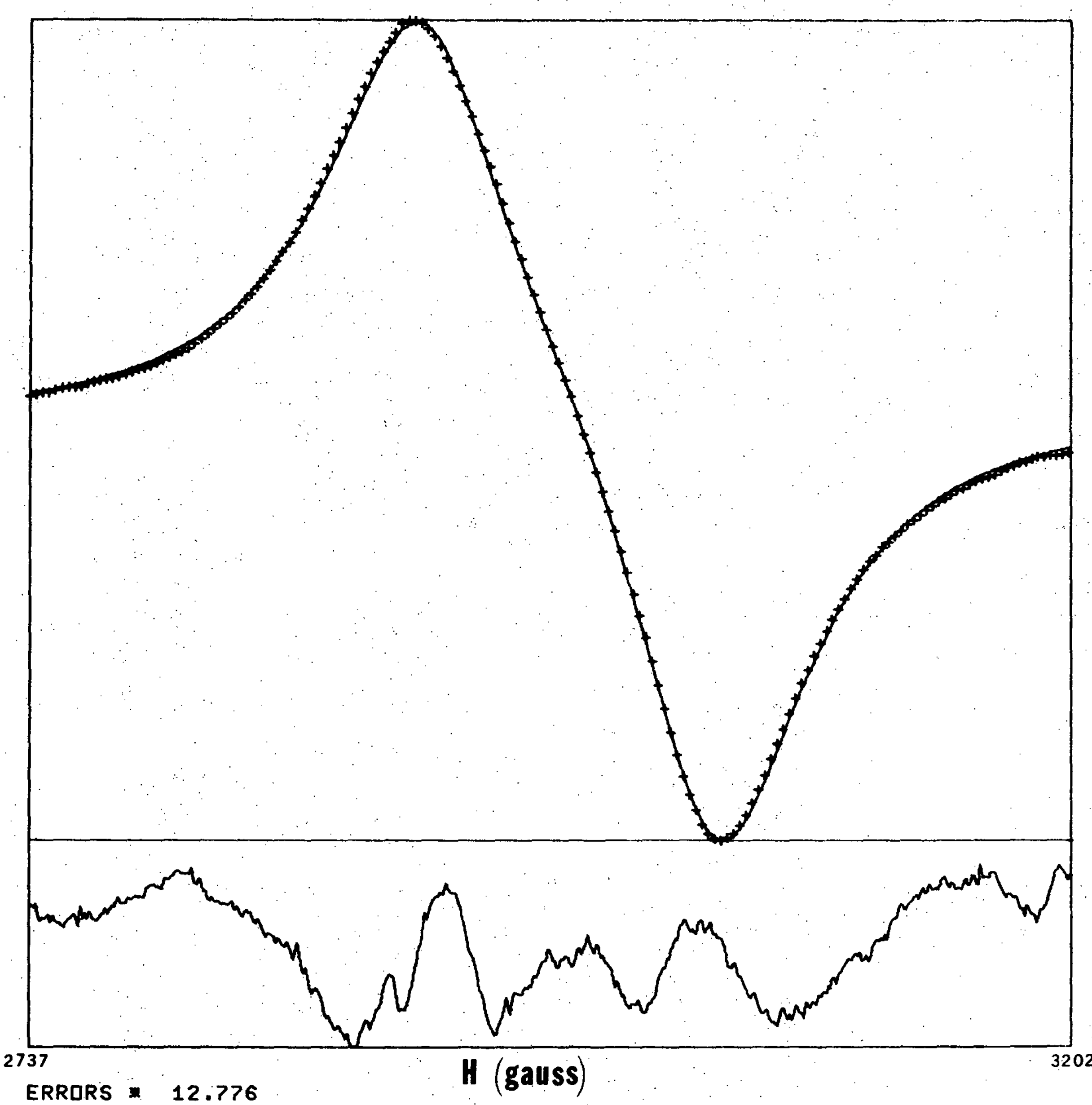

Fig. 18. Example of fit to solution spectrum of $Cu(H_2O)_6^{2+}$ at 22°C.

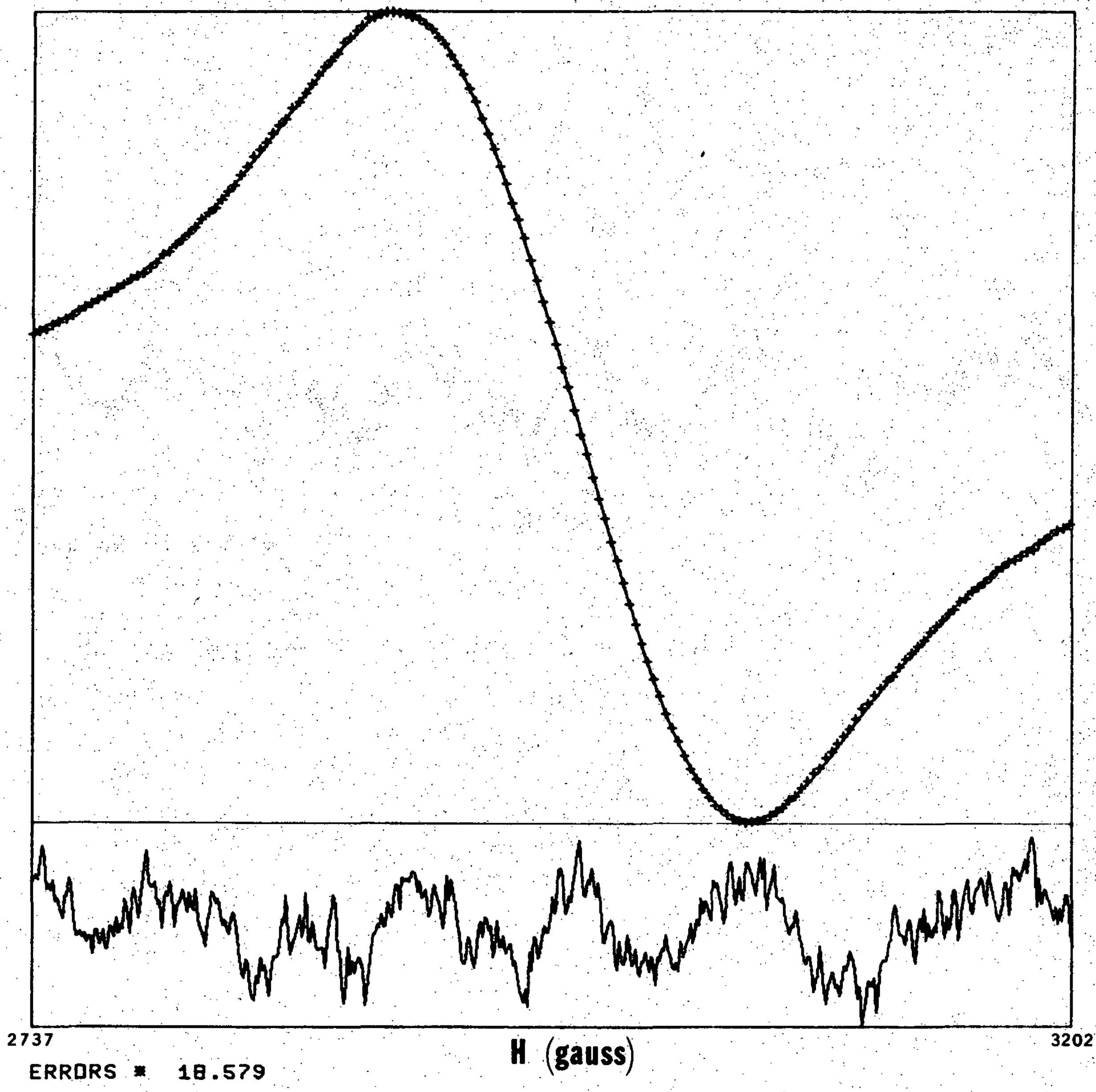

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Fig. 19. Example of fit to solution spectrum of $Cu(H_2O)_6^{2+}$ at 60°C.

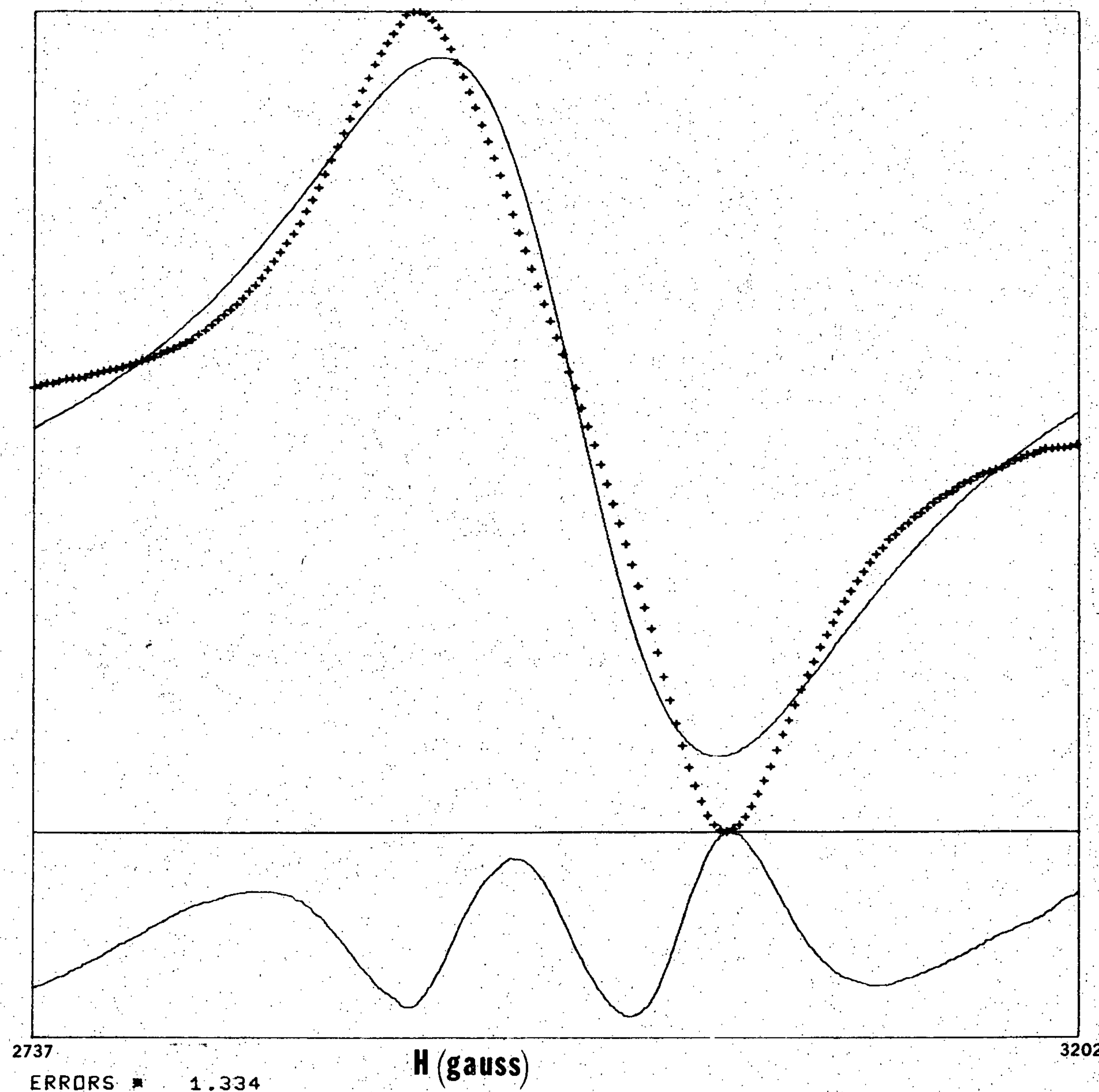

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Fig. 20. Attempt to fit spectrum of Fig. 18 with 1 Lorentz line.

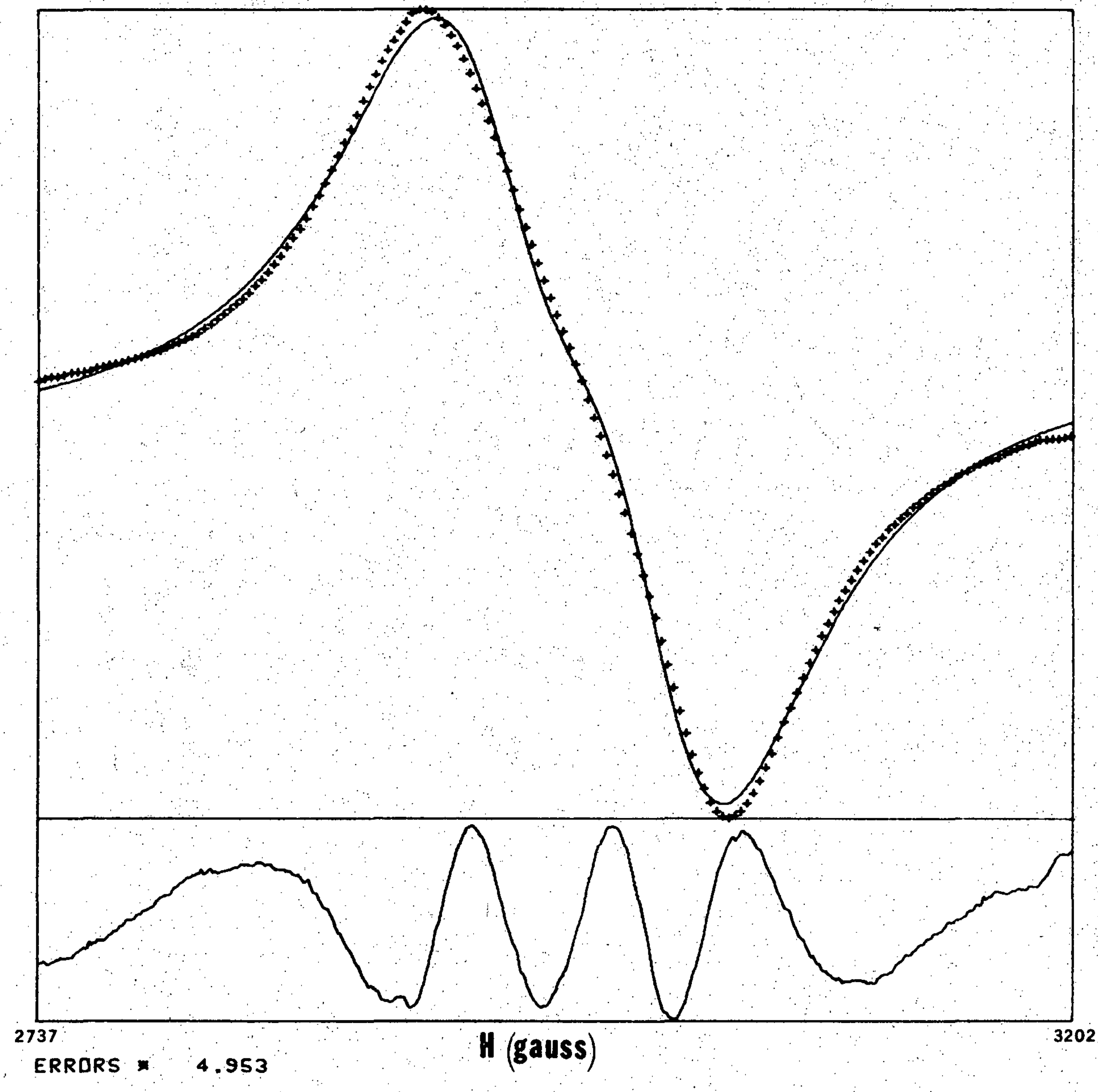

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Fig. 21. Attempt to fit spectrum of Fig. 18 with 2 Lorentz lines.

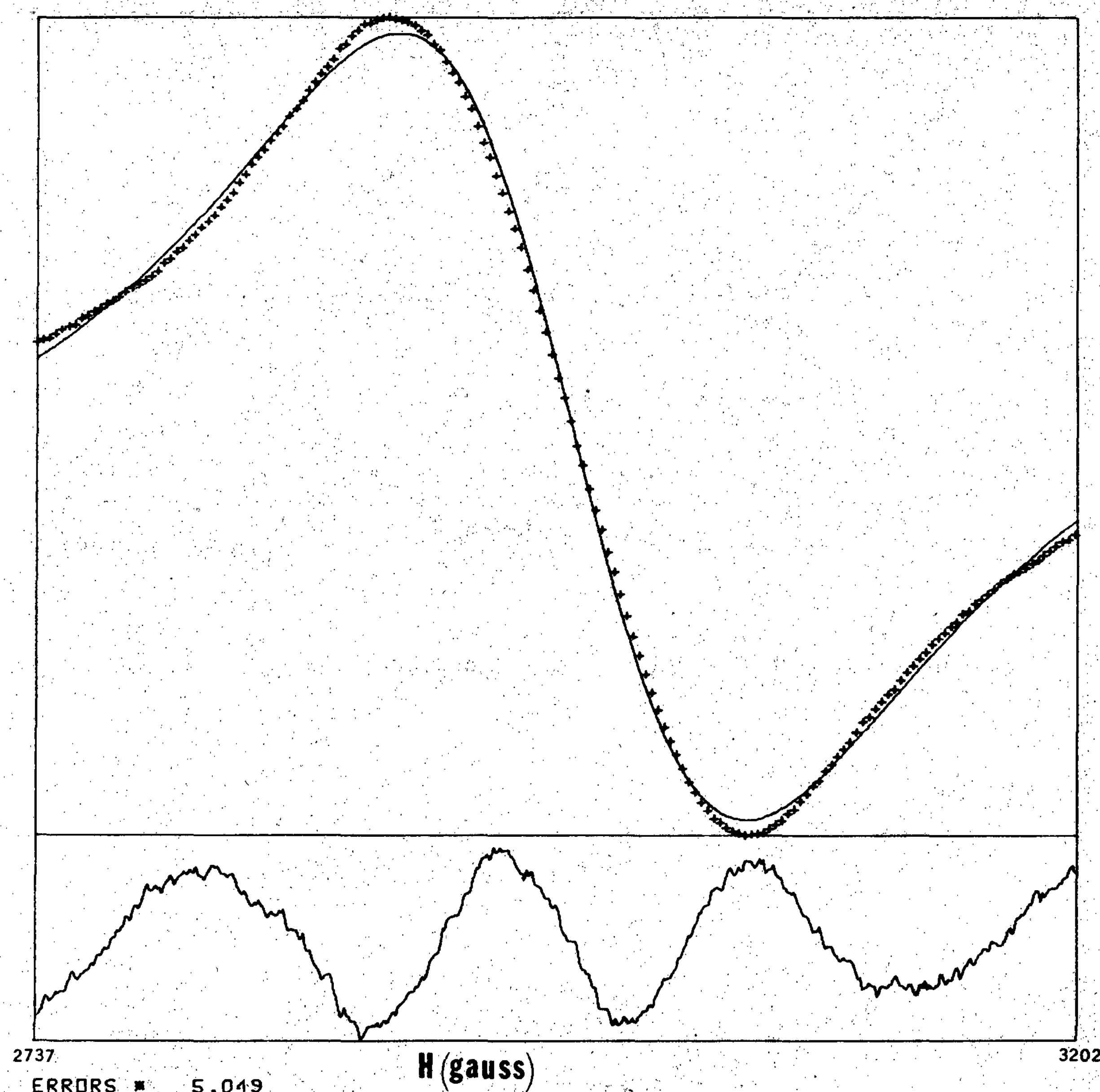

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Fig. 22. Attempt to fit spectrum of Fig. 19 with 1 Lorentz line.

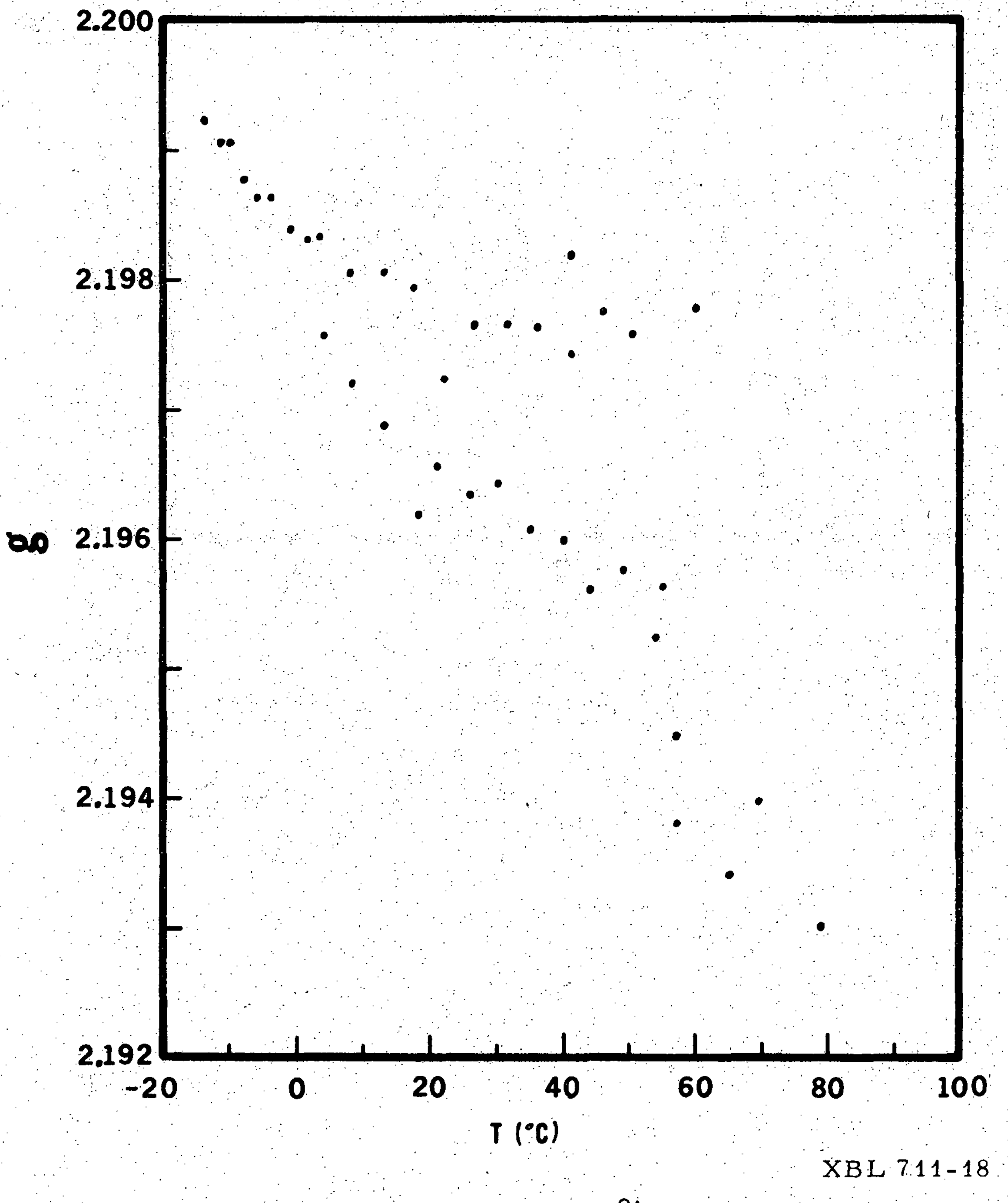

Fig. 23. g vs. T for $Cu(H_2O)_6^{2+}$?

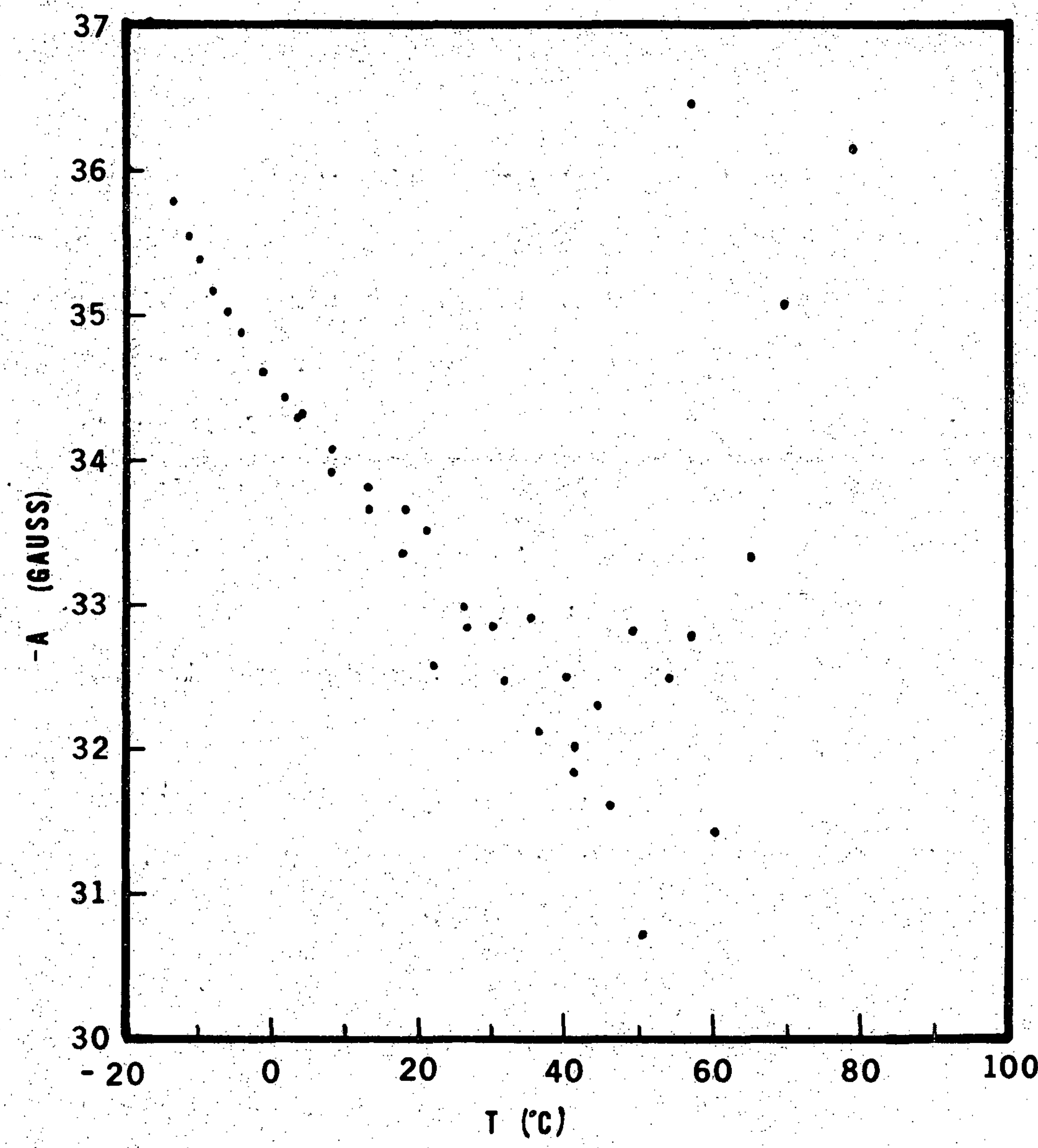

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Fig. 24. -A vs. T for $Cu(H_2O)_6^{2+}$.

measure of the true width. Without knowledge of the low temperature spectra we would also be tempted to use the overall width as the true width. However, we can convince ourselves that this is incorrect by examining the spectra closely.

The results of an attempt to fit the room temperature spectrum with a single Lorentz line is shown in Fig. 20. This is the same spectrum that was presented in Fig. 18. The spectrum quite clearly does not possess a Lorentz lineshape. In fact close examination of the spectrum reveals several inflections near the center of the spectrum . This is shown more clearly in Fig. 21 which shows the result of fitting two Lorentz lines to the same spectrum. We may confidently infer from this that the observed spectrum consists of more than two lines. It is, therefore, quite reasonable to fit the spectrum with four hyperfine components.

Figure 22 shows the result of fitting the spectrum of Fig. 19 with one Lorentz line. Even at 60°C the spectrum is not Lorentz in shape. Hence, a lineshape analysis indicates that the EPR spectra for hexaquocopper (II) must be analyzed in terms of four hyperfine components.

The variation with temperature of the isotropic and A values for hexaquocopper (II) is shown in Figs. 23 and 24. A variation of these parameters with temperature is not unexpected since such variations were observed for the aqueous vanadyl system and for vanadyl acetylacetonate (Wilson and Kivelson, 1966a). However, the usual observation is that the magnitudes of the g and A value change in opposite directions as the temperature is changed, that is, the g value decreases as the A value increases. In the present case the g and A values change in the same direction.

One might at first consider this effect to be an artifact because of the method of analysis. The line positions are determined by a second order spin Hamiltonian. The effect of the second order term is to shift all of the lines downfield. If the second order term is neglected, an apparent g value is obtained which is higher than the true g value. Furthermore, if the least squares fit erroneously causes the A value to decrease, then, the shift due to the second order term would decrease and the apparent g value would decrease. However, the shifts due to the second order term are on the order of a gauss and the changes in the second order term are somewhat less. Since the changes in the g value correspond to shifts of several gauss, the effect must be real.

The usual interpretation of the temperature variation is that changes in solvation and bonding are occurring (Wilson and Kivelson, 1966a). However, this theory would require that the g and A values change in opposite directions since changes in bonding affect these parameters in opposite ways. Therefore, the variation in the hexaquocopper (II) system cannot be explained by this mechanism.

A number of mechanisms may be responsible for variations of the g value or of the A value with temperature. Van Gerven, Talpe, and van Itterbeck (1967) have suggested a shift due to demagnetizing effects. They show that the shift in the g value, Δg is approximately given by

$$\Delta g \sim (2N_s - N_l)\ \chi_s \qquad (4.2)$$

where N_s and N_l are so-called demagnetizing factors, which are computed from the geometry of the sample, and χ_s is the static volume susceptibility of the sample. The g value variation is expected to follow a Curie law. However, the magnitude of this effect is quite small and would not account for the large g value changes which are observed. Furthermore, this mechanism is not expected to cause a variation in the hyperfine coupling constant.

A second source of shifts are dynamic effects due to relaxation effects in solution. Such effects have been discussed by Fraenkel (1967) and by Kivelson (1960). These effects are found in most treatments of relaxation theories but are generally ignored by assuming that the static Hamiltonian can be redefined to include these terms (Slichter, 1963). The spin Hamiltonian is rarely redefined in practice. Kivelson derives a nonsecular shift to be

$$\Delta = \tau_c \omega_o T_1^{-1} \tag{4.3}$$

where here T_1^{-1} is the nonsecular contribution from the linewidth theory and is dependent upon m_I. The shift is then dependent upon the hyperfine component and follows a temperature dependence involving the correlation time and linewidth. Since the shifts are different for each hyperfine component, the hyperfine coupling constant may change as well as the g value although the effect of the shifts on the least squares determination is not clear. The effect of Eq. 4.3 can be estimated if the full linewidth is assumed to be due to T_1^{-1}. In fact the magnitude of the changes with temperature could account for the magnitude of the g value changes. However, the computed shift is a downfield shift which increases with temperature. This should cause an increase of the g value with temperature whereas the g value decreases with increasing temperature. Hence, nonsecular shifts cannot be the reasons for the g value variation.

Another possible dynamic effect is the thermal vibrations of the ligands. Benedek, Englman, and Armstrong (1963) have studied the temperature dependence of NMR chemical shifts due to thermal vibrations. The effective crystal field splitting changes because the amplitudes of vibration change as a function of temperature. Unfortunately this effect would predict that the g and A values should change in opposite directions.

Walsh, Jeener, and Bloembergen (1965) and Soos (1968) have studied the variation of the g tensor as a function of temperature in the solid state. Soos explains his variations for organic radicals in terms of delocalization of the electrons over radicals with slightly different g tensors. As the temperature changes, the delocalization changes and the observed g tensor changes. Walsh, et al., explain their behavior in terms of changes in the crystal field due to thermal expansion effects. In these experiments, the g value decrease with increasing temperature was well explained by crystal field changes due to lattice expansion.

However, Walsh observed that the hyperfine interaction (for Mn^{2+}) decreased as the temperature increased, whereas the explanation for the g value change would predict an increase in the A value. Orbach (Simanek and Orbach, 1966; Calvo and Orbach, 1967) has studied this behavior and proposed that excited state configurations were mixed into the ground state by a "dynamic phonon-induced" field. This explanation was proposed for S state ions but might be applicable to other states.

Admittedly, these solid state explanations are not directly applicable to solution, but temperature dependent mixing of excited state configurations with the ground state is a possible explanation for the g and A value variation. Indeed, the hexaquocopper (II) complex is expected to have a low lying excited state due to the Jahn-Teller effect. This state could have an appreciable effect on the g and A tensors.

The source of the variation of the g and A tensors is not well understood. Fortunately, the variation in the parameters is relatively small so that the variation is neglected for the linewidth theories. The values of the isotropic parameters used for the linewidth analysis are $g=2.1983$ and $A = -34.4$ gauss.

2. Relaxation

The linewidths for hexaquocopper (II), which were also determined from the least squares fits, are presented in Figs. 25-28. The components are identified by m_I, the nuclear magnetic quantum number, and since the hyperfine coupling constant is assumed to be negative, the $m_I = -3/2$ line is the lowest field line and the $m_I = +3/2$ line is the highest field line. The linewidths for the components show a smooth functional dependence on the temperature, increasing monotonically with the temperature. Below 40°C the deviations in the data are small. Above this temperature, there is increasing scatter in the data. At the lowest temperatures where hyperfine components are distinctly visible, the linewidths are known to about .5%. Near room temperature where the line is unresolved, but definitely not lorentzian, the error is expected to be sbout 1%. There is much less confidence in the data at higher temperatures where the line is near Lorentzian, and the error is expected to be several per cent. The dashed curves in the figures are arbitrary interpolation curves.

The linewidths for the hyperfine components are compared in Fig. 29. Examination of the low temperature region reveals a distinct dependence on hyperfine component, with the narrowest line being the $m_I = +3/2$ or

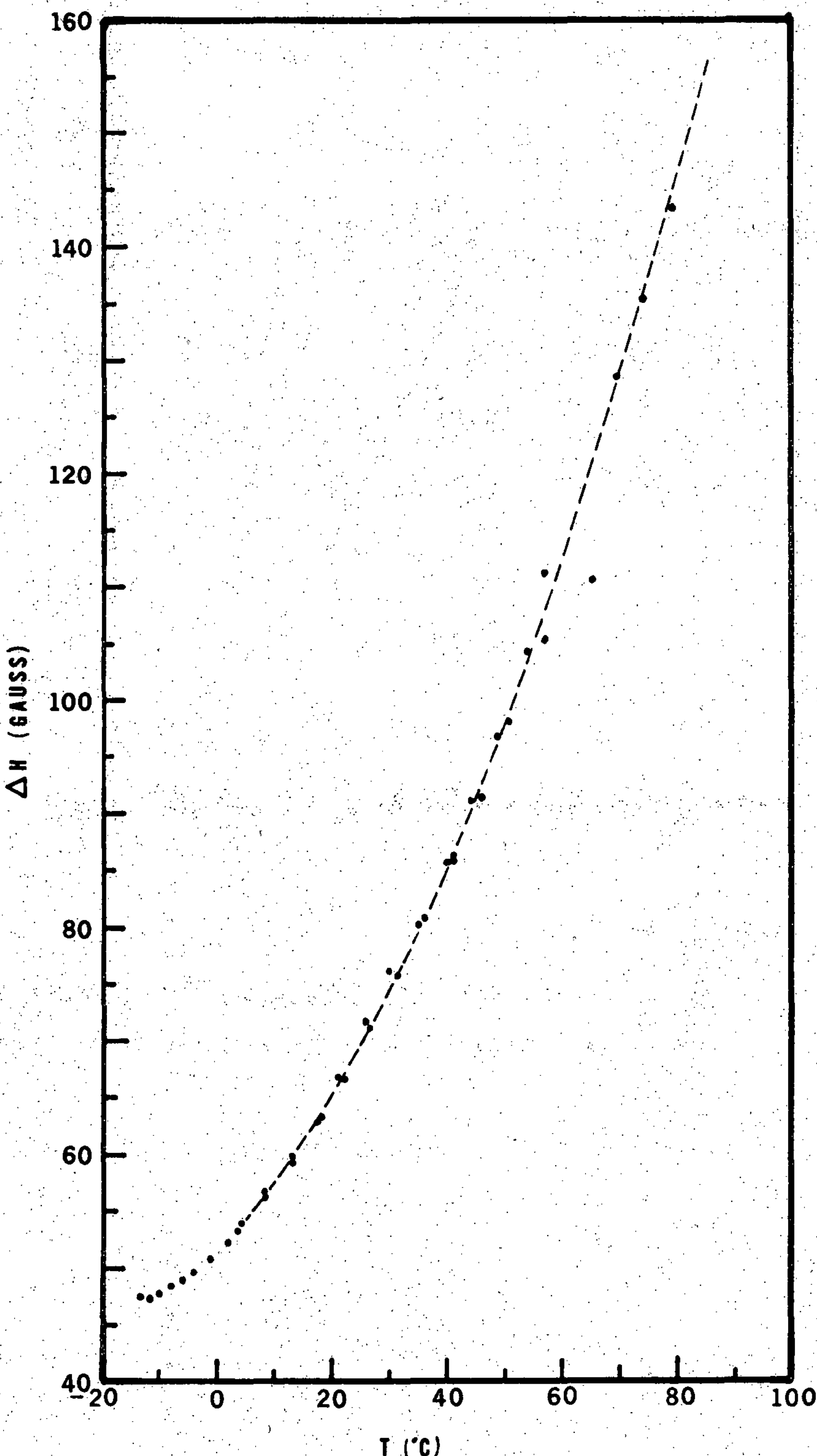

Fig. 25. Peak-to-peak linewidth of -3/2 component vs. T. Dashed curve is interpolation graphical.

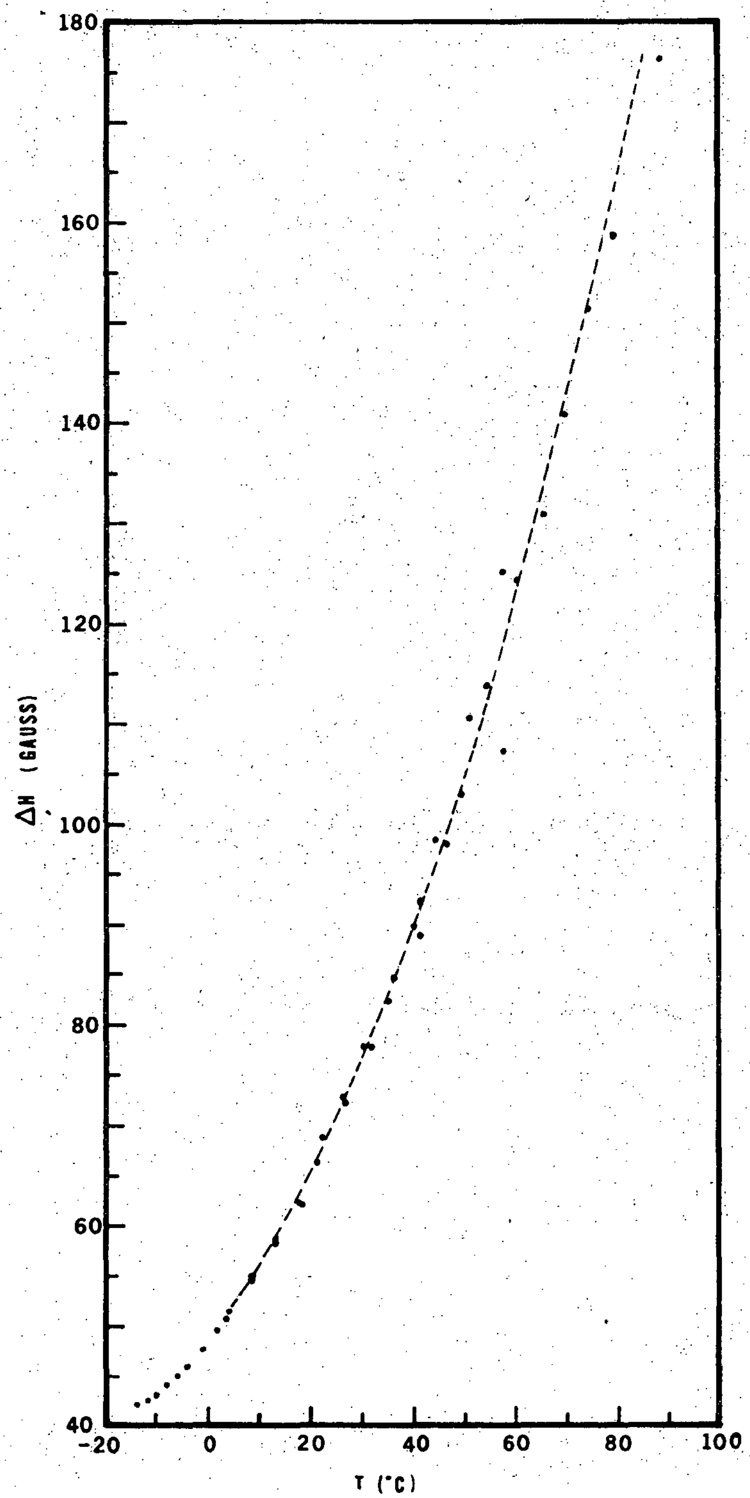

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Fig. 26. Peak-to-peak linewidth of -1/2 component vs. T.

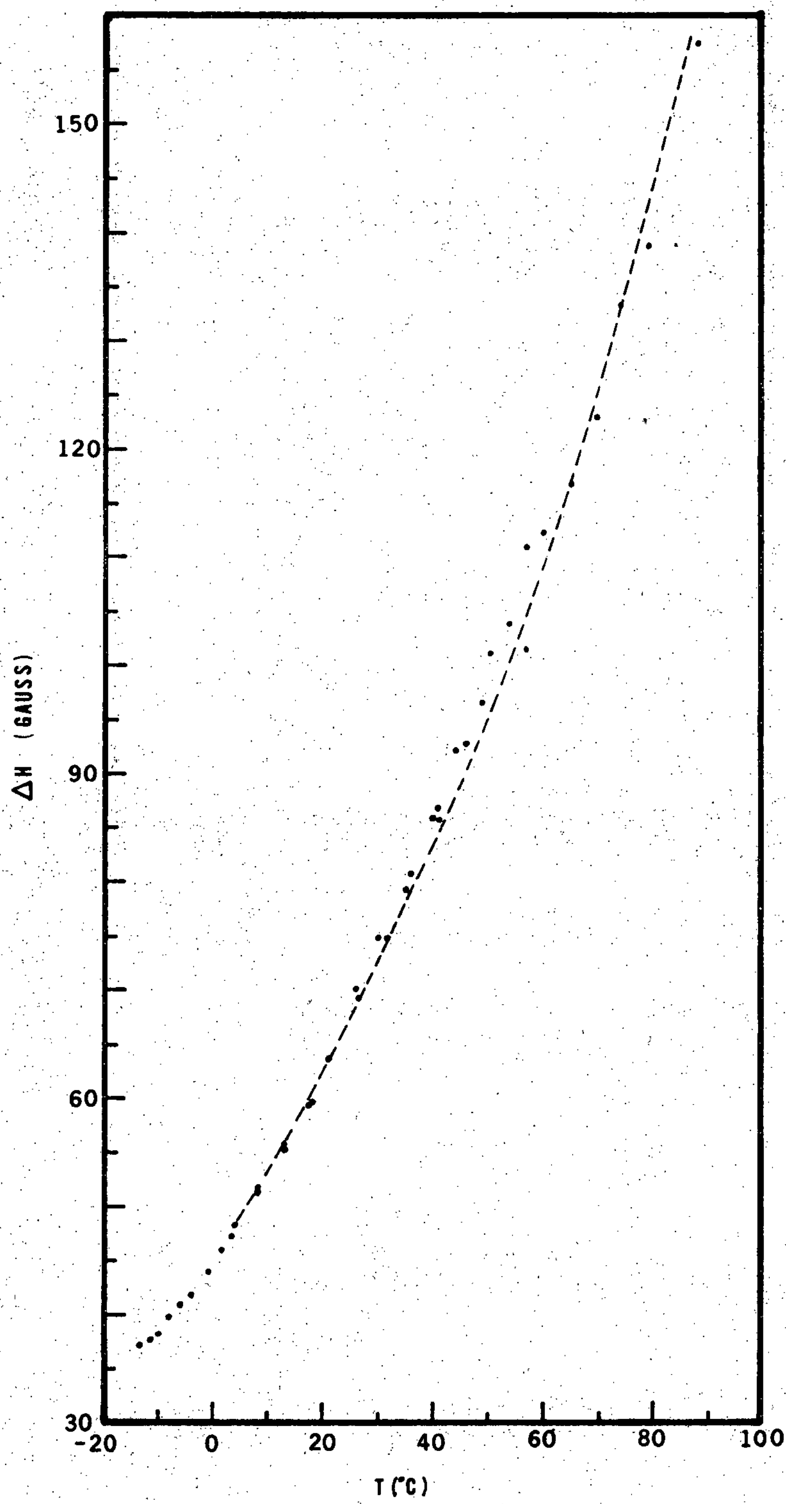

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Fig. 27. Peak-to-peak linewidth of +1/2 component vs. T.

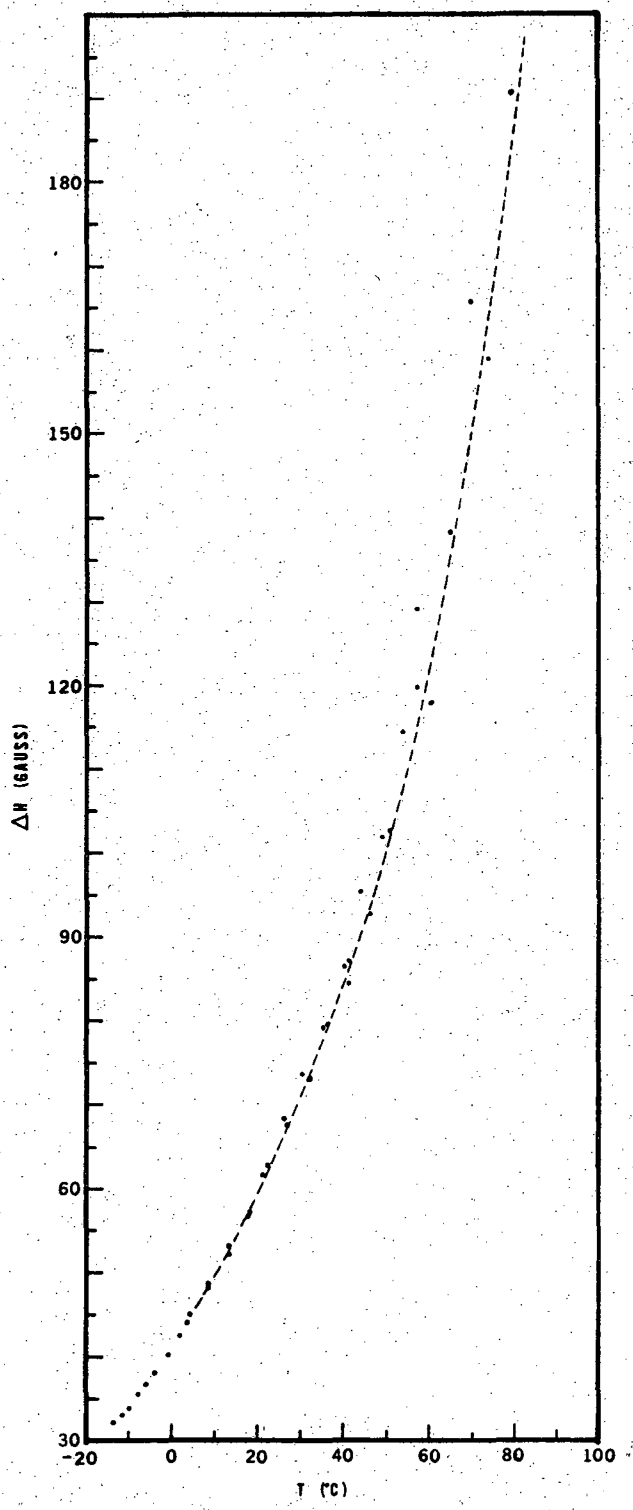

Fig. 28. Peak-to-peak linewidth of +3/2 component vs. T.

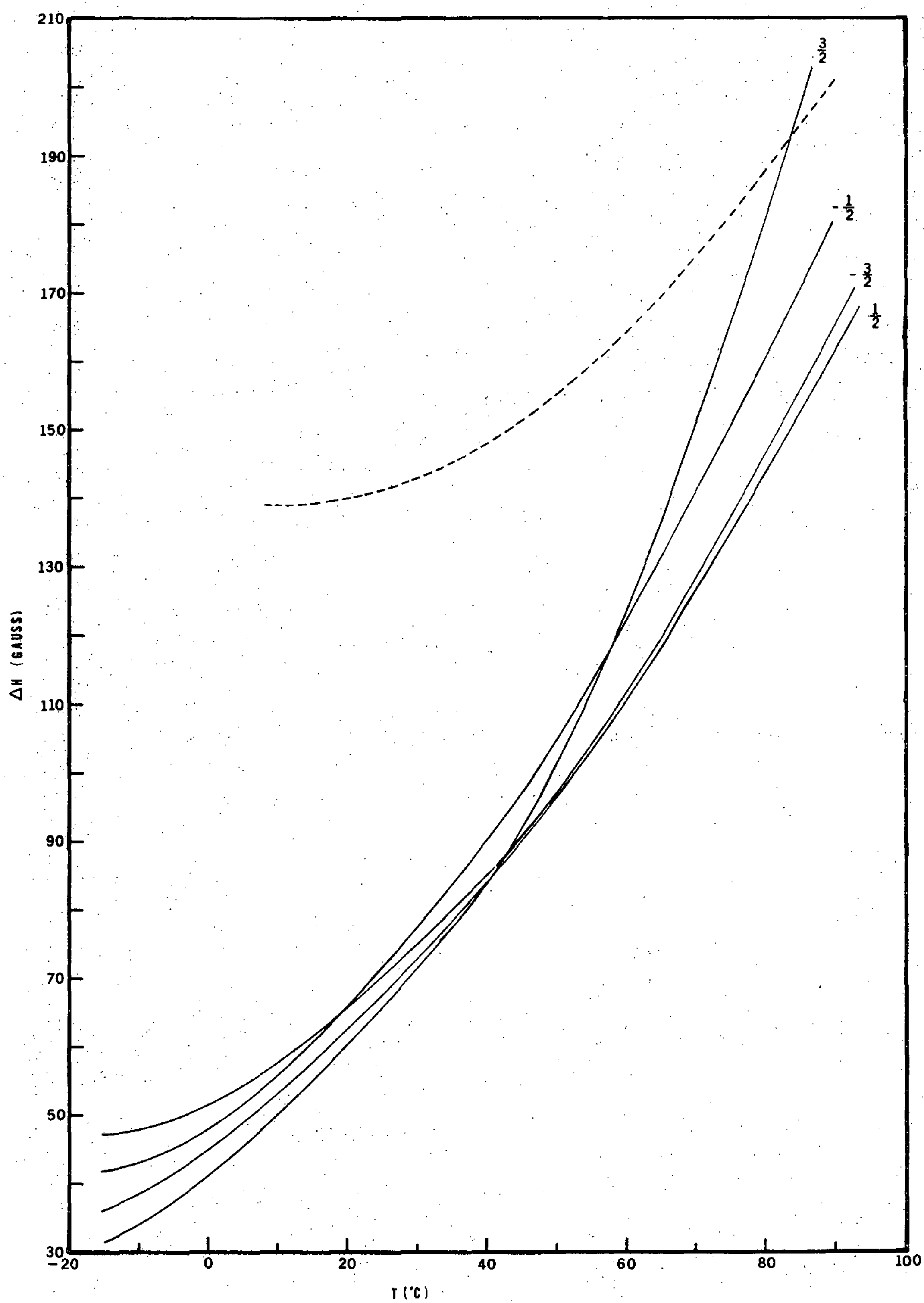

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Fig. 29. Comparison of linewidths for hyperfine components of $Cu(H_2O)_6^{2+}$.

highest field line. The lines are progressively broader as m_I is decreased, with $m_I = -3/2$ as the broadest line. As the temperature is increased, the relative widths change until the $m_I = -1/2$ line becomes the broadest line. At still higher temperatures, the $m_I = +3/2$ line appears to become the broadest line. We are not certain that this behavior is real. At the high temperatures least squares procedures are quite difficult. Noise and drifts in the spectrum could cause large changes in the least squares fits. However, the linewidths definitely depend on the hyperfine component at low temperatures and appear to depend on the hyperfine component at higher temperatures.

The dashed line in Fig. 29 is the linewidth determined from the overall peak-to-peak distance of the unresolved line. The fallacy of using the overall width as the true width is clearly seen. The temperature dependence and the magnitudes of the width are incorrect. Valiev and Zaripov (1966) indicate that their mechanism is consistent with this data, so that the mechanism is probably incorrect for the copper system.

The dependence of the linewidths on hyperfine component leads one to suspect a Kivelson tumbling mechanism (Wilson and Kivelson, 1966a) to be contributing to the linewidth. In accord with this idea, the linewidths were fit to a cubic polynomial. The polynomial is exactly determined by four linewidths, so that the polynomial coefficients may be strongly influenced by small errors in the linewidths. The parameters which were determined are presented as the points in Figs. 30-32. The alpha parameter appears to vary quite smoothly with temperature. The beta and gamma parameters exhibit much scatter which is extreme at high temperatures. The delta parameter is even worse (not presented). (The correlation of temperature with viscosity divided by temperature is presented in Table II.)

As was done with the vanadyl data, the beta parameter was used to determine a hydrodynamic radius for the complex using Eqs. 2.6 and 2.3. The theoretical values for α' and γ were then computed from Eqs. 2.5 and 2.7 and are presented as the smooth curves in Figs. 30-32. These curves were computed using the anisotropic magnetic parameters which were determined in this work (see Sec. IV.C.1). The curves computed with the Lewis, Alei, and Morgan parameters are quite similar, and, therefore, are not plotted. We can see immediately that the theoretical and experimental parameters are in marked disagreement. The beta fit is relatively good at low temperatures. However, the experimental values for the gamma parameter are negative until the lowest temperatures are reached. The theory predicts that the gamma parameter should be positive over the entire temperature range. The theoretical prediction of the alpha parameter is also far from agreement with experiment.

Furthermore, the values of the correlation time and the hydrodynamic radius which are determined from the fit to the beta parameter are anomalously low. The radius, r=1.71 A, which was determined using the anisotropic parameters from this work, is of the order of the ionic radius for copper. If the Lewis, Alei, and Morgan (1966) magnetic parameters are used, the radius is r=1.83 A, which, although better, is still too small. By analogy to the vanadyl system, the radius is expected to be on the order of 3 A. Cox and Morgan (1959) and Morgan and Nolle (1959) have measured the proton NMR for copper solutions. The proton relaxation is due to a dipolar interaction modulation by molecular tumbling, so that the correlation time is related to the hydrodynamic radius by Eq. 2.3. These workers obtain a radius r=2.8 A. Frankel (1968) in a more recent study obtained r=2.3A.

The validity of the Kivelson tumbling model for the hexaquocopper (II) system is doubtful. Further evidence is obtained from the dependence of the theory on magnetic field. The EPR spectrum for hexaquocopper (II) was measured at S band (3.12 GHz) at room temperature (about 22°C). The spectrum is presented in Fig. 33. The linewidths obtained from a least squares fit to the S band spectrum are 67.8, 66.9, 65.7 and 65.9 gauss, respectively, for the -3/2 to +3/2 component. The corresponding linewidths for the X band spectrum are 66.6, 67.7, 64.1, and 62.0 gauss (from Fig. 29). Although there is a definite dependence upon hyperfine component, there is relatively little difference between the S band and X band linewidths. The Kivelson theory would predict a strong dependence of the linewidths with magnetic field. In addition, if we ignore these problems and continue to use the Kivelson mechanism, we may compute a linewidth contribution from the spin-rotation mechanism. If this is done, we compute linewidth contributions which are five times the experimental linewidths. Therefore, this procedure cannot be used to explain the linewidths, although it was very successful for the vanadyl case.

We must, therefore, proceed in another manner to explain the linewidths. The increase of the linewidths with temperature strongly indicates a spin-rotation mechanism. Ignoring the m_I dependent terms for the present, we plot the m_I independent linewidth, the alpha term, vs. T/η in Fig. 34. The alpha term is quite linear with temperature divided by viscosity. (The alpha term has not been corrected for a contribution from the tumbling mechanism because of the uncertainty with the theory). This is consistent with the prediction of a spin-rotation mechanism except that the extrapolation of alpha to zero temperature does not pass through zero. Nevertheless, we may use the slope of a straight line fit to the data with Eq. 2.12 to determine a hydrodynamic radius of r=3.08 A. This is a reasonable value.

If we assume the spin-rotation mechanism to be dominant, we may compute a contribution from the tumbling mechanism using the new hydrodynamic radius. If this is done, the predicted linewidth parameters are found to be much larger than the experimental parameters. Since we expect the tumbling mechanism and the spin-rotation mechanism to be consistent with each other, we must conclude that these mechanisms cannot both be fully operative in the hexaquocopper (II) system.

Lewis, Alei, and Morgan (1966) propose that the anisotropy of the copper complex is less in the aqueous solution than in the glass. They reduce the anisotropies, Δg and b, and compute a contribution of the tumbling mechanism to the linewidth. After correcting the m_I independent term for the tumbling contribution, they fit the remainder to a spin-rotation mechanism. They also include a term quadratic in temperature which they describe as a Raman process (see Eq. 4.1). This term is necessary to account for the curvature which appears in the alpha term after the tumbling correction is made.

The Raman mechanism was proposed on the basis of an extrapolation from the solid state work of Gill (Gill, 1965; Stoneham, 1965) on copper ions in Tutton salts. However, the more recent calculations of Kivelson (1966) have shown that the contributions of the Raman process in liquids is small. Therefore, although Lewis, Alei, and Morgan fit the m_I independent term well with a spin-rotation interaction and a T^2 term, the Raman process is not indicated.

Furthermore, Lewis, et al., are slightly inconsistent in their adjustment of the anisotropies. Although they adjust the anisotropies to compute the tumbling width, they do not adjust the g values in computing the spin-rotation width. Furthermore, they show that the magnitude of the ^{17}O coupling constant, which they measure from temperature dependent shifts of the ^{17}O NMR line, is consistent with the anisotropic parameters determined in a glass. In addition, they argue from Stoneham's work (Stoneham, 1965) that the first orbitally excited state for the hexaquocopper (II) complex is expected to be 7700 cm^{-1} above the ground state. This is consistent with a large tetragonal distortion and, hence large anisotropy.

The linewidths in hexaquocopper (II) are then somewhat of a mystery. The solution Raman process is unlikely. The solution Orbach process is unlikely if the lowest excited state is 7700 cm^{-1} above the ground state. The increase of the linewidth with increasing temperature is most likely explained by a spin-rotation interaction. However, the contribution from a tumbling mechanism consistent with the spin-rotation interaction and with the large anisotropy is too large. The tumbling mechanism cannot contribute its full effect and must be interrupted by some other relaxation process which is also m_I dependent. This would be something similar to the inversion mechanism discussed by Spencer (1965). Spencer treated both mechanisms separately. A more proper treatment is probably to treat both the tumbling process and the inversion process together. The linewidths in hexaquocopper (II) are then due to a spin-rotation interaction, a tumbling mechanism, and a third process, similar to inversion, which interrupts the tumbling mechanism, and which is essentially independent of magnetic field.

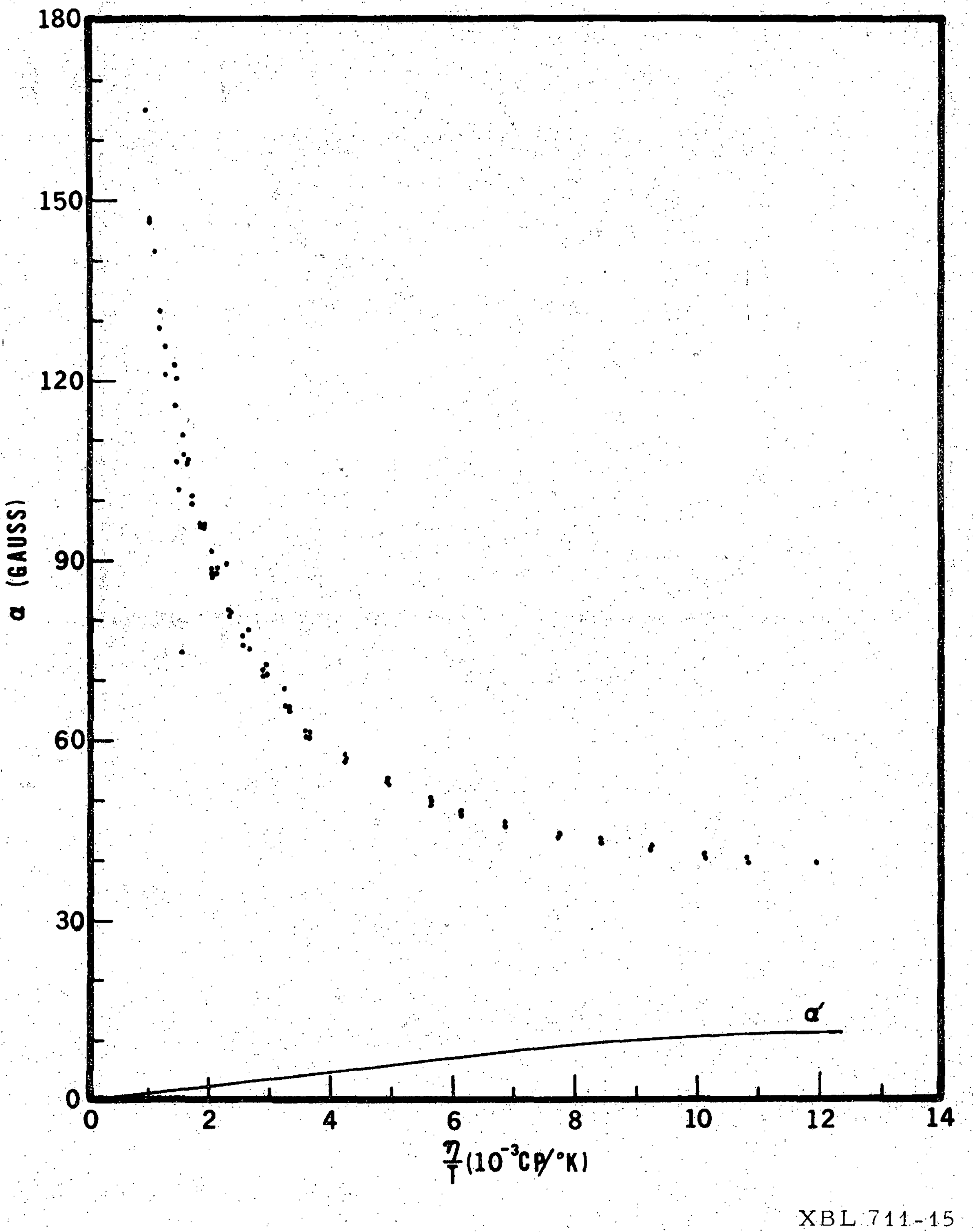

Fig. 30. Alpha parameter vs. η/T for $Cu(H_2O)_6^{2+}$.

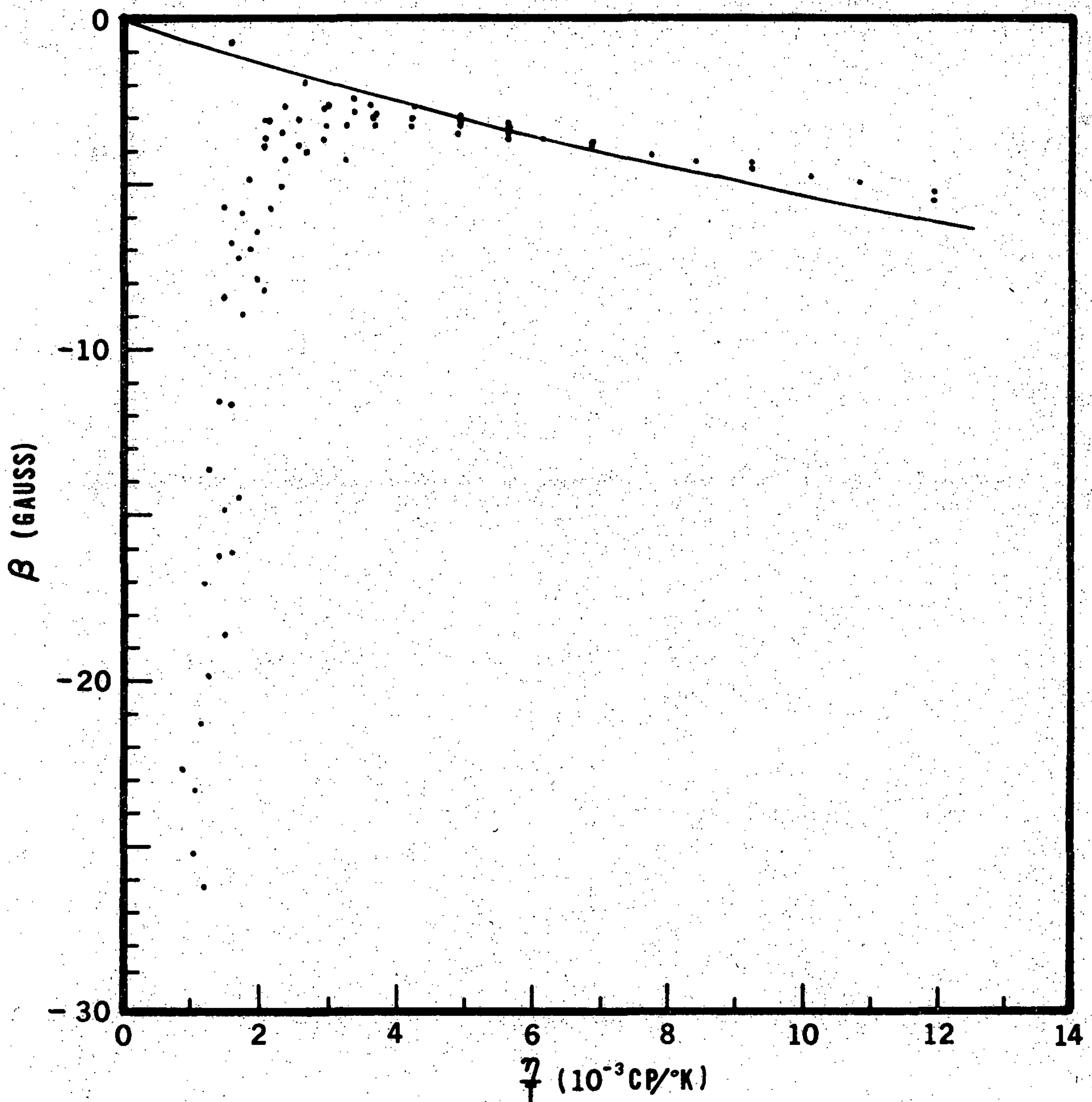

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Fig. 31. Beta parameter vs. η/T for $Cu(H_2O)_6^{2+}$.

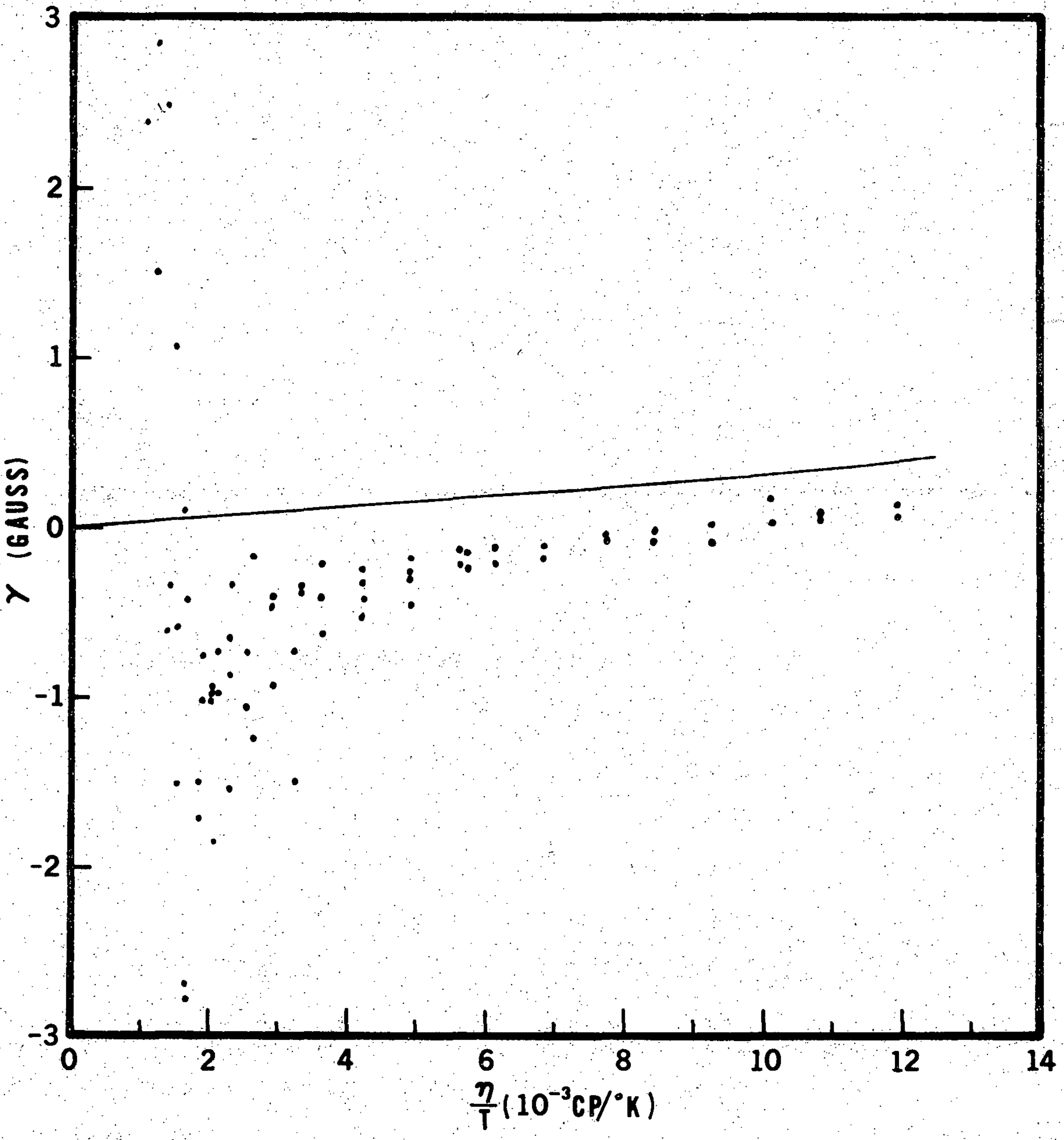

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Fig. 32. Gamma parameter vs. η/T for $Cu(H_2O_2)_6^2$.

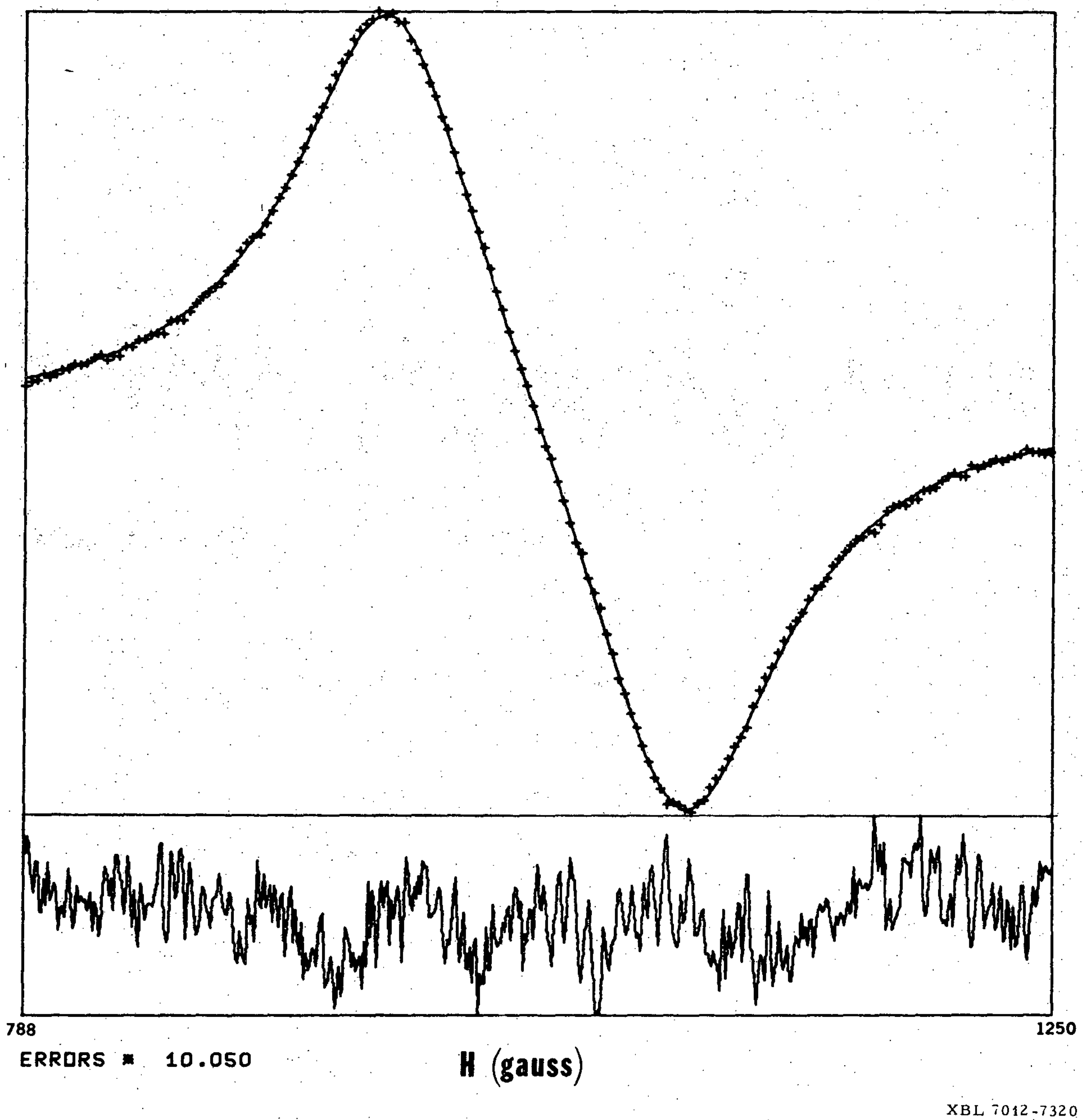

Fig. 33. Example to fit to solution spectrum of $Cu(H_2O)_6^{2+}$ at room temperature with a microwave frequency of 3.12 GHz.

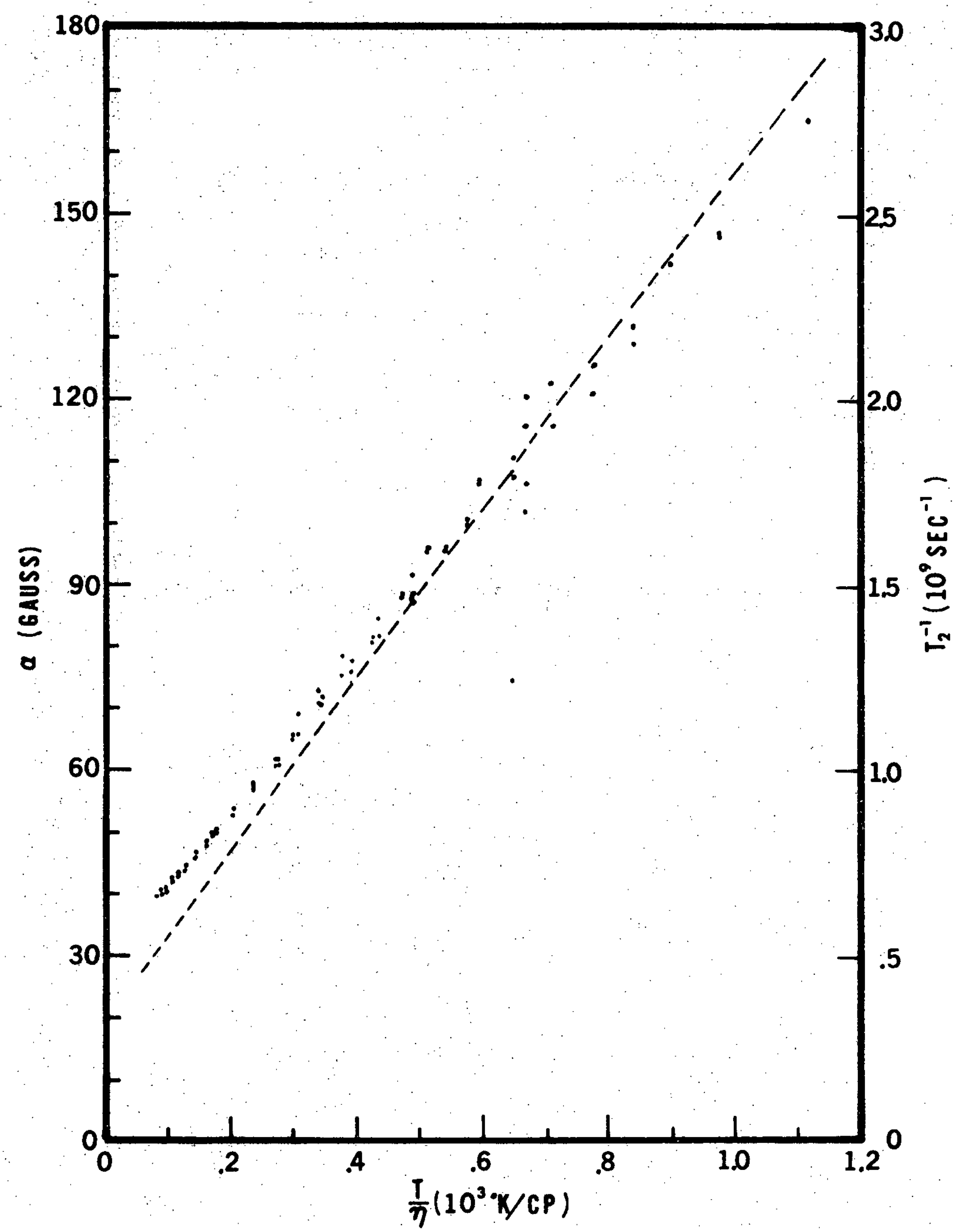

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Fig. 34. Alpha parameter vs. T/η for $Cu(H_2O)_6^{2+}$. The dashed curve is plotted with Eq. 4.1 (see text).

V. SPIN-LATTICE RELAXATION TIME MEASUREMENTS WITH AN ON-LINE COMPUTER

A. Introduction

The longitudinal or spin-lattice relaxation time is extremely important in magnetic resonance, for magnetic resonance phenomena would not be observable if satisfactory relaxation mechanisms did not exist. The spin-lattice relaxation times of transition metal ions diluted in various host lattices is of considerable interest. A knowledge of these times aids in the theoretical understanding of electron paramagnetic resonance and in the interpretation of the interactions which may occur in solids. Furthermore, the relaxation times which are related to transition probabilities are important in understanding the operation of masers (Bloembergen, 1956). Stevens (1967) and Standley and Vaughan (1969) have recently reviewed the theoretical and experimental aspects of the spin relaxation measurements.

A number of techniques have been developed for the measurement of relaxation times. One of the most popular is the pulse saturation-recovery method (Davis et al., 1958). In this method the spin system to be studied is saturated with a relatively high power pulse, and the recovery of the absorption signal as a function of time is monitored, usually on an oscilloscope. The relaxation time is determined either by measuring the slope of a plot of the lograithm of the recovery curve or by comparing the recovery curve with standard exponentials whose time constants are known. The logarithmic method requires a knowledge of the baseline to which the recovery curve is returning. This is done experimentally by providing a second scan at low power to show the recovered signal on the oscilloscope. This could involve experimental complications. The comparison method suffers if the recovery curve is not a single exponential. Furthermore, in many cases, the recovery curve contains a large amount of noise which makes the measurements from the oscilloscope traces difficult and inaccurate. Much experimental effort is usually expended to reduce this noise. Indeed, the improvement of the signal-to-noise ratio is one of the most serious problems in experimental science.

A technique for improving signal-to-noise is that of signal averaging. The usual method is to use a highly specialized computer of averaged transients (CAT) to acquire the data. Successive recovery curves are accumulated with the CAT until the signal-to-noise is acceptable. The data are then usually printed for analysis by the techniques described above, or punched for analysis with a digital computer.

However, we had been interested for some time in the application of small computers to laboratory problems. The advantages of using a computer are now well known. Interest in the technique has grown to such an extent that the January, 1969, issue of the IBM J. of Research and Development is devoted to laboratory automation. The problem of spin-lattice relaxation time measurements appears to be tailor made for a small computer. Not only can the data be acquired with the computer, for which time is a natural independent variable, but the data analysis can also be performed. In the case of simple exponential recoveries the analysis is straightforward and easily automated. Baseline problems are easily handled simply by acquiring data out to times where the baseline is well defined. More complicated recovery curves may be analyzed by an interactive technique using relatively simple conversational programs and a display oscilloscope. An additional advantage of a computer is that an analysis of the data can be performed quickly so that results are known instantly.

The Ni^{2+} ion was chosen for study since this was a transition metal ion of current interest in the laboratory (Jindo, 1971 ; Batchelder, 1969). Of interest is the D value which is negative for most nickel compounds. However, in nickel sulfate the D value is positive. This behavior is discussed by Jindo, 1971. Studies of nickel ions in other lattices were undertaken to obtain information to aid in a theoretical interpretation of this behavior. The EPR spectrum of nickel ion in a lanthanum magnesium nitrate host (Ni/LMN) has been studied in this laboratory (Jindo, 1971) and was selected as a suitable system in which to study relaxation times. Furthermore, relatively few measurements of relaxation times in nickel ions have been reported.

Bowers and Mims (1959) and Valishev (1965) have reported measurements of nickel ions diluted in zinc fluosilicate. The results did not agree with the predictions of the usual theories of spin-lattice relaxation. Indeed, Valishev's results seem to be somewhat anomalous in that the relaxation time was observed to decrease with decreasing concentrations of nickel ions. However, this may possibly be explained by a phonon bottleneck. Lewis and Stoneham (1967) and Jones and Lewis (1967) report measurements for nickel in magnesium oxide. The relaxation times were explained in terms of a direct process at low temperatures and a Raman process at higher temperatures. However, the measured relaxation times were shorter than would be predicted from the relaxation theories.

B. Experimental Methods

1. Samples

The crystals of lanthanum magnesium nitrate hydrate ($La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$) doped with Ni^{2+} were supplied by Mr. Akira Jindo. These crystals were grown by slow evaporation from a solution containing the correct proportions of $La(NO_3)_3$ and $Mg(NO_3)_2$ and a small amount of $Ni(NO_3)_2$. The crystals which are of rhombohedral symmetry, grow in the form of hexagonal plates with the crystal c axis located perpendicular to the plane of the plate. The nickel ions are substitutional impurities for the magnesium ions. There are two kinds of magnesium sites which are called site 1 and site 2 (Zalkin, et al., 1963). The spectra studied were due to nickel ions of trigonal symmetry in site 1.

Relaxation measurements were performed on two crystals one of which was more dilute in nickel ions than the other. The exact concentration of the nickel ions in the crystals is not known, but is not expected to exceed a maximum of 4%. The concentration of the more concentrated sample is expected to be 1-2%. The other crystal, which is known to be more dilute from a comparison of the relative spectrum intensities, is expected to have a concentration less than 1%.

2. Apparatus

The crystals to be studied were held in a cylindrical cavity operating in the TE_{011} mode. The crystals were oriented with the cylindrical axis of the cavity contained in the plane of the crystal so that the magnetic field could be rotated in the ac plane of the crystal. The relaxation time determinations were performed with the magnetic field oriented along the c axis which wss located with the following procedure. The magnetic field was rotated until the two high field lines in the spectrum were superimposed. This occurred at the so-called magic angle of 37° (Jindo, 1971) where the three nickel energy levels are accidentally equidistant. The magnet was then rotated by 37° to obtain the c axis.

The temperature of the sample was varied by changing the speed of pumping on the liquid helium in which the sample was immersed. The temperature, which was varied between 1.2 and 4.2°K, was determined from the equilibrium vapor pressure of the helium.

The pulse-saturation spectrometer used in these experiments consisted of the normal homodyne detection spectrometer, which has been described previously (Pratt, 1967; Batchelder, 1969), and in addition, a PIN modulator, a pulse generator, an oscilloscope, and a LAB-8/I digital computer system (see Fig. 35). The homodyne spectrometer was modified by the introduction of the Hewlett-Packard Model 8735B PIN modulator into the cavity arm of the bridge. This unit could vary the power reaching the cavity from full power to 80 dB attenuation. In practice, the modulator and the attenuator in the cavity arm were adjusted so that the saturating power reaching the cavity was about 50 milliwatts, while the observing power was more than 40 dB below the saturating power.

The modulator was pulsed to the full transmitting state by means of an Intercontinental Instruments, Inc., Model PG-2 pulse generator. The pulse widths were adjusted to about 5 milliseconds. Pulses were repeated at a maximum rate of once every 300 msec. which was sufficient to permit the spin system to return to equilibrium. The pulses were applied to the modulator through a biasing network which is also detailed in Fig. 35.

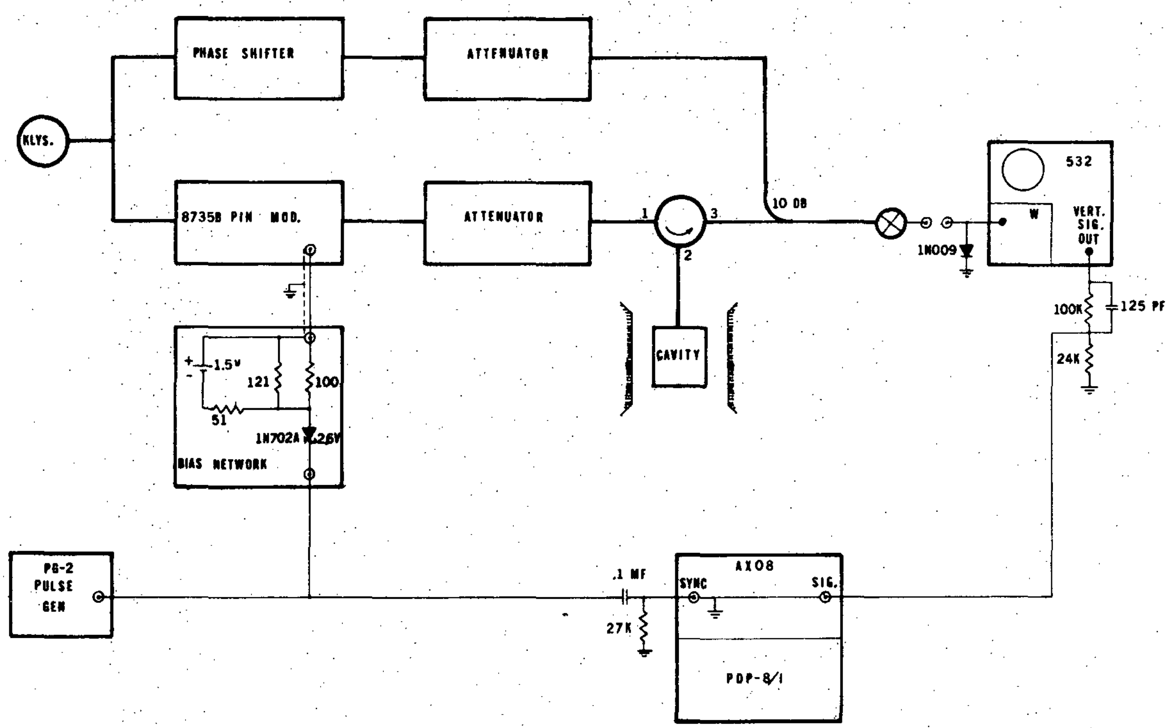

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Fig. 35. Block diagram of pulse-saturation spectrometer.

The biasing network served the double purpose of biasing the modulator to control the observing power, and to isolate the pulse generator from the modulator. The pulse generator was found to have ripple in the output in its quiescent state which could modulate the observing power and cause noise. The zener diode in the network isolates the pulse generator after the pulse has been delivered and also prevents the pulse height from accidentally becoming large enough to damage the modulator. The biasing voltage was provided by a 1.5 V dry cell which is a stable DC voltage source. The resistors were adjusted for ca. 45 dB attenuation in the modulator.

The recovery signals were observed as absorption signals using straight DC detection from the crystal diode detector. The absorption signals were on the order of millivolts and could easily be displayed on an x-y recorder or on an oscilloscope. The recovery curves were monitored with a Tektronix Model 532 oscilloscope equipped with a Type W differential amplifier plug-in. The differential amplifier was necessary to offset the detector bias voltage in order to preserve the full gain in the amplifier. The type W unit is susceptible to a thermal recovery problem if presented with a high signal level as would happen when a pulse was received. This effect was reduced by placing a clipping diode (1N009) on the input of the type W unit to prevent overdriving. The oscilloscope also served the purpose of amplifying the recovery signals for presentation to the computer system.

A synchronizing signal from the pulse generator and the recovery signal from the oscilloscope vertical signal output were presented through impedance matching networks to the LAB-8/I digital computer system.

The LAB-8/I computer system, as purchased from Digital Equipment Corp. consists of only a 4K PDP-8/I computer with teletype, and an AX08 laboratory peripheral. Our system includes, in addition, a DF32 disk (32K words), a PC08 high speed paper tape reader and punch, a KE8I extended arithmetic element, and an extra 4K of memory. The AX08 laboratory peripheral processes all analog signals and contains an analog-to-digital converter (ADC) which is multiplexed between four inputs, a crystal clock and an RC timing clock, a display control consisting of two analog outputs from a digital-to-analog converter and an intensify signal, and some trigger inputs for synchronization. There are also a number of miscellaneous digital inputs and outputs. The ADC is a 9 bit successive approximation converter and can perform a conversion in 17 microseconds. This is the ultimate limitation of how short a relaxation time may be measured with the computer system. The preamplifier of the ADC has a ±1V input range.

The operation of the spectrometer is relatively straight-forward. The spectrometer is first tuned and adjusted in the normal manner, except that the klystron is not locked to the cavity. The klystron frequency lock is not used in order to prevent the lock recovery after a pulse from interfering with the signal recovery. The PIN modulator is adjusted to provide the proper attenuation for the observing power. The magnetic field is then adjusted to the proper resonance, and the pulse generator is turned on. The averaging program is then started (presently this is the BASIC AVERAGER provided by DEC). After a sufficient numer of scans have been accumulated, the averaging program is halted. At this time the LOGLINE overlay (see Appendix) is started to either punch the data on the high speed punch, or to analyze the data for relaxation times. The data are normally punched either for later analysis or to save the data.

C. Rate Equations

In a two level system relaxation can be viewed simply as a process of transferring spin population from one level to the other level. This process is readily described by a single decaying exponential. In a three level system the problem is somewhat more complicated. The population in one level may transfer to either of the two remaining levels. The signal observed in a relaxation experiment is proportional to the population difference between the two levels being observed. We must consider the form of the signal expected in a pulse saturation experiment. This is normally done by means of the rate equations.

We shall consider the rate equations for the 3 level system shown in Fig. 36. Each of the levels, i, contains an instantaneous population N_i^o, and the excess population, n_i, by

$$N_i = N_i^o + n_i \tag{5.1}$$

The levels are connected by the spontaneous transition probabilities w_{ij} (probability $i \rightarrow j$). The rate equations are then

$$\begin{aligned} \dot{N}_1 &= N_3 w_{31} + N_2 w_{21} - (w_{12} + w_{13}) N_1 \\ \dot{N}_2 &= N_3 w_{32} + N_1 w_{12} - (w_{21} - w_{32}) N_2 \end{aligned} \tag{5.2}$$

where the third equation for $\dot{N}_3$ has been omitted since it is related to the other two by

$$\dot{N}_1 + \dot{N}_2 + \dot{N}_3 = 0 \tag{5.3}$$

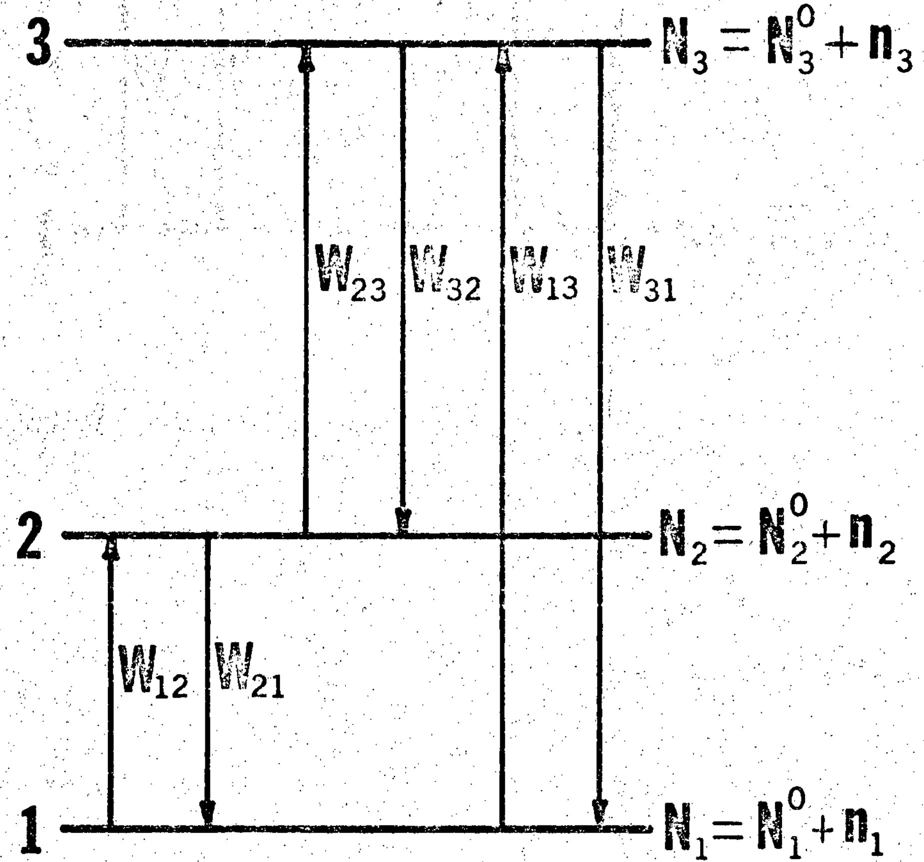

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Fig. 36. Transitions and populations of a three level system.

However, since

$$n_3 = -n_1 - n_2 \tag{5.4}$$

and

$$N_1^o/N_2^o = \exp(-E_{12}/kT) \tag{5.5}$$
$$w_{12}/w_{21} = \exp(E_{12}/kT)$$

where E_{12} is the energy difference between levels 1 and 2, and with similar relations for the other pairs of levels we may obtain the following equations

$$\begin{aligned} \dot{n}_1 &= -(w_{12} + w_{13} + w_{31})n_1 + (w_{21} - w_{31})n_2 \\ \dot{n}_2 &= (w_{12} - w_{32})n_1 - (w_{21} + w_{23} + w_{32})n_2 \end{aligned} \tag{5.6}$$

These are simultaneous linear differential equations of the form

$$\begin{aligned} \dot{n}_1 &= a_1 n_1 + b_1 n_2 \\ \dot{n}_2 &= a_2 n_1 + b_2 n_2 \end{aligned} \tag{5.7}$$

where

$$\begin{aligned} a_1 &= -(w_{12} + w_{13} + w_{31}) \\ a_2 &= w_{12} - w_{32} \\ b_1 &= w_{21} - w_{31} \\ b_2 &= (w_{21} + w_{23} + w_{32}) \end{aligned} \tag{5.8}$$

These equations may be solved using standard techniques (Kaplan, 1958). The solutions are of the form

$$n_1 = \alpha \exp(\lambda t) \qquad n_2 = \beta \exp(\lambda t) \tag{5.9}$$

where λ may be obtained from the related homogeneous equations obtained from Eq. 5.9 and 5.7

$$\begin{aligned} (a_1 - \lambda)\alpha + b_1 \beta &= 0 \\ a_2 \alpha + (b_2 - \lambda)\beta &= 0 \end{aligned} \tag{5.10}$$

These equations have a solution is the determinant is zero so that we may obtain

$$\lambda = 1/2 \left((a_1 + b_2) \pm \sqrt{(a_1 + b_2)^2 - 4(a_1 b_2 - a_2 b_1)} \right) \tag{5.11}$$

Ratios of alpha and beta may be obtained from Eq.s 5.10 and 5.11. In any case, the general solutions are

$$\begin{aligned} n_1 &= C_1\, \alpha_1\, e^{\lambda_1 t} + C_2\, \alpha_2\, e^{\lambda_2 t} \\ n_2 &= C_1\, \beta_1\, e^{\lambda_1 t} + C_2\, \beta_2\, e^{\lambda_2 t} \end{aligned} \tag{5.12}$$

where the C's are determined by the initial conditions. The solutions in which we are interested is the population difference given by

$$n_2 - n_1 = C_1(\beta_1 - \alpha_1)\, e^{\lambda_1 t} + C_2(\beta_2 - \alpha_2)\, e^{\lambda_2 t} \tag{5.13}$$

Similar solutions may be obtained for the other level pairs. We can see that the observed recovery curve will be a sum of two exponentials rather than a simple single exponential. The relaxation times will be the reciprocals of the λ's, and are related in a complicated manner by Eqs. 5.11 and 5.8 to the transition probabilities. Theoretical results will, in general, be for the transition probabilities. Hence, a complete comparison of experiment with theory requires experimental values for the w's. This will necessitate a detailed consideration of the coefficients of the exponentials as well as the λ's. This will not be considered here since we have shown what we wished: the recovery curve is a sum of two exponentials. Furthermore, for a constant field, the same relaxation times should be obtained for each of the transitions.

D. Discussion and Results

With the magnetic field oriented along the c axis of the crystal, the EPR spectrum of the Ni/LMN system consists of three lines which correspond to the transitions indicated in Fig. 37. The first and third lines, if the lines are numbered from low to high field, are strong allowed transitions. The second line is a "forbidden" transition. Jindo (1971) determined the spin Hamiltonian parameters to be $g_{\parallel}$ =2.235, $g_{\perp}$ =2.233, D=+.2005 cm^{-1}, and E=.0007 cm^{-1}. The small E value was necessary to fit the data, though the ion with no lattice distortion is expected to be at a site of trigonal symmetry. These parameters have a small temperature dependence which may require minor modifications to any theoretical relaxation treatment of the system.

Relaxation time measurements have been made for each of the lines over a temperature range of 1.3 to 4.2°K using the pulse saturation-recovery method. An example of a typical recovery curve is shown in Fig. 38 which shows the recovery of the high field line for T=1.37°K. The data show an excellent signal to noise ratio and have been collected to essentially complete recovery so that the baseline of the recovery is well known. A logarithmic presentation of the data with the baseline substracted is shown in Fig. 39. The logarithm is essentially linear at long times but shows curvature near the start of the recovery curve. Possible reasons for this behavior are discussed later. A reasonable relaxation time may be obtained from the linear portion of the curve.

The relaxation data obtained for the low and high field lines of the fairly concentrated sample are presented in Figs. 40 and 41. The data are

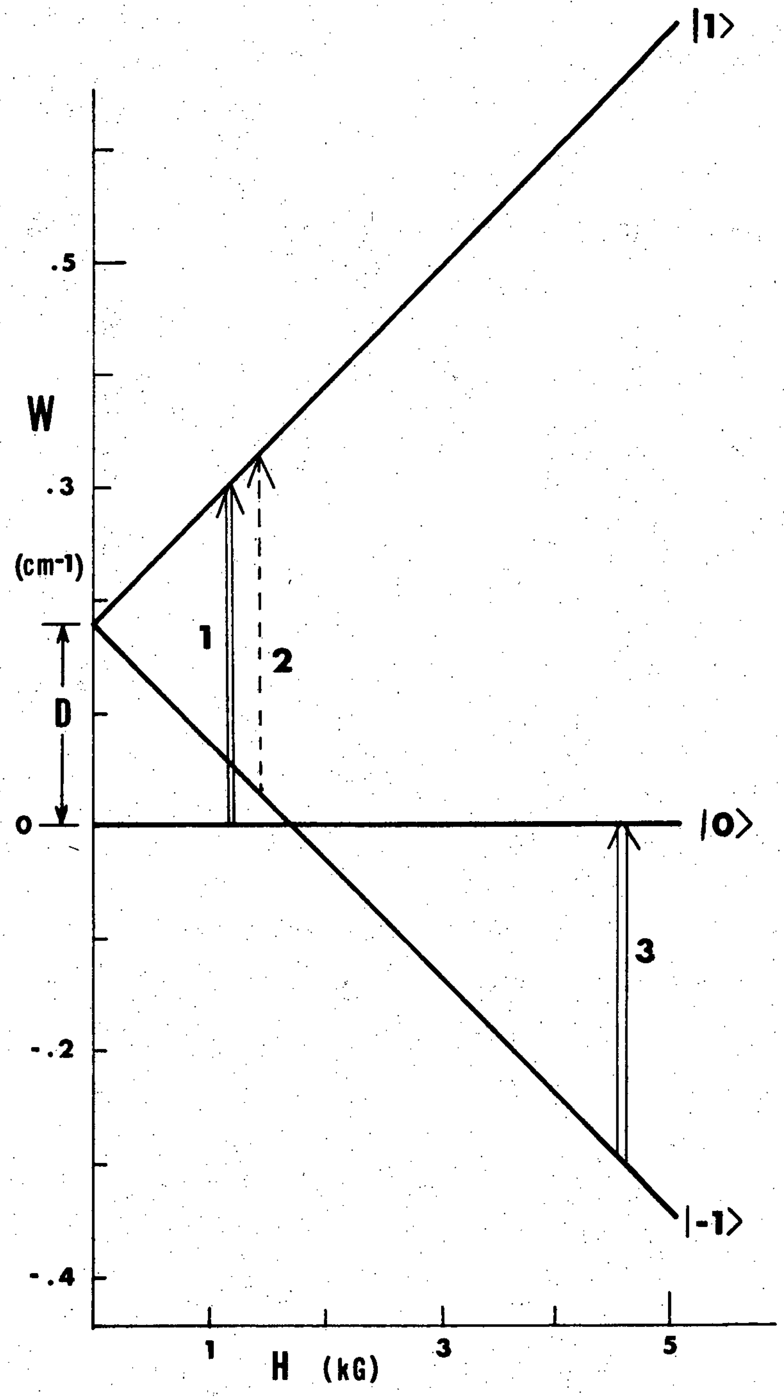

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Fig. 37. Energy levels and transitions for Ni^{2+} in lanthanum magnesium nitrate hydrate with the magnetic field oriented along the c axis (Jindo, 1971)

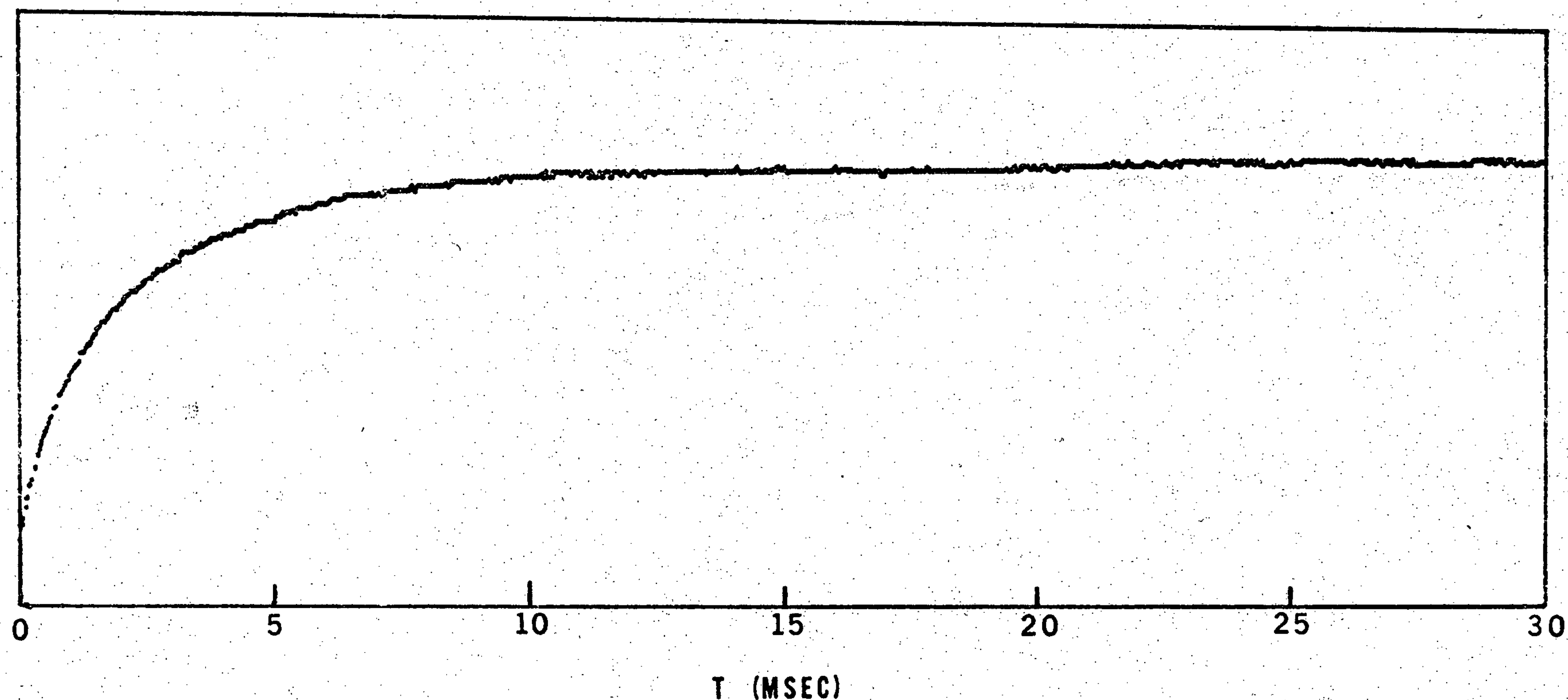

Fig. 38. Exponential recovery curve for the low field line at 1.37 °K. An average of 50 experiments.

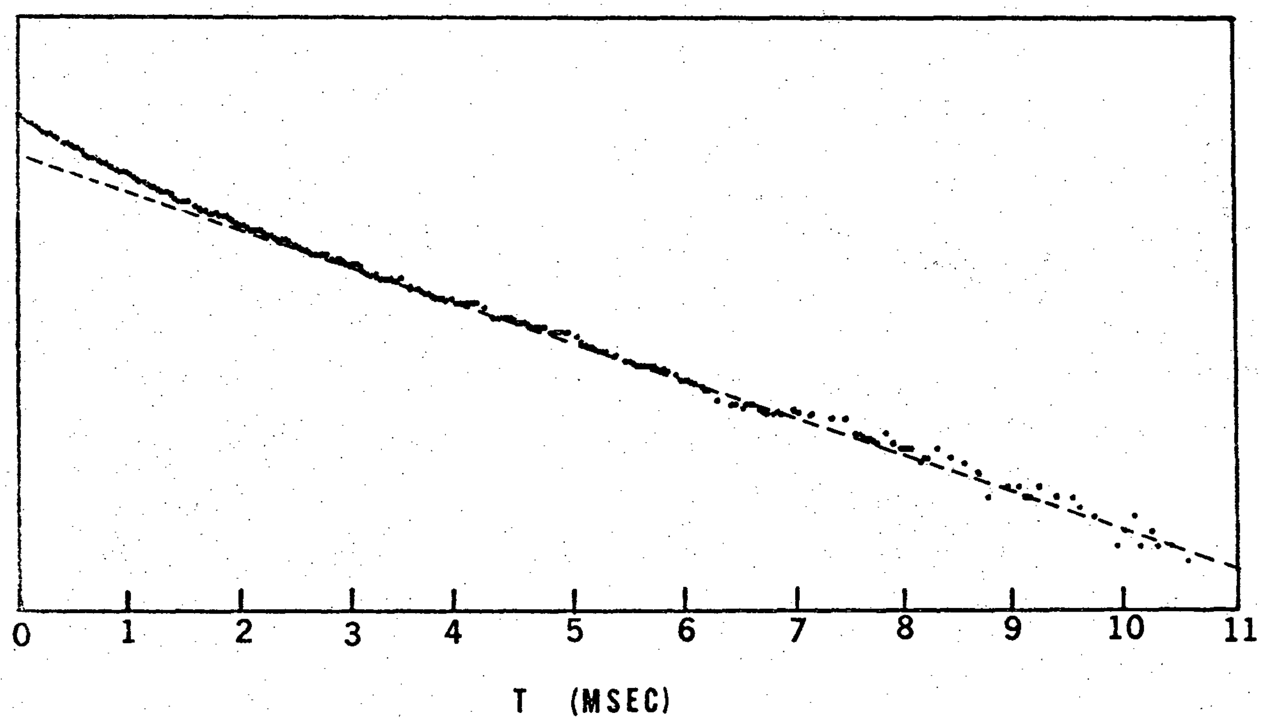

Fig. 39. Logarithm of the data in Fig. 38 with the baseline removed. Dashed line is a straight line fit to the data with a time constant (reciprocal slope) of 3.15msec. Curvature at start of data may indicate the presence of a second shorter time constant.

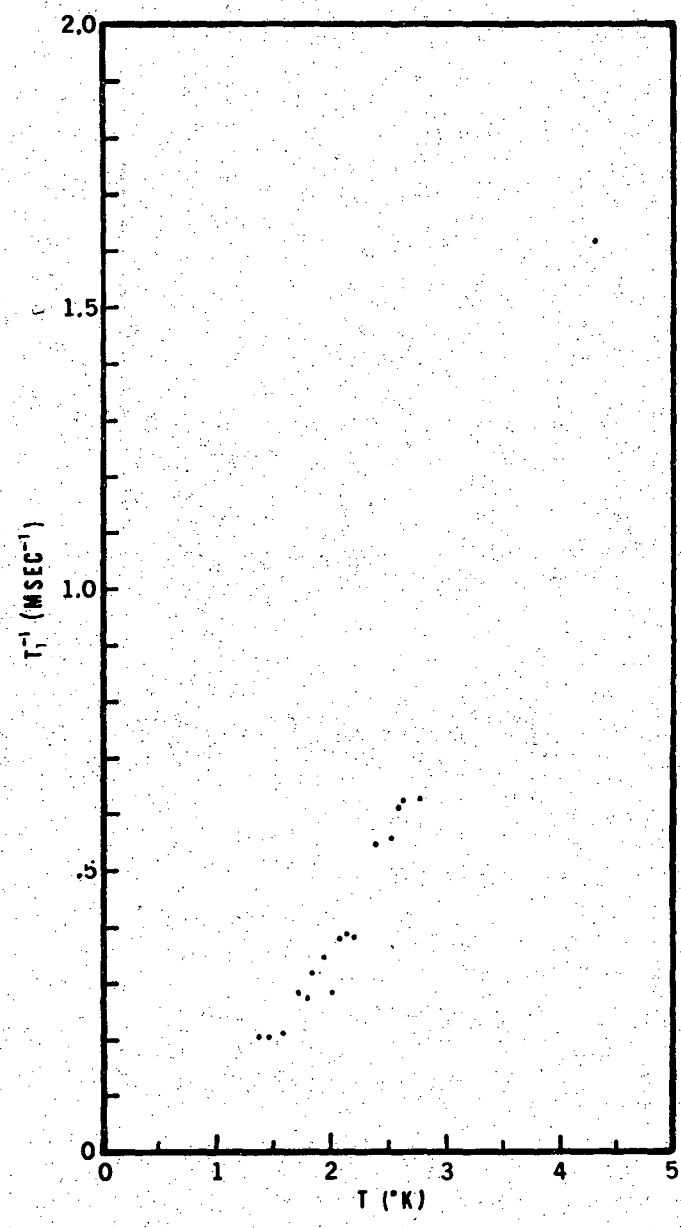

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Fig. 40. T_1^{-1} vs. T for the low field line.

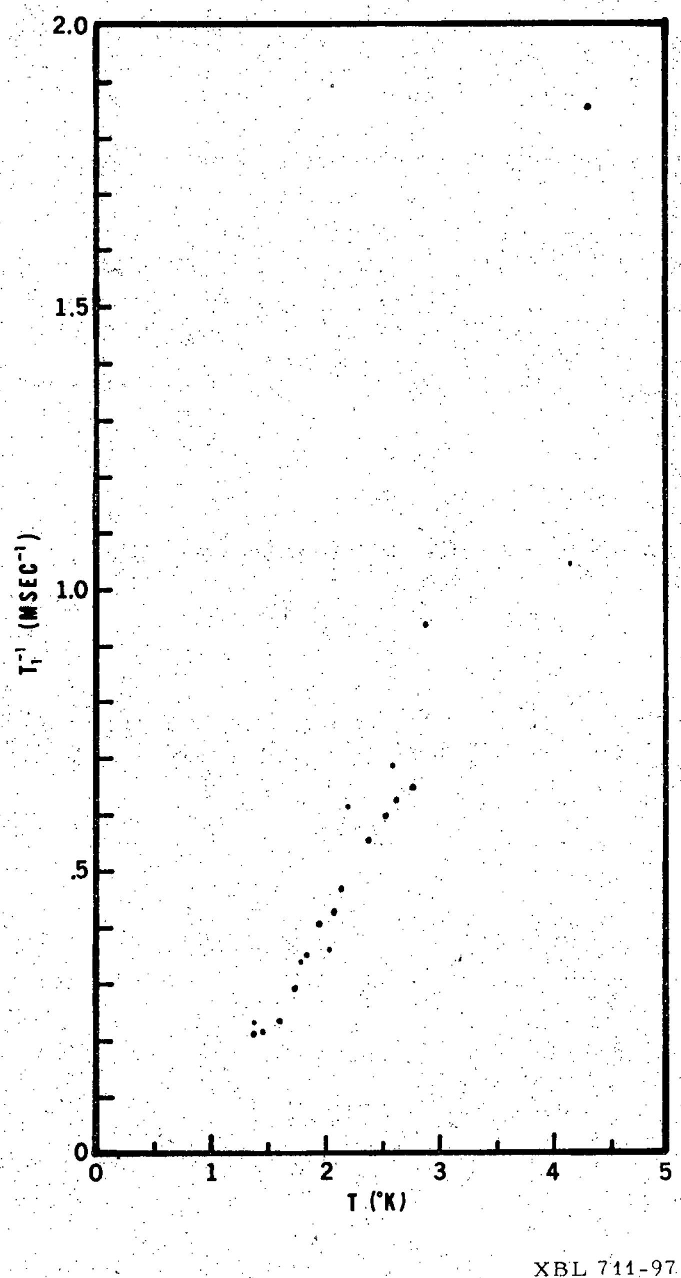

Fig. 41. T_1^{-1} vs. T for the high field line.

somewhat scattered so that a functional relationship between T_1^{-1} and the absolute temperature may not be established with confidence. The lack of data between 3 and 4°K is also somewhat unfortunate. This data was not obtained in these preliminary experiments because of the difficulty of regulating and measuring the temperature with our present apparatus. The data suggest that the inverse relaxation time is linear in the absolute temperature, but the scatter is such that a quadratic could also fit the data.

The data obtained for the dilute sample are similar to that for the concentrated sample. The data were more difficult to obtain since the signal was weaker than in the concentrated sample. The data seem to indicate a slightly shorter relaxation time in this sample, but this may in fact be experimental error.

Relaxation times were also determined for line 2, the "forbidden" line in the spectrum. The intensity of this transition was very much weaker than that of the other two transitions and the data were correspondingly more difficult to obtain. The relaxation times for this line were much longer than those for the other two lines, but this result is doubtful at best. In fact, the relaxation times varied quite widely and may be an experimental artifact.

A number of relaxation mechanisms have been utilized to explain the data in solid state measurements (Standley and Vaughan, 1969). For a non-Kramers salt, such as Ni^{2+} system, the direct process, the Raman process, and the Orbach process give rise to a linear, a seventh power, and an exponential temperature dependence, respectively, for the inverse relaxation times. The data in the Ni/LMN system could be consistent with either a linear or a quadratic function of temperature. The linear function would be consistent with a direct process. However, if a straight line is fit to the data and extrapolated to zero temperature, the line does not pass through zero, whereas the contribution from the direct process to T_1^{-1} should go to zero.

The data would seem to be fit better with a quadratic function of the form

$$T_1^{-1} = D\,T^2 \tag{5.14}$$

where D is a proportionality constant. This temperature dependence is consistent with a phonon bottleneck wherein a phonon-bath interaction rather than a spin-lattice process is observed. If we attempt to least squares fit the data with Eq. 5.14, we obtain a value of D=.0874 for the low field line (Fig. 40) and D=.0866 for the high field line (Fig. 41). These values are essentially identical. If the observed relaxation is due to a Phonon bottleneck process, we would expect D to be directly proportional to the resonance linewidth and inversely proportional to the concentration and the thickness of the crystal (Scott and Jeffries, 1962). The possibility of a shorter relaxation time in the dilute sample supports the proposal of a phonon bottleneck. The relaxation time is not drastically shorter in the dilute sample because of compensation from the dependence on the linewidth. The linewidth for the dilute sample is much narrower than that of the concentrated sample. The relaxation time seems to be well described by a phonon bottleneck, although we cannot completely rule out the posssibility of a direct process since the data are scattered.

It was mentioned earlier that the logarithm of the recovery curve exhibited curvature near the start of the recovery. This could indicate the presence of a second relaxation time in the recovery. Data was obtained for the short time constant by stripping the part of the curve due to the longer time from the data and then examining the residual recovery curve. However, the relaxation times obtained by this procedure were extremely scattered. No correlation with temperature or with the longer relaxation time was evident.

Part of the difficulty in these determinations lies in the analytical procedure. The second recovery curve is revealed by removing from the original data that portion which is due to the first recovery curve. Small errors in the determination of the first recovery curve could cause large deviation in the second curve which is much smaller than the first curve. It should be mentioned that the second curve is itself a cause of error in determining the first curve.

The short relaxation time may be due to two main sources. First, if the relaxation is phonon bottlenecked, the short relaxation could be the tail end of a T_1 relaxation which is becoming rapidly bottlenecked. This relaxation might follow a direct process, but the determination is very difficult. Secondly, if the observed relaxation is the true spin-lattice process, then two relaxation times are expected as shown in Section V-C. Furthermore, if the process is phonon bottlenecked but the short relaxation is the true relaxation time, then this short relaxation process should contain both of the relaxation times predicted in Section V-C. If this is so, the analysis of the short relaxation time is quite difficult.

It is possible that other processes are responsible for the initial relaxation. The first problem is whether the spectrometer is linear in its response to the recovery signal. The signals which are observed are quite strong so that with relatively large changes in cavity Q, the spectrometer may be nonlinear. The amplifiers may be overdriven so that the short relaxation may be the end of the recovery of an overdriven system.

A second problem is that of spectral diffusion in the line. If the nickel lines are inhomogeneously broadened, then it is possible to saturate the center of the line, but then observe a recovery due to the wings of the line growing toward the center. This would give a hyperbolic recovery curve (Mims, et al., 1961). The short relaxation time could then be an incorrect analysis of the recovery curve.

It is evident that much work remains to be done in the Ni/LMN system. Detailed studies of the relaxation times should be made for each of the transitions as a function of temperature. The crystal size and the nickel concentration should be varied to confirm the hypothesis of a phonon bottleneck. The concentration study is also important for studies of exchange effects. Studies should also be made of the dependence of the relaxation times on the pulse widths and on the value of the saturating power. (Preliminary investigations indicated no dependence). Possible anisotropy in the relaxation times should be studied by making measurements as a function of angle. Indeed, measurements at the so-called magic angle of 37° (Jindo, 1971) could prove very interesting. At this angle the nickel transitions are superimposed, since the energy levels are accidentally equidistant. The possibility of double quantum transitions exists, especially at high power levels. A double quantum transition should not occur at the power levels used for monitoring. However, the initial spin distributions produced by the saturating pulse might be studied. Furthermore, Slichter (Slichter, 1963; Hebel and Slichter, 1959) has shown that, in systems with equidistant energy levels which can be described by a spin temperature, only one relaxation time should be observed.

In summary, we have developed an experimental method which should be useful for spin-lattice relaxation time measurements. The acquisition and analysis process in our small computer system should be relatively convenient. However, the problems associated with the operation of a pulse spectrometer are still present, and they are the reason for the scatter in our data. Possible problems are the drift of the klystron frequency which would cause drifts in the recovery signal, and possible interference effects from the dispersion signal. Since the relaxation time could vary across the reasonance lineshape, the setting of the resonance magnetic field is a possible error source. These problems should be studied and eliminated.

APPENDIX I: LORENTZ LINESHAPES AND LEAST SQUARES THEORY

The real and imaginary parts of the complex susceptibility, $\chi = \chi' + i\chi''$, which are derived from the Bloch Equations are given

$$\chi'(\omega) = 1/2\ \chi_o\ \omega_o \frac{T_2^{\ 2}\ (\omega_o - \omega)}{1 + T_2^{\ 2}\ (\omega_o - \omega)^2 + \gamma^2 H_1^{\ 2}\ T_1\ T_2} \qquad \text{(A-1)}$$

$$\chi'(\omega) = 1/2\ \chi_o\ \omega_o \frac{T_2}{1 + T_2^{\ 2}\ (\omega_o - \omega)^2 + \gamma^2\ H_1^{\ 2}\ T_1\ T_2} \qquad \text{(A-2)}$$

where H_1 is the rf magnetic field, T_1 and T_2, the spin-lattice and spin-spin relaxation times respectively, χ_o the static magnetic susceptibility, and γ the magnetogyric ratio relating the resonance frequency, ω_o, to the resonance field, H_o, by $\omega_o = \gamma H_o$. In the typical magnetic resonance experiment the spectrometer is tuned to observe only the absorption, χ'' so that the dispersion, χ', is neglected. Furthermore, magnetic resonance experiments are performed at low powers so that $\gamma^2\ H_1^{\ 2}\ T_1\ T_2 << 1$ and χ'' reduces to

$$\chi''(\omega) = 1/2\ \chi_o\ \omega_o \frac{T_2}{1 + T_2^{\ 2}\ (\omega_o - \omega)^2} \qquad \text{(A-3)}$$

Examination of Eq. A-3 reveals that it is similar to the Lorentz line-shape function

$$f(\omega) = \frac{T_2}{\pi} \frac{1}{1 + T_2^{\ 2}\ (\omega - \omega_o)^2} \qquad \text{(A-4)}$$

Hence, the susceptibility is usually written in the form of a Lorentz function

$$\chi''(\omega) = F \frac{T_2}{\pi} \frac{1}{1 + T_2^{\ 2}\ (\omega - \omega_o)^2} \qquad \text{(A-5)}$$

where F is the line intensity such that

$$F = \int_{-\infty}^{\infty} \chi''(\omega)\ d\omega.$$

From Eq. A-4 we can see that the maximum in the function is T_2/π and also that T_2 is the half width at half height. We may also observe that the units of T_2 are seconds per radian.

Because of experimental convenience magnetic resonance experiments are performed with the magnetic field as the independent variable rather than the frequency so that the lineshape becomes

$$L(H) = \frac{F}{\pi} \frac{\delta}{\delta^2 + (H-H^o)^2} \tag{A-6}$$

where δ is the half width at half height (in gauss), and H^o is the resonance center of the line. Furthermore, EPR spectroscopy is done with the derivative of the absorption given by

$$\begin{aligned} L'(H) &= -\frac{2}{\pi} F\delta \frac{H - H^o}{[\delta^2 + (H-H^o)^2]^2} \\ &= \frac{2}{\pi} F\delta \frac{H^o-H}{[\delta^2 + (H^o-H)^2]^2} \end{aligned} \tag{A-7}$$

The peak-to-peak distance, ΔH, of this function is given by

$$\Delta H = (2/\sqrt{3})\,\delta \tag{A-8}$$

and is related to T_2 by Eq. 1.2.

In general an EPR spectrum consists of a number of lines with different centers, widths, and intensities, so that the spectrum is described by a sum of Lorentz lineshapes

$$g(H) = \frac{2}{\pi} \sum_k F_k \frac{(H_k^o - H)\,\delta_k}{[(H_k^o-H)^2 + \delta_k^2]^2} \tag{A-9}$$

Except in unusual cases the H_k^o are not independent of each other. A spectrum with several components is usually due to hyperfine structure so that the line centers are determined by a spin Hamiltonian. The line centers are then given to second order by (for spin 1/2 complexes)

$$H_k^o = H_o - A\,m - A^2\,((I(I+1) - m^2)/2H_o \qquad \text{(A-10)}$$

where H_o is the spectrum center, A, the hyperfine coupling constant, I, the nuclear spin, and m, the nuclear spin quantum number. The k'th line corresponds to a given value of m. In the general case the spectrum is described by more than one coupling constant and H_k^o is given by

$$H_k^o = H_o - \sum_j (A_j m_j + A_j^2((I_j(I_j+1) - m_j^2)/2H_o \qquad \text{(A-11)}$$

In the case of organic radicals the second order contribution is usually neglected.

A further simplication is usually possible when the lines are due to hyperfine structure. In this case the line intensities are usually given by the ratios of whole numbers which can be computed from the number of nuclei and the nuclear spin. The line intensity is a known fraction of the total intensity of the overall spectrum. We may then rewrite the lineshape as

$$g(H) = \frac{2}{\pi} F \sum_k R_k \frac{(H_k^o - H)\,\delta_k}{[(H_k^o - H)^2 + \delta_k^2]^2} + S + DH \qquad \text{(A-12)}$$

where R_k is the intensity ratio for the k'th hyperfine component. S and D are terms which are added to account for a baseline shift and a baseline drift. In the most general case the spectrum consists of several species each of which has a lineshape characterized by Eq. A-12. The lineshape then consists of a sum of terms similar to the first term in Eq. A-12.

We are now in possession of an analytic function to describe our experimental spectra. If we have values for the spectrum intensities at various magnetic fields, we can perform a least squares fit of the function in Eq. A-12. The theory of least squares is well known and will not be rederived here (Deming, 1938; Shoemaker and Garland, 1962). However, the object is to minimize the sum of the squares of the differences between the experimental points y(H) and the theoretical value g(H). For this purpose we require the values of the derivatives of Eq. A-12 with respect to each of the parameters which we wish to determine. These derivatives are given by

$$\frac{\partial g(H)}{\partial F} = \frac{2}{\pi} \sum_k R_k \frac{(H_k^o - H)\,\delta_k}{[(H_k^o - H)^2\ \delta_k{}^2]^2} \tag{A-13}$$

$$\frac{\partial g(H)}{\partial \delta_k} = \frac{2}{\pi} F\, R_k \frac{(H_k^o - H)^3 - 3\,(H_k^o - H)\,\delta_k{}^2}{[(H_k^o - H)^2 + \delta_k{}^2]^3} \tag{A-14}$$

$$\frac{\partial g(H)}{\partial H_o} = \frac{2}{\pi} F \sum_k (1 + f(k)) \frac{\delta_k^3 - 3\,(H_k^o - H)^2\,\delta_k}{[\delta^2 + (H_k^o - H)^2]^3}$$

$$f(k) = \sum_j \frac{A_j{}^2}{2\,H_o{}^2}\,[I_j\,(I_j + 1) - m_j{}^2] \tag{A-15}$$

$$\frac{\partial g(H)}{\partial A_i} = -\frac{2}{\pi} F \sum_k [m_j + \frac{A_j}{H_o}\,(I_j(I_j+1) - m_j{}^2)]$$

$$\times\ R_k \frac{\delta_k{}^3 - 3\,(H_k^o - H)^3\,\delta_k}{[\delta_k{}^2 + (H_k^o - H)^2]^3} \tag{A-16}$$

$$\frac{\partial g(H)}{\partial S} = 1$$

$$\frac{\partial g(H)}{\partial D} = H \tag{A-17}$$

The value of k is determined by a particular combination of m_j values. The value of the function, f(k) is different for each k since the values of m_j change. In the case of transition metal complexes with hyperfine only from the central ion, the spin Hamiltonian is given by Eq. A-10 rather than Eq. A-11 so that the sum over j reduces to one term. Using a standard least squares treatment the derivatives are formulated into a set of normal equations in the following manner.

Let us assume that the parameters which we seek are x_n. We have an initial guess x_n^o and we wish to find a value Δx_n to obtain a new value for the parameters

$$x_n = x_n^o + \Delta x_n \tag{A-18}$$

We also assume that the errors are only in the y(H) with no errors in H. Then we must solve the following set of equations

$$\begin{aligned}
&\sum_i \frac{\partial g_i}{\partial x_1}\frac{\partial g_i}{\partial x_1}\Delta x_1 + \sum_i \frac{\partial g_i}{\partial x_1}\frac{\partial g_i}{\partial x_2}\Delta x_2 + \ldots + \sum_i \frac{\partial g_i}{\partial x_1}\frac{\partial g_i}{\partial x_n}\Delta x_n = \sum_i \frac{\partial g_i}{\partial x_1}(y_i - g_i)\\
&\sum_i \frac{\partial g_i}{\partial x_2}\frac{\partial g_i}{\partial x_1}\Delta x_1 + \sum_i \frac{\partial g_i}{\partial x_2}\frac{\partial g_i}{\partial x_2}\Delta x_2 + \ldots + \sum_i \frac{\partial g_i}{\partial x_2}\frac{\partial g_i}{\partial x_n}\Delta x_n = \sum_i \frac{\partial g_i}{\partial x_2}(y_i - g_i)\\
&\sum_i \frac{\partial g_i}{\partial x_n}\frac{\partial g_i}{\partial x_1}\Delta x_1 + \sum \frac{\partial g_i}{\partial x_n}\frac{\partial g_i}{\partial x_2}\Delta x_2 + \ldots + \sum \frac{\partial g_i}{\partial x_n}\frac{\partial g_i}{\partial x_n}\Delta x_n = \sum \frac{\partial g_i}{\partial x_n}(y_i - g_i)
\end{aligned} \tag{A-19}$$

The sums are taken over all the points in the spectrum. These equations are of the form

$$\underline{A}\ \underline{X} = \underline{B} \tag{A-20}$$

where $\underline{A}$ is an N×N matrix where N is the number of parameters to be determined, X and B are vectors. These equations are solved by standard methods, for example, matrix inversion, to obtain values for the corrections Δx_n.

New values of the parameters are obtained from Eq. A-18. In the simplest case this is all that is necessary to obtain a least squares value for the parameters. In general we must perfrom an iterative procedure, using the new value for the parameter as a starting point for another solution of Eq. A-19. The iterations are then repeated until the residuals are minimized in the least squares sense. If the fitted function is linear inthe parameters, then the iterative procedure will converge rapidly to a solution. Unfortunately, the Lorentz function is not linear in the parameters.

A non-linear least squares treatment is not guaranteed to converge. In fact, the correction vectors obtained from the solution of Eq. A-19 may not be correct in magnitude. In this case the solution may diverge or may oscillate widely about the true solution. This behavior is minimized by adjusting the correction vectors so that only a fraction of the magnitude is used to compute the new value of the parameter. The fraction used will depend upon the parameter and the function.

APPENDIX II: DIGITAL PROGRAMS

A. Data Acquisition System Programs

1. SUMTAP3

The SUMTAP3* program is used to read the magnetic tapes which are produced by the data acquisition system (Model S6114) and to produce a Fortran compatible data tape for processing by FITESR (see following discussion). The program will read the data tape; select the data in a given file corresponding to either up-field or downfield sweeps, disregarding data inconsistent with smooth sweeps; smooth the y values with a second order polynomial; store the smoothed data points in predetermined channels; and sum complete sweeps to produce an averaged spectrum. The output from the program consists of a printed listing of the summed and normalized spectrum, a plot of the spectrum and its integral, and a magnetic tape of the spectral data for further processing by least squares programs.

a. Format of Input Data Tape

The data acquisition system organizes a special work mark character, the 7 digit counter measurement, and the 5 digit voltmeter measurement plus a sign into a 14 character word. A word is a measured data point. The words are organized into 80 word records and is recorded in IBM compatible NRZI format on the magnetic tape. The data belonging to a spectrum consists of a number of 80 word record blocks which make up a file. The word "file" is used with two slightly different meanings in this discussion. When applied to the input tape, the word, "file", refers to a record or number of records which is isolated from other similar records by a file mark or end-of-file gap. The data within a file may

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*Original written by Dr. Alfred Bauder (Bauder and Myers, 1968).

consist of one or more spectra. When applied to the output tape, the word, "file", refers to the data for a given spectrum. It is not separated from other such files by an end-of-file gap. (This permits the data to be read by a Fortran program without special tests for file marks.)

Both upfield and downfield sweeps may be included in a single file on the input tape. If several sweeps are included in a single file, the sweeps are averaged to form an averaged spectrum on the output tape. However, only upfield sweeps or only downfield sweeps may be averaged; upfield and downfield sweeps may not be averaged together. Two different spectra may be obtained from a mixture of upfield and downfield sweeps, one the average of the upfield sweeps, and the other the average of the downfield sweeps. The x-axis data of a given sweep must be either all increasing or all decreasing. Otherwise, the sweep may be regarded as incomplete and ignored.

The end-of-file gap on the input tape serves the purpose of indicating to the program the end of a given data set. When the file gap is encountered, the program will plot the spectrum it has found within the file and also write the spectrum on the output tape in a Fortran compatible format. If a file gap is encountered before data is found, the file is regarded as empty. Note that, therefore, empty files count as files for the purpose of numbering the files. If four sequential file marks are encountered without data, the program will assume that the tape contains no more spectra and will terminate. For this reason, all tapes should be ended with four file marks to ensure program termination.

b. Input Data Cards

The data cards are used to describe the spectra on the input tape and to indicate the processing to be performed on the spectra.

Card 1 (Format 8A10)

NAME An arbitrary name for the output tape which will contain the smoothed spectra. 10 alphanumeric characters. This name is used to identify the tape for subsequent programs.

COMMENT any arbitrary title or comment to be printed for identification

Card 2 (Format 3I5, 25X, 4A10)

NFILE1 the number of the file to be analyzed. Files must be processed in the order in which they are found on the tape. If several files are to be processed (by providing several of card 2), the files must be processed in order of increasing file number.

IK =+1 upfield sweep

=-1 downfield sweep

KK =0 do not read a new card 3. Assume the parameters are the same as provided by a previous card 3.

≠0 read new parameters from the card 3

Card 3 (Format 2I5, 2E10.0) provided only if KK≠0

KP spectra will be smoothed with 2*KP+1 points (KP must be less than 10)

NUM number of smoothed data points of the spectrum to be stored on the output tape

FMIN lower limit for sweep

FMAX upper limit for sweep; must always be greater than FMIN (FMIN and FMAX are in the units of the x axis which was recorded on the input tape)

The following cards repeat the sequence from card 2, until no further files are to be processed. A blank card at the end of the data deck (which corresponds to NFILE1=0) is used to terminate program execution.

c. Subroutines

SMOOTH2

SMOOTH2 is used to perform digital filtering (Savitzky and Golay, 1964) of the data and to select the absorption value for a given channel. It is assumed that measurements of the frequency (x axis) and the derivative absorption signal (y axis) are made at equal intervals of time. Both of the measurements are subject to noise, which is to be minimized with a smoothing function. The x axis is smoothed with a linear function x = r + s*t. The y axis is smoothed with a quadratic, y=a+b*t+c*t**2. Here, t is the relative time of the measurement.

The program uses 2*KP+1 points and automatically selects those points which are evenly distributed on both sides of a channel. It uses the linear function to calculate r and s and then uses these constants to determine the time difference from the center of the current channel to the nearest experimental point. The y values are smoothed simultaneously with the quadratic to determine the constants, a, b, and c. A smoothed value for y at the center of the channel is then computed.

The determination of the constants a, b and c, is simplified by the assumption of equal time intervals in the measurements. The time interval is assumed to be unity so that the relative time is an integer between -KP and +KP. The constants are then determined by a least squares procedure by solving the following normal equations: (k=kP)

$$a \sum_{-k}^{k} 1 + b(0) + c \sum_{-k}^{k} I^2 = \sum_{-k}^{+k} y_I$$

$$a\,(0) + b \sum_{-k}^{k} I^2 + c\,(0) = \sum_{-k}^{+k} I\, y_I$$

$$a \sum_{-k}^{+k} I^2 + b\,(0) + c \sum_{-k}^{k} I^4 \sum_{-k}^{+k} I^2\, y_I$$

The solution is simplified with the following summation formulae:

$$\sum_{-k}^{+k} I = \sum_{-k}^{+k} I^3 = 0$$

$$\sum_{0}^{k} I^2 = (1/6)k(k+1)\,(2k+1)$$

$$\sum_{0}^{k} I^4 = (1/30)k(k+1)\,(2k+1)\,(3k^2+3k-1)$$

IBITS (I1,I2,X)

IBITS is an ASCENTF coded subroutine which selects the bits I1 to I2, inclusive, of X and stores them right justified in IBITS. The bits are numbered from 1 to 60 from left to right. The spectral data on the input tape is read by SUMTAP3 as BCD coded information without conversion to a binary number. SUMTAP3 performs the BCD to binary conversion. The IBITS subroutine is used to locate a digit from the tape so that SUMTAP3 can perform the conversion to binary. This subroutine is coded specifically for a CDC 6600 digital computer, and may require changes if the computer or operating system is changed.

Plotting Subroutines

The following subroutines are used to plot the spectra. They are assumed to be available in the computer library as part of the FORTRAN compiler. A brief description is included to illustrate their usage.

CCGRID (5,2, 6HNOLBLS, 4). This subroutine draws a grid around the spectrum. The x axis is divided into 5 divisions each of which is sub-divided into two parts by tick marks. The y axis is divided into 4 divisions. The grid is not to be labeled with a scale.

CCLTR (20., 300., 1,2) This subroutine letters the graph at x position 20. and y position 300. in a direction specified by 1 and a size specified by 2. The information to be lettered has been previously provided.

CCPLOT (SX,SY,NUM, 4HJOIN, 0,0) Plots the NUM points in (SX,SY). The first 0 specifies a symbol for the plot, and the second 0 indicates that every point in the array is to be plotted.

CCNEXT This subroutine spaces the chart paper so that another graph may be plotted. `The previous graph is ended.

CCEND. This subroutine is called at the conclusion of the program to terminate the plotting.

Special Subroutines for the CDC 6600

BUFFER IN (1,0) (W(1), W(120)) This subroutine reads a record from the input tape into the array, W.

IF(UNIT,1) 103, 110, 105, 104 This statement checks the status of the input tape and transfers to 103 if a read is still in progress; to 110 when the read operation is complete; to 105 if an end-of-file is found on the tape; to 105 if a parity error occurs during reading.

CALL RECALL(1) This statement places SUMTAP3 in an inactive status until the read operation on the input tape is complete.

LENGTHF(1) This function computes the length of the record which was just read from the input tape. The record length is usually 80*14/10=112 words long.

IF (WARN(IME).NE.0) This statement checks the amount of time remaining to the program. If nonzero, the time limit has almost been reached and SUMTAP3 will terminate gracefully.

Note

The SUMTAP3 program was written in FORTRAN IV and ASCENTF to run on a CDC 6600 computer. If the computer is changed or if the operating system is changed, the program may require revision.

```
      PROGRAM SUMTAP3 (INPUT,OUTPUT,TAPE1,TAPE2=INPUT,TAPE3=OUTPUT,
     *                 TAPE4,TAPE5,TAPE98,TAPE99)
    1 FORMAT(A10,2I5,E20.13)
    2 FORMAT(4E20.13)
    3 FORMAT(8A10)
    4 FORMAT(1H1,25X,44H*** ESR TAPE READING AND SUMMING PROGRAM ***//
     *       10X,7A10//20X,28HRESULTS ON TAPE4, LABELED **,A10,2H**)
    5 FORMAT(3I5,25X,4A10)
    6 FORMAT(/////5X,4HFILE,I3,13X,4A10//25X,I4,17H CHANNELS BETWEEN,
     *       F13.4,4H AND,F13.4,5X,13HCHANNEL WIDTH,F12.6///)
    7 FORMAT(2I5,2E10.0)
    8 FORMAT(15X,15HSUMMED SPECTRUM,10X,10HTOTAL AREA,E20.10,5X,
     *       15H(INTEGRAL RANGE,E14.4,3H  /,E14.4,1H)//)
    9 FORMAT(25X,20HNO COMPLETE SPECTRUM,5X,11HFIRST VALUE,F9.0,5X,
     *       10HLAST VALUE,F9.0)
   10 FORMAT(1H0,16H*****INPUT ERROR)
   11 FORMAT(//20X,22HRESULTS STORED AS FILE,I3,9H ON TAPE4/)
   12 FORMAT(10(10F12.6/)/)
   13 FORMAT(5HTAPE ,A10,5X,4HFILE,I3)
   14 FORMAT(4A10)
   15 FORMAT(//15X,26HTOTAL INTEGRATED INTENSITY,E20.10)
   16 FORMAT(15X,28HSECOND ORDER POLYNOMIAL WITH,I3,11H POINTS AS ,
     *       18HSMOOTHING FUNCTION,10X,I5,16H SPECTRA FOUND (,I4,
     $       12H INCOMPLETE)/)
   17 FORMAT(//5X,4HFILE,I3,12H NOT ON TAPE)
 18     FORMAT(1H0, 10X,32HPARITY ERROR ON TAPE1 IN RECORD     , I5 ,
     1  6H FILE     , I5  )
 19     FORMAT( 1H0, 16H YOU FOOL FILE    , I5, 10H IS EMPTY    //
     1 5X, 5H*****, 80H WARNING,-- CHAOS MAY OCCUR -- ASSUMING YOU WISHE
     2D FILE + 1, AND CONTINUING                       , 5H***** // )
 20     FORMAT( 1H0 , 20H CONTENTS OF BUFFER         )
 21     FORMAT( 6X , 10A10 )
      DIMENSION COMMENT(7)
      DIMENSION FX(250),FY(250),W(120),SZ(2000)
       COMMON/ASPEC/ NSPEC
      COMMON/FSPEC/SX(2000),SY(2000)
      COMMON/FPAR/ISA,NUM,MM,MN,KP,FDIF,EMIN,EMAX,SW
      COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
      COMMON/CCFACT/FACTOR
      EQUIVALENCE (SX(21),FX(1)),(SX(321),FY(1)),(SX(601),W(1))
      DATA KP,NUM,FMIN,FMAX/3,500,300.,9700./
C     INITIALIZATION
      REWIND 1
      REWIND 4
      REWIND 5
      XMIN=0.
      XMAX=10000.
      IGRID=0
      NEOF=0
      NFILE=1
      NFILE2=1
C     INPUT SECTION
   50 READ (2,3) NAME,(COMMENT(J),J=1,7)
      WRITE (3,4) (COMMENT(J),J=1,7),NAME
   60 READ (2,5) NFILE1,IK,KK,(COMMENT(J),J=1,4)
      IF (NFILE1.LE.0) GOTO 401
```

```
      SW=1.
      IF (IK.LT.0) SW=-1.
      IF (KK.EQ.0) GOTO 61
      READ (2,7) KP,NUM,FMIN,FMAX
      IF (KP.GT.9.OR.KP.LT.3) GOTO 398
      IF (NUM.GT.2000) GOTO 398
      IF (FMIN.GE.FMAX) GOTO 398
   61 DO 62 J=1,NUM
   62 SZ(J)=0.
C     SET UP CHANNELS
   70 FDIF=(FMAX-FMIN)/(NUM+2*KP-1)
      FINT=KP*FDIF
      EMIN=FMIN+FINT
      EMAX=FMAX-FINT
      FDIF=SW*FDIF
      WRITE (3,6) NFILE1,(COMMENT(J),J=1,4),NUM,EMIN,EMAX,FDIF
   71 NREC=0
      NGO=0
      NSPEC=0
      NER=0
      MN=0
      M=1
      FX2=0.
      IF (IK.LT.0) FX2=1.E8
  100 NREC=NREC+1
  101 IPAR=0
C     READ DATA TAPE  --- SPECIAL 6600 FUNCTION
      BUFFERIN (1,0) (W(1),W(120))
  102 IF (UNIT,1) 103,110,105,104
  103 CALL RECALL(1)
      GOTO 102
C  PRINT PARITY ERROR INFORMATION FOR DEBUGGING
 104    WRITE( 3, 18 ) NREC, NFILE2
        WRITE( 3, 20 )
        WRITE( 3 , 21 ) ( W(I) , I = 1, 120 )
      GOTO 110
  105 NEOF=NEOF+1
      NFILE2=NFILE2+1
      IF (NEOF.GE.2) GOTO 400
      IF( NGO .EQ.1 ) GO TO 160
      IF( NFILE2 .NE. NFILE1 + 1 ) GO TO 71
      GO TO 300
  110 NEOF=0
  111 IF (NFILE2.NE.NFILE1) GOTO 101
  112 NL=LENGTHF(1)-1
      IF (NL.GT.112) NL=112
  113 NC=NL*10
      I=0
  120 I=I+1
  121 IF (I+13.GT.NC) GOTO 100
  122 NW=(I+9)/10
      J2=(I-(NW-1)*10)*6
      J1=J2-5
C    SEARCH FOR WORD MARK
      L=IBITS(J1,J2,W(NW))
  123 IF (L.NE.65B) GOTO 120
```

```
  124 ND=7
  125 NN=10**(ND-1)
      IX=0
  126 DO 127 J=1,ND
      I=I+1
      NW=(I+9)/10
      J2=(I-(NW-1)*10)*6
      J1=J2-5
C     GET A DIGIT
      L=IBITS(J1,J2,W(NW))
      IF (L.LT.33B.OR.L.GT.44B) GOTO 120
      IX=IX+NN*(L-33B)
  127 NN=NN/10
  128 IF (ND.LT.6) GOTO 144
C     CHECK THAT POINT IS WITHIN SPECTRAL LIMITS
  129 FX(M)=IX
      IF (NREC.EQ.1.AND.I.LT.13) FX1=FX(M)
      IF (IK.LT.0) GOTO 136
      IF (NGO-1) 130,132,135
  130 IF (IX.LT.FMIN.OR.IX.GT.EMIN) GOTO 120
  131 NGO=1
      GOTO 140
  132 IF (IX.LT.FMAX.AND.IX.GT.FMIN) GOTO 140
      IF (FX(M1).GT.EMAX).GOTO 134
      IF (IX.GT.FX2) FX2=IX
      IF (FX(M1).GT.EMIN) GOTO 140
  133 NGO=0
      GOTO 160
  134 NGO=2
      GOTO 150
  135 IF (IX.LE.FMIN) NGO=0
      GOTO 120
  136 IF (NGO-1) 137,138,139
  137 IF (IX.GT.FMAX.OR.IX.LT.EMAX) 120,131
  138 IF(IX.GT.FMIN.AND.IX.LT.FMAX) GOTO 140
      IF (FX(M1).LT.EMIN) GOTO 134
      IF (IX.LT.FX2) FX2=IX
      IF (FX(M1).LT.EMAX) 140,133
  139 IF (IX.GE.FMAX) NGO=0
      GOTO 120
  140 I=I+1
  141 NW=(I+9)/10
      J2=(I-(NW-1)*10)*6
      J1=J2-5
C     GET A DIGIT
      L=IBITS(J1,J2,W(NW))
  142 LS=1
C  CHECK FOR SIGN OF NUMBER
      IF (L.EQ.45B) GOTO 143
      IF (L.NE.46B) GOTO 120
      LS=-1
  143 ND=5
      GOTO 125
  144 FY(M)=LS*IX
      M1=M
      M=M+1
```

```
  145 IF (M.LE.250) GOTO 120
  150 MM=M-1
      M=1
      M1=250
      MN=MN+MM
      WRITE (5) (FX(J),FY(J),J=1,MM)
  151 GOTO (120,200), NGO
  160 NER=NER+1
      M=1
  161 MN=0
      REWIND 5
      IF (NEOF.EQ.0) 120,300
  200 REWIND 5
      ISA=0
  201 MM=250
      IF (MN.LT.MM) MM=MN
      READ (5) (FX(J),FY(J),J=1,MM)
      MN=MN-MM
      IF (MN.EQ.0) ISA=-1
      CALL SMOOTH2
  202 IF (ISA.GT.0) GOTO 201
  203 NSPEC=NSPEC+1
C    SUM SPECTRA
      DO 204 J=1,NUM
  204 SZ(J)=SZ(J)+SY(J)
      REWIND 5
      IF (WARN(IME).NE.0) GOTO 300
C   OUTPUT SPECTRA AND INTEGRATE
      IF (NEOF.EQ.0) GOTO 120
  300 IF (NSPEC.EQ.0) GOTO 399
      CCXMAX=1070.
      IF (NUM.GT.1000) CCXMAX=2070.
      XLTR=1140.
      IF (NUM.GT.1000) XLTR=2140.
      CALL CCGRID(5,2,6HNOLBLS,4)
      IGRID=1
      WRITE (98,13) NAME,NFILE1
      CALL CCLTR(20.,300.,1,2)
      WRITE (98,14) (COMMENT(J),J=1,4)
      CALL CCLTR(XLTR,200.,1,2)
      IF (EMAX.LE.10000.) GOTO 310
      XMIN=EMIN
      XMAX=EMAX
  310 SMIN=SZ(1)
      SMAX=SMIN
      DO 311 J=1,NUM
      IF (SZ(J).GT.SMAX) SMAX=SZ(J)
      IF (SZ(J).LT.SMIN) SMIN=SZ(J)
  311 CONTINUE
      AMP=SMAX-SMIN
      SHIFT=(SMAX+SMIN)/2.
  312 SMIN=0.
      SMAX=0.
      SX(1)=EMIN-FDIF
      IF (IK.LT.0) SX(1)=EMAX-FDIF
      SY(1)=0.
```

```
      A=0.
      J1=1
      DO 313 J=1,NUM
      SX(J)=SX(J1)+FDIF
      SZ(J)=(SZ(J)-SHIFT)/AMP
      SY(J)=SY(J1) +SZ(J)
      A=A+SY(J)
      IF (SY(J).GT.SMAX) SMAX=SY(J)
      IF (SY(J).LT.SMIN) SMIN=SY(J)
  313 J1=J
      KP1=2*KP+1
      WRITE (3,16) KP1,NSPEC,NER
      A=A*FDIF
      WRITE (3,8) A,SMIN,SMAX
      WRITE (3,12) (SZ(J),J=1,NUM)
      YMIN=-1.5
      YMAX=0.5
      CALL CCPLOT(SX,SZ,NUM,4HJOIN,0,0)
      WRITE (4,1) NAME,NFILE,NUM,A
      WRITE (4,2) (SX(J),SZ(J),J=1,NUM)
      A=A-SY(NUM)*FDIF*(EMAX-EMIN)/2.
      WRITE (3,15) A
      WRITE (3,11) NFILE
      YMIN=SMIN
      YMAX=2.*SMAX-SMIN
      CALL CCPLOT(SX,SY,NUM,4HJOIN,0,0)
      CALL CCNEXT
      NFILE=NFILE+1
        IF( WARN(TIME) ) 401, 60, 401
  398 WRITE (3,10)
      GOTO 60
  399 WRITE (3,9) FX1,FX2
      GOTO 60
C     TERMINATION PROCEDURE
 400    IF( NEOF.LE.3 ) GO TO 403
      IF (IGRID.NE.0) CALL CCEND
      WRITE (3,17) NFILE1
  401 STOP
 403    IF( NFILE2 .EQ. NFILE1 + 1 ) GO TO 405
        GO TO 71
 405    WRITE( 3, 19 ) NFILE1
        NFILE2 = NFILE2 - 1
        GO TO 71
      END
```

```
      SUBROUTINE SMOOTH2
C     2. ORDER SMOOTHING AND INTERPOLATION OF Y-VALUES ACCORDING TO
C     1. ORDER SMOOTHED AND CHECKED X-VALUES
      COMMON/FSPEC/SX(2000),SY(2000)
      COMMON/FPAR/ISA,NUM,MM,MN,KP,FDIF,EMIN,EMAX,SW
       COMMON/ASPEC/ NSPEC
      DATA (J=0)
      I=19-KP
      IM=MM+20-KP
      IF (J.GT.0) GOTO 2
C    DEFINE SMOOTHING COEFFICIENTS
    1 FAC=2.*KP+1.
      A0=((KP+1)*KP)/3.
      A3=1./((4.*KP+4.)*KP-3.)
      A1=((9.*KP+9.)*KP-3.)*A3
      A2=-15.*A3
      A3=-A2/A0
      EDIF=(EMAX-EMIN)/(MM+MN)
      GAP=10.*EDIF
      EDIF=SW*EDIF
      FF=EMIN*FAC
      IF (SW.LT.0.) FF=EMAX*FAC
      DEL=FDIF*FAC
    2 IF (ISA) 10,20,30
C      TAKE CARE OF GAPS IN DATA
   10 IM=MM+20
      DO 11 N=1,20
      N1=N+IM
      SX(N1)=SX(IM)+N*EDIF
   11 SX(N1+300)=SX(IM+300)
      IF (J.NE.0) GOTO 30
   20 DO 21 N=1,20
      SX(N)=SX(21)-EDIF*(21-N)
   21 SX(N+300)=SX(321)
      IF (ISA.EQ.0) ISA=1
      I=20
   30 I1=I+1
      T=SX(I)
      DO 35 N=I1,IM
      IF (ABS(SX(N)-T).LT.GAP) GOTO 34
      L=1
   31 IF (ABS(SX(N+L)-T).LT.(L+1)*GAP) GOTO 32
      L=L+1
      IF (L.LE.3) GOTO 31
   32 DIF=(SX(N+L)-T)/(L+1)
      DO 33 M=1,L
   33 SX(N+M-1)=T+M*DIF
      T=SX(N+L)
      N=N+L
      GOTO 35
   34 T=SX(N)
   35 CONTINUE
   40 L=I-KP
      M=I+KP
      S=0.
      DO 41 N=L,M
```

```
   41 S=S+SX(N)
      T=S
      GOTO 101
C     SET UP FOR A CHANNEL POINT
  100 IF (I.GE.IM) GOTO 110
      T=S
      I=I+1
      S=S+SX(I+KP)-SX(I-KP-1)
  101 IF (SW*(S-FF)) 100,103,102
  102 IF (SW*(S+T-2.*FF).LE.0.) GOTO 103
      I=I-1
      S=T
  103 J=J+1
      IF (J.GT.NUM) GOTO 130
C   J INDICATES THE CHANNEL     I POINTS TO NEAR CENTER OF CHANNEL
C    COMPUTE THE CHANNEL POINT
  104 L=I-KP
      M=I+KP
      Q=0.
      R=0.
      V=0.
      W=0.
      DO 105 K=L,M
      N=K-I
      Q=Q+N*SX(K)
      U=SX(K+300)
      R=R+U
      U=N*U
      V=V+U
  105 W=W+N*U
      Q=(S-FF)/Q
C   QUADRATIC INTERPOLATION OF Y WITH X FROM LINEAR INTERPOLATION
  106 SY(J)=R*A1+W*A2-Q*V+(Q*A0)**2*(R*A2+W*A3)
      FF=FF+DEL
      GOTO 101
  110 IF (ISA.LT.0) GOTO 103
  120 DO 121 N=1,20
      N1=N+MM
      SX(N)=SX(N1)
  121 SX(N+300)=SX(N1+300)
      RETURN
  130 J=0
      ISA=-1
      RETURN
      END
```

```
      ASCENTF SUBROUTINE IBITS(I1,I2,X)
          BSSZ 1               .THIS ROUTINE SELECTS BITS I1 TO I2 (INCLU-
          BSSZ 1               .SIVE) OF X, AND STORES THEM (RIGHT ADJUSTED
          BSSZ 1               .WITH ZERO FILL) IN IBITS.
          BSSZ 1               .BITS ARE 1 TO 60 LEFT TO RIGHT
          BSSZ 1
RET       BSSZ 1                                        .DCS,6/22/66
          SA1  B1              .I1=(X1)
          SB1= X1-1
          SA2  B2              .I2=(X2)
          IX2= X2-X1
          SB4= X2-59           .N=NUMBER OF BITS=I2-I1+1=(B4)-60
          SA3  B3              .X=(X3)
          LX6= B1,X3           .LEFT SHIFT (X3), I1-1 BITS
          EQ   B0,B4 RET       .DONE IF N=60
          LX6  B4,X6           .RIGHT SHIFT TO END OF WORD
          MX0  1
          SB4  B4+1
          LX0  B4,X0           .FORM 60-N BIT MASK
          BX6= -X0*X6
          EQ   B0,B0 RET       .C/EST FINI
      END
```

2. FITESR

FITESR* performs a least squares fit of Lorentz lineshapes to experimental EPR spectra using the procedure described in Appendix I. It is suitable for spectra with a second order spin Hamiltonian and different widths for the hyperfine components (of 1 nucleas). It can calculate the relative abundance of up to 5 similar compounds present in a mixture. The spectra are assumed to be stored as derivates of the absorption lines on a magnetic tape produced by SUMTAP3.

The program operates in the following manner. It starts from a given 0 th order guess of the relevant parameters for the spectrum and iteratively calculates better parameters until the sums of the squares of the deviations between the observed and calculated spectral points remains constant, or until the iteration diverges. The parameters and their corrections in successive steps, including a baseline offset and drift, are printed out. The program prints the final parameters and plots the observed and calculated spectrum based on these parameters together with enlarged curves of the errors between these spectra.

The program may operate in one of two modes. In the first mode, the spectrum is considered to be composed of up to 12 individual Lorentz lines with different intensities, linewidths, and line centers. In the second mode, the spectrum is considered to be composed of hyperfine components of one nucleus with the line centers determined by a second order spin Hamiltonian, with the same intensities for all hyperfine components, but with different linewidths. The maximum number of parameters is 38.

---

*Originally written by Dr. Alfred Bauder (Bauder and Myers, 1968).

INPUT DATA

Card 1. (Format 8A10)

NAME The name of the tape with the measured spectra which was given in SUMTAP3. Any 10 alphanumeric symbols (blanks count). This variable is used for file protection and causes the job to abort if it does not agree with the name found on the tape.

COMMENT Any arbitrary comment to be printed for identification

Card 2. (Format 4I5, 2E10.0, 4A10)

NFILE1 the number of the file to be analyzed (in order of increasing magnitude)

IFIT =0 individual lines according to first assignment of parameters

>0 the number of compounds with second order Hamiltonian (second mode of operation)

If IFIT is 0, the first mode of operation is selected; otherwise, IFIT is the number of compounds to be fit with a second order Hamiltonian

NLINE the number of hyperfine components. If IFIT=0, then NLINE is the number of individual lines to be fit.

KFIELD =0 use abritrary field calibration without nonlinearity correction.

>0 use arbitrary calibration with nonlinearity correction

<0 use the HCALIB field calibration subroutine.

This is a historically provided option. Usually KFIELD is negative and the HCALIB subroutine is used to calibrate the magnetic field.

HSTART Lower limit of the field sweep in gauss

HSTOP Upper limit of the field sweep in gauss.

If KFIELD is negative, the HCALIB routine is used, and HSTART and HSTOP are not used. They are only used if KFIELD is zero or positive.

COMMENT Any comment to be printed and plotted to identify the job.

Card 3 - and following cards (Format 8E10.0)

X(J) the 0 th order estimates of the parameters

if IFIT=0; first, all the line centers, second all the intensities and last all the linewidths of the NLINE individual absorption lines in the same order.

if IFIT> 0; for each compound separately, in the following order; first, the H_o field, second, the hyperfine coupling constant, third, the integrated intensity, and last all the linewidths of the hyperfine components ordered according to ascending azimuthal quantum number.

In both cases, the last two parameters are the baseline offset and baseline drift.

Cards are repeated from Card 2 to analyze additional spectra. A blank card at the end terminates the program execution.

SUBROUTINES

HCALIB (K,N,F) calibrates the N points in the array F according to the calibration specified by K (see listing)

MATINV (A,N,B,M, DETERM) solves the matrix equation AX=B for X. A is an N×N matrix. M is the number of column vectors in B and should be one. DETERM contains the determinant of A after the equations have been solved. The solution X is returned in B, and the inverse of A is returned in A.

NOTE

If the data for the spectrum is to be input from cards rather than from magnetic tape, the PROGRAM card must be altered so that the TAPE4 specification is changed to TAPE4=INPUT. The data cards for the spectra must be placed after card 2. The format of the data can be obtained from an examination of the program listings.

```
      PROGRAM FITESR(INPUT,OUTPUT,TAPE2=INPUT,TAPE3=OUTPUT,TAPE4,
     1      TAPE98,PLOT,TAPE99=PLOT )
      DATA (LOOP=0),(PI=.6366197723675811)
      DIMENSION G(38),X(38),FX(1000),FY(1000),FZ(1000),H(38,38)
      DIMENSION COMMENT(7),AR(5),GR(38),SP(33),IC(33)
      DIMENSION FC(33),C(33),D(33),DD(33),DS(33)
      DIMENSION G1(38)
      DIMENSION FW(1000)
      EQUIVALENCE (H,FW)
      COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
      COMMON/CCFACT/FACTOR
    1 FORMAT(8A10)
    2 FORMAT(1H1,10X,7A10//21X,37H*** LEAST SQUARES FIT OF ESR-SPECTRA ,
     *         3H***//20X,28HSPECTRA ON TAPE4, LABELED **,A10,2H**///)
    3 FORMAT(4I5,2E10.0,4A10)
    4 FORMAT(///5H FILE,I3,10X,17HESR-SPECTRUM WITH,I3,
     *         28H INDIVIDUAL LORENTZIAN LINES//)
    5 FORMAT(///5H FILE,I3,10X,15HESR-SPECTRUM OF,I2,13H SUBSTANCES, ,
     *              25HWHICH ARE EACH SPLIT INTO,I3,19H COMPONENTS DUE TO ,
     *         24HSECOND ORDER HAMILTONIAN//)
    6 FORMAT(18X,30HNUMBER OF FITTING PARAMETERS (,I2,
     *         17H) OR SUBSTANCES (,I2,2H) ,
     *         26HEXCEEDS AVAILABLE CAPACITY//)
    7 FORMAT(A10,2I5,E20.13)
    8 FORMAT(18X,4HFILE,I3,13H NOT ON TAPE ,A10//)
    9 FORMAT(10X,21HINCORRECT FILE LABEL ,A10)
   10 FORMAT(4E20.13)
   11 FORMAT(20X,I4,20H DATA POINTS ON FILE,I3,5X,I2,
     *         19H FITTING PARAMETERS///)
   12 FORMAT(8E10.0)
   13 FORMAT(5HTAPE ,A10,5X,4HFILE,I3)
   14 FORMAT(10X,33HFINAL VALUES OF LEAST SQUARES FIT,
     *         36H (STANDARD DEVIATION IN PARENTHESIS)//10X,
     *         10HTOTAL AREA,5X,8HMEASURED,E15.7,5X,10HCALCULATED,E15.7//
     $         10X,15HBASELINE (A+BX),12X,1HA,E15.7,2H (,E15.7,1H),9X,
     $         1HB,E15.7,2H (,E15.7,1H)/)
   15 FORMAT(10X,9HCOMPONENT,10X,11HLINE CENTER,18X,9HINTENSITY,21X,
     *         9HHALFWIDTH/)
   16 FORMAT(13X,I2,F18.4,2H (,F8.4,1H),E17.5,2H (,E12.5,1H),
     *         F15.4,2H (,F8.4,1H))
   17 FORMAT(10X,25HSPECTRUM MEASURED BETWEEN, F12.3,10H GAUSS AND,
     *         F12.3,6H GAUSS///25H ABSOLUTE VALUES IN GAUSS//)
   18 FORMAT(3X,3HNO.,7X,14HREL. INTENSITY,8X,17HHO-FIELD (CENTER),
     *         9X,18HSPLITTING CONSTANT,5X,5HCOMP.,10X,10HLINE WIDTH,
     $         9X,11HLINE CENTER/)
   19 FORMAT(3X,I2,F13.4,2H (,F6.4,1H),2(F15.3,2H (,F8.3,1H)),I8,
     *         F15.3,2H (,F8.3,1H),F15.3/(79X,I8,F15.3,2H (,F8.3,1H),
     $         F15.3))
   20 FORMAT(10X,34H*** FATAL ERROR TERMINATES JOB ***)
   21 FORMAT(///34H RELATIVE VALUES REFERRING TO PLOT//)
   22 FORMAT(/20X,14HITERATION STEP,I2,5X,2HF=,E20.12,5X,2HX=/(10E13.4))
   23 FORMAT(/20X,14HITERATION STEP,I2,9H DIVERGED)
   24 FORMAT(///)
   25 FORMAT(20X,11HCORRECTIONS,5X,2HG=/(10E13.4))
   26 FORMAT(20X,2H**,4A10,2H**//)
   27 FORMAT(4A10)
```

```
   28 FORMAT(8HERRORS *,F8.3)
   29 FORMAT(20X,11HTIME LIMIT.)
 30       FORMAT( 1H0, 18HERROR EXPANSION *    , F8.3 )
C     INITIALIZATION AND INPUT SECTION
  101 M1=0
      IFIN=0
      REWIND 4
C     INPUT PARAMETERS
  103 READ (2,1) NAME1,(COMMENT(J),J=1,7)
      WRITE (3,2) (COMMENT(J),J=1,7),NAME1
      LOOP=1
  110 READ (2,3) NFILE1,IFIT,NLINE,KFIELD,HSTART,HSTOP,(COMMENT(J),
     *           J=1,4)
  111 IF (NFILE1) 401,401,112
  112 IF (IFIT) 141,120,130
  120 WRITE (3,4) NFILE1,NLINE
      WRITE (3,26) (COMMENT(J),J=1,4)
      NVAR=3*NLINE+2
      GOTO 140
  130 WRITE (3,5) NFILE1,IFIT,NLINE
      WRITE (3,26) (COMMENT(J),J=1,4)
      NVAR=IFIT*(NLINE+3)+2
  140 IF ((NVAR.LE.38).AND.(IFIT.LE.5)) GOTO 150
  141 WRITE (3,6) NVAR,IFIT
      READ (2,12) (X(J),J=1,NVAR)
      GOTO 110
C     READ SECTION OF INPUT TAPE4
  150 READ (4,7) NAME,NFILE,NUM,AREA
  151 IF (EOF,4) 152,153
  152 WRITE (3,8) NFILE1, NAME1
      GOTO 400
C    CHECK FOR PROPER TAPE
  153 IF (NAME.EQ.NAME1) GOTO 155
  154 WRITE (3,9) NAME
      GOTO 400
  155 READ (4,10) (FX(J),FY(J),J=1,NUM)
  156 IF (NFILE.NE.NFILE1) GOTO 150
  160 WRITE (3,11) NUM,NFILE,NVAR
C     INITIALIZATION
      SPIN=(NLINE-1)/2.
      SPIN2=SPIN*(SPIN+1.)
      FA=1.E300
      M2=0
      M3=0
      LOOP=2
      CALL CCGRID(5,2,6HNOLBLS,5)
C     0.ORDER SPECTRAL PARAMETERS
  170 READ (2,12) (X(J),J=1,NVAR)
C     FIELD CORRECTION OR CALIBRATION
      IF (KFIELD.LT.0) GOTO 190
  171 HS=(HSTART+HSTOP-8500.)/2000.
      HS=9.04-24.72*HS-0.8*HS**2
      HSTART=HSTART+HS
      HSTOP=HSTOP+HS
      SWEEP=(1.E-4)*(HSTOP-HSTART)
      IF (SWEEP.EQ.0.) GOTO 110
```

```
      DISPL=HSTART/SWEEP
  180 IF (KFIELD.EQ.0) GOTO 200
C     CORRECTION FOR SWEEP NONLINEARITY
  181 DO 182 J=1,NUM
      FK=(FX(J)-5000.)*SWEEP/100.
  182 FX(J)=FX(J)-3.20*FK**2
      GOTO 200
C    UTILIZE USER PROVIDED FIELD CALIBRATION  IF K IS NEGATIVE
  190 CALL HCALIB(KFIELD,NUM,FX)
      SWEEP=1.
      DISPL=0.
      HSTART=FX(1)
      HSTOP=FX(NUM)
C     CLEARING OF ARRAYS USED FOR THE NORMAL EQUATIONS
  200 F=0.
      DO 201 J=1,NVAR
      G(J)=0.
      DO 201 M=J,NVAR
  201 H(J,M)=0.
C     CALCULATION OF THE PARAMETERS, USED IN THE LEAST SQUARES FIT
C     FC CONTAINS THE CENTER FREQUENCIES
C     C CONTAINS THE INTENSITIES
C     D CONTAINS THE HALFWIDTHS
  202 IF (IFIT) 215,210,215
C    IFIT = 0    USE INDIVIDUAL LINES
  210 DO 211 J=1,NLINE
      J1=2*NLINE+J
      FC(J)=X(J)
      C(J)=X(J+NLINE)
  211 D(J)=X(J1)
      GOTO 219
C    IFIT .NE. 0 USE 2ND ORDER HAMILTONIAN
  215 J1=0
      DO 217 I=1,IFIT
      X1=X(J1+1)
      X2=X(J1+2)
      C1=X(J1+3)/NLINE
      DO 216 J=1,NLINE
      K=(I-1)*NLINE+J
      SPIN3=J-SPIN-1.
      SP(J)=X2**2*(SPIN2-SPIN3**2)/2.
      FC(K)=X1-X2*SPIN3-SP(J)/(X1+DISPL)
      C(K)=C1
  216 D(K)=X(J+J1+3)
  217 J1=J1+NLINE+3
  219 A=X(J1+1)
      B=X(J1+2)
C     START OF LEAST SQUARES FIT ITERATIONS
  220 DO 271 N=1,NUM
  221 FZ(N)=A+B*FX(N)
C     CLEARING THE ARRAY FOR THE DERIVATIVES
      DO 222 J=1,NVAR
  222 GR(J)=0.
      GR(NVAR-1)=1.
      GR(NVAR)=FX(N)
      J1=0
```

```
  230 DO 262 I=1,IFIT
  240 DO 261 J=1,NLINE
C       CALCULATION OF INTERMEDIATE VALUES
      K=(I-1)*NLINE+J
      S=FC(K)-FX(N)
      T=S*D(K)
      R=S*S+D(K)**2
      P=R*R
      R=P*R
      P=PI*T/P
      Q=PI*C(K)*(D(K)**3-3.*T*S)/R
      R=PI*C(K)*(S**3-3.*T*D(K))/R
C       CALCULATION OF THE FUNCTION
  241 FZ(N)=FZ(N)+P*C(K)
C       CALCULATION OF THE DERIVATIVES
  242 IF (IFIT) 260,250,260
  250 J1=2*NLINE+J
      GR(J)=Q
      GR(J+NLINE)=P
      GR(J1)=R
      GOTO 261
  260 SPIN3=J-SPIN-1.
      W=X(J1+1)+DISPL
      U=SP(J)/W**2+1.
      V=2*SP(J)/W/X(J1+2)+SPIN3
      GR(J1+1)=GR(J1+1)+Q*U
      GR(J1+2)=GR(J1+2)-Q*V
      GR(J1+3)=GR(J1+3)+P/NLINE
      GR(J+J1+3)=R
  261 CONTINUE
      J1=J1+NLINE+3
  262 CONTINUE
C     SUM OF RESIDUALS SQUARED
  270 FD=FZ(N)-FY(N)
      F=F+FD**2
C       CALCULATION OF THE NORMAL EQUATION
      DO 271 J=1,NVAR
      G(J)=G(J)+FD*GR(J)
      DO 271 M=J,NVAR
      H(J,M)=H(J,M)+GR(J)*GR(M)
  271 H(M,J)=H(J,M)
  272 WRITE (3,22) M1,F,(X(J),J=1,NVAR)
C     SOLVE H*X=G ( X IS ACTUALLY SOLVED INTO G )
  280 CALL MATINV(H,NVAR,G,1,DET)
      WRITE (3,25) (G(J),J=1,NVAR)
C       TERMINATION CRITERIA
      IF (WARN(TIME)) 289,281,289
  281 IF (M1.GE.19) GOTO 292
      IF (FA-F.LT.F*1.E-3) GOTO 290
C       CALCULATION OF THE NEXT ORDER PARAMETERS
      M2=M1
  282 DO 285 J=1,NVAR
      IF (J.GE.NVAR-1) GOTO 284
C       CHECKING THE IMPROVEMENTS FOR THE PARAMETERS
C     ADJUST CORRECTION VECTORS TO HELP PREVENT DIVERGENCE
      IF (G(J)**2.LT.F*H(J,J)/NUM/10.) GOTO 284
```

```
      GA=ABS(G(J))
      GB=ABS(X(J))/5.
      IF (M3.NE.1) GOTO 283
      GC=ABS(G1(J))
      FAC=1.
      IF (GA.GT.GC) FAC=2.
      IF (G(J)**2.GT.F*H(J,J)/(NUM-NVAR)) FAC=FAC*2.
      IF (SIGN(GA,G1(J)).NE.G(J))  FAC=FAC*3.
      G(J)=G(J)/FAC
      GA=ABS(G(J))
  283 IF (GA.GT.GB) G(J)=SIGN(GB,G(J))
C    CALCULATE NEXT SET OF PARAMETERS
  284 X(J)=X(J)-G(J)
      G1(J)=G(J)
  285 CONTINUE
      IF (M2.NE.M1) M3=1
  286 M1=M1+1
      FA=F
      GOTO 200
  289 IFIN=1
      WRITE (3,29)
      GOTO 292
  290 IF (FA-F) 291,292,292
C    PERMIT FIT TO DIVERGE ONLY THREE TIMES
  291 WRITE (3,23) M1
      IF (F-FA.LT.F/20.) GOTO 292
      IF (M1-M2.LT.2) GOTO 282
      IF (M2.EQ.0) GOTO 360
C     CALCULATION OF THE STANDARD DEVIATIONS
  292 DO 293 J=1,NVAR
  293 G(J)=SQRT(F*H(J,J)/(NUM-NVAR))
C     OUTPUT AND PLOTTING SECTION
  300 XMIN=0.
      IF (KFIELD.LT.0) XMIN=FX(1)
      XMAX=10000.
      IF (KFIELD.LT.0) XMAX=FX(NUM)
      WRITE (3,24)
      WRITE (98,13) NAME,NFILE
      CALL CCLTR(20.,300.,1,2)
      WRITE (98,27) (COMMENT(J),J=1,4)
      CALL CCLTR(1140.,200.,1,2)
C     SEARCH FOR THE LIMITS OF THE PLOT
        YMIN = FZ(1)
       YMAX = FZ(1)
      YL=0.
      DO 301 J=1,NUM
      IF (FZ(J).LT.YMIN) YMIN=FZ(J)
      IF (FY(J).LT.YMIN) YMIN=FY(J)
      IF (FZ(J).GT.YMAX) YMAX=FZ(J)
      IF (FY(J).GT.YMAX) YMAX=FY(J)
      FW(J)=FZ(J)-FY(J)
      ZY=ABS(FW(J))
      IF (ZY.GT.YL) YL=ZY
  301 CONTINUE
      Y1=(YMAX-YMIN)/YL/8.
      WRITE (98,28) Y1
```

```
      CALL CCLTR(70.,30.,0,2)
      YMIN=(5.*YMIN-YMAX)/4.
      CALL CCPLOT(FX,FZ,NUM,4HJOIN,0,0)
      CALL CCPLOT(FX,FY,NUM,6HNOJOIN,23,3)
      YMIN=-YL
      YMAX=9.*YL
      CALL CCPLOT(FX,FW,NUM,4HJOIN,0,0)
      CALL CCNEXT
C     CHECKING OF THE INTEGRATED INTENSITIES
  310 ARE=0.
      DO 312 I=1,IFIT
      AR(I)=0.
      DO 311 J=1,NLINE
      K=(I-1)*NLINE+J
  311 AR(I)=AR(I)+C(K)
  312 ARE=ARE+AR(I)
  313 Y=FX(NUM)-FX(1)
      ARA=ARE+A*Y**2/2.+B*Y**3/6.
  320 WRITE (3,14) AREA,ARA,A,G(NVAR-1),B,G(NVAR)
C     OUTPUT OF THE RESULTS
  321 IF (IFIT) 350,340,350
  340 WRITE (3,21)
      WRITE (3,15)
      DO 341 J=1,NLINE
      CT=G(J+NLINE)
      DT=G(J+2*NLINE)
  341 WRITE (3,16) J,FC(J),G(J),C(J),CT,D(J),DT
      GOTO 360
  350 WRITE (3,17) HSTART,HSTOP
      WRITE (3,18)
      J1=0
      DO 352 I=1,IFIT
      DO 351 J=1,NLINE
      K=(I-1)*NLINE+J
      IC(K)=J
      DD(K)=D(K)*SWEEP
      SP(K)=G(J+J1+3)
      DS(K)=G(J+J1+3)*SWEEP
  351 C(K)=FC(K)*SWEEP+HSTART
      K=(I-1)*NLINE+1
      K1=K+NLINE-1
      FH=HSTART+X(J1+1)*SWEEP
      FG=X(J1+2)*SWEEP
      FS=G(J1+1)*SWEEP
      FT=G(J1+2)*SWEEP
      AR(I)=AR(I)/ARE
      GR(I)=G(J1+3)/ARE
      IF (KFIELD.LT.0) GOTO 352
      WRITE (3,19) I,AR(I),GR(I),FH,FS,FG,FT,(IC(J),DD(J),DS(J),C(J),
     *             J=K,K1)
  352 J1=J1+NLINE+3
      IF (KFIELD.LT.0) GOTO 353
      WRITE (3,21)
      WRITE (3,18)
  353 J1=0
      DO 354 I=1,IFIT
```

```
      K=(I-1)*NLINE+1
      K1=K+NLINE-1
      WRITE (3,19) I,AR(I),GR(I),X(J1+1),G(J1+1),X(J1+2),G(J1+2),(IC(J),
     *             D(J),SP(J),FC(J),J=K,K1)
  354 J1=J1+NLINE+3
  360 M1=0
       WRITE( 3, 30 ) Y1
      WRITE (3,24)
      IF (IFIN) 401,110,401
C     PROGRAM TERMINATION
  400 WRITE (3,20)
  401 IF (LOOP.EQ.2) CALL CCEND
      STOP
      END
```

```
      SUBROUTINE HCALIB ( K, N, F )
      DIMENSION F(1000)
C     SAMPLE CALIBRATION ROUTINE
C     CALIBRATE THE VALUES IN F     N POINTS
C      OR CONVERT FROM ONE UNIT TO ANOTHER UNIT
C     FOR EXAMPLE IF F CONTAINS NMR FREQUENCIES
C      DO 10 J = 1, N
C 10   F(J) = F(J) / 425775
C     FOR FIELDIAL CALIBRATION WITH COEFFICIENTS FROM PROGRAM GAUSS
C      DO 10 J=1,N
C 10    F(J) = A+B*F(J)+C*F(J)**2
C     IF DATA REQUIRE SEVERAL DIFFERENT CALIBRATIONS
C     K MAY BE USED TO SELECT CALIBRATION
C      IK=-K
C      GO TO ( 1,2,3,   ...ETC....) IK
       DO 10  J=1, N
 10     F(J) = 2834.7580+( 1.0366706E-01 -2.2958270E-07*F(J) ) *F(J)
        RETURN
        END
```

```
      FORTRAN IV SUBROUTINE MATINV(A,N,B,M,DETERM)                      F4020003
C                                                                       F4020004
C     MATRIX INVERSION WITH ACCOMPANYING SOLUTION OF LINEAR EQUATIONS   ANF40201
C                                                                       F4020002
      DIMENSION IPIVOT(38),A(38,38),B(38,1),INDEX(38,2),PIVOT(38)
      EQUIVALENCE (IROW,JROW), (ICOLUM,JCOLUM), (AMAX, T, SWAP)         F4020007
C                                                                       F4020008
C     INITIALIZATION                                                    F4020009
C                                                                       F4020010
   10 DETERM=1.0                                                        F4020011
   15 DO 20 J=1,N                                                       F4020012
   20 IPIVOT(J)=0                                                       F4020013
   30 DO 550 I=1,N                                                      F4020014
C                                                                       F4020015
C     SEARCH FOR PIVOT ELEMENT                                          F4020016
C                                                                       F4020017
C                                                                       F4020015
C     SEARCH FOR PIVOT ELEMENT                                          F4020016
C                                                                       F4020017
   40 AMAX=0.0                                                          F4020018
   45 DO 105 J=1,N                                                      F4020019
   50 IF (IPIVOT(J)-1) 60, 105, 60                                      F4020020
   60 DO 100 K=1,N                                                      F4020021
   70 IF (IPIVOT(K)-1) 80, 100, 740                                     F4020022
   80 IF (ABS(AMAX)-ABS(A(J,K))) 85, 100, 100
   85 IROW=J                                                            F4020024
   90 ICOLUM=K                                                          F4020025
   95 AMAX=A(J,K)                                                       F4020026
  100 CONTINUE                                                          F4020027
  105 CONTINUE                                                          F4020028
      IF(AMAX) 110,800,110                                              F402REV.
  110 IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1                                   F4020029
C                                                                       F4020030
C     INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL                 F4020031
C                                                                       F4020032
  130 IF (IROW-ICOLUM) 140, 260, 140                                    F4020033
  140 DETERM=-DETERM                                                    F4020034
  150 DO 200 L=1,N                                                      F4020035
  160 SWAP=A(IROW,L)                                                    F4020036
  170 A(IROW,L)=A(ICOLUM,L)                                             F4020037
  200 A(ICOLUM,L)=SWAP                                                  F4020038
  205 IF(M) 260, 260, 210                                               F4020039
  210 DO 250 L=1, M                                                     F4020040
  220 SWAP=B(IROW,L)                                                    F4020041
  230 B(IROW,L)=B(ICOLUM,L)                                             F4020042
  250 B(ICOLUM,L)=SWAP                                                  F4020043
  260 INDEX(I,1)=IROW                                                   F4020044
  270 INDEX(I,2)=ICOLUM                                                 F4020045
  310 PIVOT(I)=A(ICOLUM,ICOLUM)                                         F4020046
  320 DETERM=DETERM*PIVOT(I)                                            F4020047
C                                                                       F4020048
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT                                 F4020049
C                                                                       F4020050
  330 A(ICOLUM,ICOLUM)=1.0                                              F4020051
  340 DO 350 L=1,N                                                      F4020052
  350 A(ICOLUM,L)=A(ICOLUM,L)/PIVOT(I)                                  F4020053
```

```
  355 IF(M) 380, 380, 360                                         F4020054
  360 DO 370 L=1,M                                                F4020055
  370 B(ICOLUM,L)=B(ICOLUM,L)/PIVOT(I)                            F4020056
C                                                                 F4020057
C     REDUCE NON-PIVOT ROWS                                       F4020058
C                                                                 F4020059
  380 DO 550 L1=1,N                                               F4020060
  390 IF(L1-ICOLUM) 400, 550, 400                                 F4020061
  400 T=A(L1,ICOLUM)                                              F4020062
  420 A(L1,ICOLUM)=0.0                                            F4020063
  430 DO 450 L=1,N                                                F4020064
  450 A(L1,L)=A(L1,L)-A(ICOLUM,L)*T                               F4020065
  455 IF(M) 550, 550, 460                                         F4020066
  460 DO 500 L=1,M                                                F4020067
  500 B(L1,L)=B(L1,L)-B(ICOLUM,L)*T                               F4020068
  550 CONTINUE                                                    F4020069
C                                                                 F4020070
C     INTERCHANGE COLUMNS                                         F4020071
C                                                                 F4020072
  600 DO 710 I=1,N                                                F4020073
  610 L=N+1-I                                                     F4020074
  620 IF (INDEX(L,1)-INDEX(L,2)) 630, 710, 630                    F4020075
  630 JROW=INDEX(L,1)                                             F4020076
  640 JCOLUM=INDEX(L,2)                                           F4020077
  650 DO 705 K=1,N                                                F4020078
  660 SWAP=A(K,JROW)                                              F4020079
  670 A(K,JROW)=A(K,JCOLUM)                                       F4020080
  700 A(K,JCOLUM)=SWAP                                            F4020081
  705 CONTINUE                                                    F4020082
  710 CONTINUE                                                    F4020083
  740 RETURN                                                      F4020084
  800 DETERM = 0.                                                 F402REV.
      RETURN                                                      F402REV.
      END
```

3. GAUSS

When the digital data acquisition system is used with the Varian spectrometer system, a NMR tracking system is not normally employed. In this case the recorder x-axis drive voltage from the Fieldial is applied to a Vidar voltage-to-frequency converter and this frequency is measured as the magnetic field coordinate. In order for the least squares fitting programs to work in units of gauss, a calibration of the Vidar frequencies in terms of magnetic field must be performed. The GAUSS program relates the Vidar frequencies to the magnetic field.

A series of measurements of the magnetic field (using proton NMR) is made over the entire range of the sweep. This produces a set of paired measurements of the magnetic field (NMR frequency) and of the Vidar frequency. A quadratic equation

Y = A + B * X + C * X**2

if fit to these points to produce the coefficients A, B, C. Then, given a Vidar frequency (X),the magnetic field (Y) may be computed. These coefficients are used to write the subroutine HCALIB which is used by FITESR. The input to the program is the measurements X(I), the Vidar frequency; and Z(I), the proton frequency corresponding to Y(I) the magnetic field in gauss. The proton NMR frequency is converted to gauss by the program. The output consists of the coefficients A, B, and C and a comparison of the experimental field with the theoretical field for a given Vidar value.

INPUT DATA

Card 1 (Format I5, 7A10)

N	number of pairs of Points used in the calibration (minimum of three)
TITLE	any identification information

Card 2 (Format 8E10.0)

X(I)	Vidar reading in terms of tens of cycles (decacycles)
Z(1)	Proton NMR frequency in kilocycles
X(2)	etc. until X(N), Z(N)
Z(2)	

There are as many of Card 2 as needed to contain N points, 4 points to a card.

If several calibrations are to be performed at once, continued with data from Card 1, etc. A blank card at the end of the data will terminate processing.

The GAUSS program requires the subroutine MATINV which is described in the discussion of FITESR.

```
      PROGRAM GAUSS(INPUT,OUTPUT)
C     PROGRAM FOR LEAST SQUARES FIT TO A + B*X + C*(X**2) = Y
C   VERSION TO SEPT. 1, 1969. JAMES J. CHANG.
      DIMENSION X(25), Y(25), Z(25), DIF(25), PRED(25)
      DIMENSION A(20, 10) , B(20), SIGMA(10), TITLE(7)
C       INPUT SECTION
  1   READ 100, N, ( TITLE(I) , I= 1,7 )
      IF(N) 80,80, 3
  3   CONTINUE
      READ 101, ( X(I), Z(I), I= 1,N )
C   X(I) IS VIDAR FREQUENCY  IN TENS OF CYCLES
C   Z(I) IS PROTON NMR FREQUENCY IN KC.
      PRINT 102, ( TITLE(I) , I = 1,7 )
      PRINT 103
      PRINT 120
C     SECTION TO CLEAR STORAGE
      XSUM = 0.0
      XSUMSQ = 0.0
      XSUMC = 0.0
      XSUM4 = 0.0
      YSUM = 0.0
      XYSUM = 0.0
      X2YSUM = 0.0
C     SECTION TO COMPUTE MATRIX ELEMENTS
      DO 20 I = 1, N
C  CONVERSION TO MAGNETIC FIELD
 10     Y(I) = Z(I) * 0.234875
      XSUM = XSUM + X(I)
      XSUMSQ = XSUMSQ + X(I) * X(I)
      XSUMC = XSUMC + X(I) * X(I) * X(I)
      XSUM4 = XSUM4 + ( X(I) * X(I) * X(I) * X(I)   )
      YSUM = YSUM + Y(I)
      XYSUM = XYSUM + X(I) * Y(I)
      X2YSUM = X2YSUM + X(I) * X(I) * Y(I)
 20   CONTINUE
C  SET UP MATRIX  OF NORMAL EQUATIONS
      A(1,1) = N
      A(1,2) = XSUM
      A(1,3) = XSUMSQ
      A(2,2) = XSUMSQ
      A(2,3) = XSUMC
      A(3,3) = XSUM4
      A(2,1) = XSUM
      A(3,1) = XSUMSQ
      A(3,2) = XSUMC
      B(1) = YSUM
      B(2) = XYSUM
      B(3) = X2YSUM
      PRINT 109
      DO 40 I = 1,3
 40   PRINT 110 , ( A(I,J), J = 1,3 ) , B(I)
      CALL MATINV( A,3,B,1,DETERM)
      PRINT 152, DETERM
C    SECTION TO COMPUTE PREDICTED VALUES AND DIFFERENCES
      F = 0.0
       DO 50 I = 1, N
```

```
      PRED(I) = B(1) + B(2) * X(I) + B(3) * ( X(I) * X(I) )
       DIF(I) = Y(I) - PRED(I)
      F = F + DIF(I) * DIF(I)
 50    CONTINUE
      AN = N
      S = SQRT( F/(AN-3.0 ) )
      PRINT 121
      PRINT 122, ( X(I), Z(I), Y(I), PRED(I), DIF(I), I= 1,N )
C   SECTION TO COMPUTE STANDARD DEVIATIONS OF PARAMETERS
      DO 55 I = 1,3
      SIGMA(I) = S * SQRT( A(I,I) )
 55   CONTINUE
      PRINT 125, F, S
       PRINT 130
      PRINT 150
      PRINT 151, ( B(I) , SIGMA(I) , I= 1, 3 )
      PRINT 155, B(1), B(2), B(3)
      GO TO 1
 80   CALL EXIT
 100  FORMAT (I5, 7A10)
 101  FORMAT( 8E10.5 )
 102  FORMAT( 1H1, 20X, 7A10 )
 103  FORMAT(1H0,5X,*VIDAR FIELD CALIBRATION,SEPT 1,1969 VERSION* //)
 109  FORMAT( 1H0, 20H NORMAL EQUATIONS         )
 110  FORMAT( 10X, 3E16.7, 15X , E16.7)
 120   FORMAT(1H0, 45H INPUT POINTS, CONVERSION FACTOR = 0.234875    //)
 121  FORMAT(20X, 1HX,19X,1HZ,19X,1HY, 16X,4HPRED,18X, 3HDIF   )
 122   FORMAT( 10X, 5( F16.3 , 4X ) )
 125  FORMAT( 1H0, 10H RESIDUALS , F16.7, 5X, 6HSIGMA  , E16.7 )
 130   FORMAT( 1H0, 20X, 30H FIT TO Y = A + B*X + C*(X**2)      //)
 150  FORMAT (1H0, 20H COEFFICIENTS ARE       )
 151  FORMAT( 1H0, 5X, 2HA=, E16.7, 2H ( ,E13.7,1H),/ 6X,2HB=,E16.7,
     1  2H (,E13.7, 1H),/ 6X,2HC=,E16.7,2H (,E13.7,1H),// )
 152  FORMAT( 20X, 15H DETERMINANT     , F16.7//)
 155  FORMAT( 1H0, 6X, 6HF(J)= , F10.4, 4H + ( , E14.7, 1H+,
     1 E14.7, 15H *F(J) ) * F(J)      )
      END
```

B. Simulation Programs

1. IMITATE

The IMITATE program is used to simulate isotropic EPR spectra for both transition metals and organic radicals. The line positions are determined by a g value and the coupling constants according to Eq. A-11. The lineshapes are produced by Eq. A-12 which is expanded to account for more than one species. The program is at present capable of simulating a spectrum containing as many as four separate spectra each of which is characterized by g values and A values. The program is well suited for simulating spectra of a system containing several isotopic species.

In operation, the program first computes the resonance fields for each of the lines in the spectrum. Because of the storage limitations the program is limited to a maximum of 1600 lines. This may be changed by changing the DIMENSION statements. The intensity ratios of the lines are computed by SUBROUTINE RATIO. Again because of dimension limitation a given coupling constant should not produce more than 25 lines.

INPUT DATA

Card 1 (Format 2I5, 30X, 4A10)

NSPECY The number of species to be simulated. Maximum value of 4. If NSPECY=0, the job is terminated.

NUM The number of points to be computed in the spectrum

COMMENT(J) Any comment information

Card 2 (Format 10I5)

NCOUP(J) The number of coupling constants for each species. For one species there is NCOUP (1); for two, there are NCOUP (1) and NCOUP (2). NCOUP (1)=1 for one coupling constant; =2 for two constants, etc.

Card 3. (Format 5(I5, F10.5))

NEQ(J1,J) The number of equivalent nuclei corresponding to a particular coupling constant (which is given later), for the Jth species. All of the NEQ(J1,J) for the same species are on the same card.

S(J1,J) The nuclear spin for the NEQ nuclei. For two protons NEQ=2;S=0.5.

There are as aany of card 3 as there are species. Note that if there are more than 5 sets of equivalent nuclei for a given species, the data must be on a second card 3(maximum of 10 sets possible).

Card 4. (Format 8F10.5)

HSTART The starting field for the simulation

HSTOP The ending field for the simulation. The spectra are computed from HSTART to HSTOP

ALPHA Baseline offset

BETA Baseline drift. Normally ALPHA and BETA are zero.

Card 5. (Format 8F10.5)

FINT(J) The intensity of the Jth species. This is an arbitrary number but the relative values of FINT should correspond to the relative intensities of the different species.

HZERO(J) The resonance center for the Jth species. This should be computed from the g value and the microwave frequency.

A(J1,J) The coupling constants corresponding to the NEQ(J1,J) of card 3. for the Jth species. More than 6 constants are continued on the next card.

Card 6 (Format 8F10.5)

FLAG =0 read the widths of all of the lines

≠0 all the lines have the same width

Card 7. (Format 8F10.5)

W(K) The linewidth. If FLAG=0, the widths for <u>all</u> the lines must be provided on as many of card 7 as required. For the purpose of identifying a given line, each line is identified by a K value in addition to its identification by the m_I values. The value of K is determined by the m_I values and by the order in which the spins were presented on card 3. K=1 occurs when all the m_I have their lowest values. When the first m_I (corresponing to the first S on card 3) has the second from lowest value, with all other m_I at their lowest value, then K=2. If the second m_I is at its second from lowest value, with all other m_I at their lowest values, then $K=2S_1+2$ where S_1 is the maximum value of the first S on card 3. If FLAG≠0, only one width is provided (requires only 1 card).

There are as many of cards 5, 6, and 7 as there are species. Note that the cards 5, 6, 7 must come together. For two species the order is card 5, card 6, card 7, card 5, card 6, card 7.

If more than one spectrum is to be simulated, the data are continued from card 1. A blank card at the end of the data will terminate processing. The following is a sample data set which could be used to simulate hexaquocopper (II).

```
Col.5    10         20         30
    1    500                                        SAMPLE COPPER SPECTRUM
    1
    1      1.5
 2750.0           3250.0      0.0       0.0
  100.            3000.0    -34.4
    0.0
   60.0             58.0     56.0      56.0
 (blank card)
```

```
      PROGRAM IMITATE(INPUT,OUTPUT,TAPE98,PLOT,TAPE99=PLOT)
C PROGRAM FOR SIMULATING MANY SPECIES EPR SPECTRA
      COMMON/SPINS/NCOUP(10),NEQ(10,4),S(10,4),SMI(10,4),SM(10),NLINE(4)
      COMMON/FSPEC/NUM,AREA,FX(2000), FZ(2000)  ,NSPECY
      COMMON/STORE1/A(10,4),FINT(4),W(1600),R(1600),H(1600),JS
      COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
      COMMON/CCFACT/FACTOR
       DIMENSION COMMENT(4) , HZERO(4)
      DATA( TWOPI = .636619772367581 )
 5    CONTINUE
C  SECTION FOR INPUT OF SPECTRUM PARAMETERS
       READ 401, NSPECY , NUM, ( COMMENT(J) , J = 1,4 )
C   TERMINATION TEST
       IF( NSPECY ) 99, 99, 10
 10    CONTINUE
       READ 402, ( NCOUP(J) , J = 1, NSPECY )
      DO 20 J = 1, NSPECY
C     READ NO. OF NUCLEI AND SPIN
      JX = NCOUP(J)
      READ 404, (NEQ(J1,J),S(J1,J),J1=1,JX )
      NLINE(J) = 1
      DO 20 J1 = 1, JX
      NLINE(J) = (2*NEQ(J1,J)*S(J1,J) +1 ) * NLINE(J)
 20   CONTINUE
      DO 15 J= 1, NSPECY
      KP = KP + NLINE (J)
      IF ( KP .GT. 1600 ) GO TO 4
      GO TO 15
 4    PRINT 421, KP
      GO TO 5
 15   CONTINUE
       READ 405, HSTART, HSTOP, ALPHA, BETA
      KP = 0
      DO 25 J = 1, NSPECY
      KP = KP + 1
       JX = NCOUP(J)
      READ 405, FINT(J),HZERO(J),(A(J1,J),J1 = 1,JX )
      J2 = NLINE(J)
      READ 405, FLAG
C   FLAG = 0  IMPLIES READ WIDTHS FOR ALL LINES
C     FLAG .NE.0  ALLL LINES HAVE SAME WIDTH
      IF( FLAG ) 21, 24, 21
 21   READ 405, W(KP)
      DO 22 J1 = 1, J2
      KP=KP + 1
      W(KP) = W(KP-1 )
 22    CONTINUE
       GO TO 25
 24    CONTINUE
       KP1 = KP + J2
       READ 405, ( W(J1), J1= KP, KP1 )
       KP = KP1
 25    CONTINUE
       PRINT 410, NSPECY, NUM
       PRINT 411, ALPHA, BETA, HSTART, HSTOP
       PRINT 420, ( COMMENT(J) , J = 1, 4 )
```

```
       AR = 0.0
      DO 30 J = 1, NSPECY
      AR = FINT(J) + AR
 30    CONTINUE
       CALL RATIO
      DO 60 J = 1, NSPECY
       JX = NCOUP ( J )
      KP = 1 + NLINE(J) * ( J-1 )
      FACT = 1.0 / R(KP )
       RINT = FINT(J) / AR
       PRINT 412
      PRINT 413, J,FINT(J), RINT, HZERO(J),(A(J1,J),NEQ(J1,J),
     1  S(J1,J) , J1= 1, JX )
C$$$   START OF LARGE NESTED LOOP  FOR COUNTING  THROUGH M SUB I  AND
C       ARRIVING AT A PROPER K VALUE
C$$$  LOOP INITIALIZATION
      PRINT 415
      K = 0
      LOOP = JX
 100  SM(LOOP) = -SMI(LOOP,J )
 110  IF( LOOP . EQ. 1 ) GO TO 120
      LOOP = LOOP - 1
      GO TO 100
C$$   START OF LOOP WORK
 120  CONTINUE
C
C     START LINE COUNT
      K = K + 1
      FIRST = 0.0
      SECOND = 0.0
C     COMPUTE THE RESONANCE FIELDS
      DO 40 K1 = 1, JX
      FIRST = FIRST +SM(K1)* A(K1, J)
      SPIN = SMI(K1, J)* ( SMI(K1,J) + 1.0 )- SM(K1)*SM(K1)
      SECOND= SECOND+( A(K1,J)*A(K1,J)/(2.0*HZERO(J) ) ) * SPIN
 40   CONTINUE
      KP = K + NLINE(J) * ( J- 1 )
      H(KP) = HZERO(J) - FIRST - SECOND
      REL = R(KP) * FACT
      PRINT 416, K, W(KP), H(KP),REL,(SM(I),I=1, JX )
C$$$  ENDING OF LARGE NESTED LOOP
C     INNER LOOP CONTROL
 130  SM(LOOP) = SM(LOOP) + 1.0
      IF ( SM(LOOP) .LE. SMI(LOOP,J) ) GO TO 120
C     MOVING LOOP CONTROL
 140  LOOP = LOOP + 1
C      MAIN LOOP TERMINATION TEST
      IF( LOOP .GT. JX ) GO TO 150
      SM(LOOP) = SM(LOOP) + 1.0
      IF ( SM(LOOP) .GT. SMI(LOOP,J) ) GO TO 140
      LOOP = LOOP - 1
       GO TO 100
 150  CONTINUE
C***    LOOP IS ENDED
 60   CONTINUE
C
```

```
C     SECTION TO GENERATE FIELDS
        ANUM = NUM
      FDIF = ( HSTOP - HSTART ) / ANUM
      FX(1) = HSTART
        DO 61 N = 2, NUM
        AN = N
        FX(N) = HSTART + AN * FDIF
 61   CONTINUE
C   SECTION FOR COMPUTING THE LINESHAPE
        DO 80  N= 1, NUM
      FZ(N) = 0.0
            DO 75 J = 1, NSPECY
        JN = NLINE ( J)
      TSHAPE = 0.0
                DO 70 K = 1, JN
      KP = K + JN * (J-1 )
      FIELD = H(KP) - FX(N)
      FIELD2 = FIELD * FIELD
      TAU2 = W(KP) * W(KP)
      DENOM1 = FIELD2 + TAU2
      DENOM2 = DENOM1 * DENOM1
      SHAPE = FIELD * W(KP) / DENOM2
      TSHAPE = R(KP) * SHAPE + TSHAPE
 70   CONTINUE
      FZ(N) = TWOPI * FINT(J) * TSHAPE + FZ(N)
 75     CONTINUE
        FZ(N) = FZ(N) + ALPHA + BETA * FX(N)
 80   CONTINUE
C       SET THE PLOT SIZE
      CCXMAX = 1070.
      IF( NUM .GT. 1000 ) CCXMAX = 2070.
      CALL CCGRID(5,2,6HNOLBLS,5)
      XLTR = 1140.
      IF( NUM .GT. 1000 ) XLTR = 2140.
 82       CONTINUE
      WRITE (98,201)(COMMENT(J),J=1,4)
      CALL CCLTR( XLTR , 200. , 1, 2 )
C     SEARCH FOR THE LIMITS OF THE PLOT
        XMIN = FX(1)
        XMAX = FX(NUM)
        YMIN = FZ(1)
        YMAX = FZ(1)
        DO 85 N = 1, NUM
        IF( FZ(N) .LT. YMIN) YMIN = FZ(N)
        IF( FZ(N) .GT. YMAX ) YMAX = FZ(N)
 85     CONTINUE
      CALL CCPLOT(FX,FZ,NUM,4HJOIN,0,0)
      CALL CCNEXT
      GO TO 5
 99     CALL CCEND
      CALL EXIT
 201  FORMAT(4A10)
 401    FORMAT( 2I5, 30X, 4A10 )
 402      FORMAT ( 10I5 )
 404  FORMAT( 5 ( I5, F10.5 ) )
 405  FORMAT( 8F10.5 )
```

```
410    FORMAT( 1H1, 34H SIMULATION OF EPR SPECTRUM WITH      , I5,
     1   9H SPECIES   ,5X,I5, 8H POINTS    )
411   FORMAT( X, *ALPHA * ,E16.5,* BETA  *, E16.5, 5X, * HSTART    *,
     1 F12.3, 2X, * HSTOP   * , F12.3 )
412   FORMAT( 1H0, 3HNO., 5X,10HINTENSITY ,10X, 10H RELATIVE  ,
     1   7X, 3HH0 ,15X, 20H COUPLING CONSTANT
     2   2X, 5H NEQ    , 5X, 4H SI     )
413    FORMAT(X,I2,5X,F10.3, 10X,F7.3, 5X,F10.3,15X,F10.3,10X,I5,5X,
     1   F5.1/ ( 65X,F10.3, 10X,I5, 5X, F5.1 ) )
415   FORMAT(1H0, 10H COMPONENT  ,1X, 12H LINEWIDTH   ,1X,
     1   14H LINE CENTER     )
416    FORMAT(X,I5,F10.3,5X, F10.3,F8.1,10( 2X,F4.1 ) )
420    FORMAT( 1H0, 30X, 4A10, // )
421   FORMAT( 1H0, I7, 32H EXCEEDS NO. OF POSSIBLE LINES          )
       END
```

```
      SUBROUTINE RATIO
C     SUBROUTINE RATIO CALCULATES THE INTENSITY RATIO OF THE HYPERFINE
C     COMPONENTS
      COMMON/SPINS/NCOUP(10),NEQ(10,4),S(10,4),SMI(10,4),SM(10),NLINE(4)
      COMMON/FSPEC/NUM,AREA,FX(2000), FZ(2000)   ,NSPECY
      COMMON/STORE1/A(10,4),FINT(4),W(1600),R(1600),H(1600),JS
      DIMENSION ID(25,25)
      DIMENSION F(400)
       EQUIVALENCE ( FX, ID )
       EQUIVALENCE ( F, FZ )
      DO 4 JS = 1, NSPECY
      LIN=1
      NEQ2 = NCOUP( JS )
      KP = 1 + NLINE(JS) * ( JS-1 )
        R(KP) = 1.0
      DO 4 I = 1, NEQ2
      J1 = 2 * S( I, JS )
      J2 = NEQ( I, JS )
      N1=J1*J2+1
       IF ( N1 .GT. 25 ) GO TO 5
      SMI( I, JS) = S(I, JS) * J2
      FAC=1.
      FC=1./(J1+1)
      ID(1)=1
      DO 1 J=2,25
    1 ID(J)=0
      DO 2 J=1,J2
      J3=J+1
      FAC=FAC*FC
      DO 2 K=1,25
      J4=K-J1
      IF (J4.LE.0) J4=1
      ID(K,J3)=0
      DO 2 L=J4,K
    2 ID(K,J3)=ID(K,J3)+ID(L,J)
      L=1
      DO 3 J=1,N1
      DO 3 K=1,LIN
      KP = K + NLINE(JS) * ( JS-1 )
      F(L) = R(KP) * ID(J,J3) * FAC
    3 L=L+1
      LIN=L-1
      DO 4 J=1,LIN
      KP = J + NLINE( JS) * ( JS-1 )
4     R(KP) = F(J)
      RETURN
    5 LIN=1
       PRINT 10, N1, NEQ( I,JS), S( I,JS)
      RETURN
   10 FORMAT(20X,24H*** NUMBER OF COMPONENTS,I3,4H FOR,I3,
     *       28H EQUIVALENT NUCLEI WITH SPIN,F4.1,18H EXCEEDS LIMIT ***)
      END
```

2. VAESR*

VAESR is used to simulate polycrystalline or glass spectra for transition metal complexes with spin 1/2 and an axial spin Hamiltonian. The method used is due to Vanngard and Aasa (1962). The input essentially consists of the microwave frequency, and the spin Hamiltonian parameters. The main output is a computer drawn plot of the spectrum.

Method

The lineshape used is given by

$$I(H) = g_{\perp}^{2} \frac{1}{8(2I+1)} \int_{0}^{1} S'(H-H^{o})[(g_{\parallel}/g)^{2} + 1]\,dz$$

where z=cos θ, θ is the angle between the molecular axis and the applied magnetic fields, S' a shape function. For a Lorentz lineshape, the shape function is given by

$$S'(x) = \frac{2}{\pi}\frac{1}{\alpha^{3}} x[1 + (x/\alpha)^{2}]^{-2},\ \alpha = (\sqrt{3}/2)\Delta H$$

where ΔH is the peak-to-peak derivative width. The resonance field is given by

$$H^{o} = Ho - KM_{I}/g\beta - (1/4Ho)(g\beta)^{-2} A_{\perp}^{2} (A_{\parallel}^{2}+K^{2}) K^{-2} [I(I+1) - m_{I}^{2}]$$

$$- (1/2\,H_{o})(g\beta)^{-2} (A_{\parallel}^{2}-A_{\perp}^{2}) K^{-2} g_{\parallel}^{2} g_{\perp}^{2} g^{-4} z^{2} (1-z^{2}) m_{I}^{2}$$

$$g^{2} = g_{\perp}^{2} + (g_{\parallel}^{2}-g_{\perp}^{2}) z^{2} \qquad K^{2}g^{2} = A_{\parallel}^{2} g_{\parallel}^{2} z^{2} + A_{\perp}^{2} g_{\perp}^{2} (1-z^{2})$$

$$Ho = h\nu/g\beta$$

A variable linewidth is permitted for each hyperfine component, and the lineshape is summed over the hyperfine components. The integral is evaluated using Simpson's rule.

---

*The original version of this program was supplied by W. Burton Lewis. The program has been considerably altered.

INPUT DATA

Card 1 (Format I5, 6A10)

MCI the number of hyperfine components (maximum of 8)

LABEL any title information for the plot

Card 2 (Format 8F10.0)

XM(I) the m_I values for the hyperfine components (in order)

Card 3 (Format I5, 3F10.0)

N The number of points over which the Simpson's Rule integration is to be performed; must be odd.

DZ The size of the interval for the integration. May range from 0 to 1.0 (DZ = cosθ). For N=201, DZ = .005.

HT The lowest point in the magnetic field for the calculation and plotting of the spectrum.

HFNAL The highest point in the magnetic field.

Card 4 (Format 8F10.0)

A $A_{\parallel}$ in gauss

B $A_{\perp}$ in gauss

C leave blank (not used)

GPL $g_{\parallel}$

GPR $g_{\perp}$

XI I, the nuclear spin (eg. for I=3/2, XI=1.5)

SH $h\nu/\beta$(for ν=9.15 GHz, SH=6537.565)

CMP The value by which the magnetic field is to be stepped for calculations. The intensity of the spectrum is calculated at each point,n, where the value of the field at the nth point is HT+n*CMP.

Card 5 (Format 8F10.0)

DH(I) The linewidths for each of the hyperfine components

Card 6 (Format 8F10.0)

ZERO Vertical distance in inches from the bottom of the plot to the baseline. May be from 0 to 10 inches. This defines the baseline for the plot.

SIZE Length of the largest peak in inches from the baseline (ZERO). Note: If the peak is negative going, then SIZE is negative.

Cards are repeated from card 1 to simulate additional spectra. A blank card at the end of the data is used to terminate the program.

```
      PROGRAM VAESR( INPUT,OUTPUT,TAPE98,PLOT, TAPE99=PLOT )
C
C ESR SPECTRUM FITTING PROGRAM
C
      COMMON/CCPOOL/XMIN,XMAX,YMIN,YMAX,CCXMIN,CCXMAX,CCYMIN,CCYMAX
      COMMON/CCFACT/FACTOR
      DIMENSION HZ(201), ZS(201), T3(201), G(201),  XKM(201,8)
      DIMENSION XMS(8), XM(8), DH(8), D11(8), D12(8),  H(201,8)
      DIMENSION HAT(1002), HAV(1002), HAV2(1002),  LABEL(7)
C
      PRINT 117
      PRINT 118
 118  FORMAT(*  VERSION AS OF  8/8/70   J.J.C. * )
C SET COORDINATES FOR CALCOMP
      CCXMIN = 70.0
      CCXMAX = 1570.0
C
C  DATA SECTION  INPUT
 50   READ 115, MCI, ( LABEL(I), I = 1, 7 )
 52   READ 101, ( XM(I) , I = 1, MCI )
 1    READ 100, N, DZ, HT, HFNAL, IPT
      READ 101, A, B, C, GPL, GPR, XI, SH, CMP
      READ 101, ( DH(I) , I = 1, MCI )
      READ 101, ZERO, SIZE
      PRINT 119, ( LABEL(I) , I = 1, 7 )
      PRINT 111, N, DZ, HT, HFNAL
      PRINT 106, XI, SH, GPL, GPR, A, B
      PRINT 112, ( XM(I) , I = 1, MCI )
      PRINT116, ( DH(I) , I = 1, MCI )
         CALL CCGRID(5,6HNOLBLS,4)
       REWIND 98
       WRITE(98,120) ( LABEL(I) , I = 1,7 )
       CALL CCLTR ( 70. , 65. , 0, 2 )
 100  FORMAT( I5, 8F10.0 , I1 )
 101  FORMAT ( 8F10.0 )
 102   FORMAT(1H1,2(46H       FIELD              I(H)      NORMALIZED I  ))
 103   FORMAT( 1X, 6E16.7 )
 104   FORMAT ( 1H1 )
 106  FORMAT(1H0, 10X, 4H I= ,F5.2, 5X, 10H HNU/BETA     , F11.5, 4X,
     1  5H GPL= ,F10.5,5X, 5H GPR= , F10.5 /
     2          50X, 5H APL= , F10.5, 5X, 5H APR= , F10.5 // )
 111  FORMAT(1H0, 3H N=,I5,4H DZ=,F10.5,4H HT=,F10.3,7H HFNAL=,F10.3)
 112  FORMAT( 10H  M CAP I= 8F10.2   )
 115  FORMAT( I5, 7A10 )
 116   FORMAT( 10H  DELH I =  8F10.2  )
 117  FORMAT( 1H1, 20X,32H EPR GLASS SIMULATION PROGRAM        )
 119    FORMAT(1H0 , 16H IDENTIFICATION  ,3X, 7A10 )
 120    FORMAT( 1H  , 7A10 )
 131  FORMAT( 20X, I5, 4X, F10.3, 16X, F10.3 )
 130  FORMAT( 1H0, 10X, 16HRESONANCE FIELDS , 4X, 8HPARALLEL, 12X,
     1 14HPERPENDICULAR  / 29X, F10.3, 16X, F10.3  // )
C
C THIS SECTION CALCULATES COEFFICIENTS
      HA=HT
    2 D= A*A *GPL * GPL
      D1= B*B*GPR * GPR
```

```
      D2= D*D1
      D3= (D-D1) * (D-D1)
      D4= GPL* GPL
      D5= GPR*GPR
      D6= D*D4
      D7= D1*D5
      D8= D4-D5
      D9= D3*D4*D5
      D10= XI*( XI + 1.0)
       DO 15 I = 1, MCI
 11   XMS(I) = XM(I) * XM(I)
       D11(I) = 0.8660254 * DH(I)
 15      D12(I) = ( ( D11(I) ) ** (-3))*  0.63661977
      D13 = D5 / ( 8.0 * ( 2.0 * XI + 1.0 ) )
C
          PRINT 251
        PRINT 252, D,D1,D2,D3,D4,D5,D6,D7,D8,D9,D10,D13
 251   FORMAT( 1H0 , 10H D TO D13    )
 252   F3RMAT( 1H0 , 7E16.7 )
C
C         FIELD CALCULATION SECTION
C CALCULATES RESONANCE FIELD FOR EACH HYPERFINE  COMPONENT AS
C FUNCTION OF ANGLE
C
      DI= 0.0
      DO 3 I= 1,N
      Z= DI*DZ
      ZS(I) = Z*Z
C DO SOME SPEED OPTIMIZING FOR LOOP
       BIG= ZS(I)
        SINSQ = 1.0 - BIG
      GS = D5 + D8 * BIG
      G(I) = SQRT ( GS )
      XK = ( D6 * BIG   + D7 *  SINSQ           ) / GS
      HZ(I) = SH / G(I)
      T = 1.0 / ( GS * XK * 2.0 * HZ(I) )
      T1 = T * ( 0.5 * ( D2 + D1 * XK ) )
      T2 = T1 * D10
      T = T * D9 * ( 1.0 / ( GS * GS ) ) * BIG   *  SINSQ
      TEM = SQRT ( XK ) / G( I )
      T3(I) = ( D4 / GS ) + 1.0
      DO 4 J = 1 , MCI
      XKM ( I,J ) = TEM * XM (J)
      H(I,J) = HZ(I) - XKM(I,J) -( T2 - T1*XMS(J) ) -( T* XMS(J) )
 4    CONTINUE
      DI = I
 3    CONTINUE
      PRINT 130, HZ(N) , HZ(1)
      PRINT 131, ( J, H( N,J ) , H(1, J) , J = 1, MCI )
C
C   INTEGRATION SECTION
C    SIMPSON S RULE INTEGRATION
C    INTEGRATE OVER N ANGLES AT EVERY POINT
C    AND SUM OVER HYPERFINE COMPONENTS
C
      M = N-1
```

```
      CON = 6.0
            BIG = 0.0
   20 DO 21 L= 1,1002
      ABC = L
      SMKS = 0.0
      SMJS = 0.0
      DO 23 J= 1,MCI
      X = HA-H( 1,J)
C  USE FSIZE FOR TEMPORARY FOR SPEED
       FSIZE = D11 (J )
       Y = ( ( X/FSIZE) **2 ) + 1.0
      Y = 1.0/ (Y*Y)
       TEMP = D12 ( J )
       SMINT = T3(1) * TEMP * X * Y
      TEM = 4.0
      DO 24 I= 2,M
      X = HA  - H(I,J)
       Y = ( ( X/FSIZE) **2 ) + 1.0
      Y = 1.0/ (Y*Y)
       SUM = T3 (I)  * TEMP * X * Y
      SMINT = SMINT + SUM*TEM
      TEM = CON - TEM
   24 CONTINUE
      X = HA - H(N,J)
       Y = ( ( X/FSIZE) **2 ) + 1.0
      Y = 1.0/ (Y*Y)
       SUM = T3 ( N) * TEMP * X * Y
      SMINT = ( SMINT + SUM ) * DZ/3.0
      SMJS = SMJS + SMINT
C
C
   23 CONTINUE
      SMKS = SMKS + SMJS
   22 CONTINUE
C
C
      HAV(L) = SMKS* D13
C    START TO FIND MAXIMUM FOR SCALING
       TEMP = ABS ( HAV (L ) )
       IF( TEMP - BIG ) 30, 30, 32
  32   BIG = TEMP
  30        CONTINUE
      HAT(L) = HA
      HA = HT + CMP*ABC
      IF( HA-HFNAL ) 21, 21, 9
   21 CONTINUE
    9 M = ABC
C SECTION TO SCALE SPECTRUM FOR PLOTTING
      XMIN= HT
      XMAX= HFNAL
      YMIN= -1000.
      YMAX = 1000. * ( 1.0 - ZERO / 10. ) * (10. / ZERO )
      IF( SIZE ) 40 , 40 , 41
  40  FSIZE = ( SIZE / ZERO ) * YMIN
      GO TO 42
  41  FSIZE = ( SIZE / ( 10.0 - ZERO ) ) * YMAX
```

```
 42    SIZE = - ( FSIZE / BIG )
          DO 35 I = 1, M
  35    HAV2(I)  = HAV(I) * SIZE
        CALL CCPLOT(HAT, HAV2, M, 4HJOIN,0,0 )
C  PRINTING OF SPECTRUM IS SUPPRESSED
C  REMOVE C  S TO RESTORE PRINTING
C      PRINT 102
C      PRINT 103,     ( HAT(I) , HAV(I), HAV2(I), I= 1, M )
C TEST FOR MORE PLOTS
       READ 115, MCI, ( LABEL(I), I = 1, 7 )
         IF(MCI)  57, 57, 51
 51        CALL CCNEXT
       PRINT 104
         GO TO 52
C
  57   CALL CCEND
       CALL EXIT
       END
```

C. T_1 Analysis Program - LOGLINE

The LOGLINE program was written to operate in connection with the BASIC AVERAGER program supplied by the Digital Equipment Corp. with the LAB-8/I computer system. It is used to analyze the exponential recovery curves obtained in pulse-saturation-recovery experiments. It can, however, analyze any exponential recovery curve. The LOGLINE program can punch the experimental data acquired by the BASIC AVERAGER on the high speed punch; read in previously punched data for analysis; display the data on a storage display scope; or analyze the recovery curve for the time constant The program operates under the control from the teletype; the analysis is performed interactively, on-line, with the operator using the teletype to control the analysis, and the display oscilloscope to observe the results.

LOADING

The following program tapes must be loaded in order using the BINDARY LOADER

1. Lab-8 Basic Control Tape DEC-LB-T21A-PB
2. Lab-8 Basic Averager DEC-LB-U21A-PB
3. LOGLINE program tape
4. Floating Point Pkg. #3 DEC-08-YQ3A-PB without EAE or DIGITAL-8-25-F-BIN with EAE

At the end of the loading operation the Control tape and the Basic Averager are in Field 0. The main part of the LOGLINE program and the floating point package are in Field 1. Note that the operation of these programs requires a PDP-8/I equipped with 8K of memory, a high speed paper tape reader and punch, a DF32 disk, and an AX08 laboratory peripheral.

OPERATION

The programs are first loaded with the binary loader. The program is started at address 07603_8. The basic averager is used to acquire a recovery curve (The operation of the Basic Averager is discussed in the DEC manual, DEC-LB-T20A-B). The inputs to the AX08 should be adjusted so that the recovery curve is all negative; that is, the recovery curve grows from minus infinity to zero. The reason for this is that the data is converted to an exponential decay curve for the purpose of the logarithmic analysis simply by making all the data positive.

After the data has been acquired the LOGLINE program is entered from the basic averager by typing CTRL/P. LOGLINE types "R" to request the sample rate. The sample rate should be typed in some appropriate unit such as milliseconds. The sample rate is the time between data points and defines the time scale for the experiment. After the sample rate is typed the user may either punch the data or proceed to analyze the data. If the data is to be punched, CTRL/N is typed. LOGLINE will ask FIRST and LAST and the starting and ending channel to be punched should be provided. Note that the high speed punch should now be turned on. The user now types CTRL/P to punch the data. After the data is punched, the punch is turned off and the user may proceed to analyze the data.

The first step in the data analysis is to type the ALT MODE key. This causes the Basic Averager to be stored on the disk, thus freeing FIELD 0 for data manipulations. LOGLINE will reply with the message CORE SWAPPED after the operation is completed. At this time the baseline should be subtracted from the data. Type CTRL/N to redefine FIRST and LAST to the channels near the end of the recovery, for example, FIRST=960 and LAST=990. Now type CTRL/B to compute the baseline from the average of the data from FIRST to LAST. LOGLINE will reply with the value of the baseline. Now type CTRL/A to subtract the baseline. New values of FIRST and LAST are requested for the baseline subtraction. (Note: all operations on the data are performed with FIRST and LAST as limits).

At this time the data may be examined on the display scope by typing CTRL/D to display the data from FIRST to LAST The logarithm of the data is displayed by CTRL/F. The display may be expanded or contracted by tvping as manys X's or C's as are required.

The data are now analyzed for the time constants. CTRL/N is typed and the limits are redefined for the next command. CTRL/V is typed to command LOGLINE to fit the logarithmic data from FIRST to LAST with a straight line. At the end of this operation LOGLINE types the constants of the straight line and types the relaxation time. (A is the intercept and B is the slope of the straight line). The theoretical curve can be compared with the experimental curve by typing CTRL/L to display the theoretical logarithm. If the fit is bad, the limits should be changed with CTRL/N and the fit performed again with CTRL/V. CTRL/N may be used at any time to change limits of fitting or of displaying data.

If there are additional time constants present in the data, the theoretical logarithm should now be stripped from the data by typing CTRL/S. The analysis can then proceed with a CTRL/N, CTRL/V combination as before. These operations are repeated to extract all the time constants. The progress of the fit is checked at all times with the display commands.

At the end of the processing the BASIC AVERAGER is reentered by typing CTRL/Q. At this point LOGLINE reads the basic averager into field 0 from the disk and then jumps to the basic averager. Note that if a mistake has been made in analyzing the above data, the data can be restored by typing CTRL/Q to return to the averager and then CTRL/P to return to LOGLINE with the original data. The analysis may then be repeated from the beginning.

To analyze data which has been previously punched, the LOGLINE program is first entered from the averager with CTRL/P. The data tape is placed in the high speed reader and CTRL/R is typed. LOGLINE will read the data tape. The analysis may now proceed as if LOGLINE had just been entered from with averager with data.

LOGLINE COMMANDS

CTRL/A	strip baseline from data between FIRST and LAST
CTRL/B	compute baseline from between FIRST and LAST
CTRL/D	display data from FIRST to LAST
CTRL/E	examine the data in the channel indicated by FIRST LOGLINE will type the contents of the (FIRST) channel. The user now has 3 options: space: after typing a space the user can type a new value for the channel. line feed: typing the line feed causes FIRST to be changed to FIRST+1 and this channel is typed return: typing a carriage return terminates the CTRL/E command.
CTRL/F	display the logarithm of the data from FIRST to LAST
CTRL/H	halt current operation. Only operates during a CTRL/N or during a CTRL/P operation. Note that a CTRL/N occurs during a CTRL/A and a CTRL/S operation as part of their function. This command permits some mistakes during operation to be corrected.
CTRL/L	display theoretical logarithm from FIRST to LAST. In the special case of a CTRL/T command, this command is used to terminate the CTRL/T command.
CTRL/N	define new values of FIRST and LAST. The CTRL/N operation may be halted by CTRL/H. The values of FIRST and LAST after CTRL/H are uncertain.
CTRL/P	punch data from FIRST to LAST on high speed punch. Must be used before the ALT MODE command.
CTRL/Q	quit. return from LOGLINE to the basic averager.
CTRL/R	read a previously punched data tape. Must be used before ALT MODE.
CTRL/S	strip the theoretical logarithm from the data from FIRST to LAST.
CTRL/T	title. All information typed is echoed and ignored until CTRL/L is typed. This command is useful to provide descriptive information on the output during processing.
CTRL/V	Fit a straight line to the logarithm of the data from FIRST to LAST.
ALT MODE	swap the basic averager from field 0 to the disk; make the data positive and convert it from integer format to floating point.
X	expand the display by factor of two
C	contract the display by factor of two
CTRL/K CTRL/W CTRL/U	These commands are not presently defined. They are provided for future expansion of the program.

```
                /   LOGLINE
                /
                / NOV. 28, 1970    JAMES J CHANG
                /
                / PROGRAM OVERLAY TO BASIC AVERAGER
                /  DEC-LB-U21A-PB
                /
                / USES A WEIGHTED LOGARITHMIC LEAST SQUARES
                / TO ANALYZE EXPONENTIAL CURVES
                / OVERLAYS THE CTRL/P COMMAND TO CALL
                / THIS ROUTINE
                / PROGRAM RUNS IN FIELD 1
                / ASSUMES 1000 CHAN. AVERAGE
                /
                / PATCH FIELD 0 TO ALTER CTRL/P COMMAND
                /
                        FIELD 0
                        *7560
7560   7300             CLA CLL
7561   6002             IOF     /MAKE SURE INTERRUPT OFF
7562   6026             PLS     /INITIALIZE
7563   6046             TLS
7564   6211             CDF 10
7565   6212             CIF 10 /GET TO FIELD 1
7566   5767             JMP I .+1
7567   0200             0200
                /
                / FIELD 1 SECTION OF PROGRAM
                / PAGE ZERO CONSTANTS AND POINTERS
                /
                        FIELD 1
                        *5
0005   7400             7400    /FPP INPUT
0006   7200             7200    /FPP OUTPUT
                        *10
0010   0000     POINT,  0       /AUTO INDEX
0011   0000     POINT1, 0
0012   0000             0
0013   0000     POINT4, 0
0014   0000             0
0015   0000             0
0016   0000     SWITCH, 0       /I/O INDICATOR =1 FOR PUNCH
                /
                        *20
0020   0000     SHFR,   0       /HIGH  DATA PT. STOR. FOR SHIFTS
0021   0000             0       /LOW
0022   0000     TEMP,   0
0023   0000     ARITH1, 0
0024   0000     ARITH2, 0
0025   0000     ARITH4, 0
0026   0000     DISC,   0       /INDICATOR =1 IF FIELD 0 ON DISK
0027   0000     FIRST,  0
0030   0000     LAST,   0
0031   0166     SCL,    166     /POINTER TO SCALE LOCATION
0032   2212     BLK,    2212    /START OF DATA-1
0033   0240     K240,   240     /SPACE
0034   7766     KM12,   -12     /-10
0035   0000     PT1,    0       /POINTER
0036   0000     COUNT,  0
0037   6030     KMD1K,  -1750   /-1000
```

```
                        *62
0062  0000  ONE,        FLTG 1.0
0063  3777
0064  7774
0065  0001  TWO,        FLTG 2.0
0066  3777
0067  7774
0070  0007  HUND,       FLTG 100.0
0071  3077
0072  7776
0073  0000  A,          FLTG 0.0
0074  0000
0075  0000
0076  0000  B,          FLTG 0.0
0077  0000
0100  0000
0101  0000  SIGMA,      FLTG 0.0
0102  0000
0103  0000
0104  0000  N,          FLTG 0.0
0105  0000
0106  0000
0107  0000  SIGA,       FLTG 0.0
0110  0000
0111  0000
0112  0000  SIGB,       FLTG 0.0
0113  0000
0114  0000
0115  0000  BASE,       FLTG 0.0
0116  0000
0117  0000
0120  0000  R,          FLTG 0.0
0121  0000
0122  0000
0123  0000  X,          FLTG 0.0
0124  0000
0125  0000
0126  0000  Y,          FLTG 0.0
0127  0000
0130  0000
                        OCTAL
0131  0400  OUT,        OUTPUT /TYPE OR PUNCH
0132  0420  CLF,        CRLF
0133  0450  NSIN,       NOUT
0134  0616  SHIFT,      SHFTS
0135  0600  GET,        GETP   /GET DOUBLE PREC. DATA
0136  0500  MES,        MESAGE /PRINT MESSAGE
0137  0243  WHATP,      WHAT   /ECHO ?
0140  0213  LISTNP,     LISTEN
0141  0754  BRP,        BRAN   /BRANCH ON  AC MATCH
0142  0177  SPEC,       177    /DATA-1
0143  1013  INITP,      INIT
0144  1000  ENDT,       ENDTST
0145  0552  DACP,       DAC    /GET DATA FROM F0 TO FAC
0146  1125  THP,        TH     /COMPUTE Y=A+B*X
0147  1324  DEVP,       DEV    /COMPUTE PARAMETER STD. DEV.
0150  1407  LSP,        LSQOUT /OUTPUT LST. SQ. PARAMETERS
0151  0670  IFIXP,      IFIX   /FIX FAC
0152  0720  NEWCP,      NEWC   /GET NEW FIRST AND LAST
```

```
0153  0565  STORE,  FACD    /PUT FAC INTO F0
0154  0656  FLOATP, FLOAT   /FLOAT AC INTO FAC
            /
0155  1200  CLEARP, CLEAR   /CLEAR LST SQ.
0156  1216  SUMSP,  SUMS
0157  1247  CONSP,  CONS
0160  0253  KEYP,   KEY
0161  0344  DTSTP,  DTST
0162  1516  LINP,   LINEL
0163  0324  RDRP,   RDR
0164  2123  STP,    STD
0165  2144  CNVRTP, CNVRT
0166  2163  NUMTSP, NUMTST
0167  1741  HLTP,   HALT    /OPERATION STOP TEST
0170  0352  WLOGP,  WLOG    /COMPUTE WEIGHT,RETURN LOG
            /
            /
            / PROGRAM CONTROL AND INITIALIZATION
            /
                    *200
0200  7300          CLA CLL         /INITIALIZE
0201  6046          TLS
0202  6026          PLS
0203  4532          JMS I CLF
0204  4536          JMS I MES       /GET TIME RATE
0205  2240          TEXT "R
0206  0000  "
0207  4405          JMS I 5
0210  4407          JMS I 7
0211  6120          FPUT R
0212  0000          FEXT
0213  7300  LISTEN, CLA CLL
0214  3016          DCA SWITCH      /INSURE TTY OUTPUT
0215  4253          JMS KEY                 /GET COMMAND
0216  4541          JMS I BRP       /SEARCH EXECUTION LIST
0217  1136          TABLE
0220  5700          JMP I D+00      /CTRL V
0221  5701          JMP I D+01      /CTRL S
0222  5702          JMP I D+02      /CTRL B
0223  5703          JMP I D+03      /CTRL A
0224  5251          JMP N2         /CTRL N
0225  5704          JMP I D+04      /CTRL D
0226  5705          JMP I D+05      /CTRL L
0227  5706          JMP I D+06      /CTRL F
0230  5707          JMP I D+07      /ALT. MODE
0231  5710          JMP I D+10      /CTRL P
0232  5265          JMP C1+2        /X
0233  5263          JMP C1         /C
0234  5711          JMP I D+11      /CTRL E
0235  5712          JMP I D+12      /CTRL Q
0236  5713          JMP I D+13      /CTRL R
0237  5714          JMP I D+14      /CTRL T
0240  5715          JMP I D+15      /CTRL K  FOR EXPANSION
0241  5716          JMP I D+16      /CTRL W
0242  5717          JMP I D+17      /CTRL U
            /
0243  7300  WHAT,   CLA CLL         /ECHO ?
0244  1250          TAD WHAT+5
0245  4531          JMS I OUT
0246  4532          JMS I CLF
```

```
0247  5213          JMP LISTEN
0250  0277          0277
            /
0251  4552  N2,     JMS I NEWCP    /GET NEW FIRST AND LAST
0252  5213          JMP LISTEN
            /
0253  0000  KEY,    0      /LISTEN TO KEYBOARD
0254  7300          CLA CLL
0255  6031          KSF    /WAIT
0256  5255          JMP .-1
0257  6036          KRB
0260  4531          JMS I OUT      /ECHO
0261  1022          TAD TEMP
0262  5653          JMP I KEY
            /
0263  7240  C1,     CLA CMA        /CONTRACT
0264  7410          SKP
0265  7201          CLA IAC        /EXPAND
0266  1671          TAD I .+3
0267  3671          DCA I .+2
0270  5213          JMP LISTEN
0271  2275          VSW
            /
            /  DISPATCH TABLE
            /
                    *300
0300  0320  D,      LINE   /FIT TO LOG
0301  1347          STRIP  /STRIP LOG FROM DATA
0302  1052          BASL   /COMPUTE BASELINE
0303  1105          BSUB   /SUBTRACT BASELINE
0304  2235          DATDIS /DISPLAY DATA
0305  2222          THDIS  /DISPLAY TH. LOG
0306  2207          LOGDIS /DISPLAY LOG OF DATA
0307  2000          SWAP   /SWAP FIELD 0 ONTO DISK
0310  1600          PNCH   /PUNCH OUT DATA
0311  1551          EXAM   /LOOK AT DATA(FIRST)
0312  2042          RESTOR /RESTORE FIELD 0
0313  1650          INPT   /CTRL R  READ DATA
0314  0336          TTL    /CTRL T  GET HEADER(TITLE) INFO
0315  0243          WHAT   /CTRL K  FOR FUTURE EXPANSION
0316  0243          WHAT   /CTRL W
0317  0243          WHAT   /USER PROG.   NOT YET DEFINED
            /
0320  4561  LINE,   JMS I DTSTP    /TEST FOR DATA
0321  4562          JMS I LINP     /FIT THE LINE
0322  4550          JMS I LSP      /PRINT CONSTANTS
0323  5540          JMP I LISTNP
            /
            / ROUTINE TO READ PREVIOUSLY PUNCHED DATA
            / USES HIGH SPEED READER
            / LOC. 15=CHAR  TEMPORARY CHARACTER BUFFER
            /
0324  0000  RDR,    0
0325  7300          CLA CLL
0326  6014          RFC
0327  6011          RSF
0330  5327          JMP .-1
0331  6012          RRB
0332  3015          DCA 15
0333  1015          TAD 15
```

```
0334  5724          JMP I RDR
               /
               /  CTRL T
               / ACCEPT AND ECHO ALL INCOMING INFORMATION
               / THIS IS FOR TITLING PURPOSES
               / ALL INFORMATION TYPED IS IGNORED , BUT IS TYPED
               / UNTIL A CTRL L IS RECEIVED.
               / THIS PERMITS DOCUMENTATION OF THE PROGRESS
               / OF EXPERIMENT ANALYSIS.
               /
0335  7564          -214    /CTRL L
0336  4560   TTL,   JMS I KEYP      /GET INFO
0337  1335          TAD TTL-1       /CHECK FOR STOP SIGNAL
0340  7640          SZA CLA
0341  5336          JMP TTL                 /NO
0342  4532          JMS I CLF       /YES
0343  5540          JMP I LISTNP
               /
               / SUBROUTINE TO CHECK IF DATA IS PRESENT
               / DISC=0 IF DATA NOT PRESENT
               /     =1 IF DATA PRESENT
               / RETURN IF DATA PRESENT;  ? IF NOT
               /
0344  0000   DTST,  0       /CHECK FOR DATA
0345  7300          CLA CLL
0346  1026          TAD DISC
0347  7650          SNA CLA
0350  5537          JMP I WHATP
0351  5744          JMP I DTST
               /
               / SUBROUTINE TO GET POINT; COMPUTE LEAST SQUARES WEIGHT
               / AND RETURN WITH LOG IN FAC
               / WEIGHT Y↑2 IS STORED IN SIGA TEMPORARILY
               /
0352  0000   WLOG,  0
0353  4545          JMS I DACP      /GET A POINT
0354  4407          JMS I 7
0355  6022          FPUT TEMP
0356  0001          SQUARE         /COMPUTE WEIGHT  Y↑2
0357  6107          FPUT SIGA       /SIGA IS WEIGHT DURING SUM COMP.
0360  5022          FGET TEMP
0361  0007          LOG
0362  0000          FEXT
0363  5752          JMP I WLOG
               /
               / OUTPUT SECTION
                    *400
0400  0000   OUTPUT, 0      /SWITCH=0       TYPE
0401  3022          DCA TEMP        / .NE.0         PUNCH
0402  1016          TAD SWITCH
0403  7640          SZA CLA
0404  5212          JMP PUNCH
0405  1022          TAD TEMP
0406  6041          TSF
0407  5206          JMP .-1
0410  6046          TLS
0411  5216          JMP PUNCH+4
0412  1022   PUNCH, TAD TEMP
0413  6021          PSF
0414  5213          JMP .-1
```

```
0415  6026           PLS
0416  7200           CLA
0417  5600           JMP I OUTPUT
               /
0420  0000   CRLF,   0
0421  1226           TAD K215
0422  4200           JMS OUTPUT
0423  1227           TAD K212
0424  4200           JMS OUTPUT
0425  5620           JMP I CRLF
0426  0215   K215,   215
0427  0212   K212,   212
               /
               / RADIX DEFLATION TO GET DIGIT
               / # IN ARITH4; DEFLATION NO. IN AC
               / DIGIT RETURNED IN AC
               /
0430  0000   GDIGIT, 0
0431  3023           DCA ARITH1
0432  3022           DCA TEMP        /HOLDS FINAL DIGIT
0433  1025           TAD ARITH4
0434  3025   GLOOP,  DCA ARITH4
0435  1025           TAD ARITH4
0436  1023           TAD ARITH1      /SUBTRACT DEFLATION
0437  2022           ISZ TEMP        /COUNT SUBTRACTIONS
0440  7500           SMA
0441  5234           JMP GLOOP
0442  7200           CLA
0443  1247           TAD K257        /DIGIT IS TEMP-1
0444  1022           TAD TEMP
0445  4531           JMS I OUT
0446  5630           JMP I GDIGIT
0447  0257   K257,   257
               /
0450  0000   NOUT,   0       /CHECK SIGN
0451  3025           DCA ARITH4      /FOR CONVERSION
0452  1025           TAD ARITH4
0453  7710           SPA CLA                /POS?
0454  1276           TAD K15         /NO
0455  1033           TAD K240        /PRINT MINUS OR BLANK
0456  4531           JMS I OUT
0457  1025           TAD ARITH4
0460  7510           SPA
0461  7041           CIA     /MAKE POS.
0462  3025           DCA ARITH4      /SAVE NO. FOR CONVERSION
0463  1037           TAD KMD1K
0464  4230           JMS GDIGIT
0465  1277           TAD KMD100
0466  4230           JMS GDIGIT
0467  1034           TAD KM12
0470  4230           JMS GDIGIT
0471  7240           CLA CMA         /-1
0472  4230           JMS GDIGIT
0473  1033           TAD K240        /SPACE AFTER NO.
0474  4531           JMS I OUT
0475  5650           JMP I NOUT
               /
               /
0476  0015   K15,    015
0477  7634   KMD100, -144
```

```
                /
                / MODIFIED VERSION OF
                /DIGITAL 8-18-U
                /MESSAGE TYPE-OUT
                /CALL WITH A JMS MESAGE
                /WITH DATA FOLLOWING
                /RETURN FOLLOWING END OF MESSAGE
                /CODE(00)
                / USES NOUT FOR TEMPORARY STORAGE
                / CANNOT BE PRINTING NO. AT SAME TIME
                /PRINTING MESSAGE
                /
0500   0000   MESAGE,   0
0501   7240             CLA CMA             /SET C(AC)=-1
0502   1300             TAD MESAGE          /ADD LOCATION
0503   3010             DCA 10              /AUTO-INDEX REGISTER
0504   1410             TAD I 10            /FETCH FIRST WORD
0505   3250             DCA NOUT          /SAVE IT
0506   1250             TAD NOUT
0507   7012             RTR
0510   7012             RTR                 /ROTATE 6 BITS RIGHT
0511   7012             RTR
0512   4316             JMS TYPECH          /TYPE IT
0513   1250             TAD NOUT          /GET DATA AGAIN
0514   4316             JMS TYPECH          /TYPE RIGHT HALF
0515   5304             JMP MESAGE+4        /CONTINUE
0516   0000   TYPECH,   0                   /TYPE CHARACTER IN C(AC)6-11
0517   0344             AND MASK77
0520   7450             SNA                 /IS IT END OF MESSAGE?
0521   5410             JMP I 10            /YES: EXIT
0522   1345             TAD M40             /SUBTRACT 40
0523   7500             SMA                 /<40?
0524   5327             JMP .+3             /NO
0525   1346             TAD C340            /YES: ADD 300
0526   5342             JMP MTP             /TO CODES <40
0527   1347             TAD M3              /SUBTRACT 3
0530   7440             SZA                 /IS IT ZERO?
0531   5334             JMP .+3             /NO
0532   1227             TAD K212            /YES: CODE 43 IS
0533   5342             JMP MTP             /LINE-FEED (212)
0534   1350             TAD M2              /SUBTRACT 2
0535   7440             SZA                 /IS IT ZERO?
0536   5341             JMP .+3             /NO
0537   1226             TAD K215            /YES: CODE 45 IS
0540   5342             JMP MTP             /CARRIAGE-RETURN (215)
0541   1351             TAD C245            /ADD 200 TO OTHERS >40
0542   4200   MTP,    JMS OUTPUT      /TYPE MESSAGE
0543   5716           JMP I TYPECH
              /CONSTANTS
0544   0077   MASK77,   77
0545   7740   M40,      -40
0546   0340   C340,     340
0547   7775   M3,       -3
0550   7776   M2,       -2
0551   0245   C245,     245
              /
              / GET FIELD 0 DATA INTO FAC
              /
0552   0000   DAC,    0
0553   7200           CLA
```

```
0554  6201          CDF 0
0555  1412          TAD I 12        /12 IS PRESET POINTER
0556  3044          DCA 44
0557  1412          TAD I 12
0560  3045          DCA 45
0561  1412          TAD I 12
0562  3046          DCA 46
0563  6211          CDF 10
0564  5752          JMP I DAC       /# IS IN FAC
                /
                / PUT FAC INTO FIELD 0 DATA BLOCK
                /
0565  0000      FACD,   0
0566  7200          CLA
0567  6201          CDF 0
0570  1044          TAD 44
0571  3414          DCA I 14        /14 IS PRESET POINTER
0572  1045          TAD 45
0573  3414          DCA I 14
0574  1046          TAD 46
0575  3414          DCA I 14
0576  6211          CDF 10
0577  5765          JMP I FACD
                /
                /
                / PAGE 3
                /
                        *600
                / SUBSECTION TO GET A DOUBLE PREC. DATA PT.
                / ASSUMES POINT1 PRESET TO ARRAY
                / LEAVES POINT1 SET TO NEXT POINT
                /
0600  0000      GETP,   0
0601  7200          CLA
0602  6201          CDF 0  /POINTS IN FIELD 0
0603  1411          TAD I POINT1    /REVERSE LO AND HIGH ORDER
0604  3021          DCA SHFR+1
0605  1411          TAD I POINT1
0606  3020          DCA SHFR
0607  6211          CDF 10
0610  7344          CLA CLL CMA RAL         /MINUS TWO
0611  1013          TAD POINT4      /GET SCALE FACTOR
0612  7041          CMA IAC                 /SET FOR RIGHT SHIFT
0613  4534          JMS I SHIFT     /SCALE POINT
0614  1021          TAD SHFR+1      /RETURN WITH POINT
0615  5600          JMP I GETP      /IN AC
                /
                /SHIFTING SUBROUTINE    SEE DEC LISTINGS
                / OF BASIC AVERAGER
                /DOUB. PREC. SHIFT OF HIGH AND LOW
                /CALL   TAD KXXX        NEG. FOR RIGHT SHIFT
                /       SHFT
                /       RETURN
                / SHFR, SHFR+1 FOR SHIFT WORDS
                /
0616  0000      SHFTS,  0
0617  7100          CLL
0620  7450          SNA    /DONE IF COUNT=0
0621  5616          JMP I SHFTS
0622  7500          SMA     /RIGHT OR LEFT
```

```
0623  7061           CML CMA IAC    /LEFT
0624  3255           DCA SHCNT
0625  7430           SZL    /RIGHT?
0626  5243           JMP SHLEFT     /NO
0627  1020  SHRIT,   TAD SHFR
0630  7510           SPA    /SET L=1 IF NEG
0631  7020           CML
0632  7010           RAR
0633  3020           DCA SHFR
0634  1021           TAD SHFR+1
0635  7010           RAR
0636  3021           DCA SHFR+1
0637  7100           CLL
0640  2255           ISZ SHCNT
0641  5227           JMP SHRIT
0642  5616           JMP I SHFTS
0643  1021  SHLEFT,  TAD SHFR+1
0644  7104           CLL RAL
0645  3021           DCA SHFR+1
0646  1020           TAD SHFR
0647  7004           RAL
0650  3020           DCA SHFR
0651  7100           CLL
0652  2255           ISZ SHCNT
0653  5243           JMP SHLEFT
0654  5616           JMP I SHFTS
0655  0000  SHCNT,   0      /TEMP TO HOLD SHIFT COUNT
            /
            /
            / FLOAT THE # IN THE AC INTO FAC
            /
0656  0000  FLOAT,   0      / 0<#<2047
0657  3045           DCA 45
0660  3046           DCA 46
0661  1267           TAD C13
0662  3044           DCA 44
0663  4407           JMS I 7
0664  7000           FNOR
0665  0000           FEXT
0666  5656           JMP I FLOAT
0667  0013  C13,     0013
            /
            /
            / FIX NO. IN FAC
0670  0000  IFIX,    0
0671  7200           CLA
0672  1044           TAD 44 /GET EXP
0673  7540           SZA SMA        /CHECK FOR <1
0674  5277           JMP .+3
0675  7200           CLA    /YES: MAKE ZERO
0676  5316           JMP IFIX2+1
0677  1317           TAD M13        /NO
0700  7450           SNA
0701  5670           JMP I IFIX
0702  7500           SMA    /CHECK IF TOO LARGE
0703  5670           JMP I IFIX     /YES: IGNORE IT
0704  3044           DCA 44
0705  7100  IFIX1,   CLL
0706  1045           TAD 45 /GET MANTISSA
0707  7510           SPA    /CHECK FOR <0
```

```
0710  7020          CML     /YES
0711  7010          RAR
0712  3045          DCA 45
0713  2044          ISZ 44
0714  5305          JMP IFIX1
0715  1045  IFIX2,  TAD 45 /ANSWER IN AC
0716  5670          JMP I IFIX
0717  7765  M13,    -13     /-11
            /
            / SUBROUTINE TO GET NEW VALUES FOR
            /  FIRST AND LAST
            /
0720  0000  NEWC,   0
0721  7300          CLA CLL
0722  4532          JMS I CLF       /SPACE
0723  4536          JMS I MES       /ASK FOR FIRST
0724  0611          TEXT "FI
0725  2223  RS
0726  2440  T
0727  4000   "
0730  1027          TAD FIRST
0731  4533          JMS I NSIN      /PRINT OLD FIRST
0732  4405          JMS I 5         /GET NEW FIRST
0733  1057          TAD 57 /CHECK TERMINATOR FOR PANIC STOP
0734  4567          JMS I HLTP
0735  4551          JMS I IFIXP
0736  3027          DCA FIRST
0737  4536          JMS I MES       /ASK FOR LAST
0740  1401          TEXT "LA
0741  2324  ST
0742  4040
0743  4000   "
0744  1030          TAD LAST
0745  4533          JMS I NSIN
0746  4405          JMS I 5         /GET NEW LAST
0747  1057          TAD 57 /CHECK TERMINATOR FOR PANIC STOP
0750  4567          JMS I HLTP
0751  4551          JMS I IFIXP
0752  3030          DCA LAST
0753  5720          JMP I NEWC
            /
            / SUBROUTINE TO BRANCH ON MATCH OF AC WITH TABLE
            / CALL      BRAN
            /           TABLE
            /           ...     JMP ENTRY
            /       TABLE ENDS WITH NEG ENTRY
            /
0754  0000  BRAN,   0
0755  3023          DCA ARITH1      /SAVE CODE
0756  1754          TAD I BRAN      /GET FIRST TABLE ENTRY
0757  3024          DCA ARITH2      /SAVE TABLE ADDRESS
0760  1424  BRLOOP, TAD I ARITH2    /GET ENTRY
0761  7500          SMA     /CHECK FOR NEG.
0762  7041          CMA IAC
0763  2354          ISZ BRAN        /INDEX RETURN ADDRESS
0764  1023          TAD ARITH1      /CHECK FOR MATCH
0765  7650          SNA CLA
0766  5754          JMP I BRAN      /YES
0767  1424          TAD I ARITH2    /NO-TEST FOR END
0770  2024          ISZ ARITH2      /INDEX ENTRY POINTER
```

```
0771  7700          SMA CLA
0772  5360          JMP BRLOOP     /NOT LAST-CONTINUE
0773  2354          ISZ BRAN       /FELL THROUGH TABLE
0774  5754          JMP I BRAN     /RETURN TO DEFAULT
            /
            /
            PAUSE
            /
            / PAGE 4
                    *1000
            /
            / ROUTINE TO CHECK FOR END OF PROCESSING
            / A SECTION FROM FIRST TO LAST
            /
1000  0000  ENDTST, 0
1001  7200          CLA
1002  4407          JMS I 7        /ALSO INCREMENT X FOR NEXT POSITION
1003  5123          FGET X
1004  1120          FADD R
1005  6123          FPUT X
1006  0000          FEXT
1007  2036          ISZ COUNT      /RETURN TO CALL+2  IF DONE
1010  5600          JMP I ENDTST   /          CALL+1  TO CONTINUE
1011  2200          ISZ ENDTST
1012  5600          JMP I ENDTST
            /
            / ROUTINE TO INITIALIZE PROCESSING OF SECTION
            / SET N, COUNT, FIRST X, POINTER 12, 14 TO DATA
            / N=LAST-FIRST+1
            /
1013  0000  INIT,   0
1014  7300          CLA CLL
1015  1027          TAD FIRST      /COMPUTE -N FOR COUNT
1016  7041          CIA
1017  1030          TAD LAST
1020  7001          IAC
1021  3022          DCA TEMP
1022  1022          TAD TEMP
1023  7041          CIA
1024  3036          DCA COUNT      /SET COUNTER
1025  1022          TAD TEMP
1026  4554          JMS I FLOATP
1027  4407          JMS I 7
1030  6104          FPUT N        /SET UP N
1031  0000          FEXT
1032  7300          CLA CLL
1033  1027          TAD FIRST      /SET FIRST X
1034  4554          JMS I FLOATP
1035  4407          JMS I 7
1036  3120          FMPY R
1037  6123          FPUT X
1040  0000          FEXT
1041  7300          CLA CLL
1042  1027          TAD FIRST      /SET UP POINTERS
1043  7004          RAL           /REQUIRE 3 LOC. PER POINT
1044  1027          TAD FIRST
1045  1142          TAD SPEC       /LOC-1 OF DATA
1046  3012          DCA 12        /12= DATA TO FAC POINTER
1047  1012          TAD 12
1050  3014          DCA 14        /14=FAC TO DATA POINTER
```

```
1051  5613          JMP I INIT
               /
               / SUBROUTINE TO COMPUTE BASELINE BETWEEN
               / FIRST AND LAST
               /
1052  4543   BASL,  JMS I INITP    /INITIALIZE
1053  3115          DCA BASE       /CLEAR BASE
1054  3116          DCA BASE+1
1055  3117          DCA BASE+2
1056  4545   B1,    JMS I DACP     /GET A POINT
1057  4407          JMS I 7
1060  1115          FADD BASE
1061  6115          FPUT BASE
1062  0000          FEXT
1063  4544          JMS I ENDT     /CHECK FOR DONE
1064  5256          JMP B1
1065  4407          JMS I 7
1066  5115          FGET BASE
1067  4104          FDIV N /COMPUTE AVERAGE
1070  6115          FPUT BASE
1071  0000          FEXT
1072  4532          JMS I CLF
1073  4536          JMS I MES      /PRINT BASELINE
1074  0201          TEXT "BA
1075  2305   SE
1076  1411   LI
1077  1605   NE
1100  4075    =
1101  4040
1102  0000   "
1103  4406          JMS I 6
1104  5540          JMP I LISTNP
               /
               / SUBSECTION TO SUBTRACT BASELINE BETWEEN
               / FIRST AND LAST
               /
1105  4561   BSUB,  JMS I DTSTP    /MAKE SURE DATA PRESENT
1106  4552          JMS I NEWCP    /GET FIRST AND LAST
1107  4543          JMS I INITP    /INITIALIZE
1110  4545          JMS I DACP     /GET POINT
1111  4407          JMS I 7
1112  2115          FSUB BASE
1113  0000          FEXT
1114  4553          JMS I STORE    /STORE CORRECTED POINT
1115  4544          JMS I ENDT
1116  5310          JMP .-6
1117  4536          JMS I MES
1120  5502          TEXT "-B
1121  0123   AS
1122  0545   E%
1123  4300   #"
1124  5540          JMP I LISTNP
               /
               / SUBSECTION TO COMPUTE THEORETICAL Y=A+B*X
               / X IS ALREADY SET
               /
1125  0000   TH,    0
1126  7300          CLA CLL
1127  4407          JMS I 7
1130  5076          FGET B
```

```
1131  3123            FMPY X
1132  1073            FADD A
1133  6126            FPUT Y
1134  0000            FEXT
1135  5725            JMP I TH
            /
            / TABLE OF COMMAND CODES FOR BRAN ROUTINE
            / DISPATCH JUMPS IN PAGE 1
            /
1136  0226  TABLE,   226    /CTRL V  FIT LOG
1137  0223           223    /CTRL S  STRIP LOG
1140  0202           202    /CTRL B  COMPUTE BASELINE
1141  0201           201    /CTRL A  STRIP BASELINE
1142  0216           216    /CTRL N  GET NEW FIRST AND LAST
1143  0204           204    /CTRL D  DISPLAY DATA
1144  0214           214    /CTRL L  DISPLAY TH. LOG
1145  0206           206    /CTRL F  DISPLAY LOG DATA
1146  0375           375    /ALT. MODE  SWAP CORE
1147  0220           220    /CTRL P  PUNCH DATA
1150  0330           330    /X     EXPAND DISPLAY
1151  0303           303    /C     CONTRACT DISPLAY
1152  0205           205    /CTRL E  EXAMINE DATA(FIRST)
1153  0221           221    /CTRL Q  QUIT  RETURN TO AVERAGER
1154  0222           222    /CTRL R  READ DATA
1155  0224           224    /CTRL T  TITLE INFO
1156  0213           213    /CTRL K  EXPANSION COMMANDS
1157  0227           227    /CTRL W
1160  7553           -225   /CTRL U  USER ROUTINE
            /
            / TABLE FOR CONTROL OF CTRL E OPERATIONS
            /
1161  0240  CTAB,    240    /SPACE  CHANGE
1162  0212           212    /LF  OPEN NEXT
1163  7563           -215   /CR  CLOSE AND EXIT
            /
            / TABLE FOR CONTROL OF TAPE READING OPERATIONS
            / IDENTIFIES INPUT CHARACTERS FOR PROCESSING
            /
1164  0000  NTAB,    0      /BLANK TAPE
1165  0255           255    /-
1166  0253           253    /+
1167  7540           -240   /SPACE
            /
            EXP=6
            LOG=7
            SQROOT=2
            SQUARE=0001
            /
            / SUBROUTINES FOR PROCESSING LEAST SQUARES
            /
                     *1200
1200  0000  CLEAR,   0      /CLEAR SUMS
1201  7300           CLA CLL
1202  3044           DCA 44 /CLEAR FLOAT AC
1203  3045           DCA 45
1204  3046           DCA 46
1205  4407           JMS I 7
1206  6101           FPUT SIGMA
1207  6302           FPUT SUMX2
1210  6310           FPUT SUMXY
```

```
1211  6305          FPUT SUMX
1212  6313          FPUT SUMY
1213  6316          FPUT SUMY2
1214  0000          FEXT
1215  5600          JMP I CLEAR
1216  0000  SUMS,   0       /COMPUTE SUMS
1217  4407          JMS I 7
1220  5123          FGET X / SUMX=SUMX+X
1221  3107          FMPY SIGA       /SUMX=SUM  W*X
1222  1305          FADD SUMX
1223  6305          FPUT SUMX
1224  5123          FGET X / SUMX2=SUMX2+X*X
1225  0001          SQUARE
1226  3107          FMPY SIGA       /SUMX2=SUM  W*X↑2
1227  1302          FADD SUMX2
1230  6302          FPUT SUMX2
1231  5123          FGET X / SUMXY=SUMXY+X*Y
1232  3126          FMPY Y
1233  3107          FMPY SIGA       /SUMXY=SUM W*X*Y
1234  1310          FADD SUMXY
1235  6310          FPUT SUMXY
1236  5126          FGET Y / SUMY=SUMY+Y
1237  3107          FMPY SIGA       /SUMY= SUM W*Y
1240  1313          FADD SUMY
1241  6313          FPUT SUMY
1242  5107          FGET SIGA       /SUMY2=SUM W=SUM SIGA=SUMY2+Y*Y
1243  1316          FADD SUMY2
1244  6316          FPUT SUMY2
1245  0000          FEXT
1246  5616          JMP I SUMS
1247  0000  CONS,   0       /COMPUTE LST SQUARES CONSTANTS
1250  4407          JMS I 7
1251  5305          FGET SUMX       / DELTA=N*SUMX2-SUMX**2
1252  0001          SQUARE
1253  6321          FPUT DELTA
1254  5302          FGET SUMX2
1255  3316          FMPY SUMY2      /SUMY2←N WITH WEIGHT
1256  2321          FSUB DELTA
1257  6321          FPUT DELTA
1260  5310          FGET SUMXY      / A=(SUMX2*SUMY-SUMX*SUMXY)/DELTA
1261  3305          FMPY SUMX
1262  6073          FPUT A
1263  5313          FGET SUMY
1264  3302          FMPY SUMX2
1265  2073          FSUB A
1266  4321          FDIV DELTA
1267  6073          FPUT A
1270  5313          FGET SUMY       / B=(N*SUMXY-SUMX*SUMY)/DELTA
1271  3305          FMPY SUMX
1272  6076          FPUT B
1273  5310          FGET SUMXY
1274  3316          FMPY SUMY2
1275  2076          FSUB B
1276  4321          FDIV DELTA
1277  6076          FPUT B
1300  0000          FEXT   / FINALLY DONE
1301  5647          JMP I CONS
1302  0000  SUMX2,  FLTG 0.0
1303  0000
1304  0000
```

```
1305  0000  SUMX,   FLTG 0.0
1306  0000
1307  0000
1310  0000  SUMXY,  FLTG 0.0
1311  0000
1312  0000
1313  0000  SUMY,   FLTG 0.0
1314  0000
1315  0000
1316  0000  SUMY2,  FLTG 0.0
1317  0000
1320  0000
1321  0000  DELTA,  FLTG 0.0
1322  0000
1323  0000
            /
            / COMPUTE STANDARD DEVIATIONS
            / SIGA,SIGB,SIGMA ACTUALLY ARE VARIANCES
            / SIGA USED TEMPORARILY TO HOLD WEIGHTS
            / DURING FORMATION OF LEAST SQUARES SUMS
            /
1324  0000  DEV,    0
1325  7300          CLA CLL
1326  4407          JMS I 7
1327  5104          FGET N
1330  2065          FSUB TWO
1331  6022          FPUT TEMP
1332  5101          FGET SIGMA
1333  4022          FDIV TEMP
1334  6101          FPUT SIGMA
1335  5101          FGET SIGMA
1336  4321          FDIV DELTA
1337  6022          FPUT TEMP      /TEMP=SIGMA/DELTA
1340  3302          FMPY SUMX2
1341  6107          FPUT SIGA      /SIGA=TEMP*SUMX2
1342  5022          FGET TEMP
1343  3104          FMPY N
1344  6112          FPUT SIGB      /SIGB=TEMP*N
1345  0000          FEXT
1346  5724          JMP I DEV
            /
            / SUBROUTINE TO STRIP EXPONENTIAL FROM DATA
            / CTRL S
            /
1347  4561  STRIP,  JMS I DTSTP
1350  4552          JMS I NEWCP    /GET FIRST AND LAST
1351  4543          JMS I INITP    /INITIALIZE
1352  4546          JMS I THP      /COMPUTE Y=A+B*X
1353  4407          JMS I 7
1354  5126          FGET Y
1355  0006          EXP
1356  6126          FPUT Y
1357  0000          FEXT
1360  4545          JMS I DACP     /GET A POINT
1361  4407          JMS I 7
1362  2126          FSUB Y
1363  0000          FEXT
1364  4553          JMS I STORE    /STORE CORRECTED POINT
1365  4544          JMS I ENDT     /TEST FOR END
1366  5355          JMP STRIP+6    /KEEP GOING
```

```
1367  4536             JMS I MES
1370  0530             TEXT "EX
1371  2040  P
1372  2325  SU
1373  0224  BT
1374  2245  R%
1375  4300  #"
1376  5540             JMP I LISTNP
            /
                   OCTAL
                       *1400
            /   PAGE 5
            /
1400  0000             0       /ENTRY TO PRINT "DEV."
1401  4536             JMS I MES
1402  4040             TEXT "
1403  0405  DE
1404  2656  V.
1405  4000   "
1406  5600             JMP I 1400
            /
1407  0000  LSQOUT,    0       /PRINT LST. SQUARES PARAMETERS
1410  7200             CLA
1411  4532             JMS I CLF
1412  3055             DCA 55 /REMOVE CRLF
1413  4536             JMS I MES
1414  0175             TEXT "A=
1415  4000   "
1416  4407             JMS I 7
1417  5073             FGET A
1420  0000             FEXT
1421  4406             JMS I 6
1422  4200             JMS 1400
1423  4407             JMS I 7
1424  5107             FGET SIGA
1425  0002             SQROOT
1426  0000             FEXT
1427  4406             JMS I 6
1430  4532             JMS I CLF
1431  4536             JMS I MES
1432  0275             TEXT "B=
1433  4000   "
1434  4407             JMS I 7
1435  5076             FGET B
1436  0000             FEXT
1437  4406             JMS I 6
1440  4200             JMS 1400
1441  4407             JMS I 7
1442  5112             FGET SIGB
1443  0002             SQROOT
1444  0000             FEXT
1445  4406             JMS I 6
1446  4532             JMS I CLF
1447  4536             JMS I MES
1450  2417             TEXT "TO
1451  2401  TA
1452  1440  L
1453  2601  VA
1454  2211  RI
1455  0116  AN
```

```
1456  Ø3Ø5  CE
1457  4Ø75   =
146Ø  4ØØØ   "
1461  44Ø7          JMS I 7
1462  51Ø1          FGET SIGMA
1463  ØØØØ          FEXT
1464  44Ø6          JMS I 6
1465  4532          JMS I CLF
1466  4532          JMS I CLF
1467  4536          JMS I MES
147Ø  2461          TEXT "T1
1471  4Ø75   =
1472  4ØØØ   "
1473  44Ø7          JMS I 7
1474  5Ø62          FGET ONE
1475  4Ø76          FDIV B
1476  ØØØØ          FEXT
1477  44Ø6          JMS I 6
15ØØ  724Ø          CLA CMA
15Ø1  3Ø55          DCA 55 /RESTORE CRLF
15Ø2  42ØØ          JMS 14ØØ
15Ø3  44Ø7          JMS I 7        /GET DEV. FOR T1
15Ø4  5Ø76          FGET B
15Ø5  ØØØ1          SQUARE
15Ø6  6Ø22          FPUT TEMP
15Ø7  5112          FGET SIGB
151Ø  ØØØ2          SQROOT /SIG(T1)=SIGB/B↑2
1511  4Ø22          FDIV TEMP
1512  ØØØØ          FEXT
1513  44Ø6          JMS I 6
1514  4532          JMS I CLF
1515  56Ø7          JMP I LSQOUT
            /
            /
            / LEAST SQUARES SUBROUTINE
            / ORGANIZES FIT
            / DOES FIT TO LOGARITHM
            /
1516  ØØØØ  LINEL,  Ø       /ENTRY FOR LOG LST. SQUARES
1517  4543          JMS I INITP    /INITIALIZE POINTERS
152Ø  4555          JMS I CLEARP   /CLEAR SUMS
1521  457Ø          JMS I WLOGP    /GET LOG AND WEIGHT
1522  44Ø7          JMS I 7
1523  6126          FPUT Y
1524  ØØØØ          FEXT
1525  4556          JMS I SUMSP    /COMPUTE LST. SQ. SUMS
1526  4544          JMS I ENDT     /MOVE AND CHECK FOR DONE
1527  5321          JMP LINEL+3    /CONTINUE
153Ø  4557          JMS I CONSP    /COMPUTE CONSTANTS
1531  4543          JMS I INITP    /RESTART TO GET SIGMA
1532  4546  LST,    JMS I THP      /COMPUTE THEORY
1533  457Ø          JMS I WLOGP    /GET LOG AND WEIGHT
1534  44Ø7          JMS I 7
1535  2126          FSUB Y
1536  ØØØ1          SQUARE
1537  31Ø7          FMPY SIGA      /MULTIPLY BY WEIGHT
154Ø  11Ø1          FADD SIGMA
1541  61Ø1          FPUT SIGMA
1542  ØØØØ          FEXT
1543  4544          JMS I ENDT
```

```
1544  5332          JMP LST
1545  4547          JMS I DEVP      /COMPUTE DEVIATIONS
1546  5716          JMP I LINEL
            /
            / SUBSECTION TO HANDLE CTRL E   EXAMINE LOCATION
            / PRINTS FIRST AND DATA(FIRST)
            / RESPONDING WITH SPACE GIVES OPTION OF CHANGING
            / THE DATA POINT;CR TO CLOSE;LINE FEED TO
            / OPEN NEXT POINT
            /
1547  2027  LFN,    ISZ FIRST       /MOVE TO NEXT POINT
1550  4532          JMS I CLF
1551  7300  EXAM,   CLA CLL
1552  1027          TAD FIRST
1553  4533          JMS I NSIN      /PRINT FIRST
1554  4543          JMS I INITP     /SET POINTER
1555  4545          JMS I DACP      /GET NO.
1556  3055          DCA 55 /CLEAR CRLF
1557  4406          JMS I 6         /PRINT NO.
1560  7240          CLA CMA
1561  3055          DCA 55 /RESTORE CRLF
1562  4560          JMS I KEYP      /ASK FOR COMMAND
1563  4541          JMS I BRP       /IDENTIFY COMMAND
1564  1161          CTAB
1565  5371          JMP K  /CHANGE DATA
1566  5347          JMP LFN         /OPEN NEXT
1567  4532          JMS I CLF
1570  5540          JMP I LISTNP    /FELL THROUGH TABLE
1571  4561  K,      JMS I DTSTP     /CHECK FOR DATA PRESENT
1572  4543          JMS I INITP
1573  4405          JMS I 5         /INPUT NO.
1574  4553          JMS I STORE     /STORE IT
1575  1057          TAD 57 /GET TERMINATOR
1576  5363          JMP K-6         /IDENTIFY COMMAND
            /
                    *1600
            / PAGE 6
            /SUBSECTION TO PUNCH DATA
            /
1600  7300  PNCH,   CLA CLL
1601  4532          JMS I CLF
1602  1026          TAD DISC        /CHECK FOR AVERAGER
1603  7640          SZA CLA
1604  5537          JMP I WHATP     /AVERAGER NOT THERE
1605  1032          TAD BLK                 /SET POINTER TO AVER. BLOCK
1606  3011          DCA POINT1
1607  1030          TAD LAST
1610  4533          JMS I NSIN      /PRINT UPPER LIMIT
1611  1030          TAD LAST
1612  7040          CMA
1613  3036          DCA COUNT
1614  6201          CDF 0
1615  1431          TAD I SCL       /GET SCALE
1616  3013          DCA POINT4
1617  1411          TAD I POINT1
1620  6211          CDF 10
1621  4533          JMS I NSIN      /PRINT NO. OF SWEEPS
1622  4532          JMS I CLF
1623  2016          ISZ SWITCH      /SET FOR PUNCH
1624  1034  LOOP,   TAD KM12        /SET POSITION COUNTER
```

```
1625  3024          DCA ARITH2
1626  4567          JMS I HLTP     /CHECK FOR PANIC STOP
1627  2036          ISZ COUNT
1630  7410          SKP
1631  5240          JMP SCRAM      /DONE
1632  4535          JMS I GET      /GET A POINT
1633  4533          JMS I NSIN     /OUTPUT THE POINT
1634  2024          ISZ ARITH2     /CHECK POSITION
1635  5226          JMP LOOP+2     /GET MORE
1636  4532          JMS I CLF      /START A NEW LINE
1637  5224          JMP LOOP       /CONTINUE TILL DONE
1640  4532  SCRAM,  JMS I CLF
1641  3016          DCA SWITCH     /RESET FOR TTY
1642  5540          JMP I LISTNP
            /
                  *1650
            / THIS SECTION READS DATA IN ON THE HIGH SPEED READER
            / Y VALUES ONLY EXPECTED
            / DATA IS PLACED INTO THE BUFFER AREA
            / MAINTAINED BY THE BASIC AVERAGER IN FIELD 0
            / CORE MUST STILL BE SWAPPED TO GET AT THE DATA
            / CHAR=15; SIGN=ARITH4; NUM=17  TEMP USED HERE
            /
            / CTRL R
            /
1650  7300  INPT,   CLA CLL        /INITIALIZE
1651  3027          DCA FIRST
1652  3030          DCA LAST
1653  1032          TAD BLK        /GET THE BUFFER AREA
1654  7001          IAC
1655  3010          DCA POINT      /USED BY STD
1656  3017          DCA 17 /CLEAR NUMBER BUILDER
1657  3025          DCA ARITH4     /CLEAR SIGN
            /
1660  4563  START,  JMS I RDRP     /SEARCH FOR START OF TAPE
1661  4541          JMS I BRP      /IDENTIFY INPUT CHARACTER
1662  1164          NTAB
1663  5260          JMP START
1664  5270          JMP MINUS      /# IS NEG.
1665  5273          JMP PLUS       /# IS POS.
1666  5273          JMP PLUS
1667  5260          JMP START      /NOT IN TABLE
1670  7240  MINUS,  CLA CMA               /SET - SIGN
1671  3025          DCA ARITH4
1672  5275          JMP DAT
1673  7300  PLUS,   CLA CLL
1674  3025          DCA ARITH4
1675  4563  DAT,    JMS I RDRP     /PROCESS MAIN TAPE
1676  4566          JMS I NUMTSP   /TEST FOR NUMBERS
1677  5302          JMP .+3
1700  4565          JMS I CNVRTP   /PERFORM BCD TO BIN
1701  5275          JMP DAT               /GET REST OF #
1702  4564          JMS I STP      /STORE # IN BUFFER
1703  2030          ISZ LAST       /COUNT IT
1704  4563  FIN,    JMS I RDRP     /SEARCH FOR END OF TAPE
1705  4566          JMS I NUMTSP
1706  7610          SKP CLA
1707  5300          JMP DAT+3
1710  1015          TAD 15        /GET THE CHARACTER
1711  4541          JMS I BRP      /IDENTIFY
```

```
1712  1164              NTAB
1713  5320              JMP .+5                 /BLANK; FINISHED
1714  5270              JMP MINUS
1715  5273              JMP PLUS
1716  5273              JMP PLUS
1717  5304              JMP FIN                 /FELL THROUGH TABLE
1720  7300              CLA CLL
1721  4532              JMS I CLF
1722  4536              JMS I MES
1723  1401              TEXT "LA
1724  2324        ST
1725  4020         P
1726  1711        OI
1727  1624        NT
1730  4000         "
1731  7240              CLA CMA
1732  1030              TAD LAST
1733  3030              DCA LAST
1734  1030              TAD LAST
1735  4533              JMS I NSIN
1736  4532              JMS I CLF
1737  5540              JMP I LISTNP   /RETURN
                  /
                  / SUBROUTINE TO DO EMERGENCY HALT IF CTRL/H TYPED
                  / PRESENTLY CALLED FROM NEWC AND PNCH ONLY
                  / RETURNS TO CALL IF NORMAL
                  /
1740  7570              -210   /CTRL/H
1741  0000        HALT,  0
1742  7440              SZA     /USE AC FOR CHAR IF NONZERO
1743  5347              JMP .+4
1744  6031              KSF     /CHECK FOR TTY
1745  5741              JMP I HALT     /NO; RETUR
1746  6036              KRB     /YES ;GET COMMAND
1747  4541              JMS I BRP
1750  1740              HALT-1 /CHECK FOR CTRL/H
1751  5540              JMP I LISTNP   /YES; STOP
1752  7300              CLA CLL        /NO; IGNORE CHARACTER
1753  5741              JMP I HALT
                  /
                        *2000
                  /SUBSECTION TO DO THE DISK OPERATIONS
                  /ROUTINE TO SWAP AVERAGER OUT TO DISK
                  /AND CONVERT DATA TO FLOATING POINT
                  /
2000  7300        SWAP,  CLA CLL
2001  1026              TAD DISC       /CHECK IF ALREADY THERE
2002  7640              SZA CLA
2003  5537              JMP I WHATP    /ITS ALREADY THERE
2004  4261              JMS WRITE      /NO-WRITE IT OUT
2005  7201              CLA IAC
2006  3026              DCA DISC       /SET INDICATOR
                  /
                  /REARRANGE FIELD 0 DATA TO FL. PT. NO.
                  / DATA ASSUMED NEGATIVE AND IS MADE POS.
                  /
2007  1032              TAD BLK        /SET POINTERS
2010  7001              IAC
2011  3011              DCA POINT1
2012  1037              TAD KMDIK
```

```
2013  3036           DCA COUNT
2014  1142           TAD SPEC
2015  3014           DCA 14
2016  6201           CDF 0  /SET SCALE FOR GET
2017  1431           TAD I SCL
2020  3013           DCA POINT4
2021  6211           CDF 10
2022  4535  F1,      JMS I GET
2023  7041           CIA
2024  4554           JMS I FLOATP
2025  4553           JMS I STORE
2026  2036           ISZ COUNT
2027  5222           JMP F1
2030  4536           JMS I MES
2031  0317           TEXT "CO
2032  2205  RE
2033  4023   S
2034  2701  WA
2035  2020  PP
2036  0504  ED
2037  0000  "
2040  4532           JMS I CLF
2041  5540           JMP I LISTNP
            /
            / THIS SECTION RESTORES THE BASIC AVERAGER
            / AND RETURNS TO IT THROUGH A CTRL Q
            /
2042  7300  RESTOR,  CLA CLL
2043  1026           TAD DISC        /IS IT ALREADY PRESENT
2044  7650           SNA CLA
2045  5250           JMP RET
2046  4270           JMS READ        /NO-GET IT
2047  3026           DCA DISC        /CLEAR INDICATOR
2050  6032  RET,     KCC    /CLEAR FLAGS
2051  6042           TCF
2052  6022           PCF
2053  6601           6601   /=DCMA
2054  6201           CDF 0
2055  6202           CIF 0
2056  5657           JMP I .+1
2057  6506           6506   /BACIC AVER. CTRL/Q
            /
            / DISC HANDLING SUBSECTION
            /
2060  6605           6605   /DMAW=WRITE
2061  0000  WRITE,   0
2062  7300           CLA CLL
2063  1260           TAD WRITE-1     /SET WRITE INSTR
2064  3312           DCA INSTR
2065  4276           JMS DISK
2066  5661           JMP I WRITE
            /
2067  6603           6603   /=DMAR=READ
2070  0000  READ,    0
2071  7300           CLA CLL
2072  1267           TAD READ-1
2073  3312           DCA INSTR       /SET READ INSTR
2074  4276           JMS DISK
2075  5670           JMP I READ
2076  0000  DISK,    0
```

```
2077  1142           TAD SPEC       /MOVE LOC. 200-6377
2100  6201           CDF 0
2101  3720           DCA I CA
2102  6211           CDF 10
2103  1322           TAD WCV
2104  6201           CDF 0
2105  3721           DCA I WC
2106  6211           CDF 10
2107  1317           TAD TRACK      /USE LAST TWO DISK TRACKS
2110  6615           6615   /=DEAL  LOAD DISK EA AND EMA
2111  7200           CLA    /DISK ADDRESS IS 0
2112  0000  INSTR,   0      /READ OR WRITE
2113  6622           6622   /DFSC  WAIT FOR COMPLETION
2114  5313           JMP .-1
2115  6601           6601   /DCMA
2116  5676           JMP I DISK
2117  0700  TRACK,   0700
2120  7751  CA,      7751
2121  7750  WC,      7750
2122  1600  WCV,     1600
            /
            / PROCESSING SUBROUTINES FOR CTRL R COMMAND
            /
            / SUBROUTINE TO STORE THE SINGLE PREC. NO. READ
            / AS A DOUBLE PREC. NO. IN THE BUFFER AREA
            / IN FIELD 0
            / USES POINT AS A POINTER; SHOULD BE SET BEFORE CALL
            / IS SET TO NEXT POINT AFTER CALL
            /
2123  0000  STD,     0
2124  7300           CLA CLL
2125  1025           TAD ARITH4     /TEST SIGN
2126  7700           SMA CLA
2127  5333           JMP .+4               /POS.
2130  1017           TAD 17 /GET NUMBER
2131  7041           CIA
2132  7410           SKP
2133  1017           TAD 17
2134  6201           CDF 0
2135  3410           DCA I POINT    /STORE NO.
2136  1025           TAD ARITH4     /SAVE HIGH ORDER
2137  3410           DCA I POINT
2140  6211           CDF 10
2141  3017           DCA 17 /CLEAR NO.
2142  3025           DCA ARITH4     /CLEAR SIGN
2143  5723           JMP I STD
            /
            / ROUTINE TO PERFORM BCD TO BINARY CONVERSION
            / BY MULTIPLE CALLS
            / ASCII NO.S EXPECTED
            /
2144  0000  CNVRT,   0
2145  7300           CLA CLL
2146  1017           TAD 17 /MULTIPLY PREVIOUS PART BY 10
2147  7006           RTL
2150  3022           DCA TEMP
2151  1017           TAD 17
2152  7004           RAL
2153  1022           TAD TEMP
2154  1022           TAD TEMP
```

```
2155  3022          DCA TEMP
2156  1015          TAD 15        /GET THE INPUT DIGIT
2157  1376          TAD KM260      /REMOVE ASCII BIAS
2160  1022          TAD TEMP       /FORM NO.
2161  3017          DCA 17 /SAVE IT
2162  5744          JMP I CNVRT    /FOR NEXT CALL; OR DONE
             /
             / SUBROUTINE TO TEST WHETHER THE INPUT
             / CHARACTER IS A NUMBER
             /
2163  0000   NUMTST, 0      /RETURN TO
2164  7300          CLA CLL        /      CALL+1  IF NO
2165  1015          TAD 15 /      CALL +2 IF YES
2166  1376          TAD KM260
2167  7510          SPA
2170  5763          JMP I NUMTST   /NO;  <260
2171  1034          TAD KM12
2172  7700          SMA CLA
2173  5763          JMP I NUMTST   /NO; >271
2174  2363          ISZ NUMTST
2175  5763          JMP I NUMTST   /YES
2176  7520   KM260,  -260
             /
                  *2200
             / DISPLAY ROUTINES
             / SUBROUTINE TO SET UP DISPLAY
             /
2200  0000   XINIT,  0
2201  7300          CLA CLL
2202  4543          JMS I INITP
2203  1027          TAD FIRST      /USE FIRST FOR X ORIGIN
2204  1276          TAD XS
2205  3277          DCA XDIS       /SET START X
2206  5600          JMP I XINIT
             /
             /DISPLAY LOG OF DATA
             / CTRL F
             /
2207  4200   LOGDIS, JMS XINIT
2210  4545          JMS I DACP     /GET POINT
2211  4407          JMS I 7
2212  0007          LOG
2213  3070          FMPY HUND      /MULT. LOG BY 100 FOR VISUAL EFFECT
2214  6126          FPUT Y
2215  0000          FEXT
2216  4246          JMS DISP
2217  4544          JMS I ENDT     /CHECK FOR DONE
2220  5210          JMP LOGDIS+1
2221  5540          JMP I LISTNP
             /
             /DISPLAY THEORETICAL LOG   CTRL L
             /
2222  4200   THDIS,  JMS XINIT
2223  4546          JMS I THP
2224  4407          JMS I 7        /MULT. LOG BY 100
2225  5126          FGET Y /TO EXPAND FOR SCOPE DISPLAY
2226  3070          FMPY HUND
2227  6126          FPUT Y
2230  0000          FEXT
2231  4246          JMS DISP
```

```
2232  4544          JMS I ENDT
2233  5223          JMP THDIS+1
2234  5540          JMP I LISTNP
            /
            / DISPLAY DATA   CTRL D
            /
2235  4200  DATDIS, JMS XINIT
2236  4545          JMS I DACP      /GET DATA
2237  4407          JMS I 7
2240  6126          FPUT Y
2241  0000          FEXT
2242  4246          JMS DISP
2243  4544          JMS I ENDT
2244  5236          JMP DATDIS+1
2245  5540          JMP I LISTNP
            /
            / DISPLAY SUBROUTINE
            / INCREMENTS XDIS BY XDEL AT END
            / AND DISPLAYS SHIFTED VERSION OF Y
            /
2246  0000  DISP,   0
2247  7300          CLA CLL         /SET X COORDINATE
2250  1277          TAD XDIS
2251  6303          6303   /DXC DXL
2252  1300          TAD XDEL
2253  3277          DCA XDIS
2254  4407          JMS I 7
2255  5126          FGET Y /GET Y FOR DISPLAY
2256  0000          FEXT
2257  4551          JMS I IFIXP
2260  3021          DCA SHFR+1
2261  1021          TAD SHFR+1      /SET THE SIGN
2262  7710          SPA CLA
2263  7040          CMA
2264  3020          DCA SHFR
2265  1275          TAD VSW
2266  4534          JMS I SHIFT     /PERFORM SHIFT
2267  1301          TAD VSH         /BIAS SCOPE DISPLAY
2270  7041          CIA
2271  1021          TAD SHFR+1      /GET Y
2272  6317          6317   /DYC DYL DIS
2273  7300          CLA CLL
2274  5646          JMP I DISP
            /
2275  0000  VSW,    0       /SHIFTING FACTOR
2276  0000  XS,     0
2277  0000  XDIS,   0
2300  0001  XDEL,   0001
2301  0000  VSH,    0       /Y BIAS FOR SCOPE
            /
            /
```

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