gases, therefore, seem to be correct for explaining the third-harmonic coefficients.

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Electron-Spin-Resonance Study of High-Concentration Manganese Nitrate Aqueous Solutions*

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The electron spin resonance (ESR) of manganese nitrate aqueous solutions was studied over the concentration range 3.5×10^{-3}–8.25 mole/liter. ESR and viscosity data were obtained from 20 to 90 °C. The spectrum exhibited six well-resolved hyperfine components at low concentrations which transformed to a partially exchange-narrowed singlet at high Mn(II) concentrations. Collapse of the hyperfine structure (hfs) was analyzed from computer-synthesized spectra whose component linewidths and positions were obtained from Anderson's theory of exchange narrowing. It was found that exchange-narrowed spectra of Mn(II) ions were described by Anderson's case (b), in which transitions occur only between adjacent hyperfine components.

INTRODUCTION

Solutions of divalent manganese ions afford ideal conditions for electron-spin-resonance (ESR) studies in that the $3d^5$ free ion is in an S state with no orbital angular momentum to be quenched, resulting in a g factor close to the free-electron value 2.0023. More important, however, is the fact that in solutions of Mn(II) ions the spin-lattice relaxation time T_1 is sufficiently long to give rise to rather narrow linewidths, in contrast with solutions of many transition-metal ions which have strong spin-lattice relaxation through the spin-orbit coupling, resulting in unobservably broad spectra. The present study will confine its attention to aqueous solutions of $Mn(NO_3)_2$, which is particularly well suited to studying the phenomenon of electron-spin-exchange narrowing of spectral lines because of the high concentrations of paramagnetic ions which can be achieved. The ESR spectra of dilute aqueous $Mn(NO_3)_2$ solutions exhibit $2I+1=6$ well-resolved hyperfine lines arising from the interaction of the electronic spin with the $I=\frac{5}{2}$ nuclear spin of the Mn(II) ion. At high concentrations the hyperfine structure coalesces into a single exchange-narrowed resonance.

While a number of investigators have studied the ESR of Mn(II) ions in solution,[1-13] many of the articles that have appeared on this subject were confined to dilute concentrations,[1-8] where exchange-narrowing effects are negligible. For these dilute cases the Mn(II) ions are in such low concentration that the dominant relaxation mechanisms arise from their interaction with the surrounding solvent without any appreciable interaction between the paramagnetic ions themselves. As the concentration of Mn(II) ions is gradually increased, dipolar and spin-exchange mechanisms become important and are manifest as a broadening of the spectral lines resulting in the loss of hyperfine structure at approximately 2.0 mole/liter at room temperature.[9,13]

Pake and Tuttle,[14] the first to discuss the theory of spin exchange in liquids, developed a model in which the exchange frequency is given by

$$\omega_e = p\tau_2^{-1} \quad , \tag{1}$$

where τ_2 is the time between spin encounters and p is the probability per encounter that exchange occurs. This is essentially a model of mutual phase interruption during collisions between precessing spins. Thus spin exchange can be thought of as a lifetime-broadening mechanism in which τ_2 is the lifetime of a given spin state between collisions.

Several theoretical treatments[15-18] of exchange phenomena have obtained the following general type of expression for the probability of exchange per collision:

$$p = f[J^2\tau_1^2/(1+J^2\tau_1^2)] \quad , \tag{2}$$

where τ_1 is the encounter time of the spins during a collision, J is twice the exchange integral, and f is a statistical factor which effectively neglects collisions between electron spins which are located in identical nuclear-spin environments. Some recent experimental studies[15,19,20] of free radicals in dilute solution have used, in part, the above exchange probability or a modified form of it to analyze the results.

Kivelson[21] theoretically analyzed spin exchange as a relaxation mechanism for hyperfine structure during collisions of free radical molecules in dilute solutions by treating it as an application of Kubo and Tomita's general theory of motional narrowing.[22] This method is satisfactory in the two limits of weak exchange and strong exchange. Currin,[18] using the correlation function method as described by Kubo,[23] developed an analytic expression which covers the complete range from good hyperfine resolution to extreme exchange narrowing including the intermediate region. Currin's results are essentially the same as those obtained earlier by Anderson,[24] whose theory provides the basis for the analysis of the exchange-narrowed spectra presented in the present paper.

From the theory of Brownian motion approximate expressions for τ_1 and τ_2 as functions of concentration, viscosity, temperature, and molecular interaction radius can be obtained for the case of dilute ideal solutions characterized by the condition $\tau_2 \gg \tau_1$. The difficulty in determining τ_1 and τ_2 has largely limited the study of spin exchange to dilute solutions of free radicals, which, unlike most transition-metal ions, exhibit observable exchange effects at fairly low concentrations. Therefore, in order to obtain a more complete understanding of transition-metal ions in solution, it seems desirable to extend the range of measurements to higher concentrations. This has the effect of increasing both the viscosity of the solutions and the magnitude of the exchange interaction. At the highest concentrations both factors cause the exchange interaction to become more important than the Brownian motional narrowing, although one never reaches the extreme exchange-narrowed line that often appears in nonhydrated ionic solids.

APPARATUS AND EXPERIMENTAL TECHNIQUES

The ESR spectrometer employed in this investigation was an x-band Alpha ALX-10 model equipped with 100-kHz field modulation, a cylindrical TE_{011}-mode resonant cavity and a 12-in. Hall-effect stabilized magnet. Variable temperature measurements were carried out in a stream of heated or cooled nitrogen gas passing through an EPR heater control unit. The magnet scan was calibrated with the aid of an Alpha AL67 proton NMR magnetometer and a BC-221 frequency meter. The solid free radical α, α'-diphenyl-β-picryl hydrazyl (DPPH) was used as a g-factor calibration standard.

The data were recorded with modulation amplitudes between 0.1 G at low concentrations and 5.0 G at high concentrations which is considerably below the narrowest observed peak-to-peak linewidth of the hyperfine spectral components. The power was kept at the nominal value of 10 mW. No saturation effects were observed at considerably higher power levels. Magnet scans from 600 to 5600 G were employed. The recorder plotted the first derivative of the absorption spectrum. The viscosity measurements were carried out with a Brookfield Model LVF viscometer. The instrument was calibrated with the manufacturers primary viscosity standards.

The samples employed in this study were prepared from a 50% (5.2 molar) aqueous solution of $Mn(NO_3)_2$. The concentration of this solution was raised to 8.25 M/liter by slow evaporation in a vacuum dessicator with the aid of an infrared lamp. Lower concentrations were obtained by dilution, and the molar concentrations were determined analytically by direct titration with a standard 0.05-molar ethylenediamine-tetra-acetic acid (EDTA) solution. Oxygen was removed from several low- and high-concentration samples by the freeze-pump-thaw technique, but no significant effect was observed in the spin-resonance result. Therefore the re-

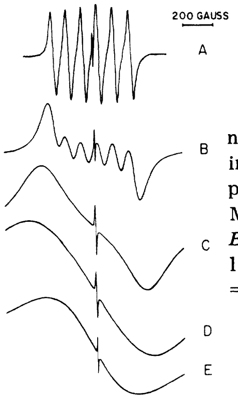

FIG. 1. Electron-spin-resonance spectra of manganese nitrate in aqueous solution at room temperature. The concentrations of Mn^{+2} are $A = 3.5 \times 10^{-3}$ mole/liter, $B = 1.45$ mole/liter, $C = 2.90$ mole/liter, $D = 4.85$ mole/liter, and $E = 8.25$ mole/liter.

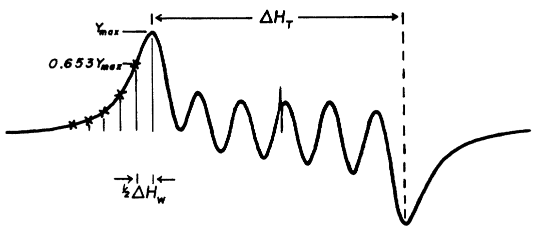

FIG. 2. Total over-all linewidth ΔH_T and linewidth fitted in the wings ΔH_W for a spectrum with partially resolved hyperfine structure. For a Lorentzian line shape the amplitude in the wings falls to 0.6531 of its peak value at a distance $\frac{1}{2}\Delta H_W$ beyond the peak. The points X give the Lorentzian fit.

maining samples were used without outgassing.

EXPERIMENTAL DATA

Several typical spectra are presented on Fig. 1. The upper spectrum exhibits the well-resolved six line hyperfine structure characteristic of low concentrations, while the lower recording is an exchange-narrowed singlet typical of the high-concentration range. Three intermediate cases are also shown. The sharp center line is the DPPH marker.

The line shapes were found to be Lorentzian at very high and very low concentrations. The low-concentration line shape is typical of low-viscosity solutions which obey the Bloch equations, while the same shape is also characteristic of an exchange-narrowed spectral line. At intermediate concentrations the hyperfine structure pattern coalesces into a broad singlet. The medium- and high-concentration spectral lines provide the total over-all peak-to-peak linewidth ΔH_T and the linewidth ΔH_W fitted in the wings, as defined on Fig. 2. The latter width is obtained from a fit of the wings of the line to a Lorentzian line shape, and is the average value calculated for the two wings. The linewidth ΔH_W is quite close to the unresolved individual linewidths. These widths are the only experimentally available parameters that characterize the line at concentrations above approximately 2.0 mole/liter. The significance of these two experimental linewidths ΔH_T and ΔH_W will be discussed later in the paper.

The linewidth ΔH_T was determined as a function of Mn^{+2} concentration and temperature, and the results are shown in Fig. 3. In order to elucidate the dependence of the line-broadening mechanism on the rotational correlation time, the viscosities of the various solutions were determined as a function of temperature, and the data are plotted

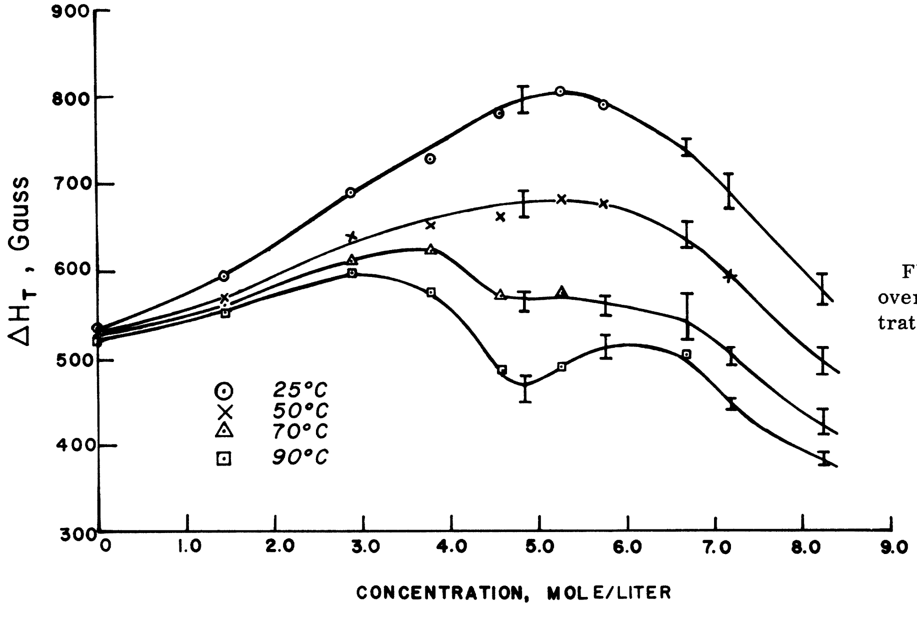

FIG. 3. Dependence of the total over-all linewidth on the concentration and temperature.

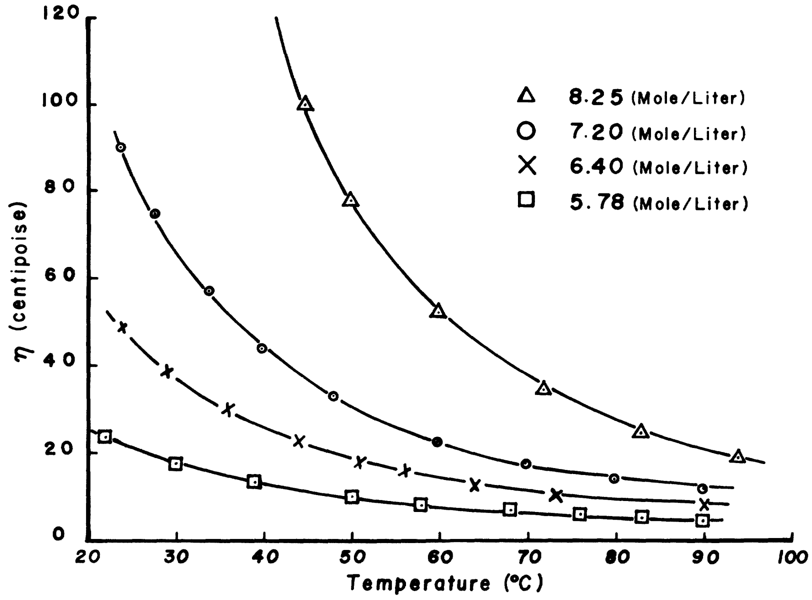

FIG. 4. Dependence of the viscosity on the temperature and concentration.

on Fig. 4. One should note how high the viscosity becomes for high Mn^{+2} concentrations.

LOW-CONCENTRATION RESULTS

At low concentrations and high temperatures the hyperfine structure is quite well resolved, and the peak-to-peak linewidths of the individual hyperfine components are related through the equation

$$\Delta H_i = B + CM_I + DM_I^2 + EM_I^3 \ , \tag{3}$$

where M_I is the nuclear-spin quantum number and $B, C, D,$ and E are constants which may be evaluated from the spectrum. The 3.5×10^{-3} M aqueous solution at room temperature has the parameters

$$B = 21.4 \text{ G}, \quad C = -1.0 \text{ G}, \quad D = 0.61 \text{ G}, \quad E = 0.16 \text{ G}. \tag{4}$$

The individual linewidths range from 21 to 25 G for this sample.

At higher concentrations when the structure merged into a single broad line it was not possible to extract the variation of the four parameters of Eq. (3), especially since the hyperfine coupling constant A is also changing. The measured values of ΔH_W were usually quite close at both ends of the spectrum, so their mean was used as a first approximation to the individual component linewidth. The smallness of the constants $C, D,$ and E relative to B of Eq. (3), and the lack of appreciable variation between ΔH_W determined from each end of the spectrum justify the validity of determining an average individual hyperfine component linewidth ΔH_i.

For a well-resolved hyperfine pattern with $I = \frac{5}{2}$, constant component linewidths ΔH_i and line separation A, the total over-all linewidth is

$$\Delta H_T = 5A + \Delta H_i \ , \tag{5}$$

as may be easily deduced from Fig. 2. The following expression allows us to obtain a first approximation to the hyperfine coupling constant A for poorly resolved or unresolved spectra:

$$A_{\text{exp}} = \tfrac{1}{5}(\Delta H_T - \Delta H_W) \ . \tag{6}$$

This provides fairly precise values for ΔH_T considerably in excess of ΔH_W, but accuracy is low in the limit of appreciable exchange narrowing.

The hyperfine components were almost equally spaced, and deviations from equal spacing arose from second-order effects. The matrix elements $\langle M_S M_I | \mathcal{H} | M_S' M_I' \rangle$ were calculated for the Hamiltonian

$$\mathcal{H} = g\mu_B H S_z + A_0[S_x I_x + S_y I_y + S_z I_z] \tag{7}$$

and the off-diagonal elements provided the corrections in second-order perturbation theory. The average second-order shifts were of the order $A_0^2/g\mu_B H \sim 3.1$ G, and the agreement with experiment is shown in Table I. Column three was calculated from the average positions of the fine structure quintet that comprise each hyperfine line for the 3.5×10^{-3}-mole/liter sample.

ANDERSON EXCHANGE-NARROWING THEORY

At high concentrations the hyperfine structure collapses due to the onset of exchange narrowing. Before presenting an analysis of the relevant experimental data it will be appropriate to discuss a theory of exchange narrowing.

TABLE I. Comparison of the observed and calculated spacings between hyperfine components.

Hyperfine interval	Observed spacing (G)	Calculated spacing (G)
$-\frac{5}{2}\to-\frac{3}{2}$	107.2	107.4
$-\frac{3}{2}\to-\frac{1}{2}$	104.4	104.2
$-\frac{1}{2}\to\frac{1}{2}$	1C2.3	101.1
$\frac{1}{2}\to\frac{3}{2}$	97.5	97.4
$\frac{3}{2}\to\frac{5}{2}$	95.0	95.4

Anderson[24] has developed a theoretical treatment of the dependence of the positions and widths of hyperfine components in the presence of a strong exchange interaction. In a separate publication[25] his matrices were converted to polynomial equations and solved in general for nuclear spins $\frac{1}{2}\leq I\leq\frac{5}{2}$. In the next paragraph the results will be summarized for Mn^{+2} where $I=\frac{5}{2}$.

Anderson discussed two possible extremes. In case (a) transitions are equally likely between each hyperfine line, while in case (b) transitions can occur only between adjacent hyperfine components. The selection rules make case (a) unlikely to occur. In addition it was found that our data could be analyzed in terms of case (b), so only this case will be discussed here.

The secular equation entails finding the eigenvalues of the following determinant

$$\begin{vmatrix} -\frac{1}{2}\omega_e+\frac{5}{2}\gamma A_0 i-\lambda & \frac{1}{2}\omega_e & 0 & 0 & 0 & 0 \\ \frac{1}{2}\omega_e & -\omega_e+\frac{3}{2}\gamma A_0 i-\lambda & \frac{1}{2}\omega_e & 0 & 0 & 0 \\ 0 & \frac{1}{2}\omega_e & -\omega_e+\frac{1}{2}\gamma A_0 i-\lambda & \frac{1}{2}\omega_e & 0 & 0 \\ 0 & 0 & \frac{1}{2}\omega_e & -\omega_e-\frac{1}{2}\gamma A_0 i-\lambda & \frac{1}{2}\omega_e & 0 \\ 0 & 0 & 0 & \frac{1}{2}\omega_e & -\omega_e-\frac{3}{2}\gamma A_0 i-\lambda & \frac{1}{2}\omega_e \\ 0 & 0 & 0 & 0 & \frac{1}{2}\omega_e & -\frac{1}{2}\omega_e-\frac{5}{2}\gamma A_0 i-\lambda \end{vmatrix}=0, \tag{8}$$

where ω_e is the exchange frequency, $A_0=101.3$ G is the hyperfine coupling constant, and $\gamma=1.76\times10^7$ rad/sec G is the gyromagnetic ratio. The product of these last two variables gives $\gamma A_0=1.788\times10^9$ rad/sec.

The roots λ_M of the secular equation are complex and when expressed in magnetic field units have the form

$$\lambda_M=-\Delta H_{iM}+iP_M\ , \tag{9}$$

where the real part ΔH_{iM} is the direct absorption half-width at half-amplitude and the imaginary part P_M is the position of the line for $|M_I|=|M|=\frac{5}{2},\frac{3}{2},\frac{1}{2}$. The positive sign corresponds to $M>0$ and the negative sign to $M<0$, so the two lines for each $\pm M$ are symmetrically located about the center point of the spectrum. We take the position P_M as positive for $M>0$, the width $H_{iM}>0$ for all lines and $P_{-M}=-P_M$. These quantities depend upon the exchange frequency in the manner shown on Fig. 5. Anderson[24] has given perturbation formulas valid for $\omega_e\ll\gamma A_0$ and $\omega_e\gg\gamma A_0$.

COMPARISON OF DATA WITH ANDERSON THEORY

The Anderson theory assumes that the individual hyperfine component linewidths are zero in the absence of exchange. They acquire widths arising from exchange when the exchange interaction is nonzero. To render the theory more realistic, it was further assumed that the component linewidths in the presence of exchange are given by $[\Delta H_c+\Delta H_{iM}]$, where ΔH_{iM} is given by Eq. (9), and ΔH_c is the linewidth that would exist if the nuclear spin were zero. For very low exchange rates where the dipolar width ΔH_{dd} greatly exceeds ω_e/γ, the width ΔH_c is given by the dipolar value. The direct absorption linewidth in gauss, ΔH_{dd}, is related to the concentration C in mole/liter through the formula[26,27]

$$\Delta H_{dd}=2.3g\mu_B\rho[S(S+1)]^{1/2} \tag{10}$$

$$=74C\ , \tag{11}$$

where $g\sim2$, $S=\frac{5}{2}$, μ_B is the Bohr magneton, and ρ is the density of Mn^{+2} ions/cm^3. At higher exchange rates where $\Delta H_{dd}\ll H_e$, the linewidth ΔH_c is exchange narrowed to give in general

$$\Delta H_c\sim\Delta H_{dd}\,,\qquad \Delta H_{dd}\gg H_e \tag{12}$$

$$\Delta H_c\sim(\Delta H_{dd})^2/H_e\,,\qquad \Delta H_{dd}\ll H_e \tag{13}$$

where $\omega_e=\gamma H_e$ relates the exchange frequency to the magnetic field associated with the exchange interaction. The fine structure contribution to the linewidth was omitted from Eq. (13) because it is negligible relative to the dipolar contribution.[4,19]

Using the linewidth $(\Delta H_c+\Delta H_{iM})$ for each Mth component and the average hyperfine coupling con-

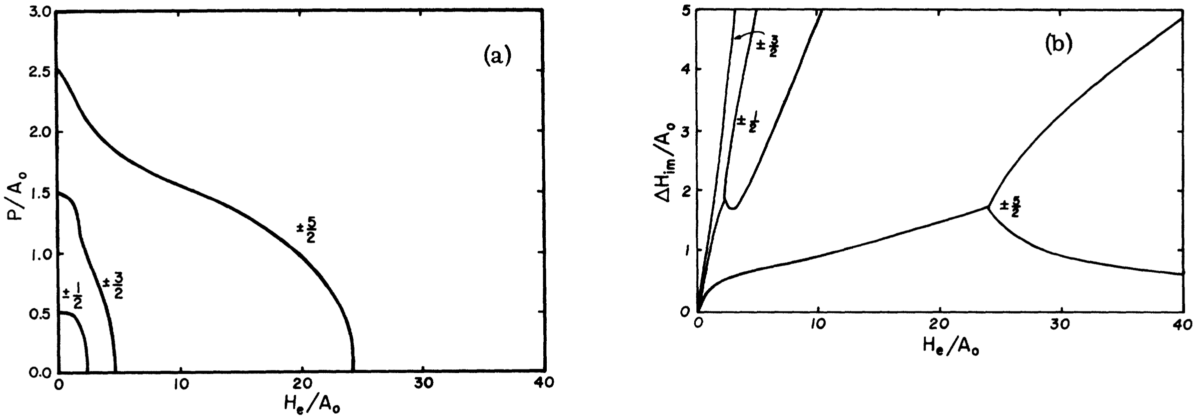

FIG. 5. Dependence of (a) the position P and (b) the individual component linewidth ΔH_{iM} on the exchange frequency (Ref. 25) where the various quantities are normalized relative to A_0.

stant $A_0 = 101.3$ G from Table I, an IBM 7040 computer was employed to fit the observed spectra to the Anderson theory. The exchange field H_e and the width ΔH_c were both considered as free parameters to be evaluated from the best fit to the data. An example of a computer fit to an experimental spectrum is shown in Fig. 6. The magnitudes of the exchange H_e deduced for various combinations of temperature and concentration are presented in Fig. 7. Figure 8 compares the computer determined linewidths ΔH_{dd} with the dipolar one arising from Eq. (11). One should note that the former are consistently greater than the latter.

The exchange field H_e determined by a fit of the data to Anderson case (b) is quite large relative to the hyperfine coupling constant A_0 even though the spectrum has not yet completely collapsed to the extreme exchange-narrowed singlet. This is intrinsic to the theory since the final coalescence point occurs where $H_e/I^2A_0 \sim 4$, which corresponds to $H_e/A_0 \sim 25$ for our high-spin case $I = \frac{5}{2}$. One should note that $H_e/\Delta H_{dd} \sim 4$ for the high-concentration samples.

EXCHANGE NARROWING

As the manganese concentration increases the line is expected to broaden due to two mechanisms: (i) the increase in the magnitude of the dipolar interaction as the average distance between Mn^{+2} ions decreases, and (ii) the decreased effectiveness of the motional narrowing as a result of the increase in viscosity with concentration.

When the concentration becomes sufficiently high the additional process of exchange narrowing becomes operative. In this investigation the Anderson theory of exchange narrowing has been employed to explain the collapse of the hyperfine pattern at high concentrations. It will be appropriate to estimate the extent to which each mechanism contributes to the individual line shape.

According to Kubo and Tomita[22] the criterion for motional narrowing is that $\gamma\delta\tau_c \ll 1$, where τ_c is the correlation time and the width δ arises from a randomly fluctuating perturbation which broadens the line. In our case δ arises from the dipolar interaction. At high concentrations the linewidth varies from 450 to 800 G corresponding to the angular frequency range of $\gamma\delta$ from 8.0 to 14×10^9 sec^{-1}. The rotational correlation time τ_c

$$\tau_c = \frac{4\pi\eta a^3}{3kT} \tag{14}$$

was calculated using $a = 3$ Å as a typical effective radius for the $[Mn(H_2O)_6]^{+2}$ group and the measured viscosities η. This gave values of τ_c ranging from 10^{-10} sec for the 5.8 molar solution at 90 °C to 10^{-8} sec for 7.75 M/liter at 25 °C. For these two cases we obtain $\gamma\delta\tau_c \sim 0.8$ and $\gamma\delta\tau_c \sim 140$, respectively. Thus the high-concentration samples are all in the region $\gamma\delta\tau_c \gtrsim 1$ and generally $\gamma\delta\tau_c \gg 1$, so motional narrowing is not appreciable.

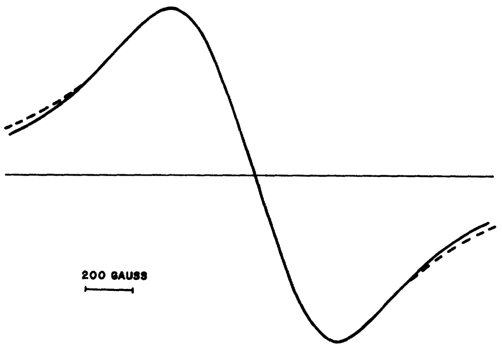

FIG. 6. Computer synthesized spectrum (dashed line) compared with the corresponding experimental spectrum for 6.7-mole/liter Mn^{+2} at 300 °K.

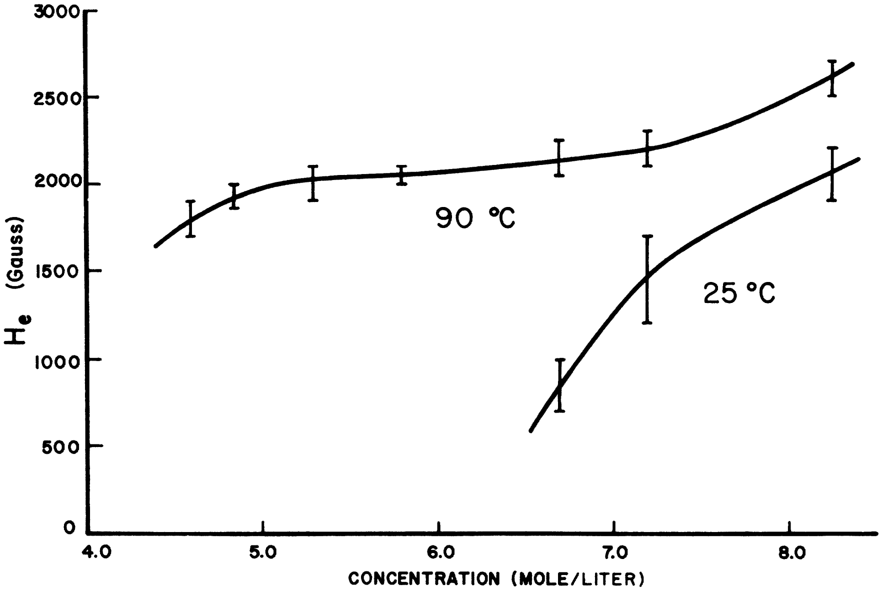

FIG. 7. Dependence of the exchange field $H_e = \omega_e/\gamma$ on the concentration and temperature.

A convenient criterion to judge the extent of exchange narrowing is the ratio $\Delta H_c/H_e$ of the component width to the exchange field obtained from the computer fitting to the data. In the range 5. 8–8. 25 M/liter the ratio $\Delta H_c/H_e$ varies from 0. 74 to 0. 25. This corresponds to a moderate amount of exchange narrowing over the region of high concentration.

The difference between H_e at low and high temperature may be attributed to the time τ_2 between collisions[21]

$$\tau_2 = \frac{750}{RC}\,\frac{\eta}{T} \quad . \tag{15}$$

Kivelson relates the effective exchange integral J' to the intrinsic exchange integral J_0 through the expression

$$\langle J'^2 \rangle = [(T_2 - \tau_2)/T_2] \times \tfrac{1}{3} S(S+1) J_0^2 \ , \tag{16}$$

where the factor $(T_2 - \tau_2)$ decreases as τ_2 increases. As a result the effective exchange will be less at room temperature than at high temperatures, as is observed (see Fig. 7).

Equations (14)–(16) are not really valid at high concentrations. Therefore the preceding argument is merely a qualitative justification for the observed increases in the exchange frequency with increasing temperature.

DISCUSSION

The ESR spectra for high-concentration aqueous solutions of Mn^{+2} have been studied, and the temperature and concentration dependence of the individual component linewidth and hyperfine coupling constant have been determined. The Anderson theory case (b) has been used to deduce the dependence of the exchange field H_e on these parameters, as presented in Fig. 7.

The simple exchange model proposed by Pake

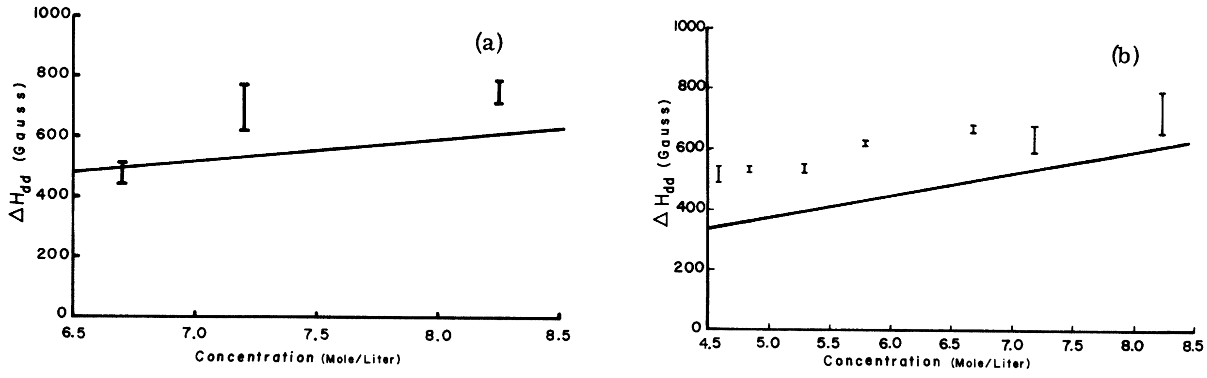

FIG. 8. Dependence of the dipolar linewidth on the concentration (a) at 25 °C and (b) at 90 °C. The Van Vleck curve from Eq. 11) is also shown.

and Tuttle[14] to explain the anomalous loss of hyperfine structure upon heating dilute solutions of various free-radical molecules is not readily applicable in the present work over the region of high concentration of Mn(II) ions. The model, while physically instructive was originally presented to estimate the magnitude of exchange in solutions sufficiently dilute to assume the validity of the Stokes-Einstein diffusion equation. On the other hand Hinckley and Morgan[13] in their rather complete paper have shown very satisfactorily that a simple rapid motion diffusion model can account for the spectral behavior of Mn(II) perchlorate solutions only up to about 1.9 mole/liter. Their study covered the concentration region dominated by dipole-dipole interactions (1–3.2 mole/liter) over which strong exchange was not observed since their spectra did not appreciably narrow. Our work extends the study of the Mn(II) system into this exchange-narrowed region for which we assume that the dominant relaxation mechanism is the exchange interaction.

The work of Plachy and Kivelson[19] in dilute solutions of the di-tertiarybutyl nitroxide radical (DTBN) is largely an extension of the Pake and Tuttle theory with five major corrections applied over the region of initial exchange broadening. At high concentrations Kivelson points out that it is not possible to carry out all the necessary corrections, and hence a comparison of his theory with experiment is not possible.

The paper by Edelstein, Kwok, and Maki[28] is also based on Pake and Tuttle's work; but it includes only one of the five corrections later made by Plachy and Kivelson. In treating the effects of pressure (viscosity) and temperature, Edelstein *et al.* were only concerned with free-radical solutions so dilute that hfs is always resolved. Therefore, the exchange interaction was so weak that it was manifest only as a broadening mechanism, and dipolar contributions to the linewidth were not explicitly considered since the solutions were sufficiently dilute that Brownian motional tumbling averaged them out. In view of these major limitations, it was not possible to obtain additional quantitative information from these papers which could be applied to our present work at high Mn(II) ion concentrations, our spectra being strongly exchange narrowed.

Kaplan[29] and Alexander[30] have applied density-matrix methods to nuclear-spin exchange and proton transfer reactions. In the same manner electron transfer reactions were later treated by Johnson and Tully,[31] and electron-spin exchange by Johnson.[16] While Freed[17] has shown that under many conditions the effects of Heisenberg spin exchange on ESR spectra will be identical to those of chemical exchange (or transfer), it has not been possible for us to apply the results of these papers to our present work. This is largely due to the difficulty in obtaining explicit values for τ_1 and τ_2 in Eq. (2) at our high concentrations. In fact, it is felt that direct application of the Anderson theory, which does not require knowledge of any spin correlation or encounter times, to the analysis of exchange-narrowed spectra of transition-metal ions in solution affords an appropriate way of circumventing these difficulties.

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Ordinary-Mode Electromagnetic Instability in Colliding Plasma Streams

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The instability of the electromagnetic linearly polarized mode propagating perpendicular to the magnetic field is studied for a system composed of two colliding plasma streams, in each of which both the electrons and the ions are streaming at the same velocity. Based on the linearized Vlasov-Maxwell equations and allowing for anisotropic temperatures, it is found that in the presence of streaming ions the instability can occur in very low-β plasmas. The higher the values of β, the streaming velocity, and the temperature ratios $T_{\parallel e}/T_{\perp e}$ and $T_{\perp e}/T_{\perp i}$, the more the plasma is susceptible to the electromagnetic instability. The ratio $T_{\parallel i}/T_{\parallel e}$ has negligible influence, except when the streaming velocity is smaller than the ion thermal speed. It is found that for β values of order unity, the streaming ions, while greatly enlarging the range of unstable wave numbers, contribute negligibly to the maximum growth rate, which is typically of the order of the electron cyclotron frequency. A comparison with the growth rates of the electrostatic two-stream instability is made.

I. INTRODUCTION

The propagation of small amplitude waves normal to an external magnetic field $\vec{B}_0$ in a collisionless plasma has been studied extensively mainly in the context of electrostatic waves, i.e., the Bernstein modes.[1] However, considerable attention has recently been given to the stability of the ordinary mode, which is a transverse electromagnetic wave with its electric field linearly polarized in the direction of $\vec{B}_0$. Hamasaki[2] and Davidson and Wu[3] studied a stationary electron plasma with anisotropic temperatures and showed that for the ordinary mode to be unstable, one of the necessary conditions is $\beta_{\parallel e} \geqslant 2$, where $\beta_{\parallel e}$ is the ratio between the electron thermal energy density in the direction of $\vec{B}_0$ and the magnetic energy density. A plasma with $\beta_{\parallel e} = 2$ is unstable only in the limit of $T_{\perp e}/T_{\parallel e} \to 0$. For a more realistic value of the temperature ratio, for example, $T_{\perp e}/T_{\parallel e} = 0.45$, the minimum value of $\beta_{\parallel e}$ required for instability is 16. Thus in a stationary plasma, the instability occurs only in high-β plasmas.

The ordinary mode in counterstreaming cold plasmas has been studied by Lee.[4-6]. For the case of two identical electron beams in a background of infinitely heavy ions, instability occurs when $u > c\Omega_e/\omega_{pe}$, where $2u$ is the relative streaming velocity, c is the velocity of light, and Ω_e and ω_{pe} are the electron cyclotron and plasma frequencies, respectively.[4] On the other hand, for a system of two colliding cold plasma streams, in each of which both the electrons and ions are streaming at the same velocity, the condition for instability is approximately $u > c\Omega_i/\omega_{pi}$, where Ω_i and ω_{pi} are the ion cyclotron and plasma frequencies, respectively.[6] Since

$$\frac{\Omega_i}{\omega_{pi}} = \left(\frac{m_e}{m_i}\right)^{1/2} \frac{\Omega_e}{\omega_{pe}} ,$$

it follows that a system with ion streaming is much more susceptible to the instability than one in which only electrons are streaming.

In a recent article, Bornatici and Lee[7] have analyzed the case of counterstreaming electrons by means of the Vlasov equation, allowing for anisotropic temperatures. Their results show that the necessary condition on $\beta_{\parallel e}$ for the existence of the ordinary-mode electromagnetic instability is $\beta_{\parallel e} \geqslant 2/(1+2u^2/V_{\parallel e}^2)$, where $V_{\parallel e}$ is the electron thermal velocity parallel to $\vec{B}_0$. Comparing with the results of Hamasaki,[2] and Davidson and Wu,[3] we see that the presence of relative streaming enables the instability to occur in low-$\beta_{\parallel e}$ plasmas. Bornatici and Lee[7] also found that typical growth rates are of the order of the electron cyclotron frequency. The pure electron problem for the case of isotropic temperatures was also considered by Tzoar and Yang.[8] However, their analysis was restricted to $(kV_{\parallel e}/\Omega_e)^2 \gg 1$ and can therefore describe the in-