Simulation of EPR Spectra of Mn\(^{2+}\) in Glasses

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The Mn\(^{2+}\) EPR spectra in glasses are treated by a computer simulation technique taking into account the distributions of the fine structure parameters \(D\) and \(E\) resulting from random variations in local environments of the paramagnetic ion. Simulated spectra are displayed for different values of the \(D_0/E_0\) ratio and for different values of the parameter distributions, \(\Delta D\) and \(\Delta E\). The good agreement observed between the simulated and experimental spectra for phosphate and silicate glasses permits determination of the spin-Hamiltonian parameters and their distributions. It is concluded that Mn\(^{2+}\) ions with \(g = 2.0\) in glasses form a distinct site characterized by the following spin-Hamiltonian parameters: \(|D_0|/g\beta = 220 \pm 20\) G, \(|E_0|/g\beta = 70 \pm 15\) G, \(A/g\beta = -93 \pm 1\) G (for the phosphate glass) and \(A/g\beta = -87 \pm 1\) G (for the silicate glass). The fine structure parameters have considerable distributions, \(\Delta D/g\beta = 80 \pm 20\) G, \(\Delta E/g\beta = 30 \pm 10\) G, due to the structural disorder of the glasses.

INTRODUCTION

Structural disorder is a characteristic feature of the vitreous state. Local environments of paramagnetic ions in glasses are subject to random distortions. This must result in substantial distributions of the spin-Hamiltonian parameters, as has been demonstrated in (1–4).

The aim of the present work is to give a detailed analysis of Mn\(^{2+}\) EPR spectra in glasses. The presence of the fine structure \(fs\) (electron spin \(S = \frac{3}{2}\)) and the hyperfine structure \(hfs\) (nuclear spin \(I = \frac{3}{2}\)) makes Mn\(^{2+}\) EPR spectra rather complex, especially in powders, where their interpretation is additionally obscured by the orientational disorder of the paramagnetic ions. On the other hand, due to their complexity, the Mn\(^{2+}\) EPR spectra contain much information about the local environment. Therefore Mn\(^{2+}\) is often used as a paramagnetic probe in structural investigations of crystals. Extending this work to disordered systems requires careful computer simulations of the spectra, in order to extract the spin-Hamiltonian parameters from the experimental data. A number of papers (5–12) have dealt with the simulations of the Mn\(^{2+}\) powder spectra. However, to our knowledge, no accurate Mn\(^{2+}\) lineshape calculations in glasses taking into account distributions of the spin-Hamiltonian parameters have been reported so far. Such calculations would be extremely useful in elucidating the structural differences between crystals and glasses. Namely, the question concerns a hypothesis advanced in some earlier publications (5) that the environments of the Mn\(^{2+}\) ions in glasses are characterized by a continuous and very broad distribution of crystal-field parameters, the \(g = 2.0\) and \(g = 4.3\) features arising...
merely from "singularities" of a powder pattern which are stationary with respect to variations of the spin-Hamiltonian parameters.

Using a computer program developed for the Mn$^{2+}$ ions in glasses, the EPR lineshapes for different cases were evaluated. By comparing the simulated spectra with the experimental ones for phosphate and silicate glasses the values of the spin-Hamiltonian parameters and their distributions were determined.

Surprisingly enough, we found that for the sharp-line portion of the $g = 2.0$ features the distribution of the $f_s$ parameters is far less broad than assumed previously. This result implies that these sharp features, at least in the glasses studied in the present work, correspond to a distinct, rather well-defined site.

**SAMPLES AND EXPERIMENTAL**

Two different types of glasses were investigated: zinc phosphate glass ZnO·P$_2$O$_5$ and potassium silicate glass K$_2$O·4SiO$_2$. The zinc phosphate glass was prepared by fusing appropriate amounts of zinc oxide and monosubstituted ammonium phosphate with 0.14 mol% Mn$_2$O$_3$ in a glazed ceramic crucible. After fusing for 0.5 hr at 1200°C in an electric muffle, the sample was cooled down rapidly to room temperature. The potassium silicate glass was made by fusing SiO$_2$ and K$_2$CO$_3$ in a fused silica crucible for 1 hr in an oil furnace at 1550°C followed by quenching to room temperature. The manganese was introduced after fusing by addition of 0.1 mol% Mn$_2$O$_3$ to the glass ground to a fine powder and heating for 1 hr at 1200°C. EPR spectra were taken at 120 K with an X-band spectrometer.

Figure 1 shows parts of the experimental spectra in the region $g = 2.0$ displaying a number of sharp features superimposed on a broad underlying resonance. In addition, much weaker features were observed for both glasses in the region $g = 4.3$, which are not discussed in the present paper. The spectra are very similar to those

![Figure 1](image-url)  
**FIG. 1.** EPR spectra of Mn$^{2+}$ observed at $v = 8900$ MHz in the phosphate (upper trace) and silicate (lower trace) glass.
reported for Mn\(^{2+}\) in different types of glasses (5, 10, 13, 14). This indicates that we are really dealing with the same valence state of manganese.

**CALCULATION OF SPECTRA**

The correct approach to the EPR lineshape calculations for Mn\(^{2+}\) in glasses requires one, in principle, to use the most general form of the spin Hamiltonian, including the fourth-order fs terms. However, data available on the EPR of Mn\(^{2+}\) ions in different solids (see, for example, 15) permit several simplifying assumptions to be made. First, the \(g\) factor and hfs constant \(A\) may be taken as isotropic, since their anisotropy is negligible. Second, as the fourth-order fs terms as well as the quadrupole term are usually much smaller than the hyperfine term, they can be neglected for glasses. Then the spin Hamiltonian is

\[
\mathcal{H} = g\beta \mathbf{H} \cdot \mathbf{S} - D \left( S_z^2 - \frac{S(S+1)}{3} \right) + E(S_x^2 - S_y^2) + A S \cdot I
\]

where \(S = \frac{5}{2}, I = \frac{1}{2}\), and all symbols have their usual meaning.

In this paper we confine ourselves to the case \(|D| \ll g\beta H, |E| \ll g\beta H, |A| \ll g\beta H. The resonance magnetic fields for the transitions between two states denoted by \(|M_m\rangle\) and \(|M_{m+1}\rangle\)

\[
H_0 = H_{M,m;M-1,m+1}(g, A, D, E, \theta, \varphi)
\]

to third-order perturbation have been given in a number of papers (see, for example, those by Bir (16) and Upreti (17)). In Eq. [2], \(M\) and \(m\) are the electronic and nuclear quantum numbers; \(i = 0\) corresponds to the allowed transitions; \(i = \pm 1, \pm 2, \ldots\), etc., correspond to the forbidden transitions; and \(\theta\) and \(\varphi\) are the polar and azimuthal angles formed by the magnetic field with the axes of the spin Hamiltonian. \(H_0\) depends on four spin-Hamiltonian parameters, \(g, A, D, \) and \(E\). Moreover parameter distributions are characterized by the mean values \(g_0, A_0, D_0,\) and \(E_0\) and respective widths \(\Delta g, \Delta A, \Delta D,\) and \(\Delta E\). Together with the linewidth \(\Delta H_{pp}\), a total of nine parameters of the experimental spectrum must be determined.

In calculating the spectra the value \(g_0 = 2.0\) was used. The ground state of Mn\(^{2+}\) ions being \(^6S\), the \(g\) factor is close to this value in all cases (15). Besides, a slight deviation from \(g_0 = 2.0\) would result simply in some shift of the whole spectrum. This can easily be taken into account after all other parameters have been fitted.

Now the question is which of the parameter distributions are determinant for the Mn\(^{2+}\) in the glasses. As these distributions arise from random variations of electric fields and strains in the glass network, some information about them can be deduced from the data concerning the effects of stresses or electric fields on the EPR of Mn\(^{2+}\) in crystals. It has been demonstrated by Feher (18) and Krebs (19) that an application of uniaxial stresses or electric fields leads to a considerable linear shift of the fs parameters, leaving the \(g\) factor and hfs constant unchanged. On the basis of these facts, it can reasonably be inferred that \(g\) and \(A\) are far less sensitive to the variations of the local environment of Mn\(^{2+}\) as compared to the fs parameters \(D\) and \(E\). Hence \(\Delta g\) and \(\Delta A\) are supposed to be small and therefore to be reflected merely in
some broadening of all the spectral features. This effect can be accounted for by choosing an appropriate value of $\Delta H_{pp}$ (which also includes the spin–spin interaction as well as the broadening caused by the omitted terms of the spin Hamiltonian).

On the other hand, as much broader distributions are expected to occur for $D$ and $E$ in glasses, a more accurate statistical approach must be used in this case (3, 4). We used the joint probability density function for $D$ and $E$ in the form (20)

$$P(D, E) = \frac{1}{\pi \Delta D \Delta E (1 - r^2)^{1/2}} \times \exp\left\{-\frac{1}{1 - r^2} \left( \frac{(D - D_0)^2}{\Delta D} - 2r \frac{(D - D_0)(E - E_0)}{\Delta D \Delta E} + \frac{(E - E_0)^2}{\Delta E} \right) \right\}. \quad [3]$$

Then the distributions of $D$ and $E$ are Gaussians with mean values $D = D_0$ and $E = E_0$, variances $\Delta D^2/2$ and $\Delta E^2/2$, and a correlation coefficient $r$, $-1 \leq r \leq 1$. When $r = 0$, $D$ and $E$ are uncorrelated and $P(D, E)$ becomes the product of two independent one-dimensional Gaussian distributions

$$P(D) = \frac{1}{\pi^{1/2} \Delta D} \exp\left[-\frac{(D - D_0)^2}{\Delta D}\right]; \quad P(E) = \frac{1}{\pi^{1/2} \Delta E} \exp\left[-\frac{(E - E_0)^2}{\Delta E}\right]. \quad [4]$$

When $r = \pm 1$ there is a total correlation between $D$ and $E$ and Eq. [3] gives $P(D, E) \neq 0$ only for $E - E_0 = \pm(D - D_0)\Delta E/\Delta D$. In this case the one-dimensional distributions, Eq. [4], should be used instead of Eq. [3] (for $D$ or $E$).

Synthesis of an EPR spectrum in a glass comprises integration over all possible orientations of paramagnetic ions as well as over the distributed values of the spin-Hamiltonian parameters. Following the approach of Taylor and Bray (6) we assume that an ensemble of randomly oriented identical sites and one of randomly distorted sites are mutually independent. Then the EPR spectrum of Mn$^{2+}$ in a glass is obtained as

$$\mathcal{P}(H) = \sum_{\substack{M = -3/2 \\ \max(|m|) = 5/2}}^{5/2} \sum_{\substack{m = -5/2 \\ \max(|m|) = 5/2}}^{5/2} \int_{-\infty}^{\infty} dD \int_{-\infty}^{\infty} dE \int_{0}^{2\pi} d\varphi \cdot P(D, E) \cdot \sin \vartheta \times W_{M,m;M-1,m+i}(D, E, \vartheta, \varphi) \cdot F\left(\frac{H - H_0}{\Delta H_{pp}}\right), \quad [5]$$

where $F\left(\frac{H - H_0}{\Delta H_{pp}}\right)$ is the lineshape function which was taken in the form of either a Gaussian or Lorentzian first derivative; $W_{M,m;M-1,m+i}(D, E, \vartheta, \varphi)$ is the transition probability between $|M, m\rangle$ and $|M-1, m+i\rangle$ states averaged over different orientations of the microwave magnetic field vector. This was calculated using the method developed by Bir (16), which provides a much better approximation that the usual perturbation approach (21). Application of Bir’s method to the calculation of the Mn$^{2+}$ EPR spectra in powders has been described in detail (12).

As has been noticed by Aasa and Vännigard (22), the integrand of Eq. [5] must be multiplied by $\partial H_0/\partial \nu$. However, in our case this multiplier can be omitted, as it
differs from unity only by a few percent. In computing the spectra the limits of integration over $D$ and $E$ were taken, respectively, as $D_0 \pm 2\Delta D$ and $E_0 \pm 2\Delta E$.

Equation [5] takes into account all the $fs$ transitions. However, as in powder EPR spectra the lines of the noncentral $fs$ transitions are much less intense than those of the central one ($|\frac{1}{2}, m\rangle \leftrightarrow |-\frac{1}{2}, m+i\rangle$) because of a stronger angular dependence of their positions, in most cases it is sufficient to confine the calculation to the central $fs$ transition. This is even more valid for the glasses. Indeed, the resonance magnetic fields for the noncentral $fs$ transitions contain the terms linear in $D$ and $E$ which vanish for the central $fs$ transition (16, 17). Therefore the parameter distributions completely smear out all the noncentral transition lines in glasses.

RESULTS OF THE COMPUTER SIMULATIONS AND COMPARISON WITH THE EXPERIMENT

Figure 2 shows the "powder patterns" (11) computed for the central hf transition. The lower curve was calculated assuming the transition probabilities to be constant and equal to one. For the upper curve the transition probabilities were calculated as described above. The drastic discrepancy between the two curves demonstrates that no convincing fit to experimental spectra can be attained without a due account of the transition probabilities.

Figure 3 displays the EPR spectra of the central $fs$ transition computed for different parameter distributions $\Delta D$ and $\Delta E$, at constant values of $D_0$ and $E_0$. Figure 4 represents a series of spectra calculated for different values of the ratio $D_0/E_0$.

Fig. 2. Powder patterns calculated to third order for some allowed (solid lines) and forbidden (dashed lines) hf transitions belonging to the central $fs$ transition. $g = 2.0$, $A/g\beta = -95$ G, $D/g\beta = 210$ G, $E/g\beta = 70$ G, $v = 8900$ MHz. Top, the transition probability is calculated using Bir's method (12). Bottom, the transition probability equals one.
Fig. 3. Series of spectra computed for different fs parameter distributions (the central fs transition).

$g = 2.0, \ A/g\beta = -93 \ G, \ D_0/g\beta = 220 \ G, \ E_0/g\beta = 73 \ G, \ \nu = 8900 \ MHz, \ \Delta H_{pp} = 7 \ G$ (the Lorentzian lineshape function). The following values of $\Delta D/g\beta$ and $\Delta E/g\beta$ have been used for different traces (in gauss): (a) 0, 0; (b) 40, 20; (c) 80, 40; (d) 120, 60; (e) 160, 80. In trace (a) the attribution of some of the spectral features to definite critical points is shown. The ciphers 1 to 6 indicate the six types of critical points (see Eq. [11]) for the allowed (A) and forbidden $i = \pm 1$ (F) hfs transitions.

Maintaining $D_0, \Delta D$, and $\Delta E$ constant. The “standard” range $-1 \leq E_0/D_0 \leq 0$ is selected (23). Because the third-order terms in the expression of the resonance field proportional to $D_0 A^2 / H_0^2$ or $E_0 A^2 / H_0^2$ are small (17), changing the sign of $D_0$ or $E_0$ does not involve appreciable variations of the calculated spectra. The fixed parameters in Figs. 3 and 4 are chosen in accordance with those actually observed in the glasses investigated in the present work (see below). Figure 5 illustrates the influence exerted on the spectral shape by the correlation coefficient $r$

Figures 6 and 7 demonstrate the comparison of the computed and experimental spectra. In order to make this procedure possible we subtracted the broad underlying resonances from the latter by means of a computer program, the broad line being simulated by a sextet of Lorentzian lineshape. The parameters of the sextet, i.e., splitting, amplitudes, and widths of the lines, were chosen so as to fit the experimental spectra outside the region of the central fs transition.

The difference spectra for the phosphate and silicate glass are shown in Figs. 6 and 7, respectively, together with the computer-simulated spectra. The parameters of the
FIG. 4. Series of spectra computed for different values of $E_0$ (the central $f$-$s$ transition). $g = 2.0$, $A/g\beta = -93 \text{ G}$, $D_0/g\beta = 220 \text{ G}$, $\Delta D/g\beta = 80 \text{ G}$, $\Delta E/g\beta = 30 \text{ G}$, $\nu = 8900 \text{ MHz}$, $\Delta H_{pp} = 6 \text{ G}$ (the Lorentzian lineshape).

FIG. 5. Series of spectra computed for different values of the correlation coefficient $r$ (the central $f$-$s$ transition). $g = 2.0$, $A/g\beta = -93 \text{ G}$, $D_0/g\beta = 220 \text{ G}$, $E_0/g\beta = 73 \text{ G}$, $\Delta D/g\beta = 80 \text{ G}$, $\Delta E/g\beta = 30 \text{ G}$, $\nu = 8900 \text{ MHz}$, $\Delta H_{pp} = 6 \text{ G}$ (the Lorentzian lineshape).
Fig. 6. Comparison of the experimental and computer-simulated spectra for the zinc phosphate glass ZnO·P₂O₅. The upper trace represents the experimental spectrum after subtracting the broad underlying resonance. The lower trace is the computed best-fit spectrum (for the central fs transition) with \( g = 2.0 \), \( A/gβ = -93 \, \text{G} \), \( D₀/gβ = 220 \, \text{G} \), \( E₀/gβ = -70 \, \text{G} \), \( ΔD/gβ = 80 \, \text{G} \), \( ΔE/gβ = 30 \, \text{G} \), \( ν = 8900 \, \text{MHz} \), \( ΔH_{pp} = 6 \, \text{G} \) (the Lorentzian lineshape).

Fig. 7. Comparison of the experimental and computer-simulated spectra for the potassium silicate glass K₂O·4SiO₂. The upper trace represents the experimental spectrum after subtracting the broad underlying resonance. The lower trace is the computed best-fit spectrum (for the central fs transition) with \( g = 2.0 \), \( A/gβ = -87 \, \text{G} \), \( D₀/gβ = 220 \, \text{G} \), \( E₀/gβ = 70 \, \text{G} \), \( ΔD/gβ = 80 \, \text{G} \), \( ΔE/gβ = 30 \, \text{G} \), \( ν = 8900 \, \text{MHz} \), \( ΔH_{pp} = 7 \, \text{G} \) (the Lorentzian lineshape).
latter are adjusted to obtain the best fit to the experimental difference spectra. The corresponding best-fit spin-Hamiltonian parameters for the two glasses turn out to be the same, with the exception of $A$: $g = 2.0$, $|D_o|/g\beta = 220 \pm 20$ G, $|E_o|/g\beta = 70 \pm 15$ G, $\Delta D/g\beta = 80 \pm 20$ G, $\Delta E/g\beta = 30 \pm 10$ G, $r = 0.0 \pm 0.2$. The values of $A/g\beta$ are $-93 \pm 1$ G for the phosphate glass and $-87 \pm 1$ G for the silicate glass. The limits of error for $D_o$, $E_o$, $\Delta D$, $\Delta E$, and $\Lambda$ indicate the regions outside which a variation of one parameter degrades the fit in such a way that it cannot be restored by any choice of the other parameters. For the correlation coefficient $r$, the limits of error are determined for fixed values of all the other parameters. It should be noted that only the absolute values of $D_o$ and $E_o$ could be determined in glasses.

DISCUSSION

First of all, we consider the effect of the $f_s$ parameter distributions on the shape of the EPR spectra, as illustrated in Fig. 3. The spectrum calculated assuming no parameter distributions (curve a) shows a number of "lines" and "peaks." As $\Delta D$ and $\Delta E$ are increased (curves b through e), these "lines" and "peaks" first broaden, some of them being completely smeared out. However, somewhat unexpected is the fact that, as $\Delta D$ and $\Delta E$ continue to grow, the remaining "lines" and "peaks" cease broadening and even get narrower (curves d through e).

In order to explain such behavior we rewrite Eq. [5] making use of Eq. [5] from the paper by Kneubühl (24), in the form

$$\mathcal{P}(H) = \sum_{M,l,m} \int dH_0 \int ds \cdot p(d, e) \cdot W_{M,m,M-1,m+i}(d, e, \vartheta, \varphi) \times F\left(\frac{H-H_0}{\Delta H_{PP}}\right) / |\text{grad} H_0|,$$

[6]

where $d = D/\Delta D$ and $e = E/\Delta E$ are new nondimensional variables,

$$p(d, e) = \frac{1}{\pi(1 - r^2)^{1/2}} \exp\left\{ -\frac{1}{1 - r^2} [(d - d_0)^2 - 2r(d - d_0)(e - e_0) + (e - e_0)^2] \right\},$$

[7]

and $d_0 = D_0/\Delta D$ and $e_0 = E_0/\Delta E$. $H_0$ is a function of four variables $d, e, \vartheta, \varphi$; hence

$$|\text{grad} H_0| = \left[ (\text{grad}_{d,\vartheta,\varphi} H_0)^2 + \left(\frac{\partial H_0}{\partial d}\right)^2 + \left(\frac{\partial H_0}{\partial e}\right)^2 \right]^{1/2},$$

[8]

where

$$|\text{grad}_{d,\vartheta,\varphi} H_0| = \left[ \left(\frac{\partial H_0}{\partial \vartheta}\right)^2 + \frac{1}{\sin^2 \vartheta} \left(\frac{\partial H_0}{\partial \varphi}\right)^2 \right]^{1/2}.$$  

[9]

The integration in Eq. [6] is performed over $H_0$ and the three-dimensional phase surface $S$ is defined by the condition $H_0(d, e, \vartheta, \varphi) = \text{const}$.

When $\Delta D = \Delta E = 0$, $p(d, e)$ becomes the two-dimensional Dirac delta function $\delta(d - d_0, e - e_0)$. Then, as $\partial H_0/\partial d = \Delta D \partial H_0/\partial D = 0$ and $\partial H_0/\partial e = \Delta E \partial H_0/\partial E = 0$, we obtain that $|\text{grad} H_0| = |\text{grad}_{d,\vartheta,\varphi} H_0|$. Therefore, it is seen from Eq. [6] that the
"lines" or "peaks" in the powder EPR spectra occur at resonance-field values for which $|\text{grad}_{\phi, \varphi} H_0| = 0$, i.e.

$$\frac{\partial H_0}{\partial \theta} = 0, \quad \frac{1}{\sin \theta} \frac{\partial H_0}{\partial \varphi} = 0.$$  \hspace{1cm} [10]$$

Such values of $H_0$ ("critical points") \cite{11} are stationary with respect to the orientation of the paramagnetic ions and therefore the relative number of ions absorbing in the region $H_0$ to $H_0 + dH_0$ is sharply increased. Making use of the resonance conditions developed to the third order of perturbations \cite{16, 17}, we have shown that, for each hfs transition, six different types of critical points occur at definite pairs of angles $\theta_0$ and $\varphi_0$, namely,

1. $\theta_0 = 0$;
2. $\theta_0 = \pi/2, \varphi_0 = \pi/4 \mp \pi/4$ (or $5\pi/4 \mp \pi/4$);
3. $\theta_0 = \pi/2, \sin 2\varphi_0 = \alpha D/E$, where
4. $\theta_0 = \pi/2, \cos 2\varphi_0 = \alpha D/E$, where

$$\alpha = \frac{2 - (2m + i)A/H_0 + 3(2m + i)(1 + i)A^2/DH_0}{18 - 73(2m + i)A/H_0}.$$  \hspace{1cm} \[ \text{(18)} \]

5, 6. $\cos^2 \theta_0 = x, \varphi_0 = \pi/4 \mp \pi/4$ (or $5\pi/4 \mp \pi/4$), where

$$x = \frac{10D \pm 6E - (2m + i)(37D \pm 35E)A/H_0 - 3(2m + i)(1 + i)A^2/H_0}{[18 - 73(2m + i)A/H_0](D \pm E)}. \hspace{1cm} [11]$$

The assignment of some of the "lines" and "peaks" to definite critical points is shown in Fig. 3, curve a. It should be noted that some of the critical points may not be present in the spectra if the conditions $|\cos 2\varphi_0| \leq 1$ and $0 \leq \cos^2 \theta_0 \leq 1$ do not hold, respectively, for the critical points 4 and 5, 6. In addition, the transition probability for the values of $\theta_0$ and $\varphi_0$ corresponding to a given critical point must not be equal to zero or small.

Now let us suppose that $\Delta D \neq 0$ and $\Delta E \neq 0$. If the parameter distributions are small enough to satisfy the conditions

$$\left| \frac{\partial H_0}{\partial D} \right|_c \cdot \Delta D, \left| \frac{\partial H_0}{\partial E} \right|_c \cdot \Delta E \ll \left| \text{grad}_{\phi, \varphi} H_0 \right|_c, \frac{\partial}{\partial \phi} \left| \text{grad}_{\phi, \varphi} H_0 \right|_c,$$  \hspace{1cm} [12]$$

where the index $c$ means that all the derivatives are taken in the critical point ($\theta_0, \varphi_0, D_0, E_0$), the values of $\partial H_0/\partial \delta$ and $\partial H_0/\sin \varphi \cdot \partial \varphi$ increase rapidly as one moves away from the critical point. In this case in Eq. [6] the main contribution in the integral over the surface $S$ containing a critical point occurs from the neighborhood of this point. For the latter, Eq. [8] becomes

$$|\text{grad} H_0|_c = \left[ \left( \frac{\partial H_0}{\partial D} \right)_c^2 (\Delta D)^2 + \left( \frac{\partial H_0}{\partial E} \right)_c^2 (\Delta E)^2 \right]^{1/2}. \hspace{1cm} [13]$$

Therefore the amplitudes of the "lines" and "peaks" decrease and their widths respectively increase in proportion to $|\text{grad} H_0|_c$. This broadening becomes significant when it approaches or exceeds the value of $\Delta H_{pp}$ which includes all other sources of line broadening.
Now, at very broad parameter distributions the probability density function begins to take up the values $D \approx 0$, $E \approx 0$. Once again, using the expression for the resonance field (16, 17), one can easily show that the point $D = E = 0$, $\cos^2 \vartheta = \frac{1}{4}$, $\cos 2\varphi = 0$ is the only "true critical point of a glass," for which $|\text{grad } H_0|$ given by Eq. [8] equals zero. Hence, the ions with $D \approx 0$ and $E \approx 0$ account for the sharp features emerging in the computer simulated spectra at broad parameter distributions (Fig. 3, curves d and e).

The situation is much more complex at intermediate parameter distributions where Eq. [12] is no longer valid, but the probability of finding an ion with $D = E = 0$ is still small. In this case the "lines" and "peaks" do not correspond, generally speaking, to the critical points of a powder. As the "true critical point" is not involved either, positions and sharpness of the spectral features are determined by the properties of the whole integrand of Eq. [6]. Therefore, no definite statement concerning their dependence on the parameter distributions can be made without a complicated analysis.

We proceed next to the dependence of the spectra on the ratio $E_0/D_0$. One may judge from Fig. 4 that even at rather broad parameter distributions ($\Delta D/g\beta = 80 \text{ G}$, $\Delta E/g\beta = 30 \text{ G}$) a strong variation in the spectral shape is produced by an increase of $E_0/D_0$. Note that particularly sensitive to this value is the low-field region of the spectra corresponding to the $|-\frac{1}{2}, -\frac{5}{2}\rangle \leftrightarrow |\frac{1}{2}, -\frac{5}{2}\rangle$ transition. At small $E_0$, when the relative number of ions with $E \approx 0$ is high, sharp features are present in the computed spectra which can be explained as follows. If $D \neq 0$, there is no "true critical point." However, the point $E = 0$, $\vartheta = 0$, which is known to be stationary with respect to the orientation of the paramagnetic ions (see Eq. [11]) is also almost stationary with respect to the variations of the fs parameters. In fact, it can be shown that in this point $\partial H_0/\partial E_0$ equals zero and $\partial H_0/\partial D = -4(2m + i)(1 + i)A^2/H_0^2$ is small (these derivatives are calculated to third order of perturbations).

It should be pointed out that the behavior of the spectra in this case is entirely different from that when only $D_0$ (12) or $\Delta D$ and $\Delta E$ (see Fig. 3) are varied. It is concluded that the computer fitting to the experimental spectra permits the determination of the ratio $E_0/D_0$ (or, rather, its absolute value), as well as the other spin-Hamiltonian parameters for Mn$^{2+}$ in glasses in a unique way and with sufficient accuracy. Furthermore, it is clear that great caution must be exercised in "qualitatively" interpreting the EPR spectra of Mn$^{2+}$ in disordered systems, since, for example, a spectrum with broad parameter distributions can easily be mistaken for one with small values of $D_0$ and $E_0$ (12), some very sharp features being present in both cases. It goes without saying that such misinterpretation is impossible with a computer simulation, because the total aspect of the spectrum in each case is quite different.

Up to this point, our discussion has concerned only the sharp spectral features in the region $g = 2.0$. The nature of the broad underlying resonance has been discussed earlier (5, 10). It was argued by Griscom and Griscom (5) that this resonance cannot arise from the noncentral fs transitions. Now this statement may be supported by direct computer simulations. Figure 8 demonstrates that the contribution of these transitions to the total EPR spectrum is indeed far too small to account for the background resonances observed. The peak-to-peak intensities of the latter relative
to the central sharp features are about 3.3 and 4.0, respectively, for the phosphate and silicate glass (Fig. 1). In view of much broader linewidths the underlying resonances must correspond to a number of sites more than an order of magnitude greater than that of the sharp features. The frequency dependence of the Mn$^{2+}$ EPR spectra, namely, the fact that the broad underlying resonances observed at the X-band collapse at the Ka-band, led Griscom and Griscom (5) to the conclusion that a broad distribution of sites with values of $|D|/h$ ranging from near zero to as high as 7 GHz (ca. 2.5 kG) and $|E_0/D_0| \approx \frac{1}{3}$ is responsible for such behavior, sites with $|D|/h \approx 2$ GHz (ca. 0.7 kG) giving rise to the background resonances. It is interesting to note that our computer simulations unambiguously result in the same $|E_0/D_0| \approx \frac{1}{3}$ value for the sharp $g = 2.0$ features with $|D_0|/g\beta \approx 220$ G (ca. 0.6 GHz). This constraint therefore seems to be of a rather general character in glasses.

However, it follows from the present investigation that, in contrast to the model suggested by Griscom and Griscom (5), the sharp $g = 2.0$ features in X-band spectra do not belong to this continuous broad distribution of sites. Indeed, if this were the case, these features would correspond to the “true critical point” $D_0 = E_0 = 0$ and not to $|D_0|/g\beta = 220$ G, $|E_0|/g\beta = 70$ G, as has been found with our experimental spectra. The fact that the accurate computer fitting to these features gives such values of the fs parameters indicates that we are actually dealing with a particular, rather well-defined site. Since the fs parameter distributions which reflect random distortions of the local environment of Mn$^{2+}$ ions are not too large ($\Delta D/g\beta = 80 \pm 20$ G, $\Delta E/g\beta = 30 \pm 10$ G), one can conclude that the short-range ordering persists to a certain extent at these sites. Thus, a concept of two different types of Mn$^{2+}$ sites in the glasses originally advanced by Tucker (25) is given support.

It follows from this result that, besides the large site-to-site distortion range, different types of sites, for which the short-range order is much better preserved, do exist in glasses.
REFERENCES