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Model calculations for the coordination of Fe^{3+} and Mn^{2+} ions in oxide glasses

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Applying the Newman superposition model to the ligand-field splitting of tetrahedrally and octahedrally coordinated Fe^{3+} and Mn^{2+} ions in glass, we have obtained analytical expressions for the dependence of the spin-Hamiltonian parameters b_2^m (D and E) on the distortion from cubic symmetry of the nearest-neighbor oxygen ligands. Quantitative estimates are made of the magnitude of the angular and/or radial distortion required to produce the frequently observed X-band $g \simeq 4.3$ ESR signal from these ions. The results of the superposition model are compared with those obtained using a point-charge model for the nuclear quadrupole splitting in the Mössbauer spectra of dilute ^{57}Fe in oxide glasses.

I. INTRODUCTION

It is generally acknowledged[1–5] that the X-band $g \simeq 4.3$ ESR signal from dilute $S = \frac{5}{2}$ ions in glass arises from a large second-order ligand-field (crystal-field) splitting in which the ratio of coupling constants $|E/D|$ lies in the vicinity of its maximum or fully rhombic value of $\frac{1}{3}$. Similarly, the Mössbauer spectra of dilute $^{57}Fe^{3+}$ in most glasses exhibit large quadrupole splittings (greater than 0.5 mm/s).[6–9] This implies that large electric field gradients exist at the nuclei which is also consistent with highly distorted environments about the S-state Fe^{3+} ions.

Several specific types of distortions from cubic symmetry have been previously suggested to account for the appearance of the $g \simeq 4.3$ ESR signal. For example, in the case of Fe^{3+} ions that are octahedrally (sixfold) coordinated with oxygen ions, Castner *et al.*[1] have considered that an angular twist of a pair of oxygens lying on an axis perpendicular to a cube symmetry axis is a possible mechanism for giving rise to the $g \simeq 4.3$ ESR signal. A similar type of angular twist of an oxygen pair has been suggested by others[2,3,10] for the case of Mn^{2+} and Fe^{3+} ions that are tetrahedrally (fourfold) coordinated with oxygen ions. Using group-theoretical techniques, Griffith has shown[11] that certain environments that are more symmetric than the overall symmetry group of the site produce the three equally spaced Kramer's doublets that are a prerequisite for the appearance of the $g \simeq 4.3$ ESR signal. The possibility has also been considered that monovalent cations such as Na^+ and Li^+ in the vicinity of the paramagnetic ions in alkali-rich glasses may be responsible for the distorted environments about the paramagnetic ions.[1,2] None of the above distortions, however, have been formulated in an analytical manner that permits a quantitative comparison with the experimental data.

In the present paper we apply the recently developed Newman superposition model[12,13] to the second-order ligand-field splitting of Fe^{3+} and Mn^{2+} ions that are octahedrally and tetrahedrally coordinated with oxygen ions in glass. This model has been successfully employed by Newman and others[12–16] to study the environment of oxygen-coordinated Fe^{3+} and Mn^{2+} ions in single crystals. Applying this model to glass we have obtained analytical expressions for the dependence of the spin-Hamiltonian parameters b_2^m on the magnitude of the distortion from cubic symmetry of the nearest-neighbor oxygens surrounding the paramagnetic ions. Several types of fully rhombic distortions are treated: (1) those involving an angular twist of an oxygen pair about a cube symmetry axis as suggested by Castner *et al.*[1]; (2) those involving a radial displacement of two or three oxygens along the symmetry axes of the ligands; and (3) those involving a variation in the polar angles of an oxygen pair along a cube symmetry axis. In addition, a number of distortions resulting in an axial ligand-field splitting are treated. Quantitative estimates are made of the magnitude of the angular and/or radial distortion required to produce the frequently observed X-band $g \simeq 4.3$ ESR signal from Fe^{3+} and Mn^{2+} ions. The results of the superposition model are then compared with those obtained using a point-charge model for the nuclear quadrupole splitting in the Mössbauer spectra of dilute $^{57}Fe^{3+}$ in oxide glasses.

In our treatment, approximately equal emphases are given to the two cases of tetrahedral and octahedral coordination since both cases have been frequently inferred from experimental measurements. For example, in sodium silicate glass, tetrahedral coordination of Fe^{3+} with oxygen has been inferred from optical and resonance absorption measurements by Steele and Douglas,[17] Kurkjian and Sigety,[18] and Pargamin *et al.*[9] However, in the same type of glass, octahedral coordination of Fe^{3+} with oxygen has been inferred from optical and resonance absorption measurements by Bamford,[19] and Bhat *et al.*,[20] as well as from XPS (x-ray photoemission spectroscopy) and EXAFS (extended x-ray absorption fine structure) measurements by Lam *et al.*[21] Levy *et al.*[22] have employed a mixture of both tetrahedral and octahedral coordinations of Fe^{3+} in calcium silicate glass in order to account for their Mössbauer-effect data.

II. SUPERPOSITION MODEL; FORMALISM

The effect of the nearest-neighbor oxygen ligands on the ESR properties of the Fe^{3+} or Mn^{2+} ions we assume to be represented by a spin Hamiltonian of the general form

$$\mathcal{H} = g\mu_B \vec{\mathrm{H}}\cdot\vec{\mathrm{S}} + b_2^0[S_z^2 - \tfrac{1}{3}S(S+1)] + \tfrac{1}{6}b_2^1(S_xS_z + S_zS_x) + \tfrac{1}{3}b_2^2(S_x^2 - S_y^2) \ , \quad (1)$$

where $g=2$, $S=\frac{5}{2}$, and the parameters b_2^m are the ligand-field (crystal-field) splitting constants related to the symmetry of the ligand field. The Newman superposition model[12–16] assumes that the parameters b_2^m can be expressed as a linear superposition of axially symmetric contributions from the individual ligand ions of the form

$$b_2^m = \bar{b}_2(R_0)\left[\sum_i \left(\frac{R_0}{R_i}\right)^{t_2} K_2^m(\theta_i,\phi_i)\right] \ . \quad (2)$$

In this expression the summation is taken only over those ligand ions involved in the local coordination of the paramagnetic ion, that is, the nearest neighbors of the paramagnetic ion. The $K_2^m(\theta_i,\phi_i)$ are coordination factors given by

$$K_2^0 = \tfrac{1}{2}(3\cos^2\theta_i - 1) \ , \quad (3a)$$

$$K_2^1 = 3\sin 2\theta_i \cos\phi_i \ , \quad (3b)$$

$$K_2^2 = \tfrac{3}{2}\sin^2\theta_i \cos 2\phi_i \ , \quad (3c)$$

where θ_i and ϕ_i are the polar and azimuthal angles, respectively, that specify the location of the ligand ion i in an xyz coordinate system having the paramagnetic ion at its center.[23] The parameter R_0 is a reference distance, and R_i is the radial distance from the paramagnetic ion to the ligand ion i. The intrinsic parameter $\bar{b}_2(R_0)$ and the power-law exponent t_2 are quantities that can be derived, for example, from crystalline-strain data of Fe^{3+} and Mn^{2+} ions in single crystals of MgO.[14]

For coordinations having rhombic symmetry or greater, the spin-Hamiltonian parameters b_2^m of Eq. (1) are properly expressed in a principal-axis coordinate system defined such that b_2^1 is zero and the ratio $|b_2^2/b_2^0|$ is minimized thereby specifying the z axis as the main ESR symmetry axis. In such a coordinate system, b_2^0 and b_2^2 represent the axial and rhombic components of the ligand-field splitting, respectively, and are related to the usual spin-Hamiltonian coupling constants D and E by

$$b_2^0 = D, \quad b_2^2 = 3E \ . \quad (4)$$

Thus the condition $|b_2^2/b_2^0| = 1$ corresponds to $|E/D| = \frac{1}{3}$, where the latter condition has been shown[24,25] to represent the maximum rhombic deviation from axial symmetry in the second-order spin Hamiltonian of Eq. (1). The structural distortion corresponding to this condition is usually termed "fully rhombic."

If the parameters b_2^m are first calculated from Eqs. (2) and (3) in an arbitrary xyz coordinate system, a transformation of coordinates may be required to relate these b_2^m to the proper principal-axis set. A transformation relation that we have frequently applied in Secs. III and IV of this paper is the following: If $b_2^0 = b_2^1 = 0$ and $|b_2^2| > 0$ in an arbitrary xyz coordinate system, then the proper set of parameters $b_2^{m\prime}$ are expressed in an $x'y'z'$ coordinate system obtained by a 90° rotation about the x or y axis, and are related to the original b_2^m by

$$|b_2^{0\prime}| = |b_2^{2\prime}| = |b_2^2/2|, \quad b_2^{1\prime} = 0 \ . \quad (5)$$

In this case $|b_2^{2\prime}/b_2^{0\prime}| = 1$ or $|E/D| = \frac{1}{3}$.

III. TETRAHEDRAL COORDINATION

As a reference we first consider that the local surroundings of the paramagnetic ion consist of four oxygens located on alternate corners of a cube giving rise to point symmetry T_d as shown in Fig. 1(a). In this cubic complex the vertical plane formed by the oxygens above the basal (xy) plane and the paramagnetic ion is perpendicular to the vertical plane formed by the oxygens below the basal plane and the paramagnetic ion. The polar angle of the upper pair of oxygens is $\cos^{-1}(1/\sqrt{3})$, and that of the lower pair of oxygens is $\cos^{-1}(-1/\sqrt{3})$. Application of Eqs. (2) and (3) to this complex gives $b_2^0 = b_2^2 = b_2^1 = 0$; hence and ESR line at $g=2$ is expected.

Two distortions of the above complex that are independently fully rhombic as well as fully rhombic when combined are the following: The first is an angular twist [Fig. 1(b)] produced by rotating the vertical plane containing the upper pair of oxygens with respect to the vertical plane containing the lower pair of oxygens about the z axis, while maintaining the same polar angles as for T_d symmetry. Denoting the angle of rotation as α, and the radial distance of all oxygens from the paramagnetic ion as R_0, the following relationships are obtained from Eqs. (2) and (3) and the transformation relation (5):

$$|b_2^0| = |b_2^2| = 2|\bar{b}_2(R_0)|\sin^2\alpha, \quad b_2^1 = 0 \ . \quad (6)$$

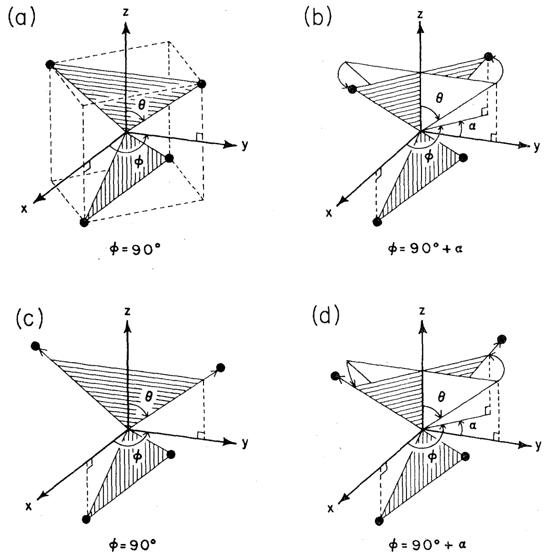

FIG. 1. Tetrahedral complex of oxygens exhibiting (a) cubic symmetry, (b) an angular twist, (c) a radial displacement, and (d) an angular twist combined with a radial displacement of oxygens lying in one vertical plane.

It is seen that the magnitudes of b_2^0 and b_2^2 increase with increasing degrees of twist and that $|b_2^2/b_2^0|=1$ or $|E/D|=\frac{1}{3}$ for any $\alpha\neq 0$. A second fully rhombic distortion is a radial displacement of two oxygens along the axes joining the paramagnetic ion to these oxygens, that is, along the symmetry axes of the ligands. In Fig. 1(c) is shown, for example, the outward radial displacement of the two oxygens above the basal plane. For this type of distortion the polar and azimuthal angles of all oxygens are the same as those for T_d symmetry in Fig. 1(a). Denoting the radial distance of the two displaced oxygens from the paramagnetic ion as R_1, and the radial distance of the two remaining oxygens from the paramagentic ion as R_0, the following relationships are obtained from Eqs. (2) and (3) and the transformation relation (5):

$$|b_2^0|=|b_2^2|=|\bar{b}_2(R_0)|\,|1-(R_0/R_1)^{t_2}|,\quad b_2^1=0\ . \tag{7}$$

Hence $|b_2^2/b_2^0|=1$ or $|E/D|=\frac{1}{3}$ for any $R_1\neq R_0$.

In Fig. 1(d) is shown the simultaneous effect of an angular twist of the upper pair of oxygens through an angle α about the z axis, combined with a radial displacement of these oxygens along their respective ligand axes. For these combined distortions the following expressions for $|b_2^m|$ are obtained from Eqs. (2), (3), and (5):

$$|b_2^0|=|b_2^2|=2|\bar{b}_2(R_0)|\left[\left(\frac{R_0}{R_1}\right)^{t_2}\sin^2\alpha+\frac{1}{2}\left|1-\left(\frac{R_0}{R_1}\right)^{t_2}\right|\right],$$
$$b_2^1=0\ . \tag{8}$$

Again $|b_2^2/b_2^0|=1$ or $|E/D|=\frac{1}{3}$. It is noted that Eq. (8) is not simply the algebraic sum of Eqs. (6) and (7), but reduces to Eq. (6) or Eq. (7), respectively, for the indicated angular twist or radial displacement applied separately.

A third distortion that is independently fully rhombic but not fully rhombic when combined with the two preceding distortions is one that involves a variation in the polar angles of two oxygens. For example, if the polar angles of the two oxygens above the basal plane in Fig. 1(a) are simultaneously increased or decreased by the same amount β (where β is positive for an increase and negative for a decrease), the magnitudes of b_2^m obtained from Eqs. (2) and (3) are given by

$$|b_2^0|=|b_2^2|=|\bar{b}_2(R_0)|\,|\sin^2\beta-2^{1/2}\sin 2\beta|,\quad b_2^1=0\ . \tag{9}$$

Hence $|b_2^2/b_2^0|=1$ or $|E/D|=\frac{1}{3}$ for any $\beta\neq 0$. However, if the above distortion is combined with either the angular twist of Fig. 1(b) or the radial displacement of Fig. 1(c), the ratio $|b_2^2/b_2^0|$ deviates from 1 by an amount that depends on the twist angle α or ratio (R_0/R_1), respectively.

Two distortions of the tetrahedral complex that result in axial symmetry in the spin Hamiltonian of Eq. (1) are the following: The first is a trigonal distortion of the complex of Fig. 1(a) produced if only one oxygen is radially displaced along its ligand axis. In this case the ligand axis of the displaced oxygen is a threefold symmetry axis. Denoting the radial distance of the displaced oxygen from the paramagnetic ion as R_1, and the radial distance of the three remaining oxygens from the paramagnetic ion as R_0, Eqs. (2) and (3) yield

$$|b_2^0|=|\bar{b}_2(R_0)|\left|1-\left(\frac{R_0}{R_1}\right)^{t_2}\right|,\quad b_2^2=b_2^1=0\ . \tag{10}$$

By comparing Eqs. (7) and (10) it is seen that the rhombic term $|b_2^2|$ in Eq. (7) arises solely from the radial displacement of the second oxygen. A second distortion resulting in axial symmetry is a tetragonal distortion corresponding to a uniform compression or elongation of the entire complex of Fig. 1(a) along the z axis. In this case the angles between the z axis and the ligand axes of all four oxygens are simultaneously increased or decreased by the same amount β. Denoting the radial distance of all oxygens from the paramagnetic ion as R_0, and taking β to be positive for a compression and negative for an elongation, the magnitudes of b_2^m obtained from Eqs. (2) and (3) are given by

$$|b_2^0| = 2|\bar{b}_2(R_0)|\,|\sin^2\beta - 2^{1/2}\sin 2\beta|, \quad b_2^2 = b_2^1 = 0 \ . \tag{11}$$

Here $|b_2^0|$ is just twice $|b_2^0|$ in Eq. (9), but the rhombic term b_2^2 vanishes. The latter result reflects the increase in symmetry that occurs if the compression or elongation is applied to both pairs of oxygens instead of one pair as represented by Eq. (9).

IV. OCTAHEDRAL COORDINATION

The local surroundings of the paramagnetic ion in an octahedral cubic complex consist of six oxygens located on three mutually perpendicular axes at $\pm x$, $\pm y$, and $\pm z$, all equidistant from the origin, giving rise to point symmetry O_h as shown in Fig. 2(a). It is again useful to visualize the oxygens as lying in two different vertical planes; one plane containing two oxygens in the basal plane and the single oxygen above the basal plane; and a second vertical plane containing the two remaining oxygens in the basal plane and the single oxygen below the basal plane. For O_h symmetry, these vertical planes are perpendicular. In this case Eqs. (2) and (3) yield $b_2^0 = b_2^2 = b_2^1 = 0$; hence an ESR line at $g = 2$ is expected.

Similar to the case of tetrahedral coordination, there are two distortions of the above complex that are independently fully rhombic as well as fully rhombic when combined. The first is an angular twist [Fig. 2(b)] produced by rotating one vertical plane of oxygens with respect to the other about the z axis, while maintaining the same polar angles as for O_h symmetry. Denoting the angle of rotation as α, and the radial distance of all oxygens from the paramagnetic ion as R_0, the following relationships are obtained from Eqs. (2) and (3) and the transformation relation (5):

$$|b_2^0| = |b_2^2| = 3|\bar{b}_2(R_0)|\sin^2\alpha, \quad b_2^1 = 0 \ . \tag{12}$$

Again it is seen that the magnitudes of b_2^0 and b_2^2 increase with increasing degrees of twist and that $|b_2^2/b_2^0| = 1$ or $|E/D| = \frac{1}{3}$ for any $\alpha \neq 0$. A second fully rhombic distortion is the radial displacement of three oxygens lying in one vertical planae. In Fig. 2(c) is shown, for example, the outward radial displacement of the three oxygens lying in the "upper" vertical plane along the $+z$ and $\pm y$ axes. It is noted that the polar and azimuthal angles of all oxygens are the same as those for O_h symmetry in Fig. 2(a). Denoting the radial distance of the three displaced oxygens from the paramagnetic ion as R_1, and the radial distance of the three remaining oxygens from the paramagnetic ion as R_0, the following relationships are obtained from Eqs. (2) and (3) and the transformation relation (5):

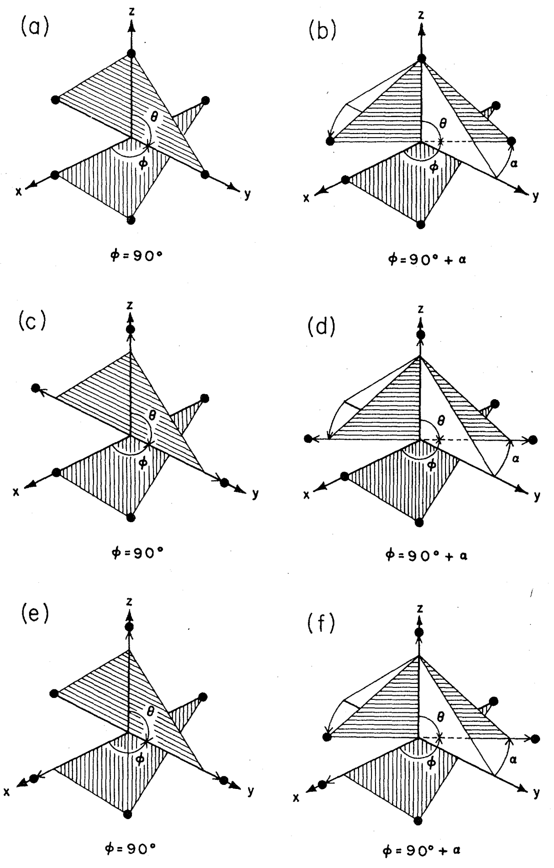

FIG. 2. Octahedral complex of oxygens exhibiting (a) cubic symmetry, (b) an angular twist, (c) a radial displacement, and (d) an angular twist combined with a radial displacement of oxygens lying in one vertical plane, (e) a radial displacement of three oxygens not lying in one vertical plane, and (f) an angular twist of oxygens lying in one vertical plane combined with a radial displacement of three oxygens not lying in one vertical plane.

$$|b_2^0| = |b_2^2| = \tfrac{3}{2}|\bar{b}_2(R_0)|\left|1 - \left(\frac{R_0}{R_1}\right)^{t_2}\right|, \quad b_2^1 = 0 \ . \tag{13}$$

Hence $|b_2^2/b_2^0| = 1$ or $|E/D| = \frac{1}{3}$ for any $R_1 \neq R_0$.

In Fig. 2(d) is shown the simultaneous effect of an angular twist of one vertical plane of oxygens with respect to the other through an angle α about the z axis, combined with the radial displacement of three oxygens in one vertical plane along their respective ligand axes. For these combined distortions the following expressions for $|b_2^m|$ are obtained from Eqs.

(2), (3), and (5):

$$|b_2^0| = |b_2^2| = 3|\bar{b}_2(R_0)| \left[\left(\frac{R_0}{R_1} \right)^{t_2} \sin^2\alpha + \tfrac{1}{2} \left| 1 - \left(\frac{R_0}{R_1} \right)^{t_2} \right| \right],$$

$$b_2^1 = 0 \ . \tag{14}$$

Again $|b_2^2/b_2^0| = 1$ or $|E/D| = \frac{1}{3}$. Also Eq. (14) is not simply the algebraic sum of Eqs. (12) and (13) but reduces to Eq. (12) or Eq. (13), respectively, for the indicated angular twist or radial displacement applied separately. It is noted that the absolute values of b_2^0 in Eqs. (12)–(14) for octahedral coordination are all $\frac{3}{2}$ of their counterparts in Eqs. (6)–(8) for tetrahedral coordination.

The radial displacement of three oxygens that do not lie in one vertical plane results in no ligand field splitting. For example, in Fig. 1(e) is shown the outward radial displacement of three oxygens lying along the $+x$, $+y$, and $+z$ axes. The point symmetry of this distorted complex is C_{3v} with a threefold axis along the [111] direction. Application of Eqs. (2) and (3) to this complex yields $b_2^0 = b_2^2 = b_2^1 = 0$. However, if this distortion is combined with an angular twist of a vertical plane of oxygens through an angle α about the z axis as shown in Fig. 2(f), the following expressions are obtained from Eqs. (2), (3), and (5):

$$|b_2^0| = |b_2^2|$$

$$= \tfrac{3}{2}|\bar{b}_2(R_0)| \left[1 + \left(\frac{R_0}{R_1} \right)^{t_2} \right] \sin^2\alpha, \quad b_2^1 = 0 \ . \tag{15}$$

The combined effect is fully rhombic since $|b_2^2/b_2^0| = 1$ or $|E/D| = \frac{1}{3}$. It is noted that Eq. (15) reduces to the pure angular twist of Eq. (12) if $R_1 = R_0$.

Similar to the case of tetrahedral coordination, we consider several distortions of the octahedral complex that result in axial symmetry in the spin Hamiltonian of Eq. (1). The first is a tetragonal distortion produced if only one oxygen in Fig. 2(a) is radially displaced along its ligand axis, or if two oxygens lying on opposite ends of the same cube symmetry axis are radially displaced the same amount from the paramagnetic ion. Denoting the radial distance of the displaced oxygen(s) from the paramagnetic ion as R_1, and the radial distance of the remaining oxygens from the paramagnetic ion as R_0, Eqs. (2) and (3) yield

$$|b_2^0| = n|\bar{b}_2(R_0)| \left| 1 - \left(\frac{R_0}{R_1} \right)^{t_2} \right|, \quad b_2^2 = b_2^1 = 0 \ , \tag{16}$$

where $n = 1$ for one oxygen and $n = 2$ for two oxygens. A second distortion resulting in axial symmetry is the radial displacement of two oxygens that do not lie on opposite ends of the same cube symmetry axis, that is, the radial displacement of two adjacent oxygens. The point symmetry resulting from this distortion is C_{2v} where the twofold axis contains the origin and the point midway between the two displaced oxygens. Denoting the radial distance of the two displaced oxygens from the paramagnetic ion as R_1, and the radial distance of the four remaining oxygens from the paramagnetic ion as R_0, Eqs. (2) and (3) yield

$$|b_2^0| = |\bar{b}_2(R_0)| \left| 1 - \left(\frac{R_0}{R_1} \right)^{t_2} \right|, \quad b_2^2 = b_2^1 = 0 \ , \tag{17}$$

which is the same as Eq. (16) with $n = 1$. A third distortion resulting in axial symmetry is a trigonal distortion corresponding to a compression or elongation of the entire complex of Fig. 2(a) along the threefold [111] direction. In this case the angles between the [111] direction and the ligand axes of all six oxygens are simultaneously increased or decreased by the same amount β. Denoting the radial distance of all oxygens from the paramagnetic ion as R_0, and taking β to be positive for a compression and negative for an elongation, the magnitudes of b_2^m obtained from Eqs. (2) and (3) are given by

$$|b_2^0| = 3|\bar{b}_2(R_0)|\,|\sin^2\beta - 2^{1/2}\sin 2\beta|, \quad b_2^2 = b_2^1 = 0 \ . \tag{18}$$

Similarly, axial symmetry results if a uniform compression or elongation is applied along the [111] direction to half of the octahedral complex (three oxygens mutually adjacent to the [111] direction). In this case the magnitude of b_2^0 is half of that given in Eq. (18).

V. QUANTITATIVE ESTIMATES: ESR

The effect of the fully rhombic distortions represented by Eqs. (6)–(9) and (12)–(15) on the ESR spectra of ions with $S = \frac{5}{2}$ will vary depending on the relative magnitudes of b_2^0 and $h\nu$, where ν is the microwave frequency in an ESR experiment. In general, any value of $b_2^0 \neq 0$ (under the constraint $|b_2^2/b_2^0| = 1$) will give an isotropic resonance associated with transitions within the middle Kramer's doublet.[5] However, this isotropic resonance will have an effective g value substantially less than 4.3 unless $|b_2^0| \gtrsim 0.6\, h\nu$.[26] For small ligand-field splittings, $|b_2^0| << h\nu$, resonances only in the vicinity of $g \simeq 2$ are expected. In a sample where there is a spread in the magnitude of b_2^0 ranging from zero to $\sim 0.6\, h\nu$ or greater, the overall spectrum is expected to display resonances in the vicinity of both $g \simeq 2$ and $g \simeq 4.3$. Hence, we consider that the fully rhombic distortions of Eqs. (6)–(9) and (12)–(15) must satisfy the relation $|b_2^0| \gtrsim 0.6\, h\nu$ in order to account for the isotropic $g \simeq 4.3$ ESR signal in glass. At a typical X-band microwave frequency of 9.0 GHz, this relation is given by $|b_2^0| \gtrsim 0.18\ \text{cm}^{-1}$.

In the Newman superposition model, the critical parameters are the intrinsic parameter $\bar{b}_2(R_0)$ and the power-law exponent t_2. These parameters depend not only on the paramagnetic ion and its distance from the ligand anions, but also on the ligand anion and cation species of the host matrix. For rare-earth Gd^{3+} ions contained in MO_4 host matrices, it has been shown[27] that there is an empirical correlation between the values of $\bar{b}_2(R_0)$ and the electronegativities (Allred-Rochow) of the matrix cations M. As yet no such correlation can be determined for Fe^{3+} and Mn^{2+} in oxide matrices due to the sparsity of experimental data. The most reliable current estimates of $\bar{b}_2(R_0)$ and t_2 in these systems, with R_0 in the range $1.9\ \text{Å} \lesssim R_0 \lesssim 2.1\ \text{Å}$, are derived from crystalline-strain data of Fe^{3+} and Mn^{2+} in MgO.[14–16] These depend on R_0 and t_2 in the following manner: for Fe^{3+}

$$|\bar{b}_2(R_0)| = (0.412\,\text{cm}^{-1})\left(\frac{2.101\ \text{Å}}{R_0(\text{Å})}\right)^{t_2}, \quad t_2=8\ , \tag{19}$$

and for Mn^{2+}

$$|\bar{b}_2(R_0)| = (0.157\ \text{cm}^{-1})\left(\frac{2.101\ \text{Å}}{R_0(\text{Å})}\right)^{t_2}, \quad t_2=7\ . \tag{20}$$

As a quantitative estimate of the smallest separation between the paramagnetic ion and its nearest oxygen neighbors in glass, we take $R_0 = 1.9\ \text{Å}$. Then Eqs. (19) and (20) reduce to $|\bar{b}_2(1.9\ \text{Å})| = 0.921\ \text{cm}^{-1}$ for Fe^{3+}, and $|\bar{b}_2(1.9\ \text{Å})| = 0.317\ \text{cm}^{-1}$ for Mn^{2+}.

The minimum values of the distortion parameters α, $R_1/R_0 > 1$, and β that are consistent with the above intrinsic parameters, power laws and the relation $|b_2^0| \geq 0.18\ \text{cm}^{-1}$ applied to Eqs. (6), (7), (9), (12), and (13) are listed in Table I. These values represent the smallest distortions able to account for the isotropic $g \simeq 4.3$ ESR signal at 9.0 GHz employing the currently available quantities pertinent to the superposition model. It is noted that some of the distortion parameters are quite large, particularly the parameter α associated with an angular twist. It is also noted that the minimum distortion parameters for Fe^{3+} are considerably smaller than the corresponding ones for Mn^{2+}. This is a consequence of the larger intrinsic parameter $|\bar{b}_2(1.9\ \text{Å})|$ employed for Fe^{3+} compared with that employed for Mn^{2+}.

VI. NUCLEAR QUADRUPOLE SPLITTING: ^{57}Fe

The magnitude of the quadrupole splitting (E_{QS}) in the Mössbauer spectrum is proportional to the electric field gradient (EFG) which interacts with the quadrupole moment of the nucleus. Since $I = \frac{3}{2}$ for the ^{57}Fe nucleus, the E_{QS} can be expressed as[28]

$$E_{QS} = \tfrac{1}{2} V_{zz} e Q (1 + \eta^2/3)^{1/2}\ , \tag{21}$$

where e is the protonic charge, Q is the quadrupole moment of ^{57}Fe (0.21 b),[29] η is the asymmetry parameter given by

$$\eta = (V_{xx} - V_{yy})/V_{zz}\ , \tag{22}$$

and V_{xx}, V_{yy}, and V_{zz} are the three components of the diagonal EFG tensor.

For the S-state Fe^{3+} ion, the contribution to the EFG from uncompensated valence electrons will be negligibly small compared with that arising from external charges. In this case the EFG may be expressed as a linear sum of contributions from external monopoles, dipoles, and quadrupoles. For simplicity, we shall assume that only monopole (point-charge) contributions are important. Hence, V_{zz} and η can be written as[28]

$$V_{zz} = e(1-\gamma_\infty) \sum_i \frac{Z_i}{R_i^3}(3\cos^2\theta_i - 1) \tag{23}$$

and

$$\eta = \frac{e(1-\gamma_\infty)}{V_{zz}} \sum_i \frac{Z_i}{R_i^3}(3\sin^2\theta_i \cos 2\phi_i)\ , \tag{24}$$

TABLE I. The minimum values of the distortion parameters α, $R_1/R_0 > 1$, and β that are consistent with an isotropic $g \simeq 4.3$ ESR signal from Fe^{3+} and Mn^{2+} ions at 9.0 GHz, calculated from the Newman superposition model with $R_0 = 1.9\ \text{Å}$.

	Tetrahedral			Octahedral	
Ion	α Eq. (6)	R_1/R_0 Eq. (7)	β Eq. (9)	α Eq. (12)	R_1/R_0 Eq. (13)
Fe^{3+}	18.2°	1.03	4.08°	14.8°	1.02
Mn^{2+}	32.2°	1.13	12.9°	25.8°	1.07

where γ_∞ is the Sternheimer antishielding factor (-9.14 for $^{57}\mathrm{Fe}^{3+}$),[30] and $Z_i=-2$ for the neighboring oxygen ions.

The parameters V_{zz} and η are conveniently written in terms of the superposition-model reference distance R_0 and coordination factors $K_2^m(\theta_i,\phi_i)$ of Eq. (3) as

$$V_{zz}=2Ze(1-\gamma_\infty)\left(\frac{1}{R_0^3}\right)\left[\sum_i\left(\frac{R_0}{R_i}\right)^3 K_2^0(\theta_i,\phi_i)\right] \qquad (25)$$

and

$$\eta=\frac{\sum_i\left(\frac{R_0}{R_i}\right)^3 K_2^2(\theta_i,\phi_i)}{\sum_i\left(\frac{R_0}{R_i}\right)^3 K_2^0(\theta_i,\phi_i)}\ . \qquad (26)$$

A comparison of η of Eq. (26) with the ratio $|b_2^2/b_2^0|$ obtained from Eq. (2) with $m=2,0$ and $t_2=3$, shows that the condition $\eta=1$ corresponds to $|b_2^2/b_2^0|=1$ or $|E/D|=\frac{1}{3}$; and that $\eta=0$ corresponds to $|b_2^2/b_2^0|=|E/D|=0$. Insertion of V_{zz} of Eq. (25) into Eq. (21) yields

$$E_{\mathrm{QS}}=Ze^2Q(1-\gamma_\infty)\left(1+\frac{\eta^2}{3}\right)^{1/2}\left(\frac{1}{R_0^3}\right)\times\left[\sum_i\left(\frac{R_0}{R_i}\right)^3 K_2^0(\theta_i,\phi_i)\right]\ . \qquad (27)$$

It is noted that the summation in square brackets in Eq. (27) is identical to that in Eq. (2) with $m=0$ and $t_2=3$. Hence, the magnitude of the E_{QS} resulting from the distortions treated in Secs. III and IV can be readily evaluated by substituting the ratios $|b_2^0/\bar{b}_2(R_0)|$ previously determined in Eqs. (6)–(18) with $t_2=3$ for the summation in Eq. (27).

In Table II are shown the minimum values of the distortion parameters α, $R_1/R_0>1$ and β calculated from Eq. (27) with $R_0=1.9$ Å and $\eta=1$ that are consistent with $|E_{\mathrm{QS}}|\geqslant 0.5$ mm/s due to the nearest-neighbor oxygens. It is noted that the *angular* minimum distortion parameters α and β in Table II are in good agreement with those obtained from the superposition model for Fe^{3+} in Table I, indicating that for angular distortions the observation of a prominent $g\simeq 4.3$ Fe^{3+} ESR signal at 9.0 GHz is consistent with a $|E_{\mathrm{QS}}|\gtrsim 0.5$ mm/s in the Mössbauer spectrum. The *radial* minimum distortion parameters R_1/R_0 in Table II are substantially larger than their ESR counterparts for Fe^{3+} in Table I. It should be remembered that distortions involving radial displacements produce different effects on the magnitude of E_{QS} compared with b_2^0 due to the different power-law exponents employed for the two splittings ($t_2=3$ for $|E_{\mathrm{QS}}|$ and $t_2=8$ for $|b_2^0|$). It can be concluded from the formal similarity between Eqs. (2) and (27) that if the same ligand-field power-law exponent is employed for both splittings, then $|E_{\mathrm{QS}}|$ would be directly proportional to $|b_2^0|$ for all types of constant-η distortions.

VII. DISCUSSION

A comparison of the minimum distortion parameters for the two types of ions Fe^{3+} and Mn^{2+} in Table I indicates that there is a wide range in the magnitude of the distortion parameters over which the condition for the appearance of the isotropic $g\simeq 4.3$ resonance is satisfied by Fe^{3+} ions but not by Mn^{2+} ions. From this it can be inferred that if two samples of the same host glass are prepared, one containing dilute Fe^{3+} ions and the other dilute Mn^{2+} ions, and if both samples contain approximately the same broad distribution of fully-rhombic distortions at the sites of the paramagnetic ions, then the relative intensity of the $g\simeq 4.3$ resonance compared with the $g\simeq 2$ resonance should be larger for Fe^{3+} than for Mn^{2+}. The paramagnetic ions are here assumed to be so dilute that one may neglect any $g\simeq 2$ resonance arising from pairs, triplets and higher-order clusters of paramagnetic ions via spin-spin interactions.[31,32] Under this assumption, the results of the superposition model are in good agreement with the experimental spectra of dilute Fe^{3+} and Mn^{2+} ions given by Loveridge and Parke,[2] Griscom and Griscom,[3] and Schreurs.[4] These spectra all indicate that for a given

TABLE II. The minimum values of the distortion parameters α, $R_1/R_0>1$, and β that are consistent with $|E_{\mathrm{QS}}|\geqslant 0.5$ mm/s due to nearest-neighbor oxygens, calculated from a point-charge model for the E_{QS} in the Mössbauer spectrum of $^{57}\mathrm{Fe}$ with $R_0=1.9$ Å.

		Tetrahedral		Octahedral	
Nucleus	α Eq. (6)	R_1/R_0 Eq. (7)	β Eq. (9)	α Eq. (12)	R_1/R_0 Eq. (13)
$^{57}\mathrm{Fe}$	19.9°	1.09	4.88°	16.2°	1.06

type of host glass the relative intensity of the $g \simeq 4.3$ resonance compared with the $g \simeq 2$ resonance is larger for Fe^{3+} than for Mn^{2+}.

As previously mentioned, the frequency dependence of the isotropic $g \simeq 4.3$ resonance is governed by the relation $|b_2^0| \geq 0.6 h\nu$. This relation may not be satisfied over the full range of the distortion parameters if the microwave frequency ν is very large. For example, at the Q-band microwave frequency of 36 GHz, the relation $|b_2^0| \geq 0.6\, h\nu$ ($=0.72$ cm^{-1}) is not satisfied by the radial distortion of Eq. (7) over the full range of the distortion parameter R_1/R_0 ($1 \leq R_1/R_0 \leq \infty$) for Fe^{3+} ions with nearest oxygens at $R_0 = 1.95$ Å. In general the relation $|b_2^0| \geq 0.6\, h\nu$ readily precludes the observation of the $g \simeq 4.3$ resonance as the microwave frequency is increased. This result also agrees with the experimental observation that the $g \simeq 4.3$ resonance disappears when the microwave frequency is increased from X band to Q band.[2–4]

The magnitude of the nuclear E_{QS} of ^{57}Fe may also be investigated for extreme values of the distortion parameters. For example, taking $R_0 = 1.9$ Å, the angular twist of a pair of oxygens in a tetrahedral complex represented by Eq. (6) results in a planar configuration of oxygens for the extreme value $\alpha = 90°$. The resultant magnitude of the E_{QS} obtained from Eq. (27) is 4.3 mm/s. Since quadrupole splittings of this magnitude are not observed experimentally,[6–9] it is reasonable to conclude that the distortion parameters are distributed closer to the values given in Tables I and II. This conclusion is still consistent with the disappearance of the $g \simeq 4.3$ ESR signal when the microwave frequency is increased.

In at least two instances the superposition model predicts a dependence of $|b_2^0|$ and $|b_2^2|$ on the distortion that is different from that considered by other authors. First, in the case of an angular twist of a pair of oxygens about a cube symmetry axis in an octahedral complex as shown in Fig. 2(b), Eq. (12) yields a dependence of $|b_2^2|$ on the twist angle α that is proportional to the second power of $\sin\alpha$. This result differs from that of Castner *et al.* (see footnote 8 of Ref. 1), who suggest that $|b_2^2|$ is proportional to the first power of $\sin\alpha$ [$|\cos(\alpha + 90°)| = |\sin\alpha|$]. Secondly, in the case of a radial displacement of two adjacent oxygens in an octahedral complex resulting in C_{2v} symmetry, Eq. (17) yields axial symmetry for the spin Hamiltonian of Eq. (1), $|b_2^0| > 0$, $b_2^2 = b_2^1 = 0$. This result differs from that of Loveridge and Parke (see Table I of Ref. 2) who classify this type of distortion as fully rhombic ($|D| = 0$, $|E| >> 0$).

It is pointed out that the analytical expressions for $|b_2^m|$ [Eqs. (6)–(18)] are applicable to S-state ions other than Fe^{3+} and Mn^{2+}, and to situations where the ligands are other than oxygens. These expressions are also not restricted in principle to glassy networks and hence may be applied to crystalline materials where the distortions at the sites of the paramagnetic ions are similar to those treated here. In all cases, however, the reliability of quantitative estimates will depend on the accuracy of the values employed for $|\bar{b}_2(R_0)|$ and t_2. It should be mentioned that the choice of fully rhombic distortions treated in the present paper was made primarily for ease of calculation and is not intended to exhaust the possibilities of distortions satisfying $|b_2^2/b_2^0| \simeq 1$. We specifically mention that the $g \simeq 4.3$ resonance observed from Fe^{3+} in ferrichrome A,[25] which is known to be associated with an octahedral oxygen complex with an apparent threefold symmetry axis, may not be generable from the particular types of distortions treated here.

VIII. SUMMARY

Employing the Newman superposition model for the ligand-field splitting of paramagnetic S-state ions, we have obtained analytical expressions for the spin-Hamiltonian parameters $|b_2^0|$ and $|b_2^2|$ as a function of several fully rhombic and axial distortions from cubic symmetry at the sites of the paramagnetic ions. These expressions are then applied to Fe^{3+} and Mn^{2+} ions in oxide glasses using the intrinsic parameters $|\bar{b}_2(R_0)|$ and power-law exponents t_2 derived from crystalline-strain data of MgO:Fe^{3+}; Mn^{2+}. It is found that the magnitudes of the fully-rhombic distortions required to account for the $g \simeq 4.3$ resonance in glass are consistent with experimental data regarding: (1) the relative intensity of the $g \simeq 4.3$ versus $g \simeq 2$ resonance for Fe^{3+} ions compared with Mn^{2+} ions at an X-band microwave frequency of 9.0 GHz, and (2) the disappearance of the $g \simeq 4.3$ resonance at Q-band microwave frequencies.

The nuclear quadrupole splitting in the Mössbauer spectra of ^{57}Fe is formulated using a point-charge model that permits direct substitution of the results obtained from the superposition model. The magnitudes of the fully rhombic distortions are then calculated assuming that the quadrupole splitting from the nearest-neighbor oxygens is at least 0.5 mm/s. The point-charge model yields angular minimum distortion parameters that are in good agreement with those obtained from the superposition model. However, the radial minimum distortion parameters behave substantially different than their ESR counterparts due to the different power-law exponents used for the two types of splittings.

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