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The dynamic Jahn–Teller effect in Cu(II) doped MgO

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The electron paramagnetic resonance spectra of Cu(II) doped MgO single crystals have been re-examined in detail within the framework of a dynamic Jahn–Teller effect. The experimental 1.8 K X-band spectra can be modeled in terms of a cubic spin Hamiltonian operating within the set of four Kramers doublets corresponding to the lowest vibronic energy levels of an $E \otimes e$ Jahn–Teller problem. This “four state” model must also include vibronic (Ham) reduction factors and a random distribution of the crystal strain. It was found to be important to treat the Zeeman, hyperfine, quadrupole, tunneling, and strain terms without recourse to perturbation theory or other approximations and this has been carried out using the eigenfield method. We find that the first excited singlet is of $A_2$ symmetry, indicating that the CuO$_6$ center has the expected $E \otimes e$ Jahn–Teller potential energy surface with three equivalent minima at tetragonally elongated octahedral geometries. Small random crystal strains have a dominant influence on the spectra and we find that the major features can be reproduced by averaging over the strain in the angular direction $\phi_2$ with a small magnitude centered about zero. Details of the strain broadening require a distribution of strains centered at zero with a larger spread; however, the use of a single intrinsic linewidth could not account for all linewidth features. Our analysis also differs from that of previous workers in that different hyperfine values ($A_1 = -20.0 \times 10^{-4}$ and $A_2 = -86.0 \times 10^{-4}$ cm$^{-1}$) are required as well as a nuclear quadrupole term ($P_2 = +8.75 \times 10^{-4}$ cm$^{-1}$) to account for the observed structure and the angular dependence. The transitions within the lowest excited singlet are observed directly, giving an estimate of the tunneling splitting as $\sim 4 \times 10^{-4}$ cm$^{-1}$. These parameter values are related to the intrinsic Jahn–Teller coupling parameters of the potential energy surface. We conclude that the Cu(II)/MgO system can be described as an almost pure dynamic Jahn–Teller case, with most spectral features accounted for by using a single isolated $\Gamma_8(7E)$ vibronic state. © 2009 American Institute of Physics. [DOI: 10.1063/1.3086038]

I. INTRODUCTION

The electron paramagnetic resonance (EPR) of the Cu(II) doped MgO system is a classic case where the dynamic Jahn–Teller effect is present even at very low temperatures.1 The study of this system has played a pivotal role in the development of many important aspects of Jahn–Teller theory including the transition between dynamic and static effects, the use of Ham reduction factors, and the effect of small random crystal strain.2

The spectrum was first studied by Orton et al.3 who noted that an isotropic spectrum at 4.2 K was replaced by an anisotropic spectrum at 1.2 K. Later work by Coffman4 found that the angular variations of the low temperature spectrum within the (100) and (110) planes were not consistent with that of a static tetragonal ion but followed the behavior expected for a tunneling quartet ($\Gamma_8$) state with the anisotropic component reduced by a factor of $\frac{1}{2}$. This reduction was reformulated in what has become to be known as the Ham vibronic reduction factor $q$, which takes a limiting value of $\frac{1}{2}$ for strong linear Jahn–Teller coupling.5,6

A seminal study by Reynolds et al.7 presented the low temperature angular variation of Cu(II) in MgO and CaO together with a model set out by Ham7 that included the important effect of coupling to a nearby vibronic singlet by the crystal strain. This became known as the “three state” model and many subsequent papers8–11 refined and applied this model to a number of related Jahn–Teller systems. The electronic ground state of the $d^9$ configuration of the Cu(II) ion in a cubic host can be described as a vibronic doublet $^2E$ state with a nearby excited vibronic singlet due to a strong $E \otimes e$ Jahn–Teller effect and higher order coupling that produces three minima.12 It was found that all three orbital states had to be included together with the small random strains of the crystal to fully describe departures of the spectrum from the expected cubic anisotropy and the observed anisotropic line shape. In addition the model allows the identification of the symmetry of the lowest excited vibronic singlet level. This in turn has the important geometric consequence that it establishes the form of the underlying potential energy surface; a lowest singlet of $A_1$ ($A_2$) symmetry corre-

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sponds to minima on the Jahn–Teller surface at tetragonally compressed (elongated) geometries. In this manner, Reynolds et al.\textsuperscript{7} established that Cu(II) in CaO is compressed, while Cu(II) in MgO is elongated. Here it is understood that the terms compression and elongation refer to the positions of the minima on the underlying potential energy surface, over which maximum vibronic probability density lies, not to a static compressed or elongated octahedral geometry of the CuO\textsubscript{6} center.

The three state model and its multistate extensions with generalized reduction factors\textsuperscript{11} went some way in explaining the line shape of the EPR spectra due to strain broadening. However, while this approach has been used with success for the related systems such as Cu(II)/CaO,\textsuperscript{7} Ag(II)/CaO, and Ag(II)/MgO,\textsuperscript{9} a satisfactory explanation for many aspects of the original Cu(II)/MgO spectrum has been lacking. It was found that a value for the ratio of the mean strain to the tunneling splitting $\delta/\Delta_2 \sim 0.12$ which was given with qualification,\textsuperscript{7} as the details of the spectrum could not be fully described. In particular these include the asymmetric line shapes observed for $H/||111)$, the lack of hyperfine splitting at $H/||111)$, and the angular variation of the hyperfine structure. An explanation was proposed that the barrier heights between the equivalent minima were small so that the splitting of the excited $A_1$, $A_2$ vibronic singlet states was also small. (In the limit of linear Jahn–Teller coupling the $A_1/|A_2$ states are degenerate.\textsuperscript{12}) The failure to fully reproduce the spectra was then proposed to be due to the failure of the three state model of taking into account the coupling with both and not just one of these singlet states. This proposal has appeal as it has been argued that in the continuous lattice of MgO, the anharmonicity of the bond stretches of a dopant will be small.\textsuperscript{13,14} These led to further studies which generalized the three state model to incorporate higher states and additional reduction parameters\textsuperscript{11} as well as an approach that utilized the vibronic wave functions directly.\textsuperscript{15}

In this work, the intention is to re-examine the Cu(II)/MgO spectrum and its analysis in detail. After a brief description of the Jahn–Teller formalism and our numerical approach, we present new X-band EPR spectra for rotations in the plane perpendicular to the (110) direction, from (001) to (110). These spectra have not previously been given in such resolution and detail and our results differ in some aspects of those previously given. We are also mindful that previous interpretations used a perturbative hierarchy, where a number of the quantities—the Zeeman, hyperfine, strain, and tunneling splitting—may be of similar magnitude in this system. In particular, it has been previously assumed the random strain is always large compared to the Zeeman interaction so that each Kramers doublet could be treated separately. This assumes that the random strain distribution is centered about a nonzero mean position $\delta$, which may not be the case in this cubic crystal system. The eigenfield method allows us to treat all terms in the Hamiltonian exactly without any particular assumptions and applies equally well independent of field orientation and microwave frequency.

We find that the observed spectra can be reproduced quantitatively using a four state model, albeit with substantially different values for the hyperfine and strain parameters to those previously reported.\textsuperscript{7} We also find that a nuclear quadrupole term is required to account for the hyperfine structure. It is shown that these parameters are fully consistent with those of related static Jahn–Teller systems and with the higher temperature isotropic spectra. Further, we show that the random strain in this system is much smaller than previously assumed and is distributed about a zero mean value. This implies that the strain is not required to modify the anisotropic cubic parameters; these features of the spectrum could equally be found from a using a “two state” $^2E$ basis. However, the strain coupling to the excited singlets is required to account for details in the relative line broadening of the various hyperfine lines. Following this we discuss the implications of the spin Hamiltonian parameter values for the molecular properties of this system.

II. EXPERIMENTAL

Single crystals of Cu(II) doped MgO where grown in an arc fusion furnace by Escete Single Crystal Technology B.V. (The Netherlands). The Cu(II) concentration was $5 \times 10^{-3}$ mol %. The sample is known to also contain impurities of Fe(II) (Ref. 13) and Mn(II). The EPR spectra were acquired on a Bruker ELEXYSYS X-band spectrometer with a microwave frequency of 9.39759 GHz. Samples were cooled with an Oxford Instruments XBR 910 cryostat and manipulated with an automatic goniometer.

III. THEORY

A. The $^2E$ spin Hamiltonian

In the octahedral double point group, the $^2E$ electronic state transforms as the fourfold degenerate $\Gamma_8$ irreducible representation.\textsuperscript{16} The calculation of the energy levels and $g$ values for a $\Gamma_8$ state can proceed using a fictitious $S=3/2$ basis.\textsuperscript{12} In this case there will be terms involving $S_i^1H_i$, which are small for a true spin 3/2 system but will be large in the present case for a $\Gamma_8$ state arising from an $^2E$ state.\textsuperscript{17} A mathematically equivalent and more natural basis for a $\Gamma_8$ state based on an orbital doublet $^2E$ is to use the orbital operators $U_\theta$ and $U_\phi$ defined as\textsuperscript{17}

$$
I = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad U_\theta = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad U_\phi = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix},
$$

(1)

$$
U_{A_2} = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.
$$

For an isolated $\Gamma_8$ state spin Hamiltonian will be of the form

$$
H = G_t I + p G_{A_2} U_{A_2} + q (G_\theta U_\theta + G_\phi U_\phi),
$$

(2)

where $G_{A_2}$, $G_\theta$, $G_\phi$, and $G_t$ are functions of the $S=1/2$ spin operators transforming as the $A_1$, $A_2$, $E_\theta$, and $E_\phi$ irreducible representations, respectively, of the octahedral point group and $p$ and $q$ are “reduction factors.” (Unfortunately $A_2$ is also the symbol commonly used as a component of the hyperfine coupling. The two cases are distinguished by context.) The
spin Hamiltonian in Eq. (2) operates on the ground state vibronic wave functions \( \Psi_\theta \), \( \Psi_e \) which can be expressed as products of electronic \( \psi_\theta \), \( \psi_e \) and an expansion of the two dimensional vibrational states \( \phi_i \) of appropriate symmetry,

\[
\Psi_\theta = \sum_i (\phi_\theta \phi_i) \psi_\theta + (\phi_\theta \phi_e) \psi_e,
\]

\[
\Psi_e = \sum_i (-\phi_{2i} + \phi_i) \psi_\theta + (\phi_{1i} + \phi_{2i}) \psi_e.
\] (3)

By integrating out the vibrational parts of the wave function, the vibronic reduction (Ham) factors \( p \) and \( q \) can be found:

\[
p = i\langle \Psi_\theta | U_{A2} | \Psi_e \rangle
\]

\[
= \sum_i \left( \langle \phi_{1i} | \phi_{1i} \rangle + \langle \phi_{2i} | \phi_{2i} \rangle - \langle \phi_{3i} | \phi_{3i} \rangle \right),
\]

\[
q = -\langle \Psi_\theta | U_{A1} | \Psi_e \rangle = \sum_i \left( \langle \phi_{2i} | \phi_{3i} \rangle - \langle \phi_{3i} | \phi_{2i} \rangle \right).
\] (4)

The reduction factors represent the change in the expectation values of the quantities in Eq. (2) which operate on an electronic basis due to vibronic coupling. In the absence of vibronic coupling, \( p = q = 1 \). To illustrate how the vibronic energy levels and reduction factors relate to the Jahn–Teller potential energy surface we briefly describe the \( E \otimes e \) potential surface and some numerical results.

The \( E \otimes e \) Jahn-Teller vibronic Hamiltonian has the form:

\[
H_{JT} = p \frac{1}{2} (Q_0^2 + Q_e^2) I + g((Q_e^2 - Q_0^2) U_\theta + 2Q_0 Q_e U_e) + K_1 Q_0^2 Q_e^2 - 3Q_e^4 U_e,
\] (5)

where \( k, g \) are the first and second order Jahn–Teller coupling constants and \( K_1 \) the anharmonic vibrational constant. Dimensionless units are used so the resulting energies are in units of the harmonic wavenumber, \( h\omega \), of the vibrational basis. A point on the energy surface due to the first two terms as a function of the Jahn–Teller active vibrational coordinates \( Q_0, Q_e \) is known as the “Mexican hat” potential energy surface as shown in Fig. 1.

When the kinetic energy terms are included in Eq. (5) the equations can be solved in a vibronic basis consisting of the product of two dimensional harmonic oscillator functions and the electronic states \( \psi_\theta, \psi_e \). The resulting energy levels as a function of first order coupling are shown in Fig. 1(a). The cylindrical symmetry of the potential surface results in a minimum that traces a circle in the angular direction. Transversing this minimum results in combinations of the \( Q_0, Q_e \) coordinates which describe an internal rotation and the energy levels are approximately characterized by combinations of a harmonic vibrational interval and rotational levels proportional to the square of an odd half-integral quantum number. Such an internal rotational motion has a dynamic mixture of the \( \psi_\theta, \psi_e \) electronic states.

The lowest vibronic level is of \( E \) symmetry while the next level is an accidentally degenerate pair of \( (A_1, A_2) \) symmetry. This degeneracy is removed by the second and higher terms in Eq. (5). Figure 1(b) shows the potential surface and the energy levels as a function of the second order Jahn–Teller coupling. The higher order coupling creates barriers between three equivalent minima as shown in Fig. 1(b) and the \( A_1/A_2 \) states split such that one approaches energy of the lowest \( E \) state while the other increases to approach the energy of a higher \( E \) state. The near triple degeneracy of the lower \( E \) and the \( A \) states reflect vibronic wave functions that are localized at the positions of the three minima, while the small \( E-A \) energy separation is the tunneling splitting cause by the barrier to free rotation. The first excited singlet is an \( A_2 \) (\( A_1 \)) state for minima at the positions \( \phi = 0^\circ, 180^\circ \) and \( 120^\circ, 240^\circ \) (\( 60^\circ, 180^\circ, 300^\circ \) and this is determined by whether the product of the first and second order coupling constants \( k \cdot g \) is positive (negative). When the first excited singlet is of \( A_2 \) (\( A_1 \)) symmetry, this corresponds to each of the three minima having a tetragonal elongated (compressed) geometry.

Figure 1 also shows the variation of the vibronic reduction factors \( p \) and \( q \) as a function of the first and second order coupling constants, and some numerical values have been included as supplementary tables S1,19 in the limit of large first order coupling \( p \to 0 \) and \( q \to \frac{1}{2} \). Choosing a particular value of \( k = 3 \), Fig. 1(b) shows the variation of \( p \) and \( q \) with the second order coupling. The factor \( p \) is further reduced and \( q \) reduces slightly below \( \frac{1}{2} \). This behavior has been previously noted.20 Of more importance is the effect on the energies of the excited \( A_1/A_2 \) states. As the second order coupling constant \( g \) increases, the barrier heights also increase, and the energy of the \( A_2 \) singlet falls to approach that of the \( E \) vibronic ground state. The energy separation between these states, \( \Delta_e \), becomes small, so that the \( E \) and \( A_2 \) vibronic states become coupled by random strain and both must be included in the spin Hamiltonian. Here we include both the \( A_2 \) and \( A_1 \) singlets in the spin Hamiltonians as we show that both are required to fully explain the observed strain broadened spectra.

The spin Hamiltonian then takes the matrix form with respect to the electronic basis \( \psi_{A_1}, \psi_{A_2}, \psi_\theta, \psi_e \):

\[
\begin{pmatrix}
\Delta_1 + G_{A_1} & 0 & r'G_\theta & r'G_e \\
0 & \Delta_2 + G_{A_2} & rG_\theta & -rG_\theta \\
r'G_\theta & rG_e & G_{A_1} - qG_\theta & qG_e \\
r'G_e & -rG_\theta & qG_e & G_{A_2} + qG_\theta
\end{pmatrix}
\] (6)

The three and two state models operating in the reduced bases are indicated by the inner brackets. The additional reduction factors \( r \) and \( r' \) are defined as follows:

\[
r = \langle \Psi_{A_1} | U_e | \Psi_\theta \rangle = -\langle \Psi_{A_2} | U_\theta | \Psi_e \rangle,
\]

\[
r' = \langle \Psi_{A_1} | U_\theta | \Psi_\theta \rangle = -\langle \Psi_{A_2} | U_e | \Psi_e \rangle.
\] (7)

The specific spin Hamiltonian terms \( G_i \) that have been used in this work are given in Table I. A number of higher order terms of \( G_{A_2} \) symmetry were also explored in fitting the spectra, but we could not find any definite experimental evidence for their requirement and so these terms have not been included in Eq. (6) and Table I. Such terms are expected to be small and are further reduced by the reduction factors \( p \) and
The random strain in Table I is specified by a magnitude $\epsilon$ and strain angle $\phi$, according to

$$S_\epsilon = \delta_s \cos \phi,$$

where $S_\theta$, $S_\epsilon$ are the two components of the strain tensor of $E$ symmetry: $S_\theta = e_{\epsilon z} - \frac{1}{3} (e_{xx} + e_{yy})$, $S_\epsilon = \sqrt{3}/2 (e_{xx} - e_{yy})$, $e_{ij} = \frac{1}{2} \left[ \partial u_i / \partial x_j + \partial u_j / \partial x_i \right]$. These have the same functional form

![Diagram](image)

FIG. 1. (a) The Mexican hat potential energy surface (upper) and the vibronic energy levels and reduction factors as a function of the first order coupling constant $k$. (b) Contour plot of the “warped Mexican hat” potential surface showing the three equivalent minima ($k = 3$, $g = 0.1$; contour interval 1) and the vibronic energy levels and reduction factors as a function of the second order coupling constant $g$ for a fixed value of $k = 3$.

TABLE I. Spin Hamiltonian terms for Eqs. (1) and (2).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Electronic Zeeman</th>
<th>Hyperfine</th>
<th>Strain$^a$</th>
<th>Nuclear quadrupole</th>
<th>Nuclear Zeeman$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{A_1}$</td>
<td>$g_1 \mu_B \mathbf{H} \cdot \mathbf{S}$</td>
<td>$A_1 \mathbf{I} \cdot \mathbf{S}$</td>
<td>$\cdots$</td>
<td>$\cdots$</td>
<td>$g_{1e} \mu_B \mathbf{H} \cdot \mathbf{I}$</td>
</tr>
<tr>
<td>$G_{\theta}$</td>
<td>$\frac{1}{2} g_2 \mu_B (3H_z S_z - H \cdot S)$</td>
<td>$\frac{1}{2} A_2 (3I_z S_z - I \cdot S)$</td>
<td>$\delta_s \cos \phi$</td>
<td>$\frac{1}{2} P_z (3I_z - I \cdot I)$</td>
<td>$\frac{1}{2} g_{2e} (3H_z I_z - H \cdot I)$</td>
</tr>
<tr>
<td>$G_{\epsilon}$</td>
<td>$\frac{1}{2} \sqrt{3} \mu_B (H_x S_x - H_y S_y)$</td>
<td>$\frac{1}{2} \sqrt{3} A_3 (I_x S_z - I \cdot S)$</td>
<td>$\delta_s \sin \phi$</td>
<td>$\frac{1}{2} \sqrt{3} P_z (I_z - I \cdot I)$</td>
<td>$\frac{1}{2} \sqrt{3} g_{2e} (H_x I_x - H_I)$</td>
</tr>
</tbody>
</table>

$^a$The strain interaction has similar symmetry properties as the other terms (see text) but is defined in terms of the magnitude ($\delta_s$) and strain angle ($\phi$) which are more useful in the present analysis.

$^b$A fixed value of $g_{1e} = 2.226$ is used; the pseudonuclear Zeeman terms involving $g_{1e}$ were not required but are included here for completeness.
as the Jahn–Teller active coordinates \(Q_\theta\) and \(Q_\epsilon\). A positive (negative) \(S_\rho\) acts as a tetragonal compression (elongation) along the \(Q_\epsilon\) coordinate and lowers the energy of the \(\psi_\theta(\psi_\epsilon)\) states. The strain distribution for Cu(II)/MgO was originally modeled by Reynolds et al.\(^7\)\(^8\) about a nonzero mean value \(\bar{\delta}\) of the form \(P(\delta_\epsilon, \phi_\epsilon) \propto \exp[-(\delta_\epsilon - \bar{\delta})^2/(2\sigma^2)]\) with equal probability in the \(\phi_\epsilon\) dimension. In the two dimensional \(S_\rho\), \(S_\epsilon\) space, such a distribution describes a ring of Gaussian probability rotated about \(\phi_\epsilon\). This distribution is required by their implicit assumption that the Zeeman splitting was at all times small relative to the random strain splitting.

Later Setser et al.\(^10\) pointed out that the random nature of the strain requires it to have the form of a two dimensional Gaussian distribution of \(S_\rho\), \(S_\epsilon\) centered at the origin. The probability of a particular strain value as a function of \(\delta_\epsilon\) and \(\phi_\epsilon\) is given by

\[
P(\delta_\epsilon, \phi_\epsilon) = \frac{2 \ln 2}{2\pi \sigma_\Delta} \exp\left[-\left(\frac{\delta_\epsilon}{\sigma_\Delta}\right)^2 \ln 2\right].\tag{9}
\]

After integrating Eq. (9) over random \(\phi_\epsilon\), one arrives at the same one dimension distribution of \(\delta_\epsilon\), \(P(\delta_\epsilon) \propto \delta_\epsilon \exp\left[-(\delta_\epsilon/\sigma_\Delta)^2 \ln 2\right]\), as given by Setser et al.\(^10\) Here we define \(\sigma_\Delta\) as the half width at half maximum spread for particular \(S_\rho\), \(S_\epsilon\) values. The probability is at a maximum at \(S_\rho = S_\epsilon = 0\) and drops to \(\frac{1}{2}\) this value for particular \(S_\rho\), \(S_\epsilon\) values which satisfy \(S_\rho^2 + S_\epsilon^2 = \delta_\Delta^2\). Due to the sensitivity of the wave functions and resulting resonant fields to the strain angle \(\phi_\epsilon\), a much finer integration grid over \(\phi_\epsilon\) is required.

**IV. COMPUTATIONAL METHODS**

In describing the computational approach we use the three state model given by the \(3 \times 3\) subset of the spin Hamiltonian in Eq. (6) for simplicity. In this case we solve the spin Hamiltonian using the 24 functions comprising the orbital \(\{|\psi_\theta, \psi_\epsilon, \psi_\epsilon\}\) and electron spin \((S=1/2)\) and nuclear spin \((I=3/2)\) functions of degeneracies 3, 2, and 4, respectively, using the eigenfield method\(^21\) described in the Appendix.

The 144 finite eigenfield solutions each involve one of the nine possible Zeeman transitions between lower and upper components as shown schematically in Fig. 2. Each Zeeman component is split into four hyperfine levels, giving rise to 16 possible transitions between the split Zeeman components, most of which will carry little or no intensity. The transitions between the same Zeeman split states \(e^- \rightarrow e^+\), \(\theta^+ \rightarrow \theta^-\), \(A_2^- \rightarrow A_2^+\) are the most intense and are shown as the solid lines in Fig. 2. There are \(32\) \(e^+, \theta^- \rightarrow A_2^+\) type transitions and \(32\) \(A_2^- \rightarrow e^+, \theta^+\) type transitions which will occur at lower and higher fields, respectively, the actual position of which depends on the \(E-A_2\) separation \(\Delta_2\). For \(\Delta_2\) greater than the wavenumber of the microwave radiation \((X\text{ band } \sim 0.31 \text{ cm}^{-1})\) these transitions will not occur. The remaining \((144-64=80)\) resonant transitions will be clustered around the \(g=2\) position.

Once the resonant fields are found, the intensity of each transition is calculated and the spectrum simulated from the stick spectrum using a finite linewidth. When a random value of the strain is used, many hundreds of these calculations must be made to generate a single spectrum. It is important to note that the strain is modeled by adding the spectra obtained for a distribution of strain values rather than relating the strain distribution to an effective bandwidth.

**V. RESULTS**

The experimental \(X\)-band EPR spectra are shown in Figs. 3 and 4. The spectra with the magnetic field oriented parallel to the \((110)\) direction results in the most highly resolved spectra. The low temperature 1.8 K spectrum shows two sets of four hyperfine lines with strain broadened line shapes similar in appearance to powder spectra, such that the

![FIG. 2. Schematic of the relevant EPR transitions in this study for \(\phi_\epsilon = 180\.\ H(\parallel(001)\). The \(A_2^+\), \(\theta^+\), \(e^+\) indicate the \(\pm M_s\) Zeeman components of the \(\phi_\epsilon\), \(\psi_\theta\), \(\psi_\epsilon\) electronic states, respectively. Strong transitions between Zeeman components of the same Kramers doublet are shown as solid lines, while the weaker transitions between different Kramers doublets are shown as the dotted lines. The total number of transitions between the hyperfine states in each of the three groups is given in brackets.](image-url)

![FIG. 3. The low temperature (1.8 K) anisotropic X-band EPR spectrum and the high temperature (6.0 K) isotropic spectrum for \(H(\parallel(110)\). Signals from Mn(II) impurities are indicated.](image-url)
low field lines are predominately positive and the high field lines predominately negative. As the temperature is raised in Fig. 3, even at the relatively low value of 6 K, the anisotropic spectrum is replaced by a spectrum that can be analyzed in terms of the isotropic $g$ and $A$ values given in Table II. This isotropic spectrum is independent of the orientation of the crystal in the magnetic field. The variation in the widths of the hyperfine lines of the 6 K spectrum can be attributed to a relaxation rate that is of the same order as the frequency differences between the hyperfine lines that are being averaged. The sharper high field lines of the 6 K spectrum correspond to the more complete averaging of spectra with a smaller energy difference compared to the low field lines. We will show the variation in the broadening of the different hyperfine lines of the low temperature spectrum to be due to the different sensitivities of the hyperfine lines to the strain broadening. The strain broadening does not allow the hyperfine structure of the two Cu isotopes to be distinguished separately.

Figure 4 shows the experimental X-band spectra as the magnetic field is rotated in the plane perpendicular to the (110) direction from $\theta=0^\circ$ (001) to $\theta=90^\circ$ (110), while Figs. 5 and 6 show the simulated spectra. The angular dependence of the strain broadened line shapes is typical of those produced by a dynamic Jahn–Teller effect. The broadest set of four hyperfine lines is at low field for $H(001)$ and at high field for $H(110)$. This is indicative of coupling of the ground vibronic $E$ state with an excited singlet of $A_2$ symmetry via the random strain of the crystal. The relationship between the symmetry of the first excited singlet and the position of the minima of the $E \otimes e$ Jahn–Teller surface is well known. The $A_2$ symmetry of the lowest excited singlet establishes that the minima and the Jahn–Teller surface is at tetragonally elongated rather than a compressed geometry. The effect of this strain coupling is to shift the low field lines lower for $H(001)$ and high field lines higher for $H(110)$. In the limit of strong strain coupling, the spectrum becomes that of a static Jahn–Teller effect of a statically elongated octahedron, with the position of the high field resonances for $H(001)$ and $H(110)$ becoming equal corresponding to tetragonal $g_\perp$ and $A_\perp$ values. In such a static situation the observed spectra will be a superposition of the spectra from three species, each a static elongation along the three cubic axes. For a rotation from (001) to (110) one would observe three sets of hyperfine lines, one set corresponding to a rotation of the field from parallel to perpendicular to the elongation axis and the other two being degenerate as the field is rotated from perpendicular to $45^\circ$ between the $\parallel$ and $\perp$ axes. The spectra shown in Fig. 4 are very different. The dynamic nature of the spectrum is indicated by the anisotropic varia-

### Table II. Spin Hamiltonian parameters for Cu(II) in selected oxide hosts. Other parameters used include $q=\frac{x}{y}, r=-\sqrt{1/2}$, and $r'=0.25$.

<table>
<thead>
<tr>
<th>Host</th>
<th>$T$ (K)</th>
<th>Strain$^a$</th>
<th>$\Delta_1$ (cm$^{-1}$)</th>
<th>$g_1$</th>
<th>$qA_1$ ($\times 10^{-4}$ cm$^{-1}$)</th>
<th>$qA_2$ ($\times 10^{-4}$ cm$^{-1}$)</th>
<th>$qP_2$ ($\times 10^{-4}$ cm$^{-1}$)</th>
<th>Ref.</th>
</tr>
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<tr>
<td>MgO</td>
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<td>...</td>
<td>...</td>
<td>2.1933</td>
<td>$\pm 18.7$</td>
<td>...</td>
<td>...</td>
<td>7</td>
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<tr>
<td></td>
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<td>$\delta=0.12$</td>
<td>...</td>
<td>2.1924</td>
<td>$\pm 18.7$</td>
<td>...</td>
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<tr>
<td></td>
<td>6.0</td>
<td>...</td>
<td>...</td>
<td>2.193</td>
<td>$\pm 18.7$</td>
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<td></td>
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<td>$\delta=0$</td>
<td>$\Delta_1=4$</td>
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<td>$\pm 18.7$</td>
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<td></td>
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<tr>
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<td>...</td>
<td>2.2205</td>
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<td>...</td>
<td>...</td>
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<tr>
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<td>...</td>
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<td>$P_{\perp}=-25$</td>
<td>22</td>
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$^a$The strain parameters are quantified by a Gaussian distribution with the mean value $\delta$ and the $\delta_1$ see text, $\Delta_1$, $\Delta_2$ are denoted by $3\Gamma$ in Ref. 7.

$^b$This work.

$^c$The small departures from tetragonal symmetry in TiO$_2$ are averaged. The hyperfine values are for the predominate $^{60}$Cu isotope.
tion for the magnetic field rotation in the (001) plane\textsuperscript{23} or equivalently, the high field spectrum being different for $H\parallel(001)$ and $H\parallel(110)$ orientations. As we will show below, both sets of hyperfine lines and the unusual structure in the spectra shown in Fig. 4 are due to a single dynamic Jahn–Teller species rather than a superposition of species.

Figure 7(a) shows the rotation in the (110) plane as an image plot, allowing the main features of the spectra to be visualized. The image plots are of the EPR spectra at 1° resolution in the field direction $\theta$ from the (001) and (110) where the field sweep is the vertical axis. At all angles, the broadening of the low field set of lines shows a positive (blue) distortion and the high field set of lines shows a negative (red) distortion of the derivative line shape. The broadening of the outer hyperfine lines is greater than the innermost lines in both the high and low field sets. For rotations away from the (001) and (110) directions, the high field hyperfine set is composed of more than four lines, particularly evident at small rotations from (001). At $H\parallel(110)$ the high field set converges so the hyperfine transitions cannot be resolved in Fig. 7. The spectra for the magnetic field approaching the (111) direction shows an increase in the apparent intensity of the spectra while the linewidth decreases. The spectra become complex, clearly showing more than two sets of four hyperfine lines. The main four positive low field and four negative high field sets appear to have an avoided crossings at (111). This complex behavior has not previously been observed. It has been reported that the spectrum coalesces to four hyperfine lines for $H\parallel(111)$\textsuperscript{29} An optimization of the fit requires a small misalignment of the rotation axis, such that at (111) the field direction is misaligned by $\sim 1.7^\circ$. However, this slight misalignment is not responsible for the complexity of the (111) spectrum. The spectrum in the (111) direction is further discussed below, and the sensitivity of the spectrum to the strain in this direction is also shown in the supplementary material (S3)\textsuperscript{19}.

The spectra simulated with the model described above and the parameters given in Table II are shown in Figs. 5, 6, and 7(b), where the calculated line spectrum has been convoluted with a single intrinsic Gaussian line-shape function for all spectra.

**VI. DISCUSSION**

**A. The hyperfine values**

Table II gives the best fit spin Hamiltonian parameters together with those obtained in from a previous analysis of Cu(II)/MgO\textsuperscript{7} While there is close agreement with the $g$ values, there is a large difference between our fitted hyperfine parameters and those reported previously. The discrepancy and its resolution can be illustrated by considering the spectra at the (001) and (110) orientations. Perturbation formula to first order\textsuperscript{5,24} give $A_1 \pm qA_3$ and $A_1 \mp qA_3$ for the hyperfine splitting in these directions, respectively, where positive and negative signs are for the high and low field sets of hyperfine lines. The observed separations for the low and high field sets of hyperfine lines correspond to the values of $\sim 60$ and $\sim 25 \times 10^{-4}$ cm\(^{-1}\) for $H\parallel(001)$ and $\sim 42$ and $< 10 \times 10^{-4}$ cm\(^{-1}\) for $H\parallel(110)$. As noted previously\textsuperscript{7} the high
field (001) and low field (110) values are the best to fit as they will be the least affected by the strain coupling to the lowest \( A_2 \) vibronic state. This gives the equations \( |A_1-qA_2| = 2.5 \times 10^{-4} \text{ cm}^{-1} \) and \( |A_1+\frac{1}{2}qA_2| = 4.2 \times 10^{-4} \text{ cm}^{-1} \), which in turn give the values \( A_1 = 0.36 \times 10^{-4} \text{ cm}^{-1} \) and \( qA_2 = 0.11 \times 10^{-4} \text{ cm}^{-1} \) assuming the positive sign of the absolute value is taken. One arrives at values similar to those found previously\(^7\) as given in Table II. However, spectral simulations using these values do not reproduce the hyperfine splittings observed at other orientations, e.g., for the high field (110) set, \( |A_1-\frac{1}{2}qA_2| = 0.30 \times 10^{-4} \text{ cm}^{-1} \) is expected whereas experimentally the hyperfine separations must be much smaller (\(<5 \times 10^{-4} \text{ cm}^{-1}\)).

We find that good agreement with the experimental hyperfine structure is obtained at all field orientations using hyperfine values, which can be found from the above equations assuming that \( qA_2 > A_1 \) so that \( A_1-qA_2 \) is negative. The values \( A_1 = 2.0 \times 10^{-5} \text{ cm}^{-1} \) and \( A_2 = 8.6 \times 10^{-5} \text{ cm}^{-1} \) also result in \( A_1-\frac{1}{2}qA_2 \) being negative, which implies that for both \( H \parallel (001) \) and \( H \parallel (110) \) the high field set of hyperfine lines corresponds to transitions of between \( m_I \) nuclear spin states of the opposite order than the low field set. At intermediate angles, \( m_I \) is not a good quantum number, and the hyperfine lines vary smoothly from low to high field sets as the magnetic field is rotated from (001) to (110); there are no “hyperfine crossings” as the hyperfine transitions are reordered. The cubic hyperfine parameters \( A_1 \) and \( A_2 \) are only determined within a sign. However, as we will show later, the interaction with other parameters allows us to establish that both hyperfine parameters are negative, in agreement with simple ligand field arguments.

As well as now accounting for the hyperfine splittings at all field orientations, the \( |qA_2| > |A_1| \) result also allows a number of other puzzling aspects of the Cu(II)/MgO spectra to be understood, in particular, the splitting of the hyperfine lines observed in the high field set of resonances for rotations away from (001). We find that this splitting can be simulated (Figs. 5–7) by a nonzero nuclear quadrupole interaction. Such a term has previously been used in a dynamic Jahn–Teller system to explain the weak forbidden \( \Delta m_I = \pm 1 \) transitions in the EPR spectra of Sc\(^{2+}\) doped in a number of hosts.\(^{25}\) However, the intensities of the \( \Delta m_I = \pm 1 \) transitions in this case were at least two orders of magnitude less than the allowed \( \Delta m_I = 0 \) hyperfine lines.\(^{25}\) In the present case the intensities of the forbidden and allowed transitions are comparable. This is clearly seen in the seven line set of high field lines at 20° rotated from (001) in Figs. 5–8. The extraordinarily large intensity observed in the present case is a direct consequence of \( |qA_2| > |A_1| \). At particular orientations of the magnetic field, \( \theta = 30° \) and \( 80° \) from (001), the \( m_I \) states are strongly mixed. At these angles the perturbation formula would incorrectly calculate the hyperfine levels as crossing (see supplementary material\(^19\)).

The mixing of the nuclear spin states by the \( |qA_2| > |A_1| \) hyperfine interaction is expected to have a much smaller effect on the intensities than would otherwise be the case.
Further, it is possible to determine the sign of the quadrupole coupling as being the opposite sign to the hyperfine coupling. If the same sign is used then a very different intensity pattern is calculated. Within the high field set of hyperfine lines for \( \theta = 30^\circ \) from (001), the “\( \Delta m_I = \pm 1 \)” transitions between the higher field hyperfine lines would be calculated to be more intense than those between the lower two hyperfine lines, opposite to what is observed. The quadrupole term in the spin Hamiltonian results from the coupling of nuclear electric-quadrupole moment with the electric field gradients which are usually associated with low symmetry ligand field environments. More rarely is a quadrupole interaction observed that is attributed to the electric field gradients produced by asymmetric electronic charge distributions. Here it is the different charge distributions of the \( \psi_\theta \) and \( \psi_e \) electronic parts of the vibronic states that give rise to the observed quadrupole interaction. For a nondegenerate electronic state in a cubic environment, the quadrupole term is required to be zero. For degenerate electronic states the isotropic quadrupole parameter is similarly required to be zero, while the anisotropic quadrupole parameter \( P_2 \) is nonzero. The quadrupole interaction is then characterized by a single value as given in the spin Hamiltonian in Table I. The fitted value (Table II) is not an abnormally large value, and we show below that both the sign and magnitude of this parameter are consistent with values obtained in related systems.

In addition, with these new values of the spin Hamiltonian parameters for the low temperature spectrum, the isotropic part of the hyperfine coupling, \( A_1 \), is now very close to that found for the isotropic “high” temperature 6 K spectrum. This is intuitively as one would expect; relaxation effects at higher temperatures only average the anisotropic parts of the (cubic) spin Hamiltonian and the isotropic terms \( g_1 \) and \( A_1 \) terms remain the same. As we discuss below, the \( |qA_2| > |A_1| \) result is entirely consistent with that expected from simple ligand field arguments and could have been predicted by comparison to related Cu(II) systems with a static Jahn-Teller effect. Another consequence of \( |qA_2| > |A_1| \) is that the perturbation formulae previously derived for a \( \Gamma_8(2E) \) state are not valid for this system, as they are derived assuming \( |qA_2| \leq |A_1| \). However, we show (supplementary material figure S2, Ref. 19) that these expressions remain good approximations for the orientations \( H \parallel (001) \) and (110).

**B. The strain distribution**

Figure 8(a) shows the eigenfields calculated as a function of the magnetic field direction using the parameters listed in Table II and a particular value of the strain \( \delta = 0.05 \) \( \text{cm}^{-1} \), \( \phi_0 = 180^\circ \). We label the two sets of lines the \( \theta \) and \( e \) branches corresponding to \( \psi_\theta \rightarrow \psi_\theta^+ \) and \( \psi_e^+ \rightarrow \psi_e^+ \) transitions, respectively. The line thickness is proportional to the transition intensity. The small nonzero value of \( \delta \) has been used for clarity as it removes the weak \( \theta \rightarrow e^+ \) and \( e^- \rightarrow \theta^+ \) resonant transitions to lower and higher mag.
netic fields, respectively. Figure S3 (supplementary material) shows, for example, how the complex spectrum at the (111) orientation is removed for small values of $\delta_s$. As noted by others, for a lowest excited singlet of $A_2$ symmetry, the inclusion of a static strain corresponding to negative $S_\theta (\phi_s=180^\circ)$ mixes the $\psi_e$ and $\psi_{A_2}$ states, shifting the $e$ low field lines at $H||$001 lower and high field lines at $H||$110 higher until the static tetragonally elongated limit where the high field lines at (001) and (110) are equal. It should again be noted that for this static case, the EPR spectrum will be a superposition of three tetragonally elongated species, whereas the spectra presented here are from a single species.

The strain broadened line shapes of the EPR spectra can be understood by considering the plots in Figs. 8(b) and 8(c) where the eigenfields are calculated as a function of the strain angle $\phi_s$ for the field directions (001) and (110), respectively. The $e$ and $\theta$ branches interchange as the strain changes from a compressed ($\phi_s=0^\circ$) to an elongated ($\phi_s=180^\circ$) direction. For the small values of $\delta_s$ used in Fig. 8, the resonant field positions at $\phi_s=0^\circ$ and $\phi_s=180^\circ$ are the same. The dynamic wave functions are not being perturbed to any great extent. For random values of the strain there is an equal probability of $\phi_s$, taking any value within this range, the spectra will be a superposition of the many resonant transitions that range between these field positions at $\phi_s=0^\circ$ and $180^\circ$. The superposition of the derivative spectrum essentially cancels in the interior region with peaks remaining at the extreme values $\phi_s=0^\circ$ and $\phi_s=180^\circ$ where $dH/d\phi_s=0$. This results in the strain broadened line shapes where the lower field side has a distorted derivative shape with a larger positive component, while the high field side has a larger negative part.

Figure 8(b) shows that at $H||$(001) the extreme values of the eigenfields, $dH/d\phi_s=0$, occur at $\phi_s=0^\circ$ and $180^\circ$. For small values of $\delta_s$, the eigenfield positions are approximately the same for both $\phi_s=0^\circ$ and $180^\circ$. The eigenfield calculation of Fig. 8(a) for $\phi_s=180^\circ$ should be the expected experimentally observed positions of the resonant fields for $H||$(001). The same is not true for $H||$(110) as in this case as shown in Fig. 8(c), the extreme position of the eigenfields occurs at values of $\phi_s$ different from $0^\circ$ and $180^\circ$. This illustrates that while Fig. 8(a), calculated for a single strain value at $\phi_s=180^\circ$, superficially resembles the observed angular dependence in Fig. 7(a) and is instructive in understanding the spectra, a full calculation over many values of $\phi_s$ is required to reproduce both the observed line shape and the resonant field positions.

Figure 9 illustrates the behavior of the eigenfields as a function of the strain magnitude $\delta_s$ for $H||$(001), where the values for both $\phi_s=0^\circ$ and $180^\circ$ are shown in the same plot. Looking at the lower field lines, for $\phi_s=180^\circ$ these indeed shift the resonant fields lower as calculated by others. This shift in the resonant field from the dynamic values has previously been used to fit a value for the mean strain. This implies that this nonzero mean strain value is for $\phi_s$ fixed at $180^\circ$, as setting $\phi_s=0^\circ$, as shown in Fig. 8(a), results in a shift in the spectrum in the opposite direction. However, a fixed value of $\phi_s$ will not give rise to strain broadened line shapes as discussed above, so there is an inconsistency in the interpretation of the effects of random crystal strain in the previous analyses of these spectra.

The relative sensitivity of the different hyperfine lines to the strain splitting exactly reflects the relative line broadening observed in the spectra, with the “outer” hyperfine lines
being broader than the inside ones. The high field lines for \( H \parallel (001) \) shown in Fig. 9(a) split in a similar manner \( \phi_z=0, \) \( 180^\circ \), but to a lesser extent. This splitting is entirely due to coupling with the higher energy \( A_1 \) singlet state and in the three state model this splitting is absent. The four state model must be used to reproduce the relative broadening of the high field hyperfine lines at \( (001) \) and the low field lines at \( (110) \). We estimate the energy of this state \( \Delta_1 \approx 150 \text{ cm}^{-1} \) to reproduce the observed broadening and use a value of \( r' = -0.25 \) calculated for the Jahn–Teller coupling constants \( k=3, \ g =0.05 \) in Fig. 1.

The simulations shown in Fig. 6 use a single 7 G linewidth and \( (\delta_0=2 \text{ cm}^{-1}) \) reproduces a number of the features in the experimental spectra in Fig. 4. At \( \theta=0^\circ \) the relative broadening of each set of hyperfine lines is well reproduced, with the outer hyperfine lines broader than the inner. At small angles away from \( (001) \) the higher field hyperfine lines split in the manner observed experimentally due to the quadrupole coupling. At \( (110) \) the high field hyperfine lines collapse to a double peak as observed experimentally. Features of the spectra which are less well reproduced include the relative broadening of the low field lines in the \( (110) \) direction. In general the experimental spectrum away from the \( (111) \) direction is broader than simulated; however, a larger spread of strain values and/or a larger intrinsic line-shape width results in much broader lines around \( (111) \) than is observed experimentally. In addition the larger strain range cancels the weak spectrum due to the populated singlet state (see Sec. VI E below). A smaller strain spread and smaller width \( (\delta_0 =0.1 \text{ cm}^{-1}, 5 \text{ G}) \) shown in Fig. 5 better reproduce the experimental linewidth at \( (111) \) and the weak singlet spectrum 3030–3100 G. However, the spectrum away from \( (111) \) is not as broad and has too much of a derivative line shape when compared to experiment. It appears that single Gaussian distribution of the random strain cannot reproduce all experimental features.

One additional difference in the calculated spectra is the resonance at \( \approx 3130 \) G for \( \theta=0^\circ \) that appears in the spectrum calculated with the larger strain spread (Fig. 6) and not in spectra shown in Fig. 5. This feature is only calculated for strain magnitudes \( \delta_0 > 0.35 \text{ cm}^{-1} \) for angles close to \( \theta=0^\circ \). It is associated with the crossing of the eigenfields at \( \phi_z=60^\circ, \) \( 120^\circ \) shown in Fig. 8(b) and may be a way of placing an upper limit on the strain spread. Unfortunately this part of the spectrum is obscured by the lowest field Mn(II) transition. It would be of interest to use a different microwave frequency to examine this region.

### C. Comparison with parameters from other systems

It is useful to compare the spin Hamiltonian parameters found in the present work with those of similar systems where the dynamic Jahn–Teller effect is quenched. We give the parameters for Cu(II) doped TiO\(_2\) in Table II, chosen as an oxide system in which narrow linewidths \( (0.5 \text{ G at } 20 \text{ K}) \) have allowed both magnitude and sign of the \( g, A, \) and \( P \) tensors to be determined.22 In this system the Cu(II) ions substitute for the Ti\(_{3+}^+\) which has six coordinates with slightly elongated bond lengths of \( 1.949 \text{ Å (4)} \) and \( 1.980 \text{ Å (2)} \).25

The site symmetry is \( D_{2h} \) due to angular distortions and this, together with charge compensating vacancy, results in a slight departure from tetragonal symmetry. The \( x \) and \( y \) values for the Cu(II)/TiO\(_2\) parameters have been averaged in Table II, allowing them to be related to the dynamic parameters according to \( g_x = g_1 + g_2, \ g_y = g_1 - \frac{1}{2} g_2 \) with the analogous expressions for the \( A \) and \( P \) values. This gives rise to the following hypothetical dynamic parameters for Cu(II)/TiO\(_2\), if it were considered as a static distortion of a dynamic system:

\[ g_1 = 2.283, \quad A_1 = -14.0 \times 10^{-4} \text{ cm}^{-1}, \quad P_1 = 0, \]
\[ g_2 = 0.163, \quad A_2 = -72.0 \times 10^{-4} \text{ cm}^{-1}, \]
\[ P_2 = + 5.0 \times 10^{-4} \text{ cm}^{-1}. \]

These parameters are similar to the values found here for Cu(II)/MgO. It also agrees with \( \frac{1}{2} |A_2| > |A_1| \) and gives a \( P_2 \) value of opposite sign to \( A_2 \).

It is noted that the anisotropic parameters \( g_x, A_x, P_x \) are all less than \( 2q \) the values for Cu(II)/MgO, indicating that while demonstrating our parameters set is reasonable and consistent with similar systems, the values in Eq. (10) cannot be used to estimate any possible deviation of \( q \) from \( \frac{1}{2} \) for Cu(II)/MgO. While strictly our simulations only determine the quantities \( g_2, A_2, \) and \( P_2 \), a rough estimate of \( q \) may be obtained from equating the \( g_1 \) shift from the free electron value \( g_e \) using first order expressions from ligand field theory,4

\[ q \approx g_2/(g_1 - g_e), \]

which gives a value of \( q = 0.55 \), confirming that we are in the strong Jahn–Teller coupling regime.

We also include the values previously obtained for Cu(II)/CaO in Table II as the only other Cu(II) dynamic Jahn–Teller system that has been studied in detail.7 The isotropic hyperfine value obtained from the high temperature spectrum is \( A_1 = \pm 21.8 \times 10^{-4} \text{ cm}^{-1} \), similar in magnitude to that found for Cu(II)/MgO. However, as in the previous fit of Cu(II)/MgO, the low temperature \( A_1 \) hyperfine value is quite different. A direct comparison is not possible in this case as the copper is modeled having a potential surface with tetragonally compressed minima, resulting in strain coupling to a lowest excited singlet of \( A_1 \) symmetry. The difference in the isotropic \( A_1 \) hyperfine values derived from the low and high temperature spectra of Cu(II)/CaO may indicate that a different set of low temperature hyperfine values may also fit the spectra, although the reported values are known to successfully account for the observed spectra.7,15

### D. The Mn(II) spectra

The image plot of the spectra in Figs. 7 and 10 also show well known resonances that are due to Mn(II) ions.28 As we wish to interpret weak features in our spectra we must first account for those due to Mn(II) impurity ions. In MgO the Mn(II) hyperfine interaction is greater than the cubic zero-field splitting parameter and the resulting \( S=5/2, I=5/2 \) spectra consist of a sextet of \( \Delta m_I=0 \) transitions, each
consisting of a pentad of $\Delta m_s=1$ transitions. The three lowest field pentads are visible in spectra of Fig. 10. The most conspicuous transition within each pentad is the $m_s=-\frac{1}{2} \rightarrow m_s=+\frac{1}{2}$ transition which shows no angular dependence. The other four $m_s\rightarrow m_s+1$ transitions oscillate in pairs in either side of the $-\frac{1}{2} \rightarrow +\frac{1}{2}$ transition with maximum separation at the (111) and (001) directions and crossing at $\theta \sim 30^\circ$. Of interest in the spectra shown in Fig. 10 are the additional pairs of lines (marked by asterisks) that also show no angular dependence and occur between the $-\frac{1}{2} \rightarrow +\frac{1}{2}$ transition of neighboring sextets. These are the forbidden $m_s=-\frac{1}{2}, m_i=m_s=+\frac{1}{2}, m_s+1$ and $m_i=-\frac{1}{2}, m_s=+\frac{1}{2}, m_s+1$ transitions. These forbidden transitions are more intense than previously described for Mn(II)/MgO. The appearance of these forbidden transitions has been shown to be due to nuclear quadrupole and nuclear Zeeman terms in a related system. The angular dependence of the linewidths of the $m_s\rightarrow m_s+1 (m_i=\frac{1}{2})$ transitions show minima at (111) and this has been interpreted as due to a distribution of strain in the MgO host.

E. The excited vibronic singlet

The fit of the spin Hamiltonian parameters given in Table II is relatively insensitive to the value of the energies of the excited state singlets $\Delta_2$ and $\Delta_1$, apart from their influence on the relative strain broadening as discussed above. In addition, the overall strain distribution quantified here by $b$ can only be accurately determined as a ratio with respect to the energy gaps to the excited singlets. For these reasons the direct observation of the $A_2$ excited singlet energy gap $\Delta_2$ is desirable. Not only would this help quantify the strain distribution but it would also give information on the barrier heights between the Jahn–Teller minima. The observation of direct $\theta, e \rightarrow A_2$ EPR transitions at high frequency and high magnetic fields is likely to be difficult for reasons discussed below. The population of the singlet to observe EPR transitions within this singlet is also difficult as relaxation (which is likely to involve this population process) occurs at a low temperature (Fig. 3). For the small strain values found here at X band the eigenfields for the singlet state are calculated to be insensitive to the strain angle $\phi_s$. This implies that, while they have a low population at 1.8 K, the relative intensities of the singlet state transitions will be large compared to those of the $E$ state where most of the transitions canceled each other except at the extrema points, where $dH/d\phi_s=0$.

The small strain coupling also makes the eigenfields of the $A_2$ state relatively insensitive to the rotation angle $\theta$. We calculate that the singlet spectra should appear as weak close lying hyperfine lines separated by $\sim 10$ G between 3040 and 3100 G. These transitions are difficult to observe in any one spectrum, but they become clear in the image plot shown in Fig. 10, appearing as horizontal streaks due to their insensitivity to the rotation angle. We assign these features to the $A_2^- \rightarrow A_2^+$ singlet transitions. To our knowledge this is the first time that the isotropic singlet spectrum of a Cu(II) dynamic Jahn–Teller system has been reported. Simulation of the spectra gives an estimate for $\Delta_2$ as 4 cm$^{-1}$.

F. The transitions between different Kramers doublets

Given that we now have a reasonable description of the lower vibronic levels in terms of the spin Hamiltonian given in Tables I and II, it is of interest to speculate on the possibility of observing EPR transitions between the different Kramers doublets. These are the transitions given as the dashed lines in Fig. 2. At any particular value of the strain parameters one can calculate the eigenfields as a complex pattern of very weak transitions. The $32 \psi_{\theta}^- \rightarrow \psi_{\phi}^e$ and the $32 \psi_{A_2}^- \rightarrow \psi_{\phi}^e$ transitions will be absent for this system as the energy to the first excited singlet is greater than that of the X-band microwaves. The $32 \psi_{\theta}^- \rightarrow \psi_{\phi}^e$ and $\psi_{\phi}^- \rightarrow \psi_{\phi}^e$ type transitions, however, are calculated to occur at X-band frequencies.

The strain determines the electronic composition of the two Kramers doublets in the vibronic $E$ state according to

$$\psi_e = \sin(\phi_e/2)\psi_\theta + \cos(\phi_e/2)\psi_\phi,$$

$$\psi_e = \cos(\phi_e/2)\psi_\theta - \sin(\phi_e/2)\psi_\phi$$

(12)

and to a lesser extent by coupling with the excited singlet states. The net effect is to distribute the eigenfield transitions within either of the Kramers doublets in Eq. (12) over a limited range as a function of the strain angle $\phi_s$. For $H=(001)$ this range is between the resonant field positions given by $H=(g_{1} \pm qg_{2})\alpha/\omega$. The eigenfields are limited to occur within this range for all values of the strain. Even for very large strain values, the range of resonant fields will only

FIG. 10. Enhanced image plot of the 1.8 K X-band spectra showing weak transitions that we attribute to the isotropic singlet spectrum. Signals due to Mn(II) impurities are also indicated by arrows, and the asterisks denote forbidden transitions at the $\theta$ direction. We assign these features to the isotropic singlet spectrum. Signals due to Mn(II) impurities are also indicated by arrows, and the asterisks denote forbidden transitions at the $\theta$ direction. We assign these features to the isotropic singlet spectrum.
be increased to the limiting static range of \( H = (g_1 + g_2)B/\omega \) and \( (g_1 - g_2)B/\omega \). This can be contrasted with the role of the strain in determining the resonant field positions for transitions between different Kramers doublets, where the energy gap is a direct function of the strain. Without a very narrow range of strain values or some other selection mechanism, there is an infinite number of resonant fields and the transitions will broaden into the background.

One particular orientation that may be the most favorable to observed these \( \theta^* \rightarrow e^* / e^- \rightarrow \theta^* \) transitions are close to (111). While the eigenfield values of these transitions are very sensitive to the strain magnitude \( \delta_e \), they are relatively independent of the strain angle \( \phi_e \) in this orientation. At orientations away from (111) these \( \theta^* \rightarrow e^* / e^- \rightarrow \theta^* \) transitions are sensitive to both \( \delta_e \) and \( \phi_e \). A careful examination of the spectra (Fig. 10) shows approximately five very weak transitions close to (111) on the low field side of the main transitions. While we are unable to reproduce these weak transitions, we note that the eigenfield transitions calculated in this region for a particular strain value always have five points where the hyperfine lines cross. These crossing are always close to (111) [calculated to be exactly at (111) for \( P_2 = 0 \)], and the observed vertical streaks may be related to these transitions.

VII. CONCLUSIONS

The EPR spectrum of the Cu(II) doped MgO single crystals at 1.8 K, recorded as a function of the field orientation, has been explained in detail. The experimental spectra can be modeled in terms of a cubic spin Hamiltonian appropriate to a \( \Gamma_8 \) (\( ^2E \)) state operating within the set of four Kramers doublets corresponding to the lowest vibronic levels of an \( E \otimes e \) Jahn–Teller problem. We find that the first excited singlet is of \( A_2 \) symmetry, indicating that the CuO\(_6\) center has the expected Jahn–Teller potential energy surface with three minima at three equivalent tetragonally elongated octahedral geometries. Small random crystal strains have a dominant influence on the spectra and we find that the spectra can be best reproduced with a distribution of the random strain centered at zero. However, a single Gaussian distribution of the random strain together with a single intrinsic linewidth cannot reproduce all the observed linewidths. Our analysis differs from previous workers in that we find a much larger cubic anisotropy in the hyperfine values (\( A_1 = -19.0 \times 10^{-4} \) and \( qA_2 = -42.0 \times 10^{-5} \) cm\(^{-1}\)) as well as a nuclear quadrupole term (\( qP_2 = 5.5 \times 10^{-4} \) cm\(^{-1}\)), both of which are required to account for the hyperfine structure. The transitions within the lowest excited singlet are observed directly given an estimate of the tunneling splitting as \( \sim 4 \) cm\(^{-1}\). We conclude that the Cu(II)/MgO system can be described as an almost purely dynamic Jahn–Teller case, with most spectral features accounted for by a single isolated \( \Gamma_8 \) (\( ^2E \)) vibronic state.

APPENDIX: EIGENFIELD DETAILS

In the notation of Belford et al.,\(^{21}\) the matrix obtained from the evaluation of Eq. (6) in the basis described in Sec. IV is split into parts that are dependent (\( G \)) and independent (\( F \)) of the applied magnetic field. These 24×24 Hermitian matrices are then used to construct the two 576×576 “supermatrices,”

\[
A = \omega I \otimes 1 - F \otimes 1 + 1 \otimes F^* ,
\]

\[
B = G \otimes I - 1 \otimes G^* .
\]

The matrices \( A \) and \( B \) are also Hermitian and the solution of the generalized eigenvalue equation

\[
AZ = \lambda BZ
\]

(A2)

gives the resonant magnetic fields at the microwave frequency \( \omega \) as the eigenvalues \( \lambda \) and the transition probabilities as the eigenvectors \( Z \). It is advantageous to prediagonalize \( F \) and to transform \( G \) into the same basis. This makes \( A \) diagonal and Eq. (A2) can be converted into the ordinary eigenvalue equation

\[
B'Z' = (1/\lambda)Z'
\]

(A3)

using

\[
B'_{ij} = B_{ij}/\sqrt{A_{ii}A_{jj}}
\]

(A4)

This is only possible if \( A \) is positive definite so that it has the real positive eigenvalues \( A_{ii} \). In practice this means that the microwave frequency is greater than the zero-field energy separations, which will be fulfilled, for example, when \( \omega > \Delta_2 \) for the three state case. If this condition is not fulfilled, then Eq. (A2) must be solved directly. This approach of prediagonalizing \( F \) has the effect of filling in the zeros of matrix \( G \), but \( B \) remains suitably sparse to make the problem tractable. We use the implicitly restarted Arnoldi methods implemented in ARPACK (Ref. 33) for the solution of large sparse eigensystems. We have found that the performance of this package depends critically on the clustering behavior of the eigenfields of this problem.

Of the 276=\( 1/5 \) (576−24) possible positive eigenfield solutions, 132 will be at infinite field, corresponding to transitions between levels within the (or within the upper) Zeeman split components and are calculated as zeros in Eq. (A3). The remaining 144 transitions each involve 1 of the 9 possible Zeeman transitions between lower and upper components as shown schematically in Fig. 2. Each Zeeman component is split into four hyperfine levels, giving rise to 16 possible transitions between the split Zeeman components, most of which will carry little or no intensity. The transitions between the same Zeeman split states \( e^- \rightarrow e^+ \), \( \theta^* \rightarrow \theta^* \), \( A_2^- \rightarrow A_2^+ \) are the most intense and are shown as the solid lines in Fig. 2. There are also 32 \( e^- \rightarrow A_2^+ \) transitions and 32 \( A_2^- \rightarrow e^+ \), \( \theta^* \) type transitions which will occur at lower and higher fields, respectively, the actual position of which depends on the \( E \rightarrow A_2 \) separation \( \Delta_2 \). For \( \Delta_2 \) greater than the wavenumber of the microwave radiation (\( X \)-band \( \sim 0.31 \) cm\(^{-1}\)) these transitions will not occur. The remaining (144−64=80) resonant transitions will be clustered around the \( g=2 \) position. Typically the ARPACK routines will fail unless all transitions within a cluster (i.e., all 80) are requested. We find an improvement in the performance using the shift-invert methods in ARPACK used together with the sparse direct linear solver from the CXML library.\(^{34}\)
Once the resonant fields are found, the intensity of each transition can be calculated directly from multiplying the eigenvectors $Z^*$ with the “flattened” matrix of the dipole moment operator perpendicular from the static field direction $\langle \mu_\perp \rangle$, after first transforming $\langle \mu_\perp \rangle$ into the same basis that diagonalizes $F$ above. The relative energy of the initial state of the transition can be obtained by substituting each resonant field into Eq. (6) and diagonalization of the $24 \times 24$ matrix, and then the energy level differences are searched to match the microwave wavenumber used in the eigenfield calculation. Thus for a single field orientation, a “stick” spectrum is calculated from one $576$ eigenfield calculation. Thus for a single field orientation, a “stick” spectrum is calculated from one $576$ eigenfield calculation and then the energy level differences are searched to match the microwave wavenumber used in the eigenfield calculation. Thus for a single field orientation, a “stick” spectrum is calculated from one $576$ eigenfield calculation and further $80$ $24 \times 24$ diagonalizations of complex matrices.

19. See EPAPS Document No. E-JCPA6-130-045909 for Tables of reduction factors (S1) and further examples of the eigenfield calculations (S2,S3). For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
34. CXML, compaq extended math library, VISUAL FORTRAN 6.6.