Isotope effects in the ESR of Mn^{++} in Ca(OH)₂ and Ca(OD)₂[†]

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Large differences in the values of the spin-Hamiltonian parameter b_2^0 were observed in Ca(OH)₂ and Ca(OD)₂ at low temperatures, but were not detected in the remaining measured parameters. b_2^0 were analyzed in terms of lattice vibrations. The significance of the results for the remaining parameters is also discussed.

I. INTRODUCTION

The simplicity and high symmetry of the unit cell of Ca(OH)₂ and the absence of H bonding between its OH⁻ ions makes this crystal unique as a host of paramagnetic impurities. Recently completed investigations of the ESR spectra of several impurities (Mn⁺⁺, Cu⁺⁺, and Gd⁺³) revealed large temperature variations.¹⁻³ A study of the Mn⁺⁺ spectra in the range 4.2–800 °K confirmed some unusual features.³ In particular, the hyperfinestructure parameter A changed by over 4.3% and the axial parameter b_2^0 reversed its sign in this temperature range.

The thermal changes of the g factors, of the cubic parameters, and of A were first treated phenomenologically by Walsh *et al.*⁴ Their analysis recognized that in order to explain these changes one must consider at least two separate contributions: an implicit one originating from the thermal expansion and an explicit one originatirg from the lattice vibrations.

It is at once obvious that an implicit contribution to temperature variations, though significant numerically, fails to account for all the observable features. The explicit contribution, on the other hand, suffers from a lack of adequate theories. Simanek and Orbach⁵ calculated an orbit-lattice contribution to A in the MgO: Mn⁺⁺ system, but their results fell far too short of the experimental value. Subsequently, basing their calculations on the covalent reduction theories, Simanek and Muller⁶ obtained values for A that were closer to the experimental ones. Subsequent refinements of the orbitlattice model⁷ did not improve much the situation theoretically.

Other spin-Hamiltonian parameters have not been adequately treated, although an attempt was made by Holuj *et al.*³ to treat the thermal changes of the parameter b_2^0 as originating from the modulation of the crystal field by lattice vibrations.

The present work was undertaken in the hope that the substitution of deuterium for hydrogen in the $Ca(OH)_2$: Mn⁺⁺ system might yield additional information concerning the influence of lattice vibrations on the spin-Hamiltonian parameters.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The Ca(OD)₂ structure [such as that of Ca(OH)₂] consists of two sheets of hydroxyl ions located in the (0001) plane. A sheet of Ca ions is sandwiched between them. Each Ca ion is surrounded by six OH groups forming a slightly compressed octahedron (Fig. 1). Neutron-diffraction studies revealed that the motion of hydrogen ions is restricted to the (0001) plane only.⁸ Consequently, there are no hydrogen bonds. The crystal is very soft (2 on Moh's scale) and has perfect cleavage along (0001).

Single crystals of $Ca(OD)_2$ were obtained by slow diffusion of NaOD and $CaCl_2$ in an aqueous solution which was free of CO_2 and O_2 . They were doped with Mn^{**} during their growth.

All investigations reported here were carried out using an x-band bridge and a heterodyne ESR spectrometer of a conventional design. Two microwave cavities, each operating in the cylindrical TE_{011} mode, were either fitted with a crystal rotating de-



FIG. 1. The site symmetry of Ca⁺⁺ is a compressed octahedron with $\gamma = 61^{\circ}$. $\gamma = 54$ represents a regular octahedron (line D). The coordinate axes (x, y, z) have the Ca site as their origin.

TABLE I.	The spin-Hamiltonian parameters of	f
$Ca(OD)_2: Mn$	at 293 °K (in G when applicable).	

<i>g</i> u	g,	A ₁₁	A	b ⁰ ₂	54
2.0011	2.0010	-92,07	-90.41	-2.15	62.07
±0.0001	±0.0001	±0.14	±0.15	±0.07	±1.7

vice described earlier, ⁹ or with an electric heater. The former was used at temperatures of 4.2, 77, and 300 °K only. At other temperatures the crystal was preoriented at room temperature and then glued to the heater pin. Both cavities had a loaded $Q \approx 4000$.

The temperatures were measured with uncalibrated copper-constantan thermocouples in the range 80-300 °K and Pt/Pt-10%-Rh thermocouples above 300 °K, with an estimated accuracy ± 2 °C. Experimental resonant fields were measured at a minimum of five crystal orientations, one of which was along the *c* axis. Although it would be best to use the same orientations throughout the experiment, this was not always possible since the relative movements and overlaps experienced by various lines made accurate measurements impossible.

The spin-Hamiltonian parameters were determined in the usual way from the equation

$$\mathcal{K} = \mu_{B} \vec{H} \cdot \vec{g} \cdot \vec{S} + \frac{1}{3} b_{2}^{0} O_{2}^{0} + \frac{1}{60} (b_{4}^{0} O_{4}^{0} + b_{4}^{3} O_{4}^{3}) + \vec{I} \cdot \vec{A} \cdot \vec{S} .$$
(1)

The analysis was based on the coordinate system indicated in Fig. 1. Table I lists the spin-Hamiltonian parameters obtained at 293 $^{\circ}$ K.

The results for $A = (2A_1 + A_{\parallel})/2$, b_2^0 , and for $|b_4^3|$ are shown in Figs. 2-4. These figures also show variations of A, b_2^0 , and $|b_4^3|$ for Ca(OH)₂, since this crystal had to be re-examined in conjunction with the determination of b_4^3 . The g factors did not vary appreciably with temperature in either crystal. The results for b_4^0 showed too large a scatter to be of any interest and therefore have been omitted.



FIG. 2. Temperature variation of A of Mn^{*} in Ca(OH)₂ (circles) and Ca(OD)₂ (squares).

III. INTERACTION OF VIBRATIONS WITH THE CRYSTAL FIELD

We reproduce for convenience some pertinent expressions which have been already presented,³ but which contain errors in derivations and interpretation.

The crystal field may be expanded as follows in terms of the ionic displacement $\vec{\sigma}_i = \vec{s}_i - \vec{R}_i$:

$$V = V_0 + \sum_i (\vec{\nabla} V)_0 \cdot \vec{\sigma}_i + \frac{1}{2} \sum_{ij} \vec{\sigma}_i \cdot (\vec{\nabla}^2 V)_0 \cdot \vec{\sigma}_j + \cdots , \quad (2)$$

where the subscript 0 denotes equilibrium values.

The second term in Eq. (2) is the orbit-lattice interaction. It can be expressed as a sum of terms involving the normal modes of the XY_6 cluster. These normal modes transform as two A_{1g} and three E_g irreducible representations of the point group D_{3d} . Let us designate these representations as mA_{1g} and kE_g . In addition, the electron operators constructed of the second rank spherical harmonics transform according to A_{1g} and two E_g , the latter being designated as E_g^1 . Thus, the second term of Eq. (2) can be written

$$V_{\rm OL} = C(A_{1\mathfrak{g}}) \sum_{\mathfrak{m}} V(mA_{1\mathfrak{g}}) q(mA_{1\mathfrak{g}})$$
$$+ \sum_{k,l} V(kE_{\mathfrak{g}}^{l}) \sum_{i} C[E_{\mathfrak{g}}^{l}(i)] q[kE_{\mathfrak{g}}^{l}(i)] , \qquad (3)$$

where C's, V's and q's are, respectively, the electron operators, the coupling constants, and the normal modes.

All the terms of Eq. (3) are listed in Table II.



FIG. 3. Temperature variation of b_2^0 of Mn⁺⁺ in Ca(OH)₂ (circles) and Ca(OD)₂ (squares). The curves are theoretical and are discussed in Sec. IV.



FIG. 4. Temperature variation of b_4^3 of Mn⁺⁺ in Ca(OH) and Ca(OD)₂ (circles and squares, respectively).

Of course, Eq. (3) does not contribute to the parameters b_n^m in the first order, since it is linear in the ionic displacements. The third term of Eq. (2), on the other hand, does since it is quadratic in them. It can be written

$$\sum_{i} \frac{1}{2} \vec{\sigma}_{i} \cdot (\vec{\nabla}^{2} \vec{\nabla}) \cdot \vec{\sigma}_{i} = \sum_{n,m,j} r^{n} Znm(j) W_{n}^{m} \left(\frac{4\pi}{2n+1}\right)^{1/2} / R^{2},$$
(4)

where

$$W_n^m = \sum_{i=1}^n W_n^m(i) \quad ;$$

j implies the spherical polar angles of the jth electron; and

$$W_{2}^{0}(i) = (\frac{1}{2}Z_{2}C_{2} + B_{2})(\vec{\sigma}_{1} \cdot \vec{r}_{i})^{2}$$

$$- 3B_{2}\cos\gamma z_{i}(\vec{\sigma}_{i} \cdot \vec{r}_{i}) + \frac{3}{2}A_{2} z_{i}^{2}$$

$$- [\frac{1}{4}B(3\cos^{2}\gamma - 1) + \frac{1}{2}A_{2}]\sigma_{i}^{2} , \qquad (5)$$

$$W_{4}^{0}(i) = [\frac{1}{2}C_{4}Z_{4} + \frac{3}{2}B_{4}(5\cos^{2}\gamma - 1) + \frac{3}{2}A_{4}](\vec{\sigma}_{i} \cdot \vec{r}_{i})^{2}$$

$$- [\frac{1}{2}B_{4}Z_{4} + \frac{3}{4}(5\cos^{2}\gamma - 1)A_{4}]\sigma_{i}^{2}$$

$$- [\frac{5}{2}B_{4}(7\cos^{2}\gamma - 3) + 15A_{4}]\cos\gamma z_{i}(\vec{\sigma}_{i} \cdot \vec{r}_{i})$$

$$+ \frac{15}{4}A_{4}(7\cos^{2}\gamma - 1)z_{i}^{2} , \qquad (6)$$

$$W_{4}^{3}(i) = \frac{1}{2}Z_{3}C_{4}(\vec{\sigma}_{i} \cdot \vec{r}_{i})^{2} - (\frac{1}{2}Z_{3}B_{4} - 3\sqrt{\frac{35}{8}}A_{4}\sin\gamma\cos\gamma)$$

$$\times \sigma_{i}^{2} - \sqrt{\frac{35}{8}}B_{4}\sin^{2}\gamma[\sin\gamma\cos\gamma(z_{i}^{2} + 3t_{i}^{2})]$$

$$+ (3\cos^{2}\gamma + \sin^{2}\gamma)t_{i}z_{i}]$$

 $-6\sqrt[]{\frac{35}{8}}A_4\sin\gamma(t_i z_i \sin\gamma - t_i^2 \cos\gamma + \frac{1}{2}\cos\gamma z_i^2),$ (7)

where *i* implies the spherical polar angles of the *i*th ion; Z_2 , Z_3 , and Z_4 are, ¹⁰ respectively, $Z_{20}(i)(\frac{4}{5}\pi)^{1/2}$, $Z_{43}^c(i)(\frac{4}{9}\pi)^{1/2}$, and $Z_{40}(i)(\frac{4}{9}\pi)^{1/2}$. $\mathbf{\tilde{r}}_i$ is the unit vector of the Ca-O (or Ca-H) bond expressed in the frame of reference of Fig. 1. Furthermore,

$$A_{n} = ee'/R^{n+1}, \quad B_{n} = R^{n+1} \nabla (A_{n} / R^{n}) \quad ,$$

$$C_{n} = R^{n+3} \nabla (B_{n} / R^{n+2}); \qquad (8)$$

 t_i and z_i are related by $\overline{\sigma}_i \cdot \overline{\mathbf{r}}_i = t_i \sin \gamma + z_i \cos \gamma$. Using the notation of Ref. 3, the crystal-field operator is

TABLE II. Orbit-lattice coupling coefficients and normal coordinates of XY_6 molecule having D_{3d} symmetry.

$C[j\Gamma_i(n)]$	$RV(j\Gamma_i^k)$	$q[j\Gamma_i^k(n)]$	Symmetry	Abbreviated designation
$[\frac{1}{2}(3z^2-r^2)]$	$+\sqrt{\frac{3}{2}}B_2(3\cos^2\gamma - 1)\sin\gamma + \sqrt{6}A_2\sin\gamma$	$[x_1 + x_2 - 2x_3 - \sqrt{3}(y_1 - y_2)]/2\sqrt{6}$	1A _{1g}	<i>a</i> ₁
	$-\sqrt{\frac{3}{2}}B_2(3\cos^2\gamma-1)\cos\gamma+2\sqrt{6}A_2\cos\gamma$	$(z_1 + z_2 + z_3)/\sqrt{6}$	2A ₁	a_2
$[\sqrt{3}/2(x^2-y^2)]$ $[\sqrt{3}xy]$		$[x_1 + x_2 + 4x_3 - \sqrt{3}(y_1 - y_2)]/\sqrt{48}$	$1E_{g}^{1}(1)$	<i>c</i> ₁
	$-\frac{3}{2}B_2\sin^3\gamma + 6A_2\sin\gamma$	$+[x_1-x_2-\sqrt{3}(y_1+y_2)]/\sqrt{16}$	$1E_{g}^{1}(2)$	<i>s</i> ₁
		$(z_1 + z_2 - 2z_3)/\sqrt{12}$	$1E_{g}^{2}(1)$	c_2
	$rac{3}{2}B_2\sin^2\gamma\cos\gamma$	$(+z_1 - z_2)/2$	$1E_{g}^{2}(2)$	s_2
	$-3\sqrt{2} A_2 \sin\gamma$	$(x_1 + x_2 + x_3)/\sqrt{6}$	$1E_{\ell}^{3}(1)$	c_4
		$-(y+y_2+y_3)/\sqrt{6}$	$1E_{f}^{3}(2)$	$-s_4$
		$=q[1E_{\boldsymbol{\ell}}^{1}(1)]$	$2E_2^1(1)$	c_1
- 3 B	$-3B_2\sin^2\gamma\cos\gamma$	$= -q[1E_{\ell}^{1}(2)]$	$2E_{2}^{1}(2)$	$-s_1$
(√3 zx) (√3 zy)	$3B_2 \sin\gamma \cos^2\gamma - 3A_2 \sin\gamma$	$=q[1E_{f}^{2}(1)]$	$2E_2^2(1)$	c_2
		$= -q[1E_{f}^{2}(2)]$	$2E_2^2(2)$	$-s_{2}$
	_	$=q[1E_{f}^{3}(1)]$	$2E_2^3(1)$	c_4
	$3\sqrt{2} A_2 \cos\gamma$	$= -q[1E_g^3(2)]$	$2E_2^3(2)$	<i>s</i> ₄

$$V = \sum_{nmj} \left(\frac{4\pi}{2n+1} \right)^{1/2} r^n Z_{nm}(j) B_n^m \left(1 + \frac{W_n^m}{B_n^m} \right) .$$
 (9)

The spin-Hamiltonian parameters therefore are

$$b_n^m(T) = (1 + W_n^m / B_n^m) \ b_{nR}^m \ , \tag{10}$$

where b_{nR}^{m} are appropriate for a rigid lattice.

Of course, if one assumes that the square of the average values of (x_i, y_i, z_i) have equal weight, expressions (4)-(7) are identically zero. However, we believe that for a system involving d electrons, only ionic displacements which preserve the center of symmetry are active, i.e., the "gerade" modes, in which case we have, for example,

$$z_{i}^{2} + z_{i+3}^{2} = \frac{1}{2} \left(z_{i} - z_{i+3} \right)^{2} + \frac{1}{2} \left(z_{i} + z_{i+3} \right)^{2} \quad . \tag{11}$$

Therefore, expressions for W_n^m contain two identical components: one for g and one for u modes. Limiting ourselves to the former, we obtain

$$\sum_{i=1}^{6} (\vec{\sigma}_{i} \cdot \vec{r}_{i})^{2} = Q_{A}^{2} + Q_{u}^{2} + Q_{v}^{2} , \qquad (12)$$

$$\sum_{i=1}^{6} t_i^2 = a_1^2 + c_1^2 + s_1^2 \quad , \tag{13}$$

$$\sum_{i=1}^{6} z_i^2 = a_2^2 + c_2^2 + s_2^2 \quad , \tag{14}$$

$$\sum_{i=1}^{6} t_i z_i = -(a_1 a_2 + c_1 c_2 + s_1 s_2) . \qquad (15)$$

 s_i , c_i , and a_i are defined in Table II. Q_A , Q_u , and Q_v are, respectively, $a_2 \cos\gamma - a_1 \sin\gamma$, $c_2 \cos\gamma - c_1 \sin\gamma$, and $s_2 \cos\gamma - s_1 \sin\gamma$. While these transformations are not essential, they do help to visualize cluster vibrations: Q_A , for example, is the "breathing" mode. Figures illustrating Q_u and Q_v were given in Ref. 2.

The advantage of this formulation is that it enables us to use the same computational method as the one used in Ref. 3. For example, we have for the pair of i and i+3 ions

$$z_{i}^{2} = \sum_{\sigma} \frac{V\hbar}{NM_{i}\pi^{2}} \int \coth \frac{B\hbar\omega}{2} \langle zzii \rangle_{\sigma} \frac{k^{2}dk}{\omega} .$$
 (16)

The quantity $\langle \rangle_{\sigma}$, which is also a function of k, is defined in Ref. 3 and elsewhere, and occurs only with lattices with a base.⁷

We note in passing that Eqs. (5)-(7) and (16) do not involve cross products of different kinds of atoms except those related by the center of inversion. Hence, the various atoms contribute to W_n^m as squares of their zero-point vibration amplitudes, i.e., inversely as their masses. We note, furthermore, that this property is absent in the expressions for orbit-lattice contribution to A.

A. Hyperfine parameter A

Any effect instrumental in admixing the $(3d^44s)$ configuration into the $3d^5$, ⁶S state would contribute to A. As explained in Secs. I and III only two of these have been treated theoretically in any detail. The orbit-lattice interaction contributing only a very small amount⁵ and the covalency reduction contributing somewhat more.⁶ One simple model of the former involves Coulomb crystal field. The latter, on the other hand, involves the chemical bond between Mn and its ligand OD⁻. On intuitive grounds, therefore, one can expect that a substitution of D for H would have a larger influence on the orbit-lattice interaction than on the chemical bond.

Indeed, a notable result in Fig. 2 is that there is no noticeable difference in the temperature variations between A's measured in the two crystals.

B. Crystal-field parameters

As seen from Figs. 3 and 4, the results for b_2^0 show a large isotope effect, while those for b_4^3 do not. We have attempted to analyze these results for b_2^0 on the basis of Eq. (5).

Using a positive value for e' in Eq. (8) the coefficient of the first and the third terms are negative. For reasons given below, however, the contribution of the "umbrella" mode $\sum_i (y_i^2 + x_i^2)$, which can be easily computed from Eq. (5), is of particular interest. Its contribution is such that it can be fitted to experimental results easily with adjustable parameters.

One such computation was carried out for a set of parameters listed in Table III and resulted in the curves shown in Fig. 3. The agreement is quite satisfactory. A good agreement with experimental results could also be obtained using a common Debye temperature and that fraction of the density of the crystal which is attributable to H or D, i.e., $\frac{2}{12}$ and $\frac{4}{72}$, respectively [see Eq. (29) in Ref. 3].

We can understand these results, semiquantitatively at least, near 0 $^{\circ}$ K. Using Eq. (16) (Ref. 3) we see that this contribution should be inversely proportional to the masses of H and D since, in the case of the acoustical modes, it is proportional to the square of Debye temperature (and so to the in-

TABLE III. Contribution of the umbrella mode $\sum_i (x_i^2 + y_i^2)$ to b_2^0 .

	Debye temperature (°K)	b_{2R}^0	Optical frequency (cm ⁻¹)
Ca(OH) ₂	300	-21.5	175
$Ca(OD)_2$	200	-26.25	130

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verse of masses), and in the case of the optical modes it involves the inverses of the masses explicitly.

The umbrella mode $\sum_i (x_i^2 + y_i^2)$ is of particular interest here because of the following: H was shown by neutron diffraction by Busing and Levy⁸ to be able to perform this umbrellalike motion of exceptionally large amplitude. We believe that this mode may be responsible for some of the peculiarities of the b_2^0 parameter.

The results for b_4^3 in Ca(OH)₂, although showing a considerable scatter in Fig. 4, do not differ much from those for Ca(OD)₂. They can be thought, however, to be consistent with an observation recently reported by Michoulier and Gaite, ¹¹ that the quartic

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terms of the spin-Hamiltonian are very strongly influenced by the nearest neighbors. We also point to another peculiarity. There seems to be a discontinuity in temperature variation of b_4^3 around 0 °C. A similar discontinuity, though at somewhat lower temperature, is also evident in the curve for the longitudinal velocity of sound presented in Ref. 3. One wonders if these abnormalities are connected somehow with an observation reported by Megaw, ¹² who found a small discontinuous change of spacing of planes perpendicular to the triad axis at a temperature just above the boiling point of nitrogen. Its magnitude was about 0.07% and it was reversible. In view of the above, b_4^3 would be expected to be influenced most strongly by any phase changes.

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