

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

g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	b_2^0	$ b_4^3 $
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

$$\mathcal{H} = \mu_B \vec{H} \cdot \vec{g} \cdot \vec{S} + \frac{1}{3} b_2^0 O_2^0 + \frac{1}{60} (b_4^0 O_4^0 + b_4^3 O_4^3) + \vec{I} \cdot \vec{A} \cdot \vec{S} \quad (1)$$

The analysis was based on the coordinate system indicated in Fig. 1. Table I lists the spin-Hamiltonian parameters obtained at 293 °K.

The results for $A = (2A_{\perp} + A_{\parallel})/2$, 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 $\text{Ca}(\text{OH})_2$, 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.

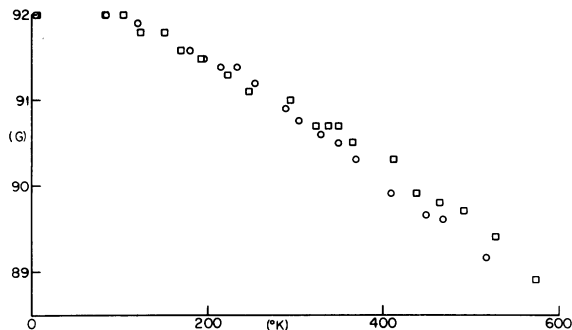


FIG. 2. Temperature variation of A of Mn^{2+} in $\text{Ca}(\text{OH})_2$ (circles) and $\text{Ca}(\text{OD})_2$ (squares).

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 $\vec{\sigma}_i = \vec{s}_i - \vec{R}_i$:

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

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 $m A_{1g}$ and $k E_g$. 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^i . Thus, the second term of Eq. (2) can be written

$$V_{OL} = C(A_{1g}) \sum_m V(m A_{1g}) q(m A_{1g}) + \sum_{k,i} V(k E_g^i) \sum_i C[E_g^i(i)] q[k E_g^i(i)] \quad (3)$$

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.

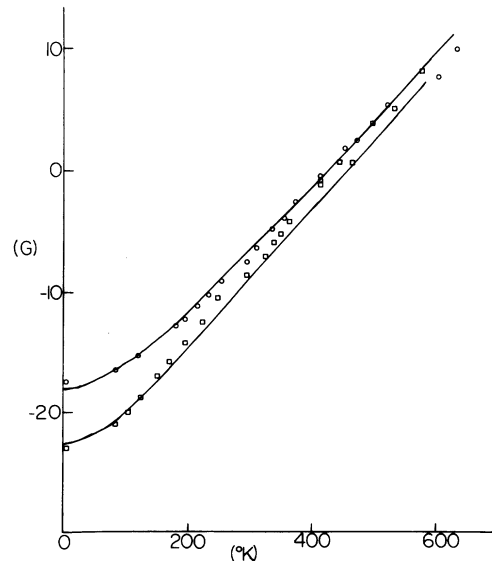


FIG. 3. Temperature variation of b_2^0 of Mn^{2+} in $\text{Ca}(\text{OH})_2$ (circles) and $\text{Ca}(\text{OD})_2$ (squares). The curves are theoretical and are discussed in Sec. IV.

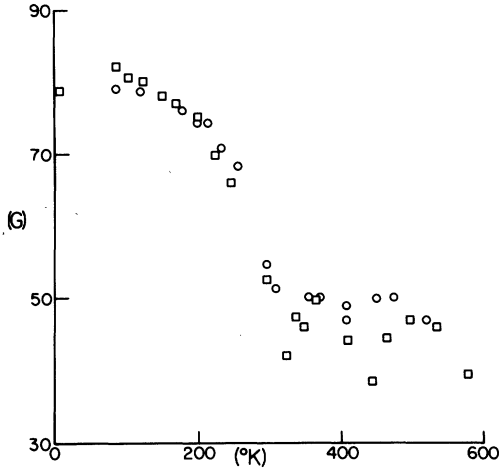


FIG. 4. Temperature variation of b_4^3 of Mn^{++} in $Ca(OH)_2$ and $Ca(OD)_2$ (circles and squares, respectively).

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

$$\sum_i \frac{1}{2} \vec{\sigma}_i \cdot (\vec{\nabla}^2 \vec{V}) \cdot \vec{\sigma}_i = \sum_{n,m,j} \gamma^n Znm(j) W_n^m \left(\frac{4\pi}{2n+1} \right)^{1/2} / R^2, \quad (4)$$

where

$$W_n^m = \sum_{i=1}^3 W_n^m(i);$$

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

$$W_2^0(i) = \left(\frac{1}{2} Z_2 C_2 + B_2 \right) (\vec{\sigma}_i \cdot \vec{r}_i)^2 - 3B_2 \cos \gamma z_i (\vec{\sigma}_i \cdot \vec{r}_i) + \frac{3}{2} A_2 z_i^2 - \left[\frac{1}{4} B (3 \cos^2 \gamma - 1) + \frac{1}{2} A_2 \right] \sigma_i^2, \quad (5)$$

$$W_4^0(i) = \left[\frac{1}{2} C_4 Z_4 + \frac{3}{2} B_4 (5 \cos^2 \gamma - 1) + \frac{3}{2} A_4 \right] (\vec{\sigma}_i \cdot \vec{r}_i)^2 - \left[\frac{1}{2} B_4 Z_4 + \frac{3}{4} (5 \cos^2 \gamma - 1) A_4 \right] \sigma_i^2 - \left[\frac{5}{2} B_4 (7 \cos^2 \gamma - 3) + 15 A_4 \right] \cos \gamma z_i (\vec{\sigma}_i \cdot \vec{r}_i) + \frac{15}{4} A_4 (7 \cos^2 \gamma - 1) z_i^2, \quad (6)$$

$$W_4^3(i) = \frac{1}{2} Z_3 C_4 (\vec{\sigma}_i \cdot \vec{r}_i)^2 - \left(\frac{1}{2} Z_3 B_4 - 3 \sqrt{\frac{35}{8}} A_4 \sin \gamma \cos \gamma \right) \times \sigma_i^2 - \sqrt{\frac{35}{8}} B_4 \sin^2 \gamma [\sin \gamma \cos \gamma (z_i^2 + 3 t_i^2) + (3 \cos^2 \gamma + \sin^2 \gamma) t_i z_i] - 6 \sqrt{\frac{35}{8}} A_4 \sin \gamma (t_i z_i \sin \gamma - t_i^2 \cos \gamma + \frac{1}{2} \cos \gamma z_i^2), \quad (7)$$

where i implies the spherical polar angles of the i th ion; Z_2 , Z_3 , and Z_4 are, ¹⁰ respectively, $Z_{20}(i)(\frac{4}{3}\pi)^{1/2}$, $Z_{43}^c(i)(\frac{4}{3}\pi)^{1/2}$, and $Z_{40}(i)(\frac{4}{3}\pi)^{1/2}$. \vec{r}_i is the unit vector of the Ca-O (or Ca-H) bond expressed in the frame of reference of Fig. 1.

Furthermore,

$$A_n = ee' / R^{n+1}, \quad B_n = R^{n+1} \nabla(A_n / R^n), \quad (8)$$

$$C_n = R^{n+3} \nabla(B_n / R^{n+2});$$

t_i and z_i are related by $\vec{\sigma}_i \cdot \vec{r}_i = t_i \sin \gamma + z_i \cos \gamma$.

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
$[\frac{1}{2}(3z^2 - r^2)]$	$+\sqrt{\frac{3}{2}} B_2 (3 \cos^2 \gamma - 1) \sin \gamma + \sqrt{6} A_2 \sin \gamma$	$[x_1 + x_2 - 2x_3 - \sqrt{3}(y_1 - y_2)] / 2\sqrt{6}$	$1A_{1g}$	a_1
	$-\sqrt{\frac{3}{2}} B_2 (3 \cos^2 \gamma - 1) \cos \gamma + 2\sqrt{6} A_2 \cos \gamma$	$(z_1 + z_2 + z_3) / \sqrt{6}$	$2A_{1g}$	a_2
$[\sqrt{3}/2(x^2 - y^2)]$	$-\frac{3}{2} B_2 \sin^3 \gamma + 6A_2 \sin \gamma$	$[x_1 + x_2 + 4x_3 - \sqrt{3}(y_1 - y_2)] / \sqrt{48}$	$1E_g^1(1)$	c_1
	$\frac{3}{2} B_2 \sin^2 \gamma \cos \gamma$	$+ [x_1 - x_2 - \sqrt{3}(y_1 + y_2)] / \sqrt{16}$	$1E_g^1(2)$	s_1
$[\sqrt{3}xy]$	$-3\sqrt{2} A_2 \sin \gamma$	$(z_1 + z_2 - 2z_3) / \sqrt{12}$	$1E_g^2(1)$	c_2
	$-3B_2 \sin^2 \gamma \cos \gamma$	$(+z_1 - z_2) / 2$	$1E_g^2(2)$	s_2
$(\sqrt{3}zx)$	$-3\sqrt{2} A_2 \sin \gamma$	$(x_1 + x_2 + x_3) / \sqrt{6}$	$1E_g^3(1)$	c_4
	$-3B_2 \sin^2 \gamma \cos \gamma$	$-(y + y_2 + y_3) / \sqrt{6}$	$1E_g^3(2)$	$-s_4$
$(\sqrt{3}zx)$	$3B_2 \sin \gamma \cos^2 \gamma - 3A_2 \sin \gamma$	$= q[1E_g^1(1)]$	$2E_g^1(1)$	c_1
		$= -q[1E_g^1(2)]$	$2E_g^1(2)$	$-s_1$
$(\sqrt{3}zy)$		$= q[1E_g^2(1)]$	$2E_g^2(1)$	c_2
		$= -q[1E_g^2(2)]$	$2E_g^2(2)$	$-s_2$
		$= q[1E_g^3(1)]$	$2E_g^3(1)$	c_4
	$3\sqrt{2} A_2 \cos \gamma$	$= -q[1E_g^3(2)]$	$2E_g^3(2)$	s_4

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

The spin-Hamiltonian parameters therefore are

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

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,

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

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

$$\sum_{i=1}^6 (\vec{\sigma}_i \cdot \vec{r}_i)^2 = Q_A^2 + Q_u^2 + Q_v^2, \quad (12)$$

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

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

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

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

$$z_i^2 = \sum_{\sigma} \frac{V \hbar}{NM_i \pi^2} \int \coth \frac{B \hbar \omega}{2} \langle z z i i \rangle_{\sigma} \frac{k^2 dk}{\omega}. \quad (16)$$

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 $(3d^4 4s)$ 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_4^0 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 $\frac{1}{12}$, respectively [see Eq. (29) in Ref. 3].

We can understand these results, semiquantitatively at least, near 0 °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

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: It 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

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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