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Paramagnetic Resonance of Impurities in $CaWO_4$. I. Two S-State Ions

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Paramagnetic resonance measurements have been made on Mn^{2+} and Gd^{3+} ions in single crystals of $CaWO_4$ grown from the melt. In both cases the four different possible substitutional sites in the unit cell lead to identical resonance spectra with tetragonal symmetry. The splitting of the electronic levels in zero magnetic field is much greater for Gd^{3+} than for Mn^{2+}, e.g., b_2^0 is 6.7 times greater and b_4^4 is 13 times greater. (b_n^m is the coefficient of an operator function having the same transformation properties as the corresponding spherical harmonic Y_n^m used in expanding the crystalline electric field.) The large value of b_2^0 (-0.0917 cm^{-1}) for Gd^{3+} makes it a potentially useful material for three-level masers. The lines are narrow, and the hfs due to $Gd^{155,157}$ is well resolved: the ratio A^{155}/A^{157} of the hyperfine splitting constants for the two isotopes was determined as 0.763 ± 0.006.

1. INTRODUCTION

We are investigating the paramagnetic resonance spectra of various paramagnetic ions introduced into a $CaWO_4$ host lattice. The principal advantages of using $CaWO_4$ are:

(1) It accepts ions of both the $3d$ and the $4f$ transition groups, and by adding a small amount of Na, it accepts not only divalent but also trivalent ions.

(2) As long as the paramagnetic ion substitutes for a Ca ion, the four possible positions for the paramagnetic ion in the unit cell all lead to identical paramagnetic resonance spectra. There is thus just a single spectrum for each paramagnetic impurity introduced into the host lattice. Furthermore the spectrum has tetragonal symmetry about the morphological tetragonal axis if $S \geq 2$, and axial symmetry about this morphological axis if $S < 2$. The resonance spectrum is thus especially easy to interpret.

(3) The limiting linewidth is very small, since the width contribution from the nuclear magnetic moments of the neighboring atoms is practically negligible. The nearest neighbors to the paramagnetic ion are oxygen atoms, of which over 99.9% have zero nuclear magnetic moment, and the effect of the small abundances of odd Ca and W isotopes is tiny.

(4) $CaWO_4$ is a hard and very stable material.

In this paper we give the results for the two S-state ions $Mn^{2+}(^6S_{5/2})$ and $Gd^{3+}(^8S_{7/2})$. Results on other ions will be described in future publications.

2. CRYSTAL STRUCTURE

The crystal structure is discussed by Wyckoff[1]: the space group is $C_{4h}^6(I4_1/a)$ with four molecules in the unit cell. There appears to be some uncertainty about the positions of the oxygen atoms in $CaWO_4$ and so, following Wyckoff, we shall use for illustrative purposes the positions deduced for KIO_4. It should however be emphasized that our main deductions are based solely on the symmetry of the crystal, and not on the positions of particular atoms.

Each Ca atom is surrounded by eight O atoms, with the Ca—O distance close to 2.5A. The four Ca sites are equivalent in pairs, one pair being derived from the other by body centering. Figure 1 shows the projections of the eight O atoms on the (001) plane through the Ca atom for the two sites: we see that they are related to each other by reflection in the (001) plane, and from this it follows that the paramagnetic resonance spectra for the two sites will be identical. This diagram also indicates that the two principal axes of the crystal field which lie in the (001) plane will not coincide with the axes of the unit cell, and hence not with the morphological axes.

3. EXPERIMENTAL PROCEDURE

The experiments were performed at low temperatures (77°K and ~2°K) using radiation of ~23 kMc/sec. The microwave spectrometer which was used is conventional except for a special absorption cavity with adjustable coupling to the waveguide.[2] This coupling was adjusted to be very near to critical (with the sample in place), and in this way high sensitivity is obtained to small changes in either absorption or

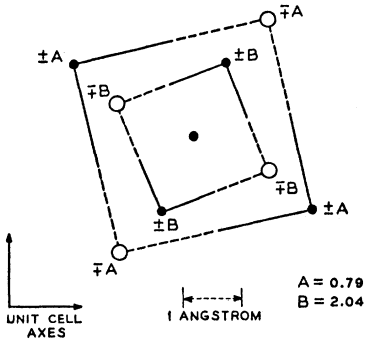

FIG. 1. Projection on the (001) plane through the Ca atom of the positions of the eight neighboring oxygen atoms. These projections for the two different sites are related to each other by reflection in the plane of the paper.

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[1] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948), Vol. II, Chap. 8.

[2] J. P. Gordon (to be published).

dispersion. This system is similar to a balanced bridge, but easier to adjust: a "balance" of about −60 db is readily obtainable without introducing appreciable instability noise. A superheterodyne receiver was used; to increase its sensitivity for weak signals, two phase sensitive detectors could be used. One employed small amplitude modulation of the magnetic field, and the other utilized the 60 Mc/sec intermediate frequency. Oscilloscope display is, however, more convenient and was used when measuring the stronger lines, and following them as the field direction was changed.

Magnetic field strengths of up to 10.5 koe were provided by a modified 12-inch Varian electromagnet rotatable about a vertical axis. Large Helmholtz coils provided field modulation of up to 50 oe at 100 cps while maintaining excellent homogeneity over the sample volume. Simultaneous slow sweep of the field was controlled by a function generator.

The crystal habit of $CaWO_4$ is a tetragonal bipyramid having an apex angle of 49°40′. This shape provides a convenient method of orienting a sample. A steel rod, ground to the appropriately shaped point, is heated and then pushed into an accurately machined piece of Lucite. The resulting hole holds the sample in place and orients it automatically. The Lucite is supported in a polyfoam plug in the cavity.

Measurements of both the microwave frequency (actually a subharmonic) and the magnetic field (using a "Numar" nuclear resonance probe) were made with a 10 Mc/sec decade counter whose clock was the Bell System frequency standard. Thus all data are referred to a very stable base, and the main limitation of accuracy is the width of the paramagnetic resonance lines themselves. With sufficiently strong lines, position measurements were made by displaying simultaneously on an oscilloscope the line itself (using field modulation) and the resonance of the "Numar" probe. Measurements were easily repeated to a precision of about $\frac{1}{5}$ of a linewidth, by simply bringing traces into superposition. With weaker lines, magnetic field modulation with phase sensitive detection was used to locate the center of a line. The excellent dc stability of the magnetic field permitted repeating of measurements again to about $\frac{1}{5}$ of a linewidth.

4. MANGANESE Mn^{2+}

The paramagnetic resonance spectrum due to Mn^{2+} was investigated in a crystal for which $Ca/Mn > 10^4$. Unless stated otherwise, the measurements described were made at 77°K.

The spectrum consisted of just $2S(2I+1)=5\times 6=30$ lines, indicating that the various paramagnetic complexes in the crystal all give identical resonance spectra. The lines were quite narrow: for the $M=\frac{1}{2}\leftrightarrow -\frac{1}{2}$ transitions, the peak-to-peak separation of the derivative of the line was only 0.34 oe; the $M=\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ lines were about twice as wide as this, and the $M=\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$ lines nearly four times as wide. These width variations may be explained by statistical fluctuations in the local crystalline field caused by strains in the crystal. Transitions associated with larger quantum numbers are more dependent on crystalline field. Some of the $M=\frac{1}{2}\leftrightarrow -\frac{1}{2}$ lines were observed carefully to determine their shape. They appeared to be closely Lorentzian from the center to about a full line width on either side. Beyond this the "tails" dropped more rapidly, as if of Gaussian shape.

The applied magnetic field was first rotated in a plane through the [001] axis, and the spectrum was observed to reach an extreme in this direction, which we shall denote by $\theta=0$. Next the field was rotated in the (001) or $\theta=\pi/2$ plane. It was found that the spectrum repeated precisely every $\Delta\varphi=\pi/2$, reaching two different extremes at $\varphi'=\delta$ and $\varphi'=\delta+\pi/4$, where φ' is the angle in the (001) plane measured from the edge of the bipyramid and δ was determined as $9°\pm 2°$. The fields at which the lines occurred were measured for the three extremes, i.e., $\theta=0$; $\theta=\pi/2$, $\varphi'=9°$; and $\theta=\pi/2$, $\varphi'=54°$.

The results can be interpreted in terms of the spin Hamiltonian,

$$\begin{aligned}\mathcal{H}=\,&g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)\\&+(a/6)(S_z^4+S_x^4+S_y^4-707/16)+D(S_z^2-35/12)\\&+(7/36)F[S_z^4-(95/14)S_z^2+81/16]\\&\qquad\qquad+AS_zI_z+B(S_xI_x+S_yI_y),\end{aligned}\tag{1}$$

with $S=I=\frac{5}{2}$. The first two terms give the interaction with the applied magnetic field, and the last two the nuclear hyperfine structure. The middle three terms relate to the splittings of the electronic levels in zero magnetic field produced by the crystalline electric field: the term in a corresponds to a cubic field, and the terms in D and F correspond, respectively, to tetragonal fields of the second and fourth degree. For our purposes it is probably more illuminating to rewrite these three terms as

$$B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4,$$

where each O_n^m is an operator function[3] having the same transformation properties as the corresponding spherical harmonic Y_n^m and the coefficients B_n^m are parameters to be determined by experiment. To simplify the expressions, these and other constants to be used below are redefined as follows:

$$\begin{aligned}b_2^0/B_2^0&\equiv 3,\\ b_4^0/B_4^0=b_4^4/B_4^4=b_6^4/B_6^4&\equiv 60,\\ b_6^0/B_6^0&\equiv 1260.\end{aligned}$$

Then the two expressions for the middle three terms of Eq. (1) are equivalent when

$$\begin{aligned}D&=b_2^0,\\ 3a+2F&=6b_4^0,\\ 5a&=2b_4^4.\end{aligned}$$

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[3] The operators are given explicitly by J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) A247, 141 (1958).

Under our experimental conditions, the effect of the applied field is so dominant over all the other interactions that only the $\Delta M=\pm1$, $\Delta m=0$ transitions are observed, and that it suffices to use second order perturbation theory. With H at $\theta=0$, these transitions occur at fields given by

$$M=\pm\tfrac{5}{2}\leftrightarrow\pm\tfrac{3}{2}:\ g_{\parallel}\beta H=h\nu\mp[4b_2^0+4b_4^0]-[Am+B^2(35-4m^2\pm16m)/8h\nu],$$

$$M=\pm\tfrac{3}{2}\leftrightarrow\pm\tfrac{1}{2}:\ g_{\parallel}\beta H=h\nu\mp[2b_2^0-5b_4^0]-[Am+B^2(35-4m^2\pm8m)/8h\nu],$$

$$M=+\tfrac{1}{2}\leftrightarrow-\tfrac{1}{2}:\ g_{\parallel}\beta H=h\nu-[Am+B^2(35-4m^2)/8h\nu],$$

and with H at $\theta=\pi/2$, at fields given by

$$M=\pm\tfrac{5}{2}\leftrightarrow\pm\tfrac{3}{2}:\ g_{\perp}\beta H =h\nu\mp\tfrac{1}{2}[-4b_2^0+3b_4^0+b_4^4\cos4\varphi]+(b_2^0)^2/h\nu-[Bm+(A^2+B^2)(35-4m^2)(16h\nu)^{-1}\pm2ABm/h\nu],$$

$$M=\pm\tfrac{3}{2}\leftrightarrow\pm\tfrac{1}{2}:\ g_{\perp}\beta H =h\nu\mp\tfrac{1}{8}[-8b_2^0-15b_4^0-5b_4^4\cos4\varphi]-(5/4)(b_2^0)^2/h\nu-[Bm+(A^2+B^2)(35-4m^2)(16h\nu)^{-1}\pm ABm/h\nu],$$

$$M=+\tfrac{1}{2}\leftrightarrow-\tfrac{1}{2}:\ g_{\perp}\beta H=h\nu-2(b_2^0)^2/h\nu-[Bm+(A^2+B^2)(35-4m^2)/16h\nu].$$

The measurements at $\theta=0$ thus effectively determine $g_{\parallel}$, b_2^0, b_4^0, and A; b_4^4 is determined from the variation with φ in the $\theta=\pi/2$ plane, and measurements in this plane also give $g_{\perp}$ and B, as well as checks on b_2^0 and b_4^0. The results are summarized in Table I. The relative signs of b_2^0 and b_4^0 were determined from the equations given above; the relative sign of b_4^4 is really indeterminate, as we have no means of knowing which direction in the $\theta=\pi/2$ plane corresponds to $\varphi=0$, as opposed to $\varphi=\pi/4$. If we arbitrarily assign $\varphi=0$ to the direction in which the spectrum reaches an extreme, 9° from the edge of the bipyramid, then b_4^4 would have the same sign as b_2^0 and b_4^0. The relative signs of b_2^0 and A were deduced by comparing the second-order shifts in the separations between the hyperfine components for the various electronic transitions. The absolute sign of b_2^0 was determined at ~2°K, where it was observed that when H is in the $\theta=\pi/2$ plane, the low-field lines lose intensity. The measurements at ~2°K showed incidentally that $|b_2^0|$ is 2% less at this temperature.

We note here that for a cubic environment we would have $b_4^4=+5b_4^0$, whereas we find experimentally that $b_4^4\simeq10b_4^0$. This indicates that the arrangement of the eight oxygen atoms surrounding the Mn^{2+} ion must differ considerably from that of a cube—in agreement with Wyckoff's discussion of the crystal structure.

TABLE I. Mn^{2+} in CaWO$_4$ at 77°K.

$g_{\parallel}$	1.99987 ± 0.0001
$g_{\perp}$	1.99980 ± 0.0002
$b_2^0=D$	$-137.6\pm0.3\times10^{-4}$ cm^{-1}
$b_4^0=a/2+F/3$	$-1.2\pm0.3\times10^{-4}$ cm^{-1}
$b_4^4=5a/2$	$(-)$[a]$11.5\pm0.3\times10^{-4}$ cm^{-1}
A	$-88.93\pm0.1\times10^{-4}$ cm^{-1}
B	$-89.53\pm0.1\times10^{-4}$ cm^{-1}

[a] See text.

TABLE II. Gd^{3+} in CaWO$_4$ at 77°K.

$g_{\parallel}$	1.9915 ± 0.0004
$g_{\perp}$	1.9916 ± 0.0004
b_2^0	$-916.7\pm1\times10^{-4}$ cm^{-1}
b_4^0	$-24.0\pm0.2\times10^{-4}$ cm^{-1}
b_4^4	$(-)$[a]$145.1\pm1\times10^{-4}$ cm^{-1}
b_6^0	$-0.6\pm0.3\times10^{-4}$ cm^{-1}
b_6^4	$0.0\pm0.3\times10^{-4}$ cm^{-1}

[a] See text.

5. GADOLINIUM Gd^{3+}

The paramagnetic resonance spectrum due to Gd^{3+} was investigated in a number of crystals for which Ca/Gd$\geq10^3$. These crystals also contained a small amount of Na(Na/Gd~1) but the experimental evidence indicates that the Na atoms do not affect the results. Unless stated otherwise, the measurements were made at 77°K.

The angular variation of the paramagnetic resonance spectrum was the same as for Mn^{2+} (see previous section): the paramagnetic complexes all gave identical resonance spectra, which reached extremes when the field was (a) parallel to [001], and (b,c) in the (001) plane 9° and 54° from the edge of the bipyramid. We shall again arbitrarily assign $\varphi=0$ to the direction 9° from the bipyramid's edge.

The spectrum consisted of $2S=7$ widely spaced strong lines, and a number of weaker ones. Some of these weaker ones were especially prominent when the field H made a large angle with the $\theta=0$ direction, and correspond to $\Delta M=\pm2$ transitions; such transitions are to be expected here as b_2^0 is so large as to be comparable with $g\beta H$. Other weak lines flanked the strong ones, and represent the hfs due to the odd Gd isotopes; the hfs will be described later.

The fields at which the strong lines occurred were measured for the three extreme directions (a,b,c) in a crystal for which Ca/Gd~10^4. The width of these lines varied from 0.4 oe (half-width at half power) for the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition when H is parallel to $\theta=0$, to about 4 oe for transitions very dependent on zero-field splittings.

The symmetry of the observed spectrum suggests that the results be interpreted in terms of the following spin Hamiltonian:

$$\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4+B_6^0O_6^0+B_6^4O_6^4,$$

with

$$S=\tfrac{7}{2}.$$

The first two terms give the interaction with the applied magnetic field, and the remaining terms relate

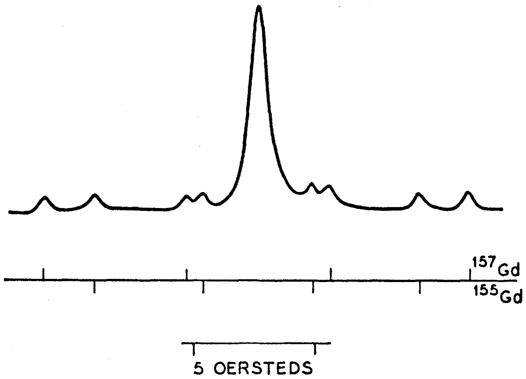

FIG. 2. The hfs due to Gd^{155} and Gd^{157}; $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition with H parallel to $\theta=0$.

to the splittings of the electronic levels in zero magnetic field. The operators O_n^m and coefficients B_n^m are defined in the preceding section. If the symmetry were cubic, we would have $b_4^4=5b_4^0$, and $b_6^4=-b_6^0$.

Since b_2^0 is so large, second-order perturbation theory is applicable only when the field H is applied parallel to $\theta=0$. For this direction, the $\Delta M=\pm1$ transitions occur at fields given by

$$M=\pm\tfrac{7}{2}\leftrightarrow\pm\tfrac{5}{2}:\ g_{\parallel}\beta H=h\nu\mp(6b_2^0+20b_4^0+6b_6^0) -p\{[0.35/(1\pm3q)]-0.75/(1\pm q)\},$$

$$M=\pm\tfrac{5}{2}\leftrightarrow\pm\tfrac{3}{2}:\ g_{\parallel}\beta H=h\nu\mp(4b_2^0-10b_4^0-14b_6^0) \pm p1.5q/(1-q^2),$$

$$M=\pm\tfrac{3}{2}\leftrightarrow\pm\tfrac{1}{2}:\ g_{\parallel}\beta H=h\nu\mp(2b_2^0-12b_4^0+14b_6^0) -p\{[0.75/(1\mp q)]-0.35/(1\mp3q)\},$$

$$M=+\tfrac{1}{2}\leftrightarrow-\tfrac{1}{2}:\ g_{\parallel}\beta H=h\nu-p0.7/(1-9q^2).$$

Here $p=(b_4^4)^2/g_{\parallel}\beta H$, and $q=b_2^0/g_{\parallel}\beta H$, and we have omitted the insignificant corrections for b_6^4.

With the help of a rough estimate for b_4^4 obtained from the variation in the $\theta=\pi/2$ plane, we can thus determine $g_{\parallel}$, b_2^0, b_4^0, and b_6^0. The remaining parameters $g_\perp$, b_4^4, and b_6^4 are determined from the data obtained with H in the $\theta=\pi/2$ plane. Unfortunately b_2^0 is too large for second-order perturbation theory to be applicable here, and the secular determinant is accordingly solved numerically for various values of b_4^4 and b_6^4 (and also $g_\perp$) with H parallel to $\theta=\pi/2$, $\varphi=0$ and $\pi/4$, until the fit with the experimental data is reasonably good.

The relative signs of b_2^0, b_4^0, and b_6^0 are determined from the equations given above, and the relative signs of b_4^4 and b_6^4 from the fit in the $\theta=\pi/2$ plane. With our choice for the $\varphi=0$ direction, this fit also demands that b_2^0 and b_4^4 have the same sign. The absolute sign of b_2^0 was determined at ~2°K, where it was observed that when H is in the $\theta=\pi/2$ plane, the low-field lines lose intensity. We note here that the signs of b_2^0, b_4^0, and b_4^4 are the same for Mn^{2+} and Gd^{3+}; also that for Gd^{3+}, as for Mn^{2+}, the environment must differ considerably from that of a cube, since the relation $b_4^4=5b_4^0$ is nowhere near being satisfied.

The large value of b_2^0 for Gd^{3+}, together with the excellent mechanical qualities of the host crystal, make this a potentially useful material for a three-level maser. It may be remarked here that the often heard argument against using materials with high values of S—that radio-frequency susceptibility is lost because the spins are divided amongst too many levels—is in fact fallacious, since the transition probabilities are higher when S is large. If $2g\beta HS\ll kT$, we can use

$$F=[S(S+1)-M(M+1)]/(2S+1),$$

for the figure of merit for the transition $M\leftrightarrow M+1$; $S=\frac{7}{2}$, $M=-\frac{1}{2}$ gives $F=\frac{3}{2}$, whereas $S=\frac{3}{2}$, $M=-\frac{1}{2}$ gives $F=1$. A comparison at temperatures such that $g\beta H\sim kT$, when only the lowest levels are appreciably populated, would make the higher values of S look still more favorable.

5.1 Hyperfine Structure of Gd^{155,157}

With the field H parallel to $\theta=0$, the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition was sufficiently narrow for the hfs due to the odd isotopes (Gd^{155}, 14.7% abundance; Gd^{157}, 15.7%) to be clearly visible (see Fig. 2). Both these isotopes have nuclear spin $I=\frac{3}{2}$,[4–6] and so each hfs component has only about 5% of the intensity of the main line, which is due to the even-even isotopes. In Table III our results are compared with those of other workers using different host crystals.

TABLE III. The hfs due to Gd^{155,157}.

Crystal	A^{155} (gauss)	A^{157} (gauss)	A^{155}/A^{157}	Reference
Bi$_2$Mg$_3$(NO$_3$)$_{12}$24H$_2$O	4.0 ±0.3	5.34 ±0.17	0.75 ±0.07	5
LaCl$_3$7D$_2$O		5.7 ±0.3		5
SrS	3.68 ±0.06	5.0 ±0.05	0.73 ±0.03	6
CaWO$_4$	4.45 ±0.02	5.84 ±0.02	0.763 ±0.006	This paper
Free atom			0.80 ±0.02	4

6. ACKNOWLEDGMENTS

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