

THE PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 153, No. 2

10 JANUARY 1967

Electron Paramagnetic Resonance of Mn^{2+} in $SrWO_4$

J. BRONSTEIN AND S. MANIV

Microwave Division, Department of Physics, The Hebrew University, Jerusalem, Israel

(Received 29 July 1966)

The spectrum of $SrWO_4:Mn^{2+}$ was measured with a Q -band spectrometer at 4.2°K. The results fit a tetragonal spin Hamiltonian. The parameters are: $g_{||}=1.9981\pm 0.0002$, $g_{\perp}=1.9973\pm 0.0002$, $b_2^0=-(107.7\pm 0.3)$, $b_4^0=-(1.0\pm 0.2)$, $b_4^4=-(5.3\pm 0.3)$, $A=-(89.0\pm 0.1)$, $B=-(90.1\pm 0.1)$ in units of 10^{-4} cm $^{-1}$. A comparison between these and the parameters for $Mn^{2+}:CaWO_4$ is made.

I. INTRODUCTION

RECENTLY, many investigations on paramagnetic ions in tungstates of the Scheelite structure have been performed. Of these, studies of the S -state ions form an important group because they could give an insight into the crystal field as well as the mechanism governing the splitting of the S states. In $CaWO_4$, the ions Fe^{3+} ,¹ Mn^{2+} ,² Eu^{2+} ,³ and Gd^{3+} ² have been investigated. Results have already been reported for Gd^{3+} in $SrWO_4$.⁴

We report here the data on Mn^{2+} in $SrWO_4$ and the method of obtaining the pertinent parameters in the Hamiltonian.

II. CRYSTAL STRUCTURE

The general Scheelite structure is given by Wyckoff,⁵ who also gives approximate values for the crystal parameters of $CaWO_4$ and $SrWO_4$. These values are given in Table I for comparison, although for $CaWO_4$ the parameters have already been measured more accurately.^{6,7} The crystals of $SrWO_4$ appear in pyramids and can therefore be easily oriented. The space group of $SrWO_4$ is $I4_1/a$ and the point group in the Ca and W

sites is S_4 . This being a cyclic group, the only nonaccidental degeneracy of the energy levels of an ion situated there is a Kramers degeneracy.

The $(3d^5)^6S_{5/2}$ ground state of Mn^{2+} in $SrWO_4$ therefore splits, owing to admixture with higher levels,⁸⁻¹⁰ into three Kramers doublets.

The natural site for the Mn^{2+} would be that of the Ca^{2+} , as no charge compensation is thus required. There are two inequivalent Ca^{2+} sites in a unit cell, which are related by reflection in the (001) plane, and are therefore magnetically equivalent. Consequently, one should expect only one tetragonal spectrum. This was indeed found.

III. THEORY

We assume that the energy levels can be obtained by a diagonalization, in the ${}^6S_{5/2}$ manifold, of an effective Hamiltonian whose magnetic field-free part is invariant under the S_4 point group. Developing this Hamiltonian in the O_n^m operators which in the above manifold have

TABLE I. Crystal parameters for $CaWO_4$ and $SrWO_4$ (from Wyckoff⁵).

	a (Å)	C (Å)	X^b (a units) ^c	Y^b (a units)	Z^b (C units) ^d
$CaWO_4$	5.24	11.38	0.25	0.15	0.075
$SrWO_4$	5.40	11.90	0.25	0.14	0.075

^a See Ref. 5.

^b X, Y, Z indicate the coordinates of the oxygens (see Ref. 5).

^c a is the side of the base of the unit cell.

^d C is the height of the unit cell.

⁸ J. H. Van Vleck and W. G. Penny, *Phil. Mag.* **17**, 961 (1934).

⁹ H. Watanabe, *Progr. Theoret. Phys. (Kyoto)* **18**, 405 (1957).

¹⁰ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **23**, 106 (1960).

¹ R. W. Kedzie and M. Kestigian, *Appl. Phys. Letters* **3**, 86 (1963).

² C. F. Hempstead and K. D. Bowers, *Phys. Rev.* **118**, 131 (1960).

³ J. Bronstein and V. Volterra, *Phys. Rev.* **137**, A1201 (1965).

⁴ M. Zaripov, A. Manenkov, and G. Chirkin, *Solid State Phys.* **8**, 262 (1966).

⁵ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1957), Vol. II, Chap. VIII.

⁶ A. Zalkin and D. M. Templeton, *J. Chem. Phys.* **40**, 501 (1964).

⁷ M. I. Kay *et al.*, *J. Chem. Phys.* **40**, 504 (1964).

matrix elements proportional to those of the spherical-harmonic operators Y_n^m , one finds for the above manifold, that only O_2^0 , $O_3^{\pm 2}$, O_4^0 , $O_4^{\pm 4}$, and $O_5^{\pm 2}$ are consistent with the S_4 symmetry. However, $O_3^{\pm 2}$ and $O_5^{\pm 2}$ are excluded from parity considerations. Hence the Hamiltonian is given by

$$\begin{aligned} \mathfrak{H}' = & g_{11}\beta S_z H_z + g_1\beta(S_x' H_{x'} + S_y' H_{y'}) + B_2^0 O_2^0 + B_4^0 O_4^0 \\ & + \bar{B}_4^4(O_4^4 + O_4^{-4}) + \frac{1}{i} C_4^4(O_4^4 - O_4^{-4}) \\ & + A S_z I_z + B(S_x' I_{x'} + S_y' I_{y'}). \quad (1) \end{aligned}$$

Transforming to a new X axis, by rotation of ϕ_0 around the C axis, one can cancel the C_4^4 term and obtain

$$\begin{aligned} \mathfrak{H} = & g_{11}\beta S_z H_z + g_1\beta(S_x H_x + S_y H_y) + B_2^0 O_2^0 + B_4^0 O_4^0 \\ & + B_4^4 O_4^4 + A S_z I_z + B(S_x I_x + S_y I_y), \quad (2) \end{aligned}$$

where from now on we write, in the usual way, O_4^4 instead of $O_4^4 + O_4^{-4}$. In Eq. (2), S is an angular-momentum operator with $S = \frac{5}{2}$ and I is the nuclear-spin operator. Mn^{2+} has one isotope with 100% abundance with $I = \frac{5}{2}$. Therefore, there are five allowed electronic transitions ($\Delta M = \pm 1$), each one splitting into six allowed hyperfine lines ($\Delta m = 0$).

If we take as the quantization axis an axis in the C plane which forms an angle φ with the new X axis, the O_n^m part of the Hamiltonian can be transformed into

$$E_2^0 O_2^0 + E_2^2 O_2^2 + E_4^0 O_4^0 + E_4^2 O_4^2 + E_4^4 O_4^4. \quad (3)$$

The O_n^m operators are defined then by

$$O_n^m(x, y, z) = O_n^m(z, x, y) \quad (4)$$

and the transformed parameters E_n^m are given by

$$\begin{aligned} E_2^0 &= -\frac{1}{2} B_2^0, & E_4^0 &= \frac{3}{8} B_4^0 + \frac{1}{8} B_4^4 \cos 4\varphi, \\ E_2^2 &= -\frac{3}{2} B_2^0, & E_4^2 &= \frac{5}{2} B_4^0 - \frac{1}{2} B_4^4 \cos 4\varphi, \\ & & E_4^4 &= (35/8) B_4^0 + \frac{1}{8} B_4^4 \cos 4\varphi. \end{aligned} \quad (5)$$

The Y_n^m used in our development are normalized so that all coefficients are integers with no common divisor.

The matrix elements of the O_n^m operators were calculated according to

$$\begin{aligned} \langle \frac{5}{2} m | O_k^q | \frac{5}{2} m' \rangle \\ = -\langle \frac{5}{2} || k || \frac{5}{2} \rangle (-)^{\frac{1}{2} - m} \begin{pmatrix} \frac{5}{2} & \frac{5}{2} & k \\ -m & m' & q \end{pmatrix} (C_k^q)^{-1}. \quad (6) \end{aligned}$$

Here C_k^q are normalization coefficients by which the Y_k^q have to be multiplied in order to conform to the

usual normalization,¹¹ and

$$\begin{aligned} \langle \frac{5}{2} || 2 || \frac{5}{2} \rangle &= 5 \left(\frac{21}{\pi} \right)^{1/2}, \\ \langle \frac{5}{2} || 4 || \frac{5}{2} \rangle &= \frac{135}{2} \left(\frac{7}{\pi} \right)^{1/2}. \end{aligned} \quad (7)$$

The magnetic field direction is taken as the axis of quantization. The off-diagonal elements at 34-kMc/sec resonance are rather small. The transitions for H in the C direction and in the C plane are hence given by a perturbation formula

$$\begin{aligned} H_0 = & H_{\pm 5/2 \pm} (a-b) + \frac{P^2}{2H_{\pm 5/2 \pm} (a-c)} - \frac{Q^2}{2H_{\pm 5/2 \pm} (b-c)} \\ & + R^2 \left[\frac{1}{4H_{\pm 5/2 \pm} (a-b)} - \frac{1}{4H_{\pm 5/2 \pm} (b-a)} \right] \\ & + \text{hyperfine interaction correction (hfc)}, \\ H_0 = & H_{\pm 3/2 \pm} (b-c) + \frac{P^2}{2H_{\pm 3/2 \pm} (a-c)} \\ & + Q^2 \left[\frac{1}{2H_{\pm 3/2 \pm} (b-c)} - \frac{1}{2H_{\pm 3/2 \pm} (c-b)} \right] \\ & + \frac{R^2}{4H_{\pm 3/2 \pm} (b-a)} + \text{hfc}, \end{aligned} \quad (8)$$

$$\begin{aligned} H_0 = & H_{1/2} - P^2 \left[\frac{1}{2H_{1/2} + a-c} + \frac{1}{2H_{1/2} + c-a} \right] \\ & + Q^2 \left[\frac{1}{2H_{1/2} + c-b} + \frac{1}{2H_{1/2} + b-c} \right] + \text{hfc}, \end{aligned}$$

here $H_{\pm M}$ denotes the $\pm M \leftrightarrow \pm M \mp 1$ transition.

The correction due to the hyperfine interaction for the electronic transition $M \rightarrow M-1$ can be written, since the fine or hyperfine structure splittings are not too large, as

$$\begin{aligned} Km + \frac{B^2}{4H_0} \left(\frac{A^2 + K^2}{K^2} \right) [I(I+1) - m^2] \\ + \frac{B^2}{2H_0} \left(\frac{A}{K} \right) m(2M-1). \quad (9) \end{aligned}$$

¹¹ J. L. Prather, Natl. Bur. Std. (U. S.), Monograph 19 (1961).

TABLE II. The lines of $Mn^{2+}:SrWO_4$ at 4.2°K at the C axis (all values in gauss).

DPPH ^a 12 379										
Line	$\frac{5}{2} \leftrightarrow \frac{3}{2}$		$\frac{3}{2} \leftrightarrow \frac{1}{2}$		$-\frac{1}{2} \leftrightarrow -\frac{3}{2}$		$-\frac{3}{2} \leftrightarrow -\frac{5}{2}$		$+\frac{1}{2} \leftrightarrow -\frac{1}{2}$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
13 114	13 114		12 875	12 875	12 429	12 428	12 190	12 189	12 652	12 651
13 018	13 018		12 777	12 778	12 332	12 330	12 091	12 091	12 556	12 555
12 923	12 923		12 681	12 683	12 235	12 233	11 992	11 993	12 459	12 458
12 829	12 829		12 587	12 588	12 138	12 137	11 895	11 895	12 364	12 363
12 735	12 736		12 493	12 494	12 042	12 042	11 798	11 799	12 268	12 268
12 642	12 644		12 400	12 401	11 946	11 947	11 702	11 704	12 174	12 174

^a Diphenylpicrylhydrazyl.

The parameters in formulas (8) and (9) are given by

	C axis	C plane	
a	$(10/3)b_2^0 + b_4^0$	$-(5/3)b_2^0 + \frac{3}{8}b_4^0 + \frac{1}{8}b_4^4 \cos 4\varphi$	(10)
b	$-\frac{2}{3}b_2^0 - 3b_4^0$	$\frac{1}{3}b_2^0 - (9/8)b_4^0 - \frac{3}{8}b_4^4 \cos 4\varphi$	
c	$-(8/3)b_2^0 + 2b_4^0$	$\frac{4}{3}b_2^0 + \frac{3}{4}b_4^0 + \frac{1}{4}b_4^4 \cos 4\varphi$	
P	0	$-(\sqrt{10})(\frac{1}{2}b_2^0 - \frac{3}{8}b_4^0 + (3/40)b_4^4 \cos 4\varphi)$	
Q	0	$-\sqrt{2}(\frac{3}{2}b_2^0 + \frac{5}{8}b_4^0 - \frac{1}{8}b_4^4 \cos 4\varphi)$	
R	$(\frac{1}{3}\sqrt{5})b_4^4$	$(\sqrt{5})(\frac{7}{8}b_4^0 + (1/40)b_4^4 \cos 4\varphi)$	
H_0	$h\nu/g_{11}\beta$	$h\nu/g_{11}\beta$	
K	A	B	

and

$$b_2^0 = 3B_2^0, \quad b_4^0 = 60B_4^0, \quad b_4^4 = 60B_4^4. \quad (11)$$

The over-all splitting of the H_M transition is given by

$$5|K|[1 + (B^2/2H_0K^2)A(2M-1)] \quad (12)$$

and from this equation one can obtain the sign of A by comparing the over-all splittings of the $H_{\pm M}$ transitions. The sign of B is supposed to be the same as that of A .

IV. APPARATUS AND EXPERIMENTAL RESULTS

Experiments were made on crystals (kindly given to us by Dr. Van Uitert of Bell Laboratories, U. S. A.), which contained a fraction 0.001 of rare-earth ions. All of the crystals were also found to contain Mn^{2+} in concentration as low as $[Ca]/[Mn] > 10^5$. All measurements were made at liquid-helium temperature, and the spectrum was also observed at 77°K and ~2°K. The spectrometer was a 34 kMc/sec V-4503 Varian spectrometer with a V-4561 microwave bridge. The field was measured with the dial of the apparatus, recalibrated by proton resonance.

In all crystals the same tetragonal spectrum was observed, the C axis being the tetragonal axis. The value of ϕ_0 was $(19 \pm 3)^\circ$, as compared to $(9 \pm 2)^\circ$ found for Mn^{2+} in $CaWO_4$.² The lines overlapped, and their order reversed when passing from the X axis to the C axis. No forbidden transitions were seen even at about 2°K.

It is important to note, as can be seen from formulas (8), (9), (10), that in the C plane there are *two* inequivalent extrema of the spectrum, which differ by 45°. In our definition, the new X axis is the one for which $b_4^4 < 0$.

The lines were identified by trying different assignments of the transitions to obtain

$$E_2^0 = -\frac{1}{2}B_2^0$$

as required by theory [Eq. (5)]. These results were supported by intensity measurements. The absolute signs of the parameters were determined from observation at about 2°K. A first iteration using the formulas (8), (9), and (10) yielded values for the parameters which gave the line positions to within experimental error (Tables II and III).

The parameters, compared with those obtained for Mn^{2+} in $CaWO_4$ are given in Table IV. The linewidths varied, at 77°K, from 3 G for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition to 5 G for the $\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$ transitions, measured between the peaks of the derivatives. The reason for the different linewidths is probably the existence of strains in the crystals which may tilt the C axis in different parts of the crystal, relative to its mean orientation. It can be seen from formulas (8)–(11) that the $H_{\pm 5/2}$ transitions are more sensitive to this than the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition when $|b_2^0|$ is large. When transforming the Hamiltonian (2) into a coordinate system in which \mathbf{H} is along the Z axis, making an angle θ with the C axis and an angle ϕ with the above-mentioned X axis, one obtains for the

TABLE III. The lines of $\text{Mn}^{2+}:\text{SrWO}_4$ at 4.2°K at the X axis (all values in gauss).

DPPH 12 412										
Line	$\frac{5}{2} \leftrightarrow \frac{3}{2}$		$\frac{3}{2} \leftrightarrow \frac{1}{2}$		$\frac{1}{2} \leftrightarrow -\frac{1}{2}$		$-\frac{1}{2} \leftrightarrow -\frac{3}{2}$		$-\frac{3}{2} \leftrightarrow -\frac{5}{2}$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
12 462	12 461	12 461	12 568	12 569	12 690	12 692	12 814	12 815	12 923	12 921
12 367	12 367	12 367	12 470	12 472	12 592	12 594	12 716	12 716	12 824	12 823
12 272	12 271	12 271	12 374	12 375	12 496	12 496	12 617	12 618	12 724	12 724
12 177	12 175	12 175	12 277	12 279	12 399	12 399	12 521	12 521	12 627	12 626
12 082	12 080	12 080	12 184	12 184	12 303	12 303	12 424	12 424	12 530	12 530
11 988	11 987	11 987	12 089	12 090	12 208	12 209	12 328	12 328	12 433	12 434

TABLE IV. Spin-Hamiltonian parameters for Mn^{2+} in CaWO_4 and SrWO_4 .^a

	Temp. ($^\circ\text{K}$)	ϕ_0^b	g_{II}	g_I	b_2^0 (in 10^{-4}cm^{-1})	b_4^0 (in 10^{-4}cm^{-1})	b_4^4 (in 10^4cm^{-1})	A (in 10^{-4}cm^{-1})	B (in 10^{-4}cm^{-1})
SrWO_4	4.2	$(19 \pm 3)^\circ$	1.9981 ± 0.0002	1.9973 ± 0.0002	$-(107.7 \pm 0.3)$	$-(1.0 \pm 0.2)$	$-(5.3 \pm 0.3)$	$-(89.0 \pm 0.1)$	$-(90.1 \pm 0.1)$
CaWO_4	77	$(9 \pm 2)^\circ$	1.9999 ± 0.0001	1.9998 ± 0.0002	$-(137.6 \pm 0.3)$	$-(1.2 \pm 0.3)$	$-(11.5 \pm 0.3)$	$-(88.93 \pm 0.1)$	$-(89.53 \pm 0.1)$

^a The CaWO_4 parameters are taken from Hempstead and Bowers [Phys. Rev. **118**, 131 (1960)].

^b ϕ_0 is the angle which the magnetic X axis makes with the unit cell's X axis.

coefficients of O_2^0 and O_4^0 the expressions

$$\begin{aligned} \Gamma_2^0 &= \frac{1}{4}B_2^0(1+3 \cos 2\theta), \\ \Gamma_4^0 &= (1/64)B_4^0(9+20 \cos 2\theta+35 \cos 4\theta) \\ &\quad + (1/64)B_4^4 \cos 4\phi(3-4 \cos 2\theta+\cos 4\theta). \end{aligned} \quad (13)$$

In first approximation we have

$$H_{\pm 5/2} = H_0 \mp 4(b_2^0 + b_4^0) + hfc$$

and therefore, because in our case $|b_4^0| \ll |b_2^0|$, we obtain for the width caused by the internal stresses the formula

$$(\Delta H)_{\text{stress}} \simeq b_2^0 \Delta(1+3 \cos 2\theta). \quad (14)$$

Therefore, from measurements parallel to the C axis we have

$$(\Delta\theta)_{\text{rms}} \simeq 2.5^\circ$$

for the mean de-orientation of the C axis, and of the whole unit-cell coordinate system as well. This causes, of course, a small asymmetry in the lines, which was indeed observed. However, the value obtained for $(\Delta\theta)_{\text{rms}}$ seems to be greater than is usually expected, and most probably the strains are not the sole contributors to the difference in linewidths between the $H_{\pm 5/2}$ and $H_{1/2}$ transitions. The angular variation of the linewidths could give an indication as to what the right mechanism is, but since here the spectrum varies slowly and the linewidths change very little, we could make no precise measurements.

V. DISCUSSION

A comparison between the parameters for $\text{Mn}^{2+}:\text{CaWO}_4$ and $\text{Mn}^{2+}:\text{SrWO}_4$ yields the following features:

(1) The $|b_n^m|$ values are smaller in SrWO_4 than those for CaWO_4 . The unit cell of SrWO_4 being somewhat bigger, this can be understood when considering the

contribution of the crystal field to the b_n^m 's. But the ratios $|b_n^m|_{\text{SrWO}_4}/|b_n^m|_{\text{CaWO}_4}$ do not show any regular behavior, being 1.28, 1.20, and 2.17 for b_2^0 , b_4^0 , and b_4^4 respectively (the change from 77° to 4.2° is of about 22%). The ratios of the A and C values (see Table I) are 1.03 and 1.05, respectively.

(2) The g values in SrWO_4 show a higher anisotropy than in CaWO_4 , the corresponding g_{II}/g_I values being 1.0004 and 1.0001. This is consistent with the change of the anisotropy, the corresponding values of C/a being 2.204 and 2.171.

(3) We see that A and B are slightly greater in SrWO_4 than in CaWO_4 . This indicates a slightly less covalent bonding for SrWO_4 , which is again consistent with SrWO_4 having a bigger unit cell.

(4) The comparison of the ϕ_0 angles shows that the charge distribution in SrWO_4 near the Mn^{2+} is quite different from that in CaWO_4 . For example, assuming a point-charge model and assuming the charge distribution in the complex WO_4^{2-} to be $W^{6\alpha}[\text{O}^{-\frac{1}{2}(1+\beta\alpha)}]_4$, $0 \leq \alpha \leq 1$, the ϕ_0 angle is a function of α , thus showing that ϕ_0 depends on the degree of covalency in the WO_4^{2-} complex. Considering the symmetry of the b_n^m parameters, one should expect $b_2^0 = 0$ and $5b_4^0 = b_4^4$ for cubic symmetry. For our case $b_2^0 \neq 0$ but the second condition is surprisingly—but, most probably, accidentally—fulfilled. Comparing these parameters with those for Gd^{3+} in the same environment,⁴ one can see a complete departure even in the signs of the b_n^m 's, b_4^4/b_4^0 being -7 for Gd^{3+} . We can see no explanation for this change of sign.

ACKNOWLEDGMENTS

The authors wish to thank to Professor W. Low and Professor M. Weger for reading the manuscript and for fruitful remarks.