

only increases the magnitude of the calculated magnetic hyperfine field. No explanation has as yet been found for this discrepancy. It is possible that the electronic configuration of the ion following the β decay of Eu^{154} is neither that of the ground state of Eu^{3+} nor Gd^{3+} . Since the electronic configuration of the Gd^{154} ion is not known, the root-mean square value of the magnetic hyperfine field $\langle \mathbf{H}_{\text{int}}^2 \rangle^{1/2}$ and, hence, the magnitude of the electronic relaxation time τ_s , could not be obtained in this case. From the values of

$\lambda\tau_N$ at 400 and 25°C we can deduce that the electronic relaxation time does not increase by more than 20% between room temperature and 400°C.

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Electron Spin Resonance of Fe^{3+} and Mn^{2+} in Single Crystals of CaO

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Single crystals of CaO doped with Mn^{2+} and Fe^{3+} have been investigated by paramagnetic resonance at 9.5 kMc/sec. Both ions are found to go in substitutionally for the Ca^{2+} ion. The spectrum of each can be described by a spin Hamiltonian for an ion in a cubic field. The parameters determined for Mn^{2+} are $g=2.0009 \pm 0.0005$, $a=(5.9 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$ and $A=(-80.8 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}$. The Fe^{3+} parameters are $g=2.0052 \pm 0.0005$ and $a=(63.8 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$. The results are discussed in relationship to the Powell, Gabriel, and Johnston theory of the ground-state splitting of Mn^{2+} by cubic crystalline fields.

INTRODUCTION

THE partial splitting of the sixfold degeneracy of $3d^5$, 6S ground-state ions by cubic crystalline fields has been a subject of considerable interest in recent years. The theory of Watanabe¹ predicts that the splitting between the doublet (Γ_7) and the quartet (Γ_8) levels is proportional to even powers of the crystal potential V , with V^2 the dominant term. One consequence of this theory is that the sign of the cubic-field splitting parameter a is independent of the sign of the cubic potential which is dependent on whether the coordination is octahedral, tetrahedral, or fluorite. To date, all values of a have been found to be positive with one exception, that of Mn^{2+} in NaCl where Watkins² has tentatively assigned a negative value of a to explain the spectra observed.

Powell, Gabriel, and Johnston³ have criticized Watanabe's arguments and pointed out that on going from a picture in terms of electrons to one in terms of holes that odd powers of V would also contribute. Calculations for Mn^{2+} based on this theory predict positive values for a with the exception of small Dq values ranging between 0 and 200 cm^{-1} . The results of Watkins² are consistent with the theory of Powell *et al.*; but Geshwind⁴ points out that the very small negative

value of a (10^{-4} cm^{-1}) could arise from excited configurations. Walsh⁵ has studied the effects of hydrostatic pressure on the paramagnetic spectra of Mn^{2+} and Fe^{3+} in cubic MgO. The results of this study showed that the pressure dependencies of a for Mn^{2+} and Fe^{3+} are identical and are proportional to V^4 . These results were found to be consistent with the calculations of Powell *et al.*³ On the other hand, in a comparison of the cubic field splittings of Fe^{3+} occupying octahedral and tetrahedral sites in yttrium gallium garnet, Geschwind⁴ found that the ratio of the two splittings was proportional to V^2 .

More recently, Gabriel, Johnston, and Powell⁶ have revised their calculation for Mn^{2+} in MgO and found that the predicted value for the cubic-field splitting using the Pratt and Coelho⁷ optical data for MnO resulted in a value which was far too small. Among the possible causes for this discrepancy was the difference in lattice parameters between MgO and MnO affecting Dq .

Because of the general interest in 6S ions, the spectra of Mn^{2+} and Fe^{3+} have been investigated in CaO. This presents an opportunity to compare the cubic-field splittings in CaO with those observed in isomorphous MgO and a further comparison with the theory of Powell *et al.*,⁶ especially with regard to the effect of a change in lattice parameter.

¹ H. Watanabe, Prog. Theoret. Phys. (Japan) **18**, 405 (1957).

² G. D. Watkins, Phys. Rev. **113**, 79 (1959).

³ M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Letters **5**, 145 (1960).

⁴ S. Geschwind, Phys. Rev. **121**, 363 (1961).

⁵ W. M. Walsh, Jr., Phys. Rev. **122**, 762 (1961).

⁶ J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, Proc. Roy. Soc. (London) **A264**, 503 (1961).

⁷ W. Pratt and R. Coelho, Phys. Rev. **116**, 281 (1959).

TABLE I. Spin Hamiltonian parameters of Mn^{2+} and Fe^{3+} .

Crystal	M-O distance of host lattice in Å	Ion	Temp. (°K)	A (10^{-4} cm^{-1})	a (10^{-4} cm^{-1})	g	Reference
CaO	2.4	Fe^{3+}	77		63.8 ± 0.3	2.0052 ± 0.0005	This paper
		Mn^{2+}	290	-80.8 ± 0.2	5.9 ± 0.3	2.0009 ± 0.0005	
MgO	2.1	Fe^{3+}	290		205	2.0037 ± 0.0007	a
		Mn^{2+}	290	-81.0 ± 0.2	18.6 ± 0.3	2.0014 ± 0.0005	b

^a W. Low, Phys. Rev. **105**, 793 (1957).

^b W. Low, Proc. Phys. Soc. (London) **B69**, 1169 (1956).

EXPERIMENTAL PROCEDURE

All measurements were performed at X band using a Varian V-4500 EPR spectrometer. The samples were placed on the side wall of a rectangular TE_{102} cavity resonating at approximately 9.5 kMc/sec. The magnetic field was produced with a rotating base 12-in. Varian magnet; field modulation of 200 cps was used.

The microwave frequency was determined by zero beating against the harmonics of a Hewlett Packard 540A transfer oscillator whose frequency in turn was measured by a Hewlett Packard 524C counter.

Magnetic field measurements were made with a Varian F-8 fluxmeter. Calibration of the field was accomplished by a comparison with the resonance of polycrystalline diphenyl picryl hydrazyl with $g=2.0036$.⁸

Single crystals of CaO were obtained from Semi-Elements Inc. The impurities were introduced with a concentration of approximately 0.05% by weight. Crystals grown from the undoped starting material were found to have both Mn^{2+} and Fe^{3+} present as trace impurities. Specimens were cleaved into pieces approximately $2 \times 10 \times 10$ mm and were x-ray oriented.

EXPERIMENTAL RESULTS

The behavior of the paramagnetic spectra of Fe^{3+} in CaO can be described accurately by the spin Hamiltonian for a 6S state in a cubic field which is of the form

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + \frac{1}{6}a[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)], \quad (1)$$

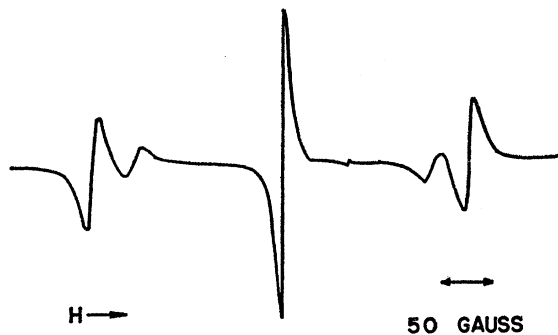


FIG. 1. First derivative of absorption spectrum of Fe^{3+} in CaO with H directed along $[100]$.

⁸ C. H. Townes and J. Turkevitch, Phys. Rev. **77**, 148 (1950).

where the positions of the resonance lines are given by

$$\begin{aligned} M = \pm \frac{5}{2} &\leftrightarrow \pm \frac{3}{2}, & g\beta H &= g\beta H_0 \mp 2pa, \\ M = \pm \frac{3}{2} &\leftrightarrow \pm \frac{1}{2}, & g\beta H &= g\beta H_0 \pm \frac{5}{2}pa, \\ M = +\frac{1}{2} &\leftrightarrow -\frac{1}{2}, & g\beta H &= g\beta H_0, \end{aligned} \quad (2)$$

where $p = 1 - 5\phi$, $\phi = \frac{1}{2}(m^2 + m^2n^2 + n^2l^2)$, and l, m, n are the direction cosines of the magnetic field relative to the principal cubic axes x, y, z .

The room-temperature measurement revealed that the Fe^{3+} ions had an unusually short relaxation time. The linewidths were so broad that the $\pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$ and $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ transitions could not be resolved at room temperature. The parameters of the spin Hamiltonian were, subsequently, measured at 77°K. The parameters g and a are given in Table I. The spectrum of the Fe^{3+} pentad with the magnetic field directed along $[100]$ is illustrated in Fig. 1. The integrated intensities of the five transitions were found to be in good agreement with the theoretical intensity ratios of 8:5:9:5:8.

The sign of the cubic-field splitting parameter a was determined by observing the relative intensities of the fine structure lines at liquid helium temperature as suggested by Low.⁹

The spectrum of Mn^{2+} is characterized by a group of six pentads as is shown in Fig. 2. This arises from the situation where the hyperfine interaction is greater than the cubic-field splitting. The hyperfine interaction is taken into account by the term $\mathbf{A} \cdot \mathbf{S}$ which must be included in the spin Hamiltonian (1). This results in an additional term which must be added to equation (2) and is of the form

$$-Am - (A^2/2g\beta H_0)[I(I+1) - m^2 + m(2M-1)], \quad (3)$$

where M and m are the magnetic quantum numbers of the electron and nuclear spin, respectively. One can notice the relative shifts of the five fine-structure lines produced by second-order effects as one proceeds to successive hyperfine groups. The integrated intensities of the Mn^{2+} pentad were found to be in good agreement with the theoretical intensity ratios 8:5:9:5:8. The sign of a was again determined by observing the relative intensities of the fine structure lines at liquid helium

⁹ W. Low, Phys. Rev. **105**, 792 (1957).

temperature. The parameters g , A , and a are given in Table I.

DISCUSSION

The Powell, Gabriel, and Johnston theory for Mn^{2+} predicts that the cubic-field splitting parameter a is most sensitive to the spin-orbit coupling, λ and Dq , varying approximately as λ^4 and $(Dq)^n$ where n varies from 3 to 6 for Dq values ranging between 700 cm^{-1} to 1500 cm^{-1} . The value for λ for iron group ions is found to be reduced from the free ion value when placed in a solid environment. Marshall and Stuart¹⁰ attribute this reduction to screening effects of ligand electrons. Consequently, Gabriel *et al.*⁶ have revised their initial calculations from Mn^{2+} using a reduced value for the spin-orbit coupling coefficient and the optical data obtained from MnO by Pratt and Coelho. By establishing an upper bound of $\lambda \approx 260\text{ cm}^{-1}$, they find that the observed ground-state splitting for Mn^{2+} in MgO can only be accounted for by their model, if Dq for Mn^{2+} in MgO is about 30% larger than the observed Dq (979 cm^{-1}) for Mn^{2+} in MnO . They suggest that the difference in lattice parameters between MnO (4.435 Å) and MgO (4.203 Å) may be the source of this discrepancy. A comparison of previous MgO results and the CaO data presented in this paper would certainly lend evidence to this suggestion. Similar effects of change in lattice parameters for noncubic $\text{MgCl}_2:\text{Mn}^{2+}$ and $\text{CdCl}_2:\text{Mn}^{2+}$ have been observed by Hall *et al.*,¹¹ but only a - F could be determined. Assuming that local lattice parameters are not changed appreciably when Mn^{2+} replaces Mg^{2+} in MgO , a calculation of the relative field strengths between MgO and MnO , based on a simple point-charge model, will account for this increase in Dq for Mn^{2+} . The ratio $a(\text{Fe}^{3+})/a(\text{Mn}^{2+})$ for CaO is 10.8 and compares favorably with the values 10.7 and 11 for MgO reported by Walsh⁵ and Low,¹² respectively. The relative constancy of the ratio $a(\text{Fe}^{3+})/a(\text{Mn}^{2+})$ shown by the MgO and CaO data can be construed as an indication that

¹⁰ W. Marshall and R. Stuart, *Phys. Rev.* **123**, 2048 (1961).

¹¹ T. P. P. Hall, W. Hayes, and F. I. B. Williams, *Proc. Phys. Soc. (London)* **A78**, 883 (1961).

¹² W. Low, *Phys. Rev.* **105**, 793 (1957).

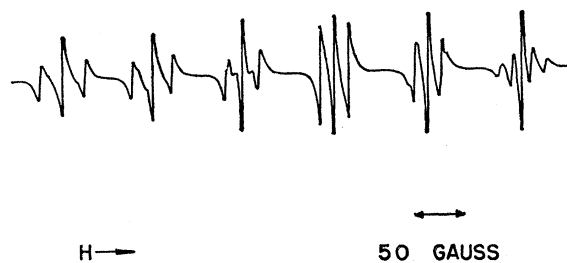


FIG. 2. First derivative of absorption spectrum of Mn^{2+} in CaO with H directed along $[100]$.

local lattice parameters in the vicinity of the impurity ion are not appreciably changed. It is difficult to picture how the trivalent ion can change the local lattice parameters in the same manner as the divalent ion and keep this ratio constant.

A calculation for Dq in CaO (4.797 Å) based on the Dq value for MnO using a simple point charge model yields a value of approximately 680 cm^{-1} . Assuming that there is no change in the value for λ between MgO and CaO , with the aid of Table V of Gabriel *et al.*,⁶ one can ascertain that the value predicted for a is considerably lower than the experimental value. For a calculated value to be in agreement with the measured value, an increase in the value for λ in CaO would be required. If screening effects of ligand electrons are responsible for the reduction of λ in the solid, an increase in the metal to oxygen distance between MgO and CaO would certainly be expected to result in an increase in λ for Mn^{2+} in CaO , since overlap effects would be expected to be reduced with an increase in the Mn-O distance. It would be interesting to perform a series of optical and electron spin resonance measurements on a series of isomorphous crystals such as V^{2+} - or Ni^{2+} -doped MgO , CaO , BaO , and SrO in order to detect whether there is a measurable change in λ as a function of lattice parameter. A further check on the validity of the above arguments could be obtained by hydrostatic pressure measurements on $\text{CaO}:\text{Mn}^{2+}$; for the theory of Powell *et al.* predicts a third power dependence on Dq for a Dq value of 700 cm^{-1} .