

Effects of Hydrostatic Pressure on the Paramagnetic Resonance Spectra of Several Iron Group Ions in Cubic Crystals*

WALTER M. WALSH, JR.†

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

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The magnetic resonance spectra of Cr^{3+} , Mn^{2+} , Fe^{3+} , and Ni^{2+} present as substitutional impurities in MgO crystals and powders, and of Mn^{2+} in cubic ZnS have been observed as functions of hydrostatic pressure at room temperature. The results are interpreted assuming the local compressibilities to be equal to those of the pure host lattices.

The measured volume dependence of the orbital contributions to the magnetic moments of the F -state ions, Cr^{3+} and Ni^{2+} , are consistent with a point-charge model within the experimental error. This simple model can only crudely account for the observed magnitudes of the orbital singlet-triplet splittings, however.

The pressure dependences of the cubic field splittings of the

S -state ions, Mn^{2+} and Fe^{3+} , are identical in MgO and correspond roughly to a fourth power law if an ionic potential is assumed. The cubic field parameter for Mn^{2+} in ZnS varies half as rapidly with volume. These results are consistent with recent calculations of Powell, Gabriel, and Johnston if it is assumed that the volume dependence of the cubic potentials in these lattices are given by the ionic model, though the relative magnitudes are not.

The hyperfine structure of the manganese spectra also proves sensitive to sample volume, particularly in the sulfide. The effect may be qualitatively understood in terms of the exchange-polarization theory of the strong electron-nuclear interaction.

INTRODUCTION

THE results to be presented in this article represent a continuation and refinement of earlier efforts to study crystalline potentials by observing paramagnetic resonance of iron group ions in samples whose strain and temperature state may be varied. Previous investigations of nickel fluosilicate, chrome alum, and chromicyanide crystals¹ proved difficult to interpret due to insufficient knowledge of the changes in *internal* structure of these complex unit cells produced by stress and temperature variations. Though these experiments served to indicate the importance of explicit lattice vibration effects as well as time-averaged geometrical parameters the analysis could at best be made only semiquantitative.

Recent paramagnetic resonance (PMR) studies have shown that a variety of magnetic ions may be substitutionally incorporated into simple cubic, diamagnetic lattices such as magnesia and zinblende, despite size and even valence disparities with respect to the host cations. The possibility of obtaining interpretable data in such straightforward geometries prompted the present research. Single crystals and powders of MgO containing several types of iron group ions in low concentrations were obtained. In particular, the PMR spectra of Cr^{3+} , Mn^{2+} , Fe^{3+} , and Ni^{2+} were examined fairly extensively. A natural crystal of cubic ZnS (zinblende) containing traces of Mn^{2+} was also studied. Following a description of some experimental details (Sec. I) the paper separates quite naturally into two parts (Secs. II and III) which deal with the F -state ions, Cr^{3+} and Ni^{2+} , and the S -state ions, Mn^{2+} and Fe^{3+} , respectively.

I. APPARATUS

Much of the equipment described earlier^{1,2} was used in these experiments though improvements in sensitivity, stability, and accuracy were required. The necessity for such refinements arose from the usually low concentrations of magnetic ions in the available samples and to the minuscule changes in spin-Hamiltonian parameters to be measured.

The sensitivity of the X-band spectrometer was increased by two to three orders of magnitude upon converting from diode (1N23C) to bolometer (Narda 610B) detection. The small conversion gain of the thermal detector required the use of a low-noise preamplifier (Millivac VS-64A) in order to profit from the improved signal-to-noise ratio. Various crude determinations of spectrometer sensitivity yielded figures near $5 \times 10^{11} \Delta H^2$ spins for unity signal-to-noise ratio at room temperature with a 1-cps bandwidth.

In order to improve the stability of the current regulated magnet, the output of the PMR spectrometer was added to the feedback signal in the control loop, thus locking the magnet to the zero-slope point of the resonance line being measured. Under optimum conditions a short-term field stability of a few parts in 10^6 could be attained by this means. The field was measured using a modified Pound nuclear magnetic resonance (NMR) spectrometer. The NMR frequency was zero-beat against a harmonic of a military-type frequency meter whose fundamental was amplified and read from an electronic counter. The short-term stability of this chain was one or two parts in 10^6 after warming up for several hours. The reproducibility and therefore the limiting relative accuracy of the best field measurements proved to be only a few parts in 10^5 , however, due to the widths of the magnetic resonance lines. The microwave frequency could be measured to better than 0.5 Mc/sec

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† Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

¹ W. M. Walsh, Jr., *Phys. Rev.* **114**, 1473, 1485 (1959).

² W. M. Walsh, Jr., and N. Bloembergen, *Phys. Rev.* **107**, 904 (1957).

using a wavemeter calibrated against a Gertsch frequency standard.

A matter of considerable practical concern in these experiments was the change in the microwave cavity frequency during a high-pressure run due principally to the varying dielectric constants of the insulators which filled the cavity. This effect causes slow leaks at "constant" pressure to be troublesome in that they lead to frequency drift of the microwave spectrometer while one is supposedly measuring the field positions of PMR lines at constant frequency. Teflon filler pieces resulted in cavity frequency shifts of nearly 800 Mc/sec over the available pressure range of 10^4 kg/cm².³ Polystyrene was used in the experiments reported here and proved roughly half as sensitive to pressure. The use of alumina in this application yields an order of magnitude improvement.⁴

Samples were obtained from a variety of sources mentioned below. Single crystals were cut into the requisite tori² by the A. D. Jones Optical Company of Cambridge, Massachusetts. Powder samples were usually blended with small amounts of stopcock grease to prevent grain motion in the microwave cavity.

II. THE *F*-STATE IONS

The orbital magnetic moments of both trivalent chromium ($3d^3, ^4F$) and divalent nickel ($3d^8, ^3F$) are suppressed to a great extent by an electrostatic field of octahedral cubic symmetry. The sevenfold orbitally degenerate levels of the free-ion *F* ground state are split into two triplets and a singlet, the latter lying lowest in octahedral coordination (Van Vleck's "upright" energy level diagram⁵). The singlet would possess no net orbital angular momentum were it not for the spin-orbit interaction, $\lambda \mathbf{L} \cdot \mathbf{S}$, which mixes some of the orbital moment of the first excited triplet into the ground state. This admixture manifests itself as an isotropic shift of the spectroscopic splitting factor, *g*, away from the free-electron value, $g=2.0023$. Weaker crystalline field components of lower symmetry split the excited triplets and lead to additional, anisotropic *g* shifts as well as partial or complete removal of the ground-state spin degeneracy remaining in the absence of a magnetic field.⁶ Whereas our earlier efforts were devoted to examining these small spin level splittings in slightly noncubic crystalline sites we now wish to focus attention on the effects of the cubic field: the singlet-triplet energy separation, Δ ,⁷ and the associated *g* shift of the ground state.

³ Two polymorphic transitions of Teflon occurring near 250 and 5400 kg/cm² at room temperature are clearly observable as discontinuities in the slope of a plot of cavity frequency versus pressure.

⁴ I. Kaminow, thesis, Harvard University, 1960 (unpublished).

⁵ J. H. Van Vleck, Phys. Rev. **41**, 280 (1932).

⁶ B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108.

⁷ The symbol Δ here represents the quantity usually designated by $10Dq$ in the American literature and by $15\bar{Q}$ in the continental literature.

TABLE I. Numerical parameters of the *F*-state ions.^a

Ion and host parameter	Cr ³⁺ in MgO	Ni ²⁺ in MgO
<i>g</i> (exp)	1.9797	2.217
$\Delta = 10Dq$ (exp), cm ⁻¹	16 100	8600
λ (exp, solid), cm ⁻¹	45.5	-231
λ (exp, free ion), cm ⁻¹	87	-335
$\langle r^4 \rangle_0$ (th, free ion), A ⁴	0.337	0.235
$\langle r^4 \rangle$ (th, solid), A ⁴	0.799	0.387
<i>d</i> (estimate), A	1.90	2.10
Δ (th), cm ⁻¹	15 130	3660
$[\partial \ln(g-g_0)/\partial P]_T \times 10^6$ (kg/cm ²) ⁻¹	1.14	1.08
$[\partial \ln(g-g_0)/\partial \ln V]_T$ (exp)	2.0±0.2	1.9±0.3
$\partial \ln(g-g_0)/\partial \ln V$ (th)	1.84	1.67

^a The experimental values were obtained at room temperature.

A. Experimental Observations

The optical and infrared absorption as well as the paramagnetic resonance (PMR) spectra of small concentrations of Cr³⁺ and Ni²⁺ in crystals and powders of MgO were first reported by Low.^{8,9} His results indicate that these magnetic impurities usually occupy sites of cubic symmetry (the existence of Cr³⁺ ions whose charge compensation is localized sufficiently near the magnetic site to produce visible axial field effects^{8,10,11} will be ignored as not of present interest). The magnetic resonance spectra are particularly simple in such high symmetry, the spin Hamiltonian consisting of an isotropic Zeeman term:

$$H = g\beta \mathbf{H} \cdot \mathbf{S}, \quad (1)$$

where $S = \frac{3}{2}$ for Cr³⁺ and $S = 1$ for Ni²⁺. The *g* values listed in Table I were obtained in the course of the present work. They differ only slightly from those measured by Low. The hyperfine structure of the chromium resonance arising from the 9.5% abundant isotope Cr⁵³ ($I = \frac{3}{2}$, $A = 16.0 \times 10^{-4}$ cm⁻¹) was observed but not investigated in detail.

The hydrostatic pressure dependences of the *g* values have been measured to 10 000 kg/cm² at room temperature. The numerical results are given in Table I as are the isothermal logarithmic derivatives of $(g-g_0)$ versus volume which is the form of theoretical interest. The compressibility of MgO as determined by Bridgman¹² and confirmed by elastic constant measurements¹³ was used to convert the measured pressure dependences to volume dependences:

$$\Delta V/V_0 = -0.59 \times 10^{-6} P + 2.2 \times 10^{-12} P^2 \quad (25^\circ \text{C}), \quad (2)$$

where *P* is measured in kg/cm². The validity of this conversion will be discussed below.

The samples used in these experiments were powders containing roughly 0.01 atomic percent of the magnetic

⁸ W. Low, Phys. Rev. **105**, 801 (1957).

⁹ W. Low, Phys. Rev. **109**, 247 (1958).

¹⁰ J. E. Wertz and P. Auzins, Phys. Rev. **106**, 484 (1957).

¹¹ J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) **73**, 948 (1959).

¹² P. W. Bridgman, Proc. Am. Acad. Arts Sci. **67**, 345 (1932).

¹³ S. Bhagavantam, Proc. Indian Acad. Sci. **A41**, 72 (1955).

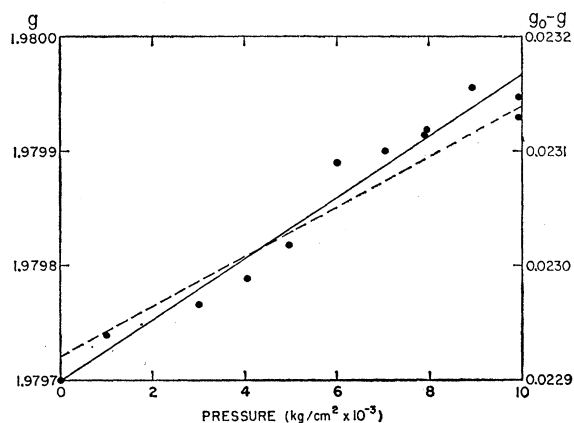


FIG. 1. Pressure dependence of the g value of Cr^{3+} in MgO . The solid curve represents an estimated best fit whereas the dashed line indicates the result predicted by a simple point charge model.

impurity. These were prepared by C. Quadros of this laboratory using coprecipitation and firing techniques similar to those described by Low.⁹ Single crystals containing Cr^{3+} as well as comparable amounts of Mn^{2+} and Fe^{3+} were obtained indirectly from the Norton Company via W. V. Smith of IBM Research, Poughkeepsie and S. Shapiro of this laboratory. A large single crystal of nickel-doped MgO containing significant amounts of Mn^{2+} , Fe^{3+} , and Cr^{3+} as well as Ni^{2+} was provided by L. Schupp of the General Electric Company, Lamp Research Division.

The pressure dependence of the chromium g value was not investigated in the single crystals because the resonance line falls almost exactly on one of the Mn^{2+} absorption peaks. Since the Cr^{3+} PMR line is quite narrow in MgO [approximately 1.5 gauss between points of maximum slope on the $(\partial\chi''/\partial H)$, recording] relatively precise g -value measurements are possible as indicated in Fig. 1. More accuracy would be desirable however, since the shift is very small.

One might hope for greater precision in the case of Ni^{2+} since the shift is an order of magnitude greater than that of Cr^{3+} . Unfortunately, the nickel spectrum proves to be quite smeared out. From 20°K (and presumably below) up to about 77°K the Ni^{2+} resonance in our best samples consists of a broad absorption peak (~ 50 gauss wide) with a slight doublet character, i.e., a relatively weak "dip" in the center (derivative width about 12 gauss). At higher incident microwave power levels the "dip" is replaced by a narrower peak (~ 5 gauss wide) which has recently been explained by Orton, Auzins, and Wertz¹⁴ as a $\Delta S_z = 2$ transition occurring at $g\beta H = h\nu$ due to simultaneous absorption of two quanta from the radiation field. As the temperature is raised above 77°K the broad linewidth increases monotonically and nonlinearly. The doublet character remains visible up to the vicinity of 400°K (see Fig. 2)

¹⁴ J. W. Orton, P. Auzins, and J. E. Wertz, Phys. Rev. Letters 4, 128 (1960).

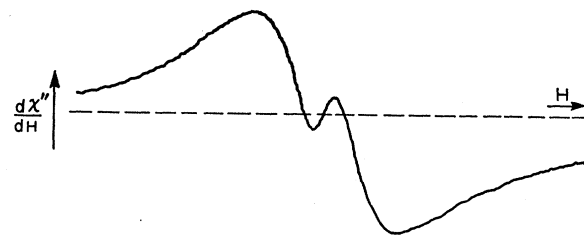


FIG. 2. Central portion of the differentiated absorption line of Ni^{2+} in MgO (powder sample) at low microwave power and room temperature.

above which temperature range only a single resonance peak is found. With the modest power (~ 25 mw) available from the 2K25 klystron we were unable to observe the double quantum transition much above 77°K. Thus the g -value determinations at room temperature were made by recording many field sweeps through the broad, slightly split line at each of three pressures. The resultant pressure dependence of the g value is given in Table I. Undoubtedly higher accuracy could be attained if the sharp high-power peak were to be used to define the line center.

Before turning to the analysis of the g -value data, a few comments on the nickel PMR line shape may be made. One is easily led to attribute the doublet character of the line to a small splitting of the zero-field spin level degeneracy, i.e., the existence of terms $DS_x^2 + E(S_x^2 - S_y^2)$ in the nickel spin Hamiltonian. The principle axes of this low symmetry perturbation presumably may assume several distinct but equivalent orientations with respect to the cubic crystalline axes. The resultant spectrum of a single-crystal sample will therefore be very similar to the isotropic average seen in a powder sample. This is indeed the case, the single-crystal Ni^{2+} line showing no anisotropy of linewidth or shape. Below 77°K the linewidth is independent of temperature and may presumably be attributed to inhomogeneous broadening by the low-symmetry distortions. The temperature-dependent broadening above 77°K is probably caused by spin-lattice relaxation. While the measurements above room temperature are not very accurate, the data are consistent with the spin-lattice relaxation time, T_1 , being proportional to T^{-2} . This temperature-dependent broadening is also found in the spectrum of $\text{MgO}:\text{Fe}^{3+}$.¹⁵

The origin of the line splitting remains a puzzle, particularly as Low⁹ reports no such behavior in his samples. We have found the linewidth and doublet character to be fairly insensitive to concentration in the range 0.1 to 0.001% but to be somewhat affected by preparation and annealing techniques. One might be tempted to ascribe the zero-field splittings to magnetic interaction between nickel ions preferentially clustered near each other. There is, however, no obvious physical reason for such segregation as divalent nickel and mag-

¹⁵ W. M. Walsh, Jr., J. Jeener, and N. Bloembergen (unpublished).

nesium are closely equal in size. Furthermore, no pressure dependence of the linewidth or loss of line intensity at low temperatures (20°K) was observed. These effects might well be expected if the postulated clustering were to give rise to appreciable (presumably antiferromagnetic) exchange coupling between nickel ions.

A simple alternative line-broadening mechanism may be the natural imperfection of the samples. A distribution of weak noncubic crystalline electric fields must exist due to vacancies, dislocations, and other lattice irregularities. Divalent nickel is extremely sensitive to such low-symmetry fields. The relative narrowness of the Cr³⁺ resonance line does not weaken this argument as the crystalline field splittings of the ground spin levels of these ions are proportional to $(g-g_0)^2$,¹ i.e., trivalent chromium is ~100 times less sensitive to axial or lower symmetry perturbations than is divalent nickel. The argument is further borne out by the relative widths of the PMR lines of the S-state ions which indicate that such a distribution of noncubic fields is indeed present. However, the magnitude of the nickel linewidth relative to that of Mn²⁺ seems excessive when one compares the over-all magnetic field widths of the PMR spectra of these two ions present as dilute impurities in the same noncubic host lattice, e.g., zinc fluosilicate.¹⁶

It is also conceivable that the Jahn-Teller effect is present to some extent despite Low's evidence^{9,17} to the contrary. A tendency of Ni²⁺ to reduce its zero field spin degeneracy by seeking sites of rhombic or lower symmetry is suggested by the excessive linewidths found in MgO (cubic) and zinc fluosilicate (trigonal) and the narrow lines found in zinc fluoride (rhombic divalent site symmetry).¹⁸

B. The Magnitudes of the Singlet-Triplet Splittings

In the crystalline field approximation the g shift of both Ni²⁺ and Cr³⁺ may be written as

$$g-g_0 = -4\lambda g_0/\Delta, \quad (3)$$

where λ is the spin-orbit coupling parameter. The energy denominator, Δ , is the singlet-triplet energy separation mentioned earlier and is proportional to the cubic moment of the lattice potential, $\Phi^{(4)}$, at the position of the magnetic ion. If the bonding in MgO is primarily ionic it is reasonable to estimate the crystal potential by treating ions as point charges. Phillips¹⁹ has recently provided theoretical encouragement for such an approach.

At a cation site the approximate cubic potential

moment is

$$\begin{aligned} \Phi^{(4)} &\sim \frac{qr^4}{24} \sum_{i=1}^6 \left(\frac{\partial^4}{\partial r^4} \frac{1}{|\mathbf{r}-\mathbf{r}_i|} \right)_{r=0} \\ &= \frac{35qr^4}{4d^5} [\sin^4\theta(\sin^4\phi + \cos^4\phi) + \cos^4\theta - \frac{3}{5}], \quad (4) \end{aligned}$$

where $q=2e$ is the charge of the nearest-neighbor oxygen ions, d is their distance from the metal-ion site and r , θ and ϕ are polar coordinates referred to [100] axes. [Limiting the summation in Eq. (4) to nearest neighbors alone causes only a small error since the net contribution of the second and third nearest neighbors is only three percent of that of the nearest-neighbor shell.] The resultant singlet-triplet splitting is^{20,21}

$$\Delta = 10e^2\langle r^4 \rangle / 3d^5. \quad (5)$$

By $\langle r^4 \rangle$ is meant the average value of r^4 over the radial part of the $3d$ orbitals. Numerical values of $\langle r^4 \rangle$ for Cr³⁺ and Ni²⁺ have been calculated using Watson's analytic Hartree-Fock wave functions²² and are listed in Table I. Since the lattice parameters of NiO and MgO differ by less than one percent, there is little risk of error in taking the Ni²⁺-O²⁻ distance in MgO as 2.10 Å. The computed value of Δ for Ni²⁺ in MgO is thus found to be 2230 cm⁻¹, whereas Low found $\Delta=8600 \pm 100$ cm⁻¹ by infrared spectroscopy.

It is not surprising that our calculated singlet-triplet splitting is smaller than the experimental number, since magnetic form factor measurements in manganous salts have indicated that the $3d$ orbitals on Mn²⁺ are significantly more spread out in the solid state than in the free ion.²³ A good fit to the neutron data may be obtained by expanding the radial scale of the free-ion orbitals by approximately ten percent. This ionic expansion in the solid results from partial shielding of the manganese nuclear charge by the over-lapping ligand orbitals. A detailed theoretical discussion of this effect has been given by Freeman and Watson.²⁴ Using the empirically determined $3d$ charge distributions, Stuart and Marshall²⁵ have obtained quantitative agreement with experimental values for the superhyperfine interaction of Mn²⁺ and F⁻ ions in ZnF₂:Mn and MnF₂. The general consequence of such radial spreading is increased values of $\langle r^n \rangle$ if $n>0$. The approximate magnitude of the effect for the particular case of Ni²⁺ in MgO may be obtained by comparing the experimental value

²⁰ J. Becquerel and W. Opechowski, *Physica* **6**, 1039 (1939).

²¹ R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.* **8**, 790 (1940).

²² R. E. Watson, Technical Report No. 12, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1959; and *Phys. Rev.* **118**, 1036 (1960).

²³ J. M. Hastings, N. Elliott, and L. M. Corliss, *Phys. Rev.* **115**, 13 (1959).

²⁴ A. J. Freeman and R. E. Watson, *Phys. Rev.* **118**, 1168 (1960).

²⁵ W. Marshall and R. N. Stuart (unpublished).

¹⁶ K. D. Bowers and J. Owen, Reports on Progress in Physics (The Physical Society, London, 1955), Vol. 18, p. 304.

¹⁷ Note that Orton *et al.*¹⁴ found the same broad, split character of the nickel PMR spectrum in their samples.

¹⁸ M. Peter (private communication).

¹⁹ J. C. Phillips, *J. Phys. Chem. Solids* **11**, 226 (1959).

of the spin-orbit coupling parameter, $\lambda = (g_0 - g)\Delta/4g_0 = -231 \text{ cm}^{-1}$, in the solid state (see Table I for values of g and Δ) with the free-ion value, $\lambda_0 = -335 \text{ cm}^{-1}$. Since λ is roughly proportional to $\langle r^{-3} \rangle$, the increased value of $\langle r^4 \rangle$ in the solid may be estimated assuming the spreading to be describable as a linear scale change:

$$\langle r^4 \rangle \simeq (\lambda_0/\lambda)^{\frac{4}{3}} \langle r^4 \rangle_0. \quad (6)$$

The corrected value of $\langle r^4 \rangle$ is 65% greater than $\langle r^4 \rangle_0$ which leads to a calculated value of $\Delta = 3660 \text{ cm}^{-1}$, still quite far from agreement with experiment.

The theory of trivalent chromium is very similar to that of divalent nickel save for the effect of the extra charge of the chromic ion on the local crystalline potential. It is difficult to estimate accurately the equilibrium distance of the six O^{2-} nearest neighbors from the trivalent ion as it is extremely sensitive to details of the repulsive part of the $\text{Cr}^{3+} - \text{O}^{2-}$ interaction potential. The distance will presumably be somewhat less than the shortest chromium-oxygen spacing found in Cr_2O_3 or garnets, i.e., the value 1.90 Å appears to be a likely upper bound on d for $\text{MgO}:\text{Cr}$.

A further complication arises due to the large electric polarizability of the O^{2-} ions. The excess charge of the trivalent chromium ion (relative to the normally divalent occupant of the site) induces electric multipole moments on the surrounding anions. These modify the electrostatic potential at the chromium site. The most important induced moment is the dipole moment, μ , whose magnitude can be calculated if we know the dipolar susceptibility, χ , of the O^{2-} ions. This, as well as the higher multipolar susceptibilities, is difficult to estimate theoretically since the free ion is unstable.^{26,27} By intercomparison of optical refractive indexes, Tessman, Kahn, and Shockley²⁸ arrived at the empirical value $\chi = 1.66 \text{ Å}^3$ for O^{2-} in MgO . Using this number and the following expression for the induced dipole moment μ :

$$\mu = \chi e \left/ \left\{ d^2 \left[1 + \frac{\chi}{d^3} \left(\frac{1+6\sqrt{2}}{4} \right) \right] \right\} \right., \quad (7)$$

we obtain $\mu = 1.46 \times 10^{-18}$ esu at the estimated equilibrium $\text{Cr}^{3+} - \text{O}^{2-}$ distance. One effect of the six induced dipoles is to increase the cubic moment of the potential at the Cr^{3+} site:

$$\Phi^{(4)} = -\frac{35}{4} r^4 \left(\frac{q}{d^5} - \frac{5\mu}{d^6} \right) [\sin^4\theta (\sin^4\phi + \cos^4\phi) + \cos^4\theta - \frac{3}{5}].$$

The expression for Δ [Eq. (5)] is similarly modified. Taking into account the 50% increase in the $\langle r^4 \rangle$ of the Cr^{3+} ion in the MgO lattice which is implied by the reduced spin-orbit coupling in the solid (see Table I) we

²⁶ R. E. Watson, Phys. Rev. **111**, 1108 (1958).

²⁷ G. Burns (to be published).

²⁸ J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

find $\Delta = 15\,130 \text{ cm}^{-1}$. The experimental value, $\Delta = 16\,100 \text{ cm}^{-1}$,²⁹ is slightly larger than the result of a rather "pushed" ionic-type calculation though the discrepancy is not as marked for Cr^{3+} as for Ni^{2+} . This degree of agreement is presumably fortuitous.

C. The Pressure Dependence of the g Shifts

Differentiation of expression (3) with respect to volume ($V \propto d^3$) which enters through the energy denominator Δ [see Eq. (4)] gives the predicted volume dependence of $g - g_0$ for Ni^{2+} in MgO subject to certain assumptions:

1. The *local* compressibility in the unit cell containing the magnetic ion is identical to that of the host lattice, as is plausible in this case where NiO and MgO are nearly identical in lattice constant.

2. The radial distribution of the magnetic orbitals does not change significantly as the solid is compressed. The g shift is sensitive to such variations through the ratio $\lambda/\langle r^4 \rangle$. If, as above, we assume the radial wave function in the solid to be linearly related to that of the free ion by a scaling factor k , i.e.,

$$f(r) \Big|_{\text{solid}} = k^{\frac{1}{2}} f(kr) \Big|_{\text{free ion}}, \quad k < 1 \quad (8)$$

then $(g - g_0) \propto k^7$. If k is insensitive to small volume changes the predicted volume dependence of the g shift is

$$\partial \ln(g - g_0) / \partial \ln V = 1.67, \quad (9)$$

which agrees with the measured value, 1.9 ± 0.3 , within the (unfortunately large) experimental error. It is possible that the sign of the discrepancy between theory and experiment indicates that the scaling factor k decreases slowly as the lattice is compressed, i.e., assumption (2) fails. This interpretation should not be unduly stressed, however, since the theory rests on an oversimplified model which is apparently incapable of yielding the observed value of the singlet-triplet splitting. It is perhaps remarkable that such a model accounts moderately well for the volume dependence of the splitting.

Assumption (1) appears rather dubious in the case of Cr^{3+} since the local binding energy is probably significantly higher in a cell containing a trivalent cation. Though no attempt will be made to estimate the magnitude of the decreased local compressibility it should be borne in mind that neglect of this factor certainly *decreases* the experimental value of $\partial \ln(g - g_0) / \partial \ln V$. Subject to assumptions (1) and (2) and allowing for the induced dipole moments on the O^{2-} neighbors, the predicted value is

$$\begin{aligned} \partial \ln(g - g_0) / \partial \ln V = 1.67 + \frac{5\chi}{2d^3} \left(1 + \frac{1+6\sqrt{2}}{4} \frac{\chi}{d^3} \right)^{-1} \\ \times \left(1 + \frac{11+6\sqrt{2}}{4} \frac{\chi}{d^3} \right)^{-1} \simeq 1.84, \quad (9') \end{aligned}$$

²⁹ D. L. Wood (private communication); Low's assignments⁸ are incorrect.

whereas the observed derivative is 2.0 ± 0.2 . The discrepancy is within experimental error but its sign implies that assumption (2) is not valid, just as indicated by the nickel results. Correction for the failure of assumption (1) would only increase the discrepancy.

Before turning to the S -state ions, it is worthwhile to mention that direct measurements of Δ as a function of pressure have been made by Parsons and Drickamer.³⁰ They observed the optical transitions between the ground singlet and the two triplets of Cr^{3+} and Ni^{2+} in several rather complex unit cells up to 130 000 atm. The general magnitudes of their results are consistent with mono- or dipolar potentials at the magnetic ions but detailed analysis is precluded by the complicated structures of the host lattices. Similar experiments using MgO or some other simple crystal would be interesting as corollary to our PMR data.

D. Conclusions

From the preceding discussion of the F -state ions in MgO, we conclude:

1. A simple model of the crystalline potential based on point charges (and induced dipole moments where appropriate) is able to account for the majority, if not all, of the observed volume dependences of the orbital part of the magnetic moments.
2. The model can only account within a factor of two for the magnitude of the singlet-triplet splittings in its present degree of crudity.

It is felt that the first conclusion justifies the simple assumptions that the local compressibilities about foreign di- and trivalent cations are essentially unchanged from that of the MgO host lattice and that the cubic potential variation with small volume changes may be closely estimated using the point-charge model.

III. THE S-STATE IONS

Divalent manganese and trivalent iron occupy a unique position within the iron group since they have no orbital angular momentum in the ground configuration ($3d^5, ^6S$). The small but readily observable interaction of the spin moment with crystalline potentials must, therefore, occur via higher multiplets of $3d^5$ and perhaps other configurations. General arguments limit the *form* which this anisotropy energy may assume in various site symmetries,^{6,31,32} but the exact mechanisms which determine the *magnitudes* of the spin-Hamiltonian parameters are still matter for discussion. By varying the strength of the crystalline potential with hydrostatic pressure, one hopes to learn something of the spin-level

³⁰ R. W. Parsons and H. G. Drickamer, J. Chem. Phys. **29**, 930 (1958).

³¹ R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 387 (1953).

³² G. Koster and H. Statz, Phys. Rev. **113**, 445 (1959). The less general spin Hamiltonian in common use accounts for the observed spectra of Mn^{2+} and Fe^{3+} in MgO within the experimental accuracy.

TABLE II. Numerical parameters of the S -state ions.^a

Ion and host parameter	Mn^{2+} in ZnS	Mn^{2+} in MgO	Fe^{3+} in MgO
g	2.0021	2.0010	2.0033
a' , gauss	8.53	20.35	217.9
$a \times 10^4$, cm^{-1}	7.97	19.01	203.8
$(\partial \ln a / \partial P)_T \times 10^6$ (kg/cm^2) ⁻¹	4.0	4.03	4.03
$(\partial \ln a / \partial \ln V)_T$	-3.2	-7.08	-7.08
A' , gauss	-68.18	-86.82	
$A \times 10^4$, cm^{-1}	-63.73	-81.11	
$(\partial \ln A / \partial P)_T \times 10^6$ (kg/cm^2) ⁻¹	-0.44	-0.035	
$(\partial \ln A / \partial \ln V)_T$	0.35	0.06	

^a These values were measured at room temperature.

splittings in exactly cubic sites. These results may be compared with recent theoretical work of Watanabe³³ and Powell, Gabriel, and Johnston.³⁴

The large hyperfine structure of the Mn^{2+} spectrum also proves sensitive to sample volume as is not surprising in view of its known variation with host lattice. The effect is qualitatively in agreement with various proposed mechanisms of the contact interaction.

A. Experimental Observations

Paramagnetic resonance of divalent manganese in natural crystals of cubic ZnS (zincblende) has been reported by Mattarese and Kikuchi³⁵ and by Watkins.³⁶ Professor Kikuchi kindly provided the sample of this material which was used in the present experiments. Low first observed Mn^{2+} and Fe^{3+} present substitutionally in MgO.^{37,38} We have examined single crystals of magnesia containing Mn^{2+} and Fe^{3+} , as well as other trace impurities, indirectly supplied by the Norton Company.

These PMR spectra may be succinctly described by the spin-Hamiltonian:

$$H = g\beta\mathbf{H} \cdot \mathbf{S} + \frac{1}{6}a(S_x^4 + S_y^4 + S_z^4) + A\mathbf{I} \cdot \mathbf{S}. \quad (10)$$

The first (Zeeman) term involves the g value which differs very little from that of the free electron in the case of S -state ions (see Table II). Since no pressure dependence of these minute g shifts^{33,39} could be measured, these parameters will be treated as constants below.

The second term of Eq. (10) describes the orienting action of the cubic crystalline potential on the spin angular momentum. The parameter a (often measured in electron-gauss: $a' \equiv a/g\beta$) is a measure of the hexadecapole (16-pole) moment of the lattice potential and of

³³ H. Watanabe, Progr. Theoret. Phys. **18**, 405 (1957).

³⁴ M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Letters **5**, 145 (1960).

³⁵ L. M. Mattarese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).

³⁶ G. D. Watkins, Phys. Rev. **110**, 986 (1958).

³⁷ W. Low, Phys. Rev. **105**, 792, 793 (1957).

³⁸ W. Low, Proc. Phys. Soc. (London) **B69**, 1169 (1956).

³⁹ I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **73**, 116 (1959).

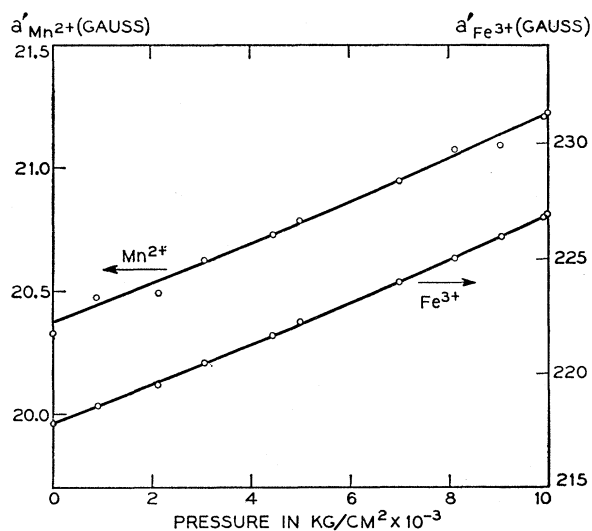


FIG. 3. Pressure dependence of the cubic field splitting parameters of Mn^{2+} and Fe^{3+} in MgO at room temperature. Units of "electron gauss" are used: $a' \equiv a/g\beta$.

the corresponding polarization of the magnetic ion. The effect of hydrostatic pressure on the a parameters of Mn^{2+} and Fe^{3+} in MgO are shown in Fig. 3 and tabulated in Table II. The data for both ions can be made to coincide by use of the scaling factor

$$\eta \equiv a(\text{Fe}^{3+})/a(\text{Mn}^{2+}) = 10.70 \pm 0.02,$$

which is independent of pressure: The percentage increases of the two cubic field splittings are identical. A similar set of measurements of a for Mn^{2+} in a zincblende crystal is illustrated in Fig. 4 and listed in Table II.

The last term of Eq. (10) represents the isotropic hyperfine coupling of the nuclear ($I = \frac{5}{2}$) and electronic moments of Mn^{55} . (A similar term is required for the 2% abundant Fe^{57} isotope which produces a weak but observable spectrum.)⁴⁰ The effect of the coupling is to split the manganese PMR spectrum into six equally intense hyperfine groups of five fine-structure lines.

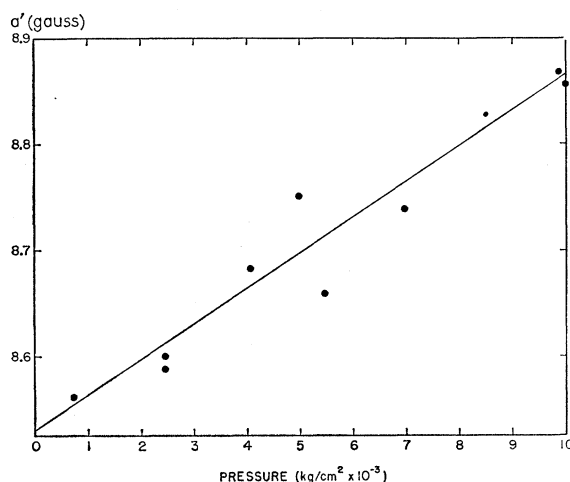


FIG. 4. Pressure dependence of the cubic field splitting parameter of Mn^{2+} in cubic ZnS at room temperature.

Detailed expressions for the resonance line positions have been given by Mattarese and Kikuchi and by Low and will not be repeated here. The spectrum of Mn^{2+} in ZnS is shown in Fig. 5 where second-order effects cause relative shifts of the five fine-structure lines as one proceeds to successive hyperfine groups. A similar pattern due to Mn^{2+} in the General Electric MgO crystal is seen in Fig. 6 as are the various differentiated absorption lines of Cr^{3+} , Fe^{3+} , and Ni^{2+} . The apparent monotonic decrease in the intensity of the Mn^{2+} spectrum as one goes to higher fields on this trace (Fig. 6) is actually a cross-relaxation effect which is absent in crystals not containing Ni^{2+} . The spin-lattice relaxation time of Mn^{2+} in MgO is sufficiently long even at room temperature that appreciable saturation of the resonances occurs at the power levels normally used (~ 10 mw incident on the cavity). The effective relaxation time of a particular transition is reduced (and its apparent intensity correspondingly increased) if energy may be transferred by spin-spin interaction to a more rapidly relaxed magnetic species (the Ni^{2+} spins in this case). Detailed studies of

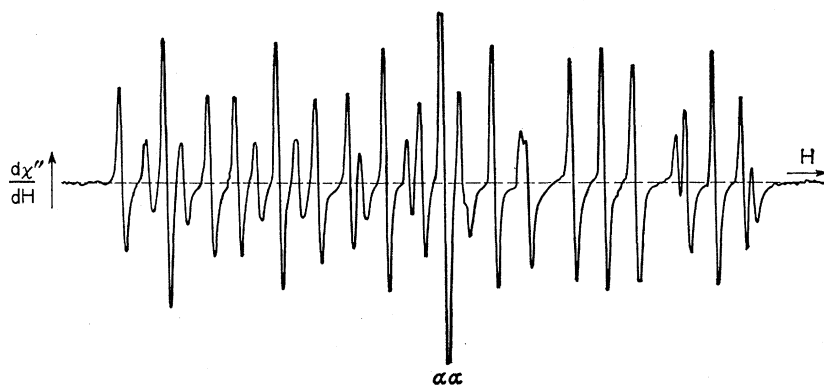
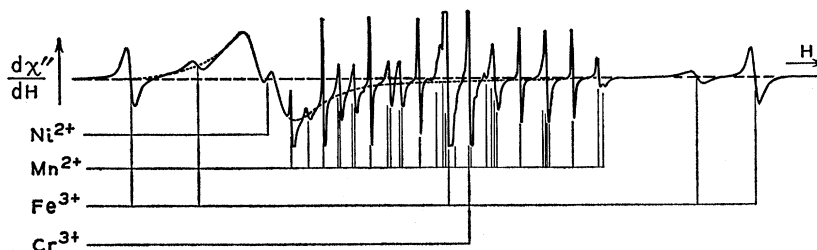


FIG. 5. PMR spectrum of Mn^{2+} in cubic ZnS ($H \parallel [100]$). The strong central resonance is a free-radical marker.

⁴⁰ G. Feher, E. Rossenwasser, and S. Geschwind (private communication).

Fig. 6. PMR spectrum of Mn^{2+} , Fe^{3+} , Ni^{2+} , and Cr^{3+} , in MgO ($H \parallel [100]$). The variation in Mn^{2+} line intensities is due to cross relaxation to the Ni^{2+} spins.



such cross-relaxation phenomena have recently been reported.⁴¹⁻⁴³

The pressure dependences of the hyperfine coupling parameters of Mn^{2+} in MgO and ZnS are shown in Figs. 7 and 8, respectively, and are summarized in Table II. The apparently great "scatter" in the case of MgO results from the expanded scale needed to display the small variation of $A' \equiv A/g\beta$ with P .

In converting the pressure data to volume dependences, we continue to use the bulk compressibilities of the host lattices. It is felt that the assumption of roughly equal bulk and "local" compressibilities is justified by the F -state ion results and the equality of the percentage variations of a for both a di- and a trivalent S -state ion. The compressibility of MgO was given earlier [Eq. (2)] and that of zincblende^{44,45} is

$$\Delta V/V_0 = -1.283 \times 10^{-6} P + 1.56 \times 10^{-12} P^2 \quad (25^\circ C). \quad (11)$$

The resultant values of $(\partial \ln A / \partial \ln V)_T$ are displayed in Table II.

B. The Cubic Field Splittings

The lack of orbital angular momentum in the ground states of the $3d^5$ ions leads to considerable difficulty in explaining the observed effects of crystalline fields. While it is possible to establish the general form that the Hamiltonian must take for a lattice site of given symmetry and thus describe the anisotropy of the PMR spectra, it is another matter to understand the magnitudes of the observed parameters in terms of explicit perturbations of the free ion by the crystalline electric field. Van Vleck and Penney⁴⁶ estimated the effect of several mechanisms involving the lattice potential and the spin-orbit interaction. Pryce⁴⁷ concluded that these perturbations could not explain the experimental splittings and suggested that spin-spin coupling and the presence of excited configurations must be taken into account. Watanabe,³³ noting the high symmetry of the half-filled shell, concluded that only perturbing schemes even in the crystalline potential could be effective within

the d^5 configuration. In particular, his numerical estimates of the effect of a cubic electric field on Mn^{2+} show the parameter a to be positive and predominantly determined by the square of the cubic potential moment in the range of experimental interest.

This problem has most recently been examined by Powell, Gabriel, and Johnston (PGJ)³⁴ who find that perturbations within d^5 and odd in Dq can produce ground spin state splittings if they are also odd in the spin-orbit coupling.⁴⁸ Their calculation, including both the spin-doublet and the spin-quartet terms of d^5 , yields a variation of a for Mn^{2+} versus Dq which agrees quite well with the few available data as shown in Fig. 9. In particular the observed values of the cubic field splittings of Mn^{2+} in MgO and in $KMgF_3$ ⁴⁹ coupled with the measured Dq values in MnO ⁵⁰ and $KMnF_3$ ⁵¹ strongly support the PGJ curve. The negative value of a found by Watkins⁵² in $NaCl$ has been placed on Fig. 9 by estimating the size of Dq from the measured value in octahedral fluorine coordination using the point charge model. A similar estimate permits crude positioning of the ground state splittings found in ZnS ⁵⁵ and CaF_2 .⁵³ Neither of these results fall near the PGJ curve. The discrepancy is perhaps not very surprising in the case

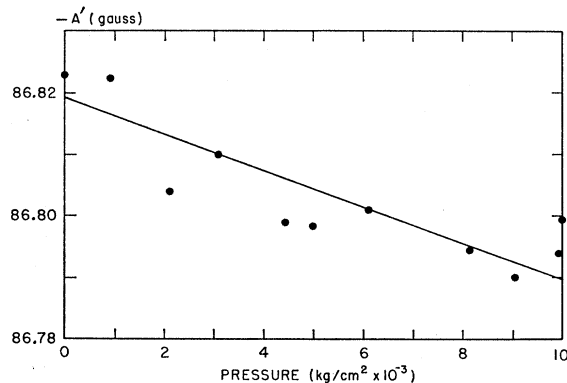


Fig. 7. Pressure dependence of the hyperfine coupling of Mn^{2+} in MgO .

⁴¹ N. Bloembergen, S. Shapiro, P. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

⁴² S. Shapiro and N. Bloembergen, Phys. Rev. **116**, 1453 (1959).

⁴³ P. Pershan, Phys. Rev. **117**, 109 (1960).

⁴⁴ P. W. Bridgman, Silliman J. **10**, 483 (1925).

⁴⁵ S. Bhagavantam and D. Suryanarayana, Proc. Indian Acad. Sci. **A20**, 304 (1944).

⁴⁶ J. H. Van Vleck and W. G. Penney, Phil. Mag. **19**, 961 (1934).

⁴⁷ M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).

⁴⁸ R. Lacroix, Helv. Phys. Acta **30**, 479 (1957) had previously noted this point in connection with calculations relative to $Gd^{3+}(4f^7, 8S)$.

⁴⁹ S. Ogawa, J. Phys. Soc. Japan **15**, 1475 (1960).

⁵⁰ G. W. Pratt and R. Coelho, Phys. Rev. **116**, 281 (1959).

⁵¹ J. Hrostowski (private communication via R. G. Shulman).

⁵² G. D. Watkins, Phys. Rev. **113**, 79 (1959).

⁵³ J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1959).

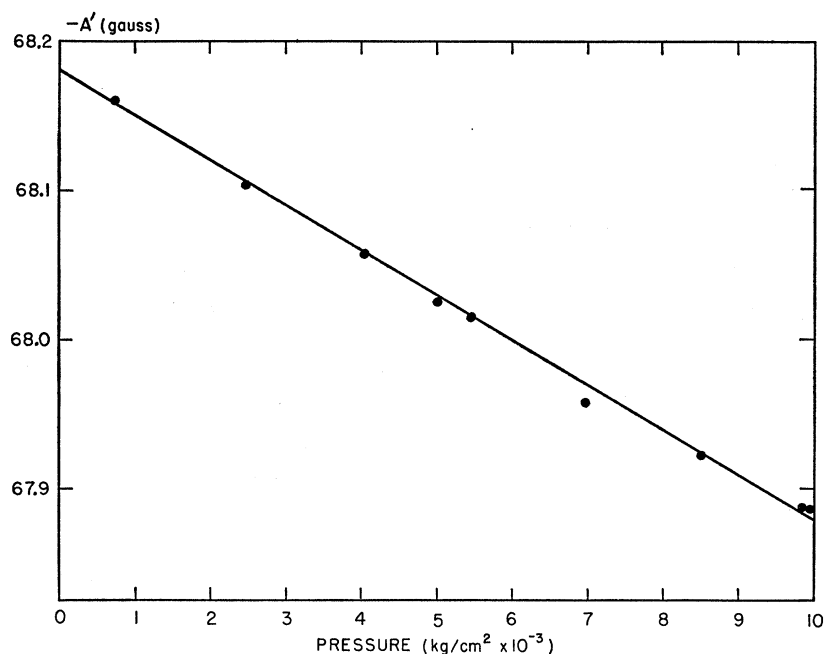


FIG. 8. Pressure dependence of the hyperfine coupling of Mn^{2+} in ZnS.

of the sulfide where the markedly reduced hyperfine interaction indicates strong interaction with the ligands.^{54,55} This holds even more strongly for CdTe:Mn.⁵⁶ It may be worthwhile re-examining the PMR of $CaF_2:Mn$,⁵⁵ however, in view of the difficulty in assigning an accurate value to a in the presence of strong superhyperfine structure and the expectation that the point-charge model might be roughly valid for

this case. Above all, experimental determinations of Dq in the tetrahedral and cubic coordinations would be most desirable, as Powell *et al.* have emphasized.

Though direct comparison of a versus Dq with PGJ theory is most desirable, in that the choice of a model is avoided, our pressure experiments may be useful in this connection if a dependable relation between volume and cubic potential variations can be established. As discussed earlier, it is felt that the point-charge model is a good approximation when only small changes in crystal field parameters are studied. On this basis, $\partial \ln Dq / \partial \ln V = -1.67$, we have

$$\partial \ln a / \partial \ln Dq = 4.25, \quad (MgO)$$

for both Mn^{2+} and Fe^{3+} in MgO. A somewhat smaller number is obtained if the observed volume dependences of the g shifts of Cr^{3+} and Ni^{2+} in MgO are presumed to measure the volume dependence of Dq exactly, i.e., $\partial \ln Dq / \partial \ln V = -1.95$, whence

$$\partial \ln a / \partial \ln Dq \approx 3.64, \quad (MgO).$$

The latter number agrees quite well with the theoretical prediction (see Fig. 10).

The use of an ionic potential for ZnS is, of course, quite indefensible, especially since we lack corroborative data on ions other than Mn^{2+} in the same lattice. Ignoring this difficulty, we find

$$\partial \ln a / \partial \ln Dq = 1.9, \quad (ZnS).$$

Since it is evident from Fig. 9 that one cannot simply calculate the magnitude of Dq in this lattice, we use the value 600 cm^{-1} deduced from the magnitude of a and the theoretical curve. As seen in Fig. 10 the measured fractional derivative falls very near the theoretical value.

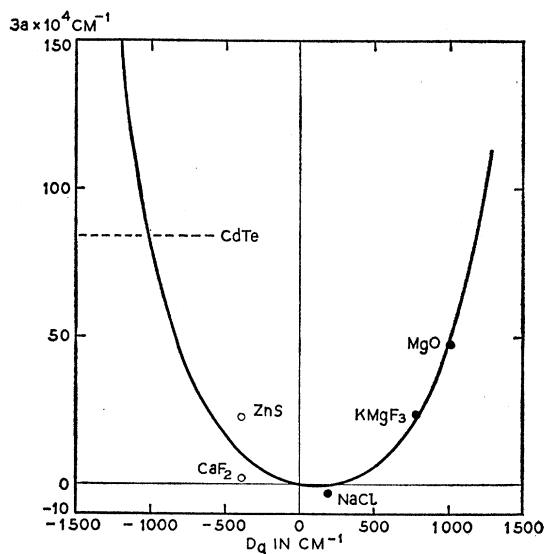


FIG. 9. Variation of the ground-state spin energy level splitting of Mn^{2+} versus the cubic crystalline field strength parameter after Powell, Gabriel, and Johnston. Various points associated with experimental data are shown and discussed in the text.

⁵⁴ J. S. Van Wieringen, *Discussions Faraday Soc.* **19**, 119 (1955).

⁵⁵ O. Matumura, *J. Phys. Soc. Japan* **14**, 108 (1959).

⁵⁶ J. Lambe and C. Kikuchi, *Phys. Rev.* **119**, 1256 (1960).

The pressure experiments thus provide further, though less direct than is desirable, support for the analysis of Powell *et al.* in the case of Mn^{2+} .

The case of Fe^{3+} is much less satisfactory since optical determinations of the various parameters (Racah, spin-orbit, spin-spin, cubic field) are made difficult by strong band absorption.⁵⁷ Geschwind's PMR data on Fe^{3+} in octahedral and tetrahedral oxygen coordination⁵⁸ indicate that a varies as the square of the cubic potential if the point-charge model may be used for intercomparison purposes. Our own data imply that a fourth power law is closer to the actual behavior in MgO. It will be very difficult to test any theory of the crystalline field effect on Fe^{3+} in the absence of data on the excited states.

It is felt that the invariance under pressure of the ratio of cubic field splittings of Fe^{3+} and Mn^{2+} in MgO supports our contention that it is primarily the environment of these ions which changes under stress not the ions themselves. Changes in spin-orbit coupling, etc., are apparently negligible compared to changes in the lattice potential. While the simple point-charge model is not sufficient to compute the magnitude of this potential, the nearly ionic variation of the various crystalline field parameters indicates that some sort of effective-charge model is appropriate.

C. The Hyperfine Couplings

The large, predominantly isotropic, coupling of the nuclear magnetic moments of the iron group ions to their electronic magnetic moments has most recently been attributed to exchange polarization of the core orbitals by the net unpaired d -electron spins.^{59,60} In particular it is the nonidentical radial distributions of the up- and down-spin electrons in the various s orbitals which leads to a net unpaired spin density at the nucleus and the resultant contact hyperfine interaction, $A\mathbf{I}\cdot\mathbf{S}$.

This coupling has been measured for $(\text{Mn}^{55})^{2+}$ in a wide variety of compounds and has been found to decrease with increasing electronegativity of the ligands. Matumura's results⁵⁵ indicate that the value $100 \times 10^{-4} \text{ cm}^{-1}$ is a reasonable extrapolation to the ionic limit. We see in Table II that MgO is fairly near this limit but ZnS is strongly covalently bonded by this criterion. It is not surprising that the greater sensitivity to lattice compression is found in the less-ionic compound.

We wish to suggest that a large part of the reduction of A with lattice parameter might be assigned to the changing radial distribution of the d orbitals of the magnetic ion. As mentioned earlier, there is good evidence for a distinct change (expansion) of these wave functions upon going from the free ion to the solid state. Further spreading under compression is to be expected though the effect appears to be quite modest (see Sec.

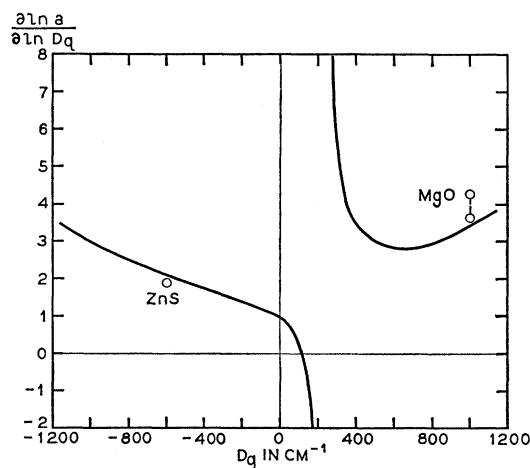


Fig. 10. Calculated fractional variation of the ground-state splitting of Mn^{2+} with cubic field strength after Powell, Gabriel, and Johnston. The results of the pressure experiments are also indicated for comparison.

II). Even small variations will affect the degree of unpairing of the up- and down-spin s orbitals via the exchange polarization mechanism and thus lead to a change in the net unpaired spin density at the nucleus. It is conceivable that a semiquantitative analysis of the change of the d orbitals under compression could be obtained by fitting the measured variation of the hyperfine coupling to a computed dependence of the contact interaction on the radial distribution of d electrons. In principle, a much more direct method for obtaining such information would be to measure the neutron scattering form factor under pressure but the experimental difficulties are formidable. The paramagnetic resonance technique is much more feasible though the interpretation will be subject to numerous pitfalls.²⁴

D. Conclusions

1. The pressure dependences of the cubic-field splittings of the divalent manganese ion energy levels are consistent with the calculations of Powell, Gabriel, and Johnston (which are quite successful in other respects) if the simple assumptions concerning local compressibility and lattice potential dependence on interionic distance are made.

2. The variation of the isotropic hyperfine interaction may be attributable to expansion of the magnetic ion's d orbitals due to increasing overlap with the nearest neighbors but quantitative interpretation appears to be quite difficult.

ACKNOWLEDGMENTS

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⁵⁷ A. M. Clogston, *J. Appl. Phys.* **31**, 198S (1960).

⁵⁸ S. Geschwind, *Phys. Rev. Letters* **3**, 207 (1959).

⁵⁹ J. H. Wood and G. W. Pratt, Jr., *Phys. Rev.* **107**, 995 (1957).

⁶⁰ V. Heine, *Phys. Rev.* **107**, 1002 (1957).