

Spin-Lattice Coupling of a Kramers Doublet: Co^{2+} in MgO

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The spin-lattice coupling constants for the Co^{2+} ion as an impurity in MgO have been measured by using a uniaxial-strain technique. The coupling tensor elements applicable to the change of g factor with strain are $F_{11} = -69/(\text{unit strain})$, $F_{12} = 32/(\text{unit strain})$, and $F_{44} = 10/(\text{unit strain})$. The coupling tensor relevant to the change of hyperfine splitting with strain is related to that for the g factor by a multiplying factor of 1.74×10^{-18} ergs. The point-charge model has been used to evaluate the same coupling constants and the theoretical results agree in sign with the experimental results but are larger in magnitude by about a factor of 9. It is also pointed out that for several ions of the iron group the point-charge model gives remarkably good values for the spin-lattice coupling constants, agreeing in both sign and magnitude with experiment.

INTRODUCTION

KRAMERS doublets are less strongly coupled to the lattice than are the levels of ions with effective spin greater than $\frac{1}{2}$, and their coupling to the lattice has not been studied in detail. Co^{2+} , even though its actual spin is $\frac{3}{2}$, has an effective spin of $\frac{1}{2}$ in the octahedral cubic field of MgO . With its low-lying excited states one would expect the spin-lattice coupling to be large for a Kramers salt and experimentally it is known as a fast-relaxing ion. With this in mind Co^{2+} has been studied both experimentally and theoretically, using the point-charge model. The results are compared with similar studies on several other iron-group ions.

Spin-lattice coupling coefficients or magnetoelastic coupling coefficients of a number of iron-group ions have been measured in recent years both by ultrasonic-attenuation methods^{1,2} and by utilization of static uniaxial stress in paramagnetic-resonance^{3,4} experiments. The agreement of the constants determined by the two methods allows one to choose the more convenient measurement technique. In this case the shift of resonant-field position produced by application of a steady uniaxial stress has been used to determine the spin-lattice coupling coefficients of Co^{2+} in MgO . This method determines absolute sign as well as magnitude and, in addition, is generally less demanding of crystal tolerances than the ultrasonic method.

SPIN-HAMILTONIAN FORMALISM FOR SPIN-LATTICE COUPLING IN KRAMERS DOUBLETS

It is most convenient to express the spin-lattice coupling results in spin-Hamiltonian form. In analogy to the usual spin Hamiltonian used for the Kramers doublet ground state of Co^{2+} the perturbation due to the applied stress is represented by

$$H' = \beta \mathbf{H} \cdot \delta \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \delta \mathbf{T} \cdot \mathbf{S}, \quad (1)$$

where $\delta \mathbf{g}$ and $\delta \mathbf{T}$ are tensors which depend linearly on the strain introduced into the lattice. These tensors

may in turn be expressed as the product of a fourth-rank coupling tensor and the strain tensor. It is most convenient to express this relationship in matrix form using Voigt notation.

$$\delta g_i = F_{ij} e_j, \quad \delta T_j = Z_{ij} e_j. \quad (2)$$

In addition to the simplification introduced by this notation it should be noted that the matrix strains (e_j) are the actual or engineering strains rather than the tensor values, in which the shear strains are just half the actual strain.

In the case of non-Kramers iron-group ions, where the quadrupole spin selection rules govern the effects of strain, the perturbation takes the form

$$H' = \mathbf{S} \cdot \delta \mathbf{D} \cdot \mathbf{S}. \quad (3)$$

The coupling matrix, related to the strain via the equation $\delta \mathbf{D}_i = G_{ij} e_j$, is simplified, beyond the limitations imposed by the symmetry of the lattice site, by the fact that the trace of Eq. (3) is not an observable. That is, the addition of the quantity $S_x^2 + S_y^2 + S_z^2 = S(S+1)$ shifts the ground-state levels uniformly and is not effective in changing the paramagnetic spectrum. The usual choice is to set the trace of Eq. (3) equal to zero. The result of this procedure in a cubic system is to require that $G_{12} = -(\frac{1}{2})G_{11}$, leaving only two independent coupling coefficients G_{11} and G_{44} . There is no such simplifying condition for the F_{ij} and the Z_{ij} coupling constants, and hence one expects the three independent matrix elements, F_{11} , F_{12} , and F_{44} allowed by symmetry, to exist.

EXPERIMENTAL RESULTS

The three independent terms of the coupling matrices require a measurement of six values of δg and δT using different stress and magnetic field directions relative to the crystal axes. The shift of resonant field δH , is given by the expression

$$g\beta\delta H = \beta\delta g_{zz}H_z - \delta T_{zz}I_z - \frac{1}{2}[(\delta T_{xx})^2/g\beta H] \times [I(I+1) - I_z^2] \quad (4)$$

neglecting second-order terms such as $(\delta H)(\delta g)$. Although a term equivalent to the last one on the right

¹ N. S. Shiren, *Bull. Am. Phys. Soc.* **7**, 29 (1962).

² E. B. Tucker, *Phys. Rev. Letters* **6**, 183 (1961).

³ G. D. Watkins and E. Feher, *Bull. Am. Phys. Soc.* **7**, 29 (1962).

⁴ E. R. Feher, *Phys. Rev.* **136**, A145 (1964).

is necessary to account for the paramagnetic spectrum, the accuracy of our experimental results is such that we can neglect it in the stress experiment analysis. The field shift is taken to be positive if the resonance field increases when stress is applied.

The shift of resonance field is determined by noting the field shift due to application of stress using as the spectrometer signal the absorption derivative. This allows very sensitive detection of field shifts even for relatively broad lines. Any frequency shift due to detuning caused by the stress should be taken into account as added terms in Eq. (4). In practice the corrections required for this purpose were minimal if the crystal was carefully positioned in the apparatus. A change in line shape, in particular the development of asymmetry, with stress would have caused difficulty in this type of measurement but insofar as we could determine the shape did not change.

The shifts observed were in some cases rather small and it was found to be desirable to measure field differences, for a given hyperfine transition, for the stress off and on conditions by successive measurements rather than to scan the eight hyperfine lines first in

one condition and then in the other. For one thing this minimized the trouble with phase changes due to the change in liquid-helium level in the cryostat, which were bothersome even though the waveguide was packed with polyfoam.

The paramagnetic g tensor is symmetric and therefore is diagonal in the coordinate system normally used for the g tensor. The application of stress to the crystal changes the crystal symmetry, and the g tensor by the addition of the δg 's. The new g tensor must also be symmetric and hence a rotation of the coordinate system will again diagonalize it. Experimentally, with the use of uniaxial static stress, the dc magnetic field is oriented along one of the principal axes of the stress modified g tensor and the δg_{11} for that direction determined. This δg value may be related to the nondiagonal tensor referred to the original g coordinate system and the values of the tensor elements in the original system determined. For the cubic system three measurements of δg for different directions of stress and magnetic field relative to the crystal axes are sufficient to determine the various values of δg . The necessary measurements are then those tabulated below

Stress axis	H axis		
[100]	[100],	stress	$\delta g = (2F_{12}S_{12} + F_{11}S_{11})X,$
[100]	[010],	\perp stress	$\delta g = (F_{12}S_{11} + F_{12}S_{12} + F_{11}S_{12})X,$
[110]	[110],	stress	$\delta g = \left\{ \left(\frac{1}{2} \right) (F_{11} + F_{12})(S_{11} + S_{12}) + F_{12}S_{12} + \frac{1}{2}F_{44}S_{44} \right\} X.$

The equations at the right result from expressing the strains of Eq. (2) in terms of the stresses by use of the elastic constants $-e_i = S_{ij}X_j$. The equations for the δT 's in terms of the Z 's are identical. The three experimental determinations of δg and δT resulting from the determination of δH in the three circumstances given above for both the lowest ($I_z = +\frac{7}{2}$) and the highest ($I_z = -\frac{7}{2}$) hyperfine lines and use of Eq. (5) provide sufficient data to solve for the E 's and F 's. There are two reasons for using these extreme transitions for the calculation of constants. Since the field separation is greatest for them the accuracy of the experimental results should be greater than for any other pair and, in addition, if there were a contribution from the quadratic term of Eq. (4) it would be smallest for the $\pm\frac{7}{2}$ transitions.

The experimental results are presented in Fig. 1 as values of δH produced by a compressional, i.e., negative, stress. The shift of resonant field is largest for the lowest of $I = +\frac{7}{2}$ level and the decrease of shift at higher fields is due to the hyperfine interaction term more than compensating for the increase of the first term due to the larger value of H . The linearity of the data is the justification for neglecting the quadratic term of Eq. (4). The δH determination for both the lowest and the

highest line for the same conditions of stress and field orientation then determine the δg and δT values. These are given in Table I. The values of δg and δT represent the result of experiments on MgO crystals containing several percent Co and which are pink in color. The results from one crystal to another vary sufficiently that the values of δg and δT vary by about $\pm 10\%$ and the values of the matrix coefficients particularly F_{44} , and Z_{44} vary by about double this amount. This presumably is due to the inhomogeneity of the crystal and certainly one of the possible sources of error is the assumption that the bulk constants assumed for the crystals are the correct ones.

The values of the constants of the spin Hamiltonian

TABLE I. Experimental data for a stress of 6.34×10^8 dyn/cm².

Stress axis	Field axis	δg	δT (erg)	$\delta T/\delta g$ (erg)
[100]	[100]	0.02025	3.57×10^{-20}	1.76×10^{-18}
[100]	[010]	-0.00980	-1.672×10^{-20}	1.71×10^{-18}
[110]	[110]	0.00330	0.573×10^{-20}	1.74×10^{-18}

⁵ W. Low, Phys. Rev. **109**, 256 (1958).

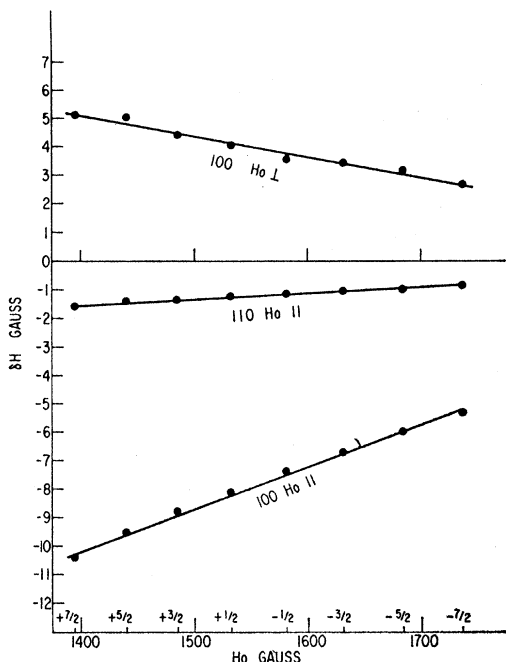


FIG. 1. Typical experimental results for the three types of measurement used to evaluate the coupling constants. The crystal direction indicates the stress axis and the symbol following the H_0 indicates the direction of the magnetic field, either perpendicular or parallel to the stress. The transitions labeled with the I_z quantum numbers are not equally spaced in magnetic field due to the second-order effects of the hyperfine coupling.

have been determined previously⁵ and the values assumed throughout this paper are

$$\begin{aligned} g &= 4.278 \\ A &= 194.229 \times 10^{-20} \text{ ergs} \\ &= 97.7 \pm 0.2 \times 10^{-4} \text{ cm}^{-1}. \end{aligned}$$

The values of the elastic constants used are those determined for a temperature of -193°C with values of⁶

$$\begin{aligned} S_{11} &= 3.839 \times 10^{-13} \text{ cm}^2/\text{dyn}, \\ S_{12} &= -0.855 \times 10^{-13} \text{ cm}^2/\text{dyn}, \\ S_{44} &= 6.380 \times 10^{-13} \text{ cm}^2/\text{dyn}. \end{aligned}$$

The stress experiments were carried out at helium temperature in two types of apparatus. An apparatus in which a vertical stress is applied via a long push rod directly on the crystal allows measurement of the field shift with stress and magnetic field at right angles to one another. This type of experiment was used as a calibration for the second type of measurement in the apparatus sketched in Fig. 2. In this case the direction of the magnetic field relative to the stress may be varied, but there is the question of the force ratio of the lever system (designed to be 1:1). In each crystal set up there exists the opportunity to determine a field shift which should be identical to that using the vertical stress above. For both the 100 and the 110 crystals the

⁶ Milo A. Durand, Phys. Rev. **50**, 449 (1936).

field is oriented at right angles to the stress and along the 100 axis. The observed field shifts in the horizontal stress experiments are then normalized to the result for the vertical stress (stress along 100, H_0 along 010) and the appropriate multiplier for that set of experiments determined. Any such normalization must take into account the difference in magnetic field at resonance, as is evident from Eq. (4) since δH depends on H as well as on the strain.

The ratio of δT to δg is within experimental error a constant and hence the coefficients of the δT tensor are related to those of δg . Since the strains are obviously identical, the F and Z tensors must be related by the same constant, i.e., $Z_{ij} = 1.74 \times 10^{-18} F_{ij}$ ergs. The components of the F matrix are found to be

$$\begin{aligned} F_{11} &= -69/(\text{unit strain}), \\ F_{12} &= 32/(\text{unit strain}), \\ F_{44} &= 10/(\text{unit strain}). \end{aligned} \quad (6)$$

COMPARISON TO SPIN-LATTICE RELAXATION-TIME MEASUREMENTS

The direct spin-lattice relaxation time depends directly on the coupling coefficients measured above. As an order of magnitude estimate one may take the value of T_1 , the spin-lattice relaxation time, to be⁷

$$\frac{1}{T_1} = \frac{\omega^2 k T (\beta H F_{ij} + \frac{1}{2} Z_{ij})^2}{2\pi \hbar^2 \rho v^5} \quad (7)$$

for the lowest hyperfine transition, characterized by $I_z = \frac{1}{2}$. The spin matrix element required in the normal formulation of the equation for T_1 has been assumed unity. The quantity in brackets corresponds to the coupling constant G used for the non-Kramers ions, and it is of interest to compare its magnitude with those of Table IV. For the moment we will simply observe that the effective coupling here is not too different in

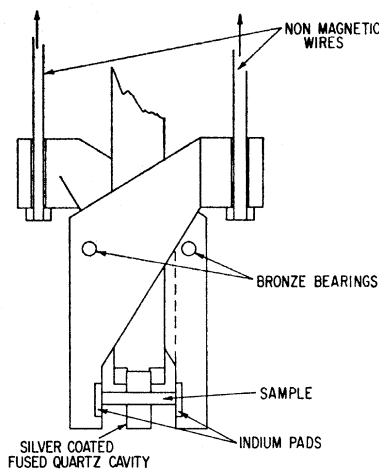


FIG. 2. Schematic of apparatus used to apply horizontal stress to the sample. The fused quartz cavity operates in the TE_{012} mode with the magnetic field vertical at the sample position.

⁷ R. L. Orbach, dissertation, University of California, 1960 (unpublished).

magnitude from that of Mn^{2+} , i.e., it is weak. On substituting values of the constants, characteristic of MgO, into Eq. (7) ($\rho = 3.58 \text{ g/cm}^3$, $\vartheta = 6.6 \times 10^5 \text{ cm/sec}$, $v = 10^{10} \text{ cps}$, $T = 4^\circ\text{K}$) a value for T_1 of approximately 60 sec results using the F and Z components characteristic of transverse waves, i.e., F_{44} and Z_{44} .

Experimentally Co^{2+} is known as a fast-relaxing ion and T_1 values tend to be in the vicinity of a millisecond.⁸ It is then very apparent that the relaxation as normally observed is not taking place through the "direct" process.

COMPARISON TO THEORY BASED ON THE POINT-CHARGE MODEL

Specific calculations of the spin-lattice coupling coefficients of Co^{2+} in MgO have not been published but the general problem of treating the spin Hamiltonian for Co^{2+} has been considered in detail by Abragam and Pryce⁹ and much of their discussion is applicable to our problem. The experimental work and the specialization of the spin Hamiltonian to the cubic field as carried out by Low⁵ is relevant and will be referred to in the development. The case of Co^{2+} in lanthanum zinc double nitrate has been treated by Culvahouse *et al.*¹⁰ and values of the δg tensor obtained in the approximation that the field is cubic but no admixture of the upper levels due to the cubic field need be considered. As will be seen, this assumption may not be carried over to the MgO host lattice. Pryce¹¹ has also calculated some of the coupling coefficients for Co^{2+} in MgO.

Theoretical values of the coupling constants are quite readily calculated by utilizing the formalism introduced by Van Vleck¹² in considering the matrix elements due to the normal modes of distortion of the octahedron surrounding a paramagnetic impurity. Because of the importance of the spin-orbit coupling in splitting the orbitally degenerate ground state, the orbit-lattice interaction is considered as a perturbation on the levels of the spin Hamiltonian in a fashion discussed by Orbach.¹³

In order to construct the appropriate eigenfunctions for the usual treatment of the cobalt ground state the following eigenfunctions, those of Abragam and Pryce,⁹ are chosen for the $\Gamma_4(T_1)$ level in the cubic field formed from the $4F$ level of the free cobalt ion (see Fig. 3)

$$\begin{aligned} \varphi_x &= \sqrt{2} \left\{ \left(\sqrt{\frac{5}{8}} \right) \psi_{33} \cos 3\varphi - \left(\sqrt{\frac{3}{8}} \right) \psi_{31} \cos \varphi \right\}, \\ \varphi_y &= \sqrt{2} \left\{ - \left(\sqrt{\frac{5}{8}} \right) \psi_{33} \sin 3\varphi + \left(\sqrt{\frac{3}{8}} \right) \psi_{31} \sin \varphi \right\}, \\ \varphi_z &= \psi_{30}, \end{aligned} \quad (8)$$

⁸ P. W. E. Smith, 14th Annual Report of the Eaton Electronics Research Laboratory, McGill University, Montreal, Canada, p. 31, 1963 (unpublished).

⁹ A. Abragam and M. H. L. Pryce, Proc. Phys. Soc. **A206**, 173 (1951).

¹⁰ J. W. Culvahouse, W. P. Unruh, and D. K. Brice, Phys. Rev. **129**, 2430 (1963).

¹¹ M. H. L. Pryce (private communication).

¹² J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

¹³ R. Orbach, Proc. Phys. Soc. **77**, 821 (1961).

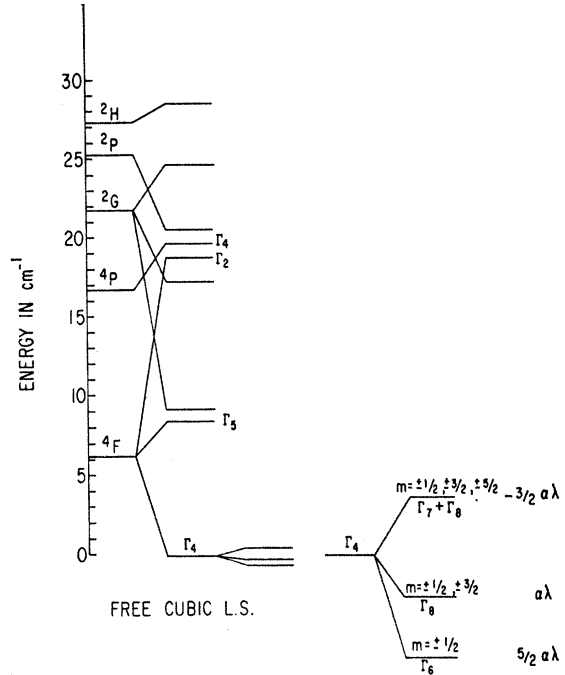


FIG. 3. Energy levels of Co^{2+} as split by a cubic field and the spin-orbit interaction. The expanded levels at the right are labeled with their symmetry properties and their eigenvalues—the value of λ is negative.

and for the $\Gamma_5(T_2)$ level

$$\begin{aligned} \psi_x &= \sqrt{2} \left\{ - \left(\sqrt{\frac{3}{8}} \right) \psi_{33} \cos 3\varphi - \left(\sqrt{\frac{5}{8}} \right) \psi_{31} \cos \varphi \right\}, \\ \psi_y &= \sqrt{2} \left\{ - \left(\sqrt{\frac{3}{8}} \right) \psi_{33} \sin 3\varphi + \left(\sqrt{\frac{5}{8}} \right) \psi_{31} \sin \varphi \right\}, \\ \psi_z &= \sqrt{2} \psi_{32} \cos 2\varphi, \end{aligned}$$

and for $\Gamma_2(A_2)$

$$\chi = \sqrt{2} \psi_{32} \sin 2\varphi,$$

where

$$\begin{aligned} \psi_{30} &= \left(\sqrt{\frac{7}{2}} \right) \left\{ \frac{5}{2} \cos^2 \theta - \frac{3}{2} \cos \theta \right\}, \\ \psi_{31} &= (21/2)^{1/2} \left\{ (5/4) \cos^2 \theta - \frac{1}{4} \sin \theta \right\}, \\ \psi_{32} &= \frac{1}{4} (\sqrt{105}) \cos \theta \sin^2 \theta, \\ \psi_{33} &= \frac{1}{8} (\sqrt{70}) \sin^3 \theta. \end{aligned}$$

In the usual fashion, the eigenfunctions of $|+1\rangle$, $| -1\rangle$, and $|0\rangle$ to be used in the treatment of Γ_4 as an effective spin=1 state are defined as

$$\begin{aligned} |+1\rangle &= -(1/\sqrt{2}) (\varphi_x + i\varphi_y), \\ |-1\rangle &= (1/\sqrt{2}) (\varphi_x - i\varphi_y), \\ |0\rangle &= \varphi_z. \end{aligned} \quad (9)$$

Similar combinations are also used for the Γ_6 orbital triplet.

The cubic field admixes some of the $4P$ level into Γ_4 , and in fact the result of combining Eqs. (8) and (9) with this admixture is wave functions for Γ_4 as follows:

$$\begin{aligned} |-1\rangle &= \epsilon \left\{ - \left(\sqrt{\frac{3}{8}} \right) \psi_{3,-1} - \left(\sqrt{\frac{5}{8}} \right) \psi_{3,+3} \right\} - \tau \pi_{1,-1}, \\ |+1\rangle &= \epsilon \left\{ - \left(\sqrt{\frac{3}{8}} \right) \psi_{3,+1} - \left(\sqrt{\frac{5}{8}} \right) \psi_{3,-3} \right\} - \tau \pi_{1,+1}, \\ |0\rangle &= \epsilon \psi_{3,0} - \tau \pi_{1,0}, \end{aligned} \quad (10a)$$

after substituting for the $\sin\varphi$ and $\cos\varphi$ and assuming the Condon-Shortley convention for signs. The function $\psi_{3,-1}$ represents $\psi_{31}e^{-\varphi}$ or $L=3, M_z=-1$. The angular momentum of the triplet is given by $-\alpha = -(\frac{3}{2}\epsilon^2 - \tau^2)$, which for small τ is just $-\alpha = -\frac{3}{2}$. The wave functions for Γ_6 , which are required later for perturbation calculations, are

$$\begin{aligned} | +1 \rangle &= (\sqrt{\frac{5}{8}})\psi_{3,-1} - (\sqrt{\frac{3}{8}})\psi_{3,+3}, \\ | 0 \rangle &= (1/\sqrt{2})(\psi_{2,+2} + \psi_{2,-2}), \\ | -1 \rangle &= +(\sqrt{\frac{5}{8}})\psi_{3,+1} - (\sqrt{\frac{3}{8}})\psi_{3,-3}. \end{aligned} \quad (10b)$$

It should be noted that these are reversed from those of Γ_4 so that $\Delta m=0$ transitions (or mixing) will occur between $|\Gamma_4+1\rangle$ and $|\Gamma_6-1\rangle$.

The wave functions of the 4P level are taken to be the p functions (also with Γ_4 symmetry)

$$\begin{aligned} | +1 \rangle &= -\frac{1}{2}\sqrt{3} \sin\theta e^{i\varphi}, \\ | 0 \rangle &= (\sqrt{\frac{3}{2}}) \cos\theta, \\ | -1 \rangle &= \frac{1}{2}\sqrt{3} \sin\theta e^{-i\varphi}. \end{aligned} \quad (10c)$$

The spin-orbit coupling splits the threefold orbital degeneracy of Γ_4 into levels of symmetry Γ_6, Γ_8 , and $\Gamma_7+\Gamma_8$ with effective spins of $\frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$. The treatment⁵ assumes a representation in which both l_z , the orbital angular momentum ± 1 or 0 in the triplet, and S_z are diagonal, sets up secular equations for each value of $m_z = l_z + S_z$, and then solves these equations for the eigenvalues. These are as indicated on Fig. 3. The eigenfunctions appropriate to the three levels into which Γ_4 is split are given by

$$| +\frac{1}{2}\Gamma_6 \rangle = \frac{1}{\sqrt{2}}| -1, \frac{3}{2} \rangle - \frac{1}{\sqrt{3}}| 0, \frac{1}{2} \rangle + \frac{1}{\sqrt{6}}| 1, \frac{1}{2} \rangle. \quad (11)$$

$$| -\frac{1}{2}\Gamma_6 \rangle = \frac{1}{\sqrt{2}}| 1, -\frac{3}{2} \rangle - \frac{1}{\sqrt{3}}| 0, -\frac{1}{2} \rangle + \frac{1}{\sqrt{6}}| -1, \frac{1}{2} \rangle.$$

$$\begin{aligned} | +\frac{3}{2}\Gamma_8 \rangle &= -(\frac{2}{5})^{1/2}| 0, \frac{3}{2} \rangle + (\frac{2}{5})^{1/2}| 1, \frac{1}{2} \rangle, \\ | +\frac{1}{2}\Gamma_8 \rangle &= (\frac{2}{5})^{1/2}| -1, \frac{3}{2} \rangle + (1/15)^{1/2}| 0, +\frac{1}{2} \rangle \\ &\quad - 2(2/15)^{1/2}| 1, -\frac{1}{2} \rangle. \end{aligned} \quad (12)$$

$$| -\frac{1}{2}\Gamma_8 \rangle = (\frac{2}{5})^{1/2}| 1, -\frac{3}{2} \rangle + (1/15)^{1/2}| 0, -\frac{1}{2} \rangle - 2(2/15)^{1/2}| -1, \frac{1}{2} \rangle.$$

$$| -\frac{3}{2}\Gamma_8 \rangle = -(\frac{2}{5})^{1/2}| 0, -\frac{3}{2} \rangle + (\frac{2}{5})^{1/2}| -1, -\frac{1}{2} \rangle.$$

$$| +\frac{5}{2}\Gamma_{7,8} \rangle = | 1, \frac{3}{2} \rangle.$$

$$| +\frac{3}{2}\Gamma_{7,8} \rangle = (\frac{2}{5})^{1/2}| 0, \frac{3}{2} \rangle + (\frac{3}{5})^{1/2}| 1, \frac{1}{2} \rangle.$$

$$\begin{aligned} | +\frac{1}{2}\Gamma_{7,8} \rangle &= (\frac{1}{10})^{1/2}| -1, +\frac{3}{2} \rangle + (\frac{3}{5})^{1/2}| 0, \frac{1}{2} \rangle \\ &\quad + (\frac{3}{10})^{1/2}| 1, -\frac{1}{2} \rangle. \end{aligned} \quad (13)$$

$$\begin{aligned} | -\frac{1}{2}\Gamma_{7,8} \rangle &= (\frac{1}{10})^{1/2}| 1, -\frac{3}{2} \rangle + (\frac{3}{5})^{1/2}| 0, -\frac{1}{2} \rangle \\ &\quad + (\frac{3}{10})^{1/2}| -1, \frac{1}{2} \rangle. \end{aligned}$$

$$| -\frac{3}{2}\Gamma_{7,8} \rangle = (\frac{2}{5})^{1/2}| 0, -\frac{3}{2} \rangle + (\frac{3}{5})^{1/2}| -1, -\frac{1}{2} \rangle.$$

$$| -\frac{5}{2}\Gamma_{7,8} \rangle = | -1, -\frac{3}{2} \rangle.$$

The spin Hamiltonian appropriate to the treatment of the Mn^{2+} spectra is given by

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{S}\cdot\mathbf{I} \quad (14)$$

similar in form to Eq. (1), and in which the constants are $g=4.278$ and $A=194.229\times 10^{-20}$ erg. Theoretical evaluation of these constants is straightforward from the treatment of Abragam and Pryce,⁹ but the procedure is worth summarizing for future reference.

There are both orbital and spin contributions to the g value in first order and an orbital contribution, due to admixture of the Γ_6 level by the spin-orbit interaction, in second order. The results is

$$g = 2\langle \frac{1}{2} | L_z + 2S_z | \frac{1}{2} \rangle \quad (15)$$

1st order:

$$\begin{aligned} g_{S1} &= 10/3, \\ g_{L1} &= \frac{2}{3}\alpha \end{aligned} \quad (16)$$

2nd order:

$$\begin{aligned} g_{L2} &= \frac{2\lambda\langle \frac{1}{2} | L_z | \Gamma_6 \rangle \langle \Gamma_6 | \mathbf{L}\cdot\mathbf{S} | \frac{1}{2} \rangle}{-\Delta} + \frac{2\lambda\langle \frac{1}{2} | \mathbf{L}\cdot\mathbf{S} | \Gamma_6 \rangle \langle \Gamma_6 | L_z | \frac{1}{2} \rangle}{-\Delta} \\ &= -\frac{15\lambda'\epsilon^2}{2\Delta}, \end{aligned}$$

where the Γ_4 to Γ_6 splitting Δ is taken as 8470 cm^{-1} ,⁵ and α is the actual angular momentum given above. The value of the hyperfine constant A is given by

$$\begin{aligned} A &= \frac{4\gamma\beta\hbar}{r^3} \langle \frac{1}{2} | L_z + (\xi L(L+1) - k)S_z \\ &\quad - \frac{3}{2}\xi[L_z(\mathbf{L}\cdot\mathbf{S}) + (\mathbf{L}\cdot\mathbf{S})L_z] | \frac{1}{2} \rangle, \\ \xi &= \frac{(2l+1) - 4S}{S(2l-1)(2l+3)(2L-1)}, \\ l &= 2, \quad S = \frac{3}{2}. \end{aligned} \quad (17)$$

The S_z term, with coefficient k , is included to allow an admixture of configurations containing unpaired s electrons and is necessary to account for the hyperfine structure. The contribution of the d electrons, given by the terms in ξ , is very small, leaving the s electron part the only important one other than the orbital factor represented by L_z .

It is necessary, in general, to make allowance for electron transfer to neighboring ions. This has been treated by Stevens¹⁴ and by Tinkham¹⁵ and for our purposes the situation may be handled by assuming that, in place of the wave functions of Eq. (8) we have a mixture of the d electron wave function on the Co^{2+} with some wave function centered on the neighbors

$$\phi' = N(\varphi + \eta\theta_{\text{neighbors}}). \quad (18)$$

For the cases referred to above, the θ 's are p and s functions. Calculation of the orbital angular-momentum

¹⁴ K. W. H. Stevens, Proc. Roy. Soc. (London) A219, 542 (1953).

¹⁵ M. Tinkham, Proc. Roy. Soc. (London) A236, 535 (1956).

TABLE II. Normal-mode matrix elements for transitions between levels of the same symmetry.

	+1	0	-1	
+1	$\sqrt{3}aQ_3$	$-b(Q_5-iQ_6)$	$-3aQ_2+i\sqrt{2}bQ_4$	
0	$-b(Q_5+iQ_6)$	$-2\sqrt{3}aQ_3$	$b(Q_5-Q_6)$	
-1	$-3aQ_2-i\sqrt{2}bQ_4$	$b(Q_5+iQ_6)$	$\sqrt{3}aQ_3$	
	a	b	C_1	C_2
${}^4F_{\Gamma_4}-{}^4F_{\Gamma_4}$	$a=(2/5)\rho_1+(25/132)\rho_2$	$b=(1/\sqrt{2})[(1/5)\rho_1+(5/11)\rho_2]$	$(3/7)$	$-(11/7)$
${}^4P_{\Gamma_4}-{}^4P_{\Gamma_4}$	$a'=(3/5)\rho_1$	$b'=-\frac{6}{\sqrt{2}5}\rho_1$	-1	0
${}^4F_{\Gamma_4}-{}^4P_{\Gamma_4}$	$a''=\frac{9\sqrt{21}}{70}\rho_1+\frac{25\sqrt{21}}{378}\rho_2$	$b''=\left(\frac{21}{2}\right)^{1/2}\left(\frac{6}{35}\rho_1-\frac{5}{126}\rho_2\right)$	$\frac{4}{\sqrt{21}}$	$\frac{3}{\sqrt{21}}$
${}^4F_{\Gamma_6}-{}^4F_{\Gamma_6}$	$a'''=0-(175/396)\rho_2$	$b'''=(1/\sqrt{2})[\rho_1+(5/33)\rho_2]$	$(3/7)$	$-(11/7)$
	$\rho_1=e\epsilon_{\text{eff}}C_1(r_0^3/R^3)$	$\rho_2=e\epsilon_{\text{eff}}C_2(r_0^4/R^4)$		

matrix elements in the ground-state results in

$$\langle \varphi_n' | L | \varphi_m' \rangle = k \langle \varphi_n | L | \varphi_m \rangle, \quad (19)$$

that is, the delocalization of the electron decreases the orbital momentum and k is referred to as the orbital reduction factor. k is related to N and η in a way which will depend on the choice of wave functions in Eq. (18), but in general N will be smaller than k .

Calculation of the orbital angular-momentum matrix elements between Γ_4 and Γ_6 which are required both for g_{L2} and for the equivalent part of A are not so simple, and the usual assumption is to take λ' , the effective value of λ , as equal to $N_{\Gamma_4}N_{\Gamma_6}\lambda$. From the experimental value of the splitting between the two lower Γ_4 levels (305 cm^{-1})¹⁶ and the first-order theory which gives the splitting as $\frac{3}{2}\alpha\lambda'$ we find that $\lambda'=135 \text{ cm}^{-1}$ ($\lambda=-180 \text{ cm}^{-1}$ for free ion) and hence that $(N_{\Gamma_4})^2=0.81$. The resultant value of g is then

$$g=10/3+\frac{2}{3}k\alpha-15\lambda'/2\Delta \quad (20)$$

and that for A is

$$A=N^2P[g_{L2}-\frac{1}{2}kg_s+(1/63)(1-15\tau^2)],$$

$$A=N^2P[\frac{2}{3}\alpha-(15/2)(\lambda'/\Delta)-(5/3)k$$

$$+(1/63)(1-15\tau^2)], \quad (21)$$

$$P=2\gamma\beta\hbar/\langle r^3 \rangle = 2g_N\beta\beta_N/\langle r^3 \rangle. \quad (17)$$

Further reference will be made to the above equations in the discussion of the comparison of the experimental results to the theory.

We now turn to the problem of calculating the spin-lattice coupling constants. The lowest order change in g due to the lattice strain, either static or dynamic, is from second-order perturbation theory and is of the form

$$\delta g = \frac{2}{H} \left\{ \frac{\langle +\frac{1}{2} | \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S}) | \Gamma_8 \rangle \langle \Gamma_8 | V_i Q_i | +\frac{1}{2} \rangle}{-\Delta} + \frac{\langle +\frac{1}{2} | V_i Q_i | \Gamma_8 \rangle \langle \Gamma_8 | \mathbf{H} \cdot (\mathbf{L} + 2\mathbf{S}) | +\frac{1}{2} \rangle}{-\Delta} \right\}, \quad (22)$$

¹⁶ P. Cossee, Mol. Phys. 3, 125 (1960).

¹⁷ γ = nuclear moment/ $I\hbar$. g_N = nuclear moment in nuclear magnetons/ I .

where the Q_i 's refer to the normal mode distortion of the octahedron as treated by Van Vleck.¹²

The normal distortions are defined as

$$\Gamma_1 Q_1 = R(e_{xx} + e_{yy} + e_{zz})/\sqrt{6},$$

$$\Gamma_3 \begin{cases} Q_2 = R(e_{xx} - e_{yy}), \\ Q_3 = R(e_{xx} + e_{yy} - 2e_{zz})/(1/\sqrt{3}), \end{cases} \quad (23)$$

$$\Gamma_5 \begin{cases} Q_4 = R(e_{xy}), \\ Q_5 = R(e_{xz}), \\ Q_6 = R(e_{yz}), \end{cases}$$

where the e_{ij} 's are the "engineering" lattice strains and R the lattice spacing. The brackets indicate to which irreducible representation of the cubic group the distortions belong (labeled according to Bethe's nomenclature).

It should be noted that the definitions of Q_4 and Q_6 are reversed from that needed in order to agree with Voigt notation.

The V_i coefficients which multiply the Q 's of Eq. (22) are given by¹²

$$V_2 = \sum_0 \{ A(x_0^2 - y_0^2) + B(x_0^4 - y_0^4) + \dots, \\ V_3 = \sum_0 \{ A(x_0^2 + y_0^2 - 2z_0^2) + B(x_0^4 + y_0^4 - 2z_0^4) \} \\ \times (1/\sqrt{3}) + \dots, \quad (24)$$

$$V_4 = \sum_0 \{ C(x_0 y_0) + E(x_0^3 y_0 + x_0 y_0^3) \} + \dots,$$

$$V_5 = \sum_0 \{ C(x_0 z_0) + E(x_0^3 z_0 + x_0 z_0^3) \} + \dots,$$

$$V_6 = \sum_0 \{ C(y_0 z_0) + E(y_0^3 z_0 + y_0 z_0^3) \} + \dots,$$

where the summations are over the d electrons, and the constants A , B , C , and E are given by

$$A = \frac{1}{2}e \times e_{\text{eff}} \left(\frac{18}{R^4} - \frac{75r_0^2}{R^6} \right), \quad B = \frac{175e \times e_{\text{eff}}}{8R^6}, \quad (25)$$

$$C = e \times e_{\text{eff}} \left(-\frac{6}{R^4} + \frac{15r_0^2}{R^6} \right), \quad E = -\frac{35e \times e_{\text{eff}}}{2R^6},$$

with e_{eff} being the effective charge of the neighboring ions.

In order to determine the effect of the strains on the spectrum the matrix elements of the coordinate

TABLE III. Normal-mode matrix elements for transitions between levels of different symmetries.

		Γ_4		
		+1	0	-1
Γ_5	+1	$aQ_2 - i\sqrt{2}bQ_4$	$-b(Q_5 + iQ_6)$	$\sqrt{3}aQ_3$
	0	$b(Q_5 - iQ_6)$	$-2aQ_2$	$-b(Q_5 + iQ_6)$
	-1	$\sqrt{3}aQ_3$	$b(Q_5 - iQ_6)$	$aQ_2 - i\sqrt{2}bQ_4$
${}^4F_{\Gamma_4} - {}^4F_{\Gamma_5}$		a	b	C_1 C_2
	$a^{IV} = \frac{2\sqrt{15}}{10}\rho_1 - \frac{25\sqrt{15}}{352}\rho_2$	$b^{IV} = \left(\frac{15}{2}\right)^{1/2} \begin{pmatrix} 1 & 2 \\ 15 & 33 \end{pmatrix} \begin{pmatrix} \rho_1 & \rho_2 \end{pmatrix}$	$\frac{3}{7}$ $-\frac{11}{7}$	
${}^4F_{\Gamma_5} - {}^4P_{\Gamma_4}$		$a^V = (\sqrt{35}) \begin{pmatrix} 9 & 20 \\ 70 & 21 \end{pmatrix} \begin{pmatrix} \rho_1 & \rho_2 \end{pmatrix}$	$b^V = \left(\frac{35}{2}\right)^{1/2} \begin{pmatrix} 6 & 1 \\ 35 & 14 \end{pmatrix} \begin{pmatrix} \rho_1 & \rho_2 \end{pmatrix}$	$\frac{4}{\sqrt{21}}$ $\frac{3}{\sqrt{21}}$
	$\rho_1 = ee_{\text{eff}}C_1(r_0^2/R^4)$	$\rho_2 = ee_{\text{eff}}C_2(r_0^4/R^6)$		

combinations appearing in Eq. (24) must be evaluated. These are given in the Appendix. The total effect of the strains is obtained by combining these matrix elements and the above constants with the results shown in Tables II and III. Some of these values have been tabulated by Van Vleck¹² but the cross terms such as ${}^4P_{\Gamma_4}$ to ${}^4F_{\Gamma_4}$ which are necessary for our purpose have been added.

The C_1 and C_2 constants are those required to convert the one-electron matrix elements such as given in the Appendix to those appropriate to Co^{2+} , the former applicable to second-degree terms and the latter to those of fourth degree.

The determination of g to second order utilizing Eq. (22) and to third order, from equations of the type

$$\frac{2\langle \frac{1}{2}\Gamma_6 | L | \frac{1}{2}\Gamma_8 \rangle \langle \frac{1}{2}\Gamma_8 | \lambda \mathbf{L} \cdot \mathbf{S} | \Gamma_5 \rangle \langle \Gamma_5 | V_i Q_i | \frac{1}{2}\Gamma_6 \rangle}{\Delta \times \frac{3}{2}\alpha'} \quad (26)$$

corresponding to the second-order g correction, involving both upper levels of Γ_4 as well as Γ_5 as intermediate states, is straightforward. The necessary matrix elements of L and $L \cdot S$ are readily obtained from the eigenfunctions of Eqs. (11), (12), (13), and (10a), (10b), and (10c).

The degenerate ground-state treatment means that the normal labels used on g factors, in which the i and j of g_{ij} refer to orbital angular-momentum operators of the spin-orbit and the Zeeman energies, are not applicable. We can however assign the δg contributions to the appropriate coupling constant by noting that the octahedral symmetry of the MgO lattice allows us to write the δg in the following form

$$\delta g = \begin{pmatrix} F_{11} & F_{12} & F_{12} & 0 & 0 & 0 \\ F_{12} & F_{11} & F_{12} & 0 & 0 & 0 \\ F_{12} & F_{12} & F_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & F_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & F_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & F_{44} \end{pmatrix} \begin{pmatrix} e_1 \\ e_2 \\ e_3 \\ e_4 \\ e_5 \\ e_6 \end{pmatrix}. \quad (27)$$

By determining the effects of various normal distortions in either δg_{11} or δg_1 the values of the F 's are obtained as follows: We write the total $\delta g = \delta g(L_2) + \delta g(L_3) + \delta g(S_2)$ indicating the orbital or spin contribution and the order of perturbation required. From Eq. (27)

$$\begin{aligned} \delta g_3 &= F_{12}e_1 + F_{12}e_2 + F_{11}e_3, \\ \delta g_5 &= F_{44}e_5. \end{aligned} \quad (28)$$

Utilizing the fact that the Q 's are equal to eR , the strain multiplied by the interionic distance in the crystal, we have

$$\delta g_3 = (1/Q_3)[\delta g_3(L_2) + \delta g_3(L_3) + \delta g_3(S_2)] \times (e_1 + e_2 - 2e_3)R, \quad (29)$$

$$\delta g_5 = (1/Q_5)[\delta g_5(L_2) + \delta g_5(L_3) + \delta g_5(S_2)]e_5R,$$

and hence

$$F_{11} = -2F_{12} = -(2/Q_3)[\delta g_3(L_2) + \delta g_3(L_3) + \delta g_3(S_2)]R, \quad (30)$$

$$F_{44} = (1/Q_5)[\delta g_5(L_2) + \delta g_5(L_3) + \delta g_5(S_2)]R.$$

Q_2 does not contribute to g_3 nor does Q_1 to the order with which we are concerned. This results in the same sort of relation between the F coupling constants as is found to the G coupling constants applicable to the ions with spin greater than $\frac{1}{2}$.

A calculation of g_3 and g_5 will then determine the theoretical values of the coupling constants F_{11} , F_{12} , and F_{44} . The former is quite straightforward and the result is given by [see Eq. (22)]

$$\begin{aligned} \delta g_3 &= \frac{4\langle \frac{1}{2} | L_x + 2S_x | + \frac{1}{2}\Gamma_8 \rangle \langle \frac{1}{2}\Gamma_8 | V_3 Q_3 | + \frac{1}{2} \rangle}{-\Delta}, \\ &= -\frac{4(2+k\alpha)}{\sqrt{3}\Delta} (\epsilon^2 a - 2\epsilon \tau a'' + \tau^2 a'), \\ &= \delta g_3(S_2) + \delta g_3(L_2). \end{aligned} \quad (31)$$

Now g_5 can be calculated either by using the $H_x \times (L_x + 2S_x)$ in combination with Q_5 or $H_x(L_x + 2S_x)$

with Q_5 : the first resulting in the spin Hamiltonian expression $H_{xz}g_{xz}S_z$, corresponding to a sort of g_{11} , and the second resulting in the form $H_{xz}g_{zx}S_x$, a g_1 term capable of inducing transitions between the lowest $\pm\frac{1}{2}$ levels. These give the same numerical result, but since the first method results in a single term rather than the two required in the second calculation, we use the former with the result

$$\begin{aligned} \delta g_5 &= \frac{4\langle +\frac{1}{2} | L_x + 2S_x | +\frac{1}{2} \Gamma_8 \rangle \langle +\frac{1}{2} \Gamma_8 | V_5 Q_5 | -\frac{1}{2} \rangle}{-\Delta}, \\ &= Q_5(2\sqrt{2}/3)[(2+\kappa\alpha)/\Delta](\epsilon^2 b - 2\epsilon\tau b'' + \tau^2 b'), \\ &= \delta g_5(S2) + \delta g_5(L2). \end{aligned} \quad (32)$$

$$\frac{\lambda(7/3)(\sqrt{5})(2+\kappa\alpha)(a^{IV}\epsilon^2 - a^V\epsilon\tau) + \lambda(15/4)\sqrt{3}\epsilon^2(\epsilon^2 a - 2\epsilon\tau a'' + \tau^2 a')}{|\alpha\lambda'| \Delta_{\Gamma_4-\Gamma_5}} Q_3 \quad (33)$$

resulting from $L_x + 2S_x$, $\lambda\mathbf{L}\cdot\mathbf{S}$, and Q_3 , from $+\frac{1}{2}$ to $+\frac{1}{2}$ with various intermediate states.

The effect of Q_5 on δg_{zx} is, in third order,

$$\frac{(7(\sqrt{30})\lambda'/12)(2+\kappa\alpha)(\epsilon^2 b^{IV} - \epsilon\tau b^V) - (9\sqrt{2}\lambda'/8)\epsilon^2(\epsilon^2 b - 2\epsilon\tau b'' + \tau^2 b')}{|\frac{3}{2}\alpha\lambda'| \Delta_{\Gamma_4-\Gamma_5}}. \quad (34)$$

COMPARISON OF THEORY AND EXPERIMENT

The numerical evaluation of the results quoted in Eqs. (31), (32), (33), and (34) is now required to obtain the values of the coupling constants F_{11} , F_{12} , and F_{44} . The major necessity is the determination of the various a and b values defined in Tables II and III.

Rather than use a calculated value of the cubic-field splitting we will make use of Van Vleck's¹² expression for the cubic-field splitting parameter based on the point-charge model

$$Dq = -\frac{1}{6}e \times e_{\text{eff}} \langle r^4 \rangle / R^5 \quad (35)$$

and evaluate the right-hand side from the experimental value of the quantity Dq . This is quite permissible since the a 's and b 's are derived from a point-charge model. The value of 960 cm^{-1} obtained by Low⁵ results in

$$e \times e_{\text{eff}} \langle r^4 \rangle / R^5 = -5760 \text{ cm}^{-1}. \quad (36)$$

There remains a factor of $\langle r_0^2 \rangle R^2 / \langle r_0^4 \rangle$ to be evaluated. This has been calculated from the wave functions given by Watson¹⁸ with a resulting value of 5.39 from the values $\langle r_0^2 \rangle = 1.251$ a.u., $\langle r_0^4 \rangle = 3.655$ a.u., and $R = 2.1$ Å = 3.79 a.u. (1 a.u. = 0.529×10^{-8} cm) (see Table V).

¹⁸ R. E. Watson, Solid State and Molecular Theory Group, Massachusetts Institute of Technology Technical Report No. 12, 1959 (unpublished).

The value of Δ is given by $\frac{3}{2}\alpha\lambda'$. It is essential that the admixture of 4P be considered, as cross terms will contribute a major portion of the theoretical value. The uppermost of the 4F levels ($\Gamma^7 + \Gamma^8$) does not contribute in second order.

The second-order contribution to the g factor of Eq. (20) amounts to about 1½%, and the third-order correction to δg should be of about the same importance. There is a contribution from Q_3 , involving the compressional strains, to the δg_{11} . The third-order expressions are complicated again by the fact that the spin-lattice coupling mixes the 4F and the 4P portions in Γ_4 . The result is

The values of the a and b constants are then

$$\begin{aligned} a &= -5150 \text{ cm}^{-1}/R, & b &= +620 \text{ cm}^{-1}/R, \\ a' &= +18\,660 \text{ cm}^{-1}/R, & b' &= -26\,350 \text{ cm}^{-1}/R, \\ a'' &= +14\,830 \text{ cm}^{-1}/R, & b'' &= -15\,540 \text{ cm}^{-1}/R, \\ a''' &= -4000 \text{ cm}^{-1}/R, & b''' &= -8440 \text{ cm}^{-1}/R, \\ a^{IV} &= -12\,800 \text{ cm}^{-1}/R, & b^{IV} &= -3890 \text{ cm}^{-1}/R, \\ a^V &= +41\,820 \text{ cm}^{-1}/R, & b^V &= +18\,300 \text{ cm}^{-1}/R. \end{aligned} \quad (37)$$

These constants depend almost directly on the value of the ratio $\langle r_0^2 \rangle R^2 / \langle r_0^4 \rangle$ and decrease as this ratio is decreased.

The evaluation of the combinations of constants occurring in Eqs. (31) through (34) rests in part on the values of the constants ϵ and τ . These have been evaluated by Low⁵ as $\epsilon = 0.980$ and $\tau = 0.204$ from measurements on the optical spectra of Co^{2+} in MgO . The sign of τ used in Eq. (10a) is the result of the sign of the cubic-field parameter and the negative sign is consistent with the ordering of the other levels. The values⁵ of $\frac{3}{2}\alpha\lambda' = 305 \text{ cm}^{-1}$ and $\Delta_{\Gamma_4-\Gamma_5} = 8470 \text{ cm}^{-1}$ are used in the final evaluation of Eqs. (31) and (32). Then we have

$$\begin{aligned} \epsilon^2 a - 2\epsilon\tau a'' + \tau^2 a' &= -11\,620 \text{ cm}^{-1}/R, \\ \epsilon^2 b - 2\epsilon\tau b'' + \tau^2 b' &= +7870 \text{ cm}^{-1}/R, \\ \epsilon^2 a^{IV} - \epsilon\tau a^V &= -20\,650 \text{ cm}^{-1}/R, \\ \epsilon^2 b^{IV} - \epsilon\tau b^V &= -7360 \text{ cm}^{-1}/R, \end{aligned} \quad (38)$$

and the resulting values of the coupling constants are

$$F_{11} = -2F_{12} = -2(285 + 35.5) = -642/\text{unit strain}$$

$$F_{44} = 83 + 5 = 88/\text{unit strain}.$$

In the above the first figure is the second-order contribution and the second the third-order part. It is noteworthy that the ${}^4F_{\Gamma_4} - {}^4P_{\Gamma_4}$ terms add so that the admixture of the 4P level into the ground state results in a substantial increase in the calculated coupling constants. If the admixture of this level into the ground Γ_4 level is neglected the values would be in somewhat better agreement with the experimental results. In any case the signs do agree but the theoretical values are approximately nine times the experimental ones.

The change of hyperfine constant with stress is, as can be seen by reference to Eq. (17), primarily a second-order calculation involving orbital and spin operators. Neglecting the d -electron contribution the result is

$$\delta A_{zz} = \frac{4\gamma\beta\hbar}{r^3} \left\{ \frac{\langle +\frac{1}{2} | L_z - \kappa S_z | +\frac{1}{2} \Gamma_3 \rangle \langle +\frac{1}{2} \Gamma_3 | V_3 Q_3 | \frac{1}{2} \rangle}{-|\frac{3}{2}\alpha\lambda'|} + (\text{reverse ordering}) \right\}. \quad (39)$$

The third-order part of g_L can easily be included and the result is

$$\delta A_{zz} = N^2 P \left\{ (\alpha - \kappa) \frac{4Q_3}{\sqrt{3}|\frac{3}{2}\alpha\lambda'|} (\epsilon^2 a - 2\epsilon\tau a'' + \tau^2 a') - \text{Eq. (33)} \right\}. \quad (40)$$

In keeping with previous assumptions¹⁵ the value is taken to be reduced by the normalization factor N^2 . This is justified by the argument that it is only the wave function in the vicinity of the nucleus, that is the d -electron part, which is effective in the hyperfine interaction. The actual contribution from the d electrons themselves is small and has been neglected, leaving the orbital contribution as well as the s -electron admixture.

Evaluating the various terms of Eq. (40) results in the expression

$$N^2 P Q_3 \{ (\alpha - \kappa)(88.3) + 9.0(\alpha - \kappa) + 6.1 \} \quad (41)$$

for the δA_{zz} . The corresponding expression for δg_{zz} is

$$Q_3 \{ 88.3(2 + k\alpha) + 9.0(2 + k\alpha) + 6.1 \} \quad (42)$$

giving a ratio of

$$\frac{\delta A_{zz}}{\delta g_{zz}} = N^2 P \left\{ \frac{97.3(\alpha - \kappa) + 6.1}{97.3(k\alpha + 2) + 6.1} \right\}. \quad (43)$$

The same ratio for the xz components differs only

TABLE IV. Coupling constants.

ion	Experiment			Theory			Normal- ization factor N^2
	G_{11}	G_{44}		G_{11}	G_{44}		
Cr^{3+}	+0.6	+4.2 ^a		+1.64	+2.81		0.72 ^b
Ni^{2+}	+57	+36 ^a		+46.6	+90.7		0.77 ^c
	F_{11}	F_{12}	F_{44}	F_{11}	F_{12}	F_{44}	
Co^{2+}	-69	32	10	-642	321	88	0.85 ^d

^a G. Watkins and Elsa Feher, Bull. Am. Phys. Soc. 7, 29 (1962).

^b W. Low, Phys. Rev. 105, 801 (1957).

^c W. Low, Phys. Rev. 109, 247 (1958).

^d W. Low, Phys. Rev. 109, 256 (1958).

slightly and is given by

$$\frac{\delta A_{zz}}{\delta g_{zz}} = N^2 P \left\{ \frac{25.6(\alpha - \kappa) + 0.68}{25.6(k\alpha + 2) + 0.68} \right\}. \quad (43a)$$

Certainly to within the accuracy of the experimental results this represents a constant ratio for the $\delta A/\delta g$ ratios.

EVALUATION OF PHENOMENOLOGICAL SPIN-HAMILTONIAN CONSTANTS

The spin-Hamiltonian representation of the Co^{2+} paramagnetic-resonance spectrum represented by Eqs. (20) and (21) involves a number of constants. Some of these are determined by the paramagnetic-resonance results but two of them, P and κ , cannot be individually determined by the paramagnetic hyperfine constant A . Low's work⁵ has determined the value of α to be 1.398 (we will use 1.40) and the value of k as 0.89. Taking the experimental value for the ratio $\delta A/\delta g$ as 1.74×10^{-18} erg and using these values of α and k , Eqs. (43) and (21) (using the experimental A value of $97.7 \times 10^{-4} \text{ cm}^{-1}$) may be solved for $N^2 P$ and κ with the result

$$N^2 P = 5.95 \times 10^{-18} \text{ erg} = 0.030 \text{ cm}^{-1}, \quad (44)$$

$$\kappa = 0.445.$$

These differ substantially from the values of $N^2 P = 0.0225 \text{ cm}^{-1}$ and $\kappa = 0.325$ which are satisfactory for

TABLE V. Mean second and fourth powers of the d electron radii for iron-group ions.^a

Ion	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}	Ni^{3+}		
$\langle r^2 \rangle$	1.893	1.644	1.447	1.286	1.150	0.9583		
$\langle r^4 \rangle$	7.069	5.446	4.297	3.446	2.790	1.971		
Ion	Ti^{2+}	V^{2+}		Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$\langle r^2 \rangle$	2.447	2.070		1.548	1.393	1.251	1.130	1.028
$\langle r^4 \rangle$	13.17	9.604		5.512	4.495	3.655	3.003	2.498
Ion	Ti^+	V^+		Mn^+	Fe^+	Co^+	Ni^+	Cu^+
$\langle r^2 \rangle$	3.508	2.819		2.026	1.774	1.576	1.401	1.256
$\langle r^4 \rangle$	31.62	20.72		10.87	8.385	6.637	5.264	4.238

^a The values in this table were calculated from the wave functions of Ref. 17 by Miss Elise Kreiger of the G. E. Research and Development Center. The values are in atomic units.

TABLE VI. Single-electron matrix elements.

		4F				4P	
		Γ_4	Γ_5	Γ_6	Γ_4	Γ_5	Γ_6
For $x^2+y^2-2z^2$ (diagonal and above) and xz (below diagonal):							
4F	Γ_4	+1	0	-1	+1	0	-1
		+56	0	0	0	28 $\sqrt{15}$	0
		+7 $\sqrt{2}$	-112	0	0	0	0
		0	-7 $\sqrt{2}$	+56	28 $\sqrt{15}$	0	0
		0	+7 $\sqrt{15}/3\sqrt{2}$	0	0	0	0
		-7 $\sqrt{15}/3\sqrt{2}$	0	7 $\sqrt{15}/3\sqrt{2}$	35 $\sqrt{2}$	0	0
		0	-7 $\sqrt{15}/3\sqrt{2}$	0	0	-35 $\sqrt{2}$	0
		0	6 $\sqrt{21}/\sqrt{2}$	0	0	-6 $\sqrt{35}/\sqrt{2}$	0
		6 $\sqrt{21}/\sqrt{2}$	0	-6 $\sqrt{21}/\sqrt{2}$	6 $\sqrt{35}/\sqrt{2}$	0	-168
		0	-6 $\sqrt{21}/\sqrt{2}$	0	0	6 $\sqrt{35}/\sqrt{2}$	84
For $x^2+y^2-2z^2$ (diagonal and above) and xz (below diagonal):							
4P	Γ_4	+1	0	-1	+1	0	-1
		28/110	0	0	0	0	0
		+12/220 $\sqrt{2}$	-28/55	0	0	+23 $\sqrt{15}/220$	0
		0	-12/220 $\sqrt{2}$	28/110	(23 $\sqrt{15})/220$	0	0
		0	(2 $\sqrt{15})/330\sqrt{2}$	0	-2/33	0	0
		-(2 $\sqrt{15})/330\sqrt{2}$	0	(2 $\sqrt{15})/330\sqrt{2}$	10/66 $\sqrt{2}$	4/33	0
		0	-2 $\sqrt{15}/330\sqrt{2}$	0	0	-10/66 $\sqrt{2}$	0
		0	(7 $\sqrt{21})/315\sqrt{2}$	0	0	-(6 $\sqrt{35})/210\sqrt{2}$	0
		(7 $\sqrt{21})/315\sqrt{2}$	0	-(7 $\sqrt{21})/315\sqrt{2}$	(6 $\sqrt{35})/210\sqrt{2}$	0	0
		0	-(7 $\sqrt{21})/315\sqrt{2}$	0	0	(6 $\sqrt{35})/210\sqrt{2}$	-24/35
		0	-(7 $\sqrt{21})/315\sqrt{2}$	0	0	0	9/105 $\sqrt{2}$

the hydrated cobalt salts.⁹ Previous attempts to compare the experimental A value with one obtained using combinations of N^2P and κ have ignored the second-order orbital contribution which in itself reduces the value of κ required [$-15/(2\Delta)=0.130$]. Even so the values of the constants appropriate to the hydrated salts have not been very satisfactory for the case of Co^{2+} in MgO .

This use of the experimental value of the $\delta A/\delta g$ value along with the value of A from the paramagnetic-resonance spectrum enables us to evaluate the constants N^2P and κ assuming that the values of k and α as previously determined are satisfactory. Since the value $\delta A/\delta g$ is evaluated in a single experimental run the uncertainties of absolute calibration are absent and only the relative effects under the same experimental condition are relevant. The conclusion from the above is that if the hyperfine constant A is to be represented by an expression such as Eq. (21) the proper constants to be used are those given by Eq. (44).

GENERAL DISCUSSION OF THE COMPARISON OF SPIN-LATTICE COUPLING CONSTANTS AS DERIVED FROM POINT-CHARGE MODEL AND EXPERIMENTAL RESULTS

In Table IV we have listed the experimental results for the spin-lattice coupling constants of a number of the iron-group ions and the theoretical values based on the same point-charge model which we have used above for cobalt. The ions Ni^{2+} and Cr^{3+} may be treated directly from Van Vleck's¹⁹ results as has been recognized by Shiren²⁰ and our values are almost identical to his except that an error in the signs of the G_{11} 's has been corrected. The values of $\langle r_0^2 \rangle$ and $\langle r_0^4 \rangle$ for a number of ions is given in Table V. It is evident that the agreement between the experimental and theoretical results is remarkably good considering the crude model which has been used.

¹⁹ J. H. Van Vleck, *Phys. Rev.* **57**, 426 (1940).

²⁰ N. S. Shiren, *Proceedings of the XIth Colloque Ampere, Eindhoven, 1962* (North-Holland Publishing Company, Amsterdam, 1963), p. 114.

The omission of the effect of overlap and covalent effects is particularly troublesome. For the three ions in Table IV the last column lists the value of the delocalization correction by giving the normalization factors N^2 . There is some correlation with the strong-field picture of the electron orbitals in that Cr^{3+} with its three t orbitals shows no hyperfine structure due to its neighbors, but the value of the spin-orbit coupling constant is reduced from that for the free ion. It is interesting to note that Ni^{2+} with its two e orbitals shows quite good agreement between theory and experiment while Co^{2+} with two e and one t orbital and approximately the same orbital reduction does not agree nearly as well. Considering the difficulty in drawing conclusions from the overlap and covalent effects^{21,22} no attempt has been made to evaluate the effect of these considerations on the spin-lattice coupling.

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APPENDIX

The single-electron matrix elements between states as indicated are given in Table VI. Conversion to the Co^{2+} matrix elements requires that the values be multiplied by C_1 for second-order terms and C_2 for fourth-order terms. C_1 and C_2 are given in Tables II and III of the main text. Some of these values are identical to those given in Ref. 9 except that the values there quoted are for charge density and hence differ in sign.

²¹ S. Sugano and R. G. Shulman, *Phys. Rev.* **130**, 517 (1963).

²² R. E. Watson and A. J. Freeman, *Phys. Rev.* **134**, A1526 (1964).