ment (~800 kc/sec) is in good agreement with that obtained from T_2 and T_{ZE} data in the plateau region (780 kc/sec). Therefore, the deviation of J_G from J is shown to be small, certainly within the experimental error of the determination of the exchange integral.

The frequency shift experiment has given an upper limit one might expect for the shift predicted by Kubo and Tomita,[3] and our results are consistent with their calculations. In view of the errors inherent to shift measurements, it is improbable that much quantitative information will be obtained even under the best conditions.

ACKNOWLEDGMENTS

The authors are very indebted to Dr. J. Winter, Dr. R. L. Garwin, and Dr. H. Reich for several helpful discussions.

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Electronic Structure of MgF$_2$:Co^{++}

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The F^{19} superhyperfine structure of the EPR spectra of Co^{++} in MgF$_2$ is interpreted with simple molecular-orbital theory. A necessary preliminary analysis is made of the g tensor and of the spacing of the six Kramers doublets derived from the $^4T_1$ ground manifold. The ligand-field parameters of the rhombic field, $\Delta \cong 510$ cm^{-1} and $\Gamma \cong -390$ cm^{-1}, and the spin-orbit coupling, $\lambda \cong -157$ cm^{-1}, are significantly different from values derived from less complete data. The reported superhyperfine interactions provide sufficient data to determine, without recourse to much less certain orbital-reduction factors, the s-, sigma-, and pi-bonding fractions: $f_s = (0.61 \pm 0.02)\%$, $f_\sigma = (3.9 \pm 0.3)\%$, and $f_\pi = (0.9 \pm 0.3)\%$ for the two equivalent fluorine ions along [110]. For the other four fluorine ions similar estimates are obtained. These results are at variance with the suggestion, made for octahedral Co^{++}, that sigma and pi bonding are of comparable magnitude.

INTRODUCTION

A PREVIOUS paper[1] describes the EPR spectra of cobalt as a dilute substitutional impurity in magnesium fluoride, and presents a complete analysis of the complex F^{19} superhyperfine structure (shfs). It is the purpose of the present paper to interpret the measured superhyperfine tensors at the simplest possible level of phenomenological molecular-orbital (MO) theory.

MgF$_2$:Co^{++} and closely related materials provide an unusually complete set of data to be correlated and interpreted.

(1) The EPR spectra are fit by a spin-Hamiltonian with completely anisotropic spectroscopic splitting and cobalt hyperfine tensors. The superhyperfine tensors of two nonequivalent F^{19} ligand-nuclei are also anisotropic. The principal-axis directions of one of these tensors are not symmetry-determined, and do not coincide with the bond direction. The nearly identical spectra of ZnF$_2$:Co^{++} have not been completely analyzed.[2,3]

(2) The infrared (IR) absorption spectrum of CoF$_2$ at low temperature[4] has several peaks near 1000 cm^{-1}.

(3) Fluorescence spectra[5] provide remarkably precise information of the energies of the lowest set of excited states.

(4) EPR[6,7] and optical[8] spectra are known for the corresponding octahedral complex KMgF$_3$:Co^{++}.

Besides these researches, there have been studies of the static susceptibility and antiferromagnetic resonance of[9–15] CoF$_2$ and of the NMR of fluorine[15] and cobalt.[16]

Simple MO theory of superhyperfine interactions has been described for similar systems,[7,17,18] but not for an orbitally unquenched octahedral ground state which is

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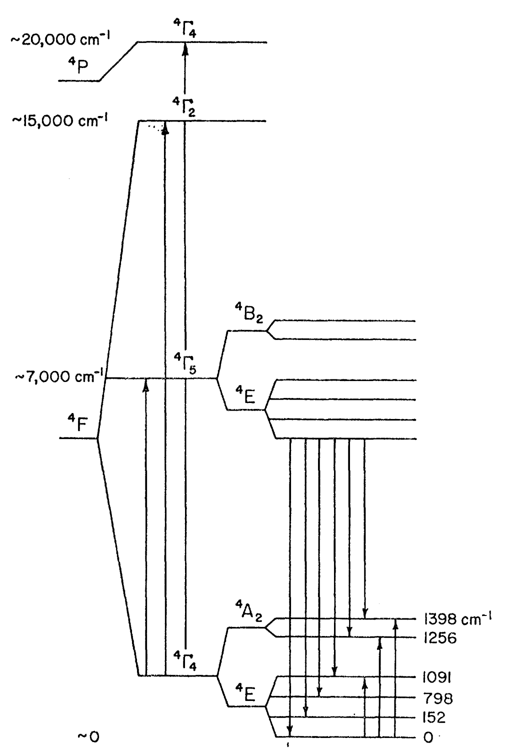

FIG. 1. Splitting of the free-ion states in a cubic field, augmented in stages by tetragonal distortion, spin-orbit coupling, and rhombic distortion. The ground $^4\Gamma_4$ manifold, a mixture of ^4F and ^4P states, is split by tetragonal fields into an orbital singlet and an orbital doublet. As for the cobalt Tutton salts, the magnetic evidence indicates that it is the doublet which lies lower [B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A208**, 143 (1951)]. However, since the spin-orbit interactions and rhombic field are not small, this statement becomes a bit specious. Spin-orbit interactions split these states into six Kramers doublets, three of symmetry $E_{3/2}$ and three of symmetry $E_{1/2}$ (under the D_{4h} spinor group). All the states belong to the single doubly-degenerate irreducible representation of the D_{2h} spinor group. Observed transitions (Refs. 4, 5, and 8) are marked.

further split by lower symmetry fields. Partly because of the attendant algebraic complexities, we do not attempt in this paper to advance conceptually from the simplest theory with sufficient structure to describe the optical and resonance spectra. Because of the large number of experimental data available, it is possible to describe the electronic structure of the rhombic d^7 ion unusually completely and precisely, with fewer approximations than is often the case. We attempt to point out all approximations, to estimate the errors incurred, and to frame the description so that they may be avoided without complicated revisions in future work.

Briefly, we adopt the following approach. The atomic states of d^7 are examined in an octahedral field to determine the composition of the lowest manifold of states. On this manifold, the matrix of the low-symmetry parts of the ligand field and of the spin-orbit interaction is diagonalized to give a representation of the ground state. The rhombic-field and spin-orbit couplings to the higher states of the octahedral problem are ignored. Because the parameters of the effective Hamiltonian are extremely difficult to evaluate from first principles they are adjusted to fit fluorescence spectra and the gyromagnetic tensor. Since the necessary matrix elements are determined empirically, and since the structure of the Hamiltonian matrix depends only on wave-function transformation properties, details of the orbitals (e.g., covalency) are irrelevant until one considers the relationship between orbitals and one-electron matrix elements. The expansion coefficients of the determinantal functions contributing to the ground state are not further modified, but the contributing orbitals are replaced by molecular orbitals which include ligand-orbital contributions. Matrices of the ligand-hyperfine interaction are written on the 10-fold MO basis and the algorithm relating these to the hyperfine perturbations in the electronic ground state, a Kramers doublet, is outlined.

We choose not to discuss the cobalt hyperfine tensor in this paper. The contact part of this interaction depends on ill-understood *s-d* hybridization effects. The orbital dipolar part is dependent on orbital reductions which are not otherwise treated below. Besides, this interaction is fairly well described by very simple theories[3] so that a description involving adjustable parameters would not represent an advance on prior work.

THEORY OF THE OPTICAL SPECTRA AND g TENSOR

The $3d^7$ ground configuration of free Co^{++} is separated by more than 40 000 cm^{-1} from the lowest terms of the first excited configuration.[19] It has ^4F and ^4P terms, as well as many doublets. Since the observed doublets are between 16 000 and 23 000 cm^{-1} above the ground state and are connected to the quartets only by spin-orbit matrix elements of the order of a few hundred cm^{-1}, they make minor contributions to the ground-state structure and may safely be ignored. On the other hand the ^4P state is not unimportant. Conveniently, its contribution is easily included in the theory. The crystal-field splittings of the free-ion states are indicated in Fig. 1.

Except for the most detailed discussions, it is customary to neglect the effects of the $^4\Gamma_5$ and $^4\Gamma_2$ manifolds. These interact with the $^4\Gamma_4$ manifold by spin-orbit splitting and by elements of the low-symmetry electric fields. The spin-orbit contribution to g has been discussed[20] for octahedral Co^{++}. Although the interval Δ' to the $^4\Gamma_5$ state is large compared to the spin-orbit coupling λ, the interaction produces a significant second-order correction, given as $-(15/2)(\lambda/\Delta')$. For KCoF$_3$, this interaction leads to a calculated change of $+0.16$ (4%) in the isotropic g value. There are also contribu-

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[20] W. Low, Phys. Rev. **109**, 256 (1958). In Ref. 7, Low's result is generalized to include the second-order effect of ^4P mixing.

tions to both the Fermi and the dipolar terms of the ligand hyperfine structure. Since they are of the order of 10% of the main terms[7] they must be considered when a refinement of the present calculations is undertaken. We omit the effects of the $^4\Gamma_5$ states principally because their inclusion would introduce two adjustable parameters, in addition to those otherwise necessary, into the description of the electrostatic field. (See Appendix A.)

We will defer also consideration of orbital-reduction factors,[21] which are important in the calculation of gyromagnetic ratios and of the Co hyperfine interaction. It is well known that direct estimation of the reduction factors is difficult and imprecise.[22] Good estimates for them will be possible when the orbitals are known from the theoretical examination of the superhyperfine structure.

The ground $^4\Gamma_4$ manifold may be described either in a weak-field representation, as a mixture of ^4F and ^4P functions, or in a strong-field representation, with t^5e^2 and t^4e^3 configurations.[23] Although the former representation is very convenient for evaluating some properties, such as the Zeeman splitting, the latter is better for the superhyperfine interactions. Wave functions may be written in terms of holes in an incomplete d shell, as te^2 and t^2e.[24] For each state of the ground manifold we write

$$|^4\Gamma_4\rangle = C|(te^2)^4\Gamma_4\rangle + D|(t^2e)^4\Gamma_4\rangle. \tag{1}$$

It is only in cubic symmetry that each state has the same mixture of te^2 and t^2e character. In lower symmetries, distortions of the molecular orbitals generally lead to different repulsion energies in different irreducible representations. However, these effects are probably small, lead to unwarranted complication in a parametric description, and will be ignored.

Since an atomic P state transforms as Γ_4 under the octahedral group, the energy matrix on the $^4\Gamma_4$ manifold may be written as the matrix of an effective Hamiltonian with pseudo-angular-momentum operators $\mathfrak{L}_x$, $\mathfrak{L}_y$, $\mathfrak{L}_z$ construed to act on P states. In rhombic fields, if we include the possible anistropy of the spin-orbit coupling, symmetry suggests the appropriate form of the effective Hamiltonian[9,12,14,22,25]:

$$\begin{aligned}\mathcal{H}_{\mathrm{eff}} = \Delta(1-\mathfrak{L}_z^2) + \Gamma(\mathfrak{L}_x^2-\mathfrak{L}_y^2) + \Lambda_x\mathfrak{L}_xS_x \\ + \Lambda_y\mathfrak{L}_yS_y + \Lambda_z\mathfrak{L}_zS_z.\end{aligned} \tag{2}$$

The matrix elements of $\mathfrak{L}$ on P states, $|M_l\rangle$, are related to those of the orbital momentum $\mathbf{L}$ on the ground manifold $|\Gamma_4M_l\rangle$ by the generalized Wigner-Eckart theorem[26,27]

$$\langle\Gamma_4M_l|\mathbf{L}|\Gamma_4M_{l'}\rangle = \mathfrak{F}\langle M_l|\mathfrak{L}|M_{l'}\rangle. \tag{3}$$

The factor $\mathfrak{F}$ is readily found if one compares elements of the z component for $M_l = M_{l'} = 1$.

$$\mathfrak{F} = -C^2 + 2CD + \tfrac{1}{2}D^2. \tag{4}$$

The ^4P mixing into the ground manifold reduces the orbital momentum, augmenting any orbital reduction. It also causes an implicit reduction in the effective spin-orbit interaction in Eq. (2).

In accordance with Kramers theorem the matrix of $\mathcal{H}_{\mathrm{eff}}$ on the $^4\Gamma_4$ basis factors into identical 6×6 matrices, which do not factor further. Since the tetragonal field, rhombic field, and spin-orbit coupling are all of the same order of magnitude, machine diagonalization is the simplest method for a sufficiently accurate representation of the ground doublet; the components may be written

$$\begin{aligned}|\pm\rangle = a|0, \pm\tfrac{1}{2}\rangle + b|\pm1, \mp\tfrac{1}{2}\rangle + c|\mp1, \pm\tfrac{3}{2}\rangle \\ + d|0, \mp\tfrac{3}{2}\rangle + e|\mp1, \mp\tfrac{1}{2}\rangle + f|\pm1, \pm\tfrac{3}{2}\rangle.\end{aligned} \tag{5}$$

If the rhombic field vanishes and the spin-orbit coupling is isotropic, then either $a=b=c=0$, corresponding to the $E_{3/2}$ irreducible representation of the D_{4h} spinor group, or $d=e=f$, corresponding to $E_{1/2}$.

The EPR experiments were reported[1] in terms of the conventional spin-Hamiltonian for an effective spin doublet.

$$\mathcal{H}_{\mathrm{sp}} = \beta\mathbf{S}^{\mathrm{eff}}\cdot\mathbf{g}\cdot\mathbf{H} + \sum_{\text{magnetic nuclei } N} \mathbf{S}^{\mathrm{eff}}\cdot\mathbf{A}^N\cdot\mathbf{I}^N. \tag{6}$$

Here the gyromagnetic and hyperfine tensors may be evaluated by comparison of the matrices of $\mathbf{S}^{\mathrm{eff}}$ on $|\pm\frac{1}{2}\rangle$ spin eigenfunctions with matrices of $(\mathbf{L}+2\mathbf{S})$ and of the coefficients of $\mathbf{I}^N$ in the nuclear hyperfine operators on the Kramers doublets, Eq. (5). Thus,[28]

$$\begin{aligned}g_z &= 2(a^2-b^2+3c^2-3d^2-e^2+3f^2) \\ &\quad + 2\mathfrak{F}(b^2-c^2-e^2+f^2), \\ g_{x,y} &= 4(a^2+\sqrt{3}bc\pm\sqrt{3}ad\pm2be+\sqrt{3}ef) \\ &\quad + 2\sqrt{2}\mathfrak{F}(ab+df\pm ae\pm cd),\end{aligned} \tag{7}$$

where the + goes with x and the − with y.

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[21] K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

[22] H. M. Gladney and J. D. Swalen, J. Chem. Phys. **42**, 1999 (1965).

[23] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1961), p. 235, gives the relationship between the two representations and the matrix of the cubic field and electron repulsion.

[24] It is conventional and convenient to discuss the d^7 electron problem as d^3 holes in a complete shell. As is well known (Ref. 23, pp. 245–256) this replacement requires only trivial changes in the matrix elements.

[25] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951). These authors show how an effective anisotropy of the spin-orbit interaction can arise on the ground manifold from ^4P and $^4\Gamma_5$ mixing, even if the orbitals are all radially identical.

[26] See, for example, S. R. Polo, "Studies on Crystal-Field Theory," RCA Laboratories Monograph, Princeton, New Jersey, 1960, p. 11–5 (unpublished). Equation (5) is strictly valid only in cubic symmetry. In D_{2h}, completely anisotropic orbital-reduction factors enter. The anisotropic form of the spin-orbit coupling suggests a parallel anisotropy in the orbital momentum matrix elements. This is not included in the text, since the anisotropy of spin-orbit is partly related to different radial behavior of different MO's, unlike that of the orbital momentum.

[27] The customary assumption that the radial distribution of all d orbitals is the same is implicit in Eq. (3).

[28] For tetragonal symmetry, Abragam and Pryce (Ref. 25) show how to take orbital reduction into account in these formulas.

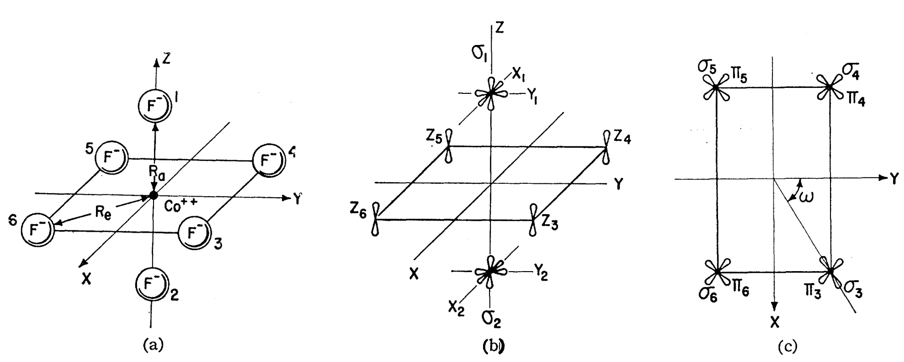

FIG. 2. Geometry and orbitals about the Co⁺⁺ site: In the text, anions 1 and 2 are referred to as axial, and anions 3, 4, 5, and 6 as equatorial.

THEORY OF THE LIGAND HYPERFINE STRUCTURE

Matrix elements of the hyperfine-interaction Hamiltonian are readily written on a molecular-orbital basis. Then the hyperfine terms of the spin Hamiltonian may be evaluated by substitution of determinantal three-electron functions for the symbolic space-spin basis $|M_lM_s\rangle$ [in Eq. (5)] and execution of the transformations expressing the ground-state eigenfunctions as expansions in determinants. Below, we first describe the molecular orbitals adopted and the calculation of elements of the hyperfine operators. Then the basis transformations are outlined, followed by the algorithm for extraction of the spin-Hamiltonian parameters.

The Co⁺⁺ ion is surrounded by six F⁻ ions in a distorted octahedron of orthorhombic symmetry (Fig. 2); the anions are numbered for identification.[29] We assume that, of the anion atomic orbitals, only $2s$ and $2p$ orbitals participate in covalent bonding. Symmetry requirements do not dictate a special choice in the xy plane for the p orbitals of the equatorial fluorides, but since the symmetry is nearly D_{4h}, we choose these orbitals along and perpendicular to the bond directions. If we assume that those linear combinations of anion orbitals which are nonbonding under D_{4h} make only negligible contributions in the present case, then the molecular orbitals may be written[30]

$$\begin{aligned}\psi_1&=N_1^{-1/2}[d_{z^2}+\alpha_s(s_1+s_2)+\alpha_\sigma(\sigma_1+\sigma_2)\\&\qquad+\beta_s(s_3+s_4+s_5+s_6)+\beta_\sigma(\sigma_3+\sigma_4+\sigma_5+\sigma_6)],\\\psi_2&=N_2^{-1/2}[d_{xy}+\gamma_s(s_3-s_4+s_5-s_6)\\&\qquad+\gamma_\sigma(\sigma_3-\sigma_4+\sigma_5-\sigma_6)],\\\psi_3&=N_3^{-1/2}[d_{x^2-y^2}+\delta(\pi_3-\pi_4+\pi_5-\pi_6)],\\\psi_4&=N_4^{-1/2}[d_{yz}+\alpha_y(y_1+y_2)+\epsilon(z_3-z_4-z_5+z_6)],\\\psi_5&=N_5^{-1/2}[d_{xz}+\alpha_x(x_1+x_2)+\zeta(z_3+z_4-z_5-z_6)].\end{aligned}\tag{8}$$

The Hamiltonian for the interaction of an electron with an F¹⁹ nucleus is

$$\mathcal{H}^{19}=\Upsilon\mathbf{I}\cdot\left\{\frac{\mathbf{l}}{r^3}-\frac{\mathbf{s}}{r^3}+\frac{3(\mathbf{s}\cdot\mathbf{r})\mathbf{r}}{r^5}+\frac{8\pi}{3}\delta(r)\mathbf{s}\right\},\tag{9}$$

$$\Upsilon=2\gamma\beta\beta_N.$$

The expectations of $\mathcal{H}^{19}$ are best evaluated directly[31] with the algebra arranged so that tedious manipulation may be done computationally. Marshall[32] breaks up the operator into three types of terms: elements on central-atom orbitals, elements on ligand-atom orbitals, and overlap-type elements. He indicates that the overlap elements have the same symmetry as the central-atom elements and therefore may be included by readjusting certain radial distribution integrals which are, in any case, uncertainly known. The elements on central-atom orbitals are evaluated by replacing the electron-nucleus vector $\mathbf{r}$ by $\mathbf{R}+\mathbf{r}_0$, where $\mathbf{R}$ is the internuclear displacement and $\mathbf{r}_0$ the vector from the Co⁺⁺ nucleus to the electron. Then the operator is expanded as a multipole series in (r_0/R). We retain only the first terms.[33] The central-atom spin-dipolar contributions are evaluated with

$$\mathcal{H}_1=\Upsilon(3s_\sigma I_\sigma-\mathbf{s}\cdot\mathbf{I})R^{-3}\tag{10}$$

and the central-atom orbital dipolar with

$$\mathcal{H}_2=\Upsilon(3l_\sigma I_\sigma-\mathbf{l}\cdot\mathbf{I})R^{-3}.\tag{11}$$

Here $\mathbf{l}$ is the orbital-momentum operator centered at the Co⁺⁺ nucleus; subscript σ indicates the component along the bond direction. The contributions from orbital and spin momentum on the ligands and from the Fermi

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[29] The choice of axes differs from that of the previous paper (Ref. 1).

[30] In D_{2h} these functions are not orthogonal; e.g., $(s_3+s_4+s_5+s_6)$ has a finite overlap with $d_{x^2-y^2}$. But these overlaps are negligibly small. The axis conventions for the ligand orbitals are, in each case, the positive σ axis directed toward the central ion; for the axial ligands, the positive x axis lies along the crystal x axis and the y axis completes the right-handed orthogonal triad; for the equatorial ligands the z axis is perpendicular to the symmetry plane, and the π axis is perpendicular to the bond but in the symmetry plane.

[31] For Co⁺⁺, the simplifications possible for Mn⁺⁺ (Ref. 17) by means of the Wigner-Eckart theorem may not be employed. For the d^5 ion, the orbital contributions to the hyperfine effect cancel; because the spin-orbit coupling is small compared to the separation of the ^6S ground manifold from excited states, it is a good approximation to assume that spin-space is isotropic, and that the electron spin operator transforms as an irreducible representation of the spin symmetry group. Since spin-orbit mixings are large for Co⁺⁺, space and spin symmetries may not be separated.

[32] W. Marshall, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962,* edited by W. Low (Academic Press Inc., New York, 1963), Vol. I, p. 347.

[33] The higher terms contribute an additional 3% to these parts of the interaction (Ref. 7).

contact term are estimated with $\mathcal{H}^{19}$ directly. Contributions at one ligand from electron density at another are assumed negligible. Also assumed negligible are contact terms arising from the finite density of a Co^{++} d orbital at the F^{19} nucleus. The effects of core polarization at the anion on estimates of the unpaired electron density have been shown to be small.[7] $\mathcal{H}^{19}$ need be evaluated only for one axial and one equatorial anion. To conserve space the matrices of the coefficients of I_x, I_y, and I_z in Eq. (9) are not included below, but may be obtained from the author.

The total hyperfine interaction is evaluated as the expectation of $\mathcal{H}^{19}$ summed over three holes following expansion of the ground-state wave functions Eq. (5) into sums over determinantal functions. Quartet functions with $M_s=\frac{3}{2}$ may be separated into orbital and spin factors. Take as the orbital parts of these the determinants

$$\begin{aligned}
\Phi_1&=|\psi_1\psi_2\psi_3|,\\
\Phi_2&=|\psi_1\psi_2\psi_4|,\\
\Phi_3&=|\psi_1\psi_2\psi_5|,\\
\Phi_4&=|\psi_1\psi_4\psi_5|,\\
\Phi_5&=|\psi_1\psi_3\psi_5|,\\
\Phi_6&=|\psi_1\psi_3\psi_4|,\\
\Phi_7&=|\psi_2\psi_3\psi_5|,\\
\Phi_8&=|\psi_2\psi_3\psi_4|.
\end{aligned} \tag{12}$$

Then the strong-field functions transforming as Γ_4 of O_h are

$$\begin{aligned}
|(te^2)\Gamma_4z\rangle&=\Phi_1,\\
|(te^2)\Gamma_4x\rangle&=\Phi_2,\\
|(te^2)\Gamma_4y\rangle&=\Phi_3,\\
|(t^2e)\Gamma_4z\rangle&=-\Phi_4,\\
|(t^2e)\Gamma_4x\rangle&=\tfrac{1}{2}\Phi_6-\tfrac{1}{2}\sqrt{3}\Phi_7,\\
|(t^2e)\Gamma_4y\rangle&=\tfrac{1}{2}\Phi_5-\tfrac{1}{2}\sqrt{3}\Phi_8.
\end{aligned} \tag{13}$$

Combining Eq. (1) with Eq. (13) and replacing the complex form of the Γ_4 functions by the real form, we have the spatial transformation

$$|M_lM_s\rangle=\sum_j|\Phi_jM_s\rangle C_{jM_l}, \tag{14a}$$

$$\mathbf{C}=\begin{bmatrix}
C & 0 & 0\\
0 & (i/\sqrt{2})C & (i/\sqrt{2})C\\
0 & -(1/\sqrt{2})C & (1/\sqrt{2})C\\
-D & 0 & 0\\
0 & -(i/2\sqrt{2})D & -(i/2\sqrt{2})D\\
0 & -(1/2\sqrt{2})D & (1/2\sqrt{2})D\\
0 & (\sqrt{3}/2\sqrt{2})D & -(\sqrt{3}/2\sqrt{2})D\\
0 & (\sqrt{3}i/2\sqrt{2})D & (\sqrt{3}i/2\sqrt{2})D
\end{bmatrix}. \tag{14b}$$

Since the $M_s=\pm\frac{1}{2}$ components of quartet spin functions cannot be written as single products, it is convenient to perform one additional transformation, so that the ground state is expressed entirely as an expansion on determinants. Let N_s denote a simple product spin function. We have

$$|\Phi_jM_s\rangle=\sum_{N_s}|\Phi_jN_s\rangle D_{N_sM_s}, \tag{15a}$$

$$\mathbf{D}=\begin{array}{cccc|c}
|\frac{3}{2}\rangle & |\frac{1}{2}\rangle & |-\frac{1}{2}\rangle & |-\frac{3}{2}\rangle & \\
1 & 0 & 0 & 0 & \alpha\alpha\alpha\\
0 & 1/\sqrt{3} & 0 & 0 & \alpha\alpha\beta\\
0 & -1/\sqrt{3} & 0 & 0 & \alpha\beta\alpha\\
0 & 1/\sqrt{3} & 0 & 0 & \beta\alpha\alpha\\
0 & 0 & 1/\sqrt{3} & 0 & \alpha\beta\beta\\
0 & 0 & -1/\sqrt{3} & 0 & \beta\alpha\beta\\
0 & 0 & 1/\sqrt{3} & 0 & \beta\beta\alpha\\
0 & 0 & 0 & 1 & \beta\beta\beta
\end{array}. \tag{15b}$$

To relate F^{19} hyperfine tensors of the spin Hamiltonian to the preceding formalism, write

$$\mathcal{H}^{19}\equiv\mathcal{H}_zI_z+\mathcal{H}_xI_x+\mathcal{H}_yI_y \tag{16}$$

and

$$\mathcal{H}_{sp}{}^{HFS}\equiv A_zS_zI_z+A_xS_xI_x+A_yS_yI_y+A_{xy}(S_xI_y+S_yI_x). \tag{17}$$

Then

$$\begin{aligned}
A_z&=2\langle+|\mathcal{H}_z|+\rangle,\\
A_x&=2\,\mathrm{Re}\langle+|\mathcal{H}_x|-\rangle,\\
A_y&=-2\,\mathrm{Im}\langle+|\mathcal{H}_y|-\rangle,\\
A_{xy}&=-\mathrm{Im}\langle+|\mathcal{H}_x|-\rangle+\mathrm{Re}\langle+|\mathcal{H}_y|-\rangle.
\end{aligned} \tag{18}$$

ANALYSIS OF THE OPTICAL SPECTRA AND GYROMAGNETIC TENSOR

Good estimates of B and Dq are available without lengthy calculations from the carefully analyzed spectrum of $KMgF_3$:Co^{++},[8] which has bands quite similar to those of MgF_2:Co^{++}.[5] (Figure 1.) Ferguson *et al.* estimate $B\cong880$ cm^{-1} and $Dq\cong800$ cm^{-1} at 20°K, so that

$$D\cong-0.2887$$

and

$$\mathcal{F}\cong-1.428.$$

Thus, the ground state has about 3% ^4P character, or about 8% t^2e character, and the ^4P mixing decreases the orbital angular momentum about 5%.

The $^4\Gamma_4\leftarrow{}^4\Gamma_5$ fluorescence spectrum of MgF_2:Co^{++} at 20°K provides unusually excellent data for the energies of the ground manifold.[5] (See Table I and Fig. 1.) It consists of a series of sharp (~10 to 25 cm^{-1} wide) lines superposed on a broad band. Six of the strongest lines have been assigned as zero-phonon transitions from a single emitting state. The earlier, less complete far-IR spectrum of CoF_2[4] substantially confirms the assignment made by Johnson *et al.*

We have used iterative least-squares calculations[34] to

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[34] We have prepared a flexible iterative least-squares computer program for arbitrary nonlinear relationships. Where **f** denotes a theoretical relationship between a set of variables **y** and sets of parameters **x** and of constants **c**, that **x** which locally minimizes the difference between the theoretical estimate **y** and an experimental vector **y** is found. The statement of the theory **f** is left as a subroutine to be specified by the user. The program is available from the author. A less complete program has been described by T. H. Brown and R. L. Taylor, J. Chem. Phys. **42**, 3979 (1965).

TABLE I. Ligand-field theory of the $^4\Gamma_4$ optical spectrum and the g tensor.

	Observed[a]	Kamimura[b]	This work (1)	(2)	(3)	(4)
Δ		627	511	511	621	528
Γ		-262	-400	-392	-350	-357
Λ_z		235	223	237	223	246
$\Lambda_z-\frac{1}{2}(\Lambda_x+\Lambda_y)$		0	0	19	0	20.5
$\Lambda_x-\Lambda_y$		0	0	1.3	0	8.5
Wt of g tensor			10^3	10^3	10^5	10^5
Optical levels	1398	1385	1403	1393	1414	1388
	1256	1288	1261	1259	1301	1268
	1091	960	1083	1094	1024	1083
	787	654	786	792	751	768
	152	181	136	142	141	160
g_x	4.240	3.919	4.637	4.228	4.169	4.121
g_y	2.296	2.261	2.261	2.117	2.139	2.144
g_z	6.027	6.157	5.277	5.795	5.744	5.836
a			-0.2953	-0.2864	-0.2796	-0.2982
b			0.3714	0.3407	0.3478	0.3389
c			0.7809	0.8070	0.8121	0.8171
d			-0.0556	-0.0483	-0.0457	-0.0474
e			0.2278	0.2015	0.1985	0.1874
f			0.3318	0.3280	0.3161	0.3019

[a] References 1 and 5.

[b] Reference 13.

fit the ligand-field parameters of $\mathcal{H}_{\text{eff}}$ to the optical energy levels and the principal values of the g tensor.[35] Several series of calculations have been performed (Table I). Although the symmetry of the problem allows the spin-orbit coupling to be anisotropic, adjustment of five free parameters to eight experimental data may be criticized. Therefore in some of the calculations the spin-orbit interaction is constrained to isotropy; these show very good agreement with the experimental data. As measured by the weighted sum of squares of residuals, inclusion of spin-orbit anisotropy is significant, although the indicated anisotropy is a modest 10%. The spin-orbit interaction is very nearly axial, the rhombic distortion being only 1%. The mean value of Λ is unchanged between the various calculations.[36] Since the g tensor is relatively insensitive to the crystal-field parameters, we have calculated fits weighting g by 10^3 and 10^5 relative to the optical levels. As expected, the fit to the g tensor is somewhat better in the latter calculations, and that to the optical levels remains within the experimental uncertainties. The wave-function expansions, to be used in interpreting the shfs, are relatively insensitive to the method of fitting the data.

Kamimura[13] has given ligand-field parameters based on the far-IR spectra.[4] The principal difference between these and the present sets depends on a corrected assignment of the principal axes of the gyromagnetic tensor to directions at the Co site.[1] In Table I we include Kamimura's values, adjusted to the directions determined, and a recalculation of the optical spectrum and gyromagnetic tensor (without the effect of ^4P mixing). The agreement with the lower optical levels, which were not available to Kamimura, is quite poor.

ANALYSIS OF THE F^{19} Hfs

Because of the complicated form of the relationship between the hyperfine interaction and the molecular orbitals, iterative least-squares calculations[34] have been used to fit the linear combination of atomic orbitals coefficients to the spin Hamiltonian. Unfortunately, even the approximate form of the orbitals, Eq. (8), involves more parameters than there are experimental data. Four mixing parameters relate to three principal values of the axial-fluorine hyperfine tensor $\mathbf{A}^{2\mathrm{F}}$, and seven parameters to three diagonal values and one off-diagonal component of the equatorial-fluorine hyperfine tensor, $\mathbf{A}^{4\mathrm{F}}$. It seems reasonable to assume that certain of the covalency parameters are proportional to the corresponding orbital overlap integrals.[37] We take, in the estimation of $\mathbf{A}^{2\mathrm{F}}$,

$$\alpha_x/\alpha_y=\langle x_1|d_{xz}\rangle/\langle y_1|d_{yz}\rangle \tag{19a}$$

and, in that of $\mathbf{A}^{4\mathrm{F}}$,

$$\beta_s/\sigma_s=\langle s_3|d_{z^2}\rangle/\langle s_3|d_{xy}\rangle\ ,\quad \beta_\sigma/\gamma_\sigma=\langle\sigma_3|d_{z^2}\rangle/\langle\sigma_3|d_{xy}\rangle$$

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[35] To ensure that the numbers reported represent a unique solution, we have diagonalized Eq. (4) for many sets (Δ,Γ). Apart from the sixfold multiplicity associated with permutations of the coordinate directions no other solutions were found to fit the optical levels.

[36] The usual spin-orbit parameter $\lambda=\Lambda\mathfrak{F}^{-1}$ is about -157 cm^{-1}. This value is the same as that determined from the high-temperature static susceptibility of KCoF$_3$ (Ref. 7) and somewhat smaller than that estimated from the spectrum of KCoF$_3$ (Ref. 8). It is about 10% reduced from the value -178 cm^{-1} appropriate to the ^4F state of the free ion, and close to the value -152 cm^{-1} for the ^4P state (Ref. 19).

[37] This is probably slightly better than choosing identical mixing coefficients in, for example, ψ_4 and ψ_5, as has been occasionally done, e.g., B. R. McGarvey, J. Chem. Phys. 41, 3743 (1964).

and (19b)

$$\epsilon/\zeta = \langle z_3 | d_{yz} \rangle / \langle z_3 | d_{xz} \rangle .$$

It happens that the contributions of π_3 and z_3 are nearly linearly dependent, so that ζ and ϵ cannot be separately determined. We take

$$\epsilon/\delta = \langle z_3 | d_{yz} \rangle / \langle \pi_3 | d_{x^2-y^2} \rangle . \tag{19c}$$

Estimates of the required radial integrals have been made with the analytic form[18] of Froese's wave functions[38] for the free fluorine ion, as[39]

$$|\psi_{2s}(r=0)|^2 = 9.852 \text{ atomic units (a.u.)}^{-3},$$
$$\langle r^{-3} \rangle_{2p} = 6.632 \text{ (a.u.)}^{-3},$$

as well as these integrals, overlap integrals between Co^{++} d orbitals and the F^- s and p orbitals are required. These are estimated from an analytic Hartree-Fock solution for the ground ^4F state of Co^{++} and the Froese wave functions (see Appendix B).

The fractional orbital occupations, chosen to reduce to the conventional[7] definitions in octahedral symmetry, are, for the axial and equatorial F^{19}'s, respectively,

$$f_{sa} \equiv (\alpha_s^2/N_1) = (0.61 \pm 0.02)\%,$$
$$f_{\sigma a} \equiv (\alpha_\sigma^2/N_1) = (3.9 \pm 0.3)\%,$$
$$f_{\pi a} \equiv (\alpha_y^2/N_4) = (0.9 \pm 0.3)\%,$$
$$f_{se} \equiv (\beta_s^2/N_1) + (\gamma_s^2/N_2) = (0.52 \pm 0.03)\%,$$
$$f_{\sigma e} \equiv (\beta_\sigma^2/N_1) + (\gamma_\sigma^2/N_2) = (4.5 \pm 1)\%,$$
$$f_{\pi e} \equiv (\delta^2/2N_3) + \tfrac{1}{4}(\epsilon/N_4^{1/2} + \zeta/N_5^{1/2})^2 = (0.2 \pm 1)\%.$$

Here the error estimates are derived from the experimental uncertainties in the hyperfine interactions, and do not reflect any of the theoretical approximations. They are particularly large for the equatorial ions because of the errors incurred in separating the x, y, and xy tensor components.[1]

DISCUSSION

The theory for part of the optical spectrum and for the EPR spectrum of Co^{++} in a rhombic environment has been developed and used to interpret the hyperfine structure of F^{19} nuclei of Co^{++}-doped MgF_2. Because of the low site symmetry, the extensive available experimental data permit more stringent tests of some features of the theory than have previously been possible. Several conclusions expressed in prior studies may be shown questionable.

Because the optical spectrum is insensitive to details of the orbitals, this study could be separated into two parts, with a preliminary discussion of the excitation energies and the gyromagnetic tensor. A simplified, three-parameter form of ligand-field theory, omitting perturbations from the $^4\Gamma_5$ manifold and orbital reduction factors, gave a good fit to the five low excited states and the g tensor, but was still significantly improved by a moderate anisotropy of the spin-orbit interaction. The ligand-field parameters do differ considerably from prior estimates.[13]

Tinkham[3] has given simple formulas for the g tensor of rhombic cobalt on the presumption of small perturbations by axial and rhombic fields on the ground state calculated by diagonalization of the spin-orbit interaction. The overlap between this unperturbed state and the ground state (2) of Table I is only 0.875, so that the use of the simple formulas to estimate orbital-reduction factors must be regarded with suspicion.[40] Further, although it is correct to describe the low-lying levels with only two electrostatic parameters, their relationship to quadratic crystal-field potential terms, with quartic omitted,[3] is spurious.

In this paper, orbital reduction factors were not estimated, although they can be calculated directly from the orbitals given. They will be included in more refined calculations, together with the influence of $^4\Gamma_5$ manifold. Then, the final two degrees of freedom of the ligand field will be involved; since several states of $^4\Gamma_5$ are known,[5] experimental data will still exceed parameters.

The excitation energy of the lowest Kramers doublet is about 15% smaller than the estimate used in a recent analysis of the magnetic properties of CoF_2.[12] The revised estimate reduces small discrepancies between experiment and theory. In particular, the estimate of the combined exchange integrals, revised upwards 10% to 33.1 cm^{-1}, is substantially closer to the value required to reproduce the deviation of the mean spin from its value at the absolute zero of temperature. A recalculation of the NMR frequency of Co^{59} as 171 Mc/sec is only 5% less than the value observed by Jaccarino[16]; this is close enough so that the assumption that hyperfine constants for CoF_2 and for Co^{++}-doped ZnF_2 are the same is not seriously jeopardized. Our reassignment of directions of the g tensor with respect to the site axes[1] does not affect any of Lines' results. However, when the more complete theory of the g tensor is available, the spin contributions will be altered, so that further small numerical corrections may be necessary.

Because the p-orbital occupations were estimated from F^{19} hyperfine structure only, they are considerably more precise than estimates which depend on a theory of orbital-reduction factors. Although the mean of the σ and π contributions, about 2.4% for each type of anion, is close to that given for octahedral Co^{++},[7] the present results have the σ bonding significantly larger than the

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[38] C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

[39] These values are recomputed from the functions given by S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963), Eqs. (4.2) and (4.3), but differ by about −8% and +3% from the values quoted by these authors (Ref. 18) and cited in subsequent papers (Refs. 6 and 7).

[40] Also, orbital reductions cannot be reliably estimated in a theory ignoring the ^4P interaction, which itself reduces matrix elements of L by about 5%.

TABLE II. Bonding integrals.

		MgF$_2$:Co^{++} Axial F^{19} (a.u.)$^{-3}$	MgF$_2$:Co^{++} Equatorial F^{19} (a.u.)$^{-3}$	KMgF$_3$:Co^{++} (a.u.)$^{-3}$
s bonding	$f_s\lvert 2s(r=0)\rvert^2$	0.0060±0.0002	0.0051±0.0003	0.0058±0.0003
σ bonding	$f_\sigma\langle r^{-3}\rangle_{2p}$	0.26 ±0.02	0.30 ±0.07	0.26
π bonding	$f_\pi\langle r^{-3}\rangle_{2p}$	0.06 ±0.02	0.02 ±0.06	0.07

π bonding.[41] The p-bonding fractions are roughly proportional to the associated overlap integrals squared:

$$f_{\sigma a}/|\langle\sigma|d_{z^2}\rangle|^2=11\,,\quad f_{\pi a}/|\langle\pi|d_{xy}\rangle|^2=9\,,$$

and

$$f_{\sigma e}/|\langle\sigma|d_{z^2}\;|^2=13\,,\quad f_{\pi e}/|\langle\pi|d_{x^2-y^2}\;|^2=19\,,$$

which confirms that it is better, where not all the parameters can be separately determined, to assume proportionality to overlap integrals than to assume equality. To compare the bonding in KMgF$_3$:Co^{++} with that in MgF$_2$:Co^{++}, we have recomputed the fractions replacing the use of orbital-reduction factors with the assumption that σ and π coefficients in Eq. (8) are proportional to the overlaps and with the revised atomic-orbital integrals.[39] The result

$$f_s=0.59\%\,,\quad f_\sigma=3.9\%\,,\quad \text{and}\quad f_\pi=1.1\%$$

is in essential agreement with the results for rhombic Co^{++} and not outside the confidence limits estimated by Thornley.[7] The σ bonding is now very close to the value estimated by Shulman and Sugano[18] for octahedral Ni^{++}.

The s-orbital occupation decreases about 16% for an increase of bond length of 0.014 Å. This decrease seems rather large compared to the 10% change observed in the isotropic interaction in Mn^{++}, where the bond length changes by 0.03 Å.[17] If a linear relationship between f_s and bond length is assumed, the Co-F distance in KMgF$_3$:Co^{++} may be estimated at about 2.035 Å, which is somewhat larger than on Thornley's estimate.[7] The Co-F spacing in KCoF$_3$ has recently been measured as (2.0345±0.0005) Å at room temperature.[42]

Fractional occupations, f_s, f_σ, and f_π are not a particularly good way to report the analysis of hyperfine interactions, since they depend on details of the atomic orbital basis—details which have no good physical basis and, even within the model employed, are extremely uncertain. Most obvious is that the use of free F$^-$ ion orbitals has no special claim of validity in the crystal environment. If the small effects of overlaps are ignored, the products of the fractional occupations with the corresponding radial integrals, $|2s(r=0)|^2$ and $\langle r^{-3}\rangle_{2p}$, are independent of the atomic orbital basis chosen, and therefore seem more apt descriptives. It should be the object of *ab initio* theories of the electronic structure to reproduce such measures of covalent bonding, rather than the fractional occupations, which have a built-in theoretical bias. In these terms, our results are listed in Table II.

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APPENDIX A

To facilitate comparison of the present formalism with crystal-field descriptions previously used,[3] we relate the parameters of Eq. (2) to the matrix of the effective ligand potential on the one-electron basis Eq. (8). In terms of the cubic ($10Dq$), tetragonal (τ_1,τ_2), and rhombic (ρ_1,ρ_2) parts of the potential, the matrix is

$$\begin{bmatrix} 6Dq+\frac{1}{2}\tau_2 & \frac{1}{2}\rho_2 & 0 & 0 & 0 \\ \frac{1}{2}\rho_2 & 6Dq-\frac{1}{2}\tau_2 & 0 & 0 & 0 \\ 0 & 0 & -4Dq-\frac{1}{3}\tau_1-\frac{1}{2}\rho_1 & 0 & 0 \\ 0 & 0 & 0 & -4Dq+\frac{1}{3}\tau_1+\frac{1}{2}\rho_1 & 0 \\ 0 & 0 & 0 & 0 & -4Dq-\frac{2}{3}\tau_1 \end{bmatrix}. \tag{A1}$$

If the simple crystal-field model is adopted, the parameters of Eq. (A1) are related to integrals of d electron on

$$V=\sum A_l{}^m r^l Y_l{}^m(\theta,\phi) \tag{A2}$$

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[41] K. Hirakawa, J. Phys. Soc. Japan **19**, 1678 (1964), estimates from F^{19} NMR measurements in KCoF$_3$ that $f_\sigma-f_\pi=(5.7\pm0.3)\%$. Although the difference seems large, his work supports our evidence that σ bonding exceeds π bonding significantly.

[42] A. Okazaki and Y. Suemune, J. Phys. Soc. Japan **16**, 671 (1961).

by

$$Dq=\frac{1}{36}\left(\frac{9}{4\pi}\right)^{1/2}\left[A_4{}^0\langle r^4\rangle+\left(\frac{10}{7}\right)^{1/2}A_4{}^4\langle r^4\rangle\right],$$

$$\begin{aligned}\tau_1&=\frac{3}{7}\left(\frac{5}{4\pi}\right)^{1/2}A_2{}^0\langle r^2\rangle-\frac{5}{21}\left(\frac{9}{4\pi}\right)^{1/2}A_4{}^0\langle r^4\rangle\\&\qquad+\frac{1}{3}\left(\frac{10}{7}\times\frac{9}{4\pi}\right)^{1/2}A_4{}^4\langle r^4\rangle,\\ \tau_2&=\frac{4}{7}\left(\frac{5}{4\pi}\right)^{1/2}A_2{}^0\langle r^2\rangle+\frac{1}{3}\left(\frac{9}{4\pi}\right)^{1/2}A_4{}^0\langle r^4\rangle\\&\qquad-\frac{1}{3}\left(\frac{10}{7}\times\frac{9}{4\pi}\right)^{1/2}A_4{}^4\langle r^4\rangle,\\ \rho_1&=\frac{2(6)^{1/2}}{7}\left(\frac{5}{4\pi}\right)^{1/2}A_2{}^2\langle r^2\rangle+\frac{4}{7}\left(\frac{10}{3}\times\frac{9}{4\pi}\right)^{1/2}A_4{}^2\langle r^4\rangle,\\ \rho_2&=-\frac{8\sqrt{2}}{7}\left(\frac{5}{4\pi}\right)^{1/2}A_2{}^2\langle r^2\rangle+\frac{4}{7}\left(30\times\frac{9}{4\pi}\right)^{1/2}A_4{}^2\langle r^4\rangle.\end{aligned}\tag{A3}$$

The parameters of the effective Hamiltonian are related to the one-electron elements by

$$\begin{aligned}\Delta&=C^2\tau_1-D^2(\tau_1+\tfrac{1}{4}\tau_2),\\ \Gamma&=-\tfrac{1}{2}C^2\rho_1+\tfrac{1}{2}D^2(\rho_1+\tfrac{1}{2}\sqrt{3}\rho_2).\end{aligned}\tag{A4}$$

Thus, although only two parameters are involved in the description of the ground manifold, they do include quartic as well as quadratic contributions.

APPENDIX B

To estimate the necessary overlap integrals, we have made a matrix Hartree-Fock calculation for the $(1s^22s^22p^63s^23p^63d^7)^4F$ state of Co^{++} with the Chicago self-consistent-field (SCF) program supplied by Professor C. C. J. Roothaan (Table III). The energy for the optimized "double ζ" basis set,[43] −1380.497 a.u. compares favorably with −1380.599 calculated with a more extensive basis.[44] The overlap integrals, collected in Table IV with sundry other constants, were calculated with the Corbato-Switendick program.[45] Corresponding quantities for octahedral $CoF_6{}^{4-}$ are included.

TABLE III. SCF calculation of $Co^{++}(^4F)$.

Basis functions (principal quantum numbers, orbital exponents)

s	p	d
1 23.78200	2 10.99710	3 2.77397
1 29.68650	2 20.29760	3 6.40638
2 10.95270	3 6.45680	
2 16.54220	3 3.97720	
3 4.17306		
3 6.04395		

Orbital energies and eigenvectors

$1s$	$2s$	$3s$	$2p$	$3p$	$3d$
−283.71515	−35.50732	−5.17492	−30.76296	−3.66428	−1.32788
0.55219	−0.46748	0.13803	0.91126	−0.38110	0.71308
0.45546	0.07641	−0.00205	0.07506	−0.01494	0.41074
0.00376	1.18925	−0.67281	0.05579	0.29138	
−0.00729	−0.11716	0.15286	−0.01250	0.81506	
0.00040	−0.00730	0.70166			
−0.00090	0.03193	0.45125			

TABLE IV. Parameters used in the hyperfine calculation.

	MgF_2:Co^{++}	$KMgF_3$:Co^{++}
R_a	2.032±0.013 Å[a]	2.02[b]
R_b	2.046±0.009 Å	
ω	50.7°	
T	74.316 Mc/sec $(Å)^3$	
$\langle s_1\|d_{z^2}\rangle$	0.03710	0.03829
$\langle \sigma_1\|d_{z^2}\rangle$	0.05998	0.06096
$\langle x_1\|d_{xy}\rangle$	0.03137	0.03128
$\langle y_1\|d_{yz}\rangle$	0.03137	0.03128
$\langle s_3\|d_{z^2}\rangle$	−0.01788	
$\langle s_3\|d_{xy}\rangle$	0.03030	
$\langle \sigma_3\|d_{z^2}\rangle$	−0.02943	
$\langle \sigma_3\|d_{xy}\rangle$	0.04986	
$\langle z_3\|d_{xz}\rangle$	0.01916	
$\langle z_3\|d_{yz}\rangle$	0.02367	
$\langle \pi_3\|d_{x^2-y^2}\rangle$	0.02979	

[a] W. H. Baur, Acta Cryst. **9**, 515 (1956); **11**, 488 (1958). These values are for CoF_2, which seem more appropriate than the lattice parameters of MgF_2.

[b] Value assumed in Ref. 7.

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[43] E. Clementi, J. Chem. Phys. **40**, 1944 (1964).

[44] E. Clementi, IBM J. Res. Develop. **9**, 2 (1965).

[45] F. J. Corbato and A. C. Switendick, Quantum Chemistry Program Exchange, No. 29A (unpublished).