

tions allowed and not experimentally observed [not shown in Figs. 2(b) and 2(c)] may be too weak to be recorded on the spectrograms.<sup>7</sup>

### CONCLUSIONS

Spectrum II of  $\text{Sm}^{3+}$  in  $\text{CaF}_2$  originates from transitions between the crystal-field-split levels of the  $^4F_{5/2}$

some component irreducible representation of  $\psi_A$  which is the same as at least one component irreducible representation of  $\psi_C$ . In practice, all the above (including decomposition of  $\psi_A$  and  $\psi_C$  into component irreducible representations) is done using the table of characters of the particular symmetry group.

<sup>7</sup> Also, there may be masking of such lines expected (in Fig. 2) by the background of light in certain regions on the spectrograms, e.g.,  $18\,599 \rightarrow 2228\text{ cm}^{-1}$  and  $18\,259 \rightarrow 2599\text{ cm}^{-1}$  transitions in Subgroup B, are in such background regions of the Spectrum I spectrograms.

state and those of the  $^6H_{5/2}$ ,  $^6H_{7/2}$ , and  $^6H_{9/2}$  states of the free ion. Spectrum I originates from transitions between the crystal-field-split levels of the second, and possibly the third, highest free-ion fluorescent state and those of the ground multiplet ( $^6H$ ) states.

The energies of crystal field split levels of the fluorescent states from which Spectra I and II originate are determined uniquely (to within  $5\text{ cm}^{-1}$ ) by the observed fluorescent frequencies.

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## Covalency Effects in $\text{KNiF}_3$ . I. Nuclear Magnetic Resonance Studies

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A nuclear magnetic resonance study of the  $F^{19}$  resonance in a single crystal of  $\text{KNiF}_3$  is reported. The internal fields at the fluorine nuclei were measured. Interpretation of the measured fields showed that the spin densities in the fluorine  $2s$  and  $2p\sigma$  orbitals were  $(0.538 \pm 0.05)\%$  and  $(3.78 \pm 0.2)\%$ , respectively. A comparison with the  $\text{KMnF}_3$  measurements, where  $p\pi$  interactions are allowed, indicated the importance of  $p\pi$  bonding in these crystals. It is shown that only a model which allows the  $2s$ ,  $2p\sigma$ , and  $2p\pi$  electrons individual degrees of covalency can explain the observations.

### I. INTRODUCTION

IT is the purpose of this series of papers to present a detailed study of  $d$ -electron covalency in a specific example, i.e., a  $\text{KNiF}_3$  crystal. For this purpose, we have studied experimentally the nuclear magnetic resonance (NMR) of the fluorine and the optical spectrum. The former experiment measures the covalency directly, while the latter determines parameters such as the cubic crystal field splitting which depend upon the covalency. These two experimental studies shall be presented in parts I and II of this series. In part III, a theoretical calculation will be made of the observed quantities such as the NMR frequency shift and the cubic field splitting parameter. The theory is based on the molecular orbital (MO) model of Van Vleck,<sup>1</sup> and will be shown to be very successful.

Previous<sup>2</sup> nuclear magnetic resonance studies of the

fluorine nuclei in magnetic crystals have shown the presence of large internal magnetic fields at the fluorine nuclei. These fields arise mainly from hyperfine interactions with the unpaired electrons, and they have been interpreted so as to give information about the wave functions of the unpaired electrons. The isotropic hyperfine fields have determined the spin density in the fluoride ion's  $2s$  orbitals and the anisotropic hyperfine fields the spin density in the  $2p$  orbitals. For some crystals it was difficult to understand the anisotropy because it was sometimes not possible to assign the unpaired  $3d$  electrons to meaningful spatial orbitals, while in other cases it was not possible to distinguish between the contributions of  $p\sigma$  and  $p\pi$  electrons. By  $p\sigma$  electrons we mean those in the  $\sigma$  bond having no angular momentum about the internuclear radius, while the  $p\pi$  electrons are in  $\pi$  bonds which do have angular momentum about this axis. It is the purpose of this paper to explain how the measurements in  $\text{KNiF}_3$  remove these difficulties and allow an unambiguous determination of the

<sup>1</sup> J. H. Van Vleck, *J. Chem. Phys.* **3**, 803, 807 (1935).

<sup>2</sup> R. G. Shulman, *Phys. Rev.* **121**, 125 (1961); R. G. Shulman and K. Knox, *ibid.* **119**, 94 (1960).

*p*-electron bonding. We shall also refer to our previous results on K<sub>2</sub>NaCrF<sub>6</sub> which complement the KNiF<sub>3</sub> results. Since the experimental results are unambiguous it is possible to use them to describe the electronic wave functions in the crystal. It will be shown that the LCAO (linear combination of atomic orbitals) molecular orbital description is particularly suitable to describe the electrons. Recent attempts to describe these hyperfine interactions as arising from orthogonalized atomic orbitals or exchange polarization are shown to be inadequate. In order to obtain the best value of the wave function, all refinements of the theory recently proposed have been included and are discussed in detail.

## II. MOLECULAR ORBITAL DESCRIPTION

Before describing the NMR experiment, it is convenient to present molecular orbitals which are used in the later discussion. A general discussion of the theoretical principle involved in the molecular orbital (MO) method is given in Van Vleck's<sup>1</sup> papers. Although his discussion is confined to the case of strong bonding, Fe(CN)<sub>6</sub><sup>3-</sup>, the principle is also applicable to the case of weak bonding.

For *d* electrons in a cubic environment, the molecular orbitals of interest are two antibonding MO's expressed as follows:

$$\begin{aligned}\Psi_e^a &= N_e^{-1/2}(\varphi_e - \lambda_s \chi_s - \lambda_\sigma \chi_\sigma), \\ \Psi_t^a &= N_t^{-1/2}(\varphi_t - \lambda_\pi \chi_\pi),\end{aligned}\quad (2.1)$$

where  $\varphi$ 's are atomic *d* functions with the appropriate symmetry denoted by subscripts, and  $\chi$ 's are appropriate linear combinations of the ligand atomic orbitals whose symmetry is designated by the subscript. Subscripts *t* and *e* are the abbreviation of *t<sub>2g</sub>* and *e<sub>g</sub>* which are Mulliken's notation for the irreducible representation of a cubic group, and  $\sigma$  and  $\pi$  mean *p $\sigma$*  and *p $\pi$* , respectively. Both  $\varphi$ 's and  $\chi$ 's are normalized, so that the normalization factors,  $N_e$  and  $N_t$ , are

$$\begin{aligned}N_e &= 1 - 2\lambda_s S_s - 2\lambda_\sigma S_\sigma + \lambda_s^2 + \lambda_\sigma^2, \\ N_t &= 1 - 2\lambda_\pi S_\pi + \lambda_\pi^2,\end{aligned}\quad (2.2)$$

where the *S*'s are overlap integrals between  $\varphi$ 's and  $\chi$ 's. As is well known, the *e* and *t* orbitals are doubly and triply degenerate, respectively. In order to denote the degenerate components, we have added the subscript  $\gamma$  to the expressions in (2.1). When  $\gamma$ 's are written as *u* and *v* for *e* and  $\xi$ ,  $\eta$ , and  $\zeta$  for *t*, it is no longer necessary to use *e* and *t* besides  $\gamma$ . Therefore,  $\varphi_\gamma$  is often used in place of  $\varphi_e$  or  $\varphi_t$ , and  $\chi$ 's are written as  $\chi_{\gamma k}$  ( $k=s, \sigma$ , and  $\pi$ ). Normalization factors  $N$ 's are independent of  $\gamma$ , so that they always have subscripts *e* and *t* only.

Explicit forms of  $\varphi$ 's are given as follows:

$$\begin{aligned}\varphi_u &= Y(20)R, & (3z^2 - r^2); \\ \varphi_v &= (1/\sqrt{2})[Y(22) + Y(2-2)]R, & (x^2 - y^2); \\ \varphi_\xi &= (i/\sqrt{2})[Y(21) + Y(2-1)]R, & (yz); \\ \varphi_\eta &= (-1/\sqrt{2})[Y(21) - Y(2-1)]R, & (zx); \\ \varphi_\zeta &= (-i/\sqrt{2})[Y(22) - Y(2-2)]R, & (xy);\end{aligned}\quad (2.3)$$

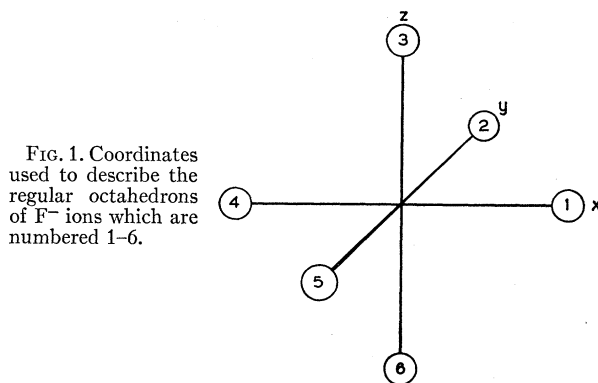


FIG. 1. Coordinates used to describe the regular octahedrons of F<sup>-</sup> ions which are numbered 1-6.

where  $Y(lm)$  is a spherical harmonic defined as  $Y(lm) = \Theta(lm)\Phi(m)$  in Condon and Shortley<sup>3</sup> and  $R$  is the normalized radial part of the *d*-wave functions. All  $\varphi$ 's are taken to be real and proportional to the expressions in brackets.

Explicit forms of the  $\chi$ 's are given by

$$\begin{aligned}\chi_{uk} &= [1/(12)^{1/2}](2\varphi_{3,k} + 2\varphi_{6,k} - \varphi_{1,k} - \varphi_{4,k} - \varphi_{2,k} - \varphi_{5,k}), \\ \chi_{vk} &= \frac{1}{2}(\varphi_{1,k} + \varphi_{4,k} - \varphi_{2,k} - \varphi_{5,k}), \quad (k=s \text{ and } \sigma) \\ \chi_{\xi\pi} &= \frac{1}{2}(\varphi_{3,y} - \varphi_{6,y} + \varphi_{2,z} - \varphi_{5,z}), \\ \chi_{\eta\pi} &= \frac{1}{2}(\varphi_{1,z} - \varphi_{4,z} + \varphi_{3,x} - \varphi_{6,x}), \\ \chi_{\zeta\pi} &= \frac{1}{2}(\varphi_{1,y} - \varphi_{4,y} + \varphi_{2,x} - \varphi_{5,x}),\end{aligned}\quad (2.4)$$

where subscript *i* of the  $\varphi_{i,k}$  ligand atomic orbital denotes the ligand position whose numbering is shown in Fig. 1. Subscripts *x*, *y*, and *z* mean that the functions are the *p $\pi$*  orbitals stretched along the *x*, *y*, and *z* axes, respectively, and the  $\sigma$  function is the *p $\sigma$*  orbital always directed towards the origin.

The bonding orbitals which are orthogonal to the antibonding molecular orbitals in (2.1) are

$$\begin{aligned}\Psi_{es}^b &= N_e'^{-1/2}(\chi_s + \gamma_s \varphi_e + \gamma_{s\sigma} \chi_\sigma), \\ \Psi_{e\sigma}^b &= N_e''^{-1/2}(\chi_\sigma + \gamma_\sigma \varphi_e + \gamma_{s\sigma} \chi_s), \\ \Psi_t^b &= N_t'^{-1/2}(\chi_\pi + \gamma_\pi \varphi_t).\end{aligned}\quad (2.5)$$

These have predominantly the nature of ligand orbitals in so-called ionic crystals. Assuming that  $\lambda$ ,  $\gamma$ , and *S* are small quantities of the order of  $\epsilon$  ( $\epsilon \ll 1$ ) and neglecting small quantities of higher order, we obtain the relations<sup>4</sup>

$$\begin{aligned}\lambda_s &= \gamma_s + S_s, \\ \lambda_\sigma &= \gamma_\sigma + S_\sigma, \\ \lambda_\pi &= \gamma_\pi + S_\pi,\end{aligned}\quad (2.6)$$

from the orthogonalities

$$(\Psi_e^a | \Psi_{es}^b) = (\Psi_e^a | \Psi_{e\sigma}^b) = (\Psi_t^a | \Psi_t^b) = 0. \quad (2.7)$$

<sup>3</sup> E. U. Condon and G. H. Shortley *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953).

<sup>4</sup> R. G. Shulman, *Magnetic Properties of Metals and Alloys* (American Society for Metals, Cleveland, Ohio, 1959), p. 56.

From another orthogonality relation

$$(\Psi_{es}^b | \Psi_{e\sigma}^b) = 0, \quad (2.8)$$

it is seen that

$$\gamma_{s\sigma} + \gamma_{\sigma s} = -(\lambda_s \lambda_\sigma - S_s S_\sigma) = O(\epsilon^2). \quad (2.9)$$

Therefore, in our approximation, we have

$$\gamma_{s\sigma} = -\gamma_{\sigma s}. \quad (2.10)$$

Let  $\gamma$  be a measure of covalency. Then, in purely ionic crystals where

$$\gamma_s = \gamma_\sigma = \gamma_\pi = 0, \quad (2.11)$$

we have

$$\lambda_s = S_s, \quad \lambda_\sigma = S_\sigma, \quad \lambda_\pi = S_\pi, \quad (2.12)$$

and

$$\gamma_{s\sigma} = \gamma_{\sigma s} = 0. \quad (2.13)$$

The  $\Psi^b$ 's constructed under the conditions of (2.12) are  $d$ -wave functions of the central metal ion orthogonalized to the ligand orbitals, and are a quantum-mechanical description of a purely ionic crystal.

Further theoretical discussions of the molecular orbitals shall be given in part III of this series.

### III. NMR EXPERIMENTS

The cubic perovskite crystal  $\text{KNiF}_3$  has offered unusual opportunities for exact measurements. Much of the ease of interpreting the measurements on the crystal arises from the high symmetry—both of the crystal and of the  $d$  orbitals of the  $\text{Ni}^{++}$  ion. The cubic perovskite crystal structure is illustrated in Fig. 2. A  $\text{Ni}^{++}$  ion is located at the body-centered position of the cubic cell while six  $\text{F}^-$  ions, located at the face-centered positions, form a regular octahedron around the  $\text{Ni}^{++}$  ion. Potassium ions are found at the corners. The edge of the cell<sup>5</sup> is 4.014 Å at 298°K and this determines all

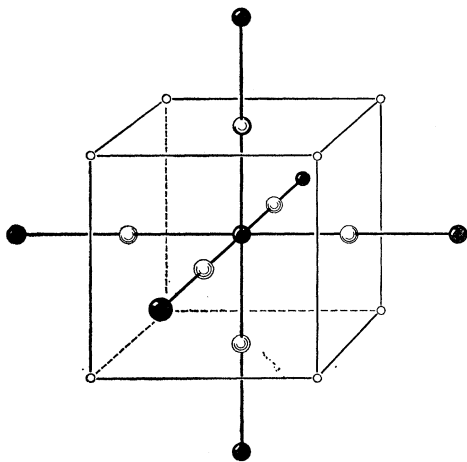


FIG. 2. Crystal structure of cubic perovskite  $\text{KNiF}_3$ .

the distances in the crystal. While each  $\text{Ni}^{++}$  has six  $\text{F}^-$  as nearest neighbors, each  $\text{F}^-$  ion is colinear with its two nearest-neighbor  $\text{Ni}^{++}$  ions.

### A. Experimental Results

The NMR measurements in the paramagnetic state on  $\text{KNiF}_3$  are very similar to those reported on the isomorphous crystal of  $\text{KMnF}_3$ . A single crystal of  $\text{KNiF}_3$  was rounded to a somewhat elliptical shape, two of whose principal axes were  $\sim 1$  cm and the third axis was  $\sim 0.5$  cm. This was mounted on the end of a glass rod with silica cement with the  $[110]$  direction parallel to the rod axis. The crystal was inserted into a Varian Associates V-4311 fixed frequency induction spectrometer operating at 60,000 Mc/sec. Two resonances were observed<sup>6</sup> and the external fields  $H_0$  required for resonance at room temperature as a function of the angle between  $H_0$  and the  $[001]$  direction are shown in Fig. 3(b). In Fig. 3(a) we have shown for comparison the same measurements made on  $\text{KMnF}_3$ . In both cases the experimental points are shown as open circles connected by a smooth solid line. The resonances are all shifted from the undisplaced field of  $\omega/\gamma = 14,979.4$  G. Both crystals exhibit isotropic and anisotropic shifts. The dashed lines describe the dipole sum over all  $i$  magnetic ions of  $\sum_i (\langle \mu_i \rangle / r_i^3) (3 \cos^2 \theta_i - 1)$  in which  $\langle \mu_i \rangle$  is the expectation value of the electronic moment at distance  $r_i$  from the fluorine site while  $\theta_i$  is the angle between  $r_i$  and  $H_0$ . The important point is that whereas the dipole sum accounts for nearly all of the anisotropy observed in the manganese compound, it does *not* account for the anisotropy in  $\text{KNiF}_3$ . As has been pointed out previously, the reason for this<sup>2,7</sup> and, in fact, the reason for doing this experiment is that the NMR measurement is only sensitive to the difference of occupancy of the  $p\sigma$  and  $p\pi$  orbitals by unpaired electrons:  $\text{Mn}^{++}$  with its  $3d^5$  configuration has unpaired spins in both  $e_g$  and  $t_{2g}$  orbitals which can mix with fluorine  $p\sigma$  and  $p\pi$  orbitals, respectively. However, the ground-state configuration of  $\text{Ni}^{++}$ ,  $t_{2g}^6 e_g^2$ , only has unpaired spins in the  $e_g$  orbitals which can only bond with the  $p\sigma$  orbitals of the fluorine. Therefore, in  $\text{Ni}^{++}$ , we can measure the absolute occupancy of the  $p\sigma$  orbital by unpaired electrons. In Fig. 3(c) we present similar measurements on  $\text{K}_2\text{NaCrF}_6$  where the large isotropic shift is missing because of the absence of electrons in the  $e_g$  antibonding orbitals. Furthermore, the large amount of  $p\pi$  bonding<sup>6</sup> is shown by the anisotropy being out of phase with the dipole sum.

### B. Calculation of Hyperfine Interactions

The geometrical relation between the hyperfine interactions and the measured NMR shifts derived<sup>2</sup>

<sup>5</sup> A. Okazaki and Y. Suemone, J. Phys. Soc. Japan 16, 671 (1961).

<sup>6</sup> R. G. Shulman and K. Knox, Phys. Rev. Letters 4, 603 (1960).

<sup>7</sup> M. Tinkham, Proc. Roy. Soc. (London) A236, 535 (1956).

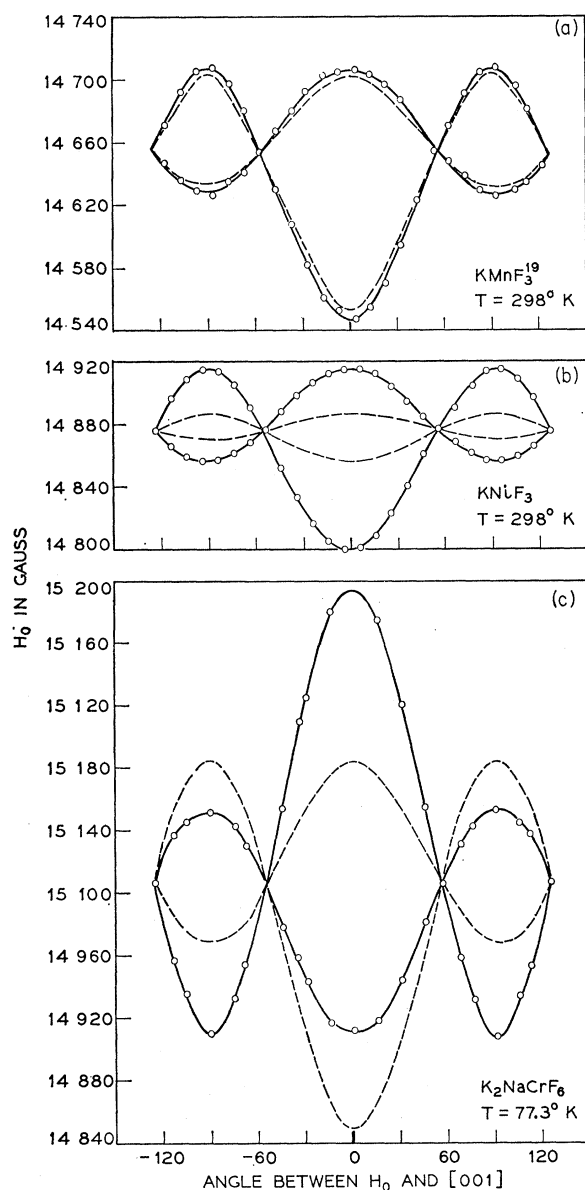


FIG. 3. (a) Resonance field for  $\text{F}^{19}$  in  $\text{KMnF}_3$  as a function of angle between  $H_0$  and  $[001]$  as  $H_0$  is rotated in  $(110)$  plane. The dipole sum, indicated by the dashed line, was performed on an IBM 704, and is seen to account for most of the observed anisotropy. For all three compounds the measurements were made at 60,000 Mc/sec; consequently, the undisplaced fluorine resonance field should be 14 979.4 G. (b) Measurements made under identical conditions on  $\text{KNiF}_3$ . Notice that since the  $p\pi$  interaction is forbidden, the  $p\sigma$  interaction accounts for most of the observed anisotropy. (c) Similar measurements made at 77.3°K for  $\text{K}_2\text{NaCrF}_6$ . Notice that the measurements are out of phase with the dipole sum as expected for  $p\pi$  interactions.

for  $\text{KMnF}_3$  is equally valid for  $\text{KNiF}_3$ . We write the measured NMR shifts in terms of  $\alpha$  where

$$h\nu = g_N \beta_N H_0 (1 + \alpha), \quad (3.1)$$

and  $g_N$  is the nuclear  $g$  factor and  $\beta_N$  the nuclear magneton. By changing the  $\text{KMnF}_3$  expression so as to

eliminate the orbital contributions to the susceptibility<sup>2</sup> we have

$$g_N \beta_N \left( \alpha_{\perp} - \frac{H_{\perp}^D}{H_0} \right) H_0 = \left( \frac{\chi_m - N\beta^2 \Delta g / \lambda}{N g \beta} \right) \times [2A_s - 2(A_\sigma - A_\pi)], \quad (3.2)$$

and

$$g_N \beta_N \left( \alpha_{\parallel} - \frac{H_{\parallel}^D}{H_0} \right) H_0 = \left( \frac{\chi_m - N\beta^2 \Delta g / \lambda}{N g \beta} \right) \times [2A_s + 4(A_\sigma - A_\pi)], \quad (3.3)$$

where  $\perp$  and  $\parallel$  refer to the orientation between  $H_0$  and the radius between the fluorine nucleus and its neighboring nickel;  $H^D$  is the dipole sum;  $\chi_m$  is the molar susceptibility;  $N$  is Avogadro's number;  $g$  is the electronic  $g$  factor;  $\Delta g$  is its deviation from the spin-only value, 2.0023;  $\beta$  is the Bohr magneton;  $A_s$  is the isotropic hyperfine interaction; and  $(A_\sigma - A_\pi)$  is the difference between the hyperfine interactions of electrons in the  $\sigma$  bond and those in the  $\pi$  bonds. As discussed above, one advantage of making these measurements in a nickel salt in a cubic environment is that  $A_\pi$  is zero.

Since our preliminary report,<sup>6</sup> accurate values of the susceptibility have been published<sup>8</sup> which differ from the estimates we made. We shall use the following numerical values to interpret the 300°K NMR data:  $\chi_m = 2.027 \times 10^{-3}$  from the measurements of Hirakawa *et al.*<sup>8</sup>;  $g = 2.28$  from a measurement<sup>9</sup> by Walsh on  $\text{KMgF}_3$ ; 0.1%  $\text{Ni}^{++}$ . The value of  $\lambda$  which is the spin-orbit interaction was derived from the expression for the  $g$  factor of

$$g = 2.0023 - 8\lambda / 10Dq, \quad (3.4)$$

in which we used the value of 7250  $\text{cm}^{-1}$  for  $10Dq$ , the cubic crystal field parameter, taken from the measurements presented in the following paper.<sup>10</sup> From Eq. (3.4) we concluded that  $\lambda = 250 \text{ cm}^{-1}$ . The value of the dipole sum  $H^D = \sum_i \langle \mu_i \rangle / r_i^3 (3 \cos^2 \theta_i - 1)$  was calculated on an IBM 7090 on the assumption that all of the magnetic moment of a site  $i$  was concentrated at the nickel nucleus. Under this assumption the values obtained were

$$H_{\parallel}^D / H_0 = 1.5686 \times 10^{-3} = -2H_{\perp}^D / H_0. \quad (3.5)$$

Marshall and Stewart<sup>11</sup> have shown that a correction must be applied to the nearest-neighbor  $\text{Ni}^{++}$  ions contribution to this dipole sum because of the cubic rather than spherical nature of the ions. This correction

<sup>8</sup> K. Hirakawa, K. Hirakawa, and T. Hashimoto, J. Phys. Soc. Japan 15, 2063 (1960).

<sup>9</sup> W. M. Walsh, Jr. (private communication).

<sup>10</sup> K. Knox, R. G. Shulman, and S. Sugano, following paper [Phys. Rev. 130, 512 (1963)].

<sup>11</sup> W. Marshall and R. Stuart, Phys. Rev. 123, 2048 (1961); and W. Marshall (private communication).

is that for the nearest neighbor instead of  $\langle\mu\rangle/\rho^3$  one should use  $(\langle\mu\rangle/\rho^3)[1+\frac{5}{2}\langle r^4\rangle_{Ni}/4]$  in which  $\rho$  is the  $Ni^{++}$ -F<sup>-</sup> distance and  $\langle r^4\rangle_{Ni}$  is the average of  $r^4$  over the nickel 3*d* function. This average was taken over Watson's<sup>12</sup> Hartree-Fock function which is given in a following paper<sup>13</sup> and we obtained  $\frac{5}{2}\langle r^4\rangle_{Ni}/4=0.036$ . This correction applied to the dipole sums (because almost all of the dipole sum comes from the nearest neighbors) yields

$$H_{11}^D/H_0=1.625\times 10^{-3}=-2H_{11}^D/H_0. \quad (3.6)$$

The measured values of the NMR shifts were

$$\alpha_{11}=1.214\times 10^{-2}, \quad \alpha_1=0.430\times 10^{-2}. \quad (3.7)$$

With these numerical values we can solve Eqs. (3.2) and (3.3) for the experimental values of the hyperfine interaction. These are

$$\begin{aligned} A_s &= 33.9\times 10^{-4} \text{ cm}^{-1}, \\ A_\sigma - A_\pi &= 8.8\times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (3.8)$$

There are additional corrections which must be made to these calculated values. Marshall<sup>11</sup> has shown that, when you take into account higher order terms such as the orbital unquenching on the fluorine, the modification of the F<sup>-</sup> spin term by spin-orbit coupling and the orbital contribution from the  $Ni^{++}$ , it is necessary to replace  $A_\sigma$  by

$$A_\sigma \left[ 1 + \frac{g-2}{\sqrt{3}} \left( \frac{A_\pi}{A_\sigma} \right)^{1/2} \right]. \quad (3.9)$$

We have in the calculation of 10 *Dq* also calculated<sup>13</sup> a value for  $A_\pi$  (really  $\lambda_\pi$ ) for a particular value of  $A_\sigma$ . This relation is

$$(A_\pi/A_\sigma)^{1/2}=0.55. \quad (3.10)$$

By substituting this value into the revised expression for  $A_\sigma$  we find that

$$\begin{aligned} A_s &= 33.9\times 10^{-4} \text{ cm}^{-1}, \\ A_\sigma &= 8.10\times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (3.11)$$

In order to convert these hyperfine interactions to the spin densities  $f_s$  and  $f_\sigma$  in the F<sup>-</sup> 2*s* and 2*pσ* orbitals, we shall use the hyperfine interactions calculated from Froese's<sup>14</sup> Hartree-Fock function for F<sup>-</sup>. These are

$$\begin{aligned} A_{2s} &= \frac{8}{3}\pi^2\mu_B\gamma_N\hbar|\varphi_{2s}(0)|^2=1.503 \text{ cm}^{-1}, \\ A_{2p} &= \frac{2}{5}\pi^2\mu_B\gamma_N\hbar\langle 1/r^3 \rangle_{2p}=0.0429 \text{ cm}^{-1}, \end{aligned} \quad (3.12)$$

which differ by a few percent from the previous values<sup>2</sup> which we have used. By using the relations given formerly we have the following values for  $f_s$  and  $f_\sigma$ , the fractional occupancy by unpaired spins of the 2*s* and

2*pσ* orbitals:

$$\begin{aligned} f_s &= 2SA_s/A_{2s}=0.451\%, \\ f_\sigma &= 2SA_\sigma/A_{2p}=3.78\%. \end{aligned} \quad (3.13)$$

As a final correction we apply the effects of the 1*s*-2*s* cross term<sup>11,15</sup> to the isotropic interaction which becomes

$$\begin{aligned} f_s &= (0.538\pm 0.05)\%, \\ f_\sigma &= (3.78\pm 0.2)\%. \end{aligned} \quad (3.14)$$

#### IV. DISCUSSION

We can recapitulate the results of these measurements on KNiF<sub>3</sub> by using the molecular orbitals presented in the previous section. The bonding orbitals in (2.5) are completely filled by 14 electrons. In cubic fields, the *t*<sub>2*g*</sub> antibonding orbital is lower than the *e*<sub>g</sub> in energy. Therefore, in the ground state of Ni<sup>2+</sup>, the  $\Psi_t^a$  antibonding orbitals are also filled, and the remaining two electrons are accommodated in the  $\Psi_e^a$  orbitals. In this event, the spin densities,  $f_s$  and  $f_\sigma$ , are related to  $\lambda_s$  and  $\lambda_\sigma$  in (2.1) as follows:

$$f_s=\lambda_s^2/3N_e, \quad f_\sigma=\lambda_\sigma^2/3N_e, \quad (4.1)$$

and similarly in the case where  $f_\pi$  is observable,

$$f_\pi=\lambda_\pi^2/4N_t. \quad (4.2)$$

In deriving (4.1) and (4.2), the explicit forms of  $\chi$ 's given in (2.4) are used. Then, by using (3.13), we obtain

$$N_e^{-1/2}\lambda_s=0.116, \quad N_e^{-1/2}\lambda_\sigma=0.337. \quad (4.3)$$

The bonding parameters obtained in the series of iron-group fluorides should be revised slightly in accordance with the values of the hyperfine interaction given in Eq. (3.12). In addition, the small changes arising from the 1*s*-2*s* cross term should be included. However, until the higher order changes in the anisotropic hfs are calculated for all of the metal ions studied, these revised values will not be published. Considering these results in conjunction with previously tabulated values, three points stand out very clearly:

1. The small value of  $f_\sigma - f_\pi$  measured in both KMnF<sub>3</sub> and MnF<sub>2</sub> is caused by a cancellation of the *pσ* bonding by a large amount of *pπ* bonding.
2. The large amount of *pπ* bonding is shown even more directly in the K<sub>2</sub>NaCrF<sub>6</sub> results where Cr<sup>3+</sup> can only form *pπ* bonds in the one-electron ground state.
3. The large amount of *pσ* bonding is determined in KNiF<sub>3</sub>.

Before proceeding with the molecular orbitals thus determined, it is important to consider two alternative interpretations of the measured F<sup>19</sup> hyperfine interactions which have been presented. The alternative interpretations have not followed the molecular orbital approach which we have used for KNiF<sub>3</sub> and in our

<sup>12</sup> R. E. Watson, Phys. Rev. **119**, 1934 (1960); and Technical Report No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology (unpublished).

<sup>13</sup> S. Sugano and R. G. Shulman, this issue [Phys. Rev. **130**, 517 (1963)].

<sup>14</sup> C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

<sup>15</sup> A. J. Freeman and R. E. Watson, Phys. Rev. Letters **6**, 343 (1961).

previous reports. We propose to show that these two alternatives cannot explain the experimental results presented in this paper.

The first alternative which has been proposed by Marshall<sup>11</sup> is a continuation of earlier work of Das and Mukherji<sup>16</sup> and of Adrian and Gourary<sup>17</sup> on color centers. It assumes a purely ionic model in which all  $\gamma$ 's in (2.5) are zero. Then, by using (2.6) and (4.1), the spin density in fluorine  $2s$  and  $2p\sigma$  orbitals are given by the overlap integrals,

$$f_s = S_s^2/3N_e, \quad f_\sigma = S_\sigma^2/3N_e. \quad (4.4)$$

On the basis of neutron diffraction form factors, Marshall and Stewart<sup>11</sup> have assumed that the  $\text{Mn}^{++}$  radial functions are more expanded in solids, by  $\sim 10\%$ , than the free ion value. On this basis they have obtained good agreement between  $f_\sigma$  with some of the reported values of  $f_\sigma - f_\pi$  for  $\text{Mn}^{++}$  in  $\text{ZnF}_2$ <sup>7,18</sup> by assuming  $f_\pi = 0$ . These assumptions would not allow them to fit our values of  $f_\sigma - f_\pi = 0.2\%$  in  $\text{KMnF}_3$  which were available.<sup>6</sup> Furthermore, the  $\pi$  interaction is not negligible and in fact it is almost as large as the  $\sigma$  interaction. The small value of  $f_\sigma - f_\pi$  observed in  $\text{Mn}^{++}$  salts must arise from a cancellation of the  $\sigma$  bond interaction by a large  $\pi$  bond effect. Consequently, in  $\text{KNiF}_3$  where the large  $\sigma$  bond interaction is not obscured by  $\pi$  bonds we can easily show that the overlaps do not account for the observed hyperfine interactions. (Before showing this, note that, whereas the neutron diffraction data indicated an expansion of the manganese wave functions in the solid, subsequent neutron diffraction<sup>19</sup> results on nickel have indicated a need to *shrink* the nickel radial function.) We will assume the Hartree-Fock function and, since our argument centers about the relative size of the  $s$  and  $\sigma$  interactions, the size of the  $\text{Ni}^{++}$  function only enters as a difference effect in second order. The point of Marshall's argument

is that the ratio  $f_\sigma/f_s$  is given by  $S_\sigma^2/S_s^2$ . Experimentally, we have shown that in  $\text{KNiF}_3$   $f_\sigma/f_s = 0.0378/0.00538 = 7.03$  while we have calculated  $S_\sigma^2/S_s^2 = (0.11071/0.08143)^2 = 1.85$  which is a clear disagreement.

By varying one parameter, i.e., the  $d$ -electron radial function, it is possible to fit one observable, i.e., the  $s$ -electron hyperfine interaction. In the case of  $\text{Mn}^{++}$  it was also possible,<sup>11</sup> by ignoring the  $p\pi$  contributions and selecting the  $\text{ZnF}_2:\text{Mn}^{++}$  data, to fit the observed anisotropic hyperfine interaction. However, since we have shown here that the  $\pi$  bonding cannot be ignored, it is clear that being able to fit two parameters in  $\text{MnF}_2$  was fortuitous. In  $\text{KNiF}_3$  where this cancellation cannot occur, this one-parameter purely ionic theory cannot explain the observations.

It has been proposed<sup>20</sup> that the  $\text{F}^{19}$  hyperfine interactions have large contributions from exchange polarization. These have been described as of the wrong sign to explain the observations but larger than the observed hyperfine interactions in magnitude. The ideal case to measure this effect is  $\text{K}_2\text{NaCrF}_6$ . In this crystal the one-electron picture of the ground state,  $t_2^3$ , does not allow the fluorine  $s$  electrons to have any hyperfine interaction.<sup>4</sup> Any isotropic hyperfine interactions observed must arise from a departure from this one electron ground state. These departures will include all the contributions of exchange polarization. In the case of  $\text{K}_2\text{NaCrF}_6$  the observed<sup>6</sup> isotropic interaction is 25 times smaller than the isotropic interaction observed when  $s$ -electron covalency mixing is allowed. Since there is no reason why the exchange polarization effects should be smaller for  $\text{Cr}^{3+}$  than they are for any other ion, it is clear that the calculations reported for  $\text{Mn}^{++}$  must be incorrect, and exchange polarization is small compared to the covalency effects.

In conclusion, we state that the molecular orbital model, where the  $s$ ,  $p\sigma$ , and  $p\pi$  electrons are allowed to bond independently with suitable  $d$  electrons, can satisfactorily describe the NMR experiments.

<sup>16</sup> A. Mukherji and T. P. Das, Phys. Rev. **111**, 1479 (1958).

<sup>17</sup> B. S. Gourary and F. J. Adrian, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, p. 127.

<sup>18</sup> A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, Phys. Rev. **117**, 1222 (1960).

<sup>19</sup> H. A. Alperin, Phys. Rev. Letters **6**, 55 (1961).

<sup>20</sup> A. J. Freeman and R. E. Watson, Bull. Am. Phys. Soc. **6**, 234 (1961).