

### C. PARAMAGNETIC AND OPTICAL ABSORPTION SPECTRA OF TRIVALENT IRON IN MgO

The paramagnetic resonance results of trivalent iron in MgO have been briefly reported previously.<sup>12,13</sup>

It was found that the spectrum can be described by a cubic spin Hamiltonian with an initial splitting of  $3a = +615 \times 10^{-4} \text{ cm}^{-1}$  and  $g = 2.0037 \pm 0.0007$ . This information is now supplemented by the observation of weak optical bands at the following wave numbers: 12 000, 15 200, 18 000, 25 500 and 38 500  $\text{cm}^{-1}$ . In addition there are a few still weaker bands at 20 600 and 21 700  $\text{cm}^{-1}$ . In all these crystals manganese was present. Manganese gives weak bands in the visible region and this makes a definite assignment of these transitions difficult. Two aspects permit, however, to make a reasonable assignment of these bands. One is the relative ease with which parts of the divalent iron can be converted into trivalent iron in these crystals and thus the intensity of these bands is enhanced. The second point is that there is a very close similarity between the optical spectra of the iron group hydrates and the oxides. Schlaefer<sup>14</sup> finds bands of 12 000–12 500, 18 500, 24 500, 27 500  $\text{cm}^{-1}$  in  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . Rabinowitch and Stockmeyer<sup>15</sup> report bands at 14 300, 18 200, and 24 600  $\text{cm}^{-1}$ . Pappalardo<sup>16</sup> measured a detailed structure stretching from 24 400–25 700  $\text{cm}^{-1}$ .

<sup>12</sup> W. Low, Proc. Phys. Soc. (London) **B69**, 1169 (1956).

<sup>13</sup> W. Low, Ann. N. Y. Acad. Sci. **72**, 69 (1958).

<sup>14</sup> H. L. Schlaefer, Z. Phys. Chem. Neue Folge **4**, 116 (1955).

<sup>15</sup> E. Rabinowitch and W. H. Stockmeyer, J. Am. Chem. Soc. **64**, 335 (1942).

<sup>16</sup> R. Pappalardo, Nuovo cimento **8**, 955 (1958).

It is likely that the bands at 12 000, 18 000, and 25 500 correspond to transition  ${}^6S \rightarrow {}^4T_{1g} \rightarrow {}^4T_{2g} \rightarrow {}^4A_{1g}$  of the parent  ${}^4G$ . The line at 32 500 is probably a transition to  ${}^4E_g({}^4D)$ . The assignment, however, is not definite.

We have also investigated to some extent the effect of heating and ultraviolet irradiation on the iron spectrum in MgO. These results can be summarized as follows.<sup>17</sup>

Heating to a few hundred degrees in hydrogen decreases the intensity of the absorption of the trivalent iron somewhat. Heating the crystal in air above 800°C. increases the absorption caused by  $\text{Fe}^{3+}$ . Irradiation with ultraviolet light produces a  $\text{Fe}^{3+}$  spectrum of fairly large intensity in some crystals, although prior to irradiation the spectrum was very weak.

### CONCLUSION

The spectrum of  $\text{Fe}^{2+}$  in MgO has been satisfactorily explained along the lines of a simple theory of a crystal field. The wide line and half-field line may be caused by local defects in the crystal structure or by a Jahn-Teller distortion. The spectrum in ZnS is at present not understood. It may arise from perturbations from  $d^5p$  or other odd configurations which may change the energy level scheme by a simple pure cubic field. Another possibility is a Jahn-Teller distortion.

<sup>17</sup> Professor Bleaney informed us that Dr. Orton has made a detailed study of the effect of irradiation on MgO crystals. Dr. J. Wertz (private communication) made an intensive study of converting divalent valencies into trivalent by irradiation and heat treatment.

## Nuclear Magnetic Resonance in Paramagnetic $\text{FeF}_2$

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A nuclear magnetic resonance study of the  $\text{F}^{19}$  resonance in paramagnetic  $\text{FeF}_2$  is reported. The hyperfine interactions with the magnetic electrons are measured and shown to be important in determining the resonance properties. The isotropic hyperfine interaction indicates the presence of  $(0.46 \pm 0.03)\%$  unpaired 2s spins in  $\text{F}^-$  orbitals from each  $\text{Fe}^{++}$  ion neighbor.

### INTRODUCTION

RECENTLY the nuclear magnetic resonance (NMR) of fluorine in magnetic fluorides has been studied<sup>1,2</sup> and shown to exhibit large displacements. These have been interpreted so as to provide values of the hyper-

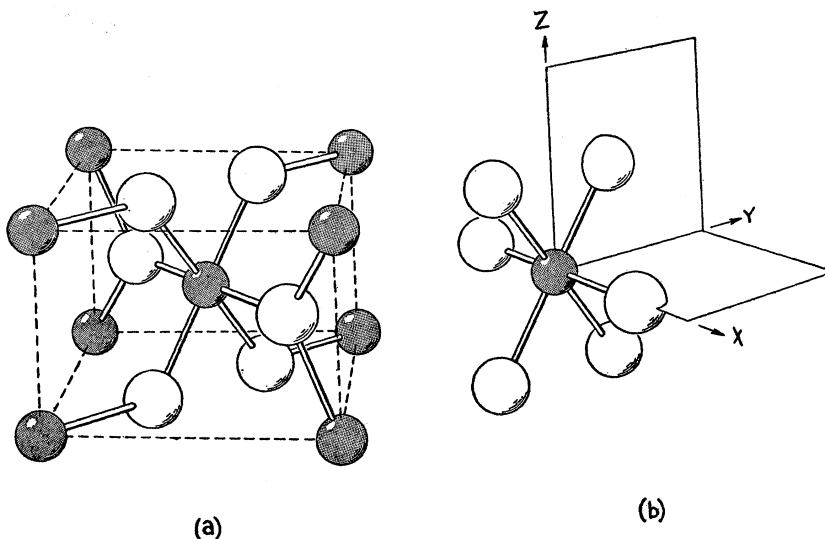
fine interactions between the fluorine nuclei and the magnetic electrons which are responsible for the shifts. In order to extend this kind of information we have measured the NMR of fluorine in paramagnetic  $\text{FeF}_2$ . A preliminary note<sup>3</sup> on these investigations was pub-

<sup>1</sup> R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).

<sup>2</sup> R. G. Shulman and V. Jaccarino, Phys. Rev. **109**, 1084 (1958).

<sup>3</sup> V. Jaccarino, R. G. Shulman, and J. W. Stout, Phys. Rev. **106**, 602 (1957).

FIG. 1. (a) Unit cell of rutile lattice. The  $\text{Fe}^{++}$  ions are represented by dark circles at the corners and the body center, the  $\text{F}^-$  ions by open circles. The origin of the coordinate system used in the text is at the lower left-hand corner; (b) Perspective drawing of  $\text{Fe}^{++}$  ion and the distorted octahedron of fluoride ions.



lished simultaneously with the results of an independent study<sup>4</sup> by Baker and Hayes. In this article we shall present additional experimental results and a general method of interpreting the measured NMR shifts in terms of the hyperfine interactions. An interpretation of the measured hyperfine interactions in terms of the spin densities in fluorine orbitals will be attempted and the attendant limitations discussed.

#### EXPERIMENTAL

$\text{FeF}_2$  is isomorphic with  $\text{MnF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$ , and  $\text{ZnF}_2$ . All these compounds have the rutile structure, space group  $D_{4h}^{14}-P4/mnm$  shown in Fig. 1. Accurate values of the crystal structures have been determined<sup>5</sup> by x-ray diffraction studies. The fluorine positions are determined by the parameter  $u$  since the fluoride ions in a unit cell are at  $\pm(u, u, 0)$  and  $\pm(\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})$ . The two metal ions at  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  are located once the lattice constants are known. The crystal structures were determined by Stout and Reed while a more recent investigation<sup>6</sup> by Baur has refined the value of the parameter  $u$ . In the opinion of one of us (J.W.S.) the best weighted mean values of  $u$  with the consequent interatomic distances are shown in Table I.

A single crystal of  $\text{FeF}_2$  was grown from the melt as described previously.<sup>7</sup> Spectrochemical analysis revealed that less than 0.004 weight percent Co, Cu, Mg, Ni, and Si were present while there was 0.08% Mn. Similar crystals had been shown to contain  $\sim 0.1\%$  Ferric ion.

The nuclear resonance experiments were made with a spherical sample  $\sim 6$ -mm diameter obtained from the crystal by cutting and grinding. This sphere was glued to a single crystal sapphire rod  $\frac{1}{4}$ -inch diameter so that

the  $[110]$  direction was parallel to the axis of the rod. During the experiment whose results are shown in Fig. 2 the crystal was inserted into a Varian Associates fixed frequency induction probe operating at 60,000 Mc/sec. The external magnetic field was in the  $(110)$  plane so that upon rotating the rod through  $360^\circ$  one passes through the positions where  $H_0$  is parallel to  $[001]$ ,  $[110]$ ,  $[001]$  at  $90^\circ$  intervals. The frequency was kept at the constant value of 60,000 Mc/sec during these experiments and the magnetic field varied to bring about resonance. These measurements include all the independent data obtainable about the hyperfine interactions from NMR measurements of this crystal at a given temperature in the paramagnetic state. With  $H_0 \parallel [001]$ , the resonance field was measured at  $300^\circ\text{K}$ ,  $220^\circ\text{K}$ , and  $90^\circ\text{K}$ . These results are presented in Table II along with the ratio of the NMR shift to the parallel susceptibility  $\chi_{11}$  at each temperature. In Table II the measured values of the NMR shifts are presented in terms of  $\alpha$  from the equation

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

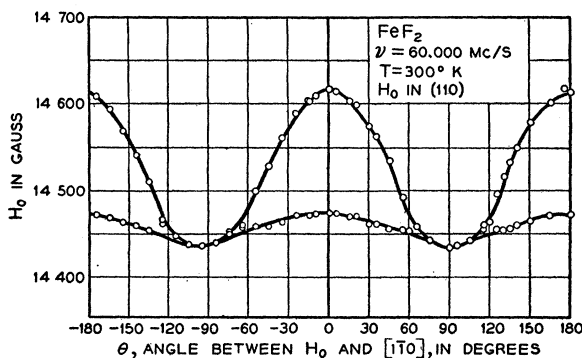


FIG. 2. Magnetic field required for resonance at a constant frequency of 60,000 Mc/sec as a function of the angle between  $H_0$  and  $[110]$  in the  $(110)$  plane.

<sup>4</sup> J. M. Baker and W. Hayes, Phys. Rev. **106**, 603 (1957).

<sup>5</sup> J. W. Stout and S. A. Reed, J. Am. Chem. Soc. **76**, 5279 (1954).

<sup>6</sup> W. H. Baur, Naturwissenschaften **44**, 349 (1957).

<sup>7</sup> M. Griffel and J. W. Stout, J. Am. Chem. Soc. **72**, 4351 (1950).

TABLE I. Weighted values of the structure parameters of the isomorphous iron group fluorides. The lattice parameters are taken from the room temperature measurements of Stout and Reed (see reference 5) while the mean values of  $u$  include the results of Baur (see reference 6).

	MnF <sub>2</sub>	FeF <sub>2</sub>	CoF <sub>2</sub>	NiF <sub>2</sub>	ZnF <sub>2</sub>
$a$ , Å	4.8734±0.0002	4.6966±0.0002	4.6951±0.0002	4.6506±0.0002	4.7034±0.0002
$c$ , Å	3.3099±0.0005	3.3091±0.0001	3.1796±0.0003	3.0836±0.0004	3.1335±0.0003
$u$	0.307 ±0.002	0.300 ±0.002	0.307 ±0.002	0.304 ±0.002	0.304 ±0.002
$d(M-F)$ Type I, Å	2.123 ±0.01	2.122 ±0.01	2.042 ±0.01	2.010 ±0.01	2.038 ±0.01
$d(M-F)$ Type II, Å	2.116 ±0.02	1.993 ±0.02	2.038 ±0.02	1.999 ±0.02	2.022 ±0.02

where the frequency  $\nu$  is related to the nuclear gyromagnetic ratio  $g_N$ , the nuclear magneton  $\beta_N$ , and the external field  $H_0$  by including the effects of the magnetic electrons in  $\alpha$ . When  $\alpha=0$  the resonance coincides with the normal fluorine resonance. For comparison the data of Baker and Hayes<sup>4</sup> are presented and it can be seen that the two independent measurements agree to within the experimental errors quoted by each source. Equation (1) was presented by Bleaney<sup>8</sup> in this particularly convenient form for use when  $H_0$  coincides with a principal axis of the hyperfine interaction. For arbitrary orientations of  $H_0$  more general expressions are available.<sup>1,9</sup>

The NMR lines were Lorentzian in shape and at 300°K with  $H_0 \parallel [110]$ , the two resolved lines had widths between derivative extrema of  $33 \pm 2$  and  $40 \pm 2$  gauss, corresponding to  $T_2 = (1.22 \pm 0.07) \times 10^{-6}$  seconds and  $T_2 = (1.01 \pm 0.05) \times 10^{-6}$  seconds, respectively. The broader line was more displaced. Similar dependence of line widths upon strength of the hyperfine interaction were reported<sup>3</sup> in CoF<sub>2</sub>. In the next section these observed variations are compared with existing theories<sup>9</sup> of line widths based upon exchange narrowing.

### INTERPRETATION

Most of the features of the fluorine resonance can be explained by interactions with the magnetic electrons.

TABLE II. Measured values of the fractional NMR shift,  $\alpha$ , where  $h\nu = g_N \beta_N H_0 (1 + \alpha)$ , at different temperatures and orientations. The comparative data of Baker and Hayes (see reference 4) are included in column 4 and agree within combined experimental errors. The last two columns list the ratio of shift to susceptibility, a relation which is discussed more fully in the text. We have used the subscripts  $B$  and  $F$  to refer to the susceptibility data of Bizette and Tsai (see reference 12) and Foner (see reference 14), respectively.

Direction of $H_0$	Temperature °K	Measured $\alpha \times 10^2$	Baker and Hayes $\alpha \times 10^2$	This study $\alpha/\chi_B$	$\alpha/\chi_F$
[001]	90°	7.49±0.03		3.52	3.79
	220°	4.58±0.03		3.49	3.72
	300°	3.77±0.03	3.62±0.13	3.51	3.82
[110]	300°	{3.49±0.03 2.48±0.03}	{3.51±0.13 2.55±0.13}	{4.03 2.86}	{4.27 3.04}
[100]	90°	6.09±0.03		3.48	3.68
	300°	2.99±0.03	3.03±0.13	3.43	3.64

<sup>8</sup> B. Bleaney, Phys. Rev. **104**, 1190 (1956).

<sup>9</sup> T. Moriya, Progr. Theoret. Phys. (Kyoto) **16**, 23, 641 (1956).

There are dipole fields at the fluorine sites arising from the magnetic electrons primarily located at the Fe<sup>++</sup> sites. In addition there are hyperfine interactions whose atomic origin we shall discuss in more detail below. As illustrated in Fig. 1, the rutile lattice of FeF<sub>2</sub> consists of two Fe<sup>++</sup> ions, one at (0,0,0) and the other at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . These two ions differ from each other by a 90° rotation about the [001] direction which is defined as the  $z$  axis of both octahedra. There are two distinct F<sup>-</sup>—Fe<sup>++</sup> bonds which have been labeled Type I and Type II by Tinkham.<sup>10</sup> Each Fe<sup>++</sup> ion has four Type I bonds to fluorines 2.12 Å away in the  $yz$  plane. Along the  $x$  axis of each octahedron lie two Type II fluorines at 1.99 Å from the Fe<sup>++</sup> ion. Consider in Fig. 1 the fluoride ion at the position  $(u, u, 0)$  having a hyperfine interaction (Type II) with one Fe<sup>++</sup> ion at (0,0,0) and a Type I hyperfine interaction with two Fe<sup>++</sup> ions, at  $(\frac{1}{2}, \frac{1}{2}, \pm \frac{1}{2})$ . Consider the origin of the coordinates to be at the lower left-hand corner. The [110] direction in the crystal is the  $x$  direction of the Fe<sup>++</sup> ions on the corners and the  $y$  direction of the Fe<sup>++</sup> ions in the cell centers. The [001] direction is the  $z$  direction of all Fe<sup>++</sup> ions and the  $[1\bar{1}0]$  is the  $y$  direction of the corner Fe<sup>++</sup> ions and the  $x$  direction of the center Fe<sup>++</sup> ions. For this geometry the energy of the fluoride ions is expressed by the Hamiltonian<sup>1,9</sup>

$$\mathcal{H} = -g_N \beta_N I \cdot (\mathbf{H}_0 + \mathbf{H}^D) + 2\mathbf{S}^I \cdot \mathbf{A}^I \cdot \mathbf{I} + \mathbf{S}^{II} \cdot \mathbf{A}^{II} \cdot \mathbf{I}. \quad (2)$$

The dipole field,  $\mathbf{H}^D$ , is

$$\mathbf{H}^D = \sum_i \frac{3(\mathbf{r}_i \cdot \boldsymbol{\chi}_i \cdot \mathbf{H})\mathbf{r}_i}{Nr_i^5} - \frac{\boldsymbol{\chi}_i \cdot \mathbf{H}}{Nr_i^3}. \quad (3)$$

The summation extends over all Fe<sup>++</sup> ions in the crystal,  $\mathbf{r}_i$  is the vector from the fluorine atom to the  $i$ th dipole,  $\boldsymbol{\chi}_i$  is the second-order tensor describing the molal susceptibility of a Fe<sup>++</sup> ion,  $N$  is Avogadro's number, and  $\mathbf{H}$  is the field at a Fe<sup>++</sup> ion. [Notice that the dipole interaction term of Eq. (A-1) of reference 1 should be multiplied by minus one.] For a spherical sample one may put  $\mathbf{H} = \mathbf{H}_0$ , the applied field, since in FeF<sub>2</sub> the difference between these two quantities, arising from the anisotropy in the dipole field as seen from a metal atom position, is throughout the paramagnetic region negligible compared to the errors in the experimental susceptibility. In the paramagnetic region we replace

<sup>10</sup> M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535, 549 (1956).

$\mathbf{S}$  by its average value  $\langle \mathbf{S} \rangle$  which will also be related to  $\mathbf{H}_0$  through a second-order tensor. In this region measurements were made with  $\mathbf{H}_0$  along the  $[110]$ ,  $[1\bar{1}0]$ , and  $[001]$  directions. The equations can be resolved into components along these axes. The symbol  $H_0$  refers to the component of  $\mathbf{H}_0$  along the axis. If one represents the experimental nuclear resonance results by (1), then

$$g_N \beta_N (\alpha_{001} - H_{001}^D / H_0) = - (1/H_0) \langle S_z \rangle (2A_z^I + A_z^{II}), \quad (4)$$

$$g_N \beta_N (\alpha_{110} - H_{110}^D / H_0) = - (1/H_0) (2\langle S_y^I \rangle A_y^I + \langle S_x^{II} \rangle A_x^{II}), \quad (5)$$

$$g_N \beta_N (\alpha_{1\bar{1}0} - H_{1\bar{1}0}^D / H_0) = - (1/H_0) (2\langle S_x^I \rangle A_x^I + \langle S_y^{II} \rangle A_y^{II}). \quad (6)$$

The dipole fields, calculated for a spherical sample are

$$H_{001}^D / H_0 = \sum_i \frac{\chi_z (3 \cos^2 \theta_i - 1)}{Nr_i^3} = 0.047 \chi_z, \quad (7)$$

$$H_{110}^D / H_0 = 0.373 \chi_x + 0.044 \chi_y, \quad (8)$$

$$H_{1\bar{1}0}^D / H_0 = -0.159 \chi_y - 0.305 \chi_x. \quad (9)$$

These numerical values were calculated by one of us (J.W.S.) and have subsequently been checked on an IBM 704 computer.

The pertinent Hamiltonian acting on a magnetic ion may be written<sup>11</sup>

$$\begin{aligned} \mathcal{H} = & D_x S_x^2 + D_y S_y^2 + D_z S_z^2 \\ & + (g_x S_x H_x + g_y S_y H_y + g_z S_z H_z) \beta \\ & - \beta^2 (\Lambda_x H_x^2 + \Lambda_y H_y^2 + \Lambda_z H_z^2) \\ & + \text{antiferromagnetic interactions}, \end{aligned} \quad (10)$$

where  $D_x + D_y + D_z = 0$  and  $\Lambda_i = (2 - g_i)/2\lambda$ . From this Hamiltonian one obtains, treating the antiferromagnetic interactions in a molecular field approximation and expanding in inverse powers of temperature,

$$\chi_z = \frac{N\beta^2(2 - g_z)}{\lambda} + \frac{2N\beta^2 g_z^2}{k(T + \Delta)} \left[ 1 - \frac{21}{10} \frac{D_z}{k(T + \Delta)} + \dots \right], \quad (11)$$

and

$$\begin{aligned} \langle S_z \rangle = & \frac{[\text{trace } S_z \exp(-\mathcal{H}/kT)]}{[\text{trace } \exp(-\mathcal{H}/kT)]} \\ = & - \frac{[\chi_z - N\beta^2(2 - g_z)/\lambda]}{Ng_z \beta} H_z, \end{aligned} \quad (12)$$

with corresponding expressions where  $z$  is replaced by  $x$  or  $y$ . Thus in order to determine  $\langle S \rangle$  in a particular direction, one has to subtract the estimated temperature independent susceptibility from the total measured and then divide by  $-Ng\beta$ . The measured susceptibilities consist of the formula given by Bizette and Tsai,<sup>12</sup>  $\chi = 3.88/(T + 117)$  for the powder and the measure-

ments<sup>13</sup> on single crystals of the anisotropy. Using this formula and the anisotropy data,  $\chi_{11} \equiv \chi_x$  and  $\chi_{\perp} \equiv (\chi_x + \chi_y)/2$  can be calculated at any temperature required for these experiments.

Tinkham<sup>10</sup> in his electron resonance experiments on  $\text{Fe}^{++}$  in  $\text{ZnF}_2$ , measured  $g_z = 2.25$  and estimated  $(g_x + g_y)/2 = 2.04$ . He also calculated from his data the parameter  $\eta = |D_x - D_y|/\sqrt{3}D_z = 0.167 \pm 0.020$  but could not tell from his data whether  $D_x$  or  $D_y$  were larger. Fortunately there is not much difference in the susceptibility in the  $x$  and  $y$  directions. We have estimated, neglecting the spin-spin interaction which is small and whose neglect enables one to relate the  $D$ 's,  $g$ 's, and  $\lambda$ , i.e.,  $[g_z - g_{av} = 2D_z/\lambda \text{ etc.}]$ , that  $|\chi_x - \chi_y|$  is about twenty percent of  $\chi_{11} - \chi_{\perp}$ . This difference almost completely vanishes, however, in the calculation of  $\langle S_x \rangle$  and  $\langle S_y \rangle$  which turn out to be identical to better than one percent between 90° and 300°K. The errors in the powder susceptibility measurement are considerably larger than this. One also needs to know the sign of  $\chi_x - \chi_y$  in calculating the dipole field. Trying both possibilities at room temperature the difference is 0.4% in the calculated value of  $2A_x^I + A_y^{II}$  and considerably less in  $2A_x^I + A_y^{II}$ . This error is also negligible. We may, therefore, to well within the accuracy of the available experimental data, consider the susceptibilities in the  $x$  and  $y$  directions equal to each other and to  $\chi_{\perp}$ . We are essentially forced to do this because there is no convincing evidence as to whether  $\chi_x$  or  $\chi_y$  is larger, but fortunately the error introduced by this approximation is negligible compared to the experimental errors.

In order to estimate the temperature-independent part of the susceptibility let us take  $\lambda = -70 \text{ cm}^{-1}$ . It is  $-103 \text{ cm}^{-1}$  in the free ion and a change to about  $-70 \text{ cm}^{-1}$  in the crystal is consistent with Tinkham's<sup>10</sup> estimates. Then  $N\beta^2(2 - g_z)/\lambda = 0.93 \times 10^{-3}$ , and  $N\beta^2(2 - g_x)/\lambda = N\beta^2(2 - g_y)/\lambda = 0.15 \times 10^{-3}$  giving

$$\langle S_z \rangle = - \frac{[\chi_{11} - 0.93 \times 10^{-3}]}{2.25 N \beta} H_0, \quad (13)$$

$$\langle S_x \rangle = \langle S_y \rangle = - \frac{[\chi_{\perp} - 0.15 \times 10^{-3}]}{2.04 N \beta} H_0. \quad (14)$$

Using the powder susceptibility data of Bizette<sup>12</sup> combined with measurements<sup>13</sup> of the magnetic anisotropy of  $\text{FeF}_2$ , and substituting into Eqs. (4), (5), (6), (13), and (14), one obtains the hyperfine coupling constants listed in Table III. The two alternatives for the  $x$  and  $y$  components arise because of the impossibility of distinguishing the two resonances observed with  $H_0$  in the (001) plane. Absolute values of these combined hyperfine interactions are only determined to  $\pm 3 \times 10^{-4} \text{ cm}^{-1}$  since they are no more accurate than the measured values of the susceptibility which we estimate to be

<sup>11</sup> A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

<sup>12</sup> H. Bizette and B. Tsai, Compt. rend. **212**, 119 (1941).

<sup>13</sup> J. W. Stout and L. M. Matarrese, Revs. Modern Phys. **25**, 338 (1953).

TABLE III. Values of hyperfine coupling constants in units of  $10^{-4}$  cm $^{-1}$ .

	300°K	220°K	90°K	Mean
$2A_z^I + A_z^{II}$	63.7	62.3	61.1	62.4
$2A_y^I + A_y^{II}$	55.8			55.8
	or			or
$2A_x^I + A_x^{II}$	51.4			51.4
$A_y^I + A_x^I + \frac{1}{2}(A_y^{II} + A_x^{II})$	53.6			53.7
$2A_z^I - A_z^{II}$			53.8 (4.2°K, $ S =1.96$ )	23.2
				37.8
				69.4

about six percent. Recent measurements by Foner<sup>14</sup> of the susceptibilities of single crystal FeF<sub>2</sub> indicate that the powder data<sup>12</sup> are too high. The use of Foner's data would increase the values of the  $A$ 's in the  $z$  direction by eight percent and in the  $x$  and  $y$  directions by six percent. However the relative values are known more accurately depending as they do upon the anisotropy of the susceptibility and the NMR shifts. These relative values are known with an accuracy of  $\pm 0.5 \times 10^{-4}$  cm $^{-1}$ .

A fourth independent measurement of the hyperfine interactions is provided by the measurements of the F<sup>19</sup> frequency in the antiferromagnetic state. This has been measured<sup>15</sup> to occur at 183.2 Mc/sec. The hyperfine interactions measured by these observations are

$$\begin{aligned} & [(2A_z^I - A_z^{II})(\text{cm}^{-1}) + 0.285 \times 10^{24} g \beta_N \beta_N] |S| \\ &= [(2A_z^I - A_z^{II})(\text{cm}^{-1}) + 7.95 \times 10^{-4}] |S| \\ &= (183.2 \times 10^6) / (2.998 \times 10^{10}), \quad (15) \end{aligned}$$

where  $0.285 \times 10^{24}$  is  $\sum_i r_i^{-3} (3 \cos^2 \theta_i - 1)$  in the antiferromagnetic state,  $g=2.25$ , and  $|S|$  is the expectation value of the spin in the antiferromagnetic state at the temperature of the measurement, namely 4.2°K. No exact value of  $|S|$  is available. Recent theory predicts<sup>16</sup> for a spin of 2 that the spins will be only 98% aligned. The results of substituting  $|S|=2.00$  and  $|S|=1.96$  into Eq. (15) are

$$\begin{aligned} 2A_z^I - A_z^{II} &= 22.6 \times 10^{-4} \text{ cm}^{-1}; |S|=2.00; \quad (16) \\ &= 23.2 \times 10^{-4} \text{ cm}^{-1}; |S|=1.96. \end{aligned}$$

The values of hyperfine interaction in FeF<sub>2</sub> measured in the paramagnetic state and presented in Table III can be compared with the similar parameters in MnF<sub>2</sub>. We have remeasured the resonances of F<sup>19</sup> in MnF<sub>2</sub> at 300°F at a frequency of 60.000 Mc/sec with greater accuracy than previously reported. The new values agree very well with the previously published<sup>1</sup> values and are

$$\begin{aligned} 2A_z^I + A_z^{II} &= 47.1 \times 10^{-4} \text{ cm}^{-1}, \\ 2A_y^I + A_y^{II} &= 48.2 \times 10^{-4} \text{ cm}^{-1}, \quad (17) \\ 2A_x^I + A_x^{II} &= 46.1 \times 10^{-4} \text{ cm}^{-1}. \end{aligned}$$

In MnF<sub>2</sub> these values have an absolute error of  $\pm 1.5 \times 10^{-4}$  cm $^{-1}$  because of uncertainties in the suscepti-

bility while the relative values of the  $A$ 's are known to  $\pm \frac{1}{2}\%$ .

It is possible<sup>10</sup> to write the six individual components of the hyperfine interaction in the form

$$\begin{aligned} A_i^N &= A_s^N + (A_\sigma^N - A_\pi^N) (3 \cos^2 \theta_{i,\sigma} - 1) \\ &\quad + (A_\pi^N - A_{\pi'}^N) (3 \cos^2 \theta_{i,\pi} - 1), \quad (18) \end{aligned}$$

where  $i=x, y$ , or  $z$ ;  $N=I$  or  $II$  for Type I or Type II bonds; and the isotropic hyperfine interaction is  $A_s^N$ . The anisotropic hyperfine interactions, associated with unpaired  $p$  electrons, are described by the differences between the unpaired spin density along two directions as compared with the third.

The isotropic interactions can be evaluated quite simply, regardless of the model used to interpret the anisotropic terms. Summing Eq. (18) over  $x, y$ , and  $z$ , the anisotropic terms cancel and substituting the values of Table III we find that for FeF<sub>2</sub>,  $2A_z^I + A_z^{II} = 56.5 \pm 2.5 \times 10^{-4}$  cm $^{-1}$ . It is interesting to compare this with the MnF<sub>2</sub> measurements where  $2A_z^I + A_z^{II} = 47.1 \pm 1.5 \times 10^{-4}$  cm $^{-1}$ . To convert the hyperfine interactions into their equivalent degree of unpaired spins in fluorine  $s$  orbitals from each bond we use the relation given by Tinkham<sup>10</sup>:

$$\text{percent } 2s = \frac{3A_s SI}{8\pi\beta_N |\Psi(0)|^2}, \quad (19)$$

where  $|\Psi(0)|^2$  is the probability for a  $2s$  electron in F<sup>-</sup> ion to be found at the nucleus. On a molecular orbital approximation the percent  $2s$  character represents the amount of its admixture in the antibonding orbital. These interpretations are given in more detail elsewhere<sup>17-20</sup> in the recent literature and need not be repeated here. Returning to the comparison between the two compounds, using the value of  $|\Psi(0)|^2$  given by Moriya,<sup>9</sup> we find the  $2s$  admixture for MnF<sub>2</sub> to be  $(0.48 \pm 0.02)\%$  while for FeF<sub>2</sub> the  $2s$  admixture is  $(0.46 \pm 0.03)\%$ . These values are equal to within the experimental errors imposed by uncertainties in the susceptibilities so that it is not possible to claim any trends as one moves across the iron group from these results alone.

<sup>17</sup> A. Mukherji and T. P. Das, Phys. Rev. **111**, 1479 (1958).

<sup>18</sup> F. Keffer, T. Oguchi, W. O'Sullivan and J. Yamashita, Phys. Rev. **115**, 1553 (1959).

<sup>19</sup> R. G. Shulman, *Magnetic Properties of Metals and Alloys* (American Society for Metals, Cleveland, Ohio, 1959), p. 56.

<sup>20</sup> W. Marshall, Bull. Am. Phys. Soc. **4**, 142 (1959).

<sup>14</sup> S. Foner (private communication).

<sup>15</sup> V. Jaccarino, R. G. Shulman, J. L. Davis, and J. W. Stout, Bull. Am. Phys. Soc. **3**, 41 (1958).

<sup>16</sup> J. C. Fisher, Bull. Am. Phys. Soc. **4**, 53 (1959).

For  $\text{FeF}_2$  we do not have enough data to determine the individual anisotropic hyperfine interaction parameters. It can be seen in Eq. 18 that six independent parameters are required to describe the interaction while only four independent measurements can be made. The main difficulty in obtaining a reasonable solution (which would then justify the assumptions made in obtaining the solution) can be seen from the relative values of the terms in Table III. When these are written in terms of components it is seen that the  $A_\sigma$  contributions to  $2A_y^I + A_z^{\text{II}}$  are both positive. For the other two measured interactions the  $A_\sigma$  contributions are smaller. On the usual assumption that  $\sigma$  interactions are much stronger than  $\pi$  interactions this term should be the largest of the three measured which it is not. The fact that the anisotropy is larger than that observed in  $\text{MnF}_2$  suggests that the interaction between the  $d\epsilon$  orbitals of the ferrous ion and the  $p_\pi$  fluorine orbitals is important. The extra electron in  $\text{Fe}^{++}$  compared to  $\text{Mn}^{++}$  is in a  $d\epsilon$  orbital and would contribute mainly to the anisotropic  $\pi$  interactions whereas in  $\text{Mn}^{++}$  the  $\pi$  interactions should be cancelled by the  $\pi'$ . More direct evidence that the  $\pi$  electron interaction is large and in fact comparable with that of the  $\sigma$  electron has been obtained lately<sup>21</sup> by NMR measurements on single crystals of  $\text{NiF}_2$ . If the  $\pi$  interactions are large then they cannot be ignored in solving Eq. (18) in terms of the values of Table III and, as mentioned above, then we do not have enough independent measurements.

We may compare our  $A_z$ 's with those that Tinkham obtained in  $\text{ZnF}_2 - \text{FeF}_2$ . His values are  $A_z^I = 100 \times 10^{-4} \text{ cm}^{-1}$  and  $A_z^{\text{II}} = 64 \times 10^{-4} \text{ cm}^{-1}$ . The correction for the dipole interaction between the  $\text{Fe}^{++}$  spin and the fluorine nucleus is  $(g\beta g_N \beta_N / \hbar c r^3) [3(z^2/r^2) - 1]$ . For the Type I bond  $(1/r^3) [3(z^2/r^2) - 1] = 0.086 \times 10^{24} \text{ cm}^{-3}$ , and for the Type II bond this number is  $-0.126 \times 10^{24} \text{ cm}^{-3}$ . The corrected  $A$ 's are then

$$\begin{aligned} A_z^I &= (100 - 10 = 90) \times 10^{-4} \text{ cm}^{-1}, \\ A_z^{\text{II}} &= (64 + 14 = 78) \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (20)$$

These are on a basis of a fictitious spin of  $\frac{1}{2}$ . To convert to the true spin they should be divided by  $4(1 - \eta^2/8) = 3.99$  to give

<sup>21</sup> R. G. Shulman (to be published).

$$\begin{aligned} A_z^I &= (22.6 \pm 1.3) \times 10^{-4} \text{ cm}^{-1}, \\ A_z^{\text{II}} &= (19.6 \pm 1.0) \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (21)$$

If we assume that  $|S| = 1.96$  we obtain

$$\begin{aligned} A_z^I &= (21.4 \pm 1.5) \times 10^{-4} \text{ cm}^{-1}, \\ A_z^{\text{II}} &= (19.6 \pm 1.5) \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (22)$$

The agreement is good, in fact better than one has any a priori right to expect. This agreement leads one to expect that a more detailed analysis of the hyperfine interactions would be possible if additional paramagnetic resonance results on  $\text{Fe}^{++}$  in  $\text{ZnF}_2$  were available.

Now we consider the line widths. Their Lorentzian shape coupled with our inability to saturate them indicates that they are exchange narrowed. Moriya<sup>9</sup> came to the conclusion that the contributions to the line widths would include nonsecular as well as secular hyperfine interactions. His expression is

$$\frac{1}{T_2} = \left(\frac{\pi}{2}\right)^{\frac{1}{2}} \frac{S(S+1)}{3\hbar^2\omega_e} \sum_i (\cos^2\theta_i + \frac{1}{2}\sin^2\theta_i) A_i^2, \quad (23)$$

where  $\theta_i$  is the angle between the  $i$ th principle axis of the hyperfine interaction and the direction of nuclear spin quantization. Included in Eq. (23) are contributions from all three principle axes to the line width observed with  $H_0$  along any particular axis. For  $H_0 \parallel [110]$ , as mentioned above, the experimental values of the two line widths are  $(1.22 \pm 0.07) \times 10^{-6}$  seconds and  $(1.01 \pm 0.05) \times 10^{-6}$  seconds. The experimental ratio of line widths is  $1.22/1.01 = 1.21 \pm 0.09$  while the theoretical ratio calculated from Eq. (23) is 1.18. This excellent agreement proves the importance of the nonsecular contributions. Substituting numerical values into Eq. (23) and including the dipole interactions in the values of  $A_i$ , we calculate that  $\omega_e = 5.3 \times 10^{12} \text{ sec}^{-1}$ . This agrees rather well with the value of  $\omega_e = 5.7 \times 10^{12} \text{ sec}^{-1}$  calculated from the molecular field approximation.

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