

## APPENDIX II

We want to prove that  $(d\|U^4\|d)=10 Dq(70)^{\frac{1}{2}}$ . According to Racah (III):

$$(d^6 {}^5DM\|U_q^4\|d^6 {}^5dM') \\ = \sum_{L'} (d^6 {}^5D\|d^5 L' d^5 D)(L' d {}^5DM\|U_q^4\|L' d {}^5dM') \\ \times (d^5 L' d^5 D\|d^6 {}^5D). \quad (1)$$

According to the Eckart-Wigner theorem the dependence on  $M$  and  $M'$  can be written

$$(L' d {}^5DM\|U_q^4\|L' d {}^5dM') \\ = (-1)^{D+M} (L' d {}^5D\|U^{(4)}\|L' d {}^5D) \\ \times [(-1)^{D-q}/(2.4+1)^{\frac{1}{2}}] (DDM'-M|DD4-q). \quad (2)$$

$U^4$  operates on  $d$  but not on  $L'$ :

$$(L' d {}^5D\|U^4\|L' d {}^5D) = (-1)^{L'+4-d-D} [(2l+1)(2l+1)]^{\frac{1}{2}} \\ \times W(dDdD; L'4)(d\|U^4\|d). \quad (3)$$

Substituting Eqs. (3) and (2) into (1) we get

$$(d^6 {}^5DM\|U_q^4\|d^6 {}^5dM') \\ = (-1)^{M-q}(5/3)(d\|U^4\|d)(22M'-M|224-q) \\ \times \sum_{L'} (-1)^{L'} (d^6 {}^5D\|d^5 L' d^5 D)W(2222; L'4) \\ \times (d^5 L' d^5 D\|d^6 {}^5D). \quad (4)$$

The sum is

$$\sum_{L=0}^4 (-1)^{L'} (d^6 {}^5D\|d^5 L' d^5 D)W(2222; L'4) \\ \times (d^5 L' d^5 D\|d^6 {}^5D) = 3/50.$$

Hence

$$(d^6 {}^5D0\|U_q^4\|d^6 {}^5D0) \\ = (-1)^{0-0}(5/3)(d\|U^4\|d)(220-0|224-0)(3/50) \\ = \frac{1}{10}(d\|U^4\|d)(36/70)^{\frac{1}{2}}. \quad (5)$$

But this matrix element is according to the usual calculation  $+6 Dq$ , therefore

$$(d\|U^4\|d) = 10 Dq(70)^{\frac{1}{2}}.$$

## Paramagnetic Resonance and Optical Spectra of Divalent Iron in Cubic Fields. II. Experimental Results\*

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The paramagnetic resonance absorption of  $\text{Fe}^{2+}$  in  $\text{MgO}$  is observed at  $g=3.428$  and  $6.86$ . The optical absorption line is found at  $10\,000\text{ cm}^{-1}$ . The paramagnetic resonance spectrum indicates considerable covalent bonding. The origin of the line at  $6.86$  is discussed.

In tetrahedral  $\text{ZnS}$  a paramagnetic line is found at  $g=2.25$  and optical absorption at  $3\text{ }\mu$  and  $0.7\text{ }\mu$ . Possible explanations of this spectrum are discussed.

A short discussion of the optical absorption spectra of trivalent iron in  $\text{MgO}$  is presented.

## INTRODUCTION

IN the preceding paper<sup>1</sup> we have calculated in detail the energy level scheme of the  ${}^5D$  level in an octahedral and tetrahedral crystal symmetry. This paper will be divided into two main sections, (A) The paramagnetic and optical spectra of  $\text{Fe}^{2+}$  in  $\text{MgO}$  and (B) The paramagnetic and optical spectra in tetrahedral sphalerite ( $\text{ZnS}$ ). Section (C) will deal with a number of additional observations on these crystals. In Secs. (A) and (B) it is shown that the spectra in  $\text{MgO}$  can be understood along the lines developed in (I), but that a definitive interpretation of the spectra in  $\text{ZnS}$  is at present still lacking.

### A. THE PARAMAGNETIC AND OPTICAL SPECTRA OF $\text{Fe}^{2+}$ IN THE OCTAHEDRAL CRYSTAL SYMMETRY OF $\text{MgO}$

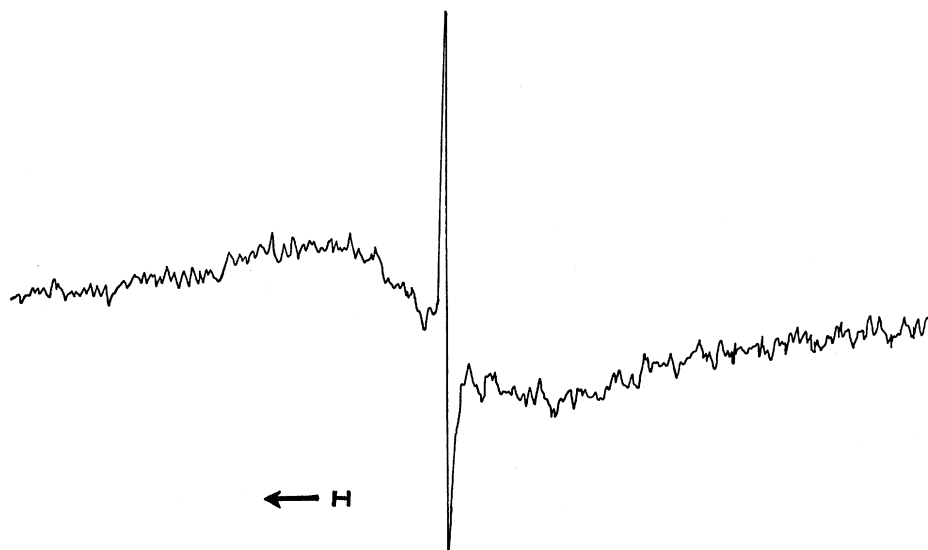
Magnesium oxide has a face-centered cubic structure. Each magnesium ion is surrounded by six equidistant oxygen ions. In this octahedral crystal field the ground state is an orbital triplet ( $\Gamma_6$ ). This triplet which is fivefold spin degenerate splits into a number of levels by spin-orbit interaction of which a triplet is the lowest. As shown in (I), this triplet gives rise to a first order Zeeman splitting in an external magnetic field. Transitions among these levels are permitted. Since the other levels are fairly close it is expected that the spin-lattice relaxation time will be short. Indeed it proved necessary to cool the crystal to liquid helium temperature in order to detect any resonance. At  $4^\circ\text{K}$  only the lowest triplet is populated to a significant degree. (The next level is removed by about  $2\lambda \sim 150\text{--}200\text{ cm}^{-1}$  or  $200\text{--}280^\circ\text{K}$ .) One will not expect, therefore, to observe resonance from the higher levels.

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<sup>1</sup> W. Low and M. Weger, preceding paper [Phys. Rev. **118**, 1119 (1960)], (to be referred to as I).

FIG. 1. Paramagnetic resonance spectrum of  $\text{Fe}^{2+}$  in  $\text{MgO}$   $g=3.428$  for both the narrow and wide line.



### Experimental Results

The paramagnetic resonance spectrum is shown in Fig. 1. The line occurs at  $g=3.428 \pm 0.002$  and is isotropic. The total width at half power at liquid helium temperature is 8–10 gauss. Superimposed on this relatively narrow line is another wide line of width  $450 \pm 50$  gauss and approximately the same  $g$  factor. At approximately half-field ( $H_0/2$  or  $2g$ ) there is another line with a peculiar shape as shown in Fig. 2. The line shape has a sharp cutoff at the high field side, rises to a maximum and then slowly tapers off to the low field side. (Note that Fig. 2 shows the derivatives of the absorption line.) We have investigated in detail the ratio of the intensity of this half-field line and the wide line relative to the narrow line at  $H_0$  for four crystals coming from different batches of crystal growing. In all the crystals (we have looked superficially

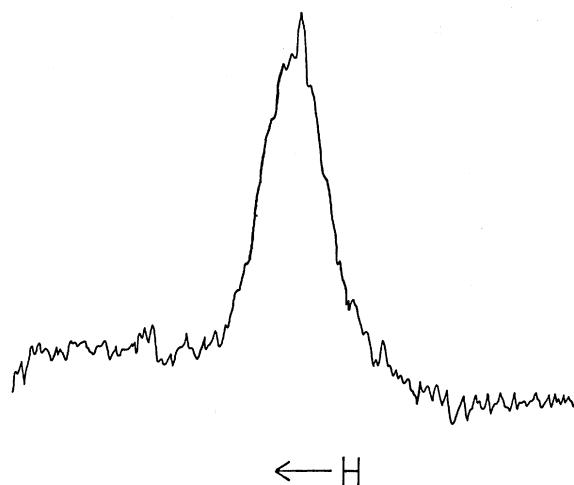


FIG. 2. Half-field transition of  $\text{Fe}^{2+}$  in  $\text{MgO}$ . The sharp cutoff at the high field side is at  $g=6.86$ .

at about 8 crystals) the wide line and the half-field appeared in addition to the narrow line at  $H_0$ . However, the ratio of the intensity of these lines varied significantly from one crystal to another. In one particular crystal the half-field and the wide line were of considerable smaller intensity.

The optical spectrum could only be observed with great difficulty since the amount of iron in the crystal was less than 0.01% and a fraction of this amount was in the trivalent state. Fortunately, we were in possession of one crystal of over 2 cm thickness which made the spectrum observable and as shown in Fig. 3. Later we were to observe this line at  $1 \mu$  even in thinner plates by reducing the  $\text{Fe}^{3+}$  present in these crystals to  $\text{Fe}^{2+}$  by heating the crystal in the presence of molecular hydrogen. The total width at half power of the optical absorption line is about  $600 \text{ cm}^{-1}$ .

### Discussion

In the previous paper we have shown that the expected  $g$  factor for the lowest triplet is about  $\frac{7}{2} + (9/25) \times (\lambda/Dq)$  (see notation in I). It is convenient to use the notation of an effective spin Hamiltonian which is given by

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

and

$$g = g_S + g_L + g_{LS} = 3(1.00114) + k\frac{1}{2} + (9/25)(\lambda/Dq). \quad (2)$$

The first factor is the contribution to the  $g$  factor by the spin of the triplet and the second factor is that of the orbital moment. We have multiplied the orbital contribution by the orbital reduction factor  $k$  as introduced by Stevens.<sup>2</sup> This factor is a measure of the ionicity of the crystal. If there is covalent bonding  $k$  will be smaller than one. This factor is defined by

$$\langle \Psi_n | L | \Psi_m \rangle = k_{nm} \langle d_n | L | d_m \rangle, \quad (3)$$

<sup>2</sup> W. K. Stevens, Proc. Roy. Soc. (London) A219, 542 (1953).

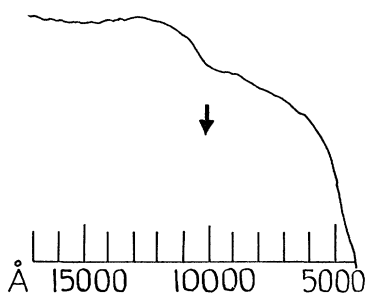


FIG. 3. The optical spectrum of  $\text{Fe}^{2+}$  in  $\text{MgO}$ . Absorption is downwards. There is a wide peak at about 10 000 Å. This peak decreases in intensity if  $\text{Fe}^{2+}$  is oxidized into  $\text{Fe}^{3+}$ .

where  $\Psi$  are the molecular orbitals appropriate for octahedral symmetry and  $d$  are the usual atomic  $d$  wave functions. The third term in Eq. (2) gives a measure of the contribution of the higher Stark level  $\Gamma_3$  admixed by the spin-orbit coupling ( $\lambda$ ). This spin-orbit coupling evaluated in the molecular orbital manifold is given by

$$\langle \Psi_n | \lambda_0 L | \Psi_m \rangle = \lambda_0 N_n N_m \langle d_n | L | d_m \rangle, \quad (4)$$

where  $\lambda = \lambda_0 N_n N_m$  and  $\lambda_0$  is the spin orbit coupling appropriate to pure  $d$  wave functions in the crystal. Presumably  $\lambda_0$  is the same as the spin-orbit coupling in a free ion although experimental verification of this is so far lacking. In general the normalization factor  $N_n N_m$  will differ from  $k_{nm}$  since the former is evaluated between two different orbital levels, whereas the latter within the same orbital level. It is found that in most crystals  $N_n N_m < k_{nm}$ . In many ions whose ground state is  $F$ ,  $N_n N_m$  is of the order of 0.75. We shall assume this to be so for the case of  $\text{Fe}^{2+}$ . At any rate an error of 10–15% in this normalization constant effects the  $g$  value only in the third decimal place.

From the optical spectrum we find that  $10Dq + 3\lambda_0 = 10\,000 \text{ cm}^{-1}$  or  $Dq = 1030 \pm 20 \text{ cm}^{-1}$ . Substituting  $N_n N_m = 0.75$ ,  $\lambda_0 = 100 \text{ cm}^{-1}$ , and  $Dq = 1030 \pm 20 \text{ cm}^{-1}$  we find  $k = 0.80 \pm 0.02$ . This is a considerable reduction factor for so called ionic crystals as well as for the covalent cyanides. This large reduction of the orbital contribution seems to indicate considerable  $\pi$  bonding with the surroundings. A comparison of various orbital reduction factors in the iron group having a degenerate ground state is given in Table I.

We have also considered the possibility of admixtures to ground Stark level of other Stark levels of the  $d^6$  configuration. The only levels which might give a contribution to the ground state are  ${}^3T_4({}^3P)$  and  ${}^3T_5({}^3H)$ . Since these levels are about 15 000–20 000  $\text{cm}^{-1}$  above the ground state their contribution to the  $g$  factor admixed by spin-orbit coupling, will be less than 0.01 and the effect on the calculation of  $k$  is negligible.

The wide line may have its origin in small deviations from cubic symmetry. In a weak axial field the center level of the ground triplet will not be exactly midway,

but either lower or higher (depending on the sign of the axial field) than the center of gravity of the Zeeman split level. The energy levels are given by (see I)

$$4Dq + 3\lambda + 2A_2 - \frac{7}{2}h,$$

$$4Dq + 3\lambda - A_2 \quad (5)$$

and

$$4Dq + 3\lambda + 2A_2 + \frac{7}{2}h.$$

If the axial field component  $A_2$  takes on continuous value from zero to a maximum and the density of ions having a certain  $A_2$  falls off as the value of  $A_2$  increases, one finds that there will be a maximum at the observed  $g$  value. The linewidth and shape will depend on the distribution function. From the measured line width of about 480 gauss one can infer that the axial component is relatively small. Another possible explanation is that the wide line is caused by dipolar broadening. This would mean that at certain places the crystal divalent iron tends to aggregate.

The half-field line corresponds to a  $\Delta M = 2$  transition. Such a transition is strictly forbidden in a cubic field. Weak transitions could be observed in axial fields. The intensity of these transitions would vary roughly as  $A_2^2/hv$ . A distribution of values  $A_2$  would lead to an unsymmetrical line shape as found experimentally by Bleaney et al.,<sup>3</sup> in many nonKramers doublets of the rare earth group, such as praseodymium.<sup>4</sup> Bleaney et al. suggested that an additional term  $\Delta_x S_x + \Delta_y S_y$  should be included in the spin Hamiltonian where  $\Delta$  measures the splitting of the doublet. Transitions will occur at

$$hv = (g^2 \beta^2 H^2 + \Delta^2)^{\frac{1}{2}} \quad \text{where} \quad \Delta^2 = \Delta_x^2 + \Delta_y^2.$$

These transitions in the nonKramers doublets can be observed when  $H_{\text{eff}}$  is directed parallel to the  $z$  axis. In our case the situation is analogous. Transitions will be observed at

$$hv = [(2g\beta H)^2 + A_2^2]^{\frac{1}{2}}, \quad (6)$$

where  $A_2^2$  is the splitting between the singlet and the doublet. These are independent of the sign of  $A_2^2$ . Assuming some kind of distribution of values of  $A_2^2$

TABLE I. Orbital reduction factor for various ions in the iron group.

Crystal	Ion	$k$	Reference
MgO	$\text{Co}^{2+}$	0.89	(a)
ZnF <sub>2</sub>	$\text{Co}^{2+}$	0.90	(b)
MgO	$\text{Fe}^{2+}$	0.80	this paper
$\text{K}_3\text{Fe}(\text{CN})_6$	$\text{Fe}^{3+}$	0.87 <sub>6</sub>	(c)
$\text{K}_4\text{Mn}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	$\text{Mn}^{2+}$	0.74	(c)

<sup>a</sup> W. Low, Phys. Rev. **109**, 256 (1958).

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

<sup>c</sup> J. M. Baker, B. Bleaney, and K. D. Bowers, Proc. Phys. Soc. (London) **B69**, 1205 (1956); B. Bleaney and M. C. M. O'Brien, Proc. Roy. Soc. (London) **B69**, 1216 (1956).

<sup>3</sup> B. Bleaney, P. M. Llewellyn, M. H. L. Pryce, and G. R. Hall, Phil. Mag. **45**, 991 (1954).

<sup>4</sup> B. Bleaney and H. E. D. Scovil, Phil. Mag. **43**, 990 (1952).

it can be shown that the intensity is given by

$$I = \frac{(2g\beta)^3}{2h\nu} \frac{\delta H}{\delta H_0} f\left(\frac{\delta H}{\delta H_0}\right) dH, \quad (7)$$

where  $\delta H = (H_0/2) - H$  is the deviation of the magnetic field from that field at which resonance occurs.

$$f(\delta H/\delta H_0) = f(A_2^{x^2}/A_{02}^{x^2})$$

is the distribution of  $A_2^{x^2}$  with a certain range parameter  $\delta H_0$ . Irrespective of the assumption about the distribution function it is seen that  $I=0$  when  $\delta H=0$ , i.e., when  $H=H_0/2$ . The intensity increases in the direction of decreasing field, i.e.,  $H < H_0$ . Assuming a Gaussian distribution the maximum intensity would occur when  $\delta H = \delta H_0$ . Experimentally one finds that the extrapolated cut off occurs at  $2145 \pm 5$  gauss,  $\Delta M = \pm 1$  line at  $4812 \pm 2$  gauss, and  $\delta H_0$  about  $32 \pm 5$  gauss, at a wavelength of 1.298 cm. It is seen that the half-field line has a smaller spread than the wide line at  $H_0$ .

Actually the line has not quite a sharp cutoff on the high field side. It seems to taper off slightly at the end of the high field side and to extend a little beyond  $H_0/2$ . Any broadening mechanism of course will cause a distortion of the line shape as given by (7) and may be the cause of this minor deviation.

The origin of the wide line and this so-called forbidden transition is not known. It is of course very tempting to consider the possibility that it may be caused by an incipient Jahn-Teller effect. The Jahn-Teller theory indicates that the system whose ground state is orbitally degenerate will be unstable.<sup>5</sup> A distortion which will lift this degeneracy will lower the energy. Some evidence for a Jahn-Teller distortion has been found in cupric salts having trigonal symmetry.<sup>6,7</sup> These crystals show a high temperature spectrum in which the  $g$  factor is isotropic. Abragam and Pryce<sup>5</sup> have explained this as an average  $g$  value of a system in which the system resonates between distortions having the same energy.

There is also a low-temperature spectrum in which the  $g$  factor is highly anisotropic, and the spectrum indicates at least 3 inequivalent sets of ions. Finally there is a range of intermediate temperatures in which both the low- and high-temperature forms coexist.

If the observed spectra were to arise from a Jahn-Teller effect then the narrow isotropic line would correspond to the high-temperature form, the wide line as well as that at  $H_0/2$  to the low-temperature anisotropic form. In view of the fact that the line shape of the low-temperature form is independent of the orientation of the crystal with respect to the magnetic field this distortion must have equal probability in nearly all directions rather than along definite orientations. If

these distortions are small, however, and there are three or more inequivalent magnetic ions, it may prove to be difficult to observe any variation of line shape with orientation.

As tempting as this explanation is, we are not convinced of its necessity or truth. As mentioned above the ratio of the intensity of the narrow line to the wide line varies from crystal to crystal. One would have to assume that the Jahn-Teller effect needs a priming agent to get it started and that its extent may depend on other factors such as concentration, strains, and dislocations.

Another explanation of the two types of spectra may be the presence of many other impurities in the crystal. Nearly all crystals of magnesium oxide have paramagnetic impurities and diamagnetic impurities in concentration comparable or larger than the iron impurity. Some of these impurities have the "wrong" valence such as  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$ . These will tend to cause distortions and dislocations either near their lattice site or at some other site. It is possible that the divalent iron may fit poorly in the lattice and tend to aggregate near dislocations.

*Note added in proof.*—Orton et al. [(J. W. Orton, P. Auzins, and J. E. Wertz, Phys. Rev. Letters 4, 128 (1960))] have suggested that the narrow line corresponds to a double quantum transition between the levels  $S_z = -1$  and  $S_z = +1$  of the ground state triplet which has an effective spin 1.

We would like to make here another comment on the Jahn-Teller effect. It has been pointed out by Öpik and Pryce<sup>8</sup> and also by Van Vleck<sup>9</sup> that a large spin-orbit coupling may stabilize the system. It seems in general preferable to diagonalize the total matrix including the spin-orbit coupling and only then use the Jahn-Teller perturbation. It is then found that the Jahn-Teller matrix elements are considerably smaller. In this connection we want to point out that it may be worthwhile to consider the Jahn-Teller effect taking into account covalent bonding with the surroundings. It is not inconceivable that certain types of covalent bonding may tend to stabilize the configurations against Jahn-Teller distortions.

## B. THE PARAMAGNETIC RESONANCE AND OPTICAL SPECTRUM IN TETRAHEDRAL ZnS

### Experimental Results

The paramagnetic resonance spectra of three ZnS sphalerite crystals were observed at 3 cm and 1.25 cm wavelength at liquid hydrogen and liquid helium temperatures.<sup>10</sup> The spectroscopic analysis of the three crystals is given in Table II.

<sup>8</sup> U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) A238, 425 (1957).

<sup>9</sup> J. H. Van Vleck (private communication).

<sup>10</sup> One of these crystals has been kindly loaned to us by Dr. L. M. Matarrese (see L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids 1, 117 (1957)). Incidental to this work we have remeasured the paramagnetic resonance spectrum of  $\text{Mn}^{2+}$  and determined

<sup>5</sup> H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937).

<sup>6</sup> A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A63, 409 (1950).

<sup>7</sup> B. Bleaney, K. D. Bowers, and R. S. Trenam, Proc. Roy. Soc. (London) A228, 157 (1955).

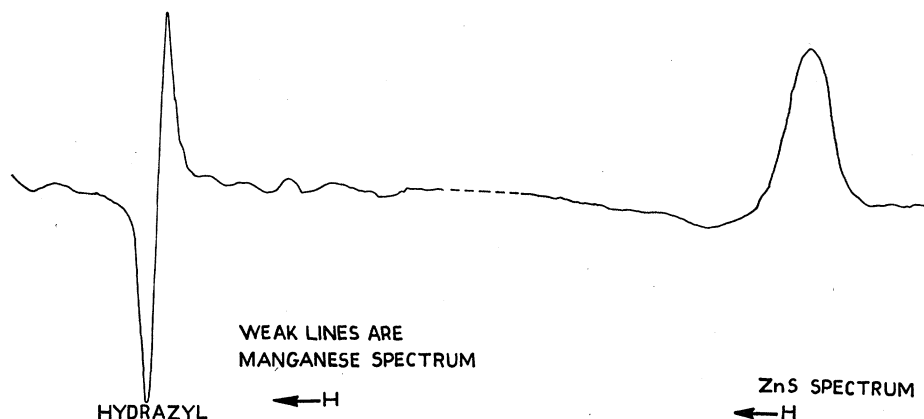


FIG. 4. Paramagnetic resonance absorption in ZnS. The spectrometer is so adjusted that a usual absorption spectrum appears at a first derivative.

The spectrum was measured at 1.25 cm wavelength to 13 000 gauss ( $g \sim 1.3$ ) and at 3 cm to about 6000 gauss ( $g \sim 1.15$ ). All three crystals gave the same spectra, one single line at  $g = 2.255$  (at 1.25 cm) and  $g = 2.245$  (at 3.3 cm). The line had the following peculiarities. When the crystal was mounted on one of its cleavage planes, i.e.,  $H_0 \parallel [111]$  plane and  $H \perp H_0$ , there was a slight anisotropy in the  $g$  factor when measured at the maximum absorption. The anisotropy was of the order of 3 parts per thousand of the  $g$  factor, of the order of the line width. The angular variation of the  $g$  factor repeats itself every  $60^\circ$ . If the crystal was mounted along the  $[001]$  plane the pattern repeats every  $90^\circ$ . Another aspect, which is not understood, was a variation in line shape. Both the line shape and intensity changes as the direction of  $H_0$  is varied. The line shape was asymmetrical for most angles (see Fig. 4). Since the derivative of the absorption is recorded it is very unlikely that part if not all of the angular variation in the  $g$  factor is caused by changes in the line shape. (We suspect that we are seeing a superposition of two different inequivalent lines which are very close. The relative intensity and separation of these line changes with the angle between the symmetry axis and the external magnetic field.)

The optical spectrum was taken on five different crystals and is shown in Figs. 5 and 6. All crystals gave the intense absorption at  $3 \mu$  although the detail of the fine structure in this band varies slightly from

crystal to crystal. The  $3 \mu$  band contains at least two resolved peaks at  $3700 \text{ cm}^{-1}$  and  $2850 \text{ cm}^{-1}$ . The band in the visible range consists of three peaks at  $13\,950 \text{ cm}^{-1}$ ,  $14\,550 \text{ cm}^{-1}$ , and  $15\,000 \text{ cm}^{-1}$ . It is less intense than the  $3 \mu$  band and was obtained on a single crystal of 1 cm thickness.

### Discussion

We cannot explain satisfactorily either the paramagnetic resonance or the optical spectrum. The following possibilities arise:

#### (a) Spectrum caused by $\text{Co}^{2+}$

The paramagnetic resonance spectrum of  $\text{Co}^{2+}$  in tetrahedral symmetry (if  $d^5p$  interaction is neglected) is expected to give a  $g$  factor of  $g = 2.0023 - 8\lambda/\Delta$ . As  $\lambda$  is of the order of  $-180 \text{ cm}^{-1}$  and  $\Delta$  about  $3500 \text{ cm}^{-1}$  the  $g$  factor would be about 2.4. If  $\lambda$  is reduced to about  $-100 \text{ cm}^{-1}$ ,  $g$  could be about 2.25. The optical transition at  $3 \mu$  corresponds in this case to the  ${}^4\text{T}_2 \rightarrow {}^4\text{T}_5$  transition, and that at  $0.7 \mu$  to  ${}^4\text{T}_2 \rightarrow {}^4\text{T}_4(P)$  transition. The fine structure separation of the last band of  $\sim 1000 \text{ cm}^{-1}$  corresponds to that expected of  $6\lambda_p$  or about  $900 \text{ cm}^{-1}$ . The following arguments speak against this assignment:

1. The spectroscopic analysis (see Table II) shows that in two of the three crystals the amount of cobalt is less than 0.001%. The amount of iron and manganese of these crystals is 0.3, 0.01 and 0.01, respectively. The intensity of the paramagnetic resonance spectrum was about half of the integrated manganese spectrum.

2. The optical spectrum of cobalt in  $\text{CaF}_2$  and in spinels has been investigated in detail.<sup>11</sup> In spinels the cobalt has a tetrahedral symmetry, as in ZnS. The spectrum always consists of three bands at  $3 \mu$ ,  $1.5 \mu$ , and  $0.6 \mu$  approximately. Furthermore the intensity of the band at  $0.6 \mu$  is by far stronger than either of the two bands. The absence of the band at  $1.5 \mu$  is difficult to understand. There exists of course the possibility that the band at  $3 \mu$  consists of two spectra, that of  $\text{Fe}^{2+}$  and of  $\text{Co}^{2+}$  superimposed one on top of the other.

TABLE II. Spectroscopic analysis of ZnS sphalerite crystals.

	Sample 1 in %	Sample 2 in %	Sample 3 in %
Mg	<0.001	<0.001	0.01
Mn	0.01	0.01	0.01–0.1
Si	0.001	0.001	...
Fe	0.03	0.03	0.1–1
Cd	0.01	0.03	0.02
Co	<0.001	<0.001	0.01–0.1

the sign of the cubic field splitting of manganese to be positive. This is in agreement with the recently published note by G. Watkins [G. O. Watkins, Phys. Rev. 110, 986 (1958)].

<sup>11</sup> R. Stahl-Brada and W. Low, Phys. Rev. 113, 775 (1959).

The spectrum of  $\text{Co}^{2+}$  at  $3\ \mu$  and at  $1.5\ \mu$  may be weaker than that at  $0.6\ \mu$ , so that the band at  $1.5\ \mu$  is not detected. The possibility that the spectrum arises from  $\text{Co}^{2+}$  is, therefore, not ruled out, although it is most unlikely.

(b) Spectrum caused by  $\text{Fe}^{2+}$  in cubic field

The energy levels of the  $d^6$  configurations in tetrahedral symmetry predict that the ground state would show isotropic lines at  $g=1\pm\frac{1}{5}\lambda/Dq$ . Similarly the large separation of the fine structure components cannot be accounted for.

Assuming  $\lambda=\lambda_0=-100\ \text{cm}^{-1}$  and  $Dq\sim 300\ \text{cm}^{-1}$ , there would be an energy level giving rise to a linear Zeeman splitting at  $g=0.93$  and another level, separated by  $18\lambda^2/5Dq\sim 10\ \text{cm}^{-1}$ , at  $g=1.07$ . Transitions corresponding to  $\Delta M=\pm 2$  are forbidden, except if there are deviations from cubic symmetry.

The optical spectrum presents some difficulty as well. The band at  $3\ \mu$  could correspond to the transition from  $\Gamma_3\rightarrow\Gamma_6$ . The width of the band, however, would be expected to be about  $5\lambda$  or maximum  $500\ \text{cm}^{-1}$ , and the fine structure consisting of three lines would have an approximate separation of about 200 and  $300\ \text{cm}^{-1}$ , respectively. The experimental separation between peaks is about  $900\ \text{cm}^{-1}$ . The band at  $0.7\ \mu$  is not understood either. It could conceivably originate from  ${}^3\Gamma_4({}^3H)$  which would be split into a triplet, through spin-orbit interaction. It is difficult, however, to account for the relative intensity of this spin-forbidden transition.

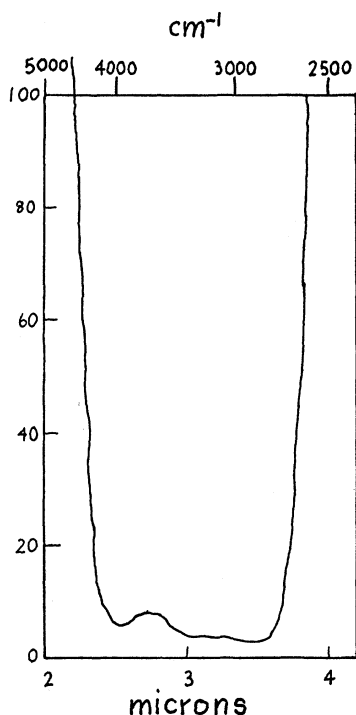


FIG. 5. The optical spectrum of ZnS in the infrared. Some of the crystals show an additional weak peak at about  $2800\ \text{cm}^{-1}$ .



FIG. 6. The optical spectrum of ZnS in the visible range.

(c) Effect of configurational mixing

If the conjectures in the preceding paper (I) are correct nearly any  $g$  factor can be expected. A relatively strong admixture of  $d^5p$  may reverse the energy levels in the ground state bringing the  $g=2.2$  level lower. The admixture of  $d^5p$  may contribute to the  $g$  value as well, i.e.,

$$g = \alpha^2 g(d^6) + \sum b_i^2 g_i(d^5p) + \sum c_j^2 g_j(d^5f),$$

where  $g(d^6)$  is the contribution of the  $d^6$  configuration and  $g(d^5p)$ ,  $g(d^5f)$  measure the  $g$  factor contributions of the various excited levels in the  $d^5p$  and  $d^5f$  configurations. The optical fine structure separation would not correspond to the 2:3 ratio but may show large deviations.

(d) Jahn-Teller distortion

If a Jahn-Teller distortion is present it is very likely to be along the cubic axes. For such an axial field one obtains a quintet at  $+2A_2$  and a similar quintet at  $-2A_2$ . The lower quintet ( $2A_2$  negative) consists of one doublet having a first order Zeeman effect at  $-3\lambda^2/5Dq \pm g\beta H(1 - \frac{2}{5}\lambda/Dq)$  and one doublet at  $-(6/5)\lambda^2/Dq$  as well as a singlet at  $-(9/5)\lambda^2/Dq$ . If  $\lambda \sim -62\ \text{cm}^{-1}$ , the  $g_{11}$  factor would be about 2.24. However, the expected  $g_1=0$ . Possibly this may account for the peculiar shape of the absorption line which is very similar to the  $\Delta M=2$  transition for  $\text{Fe}^{2+}$  in  $\text{MgO}$ . Similar considerations might hold true for a weak axial distortion along the  $[111]$  direction. The optical splitting of about  $900\ \text{cm}^{-1}$  would correspond to about  $5\lambda + 3A_2$ , from which one may infer  $A_2$  to be of the order of  $200\ \text{cm}^{-1}$ .

### 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).