

## Electron Paramagnetic Resonance of Iron in Gallium Arsenide

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The electron paramagnetic resonance spectrum of iron in GaAs has been studied at 9 Gc/sec. The spectrum corresponds to a spin  $5/2$  in a cubic environment and can be described by the two parameters in the spin Hamiltonian  $g=2.0462\pm 0.0006$  and  $a=(+339.7\pm 0.3)\times 10^{-4}$  cm $^{-1}$  at 1.3°K and  $g=2.0453\pm 0.0008$  and  $a=(+342.2\pm 0.5)\times 10^{-4}$  cm $^{-1}$  at 77°K. The iron apparently substitutes for the Ga and is observed when the defect is neutral. The temperature-independent linewidth of 54 G is attributed to hyperfine interaction with neighboring nuclei. If the interaction is assumed to be appreciable only with nearest neighbors, then the hyperfine constant is about 10 G. In addition to the allowed transitions, nine of the ten possible "quasi-forbidden" transitions between states for which the strong-magnetic-field quantum number differs by more than one unit have been identified. The angular dependence of the spectrum has been studied with the magnetic field in the  $(1\bar{1}0)$  plane. The positions and intensities of the transitions are found to agree in detail with those calculated from the spin Hamiltonian, except that the over-all intensity of the "quasi-forbidden" transitions is some 5 to 10 times too weak. The spin Hamiltonian with the Zeeman energy diagonal is given in its complete form for the magnetic field in the  $(1\bar{1}0)$  plane, from which a number of the qualitative features of the intensities of the "quasi-forbidden" transitions are readily obtained.

### I. INTRODUCTION

VERY few studies of defects in III-V compounds have been made by electron paramagnetic resonance. The first localized centers observed in a III-V compound were Mn and Fe impurities, both having a  $3d^5$  configuration, which were seen in GaP by Woodbury and Ludwig,<sup>1</sup> Almeleh and Goldstein<sup>2</sup> and later Bleekrode *et al.*<sup>3</sup> reported the observation of Mn,  $3d^5$ , in GaAs and de Wit and Estle<sup>4</sup> reported Fe,  $3d^5$ , and Ni,  $3d^7$ , in GaAs. Bleekrode *et al.*<sup>5</sup> and Goldstein and Almeleh<sup>6</sup> have reported independent studies of Fe in GaAs. Recently, Title<sup>7</sup> has observed the shallow acceptors Zn and Cd in GaAs subjected to uniaxial compression.

This investigation is concerned with the paramagnetic resonance spectrum of iron impurities in GaAs. The Fe is in an  $S$  state with spin  $\frac{5}{2}$  and is in a cubic environment. A comprehensive study of the observed "quasi-forbidden" transitions, for which the strong-field magnetic quantum number changes by more than one unit, has been made. This represents the first detailed study of the "quasi-forbidden" transitions for cubic symmetry, though some have been observed before.<sup>8</sup> The spin Hamiltonian is given in a form such that a number of the qualitative features of the position and

intensity of both the main transitions and the "quasi-forbidden" transitions become readily apparent. Precise calculations relating to these aspects of the spectrum have been performed and compared to the experimental observations.

### II. SPIN HAMILTONIAN

Gallium arsenide has the cubic zincblende structure, where each gallium atom is surrounded by arsenic atoms on the corners of a regular tetrahedron and vice versa. Iron is thought to be an acceptor in GaAs with an ionization energy of 0.37 eV.<sup>9</sup> If the iron substitutes for the gallium and is neutral, then it is expected to contribute three electrons to the bonds with the four adjacent arsenics as does the gallium in the regular lattice. The resultant configuration of the iron is then  $3d^5$  plus closed shells and saturated bonds, which results in a  ${}^6S$  ground state. A convenient way of summarizing the properties of the  ${}^6S$  term of iron in an environment having cubic symmetry is the spin Hamiltonian.<sup>10</sup>

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + \left(\frac{1}{6}a\right)[S_{\xi}^4 + S_{\eta}^4 + S_{\zeta}^4 - (1/5)S(S+1)(3S^2 + 3S - 1)], \quad (1)$$

where  $(\xi, \eta, \zeta)$  are the cubic  $\langle 100 \rangle$  axes of the crystalline field,  $\beta$  is the Bohr magneton,  $\mathbf{H}$  is the magnetic field,  $g$  is the spectroscopic splitting factor,  $S_i$  are the spin operator components,  $2S+1$  is the number of energy levels, and  $3a$  is the zero-field splitting of the lower doublet from the quartet. The electron paramagnetic resonance spectrum of Fe in GaAs has been interpreted with Eq. (1) and  $S=\frac{5}{2}$ . A total of fifteen magnetic dipole transitions are possible between the six levels

<sup>1</sup> H. H. Woodbury and G. W. Ludwig, Bull. Am. Phys. Soc. **6**, 118 (1961).

<sup>2</sup> N. Almeleh and B. Goldstein, Bull. Am. Phys. Soc. **7**, 200 (1962); Phys. Rev. **128**, 1568 (1962).

<sup>3</sup> R. Bleekrode, J. Dieleman, and H. J. Vegter, Phys. Letters **2**, 355 (1962).

<sup>4</sup> M. de Wit and T. L. Estle, Bull. Am. Phys. Soc. **7**, 449 (1962).

<sup>5</sup> R. Bleekrode, J. Dieleman, and H. J. Vegter, Philips Res. Rep. **17**, 513 (1962).

<sup>6</sup> N. Almeleh and B. Goldstein, Bull. Am. Phys. Soc. **7**, 542 (1962); B. Goldstein and N. Almeleh, Appl. Phys. Letters **2**, 130 (1963).

<sup>7</sup> R. S. Title, IBM J. Res. Develop. **7**, 68 (1963).

<sup>8</sup> J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) **73**, 948 (1959); W. Low and D. Shaltiel, J. Phys. Chem. Solids **6**, 315 (1958).

<sup>9</sup> F. A. Cunnell, J. T. Edmond, and W. R. Harding, Solid-State Electron. **1**, 97 (1960).

<sup>10</sup> A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

described by Eq. (1). If  $g\beta H \gg 3a$ , then five of these transitions will be much more intense than the other ten and will also occur at higher magnetic fields. These five are the  $\Delta M=1$  transitions and give rise to the usual  $\text{Fe}^{3+}$  fine structure. Here  $M$  is the strong magnetic field quantum number. The other ten transitions have  $\Delta M > 1$  and are referred to as "quasiforbidden" transitions because they are strictly forbidden in the limit of large magnetic fields. The "quasiforbidden" transitions have been considered previously by Kittel and Luttinger,<sup>11</sup> who calculated the intensities with the magnetic field in a  $\langle 100 \rangle$  direction. Thus far only a few superficial observations of these transitions<sup>8</sup> for  $S$ -state ions in a cubic field have been reported.

The positions and intensities of these fifteen transitions were calculated as a function of the angle  $\theta$  between the  $[001]$  axis and the magnetic field when this field is in the  $(1\bar{1}0)$  plane. The parameters  $g$  and  $a$  were obtained from data taken with  $\mathbf{H}$  along the  $[001]$  and  $[111]$  directions, since these directions were easily identifiable. The energy levels have been given as a power series<sup>12</sup> in  $a/g\beta H$ , but the convergence becomes poor at the low magnetic fields where the  $\Delta M > 1$  transitions occur. The present calculations were therefore performed on an electronic computer. For the usual experimental conditions where the magnetic field is varied and the microwave frequency is held fixed, it is necessary to obtain the magnetic field at which the energy difference between a particular pair of levels is equal to the microwave quantum. A search program for this purpose was written around an already available

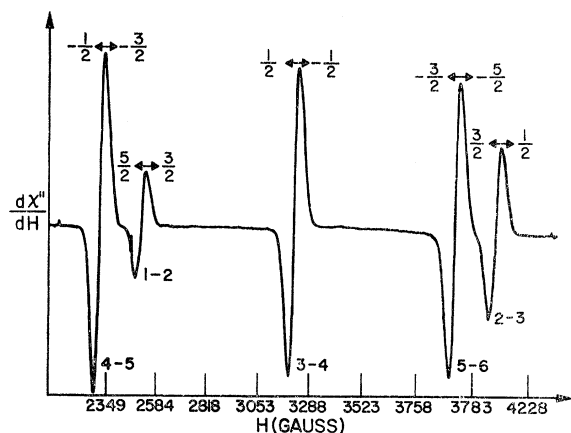


FIG. 1. The derivative of the absorption versus magnetic field for the  $\Delta M=1$  transitions of Fe in GaAs, when  $T=1.3^\circ\text{K}$ ,  $\nu=9.2$  Gc/sec, and  $\mathbf{H}$  is along the  $[001]$  direction. The pattern of the amplitudes corresponds to a positive field splitting parameter  $a$ . The levels between which the transitions occur are designated by the strong magnetic field quantum number  $M$  in the upper part of the figure or by the rank in order of decreasing energy of the level in the lower part.

<sup>11</sup> C. Kittel and J. M. Luttinger, Phys. Rev. **73**, 162 (1948).

<sup>12</sup> R. de L. Kronig and C. J. Bouwkamp, Physica **6**, 290 (1939).

eigenvalue program for an IBM-7090 computer. The eigenfunctions were also obtained and the intensities of all the transitions were calculated for a temperature of  $1.3^\circ\text{K}$ . For this calculation it is convenient to have the spin Hamiltonian in a form where the Zeeman energy is diagonal. Some of the qualitative features of the angular variation of the intensities of the  $\Delta M > 1$  transitions are then also apparent on inspection.

The spin Hamiltonian, transformed so that the Zeeman energy is diagonal and the magnetic field is in the  $(1\bar{1}0)$  plane, is

$$\mathcal{H} = g\beta HS_z + \frac{a}{120} \sum_{m=-4}^4 F_m(\theta) T_m^{(4)}(\mathbf{S}),$$

$$T_0^{(4)} = \frac{1}{8} [35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2],$$

$$T_{\pm 1}^{(4)} = \mp \frac{1}{8} (5)^{1/2} S_{\pm} (2S_z \pm 1) [7S_z^2 \pm 7S_z - 3S(S+1) + 6],$$

$$T_{\pm 2}^{(4)} = \frac{1}{8} (10)^{1/2} S_{\pm}^2 [7S_z^2 \pm 14S_z - S(S+1) + 9],$$

$$T_{\pm 3}^{(4)} = \mp \frac{1}{8} (35)^{1/2} S_{\pm}^3 (2S_z \pm 3),$$

$$F_{\pm 4}^{(4)} = \frac{1}{16} (70)^{1/2} S_{\pm}^4,$$

$$F_0 = 2(15 \cos^4\theta - 10 \cos^2\theta - 1),$$

$$T_{\pm 1} = \pm 4(5)^{1/2} \sin\theta \cos\theta (3 \cos^2\theta - 1),$$

$$F_{\pm 2} = 2(10)^{1/2} \sin^2\theta (3 \cos^2\theta - 1),$$

$$F_{\pm 3} = \pm 4(5/7)^{1/2} \sin\theta \cos\theta (5 - 3 \cos^2\theta),$$

$$F_{\pm 4} = (10/7)^{1/2} (3 \cos^2\theta - 1)(\cos^2\theta - 3), \quad (2)$$

where  $\theta$  is the angle between the direction of  $\mathbf{H}$  and the  $[001]$  axis. The  $y$  axis is the  $[1\bar{1}0]$  direction and  $S_{\pm} = S_x \pm iS_y$ . The spin Hamiltonian of Eq. (2) does not reduce to Eq. (1) when  $\theta=0^\circ$ , but differs from it by a rotation of  $45^\circ$  about the  $[001]$  axis. A method for performing the transformation of Eq. (1) into Eq. (2) has been given by Matarrese and Kikuchi.<sup>13</sup> They evaluated the diagonal term  $F_0$  for an arbitrary orientation and also<sup>14</sup> the tensor operators  $T_m^{(4)}(\mathbf{S})$ .

The microwave magnetic field was perpendicular to the applied magnetic field  $\mathbf{H}$  in the present work so that the transition probability amplitude was taken proportional to the matrix element of  $S_y$ . However, transitions are also possible when the microwave magnetic field is along  $\mathbf{H}$ .<sup>11</sup>

<sup>13</sup> L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).

<sup>14</sup> C. Kikuchi and L. M. Matarrese, J. Chem. Phys. **33**, 601 (1960).

## III. RESULTS

## A. Allowed Transitions

When the magnetic field is along the [001] direction the five lines corresponding to the  $\Delta M=1$  transitions are well resolved, and a spectrum taken at 1.3°K, is shown in Fig. 1. The parameters in the spin Hamiltonian were evaluated from the data taken at 9 Gc/sec with the field along the [001] and [111] directions and are  $g=2.0462\pm 0.0006$  and  $a=(+339.7\pm 0.3)\times 10^{-4}$  cm<sup>-1</sup>, at 1.3°K, and  $g=2.0453\pm 0.0008$  and  $a=(+342.2\pm 0.5)\times 10^{-4}$  cm<sup>-1</sup>, at 77°K. The [001] and [111] directions were located to within 0.1° by rotation of the sample about a horizontal axis and the magnetic field about a vertical axis until a maximum in the splitting was obtained.

These values are more accurate than the ones reported earlier.<sup>4</sup> When the  $g$  factor is taken to be positive, the identity of the transitions in Fig. 1 and the positive sign of  $a$  can be deduced from the relative intensities of the resonance lines at 1.3°K. The uncertainties are determined by the accuracy with which the position of the lines can be measured, all other sources of error being smaller.

Recently Bleekrode, Dieleman, and Vegter<sup>5</sup> have

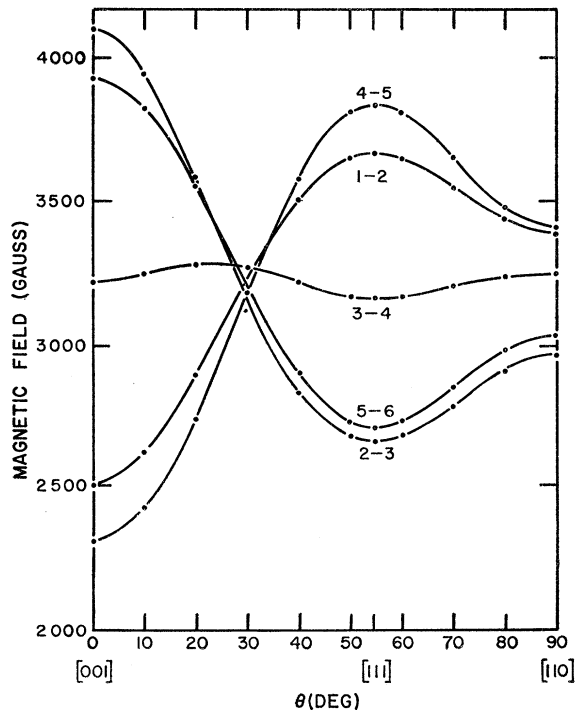


FIG. 2. The magnetic field positions versus  $\theta$  of the  $\Delta M=1$  transitions, when  $T=1.3^\circ\text{K}$  and  $\nu=9.2$  Gc/sec. The levels between which the transitions occur are designated by their rank in order of decreasing energy. The dots are the measured values, the lines are the calculated ones. The experimental uncertainty is less than the size of the dots.

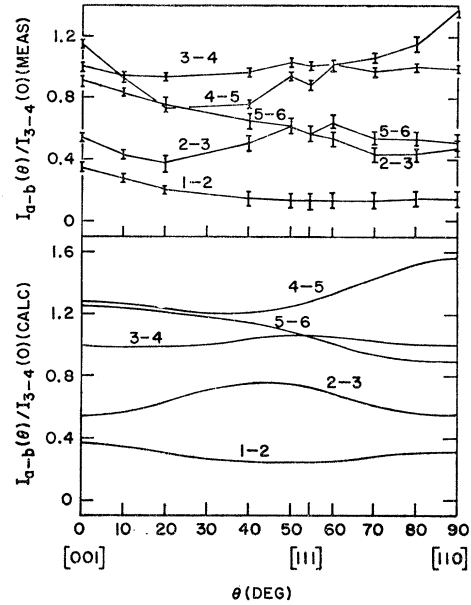


FIG. 3. The intensities versus  $\theta$  of the  $\Delta M=1$  transitions, when  $T=1.3^\circ\text{K}$  and  $\nu=9.2$  Gc/sec. The intensities are normalized to that of the 3-4 line at  $\theta=0^\circ$ . The measured values are in the upper part of the figure and the calculated values in the lower part.

reported the spectrum of Fe in GaAs at 77°K and 9 Gc/sec but obtained values of  $a$  and  $g$  significantly smaller than in the present work. The discrepancy may result from a few degrees misalignment of the sample used by Bleekrode *et al.*<sup>5</sup>

Goldstein and Almeleh<sup>6</sup> also reported on what is apparently the same spectrum, which they do not attribute to iron impurities. The quoted values of  $g$  and  $a$  are larger than those of the present work, but no uncertainties are given so that a significant comparison of the values is not possible. Their interpretation will be discussed in more detail later in this section.

The complete angular dependence of all the transitions was measured with a crystal whose axes were determined from x-ray diffraction patterns. The crystal was placed in the microwave cavity with the [110] axis vertical to within one degree. The observed and calculated positions of the  $\Delta M=1$  transitions are shown in Fig. 2. Where the spectral lines are at least partially resolved the calculated positions agree with the measured ones to within the uncertainty. No deviations in the positions that could be attributed to misalignment of the crystal in the cavity were observed. The angular dependence of the relative intensities of the  $\Delta M=1$  transitions has been calculated and compared to the measured one. The agreement is good for the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition but the other transitions are sometimes as much as 50% weaker than predicted. The comparison is shown in Fig. 3. The discrepancies are not understood.

The linewidth, taken here to be the peak-to-peak width of the derivative of the absorption curve, is  $54 \pm 2$  G for the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition and is independent of angle and temperature for  $T \leq 77^\circ\text{K}$ . When they are resolved, the widths of the other  $\Delta M = 1$  transitions are approximately the same as for the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition. The rather large linewidth can be attributed to unresolved hyperfine structure resulting from an interaction with the Ga and As nuclei. If the linewidth is attributed entirely to the hyperfine interaction with the arsenic ligands, which occur with a 100% abundant isotope of spin  $\frac{3}{2}$ , then the hyperfine interaction constant is about 10 G. The lineshape which would result from these circumstances would be approximately Gaussian. It would be somewhat more truncated than a Gaussian however, and this is consistent with the observed shape.

Efforts to observe the lines at room temperature were unsuccessful, probably indicating a considerable decrease in  $T_1$  in going to room temperature. The lines saturated somewhat easier at all temperatures than  $\text{Fe}^{3+}$  in ionic crystals.

The spectrum has been observed only in *p*-type samples obtained from iron-doped GaAs ingots. The ingots were grown using a gradient-freeze technique and contained no other impurities in appreciable concentration. A careful measurement of the iron concentration as observed by electron paramagnetic resonance was made for two samples. The intensities of the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition were compared to the mechanical damage line in silicon<sup>15</sup> at  $77^\circ\text{K}$ . The spin density of the Si sample was, in turn, calibrated by comparison with a  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  crystal. After allowance was made for the difference in spin, transition probability, linewidth, and shape, the molar iron concentrations turned out to be  $60$  and  $9 \times 10^{-6}$ . Subsequently, a carefully calibrated emission spectrographic analysis, in which these samples were burned to completion, indicated, respectively, iron concentrations of  $760$  and  $45 \times 10^{-6}$ . A similar but qualitative correlation was found for iron-doped GaAs crystals which were cut in half, one half spectroscopically analyzed and the other half observed by electron paramagnetic resonance. The iron electron paramagnetic resonance spectrum is not observed when the spectroscopic analysis showed an iron concentration less than  $10^{-6}$ . Ingots doped with other impurities, but grown in the same way, do not show the iron spectrum. Other III-V compounds show very similar spectra when heavily doped with iron.<sup>1,16</sup>

Thus, all of the experimental facts support the view that iron produces the observed center. Goldstein and Almeleh<sup>6</sup> have attributed the spectrum to intrinsic defects. It seems more likely that they have observed

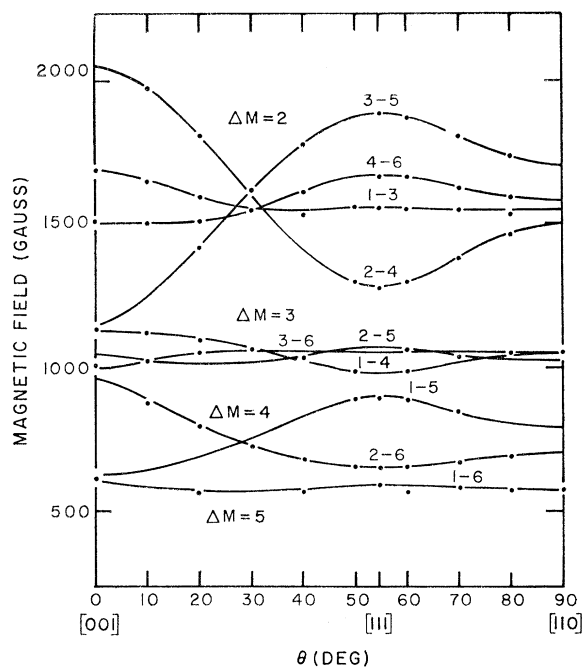


FIG. 4. The magnetic field positions versus  $\theta$  of the  $\Delta M > 1$  transitions, when  $T = 1.3^\circ\text{K}$  and  $\nu = 9.2$  Gc/sec. The levels between which the transitions occur are designated by their rank in order of decreasing energy. The dots are the measured values, the lines are the calculated ones. The experimental uncertainty is generally a few times larger than the size of the dots.

iron which has diffused into their samples during heat treatment, or which was already present and was converted from a charge state in which the resonance is not observed to the one in which it is observed. It is not understood why their intensity measurements disagree with the concentrations obtained by mass spectrographic analysis and with the present work. The substitution of iron for a gallium atom seems the most reasonable model, even though the paramagnetic resonance results do not indicate directly how the iron is incorporated in the lattice. The Fe in a Ga site will presumably transfer three electrons to the valence shell to form tetrahedral bonds and the neutral impurity will have the  $3d^5$  configuration. It would seem unlikely that the Fe would substitute for the As, but the possibility that it is incorporated in one of the two interstitial sites cannot be ruled out at present.

### B. "Quasiforbidden" Transitions

The measured positions of the  $\Delta M > 1$  lines at low magnetic fields are more uncertain than those of the  $\Delta M = 1$  transitions because of their low intensity, typically 100 to 1000 times less than that of the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition. Within the uncertainty all of the observed lines are consistent with the assignment of  $\Delta M > 1$  transitions as shown in Fig. 4. The strong

<sup>15</sup> G. K. Walters and T. L. Estle, J. Appl. Phys. **32**, 1854 (1961).

<sup>16</sup> T. L. Estle (unpublished).

magnetic field description of the energy levels breaks down at these low magnetic fields. The energy levels are simply labeled from 1 to 6 in order of decreasing energy, and  $\Delta M$  is taken to be the difference of the indices for the two levels between which the transition occurs. In particular, at the low magnetic fields where the  $\Delta M=4$  and 5 transitions occur, the level 6 changes from  $M=-\frac{5}{2}$  character for  $\theta>20^\circ$  to almost pure  $M=-\frac{3}{2}$  character at  $\theta=0^\circ$ . The positions of the transitions are given roughly by the first few terms in the power-series expansion. Since the angular dependence of these expressions is dominated by the quantity  $F_0(\theta)$  of Eq. (2), all transitions except 1-6 and 2-5 show a similar angular dependence. The exceptions occur because the first-order contribution from  $F_0$  vanishes for the 1-6 and 2-5 transitions. This dependence on  $F_0$  will produce the following properties. The splitting of a given  $\Delta M$  group will be approximately zero for  $\theta=29.7^\circ$  and a maximum at  $\theta=0^\circ$ , with a secondary maximum at  $\theta=54.7^\circ$ . The maximum magnetic field splitting of the  $\Delta M=2, 3,$  and 4 groups will be in the ratio 15:2:6. The center of gravity of a given  $\Delta M$  group will occur at about the value for the  $\Delta M=1$  group divided by  $\Delta M$ . These qualitative features are verified by the results shown in Fig. 4. The agreement between the measured positions and the exact calculation is within the experimental uncertainty.

There is no angle at which all ten of the  $\Delta M>1$  transitions have been observed and the 2-5 transition has not been observed at all. A few of the  $\Delta M>1$  transitions are sufficiently intense to be observed at 77°K, but those discussed here were observed at 1.3°K. The linewidths appeared to be the same as that of the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition although the uncertainty was often rather large.

The observed and calculated intensities of these  $\Delta M>1$  transitions at 1.3°K are shown in Fig. 5. It should be noted that the scales used for the measured and calculated results are different. The observed transitions are typically 5 to 10 times weaker than predicted, but are otherwise in excellent detailed agreement with the calculated values.

A number of the qualitative features of the intensities are readily deduced from Eq. (2). In the present experiments the microwave magnetic field  $\mathbf{H}_1$  is perpendicular to the applied field  $\mathbf{H}$ . For this geometry the only off-diagonal contributions that do not vanish at  $\theta=0^\circ$  are those proportional to  $F_{\pm 4}$ . Thus, only  $\Delta M=3$  and 5 transitions are allowed for  $\theta=0^\circ$ . For parallel orientations of the magnetic fields only  $\Delta M=4$  transitions are allowed. The observations as recorded in Fig. 5 agree with these predictions except that two of the  $\Delta M=2$  transitions are also observed at  $\theta=0^\circ$ . This can be attributed to strains or to a small misalignment of the crystal, since for these transitions the calculated intensity increases very rapidly with angle

near  $\theta=0^\circ$ . The apparent anomaly of the intensities of the 1-5 and 1-6 transitions is a result of the breakdown of the strong field quantum number description as discussed above. When  $\theta=54.7^\circ$  one has in a similar fashion, since  $F_{\pm 3}$  do not vanish, that the  $\Delta M=2, 4,$  and 5 transitions are allowed for perpendicular fields and the  $\Delta M=3$  transitions for parallel fields. When  $\theta=90^\circ$  then  $F_{\pm 2}$  and  $F_{\pm 4}$  do not vanish. Therefore,  $\Delta M=3$  and 5 transitions are allowed with perpendicular fields and  $\Delta M=2$  and 4 transitions with parallel fields. These predictions are again verified by the observations.

Some of the more detailed features of the angular dependence of the intensities can be explained with perturbation theory taken to second order. For example, the sequence of decreasing intensity of the  $\Delta M=2$  transitions in the region of  $\theta=20^\circ$  is expected to be 4-6, 3-5, 2-4, 1-3, because of the Boltzmann factor. However, the perturbation theoretic contributions to the eigenfunctions proportional to  $F_{\pm 1}$  are some three times larger than those proportional to  $F_{\pm 3}$  at  $\theta=20^\circ$ . But the relevant matrix elements of  $T_{\pm 1}^{(4)}$  vanish for the 3-5 and 2-4 transitions, and as a consequence they are weaker than the 1-3 transition. The decrease in intensity of all the  $\Delta M=2$  transitions near  $\theta=50^\circ$  can be attributed to a destructive interference between the contributions proportional to  $F_{\pm 1}$  and  $F_{\pm 3}$  in the transition probability. This becomes a constructive interference beyond  $\theta=54.7^\circ$ . The very small intensity of the 2-5 transition results from an approximate cancellation of terms in the transition probability. In a second-order perturbation calculation the various matrix elements are identical and energy denominators are opposite in sign and almost equal. A similar argument applies to the  $\Delta M=5$  transition. However, it is much more qualitative since the perturbation series does not converge as rapidly as in the  $\Delta M=3$  case, and the almost complete cancellation does not occur at all angles.

Griffiths and Orton<sup>8</sup> have observed  $\Delta M>1$  transitions for  $\text{Fe}^{3+}$  in MgO and Low and Shaltiel<sup>8</sup> have reported on some of these transitions for  $\text{Gd}^{3+}$  in  $\text{ThO}_2$ . Both of these reports indicate  $\Delta M=4$  transitions were observed for  $\mathbf{H}$  along [100]. The observation of  $\Delta M=4$  transitions may have resulted from a slight misorientation of the crystal or from a component of  $\mathbf{H}_1$  parallel to  $\mathbf{H}$ .

#### IV. CONCLUDING REMARKS

The entire observed spectrum has been interpreted as arising from a spin  $\frac{5}{2}$  system in cubic symmetry. Two parameters suffice to describe the positions and intensities of the 15 possible transitions. Nine of the ten possible transitions with  $\Delta M>1$  have been identified, but the  $\frac{3}{2} \leftrightarrow -\frac{3}{2}$  transition is expected to have a very low intensity and has not been observed. The angular dependence of the positions has been explained

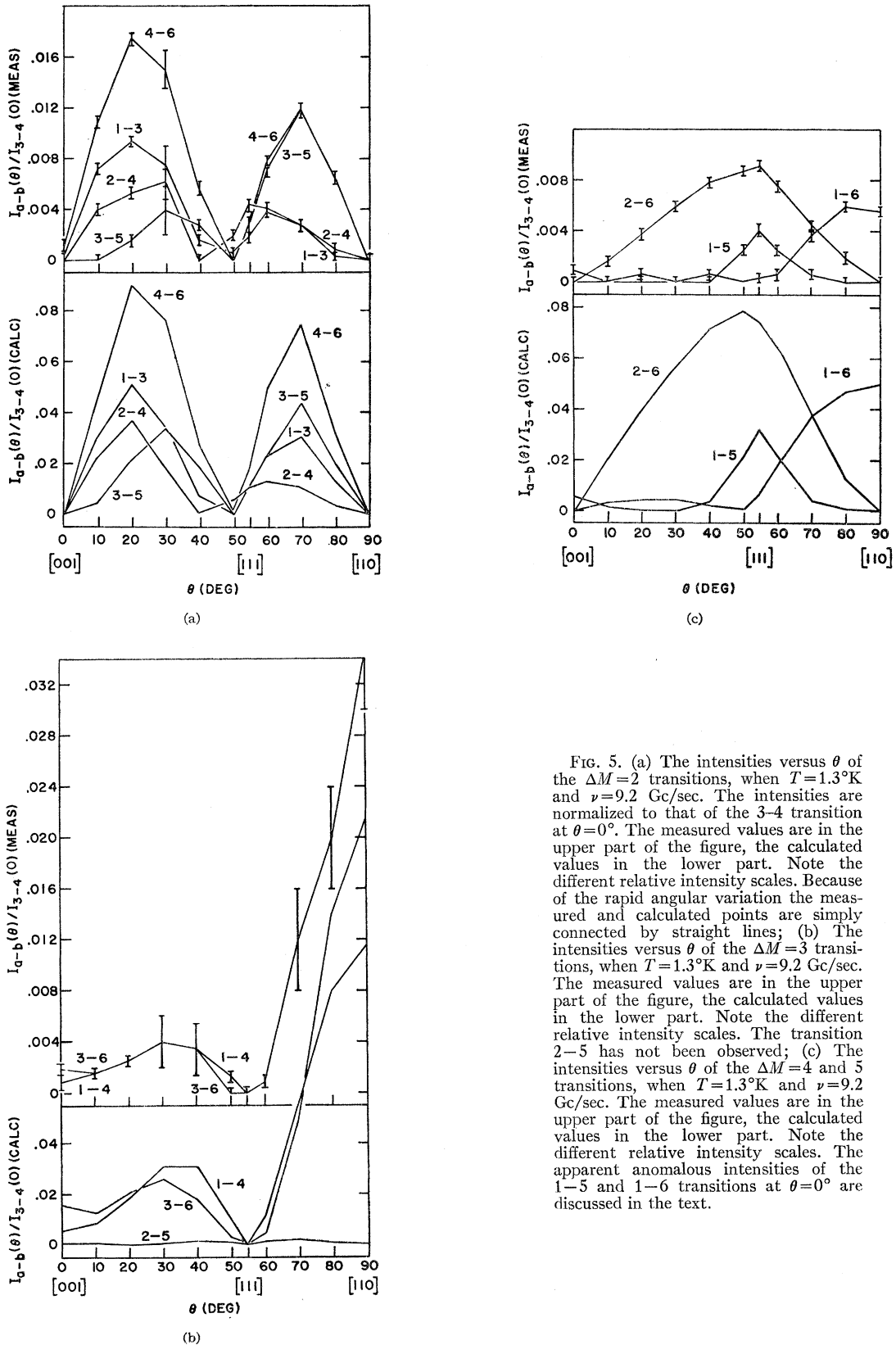


FIG. 5. (a) The intensities versus  $\theta$  of the  $\Delta M=2$  transitions, when  $T=1.3^\circ\text{K}$  and  $\nu=9.2$  Gc/sec. The intensities are normalized to that of the 3-4 transition at  $\theta=0^\circ$ . The measured values are in the upper part of the figure, the calculated values in the lower part. Note the different relative intensity scales. Because of the rapid angular variation the measured and calculated points are simply connected by straight lines; (b) The intensities versus  $\theta$  of the  $\Delta M=3$  transitions, when  $T=1.3^\circ\text{K}$  and  $\nu=9.2$  Gc/sec. The measured values are in the upper part of the figure, the calculated values in the lower part. Note the different relative intensity scales. The transition 2-5 has not been observed; (c) The intensities versus  $\theta$  of the  $\Delta M=4$  and 5 transitions, when  $T=1.3^\circ\text{K}$  and  $\nu=9.2$  Gc/sec. The measured values are in the upper part of the figure, the calculated values in the lower part. Note the different relative intensity scales. The apparent anomalous intensities of the 1-5 and 1-6 transitions at  $\theta=0^\circ$  are discussed in the text.

to within the experimental uncertainty, but the observed intensities are generally weaker than the calculated ones.

The strong correlation which has been found between the electron paramagnetic resonance intensity and the Fe concentration in the GaAs crystals, and the observation of a spin  $\frac{5}{2}$  system, lead us to the identification of the center as the  $3d^5$  configuration of Fe, presumably at a Ga site.

The values of the parameters in the spin Hamiltonian are larger than usual. The zero field splitting parameter  $a$  is about  $340 \times 10^{-4} \text{ cm}^{-1}$ , whereas it is usually less than  $200 \times 10^{-4}$  for  $\text{Fe}^{3+}$  in cubic crystals other than the III-V compounds. The value reported for GaP,<sup>1</sup>  $390 \times 10^{-4} \text{ cm}^{-1}$ , is the only other large value in the literature. The  $g$  shift,  $\Delta g = g - 2.0023$ , is  $+0.044$ , for Fe in GaAs. Again with the exception of GaP,<sup>1</sup> this is the only  $g$  shift of this magnitude which has been reported. The usual value is about ten times less, although ZnS has a  $g$  shift about half that in GaAs.<sup>17</sup> The large  $a$  and  $\Delta g$  may be related to the rather covalent nature of the III-V compounds and the resultant delocalization of the magnetic electrons of the iron impurity. The wide Gaussian lineshape is another manifestation of this delocalization. Although crystal field calculations<sup>18</sup> for  $S$ -state ions give rise to a negative

<sup>17</sup> A. Rauber and J. Schneider, Z. Naturforsch. **17a**, 266 (1962).

$g$  shift, Fidone and Stevens<sup>19</sup> have shown that covalency effects can produce a positive  $g$  shift.

The study of Fe in III-V compounds should prove very useful for the understanding of the effects of covalency on iron-group impurities. Electron nuclear double resonance should be particularly useful as should a study of  $g$ ,  $a$ , and the linewidth of Fe in a series of such compounds. Studies of this nature are currently in progress.

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<sup>18</sup> H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957); M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Letters **5**, 145 (1960); J. R. Gabriel, D. F. Johnston, and M. J. D. Powell, Proc. Roy. Soc. (London) **A264**, 503 (1961).

<sup>19</sup> I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **73**, 116 (1959).