

Paramagnetic Resonance Absorption Spectrum of Trivalent Iron in Single-Crystal Calcite*†

S. A. MARSHALL AND A. R. REINBERG

Physics Division, Armour Research Foundation, Chicago, Illinois

(Received 20 May 1963)

The electron paramagnetic resonance absorption spectrum of trace amounts of trivalent iron in single crystals of natural calcite has been observed at 9.6 kMc/sec. The spectrum is symmetric about the crystal [111] direction which, together with the doublet character of each spectral component, suggests that the trivalent iron ions occupy sites closely approximating those of the calcium ions. At 77°K, the best-fit parameters to the spin Hamiltonian are found to be $g_{11}=g_{\perp}=2.0030$, $B_2^0=343.23$ Oe, $B_4^0=-0.69102$ Oe, and $|B_4^3|=15.6$ Oe. The signs of the zero-field splitting parameters, determined by comparing relative line intensity ratios at 1.5 and at 77°K, are such that the $\pm\frac{3}{2}$ doublet spin state lies lowest. From this, it is concluded that the sign of the cubic-field splitting parameter is positive. The spectrum is found to exhibit a strong linewidth anisotropy. From the dependence of this broadening on the polar angle θ , it is concluded that the sites occupied by this ion have a mosaic structure whose width is given by $\delta\theta=0.04$ deg. An x-ray diffraction analysis of the calcite single crystal yields a mosaic angle of $\delta\theta=0.011$ deg.

I. INTRODUCTION

TRIVALENT iron has a $3d^5$ electron configuration and by Hund's rule a ${}^6S_{5/2}$ ground term. From predictions based on group theoretical arguments, such a term can have its sixfold spin degeneracy partially lifted by the application of a crystalline electric field.¹ The manner in which this spin degeneracy is lifted will depend upon the symmetry properties of the electric field. For example, in a field of cubic symmetry this state splits into two terms, one being a spin doublet and the other a spin quartet. For a field of trigonal symmetry, which is the case for the calcite structure, the sixfold spin degeneracy is lifted in such a manner as to leave three spin doublet terms. Although the theory of groups accurately predicts the manner in which the spin degeneracy of an S -state ion is lifted by a crystalline electric field, it does not predict the sign or magnitude of the splitting. This is simply a consequence of the fact that the theory of groups concerns itself with questions related to symmetry and not with the physical details of interactions operative in degeneracy removal. From the fact that S -state ions, as for example divalent manganese and trivalent iron, are observed to have their ground term spin degeneracies lifted by crystalline electric fields, it has been concluded that such terms must, in fact, be admixtures of excited states. The mechanisms by which such terms can have their spin degeneracies lifted has been treated by a number of investigators beginning with the proposals of Van Vleck and Penney.²⁻⁵

In treating the problem of term splitting of $3d^5$ ions in nearly cubic crystals, Watanabe concludes that the crystal-field splitting parameter a of the spin Hamil-

tonian should vary as the square of the crystal-field energy Dq .⁴ If this were the case, it would then follow that for a given $3d^5$ ion, the sign of a would be positive for sites having either tetrahedral or octahedral coordination. This has, indeed, been found to be the case. Watkins, for example, has found the sign of a to be positive for divalent manganese in both zincblende and germanium where the sites in question for these two structures have tetrahedral coordination.⁶ For manganese in magnesium oxide, where the sites have octahedral coordination, Low has found the sign of a to be positive.⁷ Recently, Geschwind has reported on trivalent iron in both the tetrahedrally and octahedrally coordinated sites of garnet.⁸ He similarly finds that a is positive for both sites and concludes that for the processes operative in causing removal of spin degeneracy of an S term, the dominant elements must be proportional to even powers of the crystal field energy Dq .

In a later report, Watanabe suggests that paramagnetic resonance absorption experiments on S -state ions be carried out at high hydrostatic pressure, the object of such an experiment being to see if the crystal field splitting parameter a would vary under compression in a manner predictable by theory.⁹ Such experiments have been carried out by Walsh¹⁰ on divalent manganese and trivalent iron in magnesium oxide and on divalent manganese in zincblende with results which disagree with Watanabe's predictions.

In this report, we wish to present the results of an investigation on trivalent iron in calcite single crystals. It is hoped that the information herein presented will prove to be of interest not only because it deals with an S -state ion located in an octahedrally coordinated environment, but also because of the observed temperature dependent variations in the spin-Hamiltonian

* This work supported by the U. S. Air Force, Rome, New York.
† S. A. Marshall and A. R. Reinberg, *Bull. Am. Phys. Soc.* **8**, 24 (1963); J. Wakabayashi, *J. Chem. Phys.* **38**, 1910 (1963).

¹ H. Bethe, *Ann. Physik* **3**, 133 (1929).

² J. H. Van Vleck and W. G. Penney, *Phil. Mag.* **19**, 961 (1934).

³ M. H. L. Pryce, *Phys. Rev.* **80**, 1107 (1950).

⁴ H. Watanabe, *Progr. Theoret. Phys. (Kyoto)* **18**, 405 (1957).

⁵ M. J. D. Powell, J. R. Gabriel, and D. P. Johnston, *Phys. Rev. Letters* **5**, 145 (1960).

⁶ G. D. Watkins, *Phys. Rev.* **110**, 986 (1958).

⁷ W. Low, *Phys. Rev.* **105**, 793 (1957).

⁸ S. Geschwind, *Phys. Rev.* **121**, 363 (1961).

⁹ H. Watanabe, *Phys. Rev. Letters* **4**, 410 (1960).

¹⁰ W. M. Walsh, Jr., *Phys. Rev. Letters* **4**, 507 (1960).

parameters and how such variations compare with the theory presented by Watanabe and with the experimental results of Walsh.

II. EXPERIMENTAL PROCEDURE

The magnetic resonance absorption spectrometer used in obtaining the spectrum of this crystal-ion system operates in the 3-cm wavelength region and makes use of 30 Mc/sec superheterodyne detection. Zeeman fields are provided by a rotatable 12-in. electromagnet having a 2.5-in. pole gap. Calcite samples for magnetic resonance absorption study are placed along the axis of a cylindrical cavity resonator operating in the TE_{011} mode. With this mode of operation, the microwave magnetic field vector passing through the sample is directed along the axis of the cavity and as the Zeeman field is rotated in a plane perpendicular to this axis, no spurious absorption line intensity variations are produced. Zeeman field strengths are determined by using a nuclear magnetic resonance absorption magnetometer. Proton or lithium resonance absorptions are superimposed on the absorption peaks as displayed on a cathode-ray oscilloscope screen. The Zeeman field strength is then read out by measuring the frequency of the magnetometer. Microwave frequency is determined by measuring the beat frequency resulting from mixing, at a crystal diode, a sample of the microwave oscillator output with a close-by harmonic of the output of a 10 Mc/sec quartz crystal controlled oscillator.

At temperatures below 200°K it was found necessary to use superheterodyne detection because of saturation of the resonance absorptions. To avoid strong saturation, the spectrometer was operated such that the power levels incident at the cavity resonator were not greater than one microwatt. At these power levels, resonance absorption lines identified as being due to trivalent iron and divalent manganese could be observed on a cathode-ray oscilloscope screen at signal-to-noise ratio levels of the order of ten to one. With the sample held at liquid-nitrogen temperature, the power at the cavity resonator could not be sufficiently reduced to cause negligible saturation of the iron and manganese resonance absorption lines. At this temperature, saturation effects were noticed at power levels of 10^{-8} W. At these low power levels, the feedback loops in the klystron frequency lock-in circuits failed to function partly because of the low microwave signal power and partly because of leakage of microwave power through various waveguide components.

Natural calcite single crystals were obtained from the Crystal Optics Company of Chicago, Illinois, and from the Chicago Natural History Museum. Crystals used in this investigation were analyzed by wet chemistry techniques and found to contain 4 and 5 parts per million (ppm) by weight of manganese and iron, respectively. No other iron-group impurities could be detected. Single, rhombohedral crystals having dimensions of the order of 1 in. on a side were oriented and

cut into parallelepipeds of length 1 in. with cross sections of $\frac{1}{4}$ in. \times $\frac{1}{4}$ in. Final polar angle orientation of the samples was checked by looking through crossed polaroids for a cross interference pattern. All calcite samples used were polar angle oriented to within ± 0.5 deg. The orientation of the C—O bond direction of the carbonate ion, from which the azimuthal angle is taken, was established to within ± 1 deg by referring to an x-ray diffraction pattern.

III. RESULTS AND DISCUSSION

Calcite, which is the rhombohedral form of CaCO_3 , belongs to the space group D_{3d}^6 . The structure can be visualized as that of NaCl with a compressional distortion along the crystal $[111]$ direction. The carbonate ions lie in planes perpendicular to the shortened axis and in a given plane all carbonate ions have the same relative orientation, with a given C—O bond along a crystal $[01\bar{1}]$ direction. Carbonate ions in alternate planes are related by a 60-deg rotation about the crystal c axis. This produces an alternation in direction of the carbonate ion groups and gives rise to two inequivalent cation sites in the structure. The local symmetry of each of these sites is S_6 due to a distorted oxygen octahedron of the nearest neighbors. The transformation which brings one site into the other is reflection in a plane perpendicular to a carbon-oxygen bond. If one, therefore, picks a C—O bond direction to be the x axis, the azimuthal angle ϕ for one site goes over to $\pi + \phi$ for the other.

Electron paramagnetic resonance absorption spectra of S -state ions of the first transition series have been reported in many host lattices of differing symmetries.^{11–13} For the most part, these spectra have been interpreted in terms of a spin Hamiltonian due to Bleaney and Trenam.¹⁴ In the case of trivalent iron located at the trigonally symmetric calcium ion sites of calcite, the spin Hamiltonian has five parameters which must be experimentally determined. Thus, by a proper choice of five resonance transitions, one can, in principle, determine the parameters of the Hamiltonian.

The spin Hamiltonian used to analyze the spectrum of trivalent iron in calcite is given by

$$H = \beta H \cdot g \cdot S + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^3 O_4^3 + (B_4^3 O_4^3)^*, \quad (1)$$

which is equivalent to that of Bleaney and Trenam and where the spin operators O_n^m are given by

$$\begin{aligned} O_2^0 &= 3S_z^2 - S(S+1), \\ O_4^0 &= 35S_z^2 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) \\ &\quad + 3S^2(S+1)^2, \quad (2) \\ O_4^3 &= 1/4[S_z(S_+^3 + S_-^3) + (S_+^3 + S_-^3)S_z]. \end{aligned}$$

¹¹ K. D. Bowers and J. Owens, Rept. Progr. Phys. **18**, 304 (1955).

¹² J. W. Orton, Rept. Progr. Phys. **22**, 204 (1959).

¹³ W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960).

¹⁴ B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).

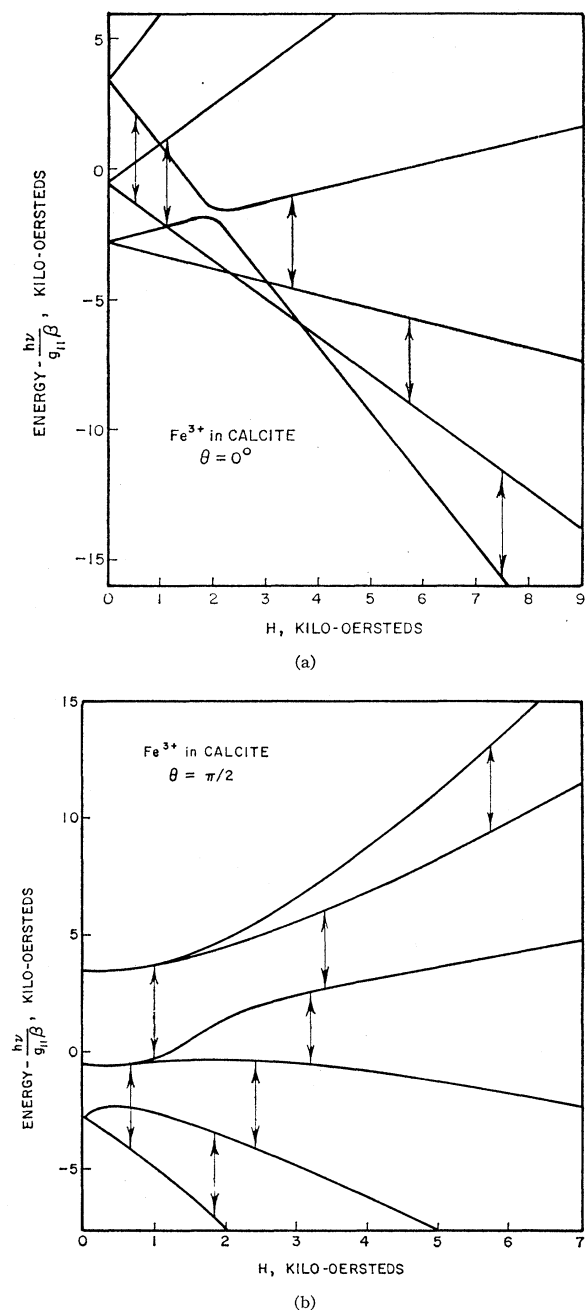


FIG. 1. Energy level diagram for the trivalent iron-calcite system at (a) $\theta=0$ and (b) $\theta=\frac{1}{2}\pi$.

The coordinate system is so chosen as to make the z axis coincide with the crystal $[111]$ direction. The matrix representation of the Hamiltonian operator given by Eq. 1, where the matrix elements are evaluated in terms of the six spin vectors which make up the $S=\frac{5}{2}$ manifold, is given by Table I. The matrix shown is for either of the two inequivalent calcium-ion sites. To obtain this matrix for the other site in our coordinate system it is necessary to replace B_4^3 by $-B_4^{3*}$. For the

particular case of the magnetic field vector oriented along the crystal $[111]$ direction, the energy eigenvalues are given by

$$\begin{aligned}
 E(\pm\frac{5}{2}) &= \pm g_{11}\beta H + B_2^0 + 90B_4^0 \\
 &\quad + [(\pm\frac{3}{2}g_{11}\beta H + 9B_2^0 - 30B_4^0)^2 \\
 &\quad\quad + 90|B_4^3|^2]^{1/2}, \\
 E(\pm\frac{3}{2}) &= \pm\frac{3}{2}g_{11}\beta H - 2B_2^0 - 180B_4^0, \\
 E(\pm\frac{1}{2}) &= \mp g_{11}\beta H + B_2^0 + 90B_4^0 \\
 &\quad - [(\mp\frac{3}{2}g_{11}\beta H + 9B_2^0 - 30B_4^0)^2 \\
 &\quad\quad + 90|B_4^3|^2]^{1/2},
 \end{aligned} \tag{3}$$

where the eigenvalues refer to the high-field limit. From these six energy states, five magnetic resonance transitions are predicted corresponding to the selection rule $\Delta M_s = \pm 1$. These transitions are given in Fig. 1(a) for the iron-calcite system at a spectrometer wavelength of approximately 3 cm. From the field positions of four of these transitions, the parameters g_{11} , B_2^0 , B_4^0 , and B_4^3 are determined with the fifth transition being used as a check. At the $\theta=90$ -deg orientation, seven strong resonance absorptions are observed [see Fig. 1(b)]. From the field position of any one of these seven absorptions, the parameter g_1 can be obtained. At intermediate orientations, the spectrum becomes complicated due to the doublet nature of each resonance absorption line and partially because of anisotropic line broadening experienced by all of the lines. A qualitative description of the observed spectrum showing the mean of the doublet positions is given in Fig. 2, where the resonance absorption field strengths are plotted as functions of the polar angle θ . No spectral dependence on the azimuthal angle was observed when the polar angle was kept at 90 deg. From this particular spectral independence of ϕ , it is concluded that the trivalent iron ions are located at sites having axial symmetry. Furthermore, since each iron resonance absorption splits into a doublet, it is concluded that the most likely site occupied by this ion is either a calcium-ion site or one which is very close to such a site.

The spectrum of this crystal-ion system was observed at nine different temperatures between 1.5 and 300°K at intervals of approximately 50°K. Over this temperature range, the spectroscopic splitting tensor was found to be constant and isotropic while the crystal field parameters were found to decrease in magnitude with increasing temperature. At 77°K the best fit parameters to the spin Hamiltonian were determined to be $g_{11}=g_1=2.0030$, $B_2^0=343.29$ Oe, $B_4^0=-0.69102$ Oe, and $|B_4^3|=15.6$ Oe. Figure 3 gives the temperature dependence of the parameters B_2^0 and B_4^0 . The signs of the crystal field parameters were established by comparing relative absorption line intensity ratios at 1.5°K with those at 77°K. The signs so determined are such as to leave the $S_z = \pm\frac{1}{2}$ Kramers doublet lowest in energy in the absence of a Zeeman field.

TABLE I. Matrix representation of the operator given by Eq. (1) evaluated within the $S = \frac{5}{2}$ manifold.
 $\alpha = g_{11}\beta H \cos\theta$; $\beta = g_{11}\beta H \sin\theta e^{i\varphi}$.

	$\frac{3}{2}$	$\frac{5}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{5}{2}$	$-\frac{3}{2}$
$\frac{3}{2}$	$\frac{3}{2}\alpha - 2B_2^0 - 180B_4^0$	$\frac{1}{2}(\sqrt{5})\beta$		$\sqrt{2}\beta^*$		
$\frac{5}{2}$	$\frac{1}{2}(\sqrt{5})\beta^*$	$\frac{5}{2}\alpha + 10B_2^0 + 60B_4^0$	$3(\sqrt{10})B_4^3$			
$-\frac{1}{2}$		$3(\sqrt{10})B_4^{3*}$	$-\frac{1}{2}\alpha - 8B_2^0 + 120B_4^0$	$\frac{3}{2}\beta$		$\sqrt{2}\beta^*$
$\frac{1}{2}$	$\sqrt{2}\beta$		$\frac{3}{2}\beta^*$	$\frac{1}{2}\alpha - 8B_2^0 + 120B_4^0$	$-3(\sqrt{10})B_4^3$	
$-\frac{5}{2}$				$-3(\sqrt{10})B_4^{3*}$	$-\frac{5}{2}\alpha + 10B_2^0 + 60B_4^0$	$\frac{1}{2}(\sqrt{5})\beta$
$-\frac{3}{2}$			$\sqrt{2}\beta$		$\frac{1}{2}(\sqrt{5})\beta^*$	$-\frac{3}{2}\alpha - 2B_2^0 - 180B_4^0$

As is shown in Eq. (1), the crystal-field parameter B_4^3 is given as a complex number. Since the secular equation at $\theta=0$ deg does not depend on B_4^3 but on its absolute value squared, its complex nature cannot be determined from the spectrum obtained at this orientation or at $\theta=90$ deg. At polar angle orientations other than these two, the complex nature of B_4^3 is demonstrated in two ways. The first is in a doubling of each of the spectral components, where the magnetic field spacing between a pair of doublets varies directly as the real component of B_4^3 . This doubling also reveals the inequivalence of the two calcium-ion sites in calcite. The second is a relative shift in the energy levels and consequently in the Zeeman field position for resonance absorption. This varies directly as the imaginary

component of B_4^3 . Such splitting and resonance absorption field shifts have been discussed by Kikuchi,¹⁵ McConnell,¹⁶ and Matarrese and Kikuchi¹⁷ for divalent manganese in calcite. In these analyses, the crystalline electric field energy is treated as a perturbation to the Zeeman field energy which is valid for this crystal-ion system at Zeeman energies of the order of 1 cm^{-1} . In the case of trivalent iron in calcite with the spectrometer operating in the 3-cm wavelength region, the crystalline electric field and Zeeman field energies are of the same order so that neither energy can be considered as a perturbation to the other. The energy operator must, therefore, be diagonalized with both terms simultaneously present. To do this we have, in a straightforward manner, expanded the 6×6 eigenvalue determinant for each calcium-ion site for small values of the polar angle. Writing $B_4^3 = a + ib$, one finds in the expansion of each of these two determinants a group of terms which are even functions of the Zeeman field, the polar angle, the absolute value of B_4^3 , and which are independent of the azimuthal angle. The remaining term in the secular equation is found to be proportional to $\sin^3\theta \cos\theta (a \cos 3\phi - b \sin 3\phi)$. The only difference between the secular equations for the two calcium ion sites in calcite is that if for one site we have B_4^3 then

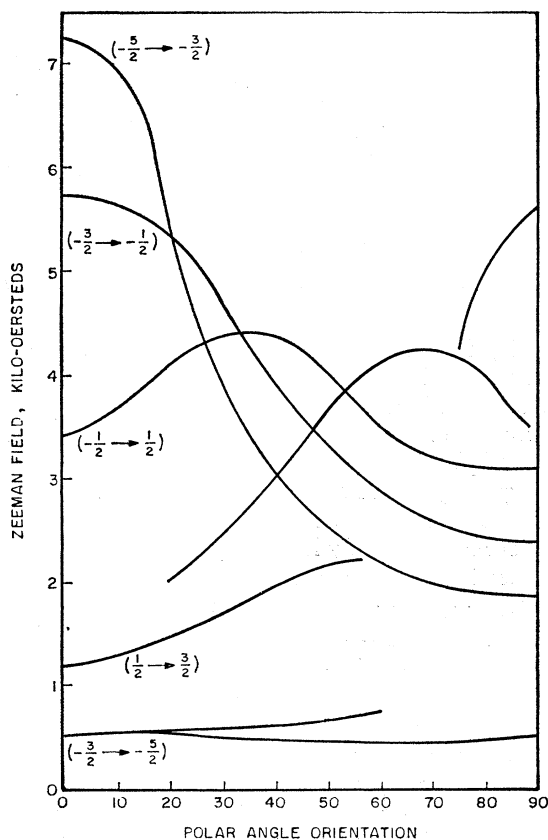
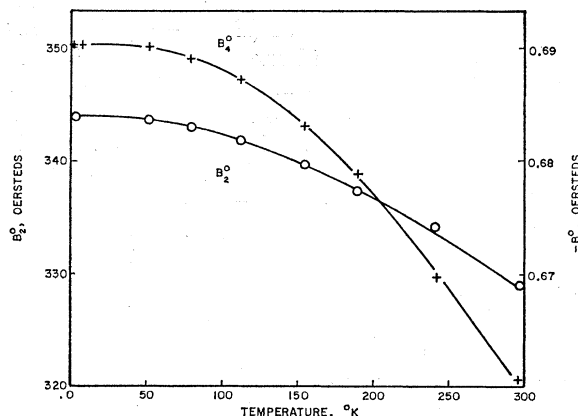


FIG. 2. Isofrequency plot of trivalent iron-calcite system spectrum.

FIG. 3. Temperature dependence of the parameters B_2^0 and B_4^0 for the trivalent iron-calcite system.¹⁵ C. Kikuchi, Phys. Rev. **100**, 1243 (1955).¹⁶ H. M. McConnell, J. Chem. Phys. **24**, 904 (1956).¹⁷ L. M. Matarrese and C. Kikuchi, J. Chem. Phys. **23**, 601 (1960).

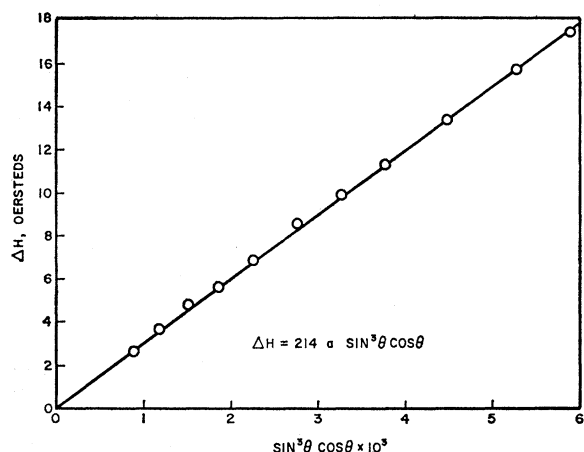


Fig. 4. Doublet separation versus $\sin^3\theta \cos\theta$ at $\phi=0$ deg for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ trivalent iron transition.

for the other site we have $-B_4^{3*}$. By taking the difference in resonance absorption field strengths for small values of the polar angle, we arrive at the following expression for the doublet separations in the spectrum of trivalent iron in calcite:

$$\Delta H = \frac{720(g_{\perp}/g_{\parallel})^3 H_0 H_i^4 a \sin^3\theta \cos\theta \cos 3\phi}{dF(E_i)/dH - dF(E_{i-1})/dH}, \quad (4)$$

where H_0 is the microwave energy converted into magnetic field, H_i is the mean magnetic field of the doublet, F is the ϕ independent part of the secular equation, $F(E_i)$ and $F(E_{i-1})$ are the function F evaluated at the roots E_i and E_{i-1} of the full secular equation, and where E_i and E_{i-1} are the energy levels between which the transitions in question occur. We thus see that for small doublet separations, ΔH varies as $a \sin^3\theta \cos\theta \cos 3\phi$ for all the iron-calcite transitions, where by small is meant a doublet separation sufficient to make the approximation $F(E_i, H_i) - F(E_i, H_i - \Delta H) = [dF(E_i)/dH] \Delta H$ a valid one. This relation between ΔH and θ has been experimentally verified for all five observed iron-calcite transitions at small values of the polar angle. This verification is shown in Fig. 4, which gives the doublet separation ΔH plotted against the function $\sin^3\theta \cos\theta$ for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition with the azimuthal angle held at zero. This particular transition yields the largest of the five doublet separations for a given value of the polar angle.

Using Eq. (4) the ratio of the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ to the $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ doublet separation is calculated to be 2.1:1 at $\theta = 10$ deg and $\phi = 0$ deg with the spectrometer operating in the region of 9600 Mc/sec. The experimentally observed ratio was found to be 2.2:1. There is, in addition to this ratio, another piece of information which one can obtain from Eq. (4); this is the sign of the doublet separation for a particular transition at a given value of the polar angle. If one could identify a specific doublet component with a specific calcium ion

TABLE II. Theoretically obtained signs of the doublet splittings for trivalent iron in calcite.

Transition	Sign of doublet splitting
$M_s = -\frac{5}{2} \rightarrow -\frac{3}{2}$	+
$M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$	-
$M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$	+
$M_s = \frac{1}{2} \rightarrow \frac{3}{2}$	+
$M_s = -\frac{3}{2} \rightarrow -\frac{5}{2}$	-

site, then the sign of the splitting for a given transition could be determined absolutely. This, unfortunately, cannot be done because of the arbitrary phase in the ϕ dependence of the Hamiltonian. Assuming, as seems almost certain to be the case, that the doublets are a consequence of iron ions located at the two inequivalent calcium-ion sites in calcite, the relative sign of the splittings can be determined provided the doublets have signatures. Such signatures do, in fact, exist for the doublet components of the iron-calcite spectrum by virtue of their unequal intensities. In all of the calcite specimens studied for this report, the intensities of the iron doublets were found to be unequal. The relative intensities varied among samples from 10:1 to close 1:1. Assuming that this difference in doublet intensity is due to a difference in population of trivalent iron in the two sites, the relative signs of the splittings of all the transitions should be predictable by fixing the sign of the splitting of one particular transition. The $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition is arbitrarily taken to have a positive splitting. Thus, for this transition, if for a given value of the polar angle the high field doublet component is the more intense, then for some other transition the splitting is called positive if the high field doublet component is the more intense and negative if it is less intense. Table II gives the predicted signs of the splittings for the five trivalent iron ion transitions where the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition doublet splitting is arbitrarily given a positive sign. The predictions are in complete agreement with the experimentally determined signs.

From the slope of the straight line given in Fig. 4, the real part of B_4^3 is determined to be 13.8 Oe and consequently the imaginary part must be 7.3 Oe with probable errors of plus or minus 10%. That B_4^3 is neither real nor purely imaginary can be demonstrated by referring to Fig. 5 which is an isofrequency plot of the $M_s = -\frac{3}{2} \rightarrow -\frac{1}{2}$ doublet transition for small values of the polar angle. As stated previously, our calcite single crystals are cut in such a manner as to have the [111] direction contained within the plane in which the Zeeman field is rotated and with the azimuthal angle set at zero. The misalignment of the polar angle is not more than 0.5 deg. If the crystal [111] direction is located precisely in the plane of rotation of the Zeeman field, then this plane will be one of constant magnitude of the azimuthal angle. On the unit sphere, $\theta = 0$ deg

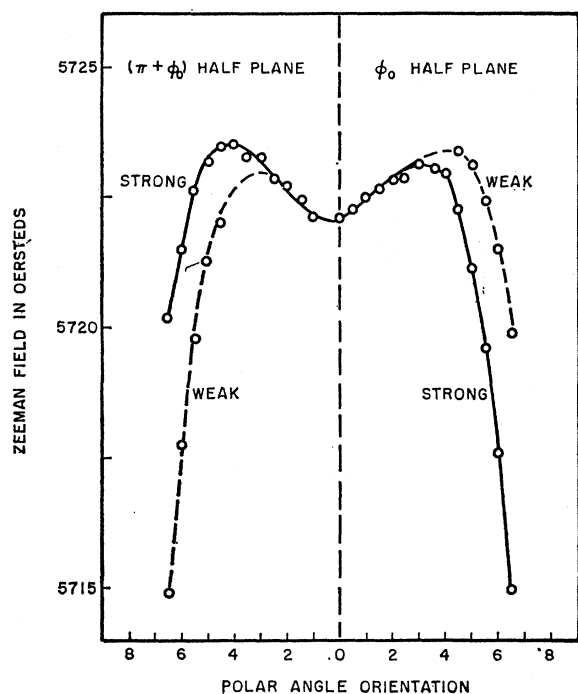


FIG. 5. Isofrequency plot of the $M_s = -\frac{3}{2} \rightarrow \frac{1}{2}$ doublets of iron-calcite.

is a singular point since at this orientation ϕ is undefined. Thus, as the Zeeman field is rotated in, say, a clockwise direction from the $\theta=0$ -deg position we say that the Zeeman field vector lies in a ϕ_0 half-plane and if the rotation is counterclockwise we say that the vector lies in a $(\pi+\phi_0)$ half-plane. If, on the other hand, the crystal $[111]$ direction does not lie precisely in the plane of rotation of the Zeeman field, then the $\theta=0$ -deg orientation cannot be achieved so that the azimuthal angle will change continuously from ϕ_0 to $(\pi+\phi_0)$ as the angle between the Zeeman field vector and the direction of minimum θ is changed continuously through $\theta=\min$ in a counterclockwise sense. The smaller the minimum angle θ , the more slowly will ϕ vary in the region of large θ and the more swiftly will it vary in the region of minimum θ . Since ϕ must assume an integral multiple value of $\frac{1}{2}\pi$ at some nonvanishing value of the polar angle, it will in a well-behaved manner do this at some finite value of θ . This behavior of ϕ will manifest itself in two ways; first, the doublet splitting will prematurely go to zero and second, the mean field position of the doublet will show either an abnormal dip or peak in the isofrequency plot at orientations near the minimum of θ . For the case shown in Fig. 5, the doublets for this transition are no longer resolved at $\theta=2$ deg which cannot be explained solely in terms of linewidths. Furthermore, the figure shows a well-resolved dip in the isofrequency plot at the position of minimum θ . The full and dashed curves correspond to the stronger and weaker doublet components, respectively. If B_4^3

were purely imaginary, there would be no doubling of the spectral components and if it were real, there would be but one extremum in the isofrequency plot near the minimum of θ which would occur at exactly $\theta=\min$. The figure also shows that the spectrum is not invariant under the transformation $\phi_0 \rightarrow (\pi+\phi_0)$. That is, the solid curve in the ϕ_0 half-plane does not go over to its mirror image in the $(\pi+\phi_0)$ half-plane. This is as it should be since the secular equation is not invariant under the transformation $\phi_0 \rightarrow (\pi+\phi_0)$. This transformation does, however, send the secular equation for a calcium-ion site over into that of an inequivalent calcium ion site.

That B_4^3 is a complex parameter is, of course, solely a consequence of our choice of coordinate system, specifically the direction of the x axis. The azimuthal dependence of the crystalline electric field potential is given by

$$V = -2 \sin^3 \theta \cos \theta (a' \cos 3\phi - b' \sin 3\phi), \quad (5)$$

where we assume that a' and b' are proportional to a and b of the parameter B_4^3 in the spin Hamiltonian. This potential has a stationary value when $\tan 3\phi_s = -b'/a'$. Substituting our values of a and b in the ratio b'/a' we find that the potential has a stationary value when the azimuthal angle is given by $\phi_s = 21 \pm 2$ deg. From the calcite structure parameters, the ϕ coordinate of the nearest oxygen-atom neighbors of the calcium-ion sites is given as 19.45 deg as measured from a C—O bond direction which is our choice of x axis.¹⁸ We thus conclude that if the crystalline electric field potential is explored along any cone of constant θ , the potential will display stationary values along or very close to the ϕ coordinates of the nearest oxygen atom neighbors of the calcium ion sites. Comparison of the Hamiltonian matrix for the two inequivalent calcium ion sites shows that these two Hamiltonians will be identical for the case where $B_4^3 = B_4^{3*}$. This will occur when B_4^3 is a pure imaginary number, which will be the situation if the x axis is taken perpendicular to a direction for which the crystal electric field potential has a stationary value. Our measurements indicate that this will occur when the magnetic field is rotated in a plane which contains the crystal c axis and where the ϕ coordinate is 90 deg with reference to the ϕ coordinate of the calcium nearest oxygen direction. Therefore, no splittings should be observed for the magnetic field along this direction.

As stated previously, the only iron-group elements to be detected in concentrations of any consequence in the calcite single crystals used for this investigation were manganese and iron. These were present to the extent of several parts per million by weight. For crystals of such low magnetic ion concentration and having a total of less than 1.5% magnetic host nuclei, it would seem that the magnetic resonance absorption

¹⁸ C. Kikuchi, AFOSR TN 59-220 (1959).

linewidths would be quite narrow and reasonably well predicted from the Van Vleck¹⁹ spin-spin interaction relation. This, in fact, turns out to be the case for both the divalent manganese and trivalent iron ion resonance absorption lines. For example, the full widths at points of half-signal intensity at $T=4.2^\circ\text{K}$ for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transitions of manganese and iron were 0.03 and 0.09 Oe, respectively. These linewidths, especially those of manganese are to within order of magnitude the widths that are predicted from spin-spin interaction broadening. Using the magnetic ion concentration obtained from the chemical analysis and the calcite structure parameters, the rms linewidth for an $S = \frac{5}{2}$ ion is found to lie between 5 and 10 mOe. The narrowness of the observed resonance absorption lines is undoubtedly due to the high degree of crystal perfection of calcite and the almost complete lack of nuclear hyperfine interaction. It also suggests that the principal sources of line broadening are spin-spin interaction and lattice-orbit-spin interaction. Temperature dependence of the manganese and iron resonance absorption line widths is given in Table III. It will be noted that for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transitions of manganese the width of the lines shows no noticeable change between 77 and 4.2°K . This lack of linewidth change plus evidence obtained from other very narrow resonance absorptions observed in the region of $g=2$ for these calcite samples suggests that the manganese resonances are very likely narrower than is indicated by our measurements. One can consider a few possible sources of line broadening arising from the spectrometer. These could be, a randomness in the signal oscillator frequency, sidebands produced by frequency modulation of the signal oscillator frequency, and Zeeman field inhomogeneities. Of these, only the Zeeman field inhomogeneities seem to be a likely source of the 30-mOe line broadening. A simple calculation indicates that the other sources of broadening could not account for linewidths greater than 4 mOe. On the other hand, since the 30-mOe linewidths are observed in the manganese spectrum, the linewidths of the iron spectrum and their temperature variations can, for the most part, be taken as observations independent of instrumentation.

TABLE III. Temperature dependence of linewidths. Linewidths in gauss.

	Temp. ($^\circ\text{K}$)	4.2	77	112	193	300
Fe^{3+}	$-\frac{1}{2} \rightarrow \frac{1}{2}$	0.09	0.25	0.45	1.4	9.5
	$\frac{1}{2} \rightarrow \frac{3}{2}$	0.63	0.58	0.94	2.8	13.0
	$\frac{3}{2} \rightarrow \frac{5}{2}$	0.94	0.92	1.4	6.4	18.0
Mn^{2+}	$-\frac{1}{2} \rightarrow \frac{1}{2}$	0.03	0.04	0.06	0.14	0.44
	$\frac{1}{2} \rightarrow \frac{3}{2}$	0.16	0.17	0.19	0.19	0.44
	$\frac{3}{2} \rightarrow \frac{5}{2}$	0.29	0.35	0.31	0.31	0.67

¹⁹ J. H. Van Vleck, Phys. Rev. 74, 1184 (1948).

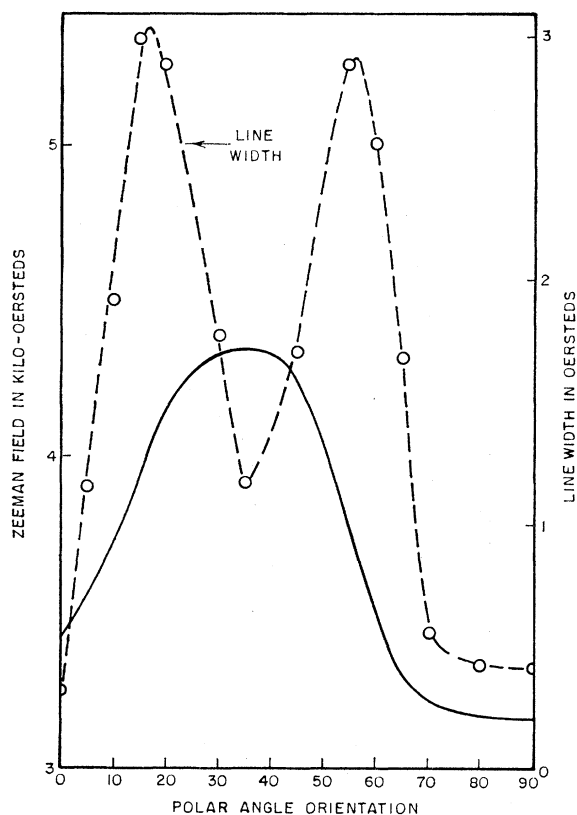


FIG. 6. Linewidth anisotropy for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition of iron-calcite.

There are, of course, other sources of line broadening such as that caused by crystal mosaic structure, vertical broadening which is due to variations in the relative slopes of the Zeeman field dependent Hamiltonian eigenvalues, and broadening due to spatial fluctuations of the parameters of the spin Hamiltonian. However, none of these effects can produce any significant broadening of the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition when the Zeeman field and crystal $[111]$ direction are parallel. Figure 6 shows the effect of crystal mosaic on the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition linewidth of iron in calcite. The solid curve is the isofrequency plot for this transition taken from $\theta = 0$ to 90 deg while the dashed curve is a plot of the resonance absorption linewidth. It will be noted that the linewidth data exhibits extrema at those values of θ for which the slope of the isofrequency plot exhibits extrema. The fact that the linewidth at $\theta = 35$ deg does not return to its $\theta = 0$ deg value is due to vertical broadening which reaches a shallow maximum at this orientation. Such a correlation is characteristic of broadening due to mosaic and, since the theory has been treated elsewhere,^{20,21} only the results will be given here. The data presented in Fig. 6 yields a crystal mosaic angle of 0.04 deg. An analysis based

²⁰ D. Shaltiel and W. Low, Phys. Rev. 124, 1062 (1961).

²¹ S. A. Marshall, T. Kikuchi, and A. R. Reinberg, J. Phys. Soc. (Japan) 17, Suppl. B-I, 450 (1962).

on x-ray diffraction data taken on a sample cut from the same calcite single crystal used for the magnetic resonance investigation yields a crystal mosaic angle of 0.011 deg. This discrepancy between the magnetic resonance absorption data and the x-ray diffraction data indicates, as does other data taken on trivalent chromium, trivalent iron and divalent nickel in α -Al₂O₃,²¹ that the sites occupied by foreign ions in a crystal differ in some sense from those sites occupied by the host ions.

At $\theta=0$ deg the linewidth contribution due to crystal mosaic becomes unimportant since at this orientation, the slope of the isofrequency plot vanishes. At this orientation, a considerable variation in linewidth is observed for different transitions of a given ion [see Table III]. The variation in linewidth is interpreted as being due to spatial fluctuation in the parameters of the spin Hamiltonian. As the resonance absorption field strength for a given transition depends in a unique manner on these parameters, it is possible to determine whether such fluctuations are, in fact, responsible for the linewidth variations at this orientation. It is a straightforward matter to show that a fluctuating g value cannot give rise to significant linewidth changes from one transition to another. This is simply a consequence of the fact that, to within first-order approximation, all transition field strengths have the same g -value dependence. Of the three remaining parameters, B_4^3 can be eliminated from consideration so long as the transitions involving the two states $M_s = -\frac{5}{2}$ and $M_s = \frac{1}{2}$ occur at field strengths reasonably well removed from the region in which these two states exhibit a near intersection in their eigenvalues, see Fig. 1(a). The linewidth squared as a function of fluctuations in B_2^0 and B_4^0 is given by

$$(\Delta H_i)^2 = (\Delta H_i^0)^2 + (\partial H_i / \partial B_2^0)^2 (\Delta B_2^0)^2 + (\partial H_i / \partial B_4^0)^2 (\Delta B_4^0)^2, \quad (6)$$

where the width of the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$ transition is substituted for ΔH_i^0 . Using Eq. (6) and the iron spectrum linewidth observed at 4.2°K we obtain 6.8×10^{-2} Oe and 1.4×10^{-3} Oe for the fluctuations in B_2^0 and B_4^0 , respectively. It is perhaps worthwhile pointing out that the relative fluctuations in these parameters differ by an order of magnitude with $\Delta B_2^0 / B_2^0 = 2.0 \times 10^{-4}$ and $\Delta B_4^0 / B_4^0 = 2.0 \times 10^{-3}$.

As stated previously, the $M_s = \pm \frac{1}{2}$ Kramers doublet lies lowest in energy. It is not, in general, possible to use this information to determine the sign of B_4^3 and from it the sign of a , the cubic-field splitting parameter, since B_4^3 is complex and may have any phase depending on the choice of crystal coordinates. From the theory developed by Watanabe, it is predicted that a should be positive. Our results show that since B_2^0 is positive causing B_4^0 to be negative and since $(a-F) = -180B_4^0$, the quantity $(a-F)$ is necessarily positive. Since F is, in general, observed to be smaller in magnitude than a

we can conclude that a is a positive quantity which is, although reassuring, not at all surprising. As is shown in Fig. 3, the parameters B_2^0 and B_4^0 exhibit well-behaved temperature dependences. No temperature dependence was found for the g values and that exhibited by B_4^3 was of questionable reliability.

According to Watanabe's theory, the cubic field splitting parameter a should vary directly as the square of the cubic electric field parameter Dq which should in the limit of a point-charge model vary as the inverse tenth power of the nearest neighbor interionic distance, or as $V^{-10/3}$ where V is the volume of the cube of nearest neighbors. If we can assume that changes in the microscopic environment of the impurity ion can be calculated on the basis of changes in the macroscopic structure parameters, we are led to the result that the temperature dependence of a may be written as

$$\frac{1}{a} \left(\frac{\partial a}{\partial T} \right)_v = -\frac{10}{3} \beta_v, \quad (7)$$

where β_v is the volume coefficient of thermal expansion.²² Since calcite exhibits an expansion anisotropy we use a combination of two linear expansion coefficients weighting the constant for the perpendicular to the [111] direction by two. We then arrive at the requirement that the right-hand side of Eq. (7) becomes $-1.21 \times 10^{-4} (\text{°K})^{-1}$. From the relation between a , F , and B_4^0 we can write

$$\left(\frac{\partial a}{\partial T} \right)_v = \left(\frac{\partial F}{\partial T} \right)_v - 180 \left(\frac{\partial B_4^0}{\partial T} \right)_v. \quad (8)$$

Although we cannot arrive at an independent value for $(\partial F / \partial T)_v$ it seems reasonable that the relative change in F will not be greater than that for a . In this connection we note that the relative temperature change in B_2^0 at 300°K is $2.4 \times 10^{-4} (\text{°K})^{-1}$, while for B_4^0 it is $3.2 \times 10^{-4} (\text{°K})^{-1}$. Thus, the relative change in B_4^0 due to F will amount to no more than 25% so that a relative change in temperature relation between a and B_4^0 can be established with reliability of 25% or better. Substituting $(F/a)(\partial a / \partial T)_v$ for $(\partial F / \partial T)_v$ in Eq. (8) we arrive at

$$\frac{1}{a} \left(\frac{\partial a}{\partial T} \right)_v = -2.64 \times 10^{-4} (\text{°K})^{-1}. \quad (9)$$

This result, which is 2.2 times greater than the value $-1.21 \times 10^{-4} (\text{°K})^{-1}$, tends to suggest that the dependence of a on the parameter Dq more closely approximates a fourth-power relation. Measurements made by Walsh on iron in cubic MgO under conditions of varying hydrostatic pressure also suggests a fourth-power relation and a discrepancy with Watanabe's theory by a factor of 2.1.

²² *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1963).

IV. SUMMARY

The results of this experimental investigation demonstrate, to within average limits of one part in three thousand for the predicted positions of resonance absorption field strength positions, that the spectrum is due to a ${}^6\text{S}_{5/2}$ ion located at a site of threefold rotational symmetry. From the lack of hyperfine structure in this spectrum, the known presence of iron in the structure and the magnitudes of the parameters to the spin Hamiltonian, it is concluded that the spectrum is due to the trivalent ion of iron. The sites at which the iron ions are located appear to be either the sites normally occupied by calcium ions or very close neighbors of such sites. The interpretation is based on the fact that each iron-ion resonance absorption as observed at orientations other than $\theta=0$ deg or $\theta=90$ deg is a doublet, which is consistent with the ion located at such a site. That the gross crystal mosaic angle as obtained from x-ray diffraction analysis is considerably less than the value obtained from the magnetic resonance spectrum and that the relative intensity ratio of the doublet spectrum varies from sample to sample tends to suggest that the sites occupied by the iron and manganese ions in calcite do not possess all the properties of the sites normally occupied by the calcium ions.

In the absence of a magnetic field the two sites of the calcite structure are physically equivalent. There, thus, appears to be no reason why impurity ions should prefer one site over the other and one would expect equal amounts in each site. In the case of calcite containing larger concentrations of impurities this is indeed observed to be the case. A similar effect to that observed in our crystals has been reported by Geschwind and Remeika²³ for Gd^{3+} in $\alpha\text{-Al}_2\text{O}_3$. They have suggested that the site population inequality is a result of an inequivalence that occurs during crystal growth. In $\alpha\text{-Al}_2\text{O}_3$ the aluminum-ion sites into which the impurities

enter lack inversion symmetry. The impurities may then preferentially lay down into those sites which are closer to oxygen atom planes. Since growth along the c axis of the corundum lattice does not explain their results, Geschwind and Remeika suggest that some type of spiral growth mechanism could give preferential site selection. The calcium-ion site in calcite, however, in which presumably the iron and manganese impurities enter is one which has inversion symmetry. It is even more difficult in this case to visualize a growth process during which the physical equivalence of the calcium sites is destroyed. One possible explanation is that, at least for the case of trivalent iron during the growth process and due to its extra charge, the inversion symmetry is lost and the ion goes in preferentially closer to one plane of carbonates. The presence of the impurity may then produce local distortion of the lattice which would further influence the deposition of other impurities in selective sites by further removing the inversion symmetry. Alternatively, the ions may select out only those sites that have been previously distorted through the presence of some other type of imperfection. The fact that both manganese and iron in a given sample show similar doublet intensity ratios argues against electrostatic attraction as being the major contributing factor in determining into which site an impurity will go.

ACKNOWLEDGMENTS

The authors are grateful to Raymond Serway for his assistance in taking data, to Miss Irene Corvin and George Klems for their x-ray analysis of the calcite mosaic structure, to Dr. Ewart Grove and Harold Combs for their chemical analysis of the calcite specimens and to Professor Chihiro Kikuchi of the University of Michigan for his stimulating discussions and encouragement during the early phase of this investigation.

²³ S. Geschwind and J. P. Remeika, Phys. Rev. **122**, 757 (1961).