

VI. MICROWAVE SPECTROSCOPY*

Prof. M. W. P. Strandberg	W. J. C. Grant	J. D. Stettler
Prof. R. L. Kyhl	J. G. Ingersoll	Winifred F. Tank
Dr. R. A. McFarlane	E. C. Ingraham	N. Tepley
Dr. G. J. Wolga	J. D. Kierstead	A. H. Thiele
Patricia A. Andre	M. S. Lipsett	M. T. Uy
J. M. Andrews, Jr.	D. W. Oliver	S. H. Wemple
P. H. Carr	W. J. Schwabe	R. M. White
P. C. Clapp	J. R. Shane	R. M-C. Wu

A. CROSSOVER TRANSITIONS

A theoretical and experimental investigation was undertaken to study the behavior of a spin 3/2 paramagnetic system with trigonal field symmetry near the Zeeman-level crossings.

The spin Hamiltonian for such a system is

$$\underline{H} = g_{\parallel} \mu_B S_z H_z + g_{\perp} \mu_B \frac{1}{2} (S_+ H^- + S_- H^+) + D \left[S_z^2 - \frac{1}{3} S^2 \right]$$

Here, the quantization axis has been chosen along the c-axis of the crystal. When the applied dc magnetic field is parallel to the c-axis, S_z is diagonal in the representation ψ_m . However, if the dc field makes some angle θ with the c-axis, the eigenfunction that diagonalizes S_z is $\Phi_m = \sum_m c_m \psi_m$. Such eigenstate mixing is particularly evident in the region of energy-level crossings. When two levels are so mixed it is possible to have dipole transitions ($\Delta m = \pm 1, 0$) between them.

The eigenfunctions Φ_m can be found by solving the secular determinant $|\hat{H} - E_m \hat{I}| = 0$ for E_m , and then substituting these eigenvalues in $\hat{H} \Phi_m = E_m \Phi_m$. However, Strandberg has shown (1) that this process is simplified by changing the quantization axis of the Hamiltonian so that it makes an angle β with the c-axis. The resulting matrix is then diagonalized by contact and rotation transformations to give the energy differences directly. For the 3/2, -1/2 crossover, Strandberg obtains

$$E_{3,-1} = (E_{3,-1})_0 \left(1 + \left[\frac{2g\mu_B(H_o - H_{or})}{\sqrt{3} D \sin^2 \beta} \right]^2 \right)^{1/2}$$

where

$$(E_{3,-1})_0 = \frac{\sqrt{3}}{2} D \sin^2 \beta$$

By applying similar operations to the rf matrix, the transition probability is found to be proportional to

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$$P = \frac{g^2 \mu_B^2 \cos^2 \beta}{1 + \left[\frac{2g\mu_B(H_o - H_{or})}{\sqrt{3} D \sin^2 \beta} \right]^2}$$

The spin system used to study these results was that of Cr^{+++} in an Al_2O_3 lattice (ruby). $(E_{3,-1})_0$ and P for ruby are shown in Fig. VI-1 and Fig. VI-2.

The crossover region was studied experimentally by observing the paramagnetic resonance with low-frequency (171-mc) equipment. This equipment has been described (2) elsewhere.

From Figs. VI-1 and VI-2 we can get a qualitative idea of how the resonance near the crossover will behave. Suppose, for instance, $\beta = 6^\circ$. Then, from Fig. VI-1, we can see that as we increase the magnetic field, we should obtain a resonance at 2018 gauss and one later at 2135 gauss. Because of spin-lattice interactions these resonances will have a finite width. Kittel and Abrahams (3) have shown that at the concentrations used in this experiment, the frequency line shape is Lorentzian with line-width $\Delta\nu$. If we maintain a fixed frequency and sweep the magnetic field through resonance, the magnetic linewidth will be $\Delta H = \frac{\Delta\nu}{\partial\nu/\partial H}$, where $\partial\nu/\partial H$ increases from

zero at the minima of $(E_{3,-1})_0$ to some finite value at higher and lower fields (Fig. VI-1).

If we now superimpose the probability restrictions given in Fig. VI-2 on our resonances, the amplitude of the lower tail of the 2135 line and that of the upper tail of the 2018 line will be increased. The resulting absorption will then look like that indicated in Fig. VI-3a, in which we have plotted $Pg(H-H_r)$ against H, for $\beta = 6^\circ$. Similarly, we obtain curves for $\beta = 8^\circ$ (Fig. VI-3b), and $\beta = 10^\circ$ (Fig. VI-3c).

The experimental results are shown in Fig. VI-4. We must remember that these experimental lines are the derivatives of the absorption. A comparison of the theoretical and experimental values for $\beta = 8^\circ$ and $\beta = 10^\circ$ are shown in Table VI-1.

Table VI-1. Comparison of line positions.

β	Theoretical		Experimental		
	H_o (gauss)	$\frac{\partial\nu}{\partial H}$ (mc/gauss)	H_o (gauss)	Linewidth (gauss)	$\Delta H \frac{\partial\nu}{\partial H}$ (mc)
8°	2065	2.29	2060	23	50
	2105		2105	23	50
10°	2100	1.34	2102	33	45

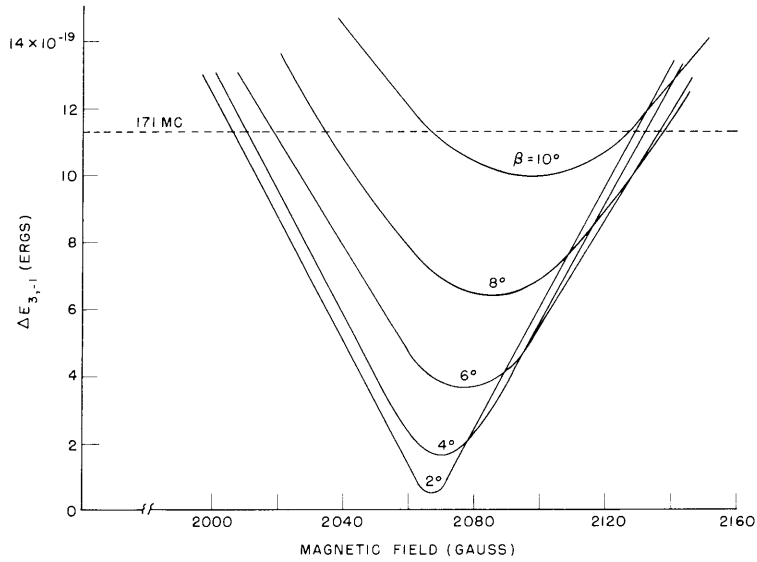


Fig. VI-1. Energy dependence $\Delta E_{3,-1}$ between the $+\frac{3}{2}$ and $-\frac{1}{2}$ levels as a function of magnetic field for $\beta = 2^\circ, 4^\circ, 8^\circ, 10^\circ$.

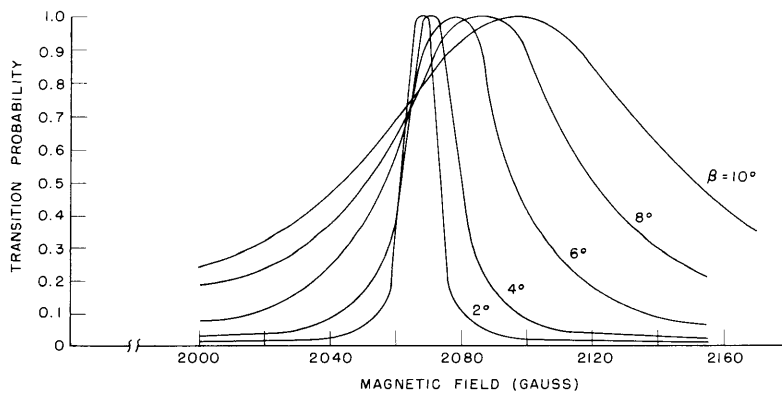


Fig. VI-2. Relative probability of $+\frac{3}{2}$, $-\frac{1}{2}$ transition as a function of magnetic field for several values of β .

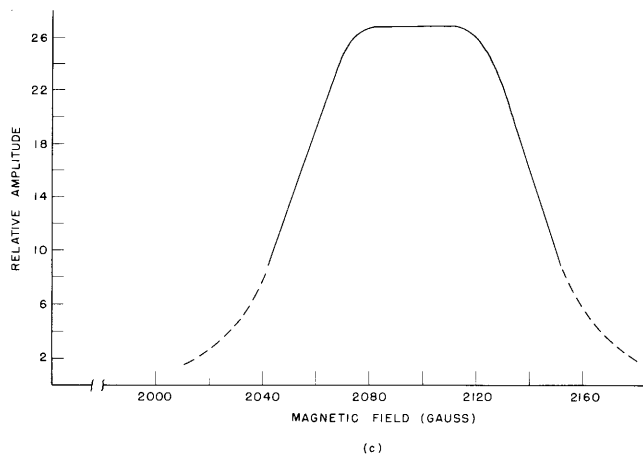
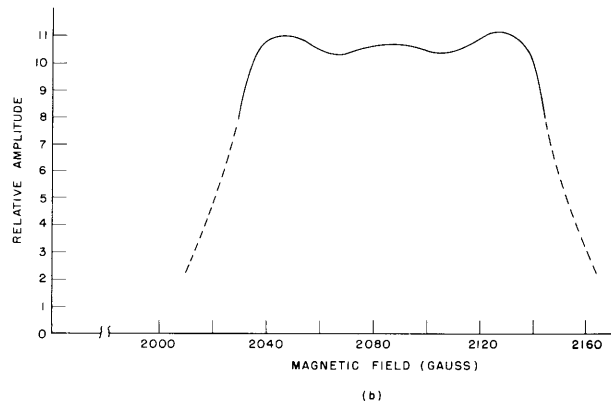
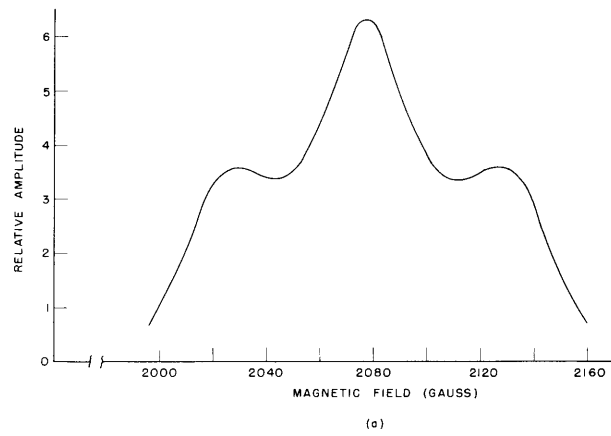


Fig. VI-3. Theoretical shape of $+\frac{3}{2}$, $-\frac{1}{2}$ absorption: (a) for $\beta = 6^\circ$; (b) for $\beta = 8^\circ$; (c) for $\beta = 10^\circ$.

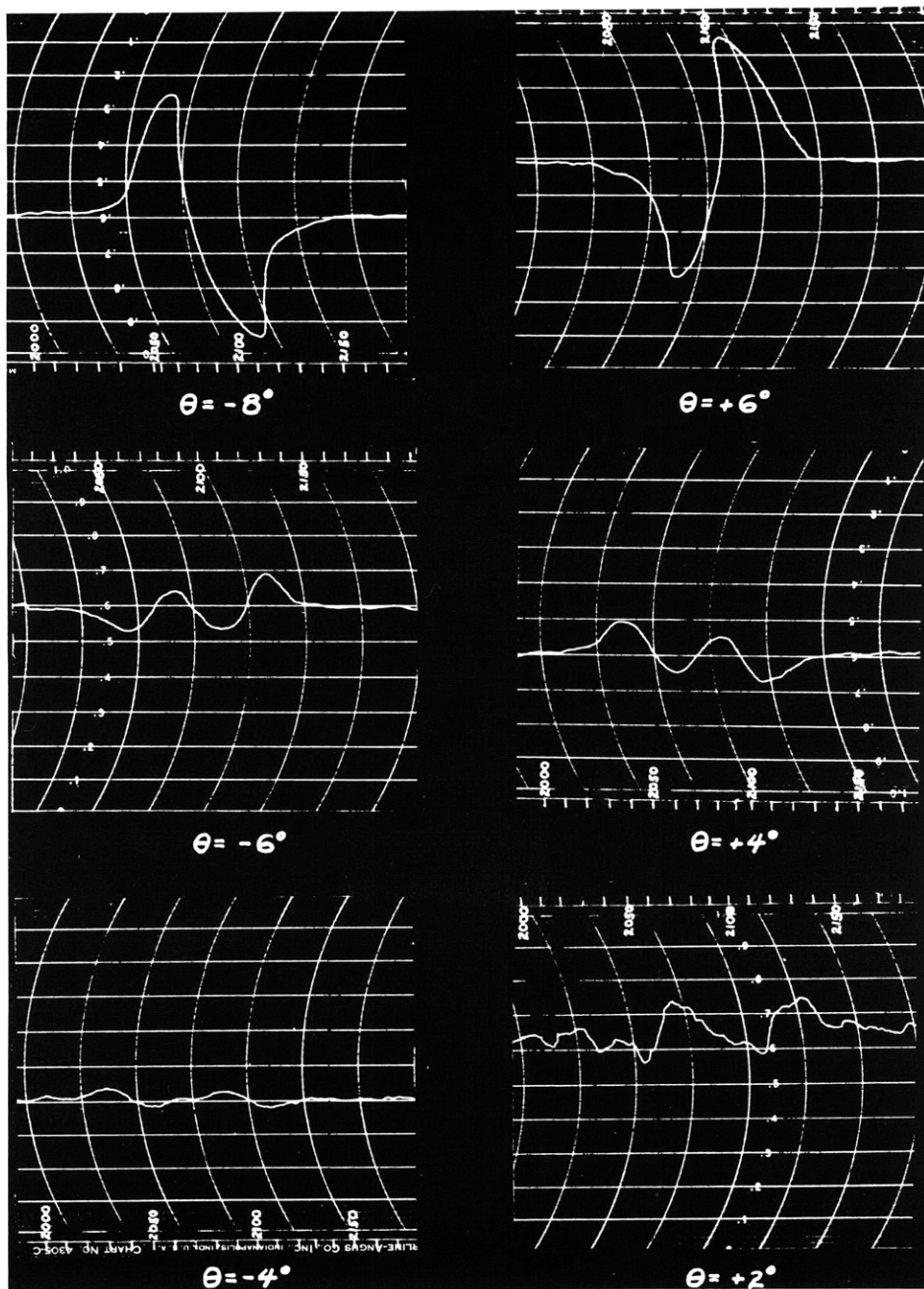


Fig. VI-4. Derivative of absorption for the $+\frac{3}{2}$, $-\frac{1}{2}$ crossover transition: θ is the angle between the c-axis and the dc magnetic field; $\nu_0 = 171$ mc; $T = 300^\circ\text{K}$; time constant, 2 sec.

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The measured spectra reflect the validity of our matrix transformations. The experiment itself points out the fact that crossover transitions produce spectra quite different from ordinary microwave transitions.

R. M. White

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B. RUBY LINEWIDTHS

In a previous discussion of ruby linewidth measurements (1), the interpretation of the procedure that was given for determining the effective chromium-ion concentration was not sufficiently stressed. For this reason, some discussion of the attitude that must be taken toward this kind of measurement will be given here.

It is apparent from the discussion of the measurements that one is determining the magnitude of the maximum slope of the imaginary part of the resonant susceptibility for a substitutionally chrome-doped sapphire lattice as a function of the amount of chromium doping. If, then, we appeal to the usual argument that we have a Lorentz-shaped line near resonance, a formula may be evoked that relates this maximum slope of the susceptibility to quantum-mechanical numbers, such as the dipole-moment matrix elements, and the physically observed properties of the resonance, such as linewidth and effective concentration of ions. However, the word "effective" should be used when we speak of the concentration of paramagnetic ions in a lattice diluted with diamagnetic ions, in our case Al²⁷. The reason is that the number that stands for the effective concentration of ions properly relates the susceptibility to the dipole moment and the linewidth, but only for a purely Lorentz-shaped line. We know, in fact, that a diluted paramagnetic crystal does not have a Lorentz-shaped susceptibility function, except near the region of resonance. There will always be broad skirts whose contribution to the line strength – that is, the frequency integral of the imaginary part of the susceptibility – can be appreciable, as compared with the contribution to the line strength from the region near the resonant susceptibility. In other words, the ion concentration given (1) before may be looked upon as a number which, if it is introduced into the conventional formulas, will allow one to calculate the susceptibility obtainable from a ruby crystal.

The fact that this concentration differs from that determined by other means, chemical means, for instance, may only indicate that, in fact, the skirt contribution to the line

strength is, indeed, appreciable and must be taken into account in any analysis that tries to relate the amount of chromium introduced substitutionally into the sapphire lattice with the maximum resonant susceptibility.

A proper discussion of paramagnetic shapes is a difficult one; this topic has been under consideration for some time. Great strides have been made toward understanding this phenomenon in the work of Anderson (2) and of Kittel and Abrahams (3). At the present time, we are trying to develop our analytical understanding of the paramagnetic-resonance line shape. We are also accumulating data on the ratio of the effective to actual ion density in other crystals that have undiluted linewidths greater than and less than those of ruby and sapphire.

Briefly, our position seems to be somewhat as follows: If Anderson's analysis (2) is used, we are led to the conclusion that the intensity of the absorption, or the imaginary part of the magnetic susceptibility, is related as $I_c = \frac{1}{2} I_1(1+c)$, where I_c is the intensity at a concentration, and I_1 is approximately the intensity with no dilution, or with $c = 1$. It is seen from this relationship that the peak intensity is diminished by a factor of 2 as we dilute the paramagnetic ions. This relationship is approximate and is restricted by the assumptions expressed in its derivation. We have been able to extend this result by a simple calculation, using Anderson's results, and have computed the slope of the intensity – the imaginary part of the susceptibility – with respect to frequency. When the concentration dependence of the linewidth is removed from the slope, the slope for a concentration of 1 is approximately π greater than the slope at vanishing concentration. This would mean, for example, if it were applied to our previous measurements (1), that if we determined the appropriate Lorentz line-shape function from the slope (which is probably what we are doing), the effective concentration would be π^{-1} as great as the actual concentration, and the discrepancy of a factor of approximately 3.5 between the EMR measurements and the chemical determinations would thus be explained. But because the calculations are somewhat restricted by their assumptions and do not describe sufficiently the actual line shape with which we are working, this explanation is not completely satisfying, and, in fact, may be merely fortuitous.

If, indeed, our present understanding of the relationship of the effective concentration of ions with the actual concentration of ions is adequate, there should be greater or less correlation between these numbers, and it would depend upon the ratio of the actual linewidth of the diluted crystal to the expected linewidth in the undiluted crystal. We have recently obtained (4) a crystal of a metal organic compound, chromium acetylacetonate, which, because of the generous proportions of the unit cell, has an undiluted linewidth that is considerably less than that of chromium in sapphire. This type of crystal will be very useful in studying the concentration dependence of line shapes.

Until this question of the actual line shape of a diluted paramagnetic crystal has been analyzed in detail, there seems to be no alternative but to compute the effective

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chromium-ion concentration, as we have done and reported (1) on the basis of a single Lorentz-shaped line.

M. W. P. Strandberg

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2. P. W. Anderson, Phys. Rev. 82, 342 (1951).
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4. We are indebted to Dr. Ellis Hormatz, of Stromberg-Carlson Company, Rochester, New York, for providing us with samples of chromium acetylacetonate.

C. PARAMAGNETIC RESONANCE IN THE MANGANOUS ION AT LOW FREQUENCIES

The present work represents an attempt to observe the paramagnetic-resonance absorption of the manganous ion at energies so low that the nuclear interaction is important and produces a mixing of the electron spin states. The ion is contained in a solution that is placed in a magnetic field. The rapid motion of the ions and dipoles in the solution averages their electric field, as seen by a paramagnetic ion, to a field of spherical symmetry over the period of a transition; thus this field produces line broadening, but no splitting. Since the experiment is carried out at room temperature, the ion is in the ground state with respect to the rest of the electrostatic terms.

The manganous ion is composed of five 3d electrons outside the argon kernel. Since the orbital angular momentum is zero, the Hamiltonian for the magnetic terms is

$$E = g_e \beta \vec{H} \cdot \vec{S} + g_I \beta_I \vec{H} \cdot \vec{I} + A \vec{I} \cdot \vec{S}$$

where \vec{S} is the total electron spin vector, \vec{I} is the nuclear angular momentum vector, \vec{H} is the externally applied magnetic field, g_e is the electronic g factor, β is the Bohr magneton, g_I is the nuclear g factor, β_I is the nuclear magneton, and A is the experimentally determined nuclear-electronic coupling coefficient. Since the Hamiltonian is expressed only in terms of angular momentum, matrix methods were used to find the eigenvalues of the Hamiltonian. The A value used has already been determined at high fields (1). The diagonalization of the Hamiltonian matrix was carried out exactly in the (F, m_F, I, S) representation by iterating a continued fraction expansion.

Since for small energy splittings the populations of the energy levels are proportional to the energy splittings, and the energy absorbed in one transition is also proportional to the difference in the energy of the two levels, the strength of the absorption signal is

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proportional to $(h\nu)^2$. This means that a compromise must be made between a high frequency, which gives a good signal-to-noise ratio, and a low frequency, at which the mixing of states is pronounced and therefore gives an interesting spectrum. The present attempt was made at a frequency of 200 mc. At this frequency, no data were obtained. The calculated energy levels predict that there are permitted transitions at 1 kmc in which the mixing of states caused by the nuclear interaction is quite strong.

The present spectrometer consists of a feedback oscillator that is held at a preset level in its linear range by a stabilizer circuit. The stabilizer controls the level by controlling the plate current of the oscillator tube. We found that the chopper modulation of the stabilizer circuit was getting into the oscillator circuit and producing modulation noise. This noise was cut down by the addition of decoupling networks and shielding between the stabilizer and signal circuits. The tank circuit of the oscillator consists of a helical coil in a cavity. The coupling is by means of probes. The coil is supported by polystyrene, foamed in place to reduce microphonics. The oscillator is equipped with built-in ports for putting in and taking out alignment signals. Isolation capacitors had to be placed in the outer conductors of the feed lines to prevent modulation ground loops.

The signal obtained is the derivative of the absorption of the sample as a function of the applied magnetic field. The applied magnetic field is modulated at an audio rate. The absorption of the sample then changes at an audio rate, and this causes the output of the oscillator to change. The time constant of the stabilizer is sufficiently large that the average level of the oscillator over a 1-sec interval is held constant. The resulting signal is then synchronously detected against the original modulation, integrated, and recorded on a strip recorder.

Attempts to obtain spectra were made with water, methanol, and acetone as solvents. Concentrations were 0.1 and 0.01 molar, except for the acetone solution, which was saturated. In all cases, enough solution was put into the cavity to reduce the Q to one-half of its initial value. For example, 0.1 cc of 0.1 molar $MnCl_2$ reduces the Q of the cavity to one-half of its original value. In no case could spectra be seen above the noise. A 1-kmc oscillator is now being constructed. It is similar in all respects to the 200-mc oscillator, except that it uses a coaxial cavity at 1-kmc.

A. H. Thiele

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