Paramagnetic Resonance Spectrum of Cr^{+++} in Emerald*

By J. E. GEUSIC, MARTIN PETER and
E. O. SCHULZ-DU BOIS

(Manuscript received October 6, 1958)

Paramagnetic resonance for the Cr^{+++} ion in emerald has been observed at X-band (8.2 to 12.4 kmc), K-band (18 to 26.5 kmc) and M-band (50 to 75 kmc). From spectra observed at these frequencies, the spectroscopic splitting factors $g_{\parallel}$, $g_{\perp}$ and D have been determined. The large value of D observed suggests the possible use of emerald as an active material in relatively high microwave-frequency solid-state masers.

I. INTRODUCTION

Survey articles by Bleaney and Stevens[1] and Bowers and Owens[2] list paramagnetic resonance data for crystals containing ions of the transition groups. A careful study of these tabulated data reveals that most of the crystals studied are hydrated or contain several magnetically nonequivalent ions and, therefore, discourages the use of many of these crystals in a practical three-level solid-state maser (3LSSM).

The present study was undertaken with a view to investigating crystals doped with paramagnetic ions which possess good chemical stability and which might be expected to have energy-level schemes suitable for extending the design of solid-state masers to higher microwave frequencies. In this article, paramagnetic resonance spectra of emerald (Cr-doped beryl) are reported. The large zero field splitting observed for the Cr^{+++} ion in this crystal might suggest emerald as a possible material for use in the design of solid-state masers for high microwave-frequency applications.

II. CRYSTAL STRUCTURE AND SPIN HAMILTONIAN OF EMERALD

The structure of beryl[3, 4, 5] is hexagonal with two molecules of ($Be_3Al_2Si_6O_{18}$) per unit cell. In the crystal, SiO_4 tetrahedra share oxygens

---

* This work is partially supported by the Signal Corps under Contract Number DA 36-039 sc-73224.

to form Si_6O_{18} rings, with each Al linked to six Si_6O_{18} rings. In the lattice, all Al sites are identical and the symmetry at each Al site includes a three-fold axis parallel to the hexagonal or c-axis of the crystal. In emerald, it is found that Cr substitutionally replaces Al in the beryl lattice and is present as Cr^{+++}.

For the Cr^{+++} ion in such a crystalline electric field of three-fold symmetry, it is well known[1] that the paramagnetic resonance spectrum is described by a spin Hamiltonian of the form

$$\mathcal{H} = \beta[g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] + D[S_z^2 - \tfrac{1}{3}S(S + 1)], \qquad (1)$$

with $S = \frac{3}{2}$ and with the z-axis taken parallel to the three-fold symmetry axis which in emerald is the c-axis. In the preceding paper[6] the energy levels of the spin Hamiltonian above were discussed for arbitrary values of the parameters $g_{\parallel}$, $g_{\perp}$ and D and for arbitrary orientation of the magnetic field H with the z-axis. The notation of the previous paper is adopted for labeling the energy levels of (1). The energy levels are labeled $W(\bar{n})$ where $\bar{n}$ is used to enumerate the levels in order of their energy and is just the high magnetic field quantum number which takes on the values $-\frac{3}{2}, \cdots, +\frac{3}{2}$. For example, $W(-\overline{\tfrac{3}{2}})$ represents the lowest energy level and $W(\overline{\tfrac{3}{2}})$ represents the highest energy level.

III. EXPERIMENTAL WORK

Initial paramagnetic resonance measurements of Cr^{+++} in a single emerald crystal were made at 9.309 kmc. The spectrometer used for these X-band measurements is similar in design to that described by Feher.[7] At 9.309 kmc and magnetic fields which were available, the spectrum of Cr^{+++} in emerald consisted of a single anisotropic line. The effective g-value, $g^e(\theta)$, of this line is plotted in Fig. 1 as a function of θ, where θ is the angle between the magnetic field H and the c-axis of the crystal. The extreme values of g^e at 9.309 kmc. are $g^e(0°) = 1.973 \pm 0.002$ and $g^e(90°) = 3.924 \pm 0.004$. This line was identified (taking the sign of D negative) as the transition $W(\overline{\tfrac{1}{2}}) \rightarrow W(\overline{\tfrac{3}{2}})$. The fact that $g^e(90°) \cong 4$ suggests that at 9.309 kmc the frequency of observation is much less than the splitting of the energy levels of (1) in zero field. Under the condition that ν, the frequency of observation, is small compared to the zero field splitting, a perturbation expression for the g^e of the $W(\overline{\tfrac{1}{2}}) \rightarrow W(\overline{\tfrac{3}{2}})$ transition is given by

$$g^e = [g_{\parallel}^2 + (4g_{\perp}^2 - g_{\parallel}^2)\sin^2\theta]^{1/2}\left[1 - \tfrac{1}{2}\left(\frac{g_{\perp}\beta H}{2D}\right)^2 F(\theta)\right], \qquad (2)$$

where

$$F(\theta) = \frac{3\sin^2\theta(\sin^2\theta - \frac{1}{3})}{\sin^2\theta + \frac{1}{3}}.$$

Specialization of (3) to $\theta = 0°$ and $\theta = 90°$ gives

$$g^e(0°) = g_{\parallel},$$

$$g^e(90°) = 2g_{\perp}\left[1 - \tfrac{3}{4}\left(\frac{g_{\perp}\beta H}{2D}\right)^2\right],$$

from which it is seen that the zero field splitting $|2D|$ can be computed from measurements of $g^e(90°)$ at two frequencies small compared to $|2D|$. Measurements at 23.983 kmc gave $g^e(90°) = 3.814 \pm 0.004$. From the measurements of $g^e(0°)$ and $g^e(90°)$ at X-band and $g^e(90°)$ at K-band, the constants in (1) were found to be

$$g_{\parallel} = 1.973 \pm 0.002,$$

$$g_{\perp} = 1.97 \pm 0.01,$$

$$2D = -52.0 \pm 2.0 \text{ kmc}.$$

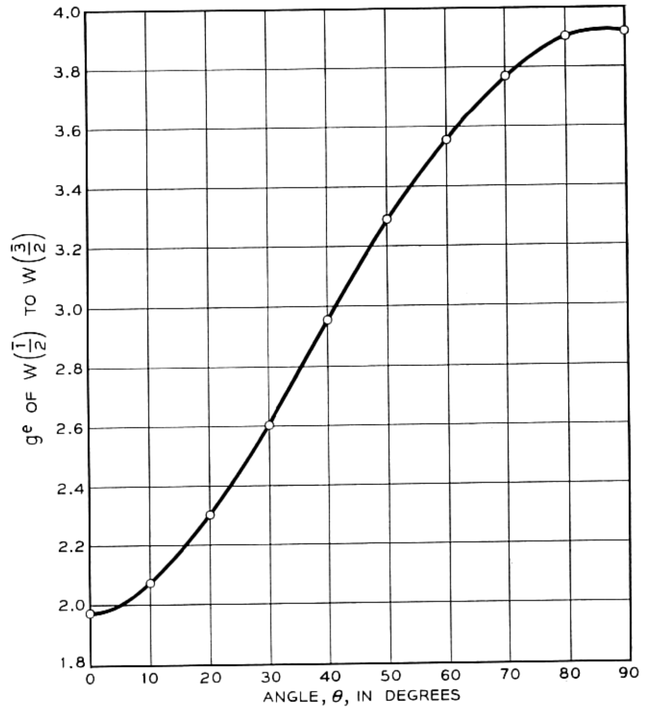

Fig. 1 — Variation of the effective g-value, g^e, of the $W(\bar{\tfrac{1}{2}}) \rightarrow W(\bar{\tfrac{3}{2}})$ transition at 9.309 kmc.

In order to establish the sign of D, the intensity of the $W(\frac{1}{2}) \rightarrow W(\frac{3}{2})$ line of Cr^{+++} in emerald was compared at two temperatures with the intensity of the same line of Cr^{+++} in ruby. The measurements were carried out with both crystals simultaneously mounted in the X-band spectrometer using temperatures of 78°K and 1.6°K, respectively. The variation of line intensity with temperature can be predicted from Boltzmann statistics if the sign of D is known. Computations were carried out, therefore, on this variation, assuming positive and negative signs of D for both ruby and emerald. The results of these calculations and of the measurement are summarized in Table I. It thus can be concluded that the sign of D for both emerald and ruby is negative.

In order to obtain $2D$ more accurately, measurements were made on Cr^{+++} in emerald at M-band. The millimeter wave paramagnetic resonance spectrometer used was constructed by one of the authors (M. Peter); a block diagram is shown in Fig. 2. Microwave power for this spectrometer is generated by free-running backward wave oscillators (BWO's). Three such BWO's are used to cover the frequency range of 48 to 82 kmc. No resonant cavity is employed in this spectrometer; instead, the sample is situated in "straight" waveguide so that the remarkably wide tuning range of the BWO's can be used. The sensitivity of this spectrometer is comparable to those at low microwave frequencies employing resonant cavities. This is because the loss of sensitivity due to the absence of a cavity is compensated for by higher microwave susceptibility and higher filling factors at these frequencies.

At M-band and for $\theta = 0°$, the two allowed transitions are, in our notation, $W(-\frac{1}{2}) \rightarrow W(\frac{3}{2})$ and $W(-\frac{3}{2}) \rightarrow W(\frac{1}{2})$; they are illustrated in Fig. 3. Both these transitions merge at zero field with the transition frequency being $|\,2D\,|$. Both transitions were studied as a function of magnetic field, as shown on Fig. 4. By following them to zero field, the value of the zero field splitting was determined to be $|\,2D\,| = 53.6 \pm 0.1$ kmc. From these X-band, K-band and M-band measurements, the best values for the constants in the spin Hamiltonian (1) for

TABLE I

$$\text{Ratio } R = \frac{I_{\text{ruby},\ 1.6°\text{K}}}{I_{\text{ruby},\ 78°\text{K}}} \times \frac{I_{\text{emerald},\ 78°\text{K}}}{I_{\text{emerald},\ 1.6°\text{K}}}$$

Computed with sign of D for			Measured R_{exp}
Emerald	Ruby	R_{theor}	
negative	negative	1.8	1.9 ± 0.1
negative	positive	2.6	
positive	negative	0.5	
positive	positive	0.7	

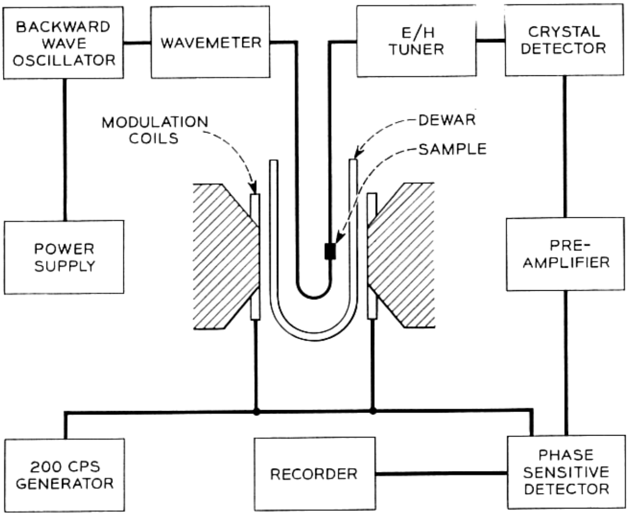

Fig. 2 — Block diagram of the M-band spectrometer.

Cr^{+++} in emerald are

$$\begin{aligned} 2D &= -53.6 \pm 0.1 \text{ kmc}, \\ g_{\parallel} &= 1.973 \pm 0.002, \\ g_{\perp} &= 1.97 \pm 0.01. \end{aligned}$$

This value of $2D$ for Cr^{+++} in emerald is, to date, the largest zero field splitting which has been reported for the Cr^{+++} ion in any crystal. Measurements on spin lattice relaxation times in this crystal are planned.

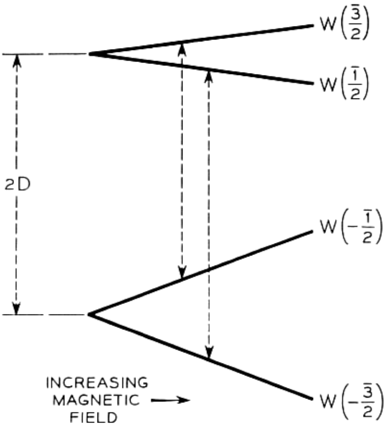

Fig. 3 — Energy level diagram of Cr^{+++} in emerald with applied magnetic field parallel to crystalline axis.

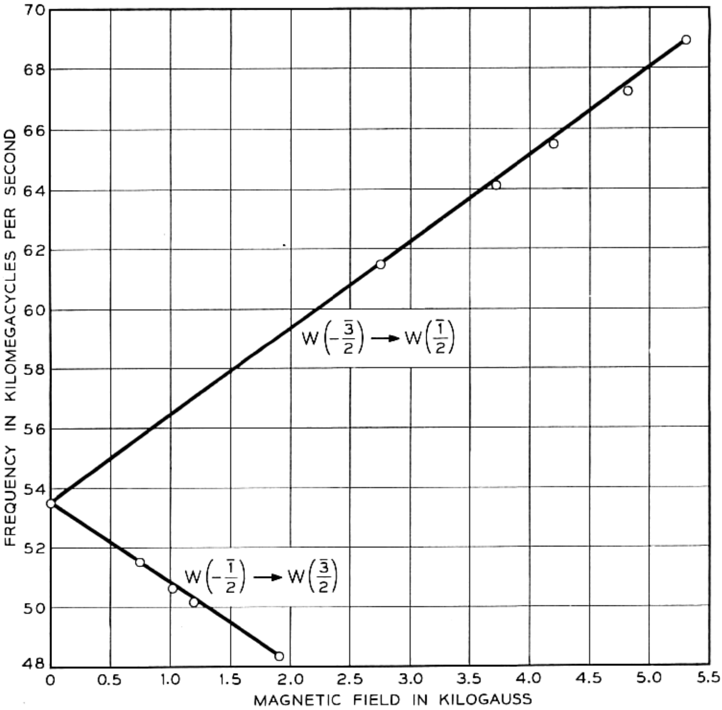

Fig. 4 — Plot of frequencies associated with transitions $W(-\frac{\bar{1}}{2}) \to W(\frac{\bar{3}}{2})$ and $W(-\frac{\bar{3}}{2}) \to W(\frac{\bar{1}}{2})$ at low applied magnetic fields and $\theta = 0°$.

IV. ACKNOWLEDGMENTS

The authors wish to thank H. E. D. Scovil for suggestions throughout the course of the work. We are indebted to S. Geschwind and D. Linn for making the K-band measurements, and to J. B. Mock for valuable assistance with the M-band measurements.

REFERENCES

1. Bleaney, B. and Stevens, K. W. H., Paramagnetic Resonance, Rep. Prog., Phys. **16,** 1953, p. 107.
2. Bowers, K. D. and Owen, J., Paramagnetic Resonance II, Rep. Prog. Phys., **18,** 1955, p. 304.
3. Bragg, W. L. and West, J., Proc. Roy. Soc. (London), **A111,** 1926, p. 691.
4. Bragg, W. L., *Atomic Structure of Minerals*, Cornell Univ. Press, Ithaca, N. Y., 1937.
5. Wyckoff, R. W. G., *The Structure of Crystals*, The Chemical Catalog Co., New York, 1931.
6. Schulz-DuBois, E. O., this issue, pp. 271–290.
7. Feher, G., Sensitivity Considerations in Microwave Paramagnetic Resonance Absorption Techniques, B.S.T.J., **36,** March 1957, p. 449.