Millimeter-Wave Paramagnetic Resonance Spectrum of ^6S State Impurity (Fe^{+++}) in $MgWO_4$

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A broad-band millimeter-wave paramagnetic resonance spectrometer has been assembled. At room temperature, with a line width of one oersted and a time constant of one second, the least number of spins that can be detected is 2×10^{14}, in reasonable agreement with theoretical prediction.

The spectrum discovered by Bowers in slightly Ni-doped $MgWO_4$ has been investigated and ascribed to an impurity in the ^6S state (Fe^{+++}). It is described by the spin Hamiltonian:

$$H=D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)+g\beta\mathbf{H}\cdot\mathbf{S},$$

with

$$S=\tfrac{5}{2};\quad D=-20.6\text{ kMc/sec};\quad E=+5.22\text{ kMc/sec};\quad g=2.0\ (T=78°\text{K}).$$

The y axis is parallel to the b axis; the z axis is turned away from the $+a$ axis towards the $+c$ axis by 41.5 degrees.

A. APPARATUS

THE millimeter-wave paramagnetic resonance spectrometer shown in Fig. 1 has been assembled. It is similar to one described by Bowers, Mims, and Korb[1] except for addition of an electromagnet and a linear detection system. From other paramagnetic spectrometers it is distinguished by the absence of a cavity. Hence, a reduction in sensitivity results which can be calculated as follows: our wave guide is filled with a sample whose length equals one wavelength λ. A comparison of attenuation in the wave guide,

$$\Delta V/V=4\pi^2\chi''l/\lambda,$$

and that in a reflection cavity,

$$\Delta V/V=\sqrt{2}\pi\chi''Q_0,$$

shows the equivalent Q of straight wave guide to be $2\sqrt{2}\pi l/\lambda$, or, in our case, $Q_{eq}\sim10$. An optimum 9-kMc/sec system has been discussed by Feher.[2] Its Q is 500 times higher, its sample volume 70 times higher, its frequency 8.3 times lower than in our case. This lets us expect a 10 times better theoretical performance limit for the 75-kMc/sec system than for the X-band system. A more direct calculation, using the formula

$$\alpha=8\pi^2\nu^2N\mu^2/ckT\Delta\nu$$

given by Gordy,[3] yields for $\Delta\nu=2.8$ Mc/sec, an observation band width of 1 cps, a power source of $P_i=10^{-4}$ watt, and an ideal noise figure, the result that 2×10^{10} spins can be detected. A more realistic noise figure is obtained by using Strandberg's formula[4]

$$d\sim(RP_i^2/f)+1,$$

where f is the modulation frequency ($=200$ cps) and R is a crystal constant ($=10^{16}$ watt^{-2} sec^{-1}). With this figure, we expect to see 10^{13} spins. Experimentally we have estimated a lower limit of 2×10^{14} detectable spins. The limit of 2×10^{10} spins could be approached through use of the well-known bridging techniques.

The microwave power was generated by backward wave oscillators, designed and lent to us by C. F. Hempstead. Frequency was measured with wavemeters, and the magnetic field was measured with a rotating-coil-type gaussmeter, which was calibrated by proton probe. The absence of resonant cavities made possible the use of the remarkable wide tuning range of

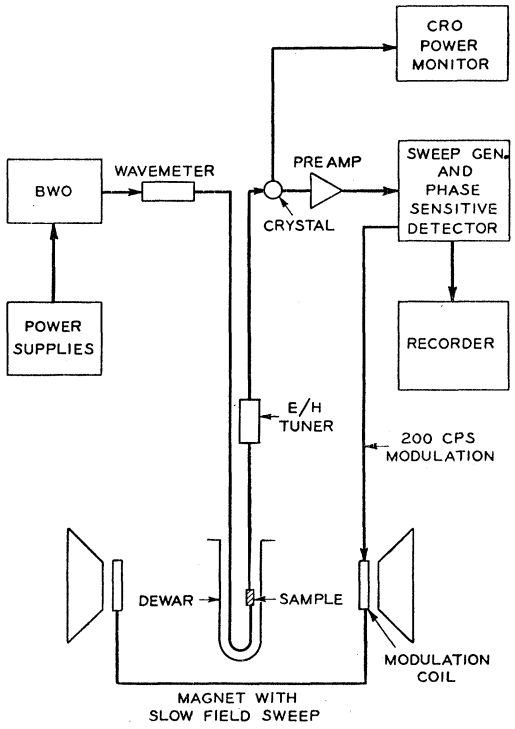

FIG. 1. Millimeter wave paramagnetic resonance spectrometer.

[1] Bowers, Mims, and Korb (unpublished).
[2] G. Feher, Bell System Tech. J. 36, 449 (1957).
[3] Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 197.
[4] M. W. P. Strandberg, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 90.

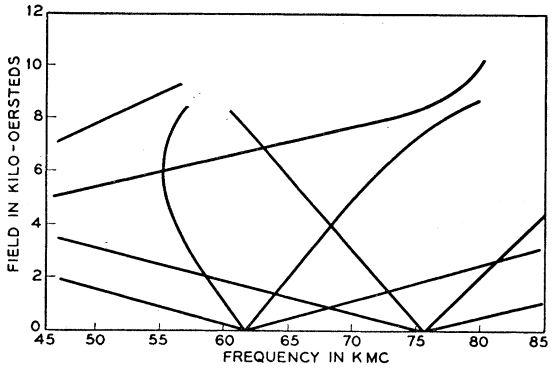

FIG. 2. Spectrum of ferric ion in $MgWO_4$.

the backward wave oscillator, as illustrated in Fig. 2 where the spectrum of a single crystal of $MgWO_4$ is shown. The magnetic field varies from 0 to 12 kilo-oersteds, the frequency from 48 to 82 kMc/sec.

B. SPECTRUM OF ^6S STATE IMPURITY IN $MgWO_4$

Monoclinic single crystals of $MgWO_4$ (space group $P2/c$), both pure and with added impurities, were grown by Van Uitert. The spectrum, shown in Fig. 2, was attributed to an impurity in the ^6S state, probably sitting on the Mg^{++} site. The absence of hfs strongly suggests Fe^{+++} as the impurity. Crystals were grown of $MgWO_4$ with and without iron doping, without changing the intensity of the spectrum. This indicates that even the "pure" $MgWO_4$ is saturated with Fe^{+++} ions, and that the doping results in an increase of Fe ions of different valency.

The oxygen positions in the isomorphous $NiWO_4$ have recently been determined by Keeling.[5] The surroundings of the Mg^{++} ion are shown in projection on the ac plane in Fig. 3. The diad axis goes through the Mg^{++} site and fixes one of the magnetic axes. The other two are shown as dotted lines.

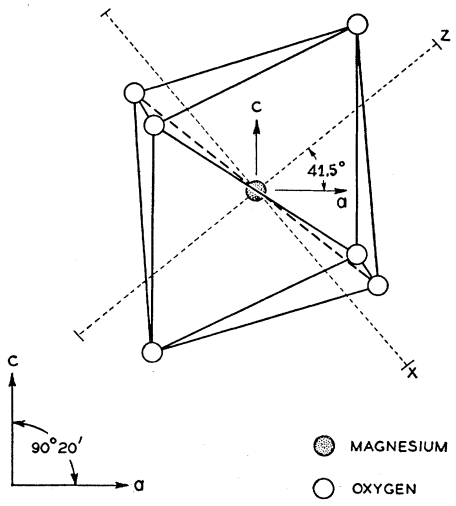

FIG. 3. Positions of oxygens surrounding Mg^{++} ion in $MgWO_4$, projected along b on the ac plane.

[5] R. O. Keeling, Jr., Acta Cryst. **10**, 209 (1957).

Since the monoclinic angle is almost 90°, the crystal could not be readily oriented from angular measurements alone. A zero-level Buerger precession camera photograph was therefore taken by Geller of a thin (010) plate that was cleaved off our crystal. The sense of the deviation of the β angle from 90° was observed and then confirmed by comparison of the intensities of the (102)-(10$\bar{2}$) and (302)-(30$\bar{2}$) pairs of reflections, as suggested in Keeling's article. In this way it was found that the y axis is parallel to the b axis, and that the z axis is turned away from the $+a$ axis towards the $+c$ axis by 41.5 degrees.

Lines as narrow as 200 Mc/sec were observed, both at 2°K and at 78°K. The levels observed and their Zeeman splitting in the z direction are shown in Fig. 4.

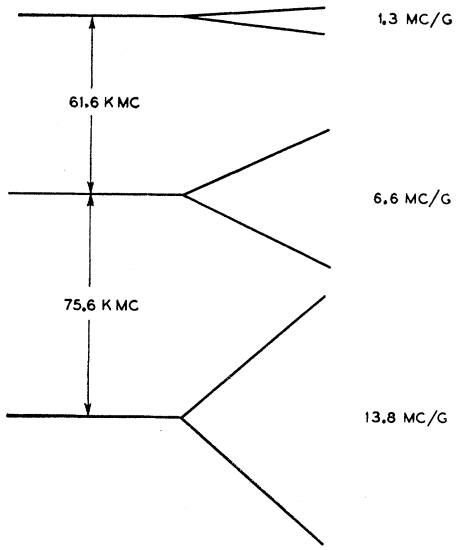

FIG. 4. Levels of ferric ion in $MgWO_4$ and Zeeman effect for $H \parallel z$ axis.

The spectrum can be described within the accuracy of our measurements by a spin Hamiltonian containing only second-order terms:

$$H=g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2).$$

The effective spin is $\frac{5}{2}$, and the impurity is assigned to be in the $3d^5\ ^6S$ state. Because of the Kramers degeneracy, the energies are given by equations of only the third degree. The theory of cubic equations allows us to relate the ratio $E/D=y$ in a simple way to the ratio of the two observed zero-field transition frequencies f_1, f_2 ($x=f_1/f_2$). We set

$$\cos\psi=[(4x^2+4x+1)/(4x^2+4x+4)]^{\frac{1}{2}}.$$

Then y^2 satisfies the cubic equation:

$$(1+3y^2)^3=0.292(1-9y^2)^2\sec^2(3\psi).$$

In this way, the values of D and E are determined from the zero-field splitting of our slightly Ni-doped sample

($T=78°K$):

$$D=-20.6 \text{ kMc/sec}, \quad E=+5.22 \text{ kMc/sec}.$$

The signs are determined by comparing intensities at 2°K and at 4°K. From the tetragonal eigenfunctions, for which m is a good quantum number, our functions are transformed by the matrix[6]

$$\begin{array}{c} \begin{matrix} \pm\frac{5}{2} & \pm\frac{1}{2} & \mp\frac{3}{2} \end{matrix} \\ \begin{bmatrix} 0.990 & -0.134 & 0.035 \\ 0.113 & 0.917 & 0.387 \\ -0.087 & -0.378 & 0.921 \end{bmatrix} \end{array}$$

[6] For an explicit description of the evaluation of a spin Hamiltonian, see T. O. Woodruff and W. Känzig, J. Phys. and Chem. Solids **5**, 268 (1958).

The fact that the linear Zeeman effect for H along the three magnetic axes as predicted from these functions agrees with our observations (for $g=2.0$) means that the fourth-order terms in the spin are small within the accuracy of our measurements.

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Electrical Conduction in Crystals and Ceramics of WO_3†

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The specific resistivities of crystals and ceramics of WO_3 have been measured from room temperature to 1000°C, and the sign and order of magnitude of the Hall coefficient have been examined near room temperature. From the results for single crystals, it was found that WO_3 behaves like an impurity semiconductor having a saturation region below 740°C and becoming intrinsic above 910°C. The specific resistivity *versus* temperature curve had a distinct anomaly at 740°C suggesting an alteration in the electronic structure at this temperature. Below 740°C, the specific resistivity of ceramic samples showed a remarkable hysteresis phenomenon, probably arising from a cracking of crystallites on heating. The sign of the Hall coefficient was positive at room temperature and its magnitude gave reasonable values for the number and mobility of the carriers. Nonohmic and rectifying characteristics were observed by means of an oscilloscope.

I. INTRODUCTION

ALTHOUGH WO_3 has attracted much notice from the viewpoint of ferroelectricity and antiferroelectricity, the measurement of the dielectric constant and the observation of D-E hysteresis loops are difficult because of its semiconductive property. On the other hand, only a few measurements of electrical conduction have been reported.[1–3] No measurements of electrical conduction in single crystals have been made. In this investigation, the specific resistivities of single crystals and ceramics were measured from room temperature to 1000°C, and the sign and order of magnitude of the Hall coefficient were examined near room temperature.

II. EXPERIMENTAL PROCEDURE

Electrical measurements were performed by the dc method using five probes.[4,5] Silver and platinum alloy-paste electrodes were found to be undesirable owing to their reactive properties with WO_3 at high temperatures and finally, as reported in a previous paper,[3] platinum electrodes pressed on the sample by springs were again used. A sample holder and furnace were devised in flat forms suitable for insertion between the poles of a magnet. Lavite was used as the heat-resistive material.

In Fig. 1 the sample holder is shown, composed of a main part A and a lid B. Two platinum plates C as

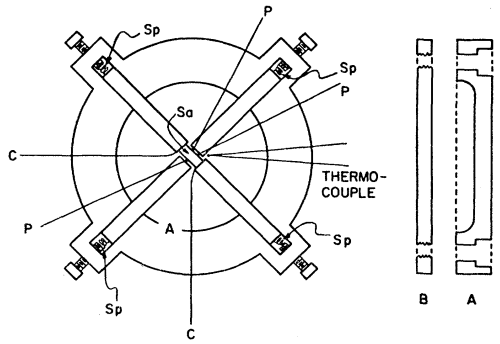

FIG. 1. Sample holder. A: main part; B: lid; Sa: sample; Sp: springs; C: current electrodes; P: potential probes.

† This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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[3] S. Sawada, J. Phys. Soc. Japan **11**, 1237 (1956).

[4] Morris, Redin, and Danielson, Phys. Rev. **109**, 1909 (1958).

[5] Redin, Morris, and Danielson, Phys. Rev. **109**, 1916 (1958).