The forbidden hyperfine paramagnetic resonance spectrum of vanadium in magnesium oxide
by David Hugh Dickey

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Physics
Montana State University

Abstract:
An X-Band electron paramagnetic resonance spectrometer has been built. The instrument's sensitivity, for a signal-to-noise ratio of unity, has been found to be 2 x 10 13 ΔH spins, under the conditions of 10-3 watts of incident microwave power and a time constant of one second. The spectrometer has been used to observe the previously unreported forbidden hyperfine spectrum of vanadium in magnesium oxide.

A quantum-mechanical justification for the existence of the forbidden spectrum is given.

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SPECTRUM OF VANADIUM IN MAGNESIUM OXIDE

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ABSTRACT

An X-band electron paramagnetic resonance spectrometer has been built. The instrument's sensitivity, for a signal-to-noise ratio of unity, has been found to be 2×10^{13} ΔH spins, under the conditions of 10^{-3} watts of incident microwave power and a time constant of one second. The spectrometer has been used to observe the previously unreported forbidden hyperfine spectrum of vanadium in magnesium oxide. A quantum-mechanical justification for the existence of the forbidden spectrum is given.

CHAPTER I

INTRODUCTION

An electron paramagnetic resonance spectrometer may be used to determine the spin state of the unpaired electrons in a sample of paramagnetic material. The spin degeneracy of the paramagnetic ion's ground state configuration is lifted by applying a magnetic field, and then transitions among these Zeeman levels are induced by exposing the sample to microwave radiation of the appropriate frequency. One can obtain the energies of all the transitions involving populated states, and from this can deduce a vast amount of information about the various mechanisms which determine the energy levels. A few of the mechanisms which can be studied are the hyperfine interaction, crystal Stark fields, dipolar interactions and lattice defects.

The phenomenon of magnetic resonance can be explained on a classical basis, as well as quantum-mechanically.[1,2] Classically, the magnetic moment μ resulting from the electron's intrinsic spin will experience a torque when the electron is placed in an external magnetic field. If the external field is uniform, this torque will induce a precession of the magnetic moment around the direction of the external field; the well known Larmor precession. If now a small magnetic field is applied at right angles to the external field H_o, and is made to rotate around H_o at the Larmor frequency, it will appear to be stationary in the reference frame of the electron's magnetic moment. The magnetic moment will then experience a torque which will try to cause a precession around the direction of H_1, the small applied field. This precession is in the rotating reference frame, where μ and H_1 are stationary relative to each other. The tendency to precess about H_1 will result in a change in the orientation of μ in the external field, to the opposite direction. The energy required for the change in orientation (spin-flip) is supplied by H_1. The occurrence of a spin-flip can therefore be detected by observing the absorption of power in the microwave beam which induces H_1.

The small field H_1, must be applied in a manner such that it appears to rotate in a plane perpendicular to H_o. This can be achieved by applying a linearly oscillating field, since such a field can be resolved into two rotating fields moving at the same frequency in opposite directions. The component which rotates in the direction opposite to the Larmor precession has no large effect on the system, since it has no stationary orientation with respect to the precessing dipole.

The condition necessary for resonant absorption, namely that the oscillation frequency of H_1 be equal to the Larmor frequency, is stated in the following equation:

$$h\nu = -2\vec{\mu}_e \cdot \vec{H}_0 = g_0 \beta H_0 \quad (1)$$

where g_o is the free electron g-value (2.0023), β is the Bohr magneton and μ_e is the magnetic moment of the electron. For fields commonly available in the laboratory, (1,000 to 10,000 gauss) the frequency ν lies in the microwave region.

A quantum-mechanical description of magnetic resonance is straightforward if one takes as a valid representation the set of sets $|M\rangle$, where M is the electron spin magnetic quantum number. The Hamiltonian function for an electron in the magnetic fields H_0 and H_1 is:

$$\mathcal{H} = g\beta\left[(\vec{H}_0 + \vec{H}_1)\cdot\vec{S}\right] = g\beta\left[H_0 S_z + H_1(\cos\omega t)S_x\right] \quad (2)$$
$$= g\beta\left[H_0 S_z + \tfrac{1}{2}H_1(\cos\omega t)(S_+ + S_-)\right]$$

where H_0 is assumed to be directed along the z axis, and H_1 is assumed to lie in the x direction. The substitution $2S_x = S_+ + S_-$ has been used. Operating on the state $|M\rangle$ with this Hamiltonian, one sees that a transition to a higher or lower spin state is possible:

$$\mathcal{H}|M\rangle = g\beta\left[H_0 M|M\rangle + \tfrac{1}{2}H_1(\cos\omega t)\times \left(\sqrt{S(S+1)-M(M+1)}\,|M+1\rangle + \sqrt{S(S+1)-M(M-1)}\,|M-1\rangle\right)\right] \quad (3)$$

The line intensity, or transition probability per unit time, for the state $|M+1\rangle$ is proportional to the matrix element squared:

$$I \sim |\langle M+1|\mathcal{H}|M\rangle|^2 = \frac{g^2\beta^2}{4}H_1^2|\cos\omega t|^2\left[S(S+1)-M(M+1)\right]. \quad (4)$$

The transition is allowed only if the condition for conservation of energy, Eq. (1), is satisfied.

There are several varieties of paramagnetic resonance spectrometer.(4-8) A common feature of all designs is a resonant cavity which contains the sample and for which there is some means of determining the amount of microwave power absorbed. It is difficult to change the resonant frequency of a cavity during an experiment, so the frequency is usually kept constant and the magnetic field is varied in order to explore the various Zeeman levels.

The purpose of this thesis is to describe the design and construction of a paramagnetic resonance spectrometer, and to indicate one application of its use.

CHAPTER II

THE SPECTROMETER

General Description of the Spectrometer

The spectrometer may be briefly described as a superheterodyne system with balanced mixer detection and magnetic field modulation. The klystrons operate at about 10 GHz, the IF amplifier operates at a nominal 30 MHz, the stabilization frequency is 22 KHz, and the field modulation is at 400 Hz. Figure I shows a block diagram of the entire system. The basic parts of the spectrometer are:

1. Signal and local oscillators, operating at X-band.
2. Microwave bridge, with magic tee.
3. Resonant cavity, containing the sample.
4. Magnet, adjustable from 0 to 10 kilogauss.
5. System to modulate magnetic field up to 50 gauss peak-to-peak at 400 Hz.
6. Microwave mixer, preamplifier, and IF amplifier.
7. Automatic frequency control system.
8. 400 Hz phase sensitive detector.
9. Strip-chart recorder.

This spectrometer is designed, with the exception of a few modifications, after the instrument described by Locher.[8]

The spectrometer's operation can be generally described as follows: microwave power, frequency modulated at 22 KHz, is fed to a reflection-type cavity which is in one arm of a balanced bridge. The cavity, containing the sample, is in a dc magnetic field of appropriate magnitude such

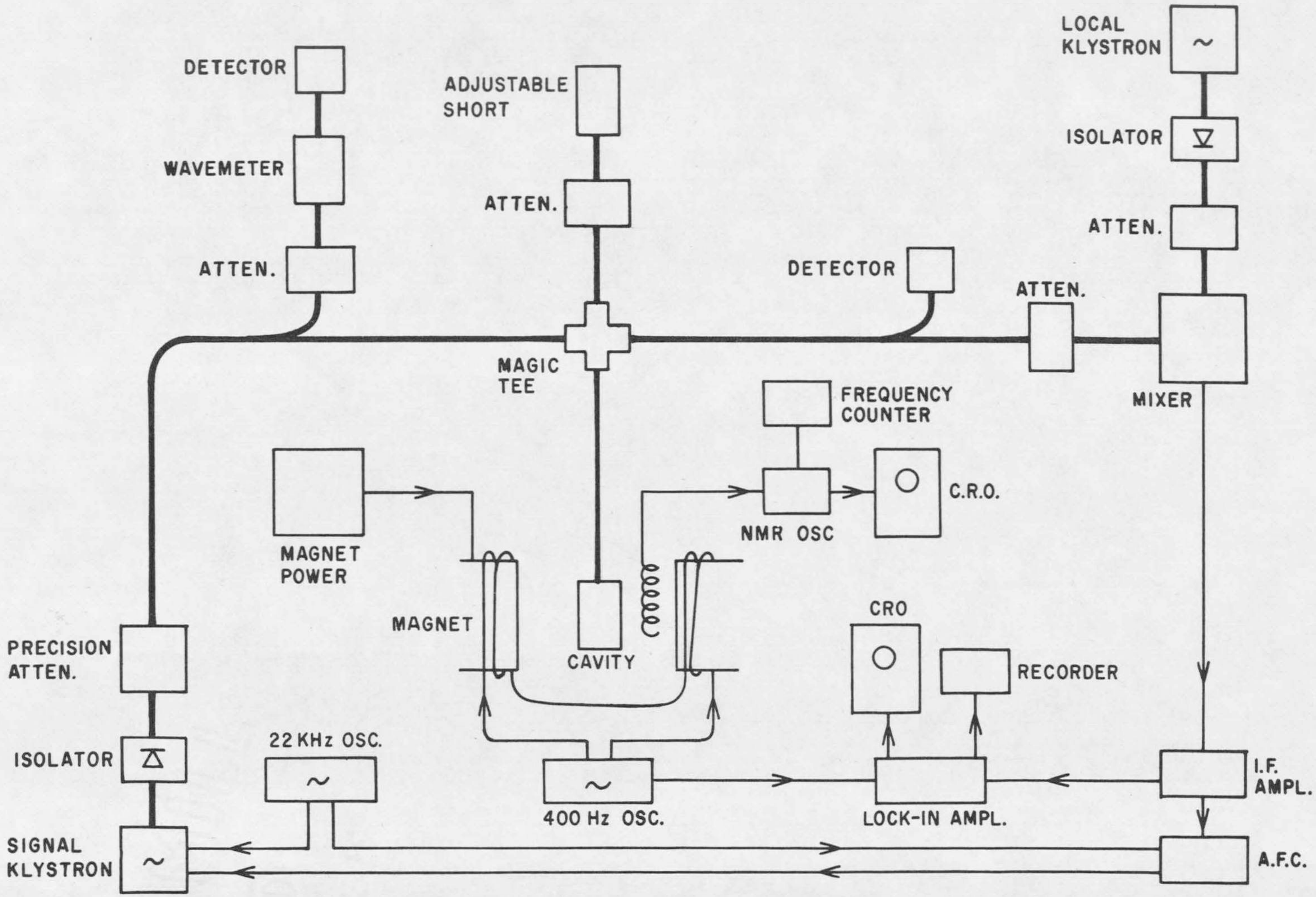

FIG. I

SPECTROMETER SCHEMATIC

as to cause paramagnetic absorption of the microwave power according to Eq. (1). The magnetic field is modulated (about one gauss peak-to-peak) at 400 Hz, so that the resonant condition of Eq. (1) is varied at that frequency. The microwave power returned from the cavity is therefore amplitude modulated at 400 Hz, the amplitude depending on the strength of the paramagnetic absorption.

The phase of the 22 KHz frequency modulation is also shifted in the returned signal. The direction of the phase shift depends upon whether the klystron frequency is above or below the cavity's resonant frequency.

The reflected power, with its modulations, is mixed with a microwave signal from the local oscillator. The local klystron oscillates at a frequency nominally 30 MHz higher than the signal klystron. The 30 MHz beat signal is preamplified and fed to the IF amplifier. At the last stage of IF amplification, the 30 MHz is detected, producing the "control" signal at 22 KHz, and the resonance signal at 400 Hz. Each of these signals is filtered and further amplified. The control signal is phase compared with a 22 KHz reference to generate a correction voltage which is applied to the signal klystron. This keeps the klystron locked to the cavity frequency. The 400 Hz signal is phase-sensitive detected, using the field-modulation source as a reference, and the resulting dc output is displayed on a strip-chart recorder. In an experiment, the magnetic field is slowly increased so that the time axis on the strip-chart can be read as a magnetic field axis.

Construction of the Spectrometer

The microwave system. The microwave power is generated by two Varian X-13 klystrons. Each klystron is enclosed in a seven inch diameter brass can filled with transformer oil, to stabilize the temperature. The microwave circuit is shown on the spectrometer's schematic diagram, Figure I. Power from the signal klystron passes first through an isolator, and then a precision attenuator which is adjustable from 0 to 50 db. A 10 db directional coupler takes off some power to the cavity wavemeter. The remaining power reaches the magic tee where it is divided into two equal beams, in the cavity arm and the balancing arm of the microwave bridge. The amplitude-modulated power reflected from the cavity is again divided at the tee, as is that returning from the balancing arm. The net signal entering the fourth arm of the bridge goes into the microwave mixer where it is beat against a microwave signal from the local klystron. The beat signal, nominally at 30 MHz, is preamplified in the mixer and is then fed to the IF amplifier. A directional coupler between the magic tee and the mixer takes a small fraction of the signal for monitoring and tuning purposes.

The cavity, which contains the sample, has a tunable iris which allows some control over the amount of microwave power which can enter or leave the cavity. The resonant frequency of the cavity is tunable. The design and construction of the cavity is described in a separate section.

The balancing arm of the bridge consists of a level-set attenuator and an adjustable short. This allows the phase and intensity of the microwave signal to be adjusted so that they closely match those of the signal reflected from the cavity.

Klystron power control. The power requirements for the klystrons are supplied by three sources, all of which are highly regulated. The heater current is supplied at 6.3 v dc from a regulated supply which has a maximum current output just slightly greater than that required by the klystrons at their operating temperature. The filaments are heated more slowly in this way, since their cold resistance is much lower than their operating resistance. The beam current is supplied at +350 v by a standard 300 v power supply modified for the higher voltage. The reflector voltage is obtained from two modified standard supplies wired in series to produce -700 v. The control circuit is shown in Figure II.

An unusual feature in this spectrometer is the single set of power supplies used to power both klystrons. The duplicated circuitry is indicated in Figure II, except that the local klystron has no interconnection with the AFC. Other features of the control circuit are a delay relay which allows the reflector voltage to build up before the beam supply is switched on, and a safety mechanism to prevent the reflector voltage from going positive with respect to the cathode. The safety mechanism consists of a diode which can support only a negative reflector voltage, in series with a 4.5 v battery which in fact prevents the reflector from reaching a potential more positive than -4.5 v.

The high voltage power supplies are hand-made from a circuit given by Elmore and Sands.[9]