

Local Molecular Spectroscopy Using the Evanescent Microwave Probe Technique: Electron Spin Resonance

Massood Tabib-Azar
Case School of Engineering
Case Western Reserve University
Cleveland, OH 44106
USA

Xiyang Li
Case School of Engineering
Case Western Reserve University
Cleveland, OH 44106
USA

J. Adin Mann, Jr
Case School of Engineering
Case Western Reserve University
Cleveland, OH 44106
USA

Abstract— a method based on evanescent microwave microscopy (EMM) was developed to spatially resolve small number of electron spin resonant (ESR) transitions in single crystal ruby (Cr^{3+}). The EMM probe operates at a resonance frequency of 3.77 GHz (S-band ESR) in a modulated electromagnetic field in the range of 0.02 to 0.6 Tesla. The current EMM probe with a magnetic dipole loop of around 1 mm radius was capable of resolving 20,000 spin transitions compared to standard ESRs with $\sim 10^7$ detection limit. We are currently improving the spatial resolution of our probe to enable detection of 2000 spin transitions with the goal of reducing it to a few spins by using a microwave probe integrated with an atomic force microscope. Even with its relatively low current resolution, the probe is unique and can be used in micro-fluidic channels and biological tissues to detect free radicals. We are pursuing applications of the probe in Alzheimer and other tissue studies where mapping the spatial distribution of free radicals may shed some light on the cause and diagnosis of disease.

for the EMM, the spatial location of the probe tip is well defined and the sample is placed at the tip of the probe. Therefore, both the density and the spatial location of the spin centers can be determined.

Table 1. Electron Transitions for Cr^{3+} at 3.77 GHz

S+1	S	f (GHz)	(2S+1)D	H_0 (Oe)
3/2	1/2	3.77	-7.62E-24	5505
1/2	-1/2	3.77	0.00E+00	1359
-1/2	-3/2	3.77	7.62E-24	2787

ESR, also called electron paramagnetic resonance (EPR), is very selective and only a molecule with unpaired electrons (also known as free radical) can generate ESR signals. High spatial resolution detection of electron spin transitions can be used to map free radicals in biological tissues that cause aging and cancer, where thousands of non-free-radical molecules may be present. In material research, defects may also be detected using this technique because they trap unpaired electrons. Additionally, ESR signal may be used in detecting explosives and food freshness. Spatial ESR detection may also facilitate quantum computing, high density memory device (Spin Net) and other applications.

Building on our previous work [2-6] that integrated a microwave waveguide on an atomic force microscope probe to simultaneously perform AFM topography and map the

I. INTRODUCTION

The size of the electronic devices is expected to reach 10 nm or less by 2010 reducing the number of electrons in the channel to about 10. With such a small number of electrons determining on/off behavior of the device, the number-fluctuation and other noise sources become more important. Thus, research groups are attempting to use other degrees of freedom of charge carriers, such as electron spins, to improve the signal to noise ratios. One of the manifestations of the unpaired electron spin is its resonant transition (flipping) in the presence of external magnetic and suitable RF fields. The aim of this study is to explore the possibility of detecting one single electron as a localized object, using an EMM probe. Among many ESR samples, Ruby has been studied extensively and it was treated as the standard ESR reference material, because of strong ESR signal and high observation temperature (room temperature). Selection rules allow three possible electron spin transitions for the Cr^{3+} ions at 3.77 GHz as shown in Table 1 [1].

For most conventional ESR experimental setups, the sample is inserted in the center of a microwave cavity. While

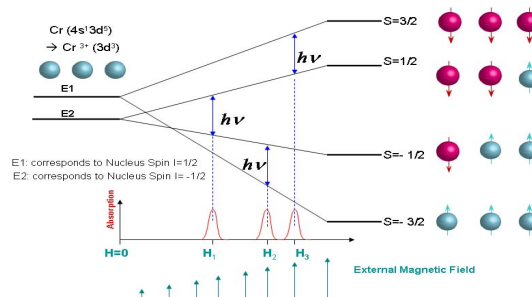


Fig. 1 Cr^{3+} Energy levels splitting with external magnetic field.

electromagnetic properties of materials, we designed and developed a magnetic dipole probe fed by a $\lambda/4$ resonator section to produce RF magnetic field in or over a sample to spatially map spin transitions. Although in its current embodiment, the probe is quite large and measures around $2 \times 3 \times 1 \text{ cm}^3$, it was needed to understand the evanescent wave-sample interactions for spin transition detection and has started revealing interesting information regarding spatial distribution of defect centers in ruby.

II. THEORETICAL BACKGROUND

A. Mathematical Model of Cr^{3+} Energy Levels

The electron configuration of Chromium is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$. In single crystal Ruby, the Cr atom replaces the Al atom in Al_2O_3 crystal and gives up 3 electrons, which results the Cr^{3+} ion electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$. The Cr^{3+} ions in ruby are surrounded by distorted octahedral of oxygen ions. The distortion of the crystal lattice (octahedral symmetry) gives the energy level degeneracy of three electrons from the 3d shell of the Cr^{3+} ion, when external magnetic field presents. As shown in Fig. 1, there are four different energy levels for the three 3d orbit electrons of Cr^{3+} ion, and according to selection rules, only three transitions are allowed. It is clearly shown that three possible magnetic fields may result this kind of transition, which is shown as three strong signal spikes in the ESR spectrum. When one of these transitions occurs, a tiny amount of energy is absorbed from the microwave energy source, which can be recorded to produce ESR signals.

To determine if the electron state transition is forbidden or allowed in quantum mechanics, the following Selection Rules must be followed.

- l (orbital): change in $l = \pm 1$
- m (orbital magnetic) : change in $m = 0$ (for linearly polarized light), $= +1$ (for right-handed circularly polarized light), $= -1$ (for left-handed circularly polarized light).
- S (spin angular momentum): change in $S = \pm 1$

The ESR occurs when the microwave energy is equal to the allowed electron spin transition energy gap:

$$E = hf = g\mu_B S H(t) \quad (1)$$

B. Magnetic Field Modulation

The ESR resonance condition occurs when the microwave energy is exactly equal to the energy difference between two electron energy states. To achieve coherent ESR measurement, two different approaches can be applied to obtain the ESR signal, one is magnetic field modulation and the other is the frequency modulation.

In this study, the magnetic field modulation is chosen and the amplitude of the modulation is less than the ESR line

width. It is practical to use the linear magnetic field sweep step as the modulation amplitude, for an instance, if the linear magnetic field is sweeping at one Gauss per step, the modulation amplitude should be close to one Gauss. Therefore the instantaneous magnetic field at any moment can be written as:

$$H(t) = H_C + \delta H_S(t) + H_m \cos(\omega t) \quad (2)$$

where $\delta H_S(t)$ is the magnetic field scanning rate (Gauss/sec.), which is much slower than the sinusoid component. The term in Eq. (1) can be treated as a constant to the sample at any moment of the scanning process.

The magnetic field $H(t)$ scans the absorption curve slowly as shown in Fig. 2. As the magnetic modulation signal scans a portion of the absorption line, which alters the ESR absorption power at the same frequency. Therefore, the field modulation can also be treated as absorption power modulation. At the left half of the absorption curve, when the modulation field is positive, the amount of power absorption increases, while the power absorption decreases at the right half of the absorption curve when the modulated field is positive. This can be observed as 180 degree phase shift when the constant field swept from the left of the peak to the right. At the resonance condition, the ESR absorption power is equal to the reflected power from the resonator, which can be isolated from the incoming microwave power by the circulator. The crystal detector is operating in its linear region, where the output is proportional to the reflected microwave power.

C. Microstrip Resonator

Instead of using a microwave cavity, this study uses a Microstrip resonator [7] to obtain useful spatial information

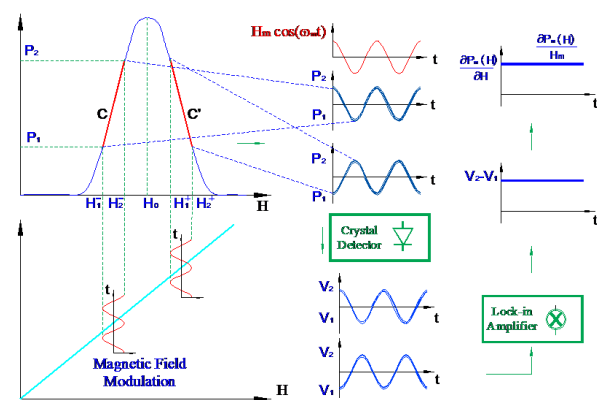


Fig. 2 The relationship between power absorption slope and the magnetic field modulation.

along with the ESR signals. The Microstrip resonator is made by a strip line with 2.3 mm width and 35 μm thick copper strip and 0.8 mm thick Duroid with permittivity of

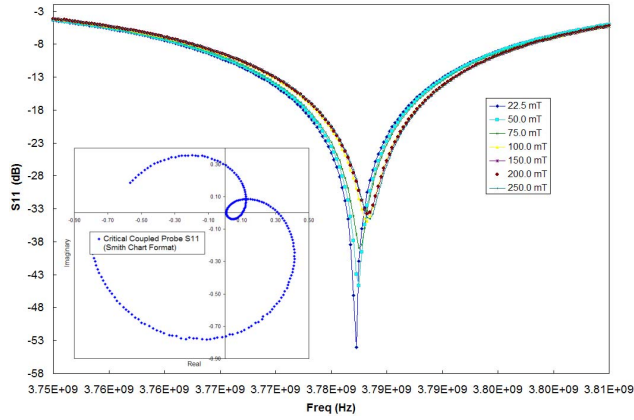


Fig. 3 The reflection coefficient S_{11} of the microstripline resonator.

2.2 as the dielectric material between the ground copper plane and the copper strip. As shown in Fig. 3, the Microstrip Resonator has been fine tuned to be critical coupled with the circulator and transmission line. The reflection coefficient is close to -42 dB and the system overall Q is around 5000.

As shown in Fig. 3, the reflected power from the EMM ESR probe is at the minimum when the magnetic field is off. During the ESR the power absorbed by Ruby sample altered the perfect match between the probe and the transmission line, which results larger amount of reflected power.

III. EXPERIMENT MEASUREMENT APPARATUS

The experiment setup is shown as Fig. 4, the EMM probe is a microwave strip line resonator with an overall Q factor of more than 5,000. The probe tip was shorted to the ground plate by a 0.15 mm copper wire to generate a strong alternating magnetic field at microwave frequency. The synthesized sweeper generates a microwave signal at 3 dBm power at 3.77 GHz, which passes through the circulator and incident on the microstripline resonator. After tuning the resonator to critical coupling condition by using the tuning screw, a standing electrical magnetic waveform was generated and sustained at the probe tip and minimum power is reflected to the crystal detector and the sensitivity of the probe is at the highest level. A 3 feet long coaxial cable was used to make certain that the electromagnetic field will not affect the circulator operation.

A large current-regulated electromagnet (0.2-1.6 T) was used to generate uniform magnetic field. A 24-turn solenoid coil was wrapped around the main pole of the electromagnet to generate the magnetic modulation field of 2 Gauss at 5.3 kHz. The probe tip was parallel to the electromagnet poles, resulting in a perpendicular main magnetic field to the RF magnetic field.

The output of the crystal detector was amplified and band passed (3 kHz and 30 kHz) and was subsequently detected

by a lock-in amplifier with synchronized with the magnetic field modulation frequency. The ESR signal was collected by a DAQ card that was also used to control the magnetic field and the experiment.

IV. ESR SIGNAL DETECTION

Real time ESR detection software was developed to precisely control the scanning magnetic field and display the ESR signal in real time. The software employed multiple loops to average out the white noise for one single ESR data point. With a scanning time of 400 ms per data point and 30 ms time constant, three distinct ESR first derivative signals were detected as shown in Fig. 5. The peak magnetic fields matched the theoretical predications based on the Standard Reference Materials: ESR Intensity Standard: SRM 2601. Based on the line shape of the ESR signal, the number of spins was in the range of 20 -100 thousands. When the sample was removed from the probe or without the magnetic field modulation, the ESR signal disappeared totally.

The first ESR signal was around 1363 Oersted and the comparison between the experimental data and the theoretical Gaussian and Lorentzian type line shape are shown in Figs. 6 and 7. Both plots show that the experimental line width is slightly larger than the theoretical prediction due to magnetic field modulation ESR line broaden.

At 3.77 GHz, the gyromagnetic ratio is $\gamma = \frac{g\mu_B}{\hbar} = 1.737 \times 10^7 \text{ Hz / Gauss}$. For an single electron the spin-spin relaxation time can be estimated as [8] $T_{\text{relaxation}} = \frac{2}{\sqrt{3}\gamma\Delta H_{pp}} = 2.753 \times 10^{-9} \text{ sec}$.

By integrating the first derivative of the ESR absorption line shape, the actual line shape can be obtained. The peak

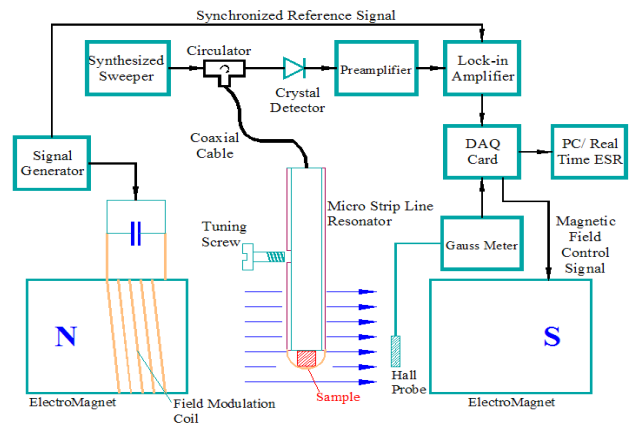


Fig. 4 The ESR experimental setup with magnetic field modulation.

of the ESR line shape is the maximum Power absorption

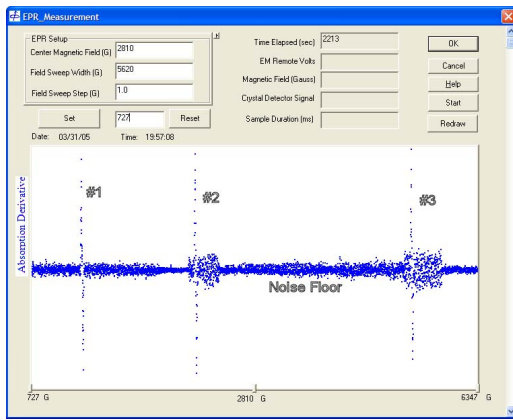


Fig. 5 Measured ESR signals.

point, therefore the peak ESR absorption power can be written as
$$P_{\text{Absorption}} = \frac{V_M / 120 \cdot 10 \mu V}{S_C \cdot G_p} = 1.24 \times 10^{-4} \mu W$$

Where the lock-in amplifier has 120 reading at full scale of 10 μV , crystal detector sensitivity S_C is 0.5 mV/ μW and

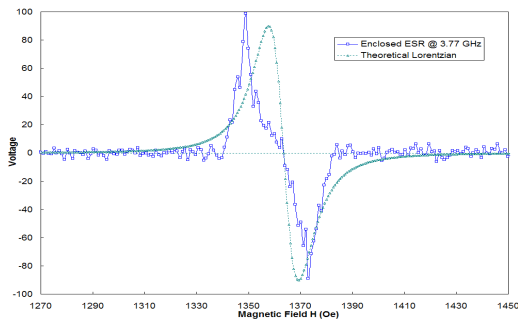


Fig. 6 The first derivative of the ESR Signal compared to a Lorentzian line shape.

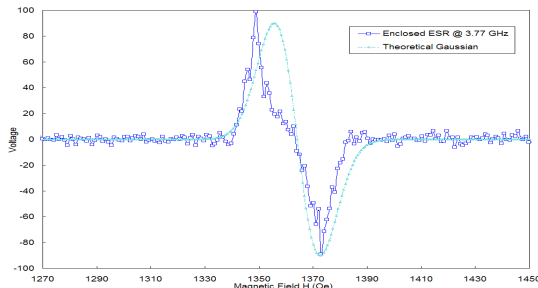


Fig. 7 The first derivative of ESR absorption signal crossed zero at 136.3 mT with the enclosed EMM probe. the preamplifier gain G_p has a gain of 1000. For one single

electron spin transition, the microwave energy absorption is $h\nu = 2.4995 \times 10^{-24} J$.

The power required at resonance condition for one single electron is $9.079E-10 \mu W$ which is the required energy divided the spin-spin relaxation time. Therefore, the maximum number of spin centers at the peak of the absorption is
$$N_{\text{max}} = \frac{P_{\text{Absorption}}}{P_{\text{Electron}}} = \frac{1.24 \times 10^{-4} \mu W}{9.079 \times 10^{-10} \mu W} = 1.37 \times 10^5$$

The estimated signal to noise ratio (SNR) is around 6.8:1, therefore, the minimum number of detectable spin centers is

$$N_{\text{min}} = \frac{N_{\text{max}}}{\text{SNR}} = 2.01 \times 10^4$$

V. CONCLUSIONS

This paper presents the ESR spatial detection in the single crystal ruby using a microwave microstripline resonator with an overall Q factor of more than 5,000. With a small modulated field imposed on the DC bias magnetic fields, the ESR signal was synchronized with the magnetic field modulation signal. Three distinct ESR signals were detected in ruby, and the magnetic fields matched the theoretical predications. Future study will be conducted to map the ESR signals on the solid surface and acquire images of localized ESR signals. Also by combining with AFM and using carbon nanotubes to replace the copper wire loop, the spatial resolution is expected to increase dramatically and it is possible to detect single electron spatially in the near future.

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