Introduction to Electron-Spin Resonance (ESR) Spectrocopy

Toni Shiroka

February 26, 2013

Abstract Electron-spin resonance (ESR) represents the resonant absorption of electromagnetic radiation by unpaired electron magnetic moments placed in a magnetic field. ESR spectroscopy has found applications in a wide range of fields, from chemistry and biology to the novel and stimulating areas of quantum computation and "single-spin" detection. By carrying out simple experiments the student will learn the basics of the ESR technique and the related microwave technology, hence gaining knowledge in one of the active areas of spectroscopy.

Contents

1 Objectives

1. Understand the basics of microwave spectroscopy, its advantages and limits. Familiarize with the concepts of waveguide, resonant cavity, quality factor, hybrid junction, etc. Determine the cutoff frequency of a waveguide.
2. Understand the concept of magnetic resonance and apply it to the case of unpaired electron spins in a magnetic field. Observe and interpret the ESR signal (both absorption and dispersion) in a typical sample. Estimate the spin-spin relaxation time from the absorption linewidth.
3. Learn how lock-in detection works and understand how its key features are used to reveal the weak ESR signal. Search the literature (see, e.g., [8]) for a more detailed explanation relating the bridge reflectivity with the sample's complex magnetic susceptibility.
4. By using the main attenuator investigate the dependence of the diode detector output from the microwave input power. Try to improve the ESR signal by balancing the microwave bridge via the reflection arm attenuator.

Previous versions of this document by B. Simovič and J. Rey.

Laboratorium für Festkörperphysik, ETH Zürich, Hönggerberg

2 Theoretical concepts

2.1 The phenomenon of ESR

As an elementary particle the electron has an intrinsic angular momentum called spin ($\boldsymbol{S}$) whose behaviour is described by the rules of quantum mechanics. For a particle with a total spin quantum number S the orientation of angular momentum in space is quantized into $2S+1$ states which, for the $S = 1/2$ electron, corresponds to two different states. These are conventionally labelled α and β and correspond (in $\hbar$ units) to spin projection values along an *arbitrary* z direction $S_z = \pm 1/2$, respectively. Due to space isotropy the α and β electron-spin states have the same energy (i.e. they are degenerate). This is not the case, though, when the electron spin is placed in a magnetic field.

Since the electron carries a charge $-e$, the presence of an angular momentum $\boldsymbol{S}$ (in $\hbar$ units) implies a magnetic moment $\boldsymbol{\mu_e}$ proportional and opposite to it

$$\boldsymbol{\mu_e} = -g\mu_{\mathrm{B}}\boldsymbol{S}, \tag{1}$$

where $\mu_{\mathrm{B}} = e\hbar/(2m) = 9.274 \times 10^{-24}$ J/T is the Bohr magneton and g is the Landé factor ($g = 2.0023$ for a free electron). The existence of a magnetic moment associated with

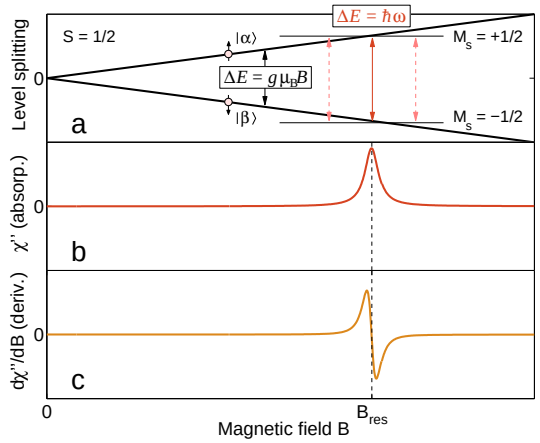

Fig. 1 (a) The electron-spin Zeeman effect. At zero field the spin states α ($M_s = 1/2$) and β ($M_s = -1/2$) have the same energy. In the presence of a static magnetic field the energy separation of the two spin states is proportional to the applied field. As the magnetic field is *swept* across the resonance ($\Delta E = g\mu_B B = \hbar\omega$), the transfer of energy from the EM radiation (with *constant* frequency ω) gives rise to an absorption line (b), which in ESR is observed by detecting its derivative $\mathrm{d}\chi''/\mathrm{d}B$ (c). Here $\chi(\omega) = \chi' - i\chi''$ represents the sample's magnetic susceptibility, with χ' the dispersive and χ'' the absorptive part, respectively.

the electron spin is the reason for the energy separation between the α and β electron spin states in the presence of a magnetic field (see Fig. 1a). As the energy of a magnetic moment $\boldsymbol{\mu_e}$ in an applied magnetic field $\boldsymbol{B}$ is given by the scalar product $E = -\boldsymbol{\mu_e}\boldsymbol{B}$, the resulting electron-spin energy levels, characterized by the magnetic quantum number M_s, are

$$E_\pm = \pm\frac{1}{2} g\mu_B B. \tag{2}$$

Here the positive sign refers to the α state and the negative one to the β state. The splitting of the electron-spin energy level into two levels in the presence of a magnetic field is called the *Zeeman effect*, and the interaction of the electron magnetic moment with an external applied magnetic field is called the electron *Zeeman interaction* (see Fig. 1a).

If electromagnetic radiation is applied at a frequency ω that corresponds to the separation between the energy levels

$$\boxed{\Delta E = E_+ - E_- = g\mu_B B = \hbar\omega,} \tag{3}$$

energy quanta are absorbed from the electromagnetic field. This is the phenomenon of ESR. The relation between the resonance frequency $\nu \equiv \omega/(2\pi)$ (in Hz) and the magnitude B of the magnetic field (in G) is $\nu = 1.3996 \times 10^6 (gB)$ which, for a typical 0.35-T magnet and assuming $g = 2$, gives $\nu = 9.5$ GHz. This radiation frequency is in the microwave X-band region (8–12 GHz).

For electrons bound in an atom or a molecule the phenomenon of ESR may not be observed at all because electron spins pair in atomic or molecular orbitals so that no net spin or orbital magnetism is exhibited, and the material is said to be *diamagnetic*. When an atom or a molecule has an odd number of electrons, however, complete pairing is not possible and the material is said to be *paramagnetic*. In this case ESR (also called electron paramagnetic resonance, EPR) can be observed.

So far we have considered a single electron interacting with an external magnetic field. In the present experiment, however, we deal with a macroscopic sample, i.e. with a *statistical ensemble* of electron magnetic moments. In thermodynamic equilibrium the relative populations of the energy levels N_+ and N_- are given by the Boltzmann distribution

$$\frac{N_+}{N_-} = \exp\left(-\frac{\Delta E}{k_B T}\right), \tag{4}$$

where $\Delta E = E_+ - E_-$, k_B is the Boltzmann constant, and T is the absolute temperature. Since microwave absorption is possible only because of a *population difference* ΔN between the energy levels (see appendix A), to detect an ESR signal this difference should be made as large as possible. At room temperature and for a Zeeman splitting corresponding to a frequency of 10 GHz, $\Delta E = g\mu_B B \ll k_B T$ and

$$\frac{\Delta N}{N} \simeq \frac{g\mu_B B}{k_B T} = 1.5 \times 10^{-3}, \quad \text{with} \quad N_+ \simeq N_- \simeq N. \tag{5}$$

The same population difference between the magnetic energy levels is responsible for the *macroscopic* magnetic response of the sample: $\boldsymbol{M} = \chi \boldsymbol{H}$, with $\boldsymbol{M} = \sum \boldsymbol{\mu_e}$ and $\chi = \chi(\omega)$ the frequency-dependent magnetic susceptibility. Since the energy of the spin system is $U = -\int \boldsymbol{M}\mathrm{d}\boldsymbol{H} = -1/2\chi\boldsymbol{H}^2$, the power absorption in resonance P can be expressed more conveniently in terms of changes in magnetic susceptibility. By taking into account the time evolution of the magnetization $\boldsymbol{M}$, determined by both the precession in the applied field and by relaxation phenomena (*Bloch equations* [9,10,14]), it can be shown that $P = \omega\chi'' H_1^2$, with H_1 the magnetic component of the oscillating EM field. Therefore, referring to Fig. 1b, the detected ESR signal is proportional to χ'', the absorption part of the sample's magnetic susceptibility, $\chi(\omega) = \chi' - i\chi''$. The dispersion part χ' instead accounts only for a slight shift in resonance frequency.

2.2 The hyperfine interaction

The hyperfine interaction represents the interaction between the magnetic moment of an electron with the magnetic moment of the nucleus in its vicinity. Nuclei with a total spin quantum number I have a magnetic moment which also has $(2I+1)$ different allowed orientations. The magnetic field associated with the nuclear moment can then add to or subtract from the applied field experienced by the electron spin system associated with it. In a bulk sample some electrons

will therefore be subject to an increased field and some to a reduced field. Consequently, the original electron resonance line is split into $(2I+1)$ components. For example, when the electron spin of a transition metal or a free radical[1] interacts with its own nuclear spin, the hyperfine interaction is described by the Hamiltonian term

$$\mathscr{H}_{hf} = A\boldsymbol{IS}, \tag{6}$$

with A the hyperfine coupling constant. The coupling constant varies with the nuclear species, and it is a measure of the strength of the interaction between the nuclear and electron spins. Figure 2 illustrates the phenomenon: the hyperfine interaction between the electron spins[2] and the nuclear $I = 5/2$ spin of the Mn^{2+} ion splits the resonance line of the $3d$ electrons into six sub-levels. In molecules, the unpaired electron is shared by several atoms and the resulting hyperfine structure is the result of a Hamiltonian term of the form

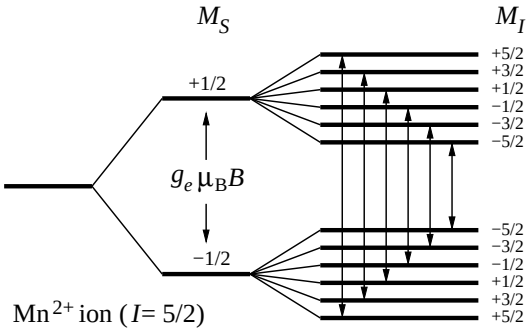

Fig. 2 Energy level splitting in Mn^{2+} due to the electron-nucleus hyperfine interaction. The arrows show the allowed $\Delta m_I = 0$ transitions induced by the microwave field radiation. As the magnetic field is swept through resonance, six lines will be observed, starting from the transition with the highest splitting.

$$\mathscr{H}_{hf} = \sum A_i m_i, \tag{7}$$

where the projection m_i of the ith nuclear spin on the magnetic field direction may take on the $2I_i + 1$ values I_i, $I_i - 1$, $I_i - 2$, …, $-I_i + 1$, $-I_i$. For example, the hyperfine interaction with the two equally coupled nitrogen nuclei ($I = 1$) in the DPPH molecule (see Fig. 3) leads to a splitting of the resonance into five components of respective intensity 1:2:3:2:1.

2.3 The dipole-dipole interaction

For a large concentration of electron spins, the electron magnetic moments also interact appreciably with each other and

[1] A free radical is an atom, molecule or ion with one unpaired electron. By contrast, a transition ion can have several unpaired electrons.

[2] The electronic configuration of the free Mn^{2+} ion is $3d^5$.

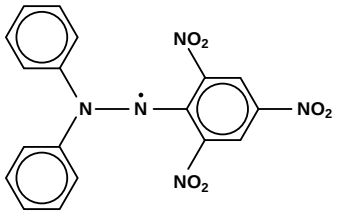

Fig. 3 Structure of the stable free-radical 2,2'-diphenyl-1-picrylhydrazyl (DPPH). Due to the two almost equivalent nitrogens it gives rise to a five-line ESR pattern. The $g = 2.0035$ value of DPPH, close to that of a free-electron, makes it a widely used standard for g-factor calibrations in ESR spectroscopy.

this can alter the ESR spectra considerably. The interaction is mediated by the dipolar field associated with the magnetic moment of the electron $\boldsymbol{\mu_e}$

$$\boldsymbol{H}(\boldsymbol{r}) = \frac{\mu_0}{4\pi}\frac{1}{r^3}\left[-\boldsymbol{\mu_e} + \frac{3(\boldsymbol{\mu_e}\boldsymbol{r})\boldsymbol{r}}{r^2}\right]. \tag{8}$$

By combining equations (1) and (2), we see that the energy of the dipole-dipole interaction between two adjacent electrons separated by r lies between E_{dd} and $-E_{dd}$ with

$$E_{dd} = \frac{\mu_0}{8\pi}\frac{1}{r^3}g^2\mu_B^2. \tag{9}$$

Therefore, the dipolar interaction induces a *broadening* of the resonance line, which increases with the concentration of the dipole moments.

3 The ESR spectrometer

Due to the tiny amount of energy absorbed by the electron spin system the detection of ESR signals is challenging. Although the typical spectrometer reflects the basic excitation-detection scheme, different additional techniques are used to increase its sensitivity. These include microwave bridge detection, resonant-cavity signal amplification, noise reduction via filtering, and lock-in detection. The ESR spectrometer consists of four essential components, as shown in Fig. 4:

- A monochromatic microwave source.
- A waveguide system for delivering the microwave power to the sample to be investigated.
- A resonating cavity designed to enhance the coupling between the sample and the electromagnetic field.
- A microwave detector to detect the response of the sample to the microwave radiation.

The reflection microwave spectrometer mimics in its operation other bridge setups, such as the resistance bridge or the Michelson interferometer. In our case the signal to be detected arises from an imbalance between two arms of the bridge.

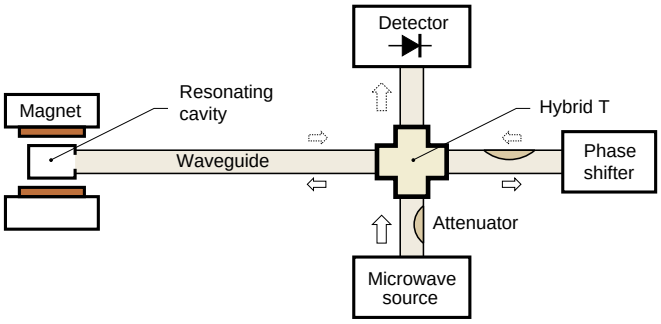

Fig. 4 Simplified diagram of an ESR spectrometer. The waveguide system also includes a phase shifter, a hybrid junction and two attenuators. Arrows indicate the propagation direction of the microwaves.

3.1 Components of the ESR system

The different components making up the ESR spectrometer are described in more detail below:

The monochromatic microwave source consists of a Gunn diode oscillator stabilized by a dielectric resonator. The fundamental frequency in our case is $\nu_0 \simeq 9.4$ GHz. By slowly turning the screw on top of the metallic case of the oscillator one can tune its frequency. The value of the latter can be read by using the frequency counter located next to the source.

Two **calibrated attenuators** are used to control the microwave power level, since the output of the source cannot be varied easily. The attenuation scale is logarithmic:

$$\text{Att. [dB]} = 10 \log \frac{P_{\text{in}}}{P_{\text{out}}}, \tag{10}$$

where P_{in} and P_{out} are the input and output microwave power, respectively, measured in the same units.

The waveguide is a rectangular open-ended metallic tube enclosing the dielectric medium where the electromagnetic waves propagate. Boundary conditions have to be fulfilled by the electric and magnetic components of the EM wave on the metallic waveguide walls. Consequently the propagation is restricted to a set of *transverse* modes occurring at well-defined frequencies. There is an upper wavelength cutoff above which no EM wave propagation is possible, which, for a rectangular waveguide of width a, corresponds to $\lambda_c = 2a$. The wavelength in vacuum λ, that in the guide λ_g, and the cutoff length satisfy the relationship $\lambda^{-2} = \lambda_g^{-2} + \lambda_c^{-2}$. For a standard $a \times b = 0.9" \times 0.4"$ waveguide (WR90) in use at X band the allowed TE_{10} modes range from 8.2 to 12.5 GHz, with 9.5 GHz being the typical frequency.

The hybrid junction ("magic" T) is a 4-port device as sketched in Fig. 5 and represents a crucial part of a reflection ESR spectrometer. The travelling TE_{10} mode from the source at input 1 (H-port) is evenly split into two waves propagating to ports 2 and 3. No transmission from port 1 to port 4 can occur, since port 1 is orthogonal to port 4 (the first is part of an H-component T-bridge, while the latter is of an E-component T-bridge, each sustaining EM waves of opposite symmetry). Owing to the presence of the source and detector,[3] no reflections occur at ports 1 and 4. Waves are therefore reflected only from ports 2 and 3, with a relative phase difference $\Delta\varphi$. If $\Delta\varphi = 0$ then the two reflected waves recombine and couple into port 1 (also known as Σ port). If $\Delta\varphi = \pi$, the two recombine and couple into port 4 (known also as Δ port). In our case, the relative phase and amplitude of inputs 2 and 3 can be controlled via a phase shifter and attenuator, respectively, both located on the right arm (port 3) of the hybrid coupler.

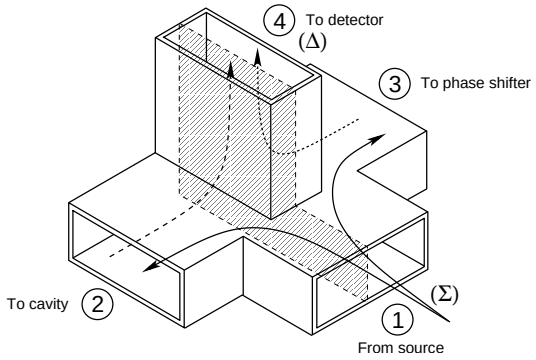

Fig. 5 A microwave hybrid (or "magic" T) junction consists of an H T-bridge (horizontal) and an E T-bridge (vertical). Due to symmetry considerations, a signal applied to H-port 1 (Σ) splits equally to ports 2 and 3 (full lines). On the other hand, only the difference of the signals applied in 2 and 3 will appear in E-port 4 (Δ) (dashed lines). Ports 1 and 4 are always isolated from each other.

The microwave detector is a crystal rectifier (planar-doped barrier diode), which converts the incident microwave power to an electrical current. The principle of operation of the detector is the rectification of microwave (mw) signals, while leaving the (slow) modulation untouched. Since the diode does not respond to the fast mw oscillations, its output is $i \propto \langle V_{\text{sig}}^2(t) \rangle_\tau$, with τ the averaging time reflecting the detector bandwidth. For $P \lesssim 1$ mW the current is proportional to the microwave power ($i \propto P$), while for $P \gtrsim 1$ mW it is proportional to $\sqrt{P}$. The best detection sensitivity is achieved in the latter regime (since there $i \propto \sqrt{P} \propto V_{\text{sig}}$), at a typical detector current of about 0.2 mA. The detection characteristics depend strongly on the slope $\text{d}i/\text{d}P$, specific to each Schottky barrier diode.

The resonating cavity consists of a closed metallic box with an iris to allow the microwaves to couple in and out (see

[3] Reflections could occur in case of an impedance mismatch along the wave path. However, both the detector and the source are designed to have (at their entrance planes) an impedance which matches that of the 50-Ohm waveguide.

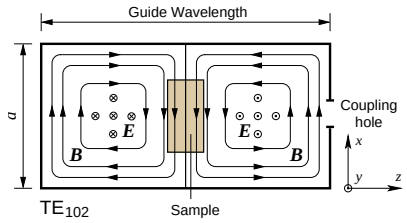

Fig. 6 Electric and magnetic field configurations in a TE_{102} mode rectangular resonant cavity. The sample is positioned where the magnetic field has a maximum. Typical iris openings are 0.2–0.25 in (X band).

Fig. 6) and is essential in amplifying the weak signal from the sample. Since the microwave magnetic field drives the ESR absorption, the sample position inside the cavity coincides with a magnetic field maximum (typ. 1 μT). A cavity possesses resonant frequencies $\nu_{\rm res}$ (related to its dimensions) at which the energy stored reaches large values. The efficiency of the energy storage in the cavity is indicated by its quality factor Q. The latter is a measure of the frequency width (FWHM, $\Delta\nu$) of the resonance, or equivalently of the cavity selectivity, and is defined as

$$Q = \frac{2\pi\,(\text{Energy stored})}{\text{Energy lost per cycle}} = \frac{\nu_{\rm res}}{\Delta\nu}, \qquad (11)$$

where $\nu_{\rm res}$ is the resonant frequency of the cavity and $\Delta\nu$ is the width at half height. In general, Q values are of the order of magnitude of the volume-to-surface ratio of the resonator, divided by the skin depth in the conductor at the frequency of resonance. Figure 7 shows a measurement of the electrical characteristics of the rectangular cavity used in the present experiment.

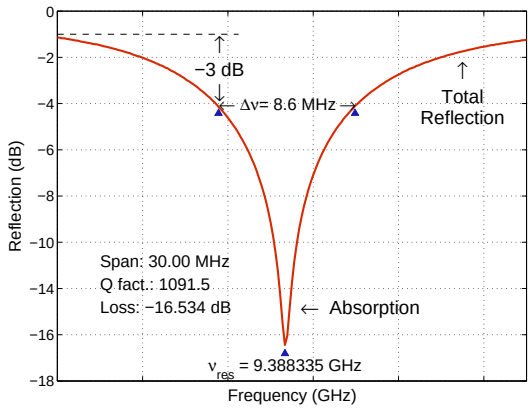

Fig. 7 The mode of the cavity used in an ESR spectrometer can be monitored with a network-analyzer, which measures the reflected power (on a logarithmic scale) versus frequency. The sharp dip shows the absorption by the cavity of part of the incident power. The amplitude of the dip quantifies the amount of power absorbed by the cavity. Note that both the amplitude of the dip and the frequency at which the mode occurs change when a sample is introduced in the cavity.

3.2 Electronic equipment

The electronic instruments listed below (see Fig. 8) are essential for carrying out the ESR experiment, the most important of them being the SR830 lock-in amplifier:

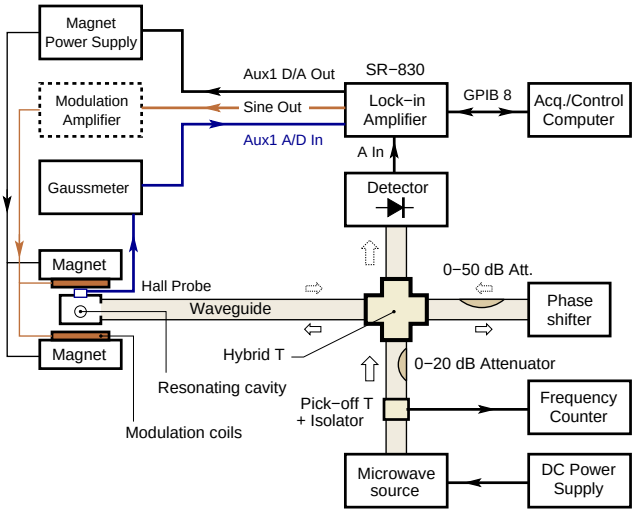

Fig. 8 Detailed ESR spectrometer schematics. Notice that the sample can be inserted into the resonating cavity only when the Hall probe has been removed. The modulation (audio) amplifier is an optional item.

1. The regulated DC power supply (A+D Products) provides typically 15 V to the 20 mW microwave source (Gunn diode oscillator stabilized via dielectric resonator). If necessary, the screw on top of the DRO-G-09000-HT source (Miteq) can be used to mechanically tune its resonance frequency.
2. The HP 5342A microwave frequency counter measures the exact (fixed) frequency used during the ESR experiments. For reliable readings let the instrument warm up for ca. 1 h during the magnetic field calibrations. Then take at least 10–20 measurements at regular intervals to estimate the microwave frequency and its fluctuations.
3. Two sets of coils (see Fig. 8) are used to generate a (large) static H_0 and a (small) modulating H_m magnetic field, respectively.
4. The SM 400 AR-4 (Delta Elektronika) power supply provides the current to the main set of coils, which generate the static magnetic field. This power supply is controlled by the SR830 lock-in amplifier via the auxiliary output (**Aux1 D/A Out**) located on the back of the instrument. To record an ESR spectrum the current (and, consequently, the magnetic field) is swept linearly in time (ramped up/down) via the LabView program.
5. An optional low- (audio) frequency amplifier can be used to drive the coils which generate the modulating magnetic field. The sinusoidal modulation signal is provided by the **Sine Out** output located on the front panel of the

SR830 lock-in amplifier. The amplitude of the modulation signal can be set in the range 4 mV to 5 V (RMS) by using the 10-turn knob on the lock-in front panel.

6. The Hall probe is used for measuring the sweeping and the modulating magnetic fields. Its principle of operation is based on the Hall effect. For maximum sensitivity position the probe perpendicular to the magnetic field at a height which provides a maximum reading. *Handle the probe carefully* since it is very fragile and expensive.
7. The F. W. Bell 600A gaussmeter is used to convert the voltage measured by the Hall probe into a magnetic field value. The output of the gaussmeter (end of scale corresponds to 1 V) can be read by and stored on a PC by means of the auxiliary input (**Aux1 A/D In**) located on the back of the SR830 lock-in amplifier. Always choose a suitable measuring range, e.g., 300 G for the modulating field and 3–10 kG for the main (sweeping) field.
8. The SR830 lock-in amplifier (Stanford Research Systems) is used primarily to detect a very weak signal at a frequency close to that of the reference (i.e. modulation) signal, which acts as an excitation. Further details on the principle of operation and the use of lock-in amplifiers are given in Sec. 4.3. As mentioned above, besides detecting and recording the ESR signal, due to its versatility SR830 is used also to provide the modulation signal (variable both in frequency and amplitude), control the amplitude of the static magnetic field, and read out the output of the Hall probe. The amplifier is fully computer-controlled from its GPIB interface via a PC running the LabView program.

4 The ESR detection scheme

4.1 The ESR signal

Most ESR spectrometers employ a *reflection* microwave resonator setup to achieve a high sensitivity. The ESR signal is detected by measuring *variations* in the microwave power reflected from the resonator as the sample absorbs or emits radiation upon achieving magnetic resonance [8]. The resonator reflection coefficient Γ, which plays a central role in the detection of the ESR signal, is given by:

$$\Gamma = \frac{Z_c - Z_0}{Z_c + Z_0}, \tag{12}$$

with Z_0 the transmission-line characteristic impedance (typically 50 Ω) and Z_c the resonator cavity input impedance. By considering the equivalent series RLC circuit shown in Fig. 9a, the cavity impedance can be expressed as $Z_c = R + jX$, with R the equivalent resistance and $X = \omega L - 1/(\omega C)$ the equivalent (frequency-dependent) reactive impedance.

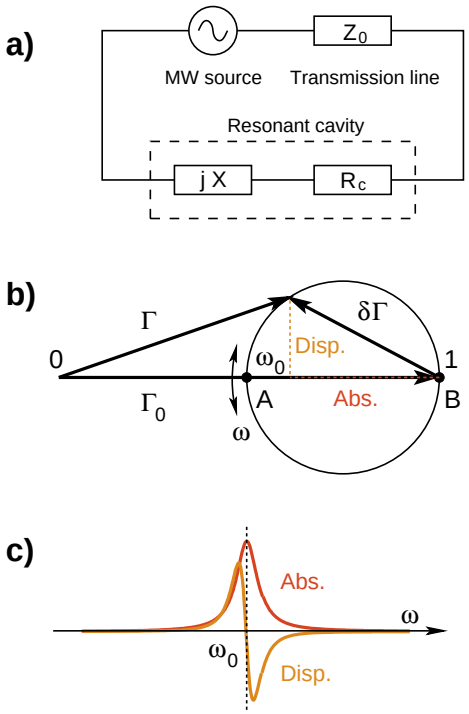

Fig. 9 Equivalent series RLC circuit representation of the ESR resonator (a). Z_0 is the transmission line characteristic impedance, while R, L, and C are the equivalent resistance, inductance, and capacitance of the cavity resonator. Graphical visualization of the resonance phenomenon (b). The vector construction shows how the absorption and dispersion components of the ESR signal (c) are connected to variations in the reflection coefficient Γ. At resonance ω_0 the signal is maximum (A), while it goes to zero both when $\omega \to 0$ or $\omega \to \infty$ (B).

Notice that L depends on the sample susceptibility χ, $L = L_0(1+\eta\chi)$, where the filling factor $0 < \eta < 1$ accounts for a sample that occupies only a fraction of the cavity volume.

In dealing with resonance, it is convenient to define two key parameters: the coupling β and the normalized offset ξ. The coupling β is defined as the ratio of the energy losses into the transmission line to the losses inside the resonator, $\beta = Z_0/R_c$. The normalized offset ξ is a measure of how far from resonance $\nu_{\rm res}$ we are, expressed in "natural" resonance half-width units, $\xi \simeq (\nu_{\rm res} - \nu)/\Delta\nu_{0.5}$.
One can now express the reflection coefficient as:

$$\Gamma = \frac{1 - \beta - j\xi}{1 + \beta - j\xi}. \tag{13}$$

which is very convenient as it depends only on the (mutually independent) tuning (ξ) and matching (β) parameters, both controllable by the experimenter. In case of *critical* coupling, realized when $\beta = 1$, it can be shown that the ESR signal is a maximum. For a cavity which is tuned on resonance ($\xi = 0$) and matched to the waveguide ($Z_c = Z_0$), $\Gamma = 0$. Far off resonance ($\xi = \infty$) the cavity is equivalent to a short, nothing goes through the iris, and consequently $|\Gamma| \approx 1$. For under-critical coupling (e.g. $\beta = 0.33$), these

two cases correspond to the points A and B in Fig. 9b, respectively.

What happens during the *field sweep*, when the electron spins become resonant with the irradiated microwave frequency? The sample absorbs additional microwave power, which drives the ESR transition and is eventually converted (via relaxation mechanisms) into heat. Due to this process the impedance of the resonator changes and the condition of critical coupling is no longer fulfilled. Hence, power is reflected from the resonator and transmitted to the detector. It can be shown that the change in input voltage at the detector, ΔV_{refl}, is given by:

$$\Delta V_{\text{refl}} = C\chi''(\omega)\eta Q_L, \tag{14}$$

with C an instrumental constant and η the filling factor of the resonator (the ratio of the integral of the microwave field amplitude B_1 over the sample volume divided by the integral of B_1 over the whole resonator).

► Sketch the variation through the resonance of χ' and χ'', the real and imaginary parts of the complex susceptibility χ, as well as that of the elementary variations δR and δX as a function of frequency.

► Based on Fig. 9 and the above considerations, explain how to detect the dispersive component "Disp." of the signal.

To summarize, in ESR a change in the effective resistance of the resonator due to resonant energy absorption from the sample[4] causes a change in resonator Q, in turn detected as a change in the reflected voltage.

4.2 Magnetic field modulation

The direct detection of the ESR signal is severely limited by the drift of the detector and by $1/f$ noise. For these reasons, most ESR spectrometers incorporate magnetic field modulation which shifts the relevant signal from DC to AC. The principle of detection is the following. When the magnetic field is modulated at the angular frequency ω_m, an alternating field $H_m \sin\omega_m t$ is superimposed to the constant magnetic field H_0. Here H_0 includes not only the main field but also the local magnetic field at the electron position due to its surroundings, which determines the broadening of the ESR line. The "constant" magnetic field is normally swept over the range ΔH_0 (from $H_0 - \frac{1}{2}\Delta H_0$ to $H_0 + \frac{1}{2}\Delta H_0$) in a time t_0, with H_0 the magnetic field strength at the center of the scan.

[4] We recall here that the absorption (dispersion) is related to the imaginary (real) part of the complex susceptibility and it changes in phase (quadrature) with the time-varying field.

At any time t during the scan, the *instantaneous* value of the magnetic field $H(t)$ is given by

$$(H_0 + H_{\text{sweep}}) + H_{\text{mod}} = H_0 + \Delta H_0 \left(\frac{t}{t_0} - \frac{1}{2}\right) + H_m \sin\omega_m t,$$

where

$$H_{\text{sweep}} = \Delta H_0 \left(\frac{t}{t_0} - \frac{1}{2}\right), \quad \text{and} \quad H_{\text{mod}} = H_m \sin\omega_m t.$$

In order to consider the linearly swept field $(H_0 + H_{\text{sweep}})$ as a constant, the scan should be slow enough so that there are many modulation cycles during the passage between the peak-to-peak (or half amplitude) points of the resonance line. If this condition is satisfied, the signal at the input of the detector is almost sinusoidal with an angular frequency ω_m and an amplitude proportional to the slope of the absorption curve evaluated at $(H_0 + H_{\text{sweep}})$.

Choosing the correct modulation field amplitude, H_m, is crucial. It should be as large as possible for a good signal-to-noise ratio, but smaller than the ESR linewidth to prevent signal distortion (typically one employs an H_m between 1/5 to 1/3 of the linewidth). The modulation frequency should also be smaller than the linewidth to prevent the appearance of sidebands (we suggest using $\nu_m = 133$ Hz).

► Plot on two separate graphs the time dependence of the magnetic field $B = B(t)$ and the field dependence of the resonance signal $\Delta V_{\text{refl}} \propto \chi''(B)$ (see Fig. 1b). From these plots try to sketch the signal at the detector. How does it relate to the final signal $\mathrm{d}\chi''/\mathrm{d}B$, shown in Fig. 1c?

4.3 Phase-sensitive detection

A phase-sensitive detector (PSD) can be thought of as a specialized AC voltmeter which measures the amplitude and phase of signals at a frequency equal to that of a reference. A PSD is basically a mixer (multiplier) followed by a low-pass filter (Fig. 10). It multiplies the modulated ESR signal from the silicon detector with a reference signal (pure sine wave at the *same* modulation frequency) and integrates the product via a low-pass filter over an adjustable time period. Mathematically speaking, phase-sensitive detection is equivalent to function convolution. The product of two harmonic functions leads to two terms containing the sum and the difference of the respective frequencies. If the two signals have the same ω, then the sum at 2ω is suppressed by the low-pass filter, while their difference is a constant whose value depends on the phase difference between the two signals (hence the name phase-sensitive detector). As the (external) reference and the signal vary together, the tracking characteristic of the PSD keeps the center frequency exactly at the signal frequency, hence the name "lock-in" amplifier.

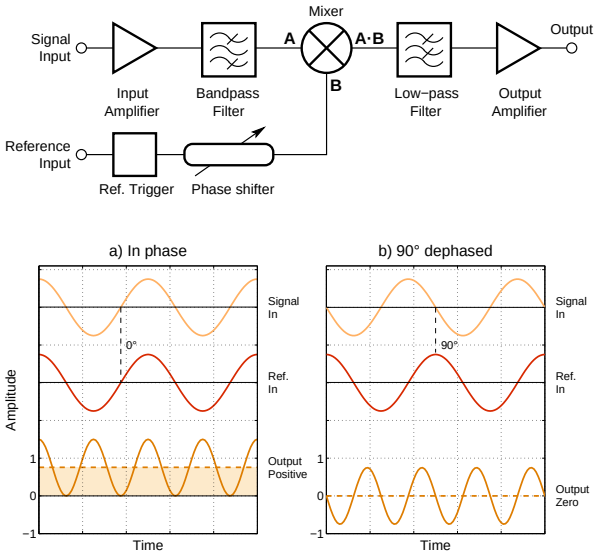

Fig. 10 Schematic of a lock-in amplifier (top) and its principle of operation (bottom). An out-of-phase signal gives little or no output.

The operation principle of the phase-sensitive (lock-in) detector is explained below. A reference oscillator produces a reference signal

$$e_r = E_r \cos(\omega t + \varphi_r),$$

where φ_r is a phase angle. At resonance the sample absorbs microwave energy and unbalances the microwave bridge, giving rise to an ESR signal at the diode

$$e_s = E_s \cos(\omega t + \varphi_s),$$

where φ_s is another phase angle, generally different from φ_r. The detector's multiplier produces an output that is the product $e_s\, e_r$ of the ESR signal and the modulating reference

$$\begin{aligned} e_s\, e_r &= E_s E_r \cos(\omega t + \varphi_s)\cos(\omega t + \varphi_r) = \\ &= \frac{1}{2} E_s E_r \left[\cos(2\omega t + \varphi_r + \varphi_s) + \cos(\varphi_r - \varphi_s)\right]. \end{aligned}$$

The low-pass filter suppresses the first (fast-oscillating) term to produce a DC output voltage

$$V_{\text{out}} = \frac{1}{2} E_s E_r \cos(\varphi_r - \varphi_s).$$

By setting the two phases at the same value (either manually or automatically), the maximum output signal

$$\boxed{V_{\text{out}} = \frac{1}{2} E_s E_r.} \qquad (15)$$

is achieved.

Signal filtering: The ESR signal to be measured by the lock-in amplifier is usually noisy. A large part of this noise can be removed by passing the signal through a low-pass filter, characterized by a time constant (or response time) τ_0. The latter is a measure of the cutoff frequency which, for a low-pass, 1st-order filter, is $\Delta\nu = 1/(2\pi\tau_0)$. The filter will suppress the signals with frequencies much above the inverse of its time constant $1/\tau_0$, will attenuate, distort, and retard those with frequencies in the vicinity of $1/\tau_0$, and will transmit those with frequencies lower than $1/\tau_0$ undisturbed.

Now the ESR signal has an effective frequency which corresponds to the inverse of the time required to scan the field through resonance from one peak to the next. The filter time constant τ_0 should satisfy two opposing requirements: it should be sufficiently long to filter out undesirable noise, yet short enough not to distort the ESR signal. Based on the above considerations, a good "rule of thumb", to avoid signal distortion (or worse yet, signal suppression) is to choose a time constant that is less than about 1/10 of the time it takes to scan through the narrowest line in the spectrum [4].

5 Carrying out the ESR experiment

■ **Warning:** High voltage ($V > 100$ V, $i > 500$ mA) is applied to the magnet! Do not let the magnet get too warm!

1. Read the manual and answer all the exercises marked with the symbol ▶.
2. Measure the magnetic field as a function of the control voltage. Observe the presence of field hysteresis.
3. Calibrate the main magnetic field.
4. Assemble the modulation equipment.
5. Measure the amplitude of the modulating field as a function of the voltage applied across the modulation coils.
6. Adjust the microwave bridge for maximum sensitivity.
7. Measure the ESR signal on a powder sample of DPPH in *absorption* mode for different modulation amplitudes and microwave powers. Estimate the linewidth and the g-factor.
8. Measure the ESR signal on a powder sample of DPPH in *dispersion* mode. How does the position of the phase shifter relate to the previous case?
9. Discuss the effect of varying the amplitude of the field modulation.

A Spin thermodynamics [2]

The interaction of the electromagnetic radiation field with an atomic system involves three different processes:

Spontaneous emission: involving a transition from the higher to the lower energy state with the spontaneous emission of a photon.

Stimulated absorption: corresponding to the absorption of a photon from the radiation field accompanied by a spin transition to the high-energy state.

Stimulated emission: is the reverse of the above process and corresponds to a spin transition to the low-energy state induced by the radiation field, accompanied by the emission of a photon coherent in phase and frequency with the radiation field.

The transition probabilities (Einstein coefficients) depend on frequency. While at optical frequencies the spontaneous transitions are significant, they can be safely neglected in case of microwave frequencies. Hence, in our case we need to consider only the stimulated emission and absorption. Both are coherent with the radiation field, whose intensity (energy density) determines the number of transitions.

In the microwave range the stimulated emission and absorption coefficients are practically the same. Consequently, the detection of an absorption (or emission) signal requires a difference in the spin population of the two energy levels (i.e. $N_+ \neq N_-$). If the radiation field is too intense, the equilibrium condition corresponds to $N_+ = N_-$ (infinite spin temperature!), with no net energy absorption and the spin system is in a so-called *saturated* state. Fortunately, the spin system is in thermal contact with other degrees of freedom ("lattice") to which it releases the excess energy via relaxation processes, hence lowering its temperature and reestablishing the condition $N_- > N_+$. Typical ESR experiments are performed with radiation fields too small to appreciably perturb the normal electron-spin thermal equilibrium. From the above considerations it is clear that, since $N_+/N_- = \exp[-\Delta E/(k_B T)]$, to maximize the signal one can lower the temperature, or increase the energy gap ΔE, by increasing the magnetic field.

B The Gunn oscillator [16]

In 1963, while studying high electric field phenomena in gallium arsenide (GaAs), J. B. Gunn observed that for fields in excess of 2 kV/cm the current showed very marked oscillations in the microwave frequency range. In addition, above V_0 the current-voltage characteristic of the diode displayed a negative differential resistance (Fig. 11)! The physical reason behind the Gunn effect is the existence of a field-dependent electron mobility. In some semiconductors, such as in GaAs, there are high-energy minima in the conduction band to which carriers can be excited under high electric-field conditions. These minima, characterized by a much lower charge mobility (see Fig. 11, right panel), are separated from the lowest minimum by energies much higher than $k_B T$. Hence, not being populated thermally, they can be occupied only by the so-called "hot" (i.e. field-accelerated) carriers. The phenomenon of hot carriers and the related *negative differential resistance* fulfill the conditions for the development of charge-modulated domains inside the semiconductor. The movement of these domains gives rise to oscillating currents and therefore to the production of microwave oscillations.

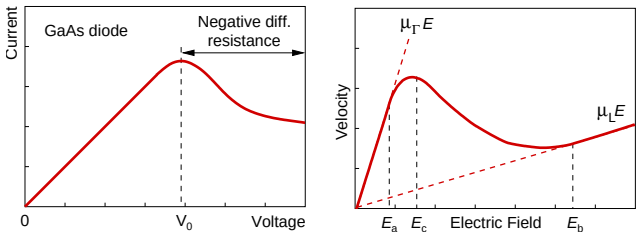

Fig. 11 Left: Current-voltage characteristic of a Gunn diode. The negative differential resistance regime above V_0 is related to the *indirect gap* which is distorted by the field. Right: Qualitative dependence of the drift velocity of electrons in GaAs on electric field.

Dielectric resonator: A dielectric resonator is a high dielectric constant material (e.g. Ba, Zr or Sn titanate, with $\varepsilon \sim 40$) usually in the shape of a disc that acts as a miniature microwave resonator. The resonant behaviour arises from the internal reflections of electromagnetic waves at the high-ε material/air boundary, resulting in EM energy confinement (mostly) within the dielectric material [5]. In fact, to a first approximation, a dielectric resonator can be assumed as a magnetic wall cavity, which is the dual case of the common metal (electric) wall cavities.

Although long known, dielectric resonators have only recently become ubiquitous microwave components, able to replace the traditional waveguide cavity resonators in most applications. Due to their small, light-weight, high-Q ($\sim 10^4$), and temperature-stable structures, dielectric resonators have been used to *stabilize Gunn diode oscillators*, by lowering their phase noise and reducing the frequency variations due to temperature or bias changes.

C Biographic notes [19]

Evgeny Konstantinovich Zavoisky (1907–1976)

Soviet physicist who discovered electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR).

Zavoisky graduated from the Kazan State University in 1930 and taught physics there for almost 15 years, becoming a popular teacher who focused on demonstrations rather than theories. During this period he started systematic studies of the interaction of electromagnetic waves with matter, which culminated in 1944 with the discovery of ESR in paramagnetic salts. His key contributions to ESR included the development of new, more sensitive electronic detectors (with respect to the previous calorimetric ones) and the introduction of AC magnetic field modulation, which dramatically increased the ESR detection sensitivity.

Later on Zavoisky moved to the Institute of Atomic Energy in Moscow, where he worked on problems of controlling nuclear fusion. In particular, his efforts were focused in the field of plasma physics, leading him to the discovery of the phenomenon of turbulent plasma heating.

For his contributions to science Zavoisky was elected member of the USSR Academy of Sciences, was awarded the Stalin Prize (1949) and, later on, the Lenin Prize (1957). Zavoisky died in 1976 in Moscow due to a serious illness.

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