

### Related topics

Zeeman effect, energy quantum, quantum number, resonance,  $g$ -factor, Landé factor.

### Principle and task

The  $g$ -factor of a DPPH (Diphenylpicrylhydrazyl) and the half-width of the absorption line are determined, using the ESR apparatus.

### Equipment

ESR resonator with field coils	09050.00	1
ESR power supply	09050.93	1
Power supply, universal	13500.93	1
Oscilloscope, 20 MHz, 2 channels	11454.93	1
Digital multimeter	07134.00	1
Screened cable, BNC, 1 750 mm	07542.11	4
Adapter, BNC-socket/4 mm plug pair	07542.27	1
Connecting cord, 500 mm, blue	07361.04	3
Connecting cord, 500 mm, red	07361.01	2
Connecting cord, 500 mm, yellow	07361.02	2
Options:		
Teslameter, digital	13610.93	1
Hall probe, tangent., prot. cap	13610.02	1

### Problems

With ESR on a DPPH specimen determination of

1. the  $g$ -factor of the free electron, and
2. the half-width of the absorption line.

### Set-up and procedure

A symmetrically fed bridge circuit (Fig. 2a) contains a variable resistor  $R$  in one branch and a high-quality tuned circuit (resonator) in the other. The specimen is located in the coil of the tuned circuit. Normally, the bridge is balanced so that the complex impedance of both branches is the same and consequently there is no voltage between points  $a$  and  $b$ . If the external magnetic field is now so adjusted that the resonance absorption occurs in the specimen, the bridge becomes unbalanced and the voltage set up between  $a$  and  $b$  rectified and amplified.

If the magnetic field is modulated with 50 Hz a.c. (voltage 2 V), the resonance point is passed through 100 times a second (Fig. 3), and the absorption signal can be displayed on an oscilloscope, provided the  $x$ -deflection is driven with the same a.c. voltage in the correct phase.

Fig. 1: Experimental set-up for determining characteristic curves.



Fig. 2a: Measuring bridge of the ESR apparatus.

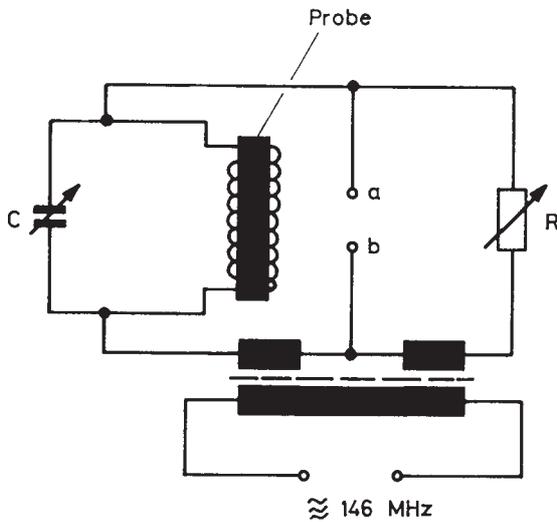


Fig. 3: The magnetic field  $B$  is compounded from a d.c. field  $B_{\pm}$  and an alternating field  $B_{\sim}$ , so that  $B = B_{\pm} + B_{\sim}$ . Through  $I_{\pm}$ ,  $B_{\pm}$  is to be adjusted so that  $B_{\pm} = B_r$ .

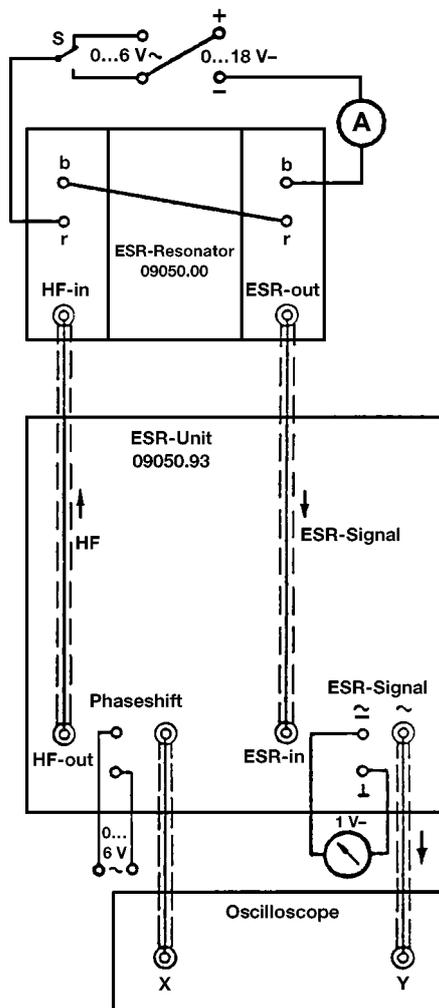
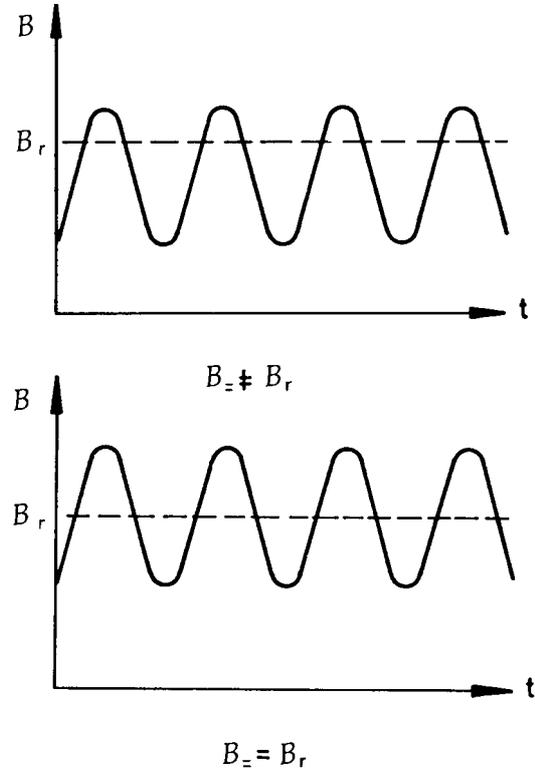


Fig. 2b: Wiring diagram.

First, the bridge has to be balanced. In doing this (without external magnetic field), "R" on the resonator is brought to its central position and "C" to the lefthand stop. On the ESR power supply, key 8 "bridge balancing" (see operating instructions) is pressed, the oscilloscope input is switched to d.c. and 1 V/cm and the line is brought to the zero with 12 "Zero" (beforehand bring to zero with "Position" in GND setting). For the wiring see Fig. 2b and operating instructions.

Now the absorption signal can be searched for: the coil current is set to about 1.3 A, button 10 "≈" pressed and the zero line again brought to the centre with 12. The signal can now be sought with 25 "C", while continuously correcting the zero point with 12.

As soon as a signal appears, both lines are made to coincide with 13 "Phase". As long as the resonance frequency of the tuned circuit does not correspond to the oscillator frequency, the signal appears asymmetrical or as a derivative. The resonator should thus be tuned with 25 "C" until a symmetrical absorption signal of maximum amplitude appears on the oscilloscope. The sensitivity of the oscilloscope is increased so that the signal reaches a height of 8-10 cm. By varying the d.c. current in the coil, the signal can be brought to the centre of the screen, so that the minimum is on the y-axis, (correct again with 13 "Phase" if necessary). The resonance magnetic field  $B_r$  can be calculated from the d.c. current  $I_{res}$  now flowing.

If the signal is now adjusted so that the x-axis goes exactly half way through the height of the signal, then, once the alter-

nating voltage modulation has been switched off, the two current values at which the moving spot crosses the x-axis can be determined by slowly varying the d.c. current in the coil. The half-width of the signal is calculated from the difference between these currents.

### Theory and evaluation

If an electron of mass  $m$  and charge  $e$  is located in an electromagnetic field with vector potential  $\vec{A}$  and scalar potential  $\phi$ , then its steady-state energy level and characteristic states are given by the solutions of the Dirac equation.

If the equation is solved for the  $\psi$ , component of the state spinor, it reads:

$$\left( \vec{\pi}^2 + \mu_B 2\vec{S} \cdot \vec{B} \right) \pi_1 = \epsilon \psi_1 \quad (1)$$

where

$$\mu_B = \frac{eh}{2mc} \quad (\text{Bohr Magneton})$$

$$= 9.27 \cdot 10^{-27} \text{ Am}^2$$

$$\vec{\pi} = \vec{p} + e/c \vec{A}$$

where  $\vec{p}$  is the momentum,  $c$  the velocity of light,  $\vec{S}$  the electron spin operator, and  $\vec{B} = \text{rot } A$  is the magnetic field.  $h$  is Planck's constant

$$h = 6.626 \cdot 10^{-34} \text{ Js,}$$

and

$$\epsilon = \frac{1}{2} \left( 1 + (E/mc^2) \right) (E - mc^2)$$

is approximately the excess of energy over the residual mass energy.

For a free electron in a uniform magnetic field, the second term (Zeeman term) interchanges with the first in the Hamiltonian operator of (1), and the energy level

$$\epsilon = \epsilon_0 + \mu_B 2S_z B_z, \quad \text{is obtained}$$

if the z-axis lies in the direction of the magnetic field.

$\epsilon_0$  is the energy of the electron without a magnetic field. If the diamagnetic contribution from the first term of (1) is disregarded in the general case, then for the electron in a uniform magnetic field, the interaction Hamiltonian operator with the magnetic field, (Zeeman effect) is

$$H_Z = \mu_B \vec{B} \cdot (\vec{L} + 2\vec{S}), \quad (2)$$

where  $\vec{L}$  and  $\vec{S}$  are the operators of the orbital and spin angular momentum respectively. In addition, the spinorbit interaction

$$H_{so} = \lambda \cdot \vec{S} \cdot \vec{L}$$

should be taken into account, so that only the total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$

is a conservation value.

In this case,  $H_Z$  (2) can be written

$$H_Z = \mu_B g_j \vec{B} \cdot \vec{J} \quad (3)$$

with the Landé factor

$$g_j = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (4)$$

Disregarding the influence of the nuclear spin, the energy levels of  $H_Z$ , for magnetic fields in the Z-direction, are

$$E_Z = \mu_B g_j B m_j$$

with

$$m_j = j, j-1, \dots -j.$$

The selection rule for magnetic transitions of the electron spin resonance experiment is

$$\Delta m_j = \pm 1$$

so that the absorption condition reads

$$\mu_B g_j B = \Delta E = hf.$$

In many cases, especially with molecular radicals, the angular momentum  $L$  of the unpaired electron is extinguished by the electric fields of the neighbouring atoms and molecules. In the case of DPPH,  $L = 0$  and therefore

$$g_j = 2.$$

In (3),

$$\vec{\mu} = \mu_B \cdot g_j \cdot \vec{J} \quad (5)$$

is the magnetic moment of an electron with the angular momentum  $\vec{J}$  in units of the Bohr magneton  $\mu_B$ . If account is also taken of the exchange of virtual photons between the electron and a radiation field in the static limit through inclusion of the vertex corrections in increasing order, a modified abnormal magnetic moment of the electron is obtained as a series in the fine-structure constant  $\alpha$ :

$$\alpha = \frac{e^2}{h \cdot c}$$

$$\vec{\mu} = \mu_B \left( 1 + \frac{\alpha}{2\pi} - 0.328 \frac{\alpha^2}{\pi^2} + \dots \right) g_j \vec{J} \quad (6)$$

The correction factor in the parentheses of equation (6) is generally taken into account in  $g_j$ , so that  $g_j$  then  $\neq 2$ .

Fig. 4 shows the energy level in the magnetic field  $B$ , for DPPH.

By supplying the corresponding energy, transitions can be induced between the levels:

$$hf = g_j \mu_B B H.$$

The probability of transition depends on the occupation number and on the transition matrix elements. The latter are the same for absorption and emission processes.

Because of the interactions of the spins with the lattice or with one another, the levels are not sharply defined, and this leads

to a line width of the absorption spectrum and prevents an equipartition of the levels (saturation) because of the corresponding relaxation processes.

The occupation numbers are given in accordance with the Boltzmann relation by:

$$\frac{N_2}{N_1} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{g\mu_B B}{kT}},$$

where  $k$  is the Boltzmann constant. It is customary to take account of other interactions in the constant  $g$  which vary linearly  $B$ , e.g. the contact of Fermi interaction with the nucleus, i.e.

$$g = g_j (1 + WW),$$

where  $g$  is specific for the measured substance and  $f$  is pre-determined at 146 MHz by the apparatus, so that  $B$  must be varied to satisfy the resonance condition.

For the magnetic field of a Helmholtz arrangement with  $w = 250$  turns, current  $I$  and radius  $R = 0.054$  m,

$$B = 0.7155 \cdot \mu_0 \cdot \frac{w \cdot I}{R}$$

on the axis of symmetry between the coils, where

$$\mu_0 = 1.256 \cdot 10^{-6} \cdot \frac{T \cdot m}{A}$$

With the numerical values stated, one obtains

$$B = 4.16 \cdot 10^{-6} \cdot I \frac{T}{A}.$$

For the  $g$ -factor, one obtains:

$$g = 10.43 \cdot \frac{1}{B_r}; B_r \text{ in teslas}$$

or

$$g = 2.507 \cdot \frac{1}{I_r}; I_r \text{ in amperes,}$$

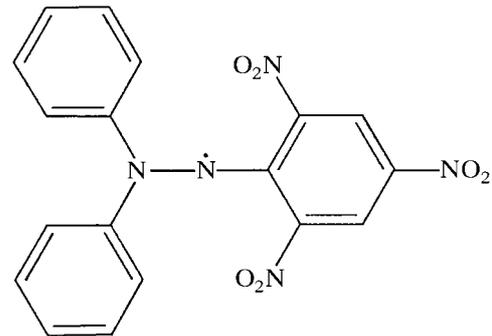
with the stated values.

A resonance current of 1.245 A was measured, corresponding to a  $g$ -factor of 2.02, and a half-width value of  $2.7 \cdot 10^{-4}$  T.

(Literature values for DPPH:  
 $g = 2.0037$ , half-width  $2.8 \cdot 10^{-4}$  T).

**Note:**

The analyzed specimen DPPH (Diphenylpicrylhydrazyl) is a organic, paramagnetic material with one stable radical. The magnetic moment of the molecule is determined only by the spin moment of the valence in the "N"-bridge.



### Electron spin resonance (ESR), model experiment

Model experiment for electron spin resonance for clear demonstration of interaction between the magnetic moment of the electron spin with a superimposed direct or alternating magnetic field.

A ball with a central rod magnet, which rotates with low friction on an air cushion, acts as model electron. Two pairs of coils allow to generate a direct magnetic field  $B_0$  and an alternating magnetic field  $B_1$ . The axes of both fields intersect perpendicularly at the centre of the ball.

The table is slightly inclined to start the electron gyroscope with an air draught (Magnus effect). If the direct magnetic field  $B_0$  acts on the ball, a precession of the magnet axis is observed. Precession frequency increases with the intensity of field  $B_0$ .

With a second pair of coils and a pole changeover switch (commutator), a supplementary alternating field  $B_1$  is generated. If the change of poles occurs at the right phase, the angle between the gyroscope axis and the direction of the direct field is continuously increased, until the magnetic axis of the ball is opposed to the field direction (spin flip).

Ask for a complete equipment list Exp.no. 12980

### Material

Gyroscope w. magnetic axis, ESR model	11208.00	1
Coil 1200 turns	06515.01	4
Iron core, short, laminated	06500.00	2
Commutator switch	06034.03	1
On/off switch	06034.01	1
Blower	13770.93	1
Pressure tube with end piece 1.5 m	11205.01	1
Variable transformer with rectifier 25 Vp/20 V-, 12 A	13531.93	1
Connecting cable		8

Fig. 4: Electron spin resonance (ESR), model experiment.

