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QUANTUM SENSOR FOR MAGNETIC FIELD

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Abstract*: Recently, the nanotechnologies are largely implemented in space technologies. The concept of magnetometer with magnetic resonance/MMR/ is considered in this paper. The device combines the advantages of the electronic devices with thin organic film and the traditional MMR. Especially, investigations are carried out on the splitting in polaron pairs in organic diodes, based on π- conjugated organic semiconductor MEH-PPV. As this spin-dependent transition of electrons controls the conductivity of the material, magnetic resonance with electrons or holes could be detected through measurement of the electric current. In fact, the diode consists of thin layer of MEH-PPV, located between two levels, injecting electrons and holes. This structure is identical with these used in the conventional organic light-emitting diodes. The properties of this organic MMR, regarding its flexibility, sensibility and limits of the magnetic field, and its response to temperature fluctuations and aging are investigated. Experiments are carried out at room temperature.*

Introduction

The measurement of absolute magnetic fields is critical for much of the research and technological applications (1),(8). While superconducting quantum interfering elements could solve this problem for extremely weak magnetic fields, the sensors, based on magnetic resonance allow quick and precise determination of weak and strong magnetic fields. The latter is based on the input of electromagnetic emissions with magnetic resonance in paramagnetic centers, which Landé factors are well known (5). At these sensors, which aim is to determine the magnetic field, the Planck's fundamental relation between the frequency of the emission v and the Zeeman energy of the paramagnetic centers is used:

$$hv=h\gamma Bo,$$

where γ is the gyromagnetic ratio, Bo is the applied magnetic field and h is the Planck's constant. The disadvantages of these elements are their price and size: the conventional magnetic resonance determining a field requires large volumes/up to hundreds of cubic meters/(5),(12). When the signals of the magnetic resonance disappear in the case of weak magnetic fields (due to the disappearance of the spin polarization), these magnetometers are weak detectors even for close fields. Until now there were several propositions for solving this problem through the use of spin-depending transport of charges, or through recombination processes in semiconductors in view of the electrical or optical detection of magnetic resonance(3),(10). Usually signals of the electrical or optical detection don't depend on the spin polarization, which make these sensors remarkably sensitive, even at very low magnetic fields. Besides, they are not volume sensitive and they can be self-generated in the nanoscale (9). The existing sensors for electrical or optical detection use silicone and nitrogen-vacancy centers in diamonds (11),(14). In the silicone case the spin-dependent signals are totally missing at room temperature or they are extremely weak. In diamond the optical detection requires the use of fluorescent microscopy (11),(13),(14).

The concept of sensor with magnetic resonance, which combines the advantages of the electronic elements with thin organic film and those of the traditional sensor with magnetic resonance, is reported in this paper. The spin-dependent splitting in polaron pairs in a π- conjugated organic semiconductor is especially investigated. As this spin-dependent transition of electrons controls the conductivity of the material, magnetic resonance with electrons or holes could be detected through measurement of the electric current. The element consists of thin layer semiconductor poly(2-methoxy-5-(2-ethylhexyloxy)-p-phenylene vynilene; MEH-PPV (7),(9), located between contacts, injecting only one electron and one hole. The properties of this sensor are studied, regarding its

sensitivity, the limits of the magnetic field, the response to fluctuations in temperature and the aging of the material. The sensitivity of the element is discussed and the expected error is calculated.

Methodology

Mechanism: Change in the resonance current

The hypothesis, that signals of the electrical detection are independent of the spin polarization over a large range of the magnetic field, is applied to the measurement of the magnetic field. This is a critical prerequisite for the realization of sensor with magnetic resonance. For the recombination of polaron pairs, the spin dependent relations are based on symmetry of the spin permutation of the pairs- charge carriers, not on the spin polarization. Therefore, slight dependence of Bo, regarding the signal of the current is expected. This model is studied in details, during the recent years, with the help of spectroscopy of the electrical and optical signals. Research is under way in the X-band (Bo=340mT) or frequencies in the same order of magnitude.

In the presence of radio-frequency emissions, a change in the current is observed, as a function of the magnetic field. This change in the current is due to a change in the spin dynamics of the charges carriers' ensembles, moving from a steady state to a spin-resonance exited state (15). When spins of the charges carriers are manipulated, the ratio between the single and the triple pairs changes (2),(7). As a result the ratio of recombination and dissociation changes too, consequently, the current changes.

When the frequency in radio-frequency emission decreases, the measurement limit of the magnetic field becomes lower. This lower limit of Bo measurement is attributed to the reduced changes in the spin-mixing: as longer the external magnetic field exceeds the local hyperfine field of the π- conjugated polymer (Bo>BHyp), the more the spin-mixing is suppressed and the more longitudinal spin relaxations relations are enlarged. The applied magnetic resonance can enlarge artificially the spin-mixing and therefore the current should change constantly. Contrary, when Bo<BHyp, the spin-mixing is almost independent of the magnetic resonance. In this case the magnetic resonance changes slightly the spin-mixing and the spin-dependent current, as a result the signal of the electrical detection disappears (10),(11).

The disappearance of the signal of magnetic resonance at Bo=BHyp confirms, that the mechanism of the polaron pair (electron-hole) is responsible for the signal of the electrical detection, as well as, for the magnetic resistance of the permanent current. This assumption will be a subject to debate. It is important to note that for the magnetometery, based on the magnetic resonance, this effect does not establish a lower limit of the magnetic field measurement: at Bo<BHyp a magnetic field could be detected though the application of a precise constant magnetic field Boff in a modulated pad(6).

$$Bdet=Bo+Boff>BHyp$$

Then $Bo= Bdet – Boff$

Accuracy and stability of the measurement

Something very important for the absolute measurement of the magnetic field, produced through this element, is the standard, which in this case is the gyromagnetic ratio γ (or the g-factor of Landé) of a polaron's spin. Multiple measurements of the electric detection with thin film samples over a wide range of magnetic fields are made in view the precise determination of γ and in order to confirm the independence of γ from the magnetic field itself. It has to be noted that for this purpose the optic detection could be used in the same way, but this is very difficult to be technologically achieved (4). For this reason the measurements are focused only on the electric detection. Measurements of transitory processes, induced by a single impulse are made. In this case the spectrum of the polaron pair shows two Gaussian peaks, corresponding to two types of current carriers. In order to maximize the accuracy of the measurement of Bo, one Gaussian peak has to be chosen, corresponding to one type of the current carriers (electron or hole).

For the determination of the sensor's operational range the stability of the gyromagnetic relation is used as a function of temperature and the purposeful aging of the element. This study is carried out through reproduction of γ at a range of temperature varying from 5K to room temperature and repeating the experiments after induced aging of the material.

Construction of the element:

The element for electric detection of magnetic resonance has the following construction:

1. Layer-indium-stannic oxide : 200 nm
2. Layer- injection of holes: 50 nm, applied in a centrifuge at 3000 RPM
3. Layer-MEH-PPV:200 nm, applied in a centrifuge at 1600 RPM in a chamber with nitrogen
4. Layer-injection of electrons:25 nm Calcium
5. Layer-aluminum: 50 nm.

The coatings of calcium and aluminum are applied by evaporation in a chamber with nitrogen at a pressure of 10^{-6} mbar.
The element is located closely to two separated electric plates, as shown on fig.1, respectively for implementing a management and modulation fields.

Experimental settings

For the studies with different radio-frequencies, direct current power supply is applied to the element and it is put in a small coil. The coil is linked to an adjustable source of frequency, with the purpose to apply a fixed frequency. The output of the element is connected to an amplifier, working as low-frequency filter (frequency of cutting fc=10Hz). The filter is connected to a computer for visualization. The experimental setting is illustrated in figure 2.

For the experiments with one single impulse, the design of resonator, which is used, is those with one plate. One single impulse with frequency 350MHz is applied to the element. The output is connected to an amplifier in high-frequency regime with current adjustment close to Io. The output is linked to a device, recording the transition process. The experimental setting is illustrated in figure 3.

For the studies of the integral sensor, direct current voltage is applied to the element. Standard frequency of 6kHz is supplied to the modulation plate through generator at 5Vpp. This represents amplitude of 0,02mT of the modulation field. The output is connected to a computer for visualization. The plates consist of copper strips on each side of the epoxy pad. Simple mechanical contact between the element and the plate is sufficient to induce resonance. The experimental setting is illustrated in figure 4

Results

On fig. 1 it is shown the construction of magnetometer with magnetic resonance and organic semiconductor. The element is located over two plates, perpendicular to each other, which is necessary to excite resonance and modulation of the field. The electrons and holes are injected in the opposite sides and they recombine in dependence of the spin in the organic semiconductor.

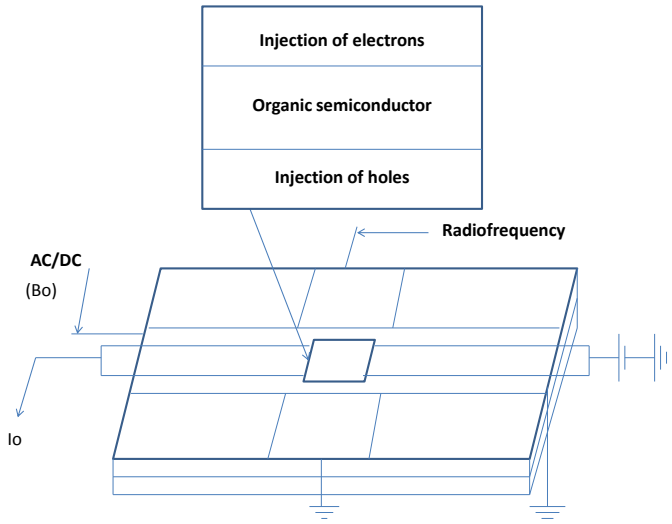

Fig.1. Construction of magnetometer with magnetic resonance and organic semiconductor

On Fig. 2 is shown the experimental setting for measurement of a constant magnetic field, when radio-frequencies of 200MHz and 50MHz are applied.

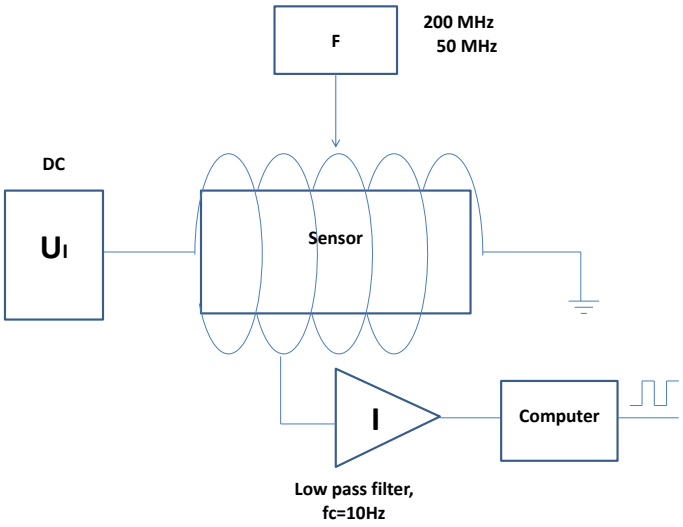

Fig. 2. An experimental setting for measurement of a constant magnetic field, when radio-frequencies of 200MHz and 50MHz are applied

On Fig. 3 is shown the experimental setting for impulse excitement of resonance.

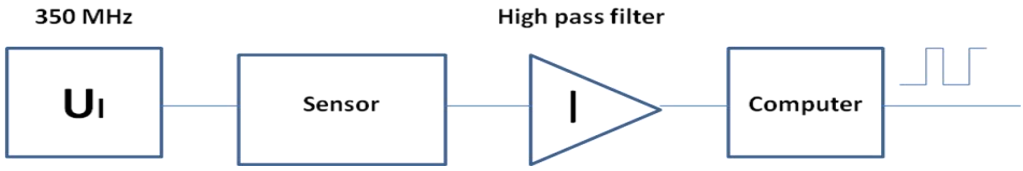

Fig. 3. An experimental setting for measurements in the case of an impulse excitement of resonance

On Fig. 4 is shown the experimental setting for a study of the integral sensor.

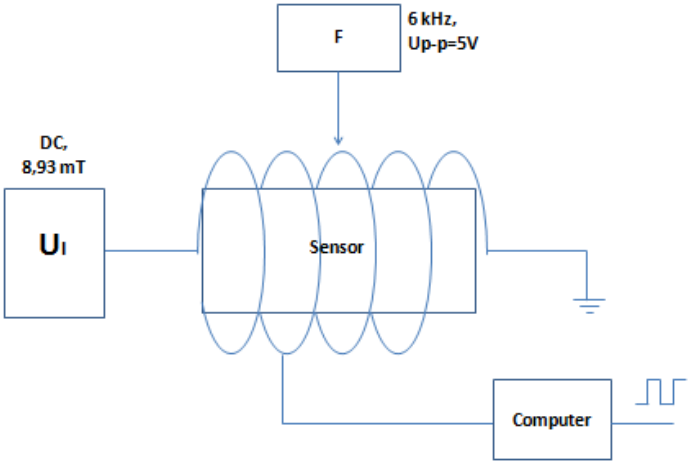

Fig. 4. An experimental setting for measurement with integral sensor

On the Fig. 5 is shown the change in the current at constant magnetic field (1,3mT<Bo<10mT) and a radio-frequency of 200MHz. Through the range of measurements, the graph shows a monotone increase of the current. This behavior is due to the strong magnetic resistance. Besides the monotone magnetic dependence of the current, the graph shows decrease of the current approximately to Bo=7,14mT. This corresponds to the condition for magnetic resonance at g=2, 0026(4). The relatively decrease of the current is 10^{-3}; $\Delta I/I=10^{-3}$

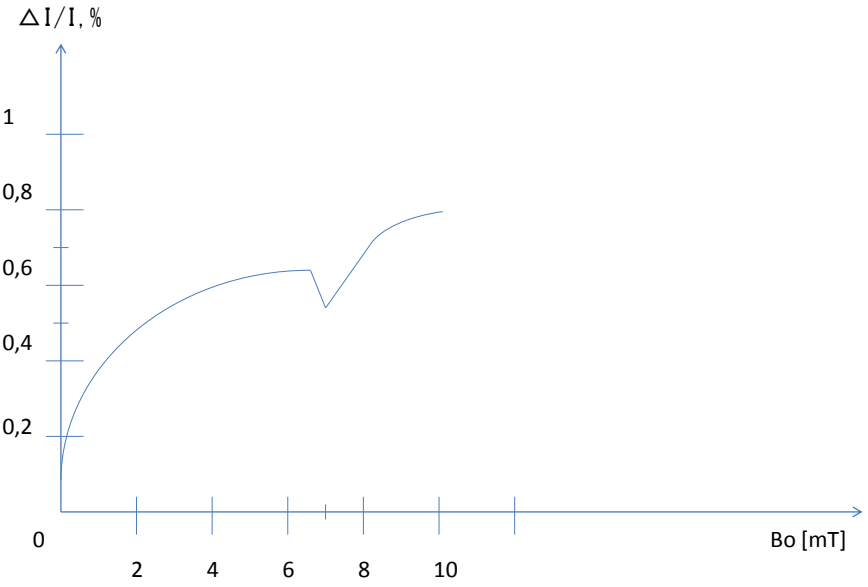

Fig. 5. Current change at constant magnetic field and frequency of 200MHz

On the Fig. 6 is shown the current change at constant magnetic field and frequency of 50MHz. The current decrease can be seen at Bo=1,79mT, but with a reduced amplitude.

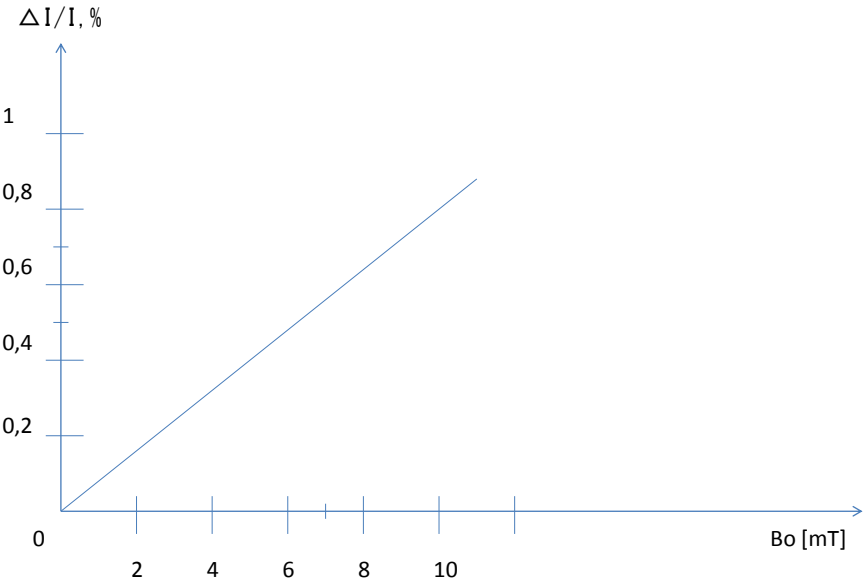

Fig. 6. Current change at constant magnetic field and frequency of 50MHz

Fig. 7 shows the current, induced by magnetic resonance, measured as a function of the applied excitation frequency. Linear approximation of data gives the gyromagnetic ratio γ=28,03 GHz.T^{-1} and corresponding g-factor g=2,0026. Therefore, the detected electric gyromagnetic ratio of an electron can be used as a standard for magnetic field.

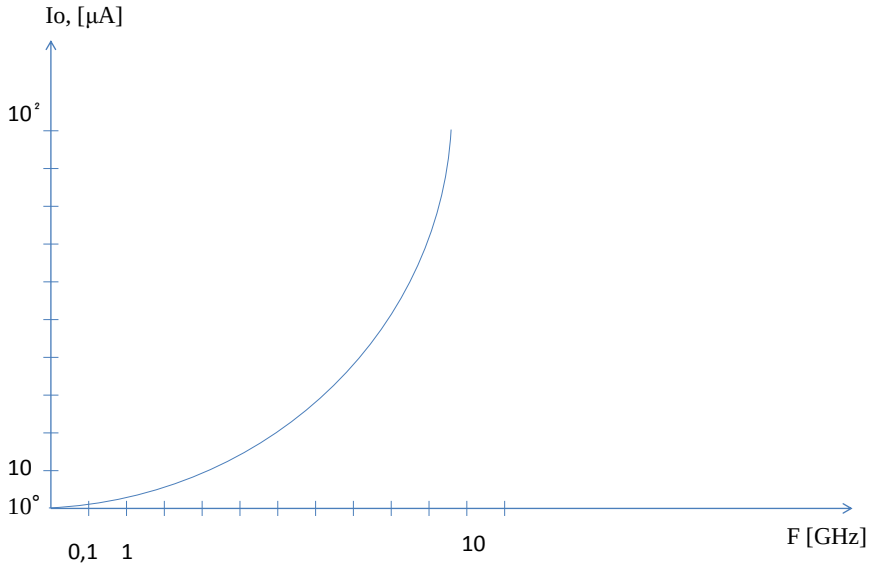

Fig. 7. The current, measured as a function of the applied exciting frequency

Fig. 8 represents the volt-ampere characteristic of the element at 5K marked with a solid line on the diagram, and after the purposeful aging, over 5K, marked with a dashed line.

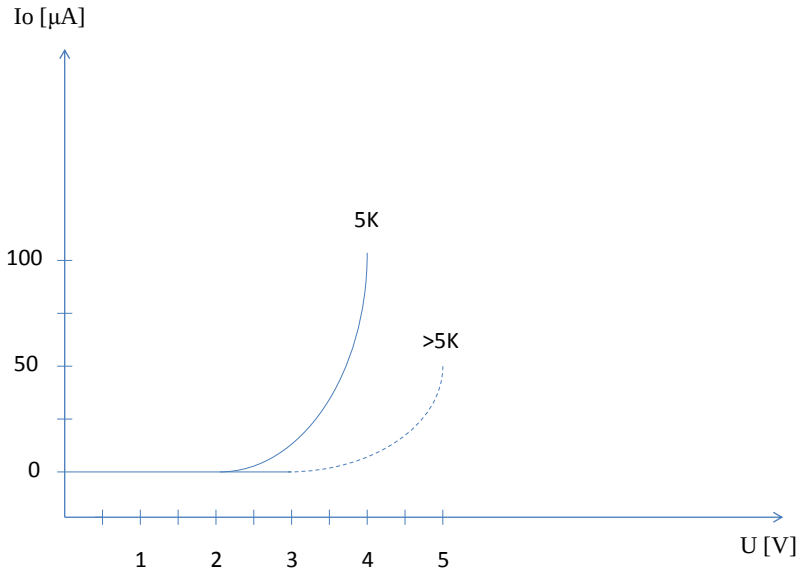

Fig. 8. Volt-ampere characteristic of the sensor

Discussion

An important parameter for each measuring device is its sensitivity (named resolution, too) δBmin of an individual measurement of a magnetic field corresponds to the error of a single measurement. Its unit is equal to the unit of the investigated magnitude –magnetic field. When a measurement is conducted during τ time with sensitivity δBmin, then the sensitivity may be improved to δBmin/√ n, through conducting of n number of measurements during nτ time and subsequent averaging of the n measured values. The sensitivity of a magnetometer depends on the time taken for conducting the measurement and it is more important to describe the element from the point of view of the spectral density of its resolution (unfortunately, often it is mentioned as "sensitivity" in the literature). The spectral density of the resolution is the magnetic field multiplied by the square root of time. Therefore its unit is [T√s] = [T/√Hz]. The sensitivity δBmin of magnetometer with magnetic resonance (2), discussed here, can be affected by noise, amplitude of the modulating field and the width of the resonance line ΔB, through the following relation:

$$\delta Bmin.Bm \frac{\partial^2 I}{\partial B^2} = Inoise,$$

$$\delta Bmin = \frac{Inoise,}{Bm \frac{\partial^2 I}{\partial B^2}}$$

Where Inoise is the noise, Bm is the amplitude of the modulating field, and $\frac{\partial^2 I}{\partial B^2}$ represents the resonance line ΔB.

The noise is equal to Inoise=√(2.e.Δf.Io).

$\frac{\partial^2 I}{\partial B^2}$ is the second derivative of the function between the current and the magnetic field I(Bo)

In the case of MEH-PPV, the Gaussian function is applied:

$$I(Bo)=\frac{Ia.Bm}{\Delta B\sqrt{2\pi}} e^{\frac{-(Bo-Bres)^2}{2\Delta B^2}},$$

Where Ia is the adjustment current.

In the center of the Gaussian distribution curve Bo=Bres. Then I(Bo) has the following expression:

$$I(Bo)=\frac{Ia.Bm}{\Delta B\sqrt{2\pi}}$$

Then the second derivative has the following expression:

$$\frac{\partial^2 I}{\partial B^2}(Bo) = \frac{Ia.Bm}{2} .\sqrt{(2/\pi)}. \frac{1}{\Delta B^3}$$

Thus, the spectral density of the resolution is δBmin/√Δf, where Δf is the width of the frequency band of the measured signal and it is defined by a low-frequency filter, placed after the range detector. Then, the spectral density of the resolution is:

$$\delta Bmin/\sqrt{\Delta f} = 2(\sqrt{(\pi e Io)}/ Ia)\Delta B,$$

where we assume that the modulating amplitude Bm is equal to the linear width ΔB. The following experimental data are used for assessing the resolution in the elements: Ia=100nA, Io=100μA, ΔB=0,35mT.

Conclusions

A magnetometer with thin organic film, based on the magnetic resonance, independent of calibration, temperature and aging, is demonstrated in this paper. The realization of such magnetic fields' sensor (Bo is in the range of 1,3mT<Bo<10mT) is illustrated. There are not fundamental restrictions, but rather technological. The upper limit is established by the high-frequency equipment and the lower limit could be overcome through a constant field, added to the modulation of Bo. The sensor is integrated in a monolithic device. It is foreseen, a large number of sensors to be placed on a separate (flexible) pad, for presenting the spatial variation of the magnetic field, with resolution lower than 100 nm.

Different experimental settings are presented to perform measurements at different excitation frequencies and at excitation with a single impulse.

When the concept of this organic magnetometer is compared to the existing devices, it can be seen that its realization could fill the gap in the precise magnetometry with small dimensions. The organic magnetometer is less sensitive than the superconducting quantum interference elements, but much more sensitive than the sensors of Hall. Unlike the superconducting quantum interference elements, which work only at cryogenic temperatures, and the sensors of Hall, which calibration is highly dependent of temperature, the organic magnetometers operate without calibration in a wide range of temperature. If compared to the conventional magnetometers with nuclear magnetic resonance, which have large dimensions and reduced sensitivity in the case of weak magnetic fields, it is seen that the organic magnetometers can be with very small dimensions and their sensitivity does not depend on the magnetic field at a large range. As the resonances in the case of nuclear magnetic resonance are narrower than the resonances of a polaron, the magnetometers with nuclear magnetic resonance provide higher sensibility at strong magnetic fields. Similarly, for the very weak magnetic fields, the superconducting quantum interference elements will continue to be the most sensitive detectors. It has to be noted, that the magnetometers with nitrogen-vacancy centers in diamond have some advantages as temperature stability and high space resolution, but opposite to the organic magnetometers there is not electrical access to them.

The error is calculated, i.e. the spectral density of sensitivity of the element is found.

Peroration

The most important challenge to magnetometers with thin organic layer is the time, needed to find the reference frequency. As in the case of conventional devices with nuclear magnetic resonance, these ones require long adjustment of the frequency. For the design, proposed here, this disadvantage could be surmounted through combination of the working regime of magnetic resonance with the magnetoresistive behavior of the polymer layer. The magnetoresistive effect allows magnetic field to be measured at a large frequency bandwidth, and the regime with magnetic resonance is used regularly for recalibration. As the recalibration of a magnetoresistive sensor is necessary only in the case of aging and major changes in temperature, this organic hybrid magnetometer may combine the advantages of two approaches: the rate of the magnetoresistive measurement with accuracy, not dependent of temperature and aging.

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