

Automated ESR spectrometer for various applications

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The paper presents a 3-cm automated ESR spectrometer providing measurements be done in the temperature range 4.2 to 300 K. The spectrometer is designed according to a standard scheme with a superhet SHF radiation receiver and magnetic field modulation. The software for the spectrometer is designed as a single program module guaranteeing performance of all types of experiments and based on the principles of structural programming and elements of object-oriented programming assuring mutual independence of algorithms and the possibility to expand the software support. Advantages of the spectrometer are illustrated taking investigations of characteristics of diluted magnetic semiconductors as an example. Preliminary investigations of both organic and inorganic substances that have been carried out on the spectrometer testify to possibilities of its effective application not only in physics but also in medicine and biology.

В статье описан автоматизированный ЭСР-спектрометр 3-см диапазона, обеспечивающий проведение измерений в температурном диапазоне 4,2–300 К. Спектрометр построен по стандартной схеме с супергетеродинным приемником СВЧ излучения и модуляцией магнитного поля. Программное обеспечение для спектрометра разработано в форме единого модуля программ, гарантирующего выполнение всех типов экспериментов и основанного на принципах структурного программирования и элементов объектно-ориентированного программирования, обеспечивающего взаимную независимость алгоритмов и возможность расширения программной поддержки. Преимущества разработанного спектрометра показаны на примере исследования функций разбавленных магнитных полупроводников. Предварительные исследования как органических, так и неорганических веществ, выполненные с помощью данного спектрометра, свидетельствуют о возможности его эффективного применения не только в физике, но также в медицине и биологии.

As a rule, most of paramagnetics are studied 3-cm ESR spectrometers; only in few cases, the particular interest in higher resolution of ESR spectra necessitates the development of higher-frequency spectrometers [1]. Development of an ESR spectrometer with high sensitivity and fully automated data retrieving and processing is of a gaining importance. This paper presents a 3-cm ESR spectrometer with fully automated process measuring of ESR line parameters, which retrieves information on magnetic properties of substances at low concentrations of paramagnetic centers.

ESR spectrometer is a part of a set-up for studying different characteristics of substances, such as conductivity, surface

characteristics, and magnetic susceptibility in the temperature range 4.2 to 300 K. The spectrometer can be tentatively presented as divided into four functional blocks: temperature, magnetic field controlling, scheme of ESR line recording and software (see Fig. 1). The temperature stabilization circuit includes three temperature sensors, a temperature measuring block, a computer, and two heaters with a power supply unit. To attain a desirable temperature, a cooling liquid (nitrogen or helium) is pumped under pressure into the lower part of cryostat. As the cooling medium evaporates, a flow of cold gas is formed, which can be regulated by a throttle. This provides wide-range temperature regulating within the cryostat. To

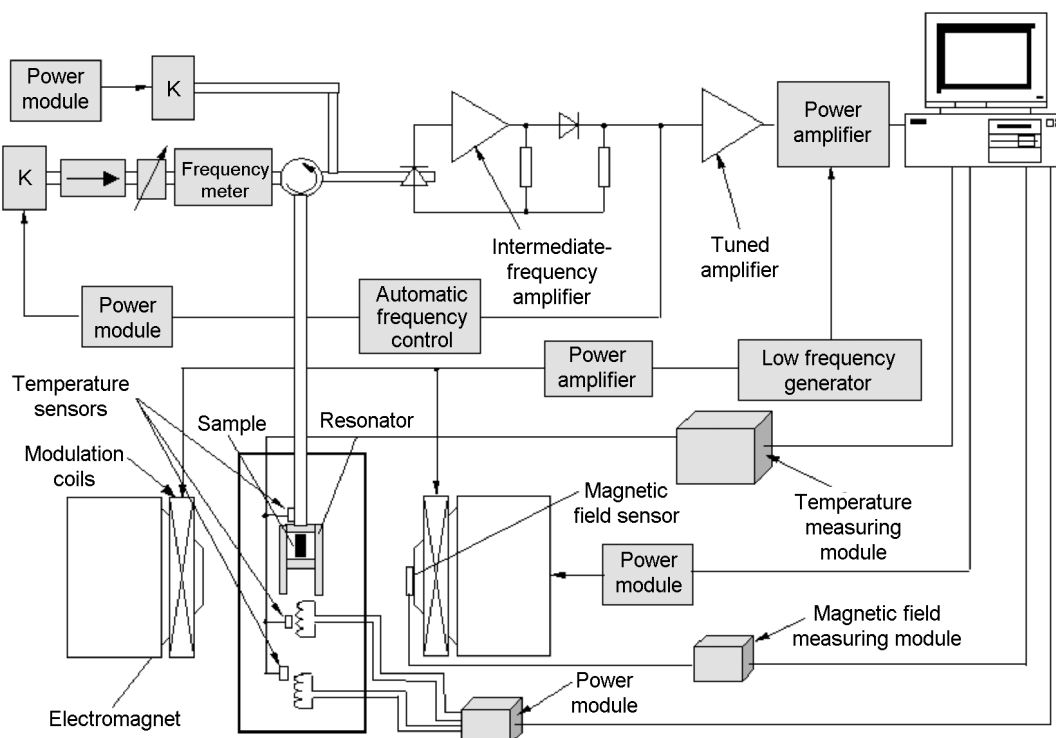


Fig. 1. Block-diagram of ESR spectrometer.

control the operating chamber temperature more precisely, we use an automatic stabilizing circuit. The precision of temperature stabilization ± 0.1 K is achieved using a proportional integral-differential (PID) control algorithm. The resonance cell is placed inside a copper cylinder so that the temperature around it is distributed homogeneously. Under the temperature stabilization regime, the resonance cell temperature reaches the preset value in 10–20 minutes and remains stable to within ± 0.1 K during the whole experiment.

The magnetic field control circuit includes a Hall sensor, a magnetic field measuring block, and an electromagnet with a computer-controlled power supply unit. The signal from the Hall sensor enters the computer which produces a monitoring signal for the electromagnet basing on the PID algorithm. The magnetic field can be regulated both with and without feedback. The latter regime is used for a preliminary recording of ESR line; in this case, the determination precision of the magnetic field value is ± 40 Gauss because of hysteresis in the magnet core. When the feedback algorithm is used in the magnetic field range 0 to 7500 Gauss, the magnetic field stabilising and measuring precision is 1.0 Gauss. When determining g-factor as well as meas-

uring narrow lines, the magnetic field interval can be considerably reduced and, therefore, the magnetic field stabilisation and measurements can be as exact as ± 0.01 Gauss.

The ESR spectrometer is designed basing on a superheterodyne receiver of SHF radiation, magnetic field modulation and recording of the first derivative of absorption line at the magnetic field modulation frequency (Fig. 1). The klystron frequency is stabilized using a scheme of automatic frequency control to the working resonator; a voltage modulation scheme on the klystron reflector at 100 kHz frequency is used. The synchronous detector that is used in the spectrometer can be operated by hardware as well as by software. The former way provides a better noise reduction during the ESR line recording. The choice of time constant is stipulated by the width of the initial spectrum. The latter way is more suitable for narrow intense lines.

The operation of the setup and the measuring of analog signals are monitored through analog-to-digital converter-digital-to-analog converter L761 of L-Card. Control over the experiment and data recording are supported by the software written in Borland C++ 5.02 using the library of API functions of a driver from L761 card. The

software operates under Windows 95, thus has expanding the possibilities for data visualization and providing a convenient interface. The software fulfils three functions: stabilization and measurement of temperature inside the cryostat, measurement and control over the magnetic field, and automatic recording of ESR lines. Temperature stabilization is performed simultaneously with control over the magnetic field and registering of ESR line. When studying substances with low concentration of paramagnetic centers, the sensitivity is increased through the regime of accumulating data from multiple measurements of the ESR line (Fig. 2). We have also introduced an additional digital integration of the signal from the synchronous detector. When the ESR line is recorded, the program shows the measured values of the absorption signal in graphic form on the screen in real time. The software uses automatic definition algorithms of ESR line width and its center. The ESR curve width is determined as the distance between the maximum and the minimum of the first derivative from the absorption line, whereas its center is defined as a point where the line intersects with x -coordinate axis. Software automated regime of the integrating voltmeter is used to compensate for the circuit error.

In cases when the ESR spectrum is a broad, low-intensity line, the curve parameters cannot be determined precisely using numerical methods because of the noises that overlap with the ESR curve. The algorithm of fitting the experimental curve to theoretical one is used to obtain a smooth curve. If a real ESR spectrum cannot be described by either Lorentz or Gauss functions, the central part of initial experimental ESR spectra is approximated with a polynomial of highest power, which looks as follows:

$$f(H) = a_0 + a_1(H_0 - H) + a_2(H_0 - H)^2 + \dots + a_n(H_0 - H)^n, \quad (1)$$

where H_0 is the line center defined as a point where the first derivative of absorption line intersects zero; a_i are coefficients of polynomial determined by approximation; n , the order of the polynomial. The determination algorithm of the ESR line width and center is as follows. First, the center of experimental curve is determined and the approximation by formula (1) is carried out. Then, the center of ESR line is determined from the approximated curve at a higher pre-

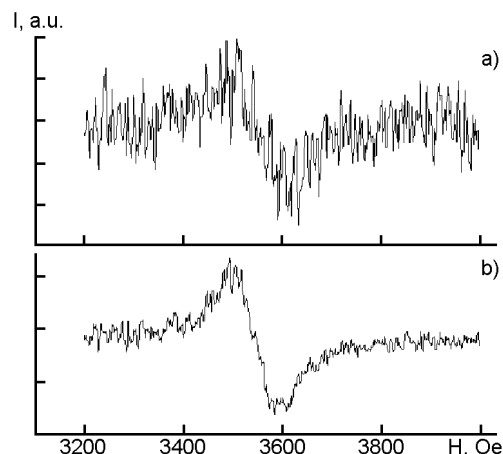


Fig. 2. ESR spectrum of the sample of $\text{Hg}_{1-x}\text{Cr}_x\text{Se}$ type with $x = 0.03$ at the temperature $T = 224.3$ K: for the only realization (a), and for 16 realizations (b).

cision, and the second approximation of the experimental line is conducted. The final width and center of the line are determined basing on the last approximated curve.

We have investigated a series of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ samples with manganese concentration x varying of 0.02 to 0.55 as well as Mn doped CdTe (CdTe:Mn) crystals grown by Bridgman method of manganese substitution for cadmium. The crystal under study has the structure of a zinc blende. The main particularities of ESR spectrum of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ at low manganese concentrations are as follows: gyromagnetic ratio g is almost equal to g -factor of free electron ($1.99 < g < 2.02$); isotropic hyperfine structure consisting of six lines can be observed as a result of interaction between $3s^23d^5$ and $3s3d^54s$ configurations; a fine structure is also visible as a result of anisotropic influence. The line shape is similar to Gaussian. As the manganese concentration increases, the spectrum fine structure disappears (at $x > 0.03$) and the line shape changes to the Lorentz one. At high concentrations, considerable broadening of ESR line can be observed as the temperature decreases, which is the result of the internal field increase due to final clusters of antiferromagnetic ordering.

The ESR lines for all the above samples are symmetrical throughout the whole temperature interval and shaped similar to Lorentz type, which correlates well with the previous results [2]. The absorption line is defined by the manganese ion Mn^{++} . Any explicit magnetic anisotropy axes cannot be observed in these samples. Fig. 3 shows

temperature dependences of ESR line width for manganese content (x) of 0.02 to 0.55. The manganese concentration range from the minimum to $x = 0.1$ shows only a slight temperature dependence in the range from room temperature to helium one. However, as the Mn^{++} increases further, the ESR line width increases, and the temperature dependence of ESR line width shows an area with anomalously high growth rate at each composition. This fact results from the increasing internal magnetic field defined by the presence of final antiferromagnetic clusters [2]. In this case, broadening of ESR line can be observed long before the transition temperature to the spin glass phase (T_g). It is just this fact that forms a base for the method of determination the spin glass transition temperature T_g using ESR method.

In order to determine the spin glass transition temperature T_g , experimental data have been approximated by the formula (2), which describes the line width increase at the temperature decrease [2]:

$$\Delta H_{pp} = A \left[\frac{T_g}{T - T_g} \right]^\alpha + B \left[\frac{\Theta}{T} + 1 \right], \quad (2)$$

where B is the temperature-independent line width; a , a critical indicator; θ is a Curie-Weiss temperature. The empirical picture of the spin glass formation for these samples has been reconstructed basing on the concept of spontaneous formation of clusters with antiferromagnetic ordering. As the temperature decreases, the volume of clusters increases. The higher manganese concentration in a sample is, the higher is the temperature at which the volume of clusters increases to the point of their contact. It is below this temperature that the whole substance transits into the spin glass phase. Unlike the paramagnetic phase where magnetic moments fluctuate in time, the spin glass phase is characterised by the presence of "frozen" magnetic moments [3]. This means that atomic magnetic moments have non-zero time-averaged vector values.

The properties of CdTe:Mn samples differ from those described above. We have measured ESR spectra of CdTe:Mn in the temperature range 80–300 K. An explicit anisotropy in the sample magnetic properties can be observed at room temperature: at a certain sample orientation, a single symmetric line corresponding to Mn^{++} can be observed. As the sample is rotated, an unre-

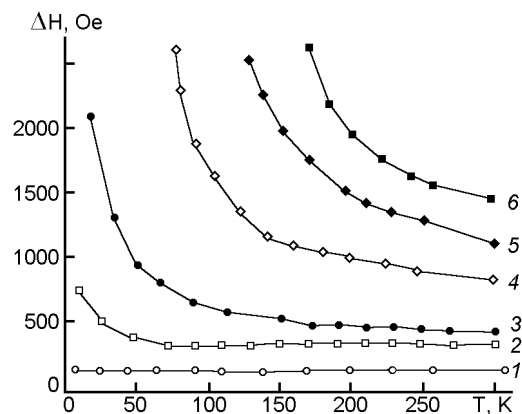


Fig. 3. Temperature dependences of ESR line width for $Cd_{1-x}Mn_xTe$ samples with different manganese concentration, x : 0.02 (1), 0.1 (2), 0.2 (3), 0.3 (4), 0.45 (5), 0.55 (6).

solved hyperfine structure appears which resolves at the temperature decrease. Bivalent Mn^{++} ions have $3d^5$ -configuration and the basic state ${}^6S_{5/2}$. The crystal field revokes partially the 6-fold degeneration of the ground state, however, it cannot revoke it fully; at best, this state can be divided into three Crammers doublets. In this case, the Mn^{++} ESR spectrum consists of five resonance lines corresponding to the thin transition structure for $\Delta M = +1$. The scheme of energy levels depends on the angle between magnetic field and crystallographic axes. As the Mn^{++} nucleus has magnetic moment $I = 5/2$, the interaction between the electron and nuclear magnetic moments results in splitting of each energy level of the fine structure into six additional levels. The simplest spin Hamiltonian for Mn^{++} in a cubic crystal looks as follows:

$$H = g\beta\mathbf{H}\cdot\mathbf{S} + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4) + A\mathbf{I}\cdot\mathbf{S}, \quad (3)$$

where g is the spectroscopic splitting factor; β , the Bohr magneton; a is a cubic field constant; A , the constant of hyperfine interaction with Mn^{55} nucleus.

As the temperature decreases, the spectrum structure becomes more resolved because of the narrowing of single resonance lines due to relaxation processes. The value of hyperfine splitting is 60.4 Gauss. When the angle between the direction of magnetic field \mathbf{H} and the polar axis of the crystal is $\varphi = 32^\circ$, a characteristic line superposition takes place, with lines corresponding to transitions with the same projection of nuclear spin onto the direction \mathbf{H} . As this case is equivalent to the crystal field absence,

the observed six peaks correspond to the transitions between the levels of hyperfine structure (Fig. 4). For other angles φ , the spectrum structure changes considerably due to combinations of different hyperfine structure lines belonging to different elements of thin structure. For the orientation $\varphi = 32^\circ$, we have determined line parameters. As the spectrum is not fully resolved, we have approximated the experimental spectra with the following function:

$$I(H) = \sum_{i=1}^6 f(H - H_0 + (i - 3.5)\Delta H_p), \quad (4)$$

where H_0 is a magnetic field value corresponding to the center of ESR signal; ΔH_p , the hyperfine splitting value; $f(H)$, a function describing the line shape of a hyperfine structure single component.

As $f(H)$, we take Gaussian function

$$f(h) = -\left(\frac{H}{\Delta H}\right) e^{-\left(\frac{H}{\Delta H}\right)^2}, \quad (5)$$

or that of Lorentz

$$f(H) = \frac{\left(\frac{H}{\Delta H}\right)}{\left(1 + \left(\frac{H}{\Delta H}\right)^2\right)^2} \quad (6)$$

for the first derivative on the absorption line. Here, ΔH is the line width.

As a result, we have determined the values ΔH_p , ΔH and H_0 . The values of resonance magnetic field and of hyperfine splitting do not change as the temperature decrease and remain $H_0 = 3526$ Gauss (corresponds to $g = 1.9807$), $\Delta H_p = 60.4$ Gauss. The width of a single resonance line decreases monotonously with decreasing temperature, and its shape remains the Gaussian. Mn^{++} ESR spectra in $Cd_{1-x}Mn_xTe$ with $x < 0.03$ have been studied in detail in [4–6].

To conclude, the 3-cm ESR spectrometer presented here has characteristics compatible with those of well-known analogues. Its key particularity, however, is the use of software making it possible to study substances with low concentration of paramagnetic centers. The programs of experimental

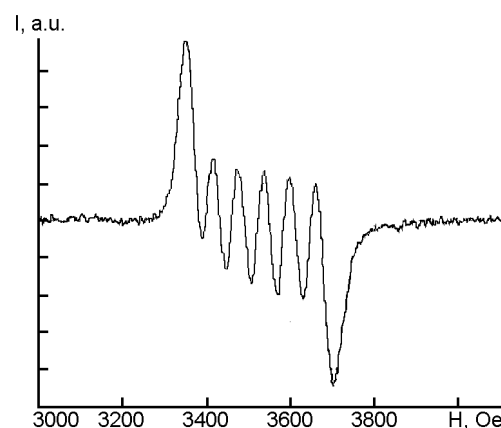


Fig. 4. ESR spectrum of CdTe:Mn crystal for $\varphi = 32^\circ$ at $T = 180$ K.

ESR spectra processing provide determination of the width and the center of ESR line as well as the function corresponding to the ESR line shape of both for single and complex absorption lines that describe fine and hyperfine structures. The advantages of this spectrometer are explicated in the presented ESR spectra of a number of diluted magnetic semiconductors of $Cd_{1-x}Mn_xTe$ type with manganese concentration x ranging from 0.02 to 0.55. Experimental results are analysed basing on existing physical models that describe diluted magnetic semiconductor properties in the given temperature range. Preliminary investigations of different substances of organic and inorganic nature show that the spectrometer can be applied in a number of experiments in medicine and biology.

Samples of $Cd_{1-x}Mn_xTe$ type have been supplied by our colleagues from the Faculty of Microelectronics at Chernivtsi National University.

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Автоматизований ЕСР спектрометр для різноманітних застосувань

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У статті представлений автоматизований ЕСР спектрометр. Спектрометр дозволяє проводити вимірювання в інтервалі температур 4,2–300 К. ЕСР спектрометр створений за стандартною схемою із супергетеродинним НВЧ приймачем та модуляцією магнітного поля. Програмне забезпечення для ЕСР спектрометра розроблено у вигляді єдиного програмного модуля, який дозволяє проводити усі види експериментів. Його структура базується на принципах структурного програмування та елементах об'єктно-орієнтованого програмування, які забезпечують взаємну незалежність алгоритмів та можливість розширення програмного забезпечення. Переваги спектрометра продемонстровано на прикладі досліджень характеристик напівмагнітних напівпровідників. Проведені на спектрометрі попередні дослідження різноманітних речовин органічної та неорганічної природи свідчать про можливість його ефективного використання також у медицині та біології.