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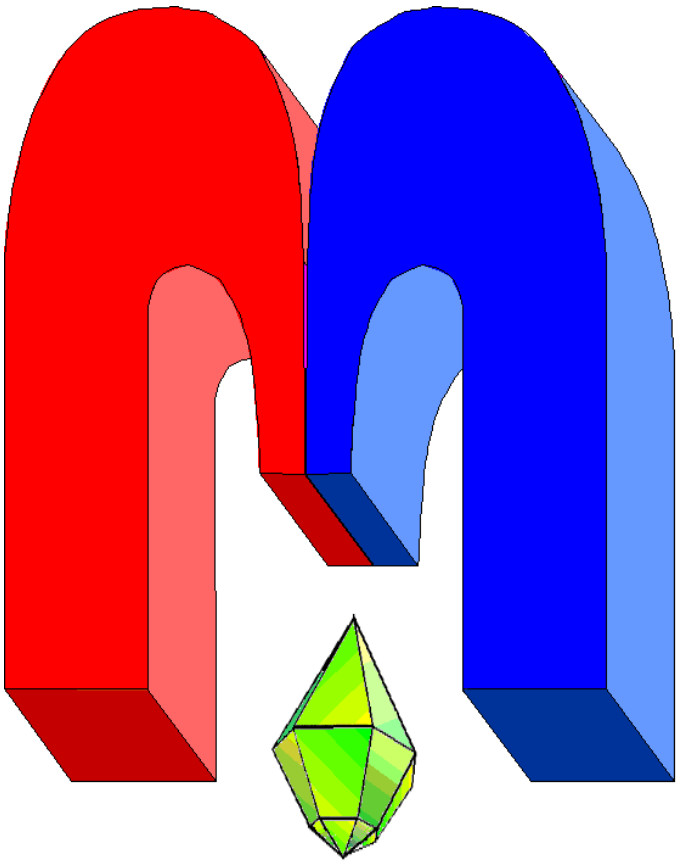

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* In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Calculation of ZnO nanoparticle size distribution based on EPR line shape analysis

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Quantum confinement of the shallow-donor electron wave function in ZnO nanoparticles is used to study nanocrystal samples by means of High-Frequency EPR. A method for deriving nanoparticle size distribution in the sample from the EPR line shape of the shallow donor is developed based on dependence of the shallow donor *g*-factor on nanoparticle size.

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Keywords: ZnO, nanoparticles, shallow donor, High Frequency EPR, *g*-factor

1. Shallow donors in zinc oxide

In recent years zinc oxide has attracted a lot of attention as a promising material for UV light-emitting diodes and diode lasers due to its wide direct bandgap of 3.4 eV. However, development of optical devices based on ZnO requires ability to grow both *n*- and *p*-type materials of high quality. ZnO can easily be doped *n*-type, even nominally undoped ZnO crystals show *n*-type conductivity. On the other hand, the *p*-type conductivity is hard to achieve. It has been suggested [1] and later experimentally proven [2] (by means of High-Frequency EPR and ENDOR spectroscopy) that this behavior is caused by the presence of hydrogen, which prefers interstitial over substitutional sites in ZnO and becomes a shallow donor.

Similar effects may be expected after the introduction of other group-I elements in ZnO. In particular, Li and Na were predicted [3] to occupy the interstitial sites and form shallow donors as well. This effect, however, has only been observed in nanoparticles, while in bulk ZnO crystals Li was only found to form the substitutional defect Li_{Zn} [4, 5].

Extension of the wave function of the shallow donor in ZnO is rather significant. Effective Bohr radius of the shallow-donor 1s-type wave function obtained from the effective mass theory [2] is about one and a half nanometers:

$$r_d = \frac{\varepsilon / \varepsilon_0}{m^* / m_e} \cdot r_B \simeq 1.5 \text{ nm} \qquad (1)$$

where $\varepsilon = 8.65$ is the dielectric constant of ZnO, $m^* = 0.3 m_e$ is the polaron mass in ZnO, and $r_B = 0.053$ nm is the Bohr radius. When a shallow donor is introduced into a ZnO nanoparticle of a comparable size to the effective Bohr radius, effects of quantum confinement of the shallow-donor wave function can be studied experimentally.

2. Quantum confinement effect in ZnO nanoparticles

Li-doped ZnO nanoparticles have been studied in great detail by means of High-Frequency EPR spectroscopy at 95 GHz [6]. It was found that position of the EPR line corresponding to the shallow donor is dependent on the size of ZnO nanocrystals.

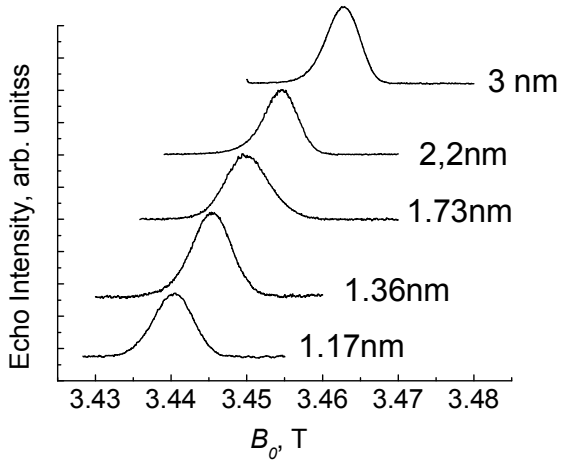

Figure 1. Position of the shallow donor EPR line in ZnO nanocrystals is strongly correlated with the size of the nanocrystals, $f = 94.9$ GHz .

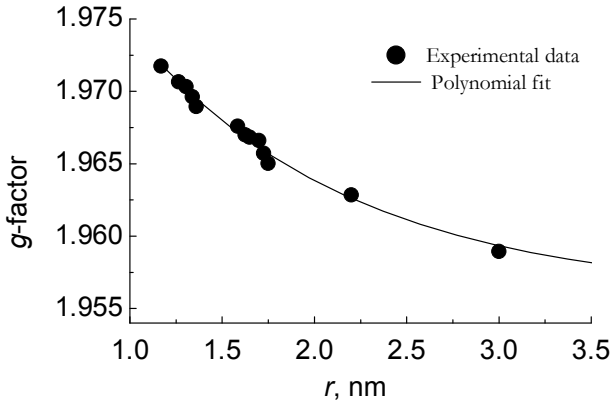

Figure 2. *g*-factor of the shallow donor as a function of ZnO nanoparticles size. The fitting function is $g(r) = 1.98835 - 0.01724 \cdot r + 0.00248 \cdot r^2$, where r is in nanometers.

This dependence is illustrated in Fig. 1. Even small changes in the size of the nanocrystals result in significant shifts of the EPR line. These spectra were recorded by means of High-Frequency Electron Paramagnetic Resonance (HF EPR) at W-band (frequency around 95GHz). It would be impossible to detect these shifts in EPR experiments at lower frequencies because the spectral resolution drops proportionally to the EPR frequency. Enhanced spectral resolution makes HF EPR spectroscopy a highly sensitive tool for studying nanoparticles. Dependence of the g-factor of the shallow donor on size of ZnO nanoparticles is shown in Fig.2. The fitting function is $g(r) = A + B \cdot r + C \cdot r^2$, with $A = 1.98835$, $B = -0.01724$ nm^{-1} and $C = 0.00248$ nm^{-2}.

The *g*-factor of the shallow donor in ZnO nanoparticles increases towards the free electron value $(g_e \simeq 2)$ when decreasing the size of the nanoparticles. This effect occurs due to quantum confinement of the shallow-donor electron wave function when its effective Bohr radius $r_d = 1.5$ nm becomes comparable to dimensions of the nanoparticles. The confinement causes an increase in the bandgap and, consequently, reduces admixture of valence-band states and higher-lying conduction bands [7].

The average nanocrystal radii can be measured by X-ray powder diffraction, based on the peak broadening due to the finite crystallite sizes (Scherrer's equation). However, sensitivity of the X-ray method decreases when decreasing the size of the nanoparticles. Dependence shown in Fig. 2 can be used to determine the average particle size in the sample from position of the EPR line. Our goal was to develop a method that would allow us to derive ZnO nanoparticle *size distribution* in the sample from the EPR line shape.

3. Calculation of ZnO nanoparticle size distribution

The shape of the shallow donor EPR line of a ZnO nanoparticle sample is determined by two factors. First, nanoparticles compose a powdered sample with all possible orientations of the individual nanocrystal axes with respect to direction of the magnetic field being equally probable. Second, the value of the shallow donor *g*-factor is dependent on the size of an individual nanoparticle. Both of these factors should be taken into account in a procedure of EPR line shape computer simulation; the second factor is that which allows the particle size distribution to be estimated.

First, let us consider the powdered nature of the sample. Zinc oxide has a wurtzite structure with an axial symmetry. The values of the shallow donor g-tensor are $g_{\perp}=1.956$ and $g_{\parallel}=1.957$ [2]. The line shape corresponding to particles of a single, fixed orientation will have the Lorentz form:

$$f_L(H)=\frac{\sqrt{3}\cdot\Delta H_{\max}}{2\pi}\cdot\frac{1}{\frac{3}{4}(\Delta H_{\max})^2+H^2}, \tag{2}$$

where $\Delta H_{\max}$ is a peak-to-peak linewidth, experimentally measured [2] and equal to 0.4 mT. This expression should be multiplied by a factor that will take into account the fact that an EPR transition probability is also a function of particle orientation [8]:

$$F(H,\theta)=\frac{g_{\perp}^2\left(g_{\parallel}^2+g^2(\theta)\right)}{2g^2(\theta)}\cdot f_L\left(H-\frac{h\upsilon}{\beta\cdot g(\theta)}\right), \tag{3}$$

where θ is an angle between an individual nanocrystal axis and the constant magnetic field direction and $g(\theta)=\sqrt{g_{\parallel}^{\,2}\cos^2\theta+g_{\perp}^{\,2}\sin^2\theta}$.

The next step is to sum (integrate) over all possible orientations. Thus we obtain the resulting expression for the EPR intensity distribution for all particles in the sample

$$F(H)=\int_0^{\pi/2}\frac{g_{\perp}^2\left(g_{\parallel}^2+g^2(\theta)\right)}{g^2(\theta)}\cdot f_L\left(H-\frac{h\upsilon}{\beta\cdot g(\theta)}\right)\cdot\sin\theta d\theta\,. \tag{4}$$

Next, let us take into account a certain size distribution that necessarily exists in a nanoparticle sample. This means that dependence of the shallow donor g-factor on the size of the nanoparticles, shown in Fig.2, should be put into consideration. This dependence results in a shift of the spectrum of nanoparticles as compared to the powder spectrum, calculated without any nano-sized effects. The smaller the size of a nanoparticle, the more its g-factor will differ from the bulk value and, consequently, the more significant this shift will be. Thus the EPR intensity distribution $F(H)$ becomes a function of size of the nanoparticles. The calculated EPR line shape with the size distribution taken into consideration can be written

$$I^{cal}(H)=\int_0^{+\infty}F(H,r)\cdot P(r)\cdot dr\,, \tag{5}$$

where $F(H,r)$ is a powder spectrum of nanoparticles of a single, fixed radius r, simulated with the use of the size dependence of the *g*-factor, shown in Fig.2. $P(r)$ is a probability of the size r in the ensemble (i.e. $P(r)$ defines the number of particles of a given size in the sample). Now the goal is to derive the size distribution $P(r)$ from the condition that the calculated spectrum, as given by (5), be as close as possible to the shallow donor EPR line shape.

Since an experimental spectrum is a discrete sequence of numbers, the integral in (5) should be written as a discrete sum

$$I^{cal}(H_i)=\sum_{j=1}^{n}F(H_i,r_j)\cdot P_j\,, \tag{6}$$

then the least-squares method can be applied.

However, since experimental data contains noise, the least-squares method in this case should be supplemented with additional conditions of smoothness and non-negativity of the resulting probability distribution. The minimization is performed by a gradient descent procedure.

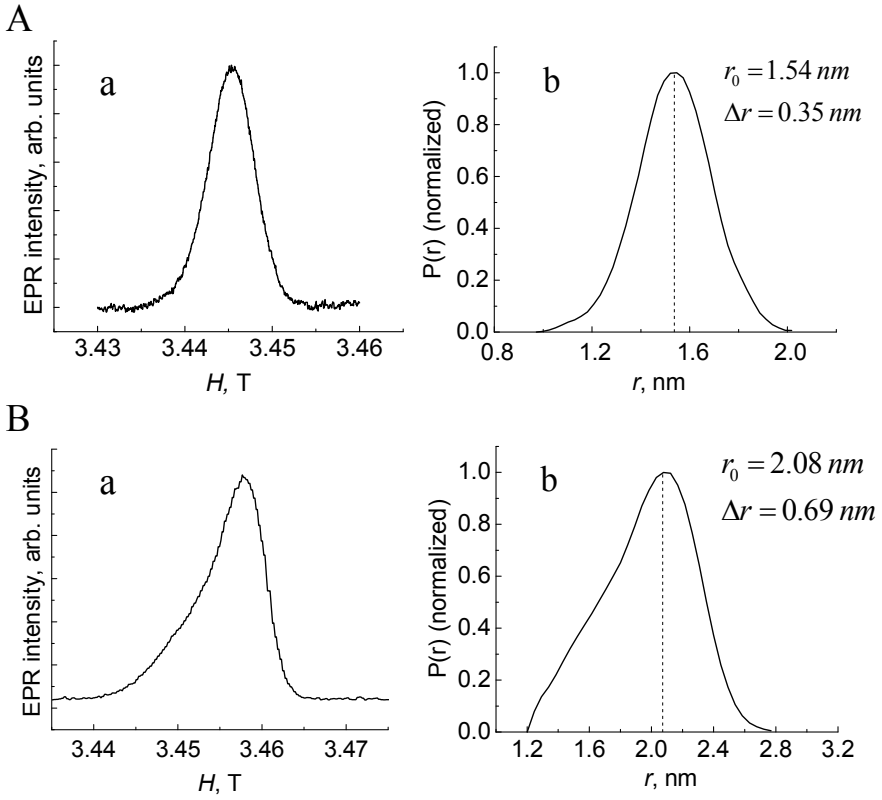

Figure 3. EPR spectrum (a) and estimated size distribution function (b) of two samples (A and B) of ZnO nanoparticles. r_0 is the size, corresponding to the peak of the distribution, Δr_0 is the distribution width on the half-height.

4. Results

The method described above allowed us to compare quality of several samples of nanoparticles produced in different laboratories.

Fig. 3 shows experimental EPR spectra and calculated functions of size distribution of two nanoparticle ensembles, grown under different conditions. The size distribution in the first case (Fig. 3A) is rather symmetrical, the average particle size r_0 is about 1.54 nm. The half-height width of the distribution Δr_0 is quite small, around 0.35 nm. The estimation error of r_0 and Δr_0 is about 0.1 nm. The result of the calculations made for another sample of nanoparticles is shown in Fig. 3B. In this case the size distribution is significantly asymmetric. Its half-height width is 0.69 nm, which is almost twice as large as in the case of the first ensemble. Such differences in the size distributions allow us to draw conclusions on the quality of the studied samples.

5. Summary

Development of nanotechnologies requires new techniques for controlling the quality of the nanoparticles produced. We developed a method of calculating the size distribution function of ZnO nanocrystals in a sample based on size dependence of the shallow donor *g*-factor. This dependence is caused by quantum confinement of the shallow-donor wave function that occurs when its effective Bohr radius is comparable to the size of the nanocrystals. Consequently, this method is inherently applicable to the case of small nanoparticle sizes, where sensitivity of other methods (the X-ray spectroscopy, for instance) decreases. We used our method to estimate the size distribution functions

of several samples grown in different laboratories and perform a comparative analysis of these samples to show that it can be used to control the quality of the grown nanoparticles.

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