

# ELECTRON PARAMAGNETIC RESONANCE FOR THE SURFACE MANGANESE IN ZnS SUBMICRON POWDERS

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A new kind of paramagnetic center (PC) associated with  $\text{Mn}^{2+}$  ions has been detected in ZnS submicron powders. The parameters of the EPR spectrum for this center are  $g = 2.001$ ,  $A = 9.5$  mT, and  $D = 8$  mT. To explain peculiar features of the spectrum, an influence of the axial crystalline field is taken into account by means of a perturbation method employed with regard for the third-order terms inclusive. A symmetry of the center environment and the proximity of a value of the hyperfine interaction (HFI) constant to that of the free  $\text{Mn}^{2+}$  ion allow us to identify the observed EPR spectrum as that originating from a surface manganese ion.

## 1. Introduction

An intense research interest in zinc sulphide, especially enhanced in recent years, has been associated with the effect of an increase in the photoluminescence efficiency observed in nanocrystalline ZnS:Mn [1], which opens new opportunities for optoelectronic applications. It has been shown that this effect, which is accompanied with a reduction in the luminescence relaxation time, is caused by the influence of impurity manganese [2]. For this reason, a solution of the problems concerned with the determination of manganese parameters, specification of its position within the zinc sulphide lattice, and investigation of technological conditions and other factors that influence the ZnS:Mn properties is one of the most urgent topics today.

Investigations of manganese-doped ZnS, carried out with the use of the EPR technique, have shown that manganese ions can form more than one type of PC. The most studied among them are  $\text{Mn}^{2+}$  ions that substitute for the ions of zinc. Due to the unfilled  $d$ -shell, these ions are paramagnetic and form PC with the electron spin  $S = 5/2$ . The EPR spectrum for the  $\text{Mn}^{2+}$ -containing center consists of five lines, each of which is split into a sextet due to the HFI of an unpaired electron with the  $^{55}\text{Mn}$  nucleus having the spin  $I = 5/2$ . Depending on a crystalline structure of zinc sulphide (cubic or hexagonal), this spectrum is characterized by either

of the following sets of parameters [3]:  $g = 2.0025$ ,  $A = 6.8$  mT,  $a = 0.78$  mT for the cubic modification or  $g = 2.0016$ ,  $A = 7.0$  mT,  $D = -10.5$  mT for the hexagonal one. Here,  $A$  is the HFI constant,  $D$  and  $a$  are the axial and cubic constants of the crystalline field, respectively. Another type of PC containing a manganese ion is interstitial  $\text{Mn}^{2+}$ . Its spectrum is characterized by a slightly greater value of  $g$ -factor, namely, 2.020 [4]. At higher impurity concentrations, more complicated PC are formed, which contain two, three, or more manganese ions that are bound to one another by the exchange interaction [5].

Recently, an EPR spectrum with the parameters  $g = 2.001$ ,  $A = 9.5$  mT, and  $50$  mT  $< D < 100$  mT was revealed in zinc sulphide [2]. This spectrum was observed only in nanosize ZnS and ascribed to  $\text{Mn}^{2+}$  ions localized on the nanocrystallite surface. It is this kind of manganese ions that is thought to be responsible for the considerable enhancement of the photoluminescence efficiency [2].

In this work, a new kind of PC that we attribute to  $\text{Mn}^{2+}$  is revealed in ZnS submicron powders. An unusual shape of the EPR spectrum for this center is explained by an influence of the axial crystalline field, which was taken into account in the third order of perturbation theory. The parameters of the spin Hamiltonian, which were determined in the work, make it possible to identify the revealed center as the surface  $\text{Mn}^{2+}$ .

## 2. Materials and Methods of Measurements

ZnS powders (ETO.035.295 TU) were used in the investigation. For these powders, a mean grain size was equal to 10–15  $\mu\text{m}$ . The powders were annealed together with  $\text{CuCl}_2$  in quartz technological test tubes at 750  $^\circ\text{C}$ . The annealing time was 2 h. A gas seal made from activated charcoal was used to restrict the atmosphere air access. Manganese was an uncontrolled impurity in  $\text{CuCl}_2$ .

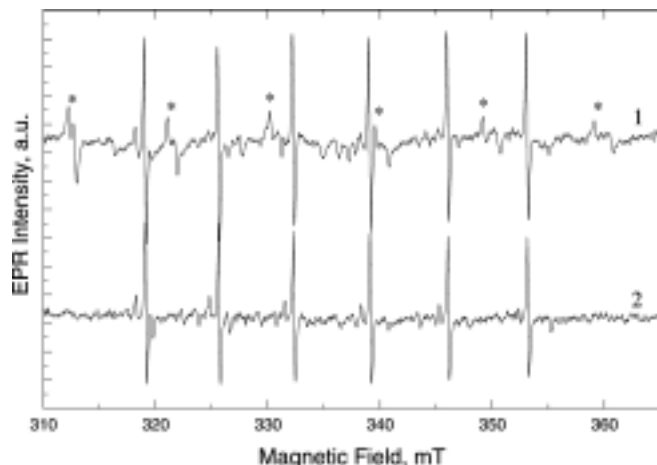


Fig. 1. EPR spectra for the  $\text{CuCl}_2$  doped ZnS powders recorded immediately after the specimen withdrawal (1) and after its holding for 3 days under conditions of the free atmosphere access (2). The lines corresponding to the PC of a new kind are denoted by asterisks

EPR measurements were carried out both immediately after a withdrawal of the powder from the technological test tube and, additionally, after its holding for 3 days under conditions of the free atmosphere access. The studies were performed at room temperature with the use of a Radiopan EPR spectrometer operating in a 3-cm frequency range ( $\sim 9.4$  GHz). The amplitude of the high-frequency (100 kHz) magnetic field modulation was 0.1 mT. To avoid saturation effects, the spectra were measured at sufficiently low powers of the microwave radiation (near 5 mW). The value of magnetic field was measured using a NMR sensor, which ensured an accuracy of measurement better than 0.01 mT.

### 3. Results of Studies and Discussion

Fig. 1 compares the typical EPR spectrum recorded directly after the specimen withdrawal with that obtained after the three-day keeping of the specimen in ambient atmosphere. The latter spectrum consists of six lines of the equal intensity, each of which is accompanied with a satellite on the low-field side (see Fig. 2, spectrum 2). It is the presence of six lines of the equal intensity that evidences for that this spectrum originates from the interaction of an unpaired electron of PC with its nucleus having the spin  $I = 5/2$ . This spectrum can be described with the parameters  $g = 2.001$ ,  $A = 9.5$  mT, which are close to those of  $\text{Mn}^{2+}$  ions in the hexagonal zinc sulphide. Such a PC has the electron spin  $S = 5/2$

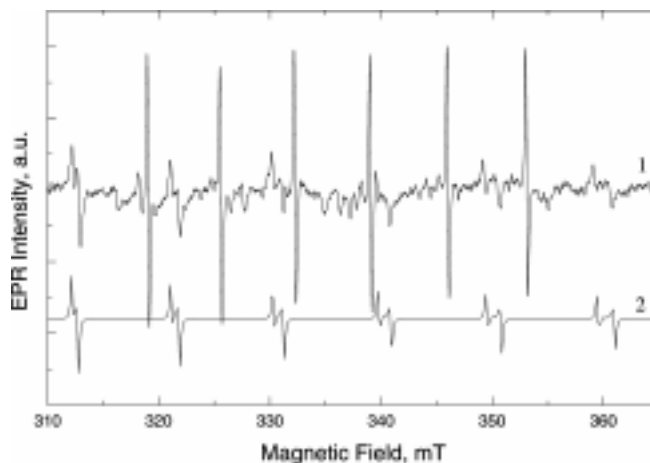


Fig. 2. EPR spectrum for the  $\text{CuCl}_2:\text{Mn}$  doped ZnS powders recorded immediately after the specimen withdrawal (1) and that calculated using the parameters  $g = 2.001$ ,  $A = 9.5$  mT, and  $D = 8$  mT (2)

and rather complicated EPR spectrum in single crystals. In powders, however, only the lines corresponding to the electron transition  $M = 1/2 \leftrightarrow M = -1/2$  are usually observed due to orientational widening. The satellite lines which accompany the lines of the main EPR spectrum can be characterized by the parameters  $g = 2.003$  and  $A = 6.8$  mT, which are close to those of  $\text{Mn}^{2+}$  ions in the cubic environment.

A peculiar feature of spectrum 1, which was recorded immediately after the withdrawal of the specimen from the technological test tube, is that, besides the lines characteristic of the manganese ions located within the volume of zinc sulphide, it comprises an additional spectrum (its lines are denoted by asterisks in Fig. 1). The latter spectrum also consists of six lines with a certain structure that changes with an increase in the magnetic field.

To analyze the spectra obtained, let us utilize the approach described in [6]. According to it, the spin Hamiltonian can be expressed as

$$\mathcal{H} = g\beta\mathbf{HS} + D[S_z^2 - S(S+1)/3] + ASI - g_I\beta\mathbf{HI}, \quad (1)$$

where  $\beta$  is the Bohr magneton value;  $S$  and  $I$  are the electron and nuclear spins, respectively, and  $g_I$  is the nuclear  $g$ -factor,  $H$  is the external magnetic field.

Considering the first term as the zero-order approximation of the operator and other terms as perturbations, a solution can be written in the third-order approximation of perturbation theory as

$$E_{Mm} = E_{Mm}^{(0)} + E_{Mm}^{(1)} + E_{Mm}^{(2)} + E_{Mm}^{(3)}, \quad (2)$$

where  $M$  and  $m$  are the quantum numbers of the projections of the electron and nuclear spins, respectively, on the direction of the external magnetic field.

It was noted above that only those EPR lines are observed in non-oriented systems which are caused by the transition  $M = 1/2 \leftrightarrow M = -1/2$ . Thus, let us limit a consideration of the solutions of Eq. (1) only to those which concern this transition and consider only the case in expression (2) where  $M = \pm 1/2$ . Then, the values of resonance fields can be written as

$$H_r = H_0 + H_1 + H_2 + H_3, \quad (3)$$

where

$$H_0 = h\nu/g\beta, \quad H_1 = -Am,$$

$$H_2 = A^2(m^2 - 35/4)/2H_0 + 2D^2 \sin^2 \theta (9\cos^2 \theta - 1)/H_0,$$

$$H_3 = (15A^3m)/4H_0^2 - 32AD^2m \sin^2 2\theta/H_0^2 - 4A^2Dm(3\cos^2 \theta - 1)/H_0^2.$$

Here,  $\theta$  is the polar angle, which characterizes an orientation of the external magnetic field, and  $\nu$  is the frequency of microwave field.

In the case where the symmetry is axial, the expression describing the PC EPR spectrum in the powder samples can be obtained by means of the substitution of  $H_r$  into the expression

$$I(H) \approx \int_0^\pi G(H - H_r) \sin \theta d\theta, \quad (4)$$

where  $G(H - H_r)$  is a function describing the EPR line shape of a separate center.

The PC parameters  $g$ ,  $A$  and  $D$  were obtained by means of a fitting of the spectrum calculated according to Eq. (4) to that obtained experimentally. The best accordance of the former to the experimental results was achieved at  $g = 2.001$ ,  $A = 9.5$  mT, and  $D = 8$  mT. As a function describing the shape of a single EPR line, we took the Lorentzian with a width of 0.2 mT. Fig. 2 compares the data obtained in experiment with those calculated using the above parameters. In our opinion, the proximity of the value of the HFI constant to that of the free ion can serve as a confirmation of the fact that the ion is located just on the surface.

The parameters  $g$  and  $A$ , obtained as a result of the fitting procedure, coincide with those characteristic of the surface  $Mn^{2+}$  ion that were observed earlier in nanosize zinc sulphide [2]. However, the value of the

constant  $D$  obtained by us is far smaller than that estimated in [2]:  $50 \text{ mT} < D < 100 \text{ mT}$ . The reason for this discrepancy is supposed to originate from a difference in the methods of estimation of  $D$ : contrary to the rough estimation procedure which was carried out in [2], we determined the parameters by means of a careful fitting of the calculated data to those obtained in experiment. To examine the results of work [2], we calculated the EPR spectrum in the  $Q$ -band, using Eqs. (1) – (4) with the parameters obtained in the latter work. The shape of the calculated spectrum sufficiently differs from that recorded in [2]. It is worth noting that the parameters of surface manganese ions in nanosize zinc sulphide were also determined in [7] and their values ( $g = 2.0013$ ,  $A = 9.0$  mT, and  $D = 16$  mT) are close to those obtained by us. A slight discrepancy between the values might be caused by a difference in the object size: nanosize powders in [7] and submicron ones in the present work.

A rather fast time decay, which is characteristic of the EPR spectrum associated with the surface manganese ions, can result from a modification of the ZnS grain surface under an influence of the external atmosphere (most likely under an action of oxygen), which may give rise to a recharge of  $Mn^{2+}$  ions. The other likely reason is the diffusion of surface manganese ions into the grain core, similarly to the process occurring with gallium ions [8].

#### 4. Conclusions

As a result of the research performed on ZnS submicron powders, a new kind of PC has been revealed, which is associated with  $Mn^{2+}$  and is similar to that observed earlier only in nanocrystalline ZnS [2,7]. Such a center is characterized by the EPR spectrum parameters  $g = 2.001$ ,  $A = 9.5$  mT, and  $D = 8$  mT. The axial symmetry of the center environment, the proximity of the HFI constant to that of free  $Mn^{2+}$  ions, as well as the proximity of the parameters of its EPR spectrum to those characteristic of the surface centers which were observed in ZnS nanosize powders make it possible to identify the revealed center as the surface  $Mn^{2+}$  in submicron powders. The unusual spectrum shape and dependence of the resonance line shape on  $m$  can be explained by the influence of the axial crystalline field taken into account in the third order of perturbation theory.

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ЕЛЕКТРОННИЙ ПАРАМАГНІТНИЙ РЕЗОНАНС  
ПОВЕРХНЕВОГО МАРГАНЦЮ  
В СУБМІКРОННИХ  
ПОРОШКАХ ZnS

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Р е з ю м е

У субмікронних порошках сульфїду цинку зареєстровано новий парамагнітний центр (ПЦ), пов'язаний з іонами  $Mn^{2+}$ . Встановлено, що спектр ЕПР цього центра характеризується параметрами  $g = 2,001$ ,  $A = 9,5$  мТ,  $D = 8$  мТ. Для пояснення спектра ЕПР було враховано вплив аксіального кристалічного поля методом збурень до третього порядку включно. Симетрія центра та близькість константи надтонкої взаємодії (НТВ) до значення, характерного для вільного іона  $Mn^{2+}$ , дозволили співвіднести спектр ЕПР з поверхневим іоном марганцю.