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Co²⁺ IONS IN ZnS_xSe_{1-x}:Co — ESR AND OPTICAL STUDIES

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The electron spin resonance of Co²⁺ ions in ZnS_xSe_{1-x}:Co mixed crystals was measured at temperature of 3 K and microwave frequency of 9.47 GHz. Trigonal Co_{Zn}²⁺-S center in the ZnS_{0.001}Se_{0.999}:Co crystal was identified and parameters of relevant spin Hamiltonian were determined. Influence of alloy disorder in the anion sublattice on the Co_{Zn}²⁺ ground and first excited states is briefly discussed.

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Transition metal (TM) impurities have been a subject of manifold investigations in the binary III-V and II-VI semiconductors. Despite the enormous progress in growth and device technology there is only little information about deep defects in ternary mixed materials. TM impurities are perfect "probes" which allow to observe a change through a composition range of fundamental characteristics of an electronic structure, compositional and structural disorder of solid solutions.

In this paper we report results of electron spin resonance (ESR) and photoluminescence (PL) measurements of solid solutions ZnS_xSe_{1-x}:Co (zinc blende structure) at the whole composition range of sulfur ($x = 0-1.0$). All samples studied were grown by a chemical transport method and were doped with Co to the level of 10^{18} cm^{-3} . The ESR measurements were performed at 3 K with a Bruker ESP 300E spectrometer and microwave frequency of 9.47 GHz. The spectra of binary ZnSe:Co and ZnS:Co crystals are dominated by the almost isotropic resonance line at g -factor 2.273 and 2.247, respectively, related to the isolated Co_{Zn}²⁺ centers (Fig. 1). This result agrees well with previously reported data for Co²⁺ ions in ZnSe and ZnS crystals [1, 2]. The spectra measured on mixed ZnS_xSe_{1-x}:Co crystals ($0 < x < 1$) show a superposition of resonance lines due to various centers (Fig. 1). Part of angular dependent ESR lines seems to arise from Co-related centers of low symmetry, created by alloy disorder in the anion sublattice. Here we give an analysis of lines assigned to a trigonal Co_{Zn}²⁺-S center in the ZnS_{0.001}Se_{0.999}:Co

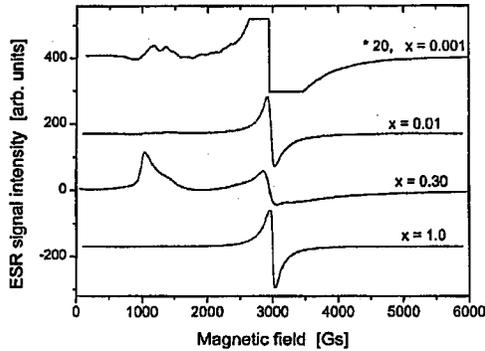


Fig. 1. ESR spectra of $\text{ZnS}_x\text{Se}_{1-x}:\text{Co}$ mixed crystals ($x = 0.001, 0.01, 0.3, \text{ and } 1.0$) measured at 3 K and microwave frequency of 9.47 GHz. The magnetic field vector was parallel to $\langle 110 \rangle$ axis of the crystals.

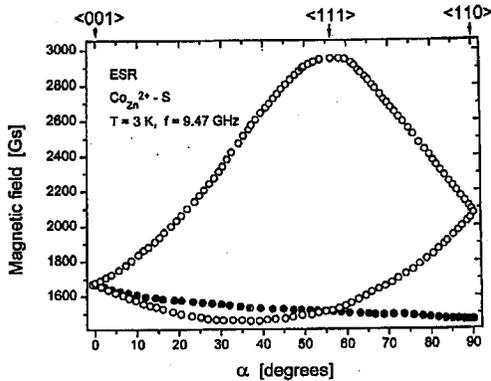


Fig. 2. Angular dependence of ESR resonance lines of $\text{ZnS}_{0.001}\text{Se}_{0.999}:\text{Co}$ crystal measured at 3 K. The magnetic field \mathbf{B} was rotated in a $\langle 11\bar{0} \rangle$ crystal plane. α is a value of angle between $\langle 001 \rangle$ axis and the vector \mathbf{B} . The transitions between $|\pm 1/2\rangle$ levels of the trigonal $\text{Co}_{\text{Zn}}^{2+}$ center are marked by circles.

crystal. The angular dependence of ESR resonance lines shown in Fig. 2 exhibits typical patterns of a trigonal paramagnetic center with an effective spin $S' = 1/2$. This spectrum was measured in the crystal with the lowest sulfur composition ($x = 0.001$).

The ground state of the $\text{Co}^{2+}(3d^7)$ ion in tetrahedral symmetry is a $^4A_2(F)$ level [3]. This spin quartet splits in trigonal symmetry into the two Kramers doublets $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$, separated by energy distance of $2D$. The energy levels of such a system can be described by the Hamiltonian with spin $S = 3/2$ in the following way:

$$H = g_{\parallel}\mu_{\text{B}}B_zS_z + g_{\perp}\mu_{\text{B}}(B_xS_x + B_yS_y) + D[S_z^2 - (1/3)S(S+1)]. \quad (1)$$

Here μ_{B} is Bohr magneton, g_{\parallel} and g_{\perp} are g -factors for magnetic field $\mathbf{B} = (B_x, B_y, B_z)$ parallel and perpendicular, respectively, to the z -axis of the coor-

dinate system (x, y, z). The z -axis coincides with the trigonal C_3 symmetry axis, parallel to the $\langle 111 \rangle$ crystallographic axis of the crystal. In a tetrahedron there are four C_3 directions and four different center positions for anion nearest neighbors. Two of them are magnetically equivalent under rotation around a $\langle 110 \rangle$ axis of the crystal.

When the trigonal crystal field splitting of the 4A_2 ground state is much larger than the microwave energy ($D \gg h\nu = 0.316 \text{ cm}^{-1}$), the observed ESR transition takes place only within $|\pm 1/2\rangle$ doublet and can be described by an effective spin $S' = 1/2$ formalism. The measured angular dependence of ESR lines (Fig. 2) was numerically fitted with the use of Hamiltonian (1) and the obtained g -factors are given in Table. The value of parameter D was estimated from additional optical absorption measurements.

TABLE
Parameters of spin Hamiltonian for the trigonal
Co_{Zn}²⁺ center in ZnS_{0.001}Se_{0.999}:Co crystal.

$S' = 1/2$	$S = 3/2$
$g'_{\parallel} = 2.270 \pm 0.020$	$g_{\parallel} = 2.270 \pm 0.020$
$g'_{\perp} = 4.601 \pm 0.042$	$g_{\perp} = 2.274 \pm 0.022$
	$ D = (4.1 \pm 0.4) \text{ cm}^{-1}$

On the other hand, it is possible to calculate (by perturbation method) the Zeeman corrections to the energies of 4A_2 states of Co²⁺(d^7). In this case, the principal values of the effective g' tensor are given by parameters of $S = 3/2$ formalism [3]: $g'_{\parallel} = g_{\parallel}$ and $g'_{\perp} = (1/2 + S)g_{\perp}$ (see Table). It is worth mentioning that g -values obtained for both the Co_{Zn}²⁺ in the pair with sulfur and the isolated Co_{Zn}²⁺ center, differ only slightly. Taking into account the simplified relation $g = g_e - 8k\lambda/\Delta$ (Ref. [4], $g_e = 2.0023$ is free electron g -factor), we find that crystal-field splitting Δ is similar in both cases. Using the spin-orbit coupling constant for free Co²⁺ ion $\lambda = -180 \text{ cm}^{-1}$ (Ref. [3]) and $\Delta_{\text{ZnSe}} \approx 3315 \text{ cm}^{-1}$ (energy of the Co²⁺ ${}^4A_2(F) - {}^4T_2(F)$ transition in ZnSe) [5], we estimate the so-called covalency reduction factor $k_{\text{ZnSe}} \approx 0.62$ for Co_{Zn}²⁺ defect in ZnSe lattice. On the other hand, for the Co_{Zn}²⁺ defect in ZnS lattice and $\Delta_{\text{ZnS}} \approx 3470 \text{ cm}^{-1}$ [6], the same estimation gives $k_{\text{ZnS}} \approx 0.59$.

The observed changes of photoluminescence spectra of ZnS_xSe_{1-x}:Co with increasing sulfur composition, depends mainly on a relative position of the excited Co²⁺ levels versus edge of conduction band in the alloys [7]. The effects related to lowering of local symmetry of the Co²⁺ centers and alloy broadening are less important in the Co²⁺ intra-shell transitions.

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