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SUPERHYPERFINE INTERACTIONS OF Mn^{2+} IN CdS CRYSTALS

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Crystals of cadmium sulphide were grown with the impurity Mn^{2+} ions from the gaseous phase by a static method using sublimation in a closed space. By the method of the electron paramagnetic resonance of Mn^{2+} ions and their interactions with the crystalline environment of cadmium sulphide the superhyperfine structure of spectra has been verified. The superhyperfine interactions are interpreted using a model with the Cd^{111} and Cd^{113} isotopes.

I. INTRODUCTION

Crystals of the semi-conductor compounds of the group II—VI are used in various photoelectric, electroacoustic and optoelectronic instruments and equipments. The compounds of this group, particularly cadmium sulphide, are also interesting in the research of crystallization from the gaseous phase. The basic physical properties of these compounds — the character of bonds, the crystalline structure, the intracrystalline field can be studied by the methods of magnetic resonances. The methods of magnetic resonances in the investigated complexes of the transition metals enable to analyse the local properties of the impurity paramagnetic ions and their interactions with the crystalline environment. Based on the EPR measurements the research into the interactions of the impurity paramagnetic Mn^{2+} ions with the ground state $3d^5\,{}^6s_{5/2}$ with the crystalline neighbourhood of cadmium sulphide crystals has been carried out. In this paper the superhyperfine structure based on the model of cadmium isotopes is interpreted.

II. EXPERIMENTAL RESULTS AND THEIR ANALYSIS

The crystal of cadmium sulphide in the pure state and doped by Mn^{2+} ions has been grown by crystallization from the gaseous phase by the static method employing the sublimation effect in a closed space. Crystallization from the

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gaseous phase enables to get large, very pure and perfect single crystals of different forms and dimensions — from thin, threadlike crystals up to single crystalline blocks of a weight from 4×10^{-2} up to 8×10^{-2} kg and more [1, 2, 3]. Optimum conditions for the growth of a crystal can be achieved using a vertical furnace with resistive heating and a large temperature gradient [3]. The works analysing the growth of cadmium sulphide and other II—VI compounds from the geseous phase assume that the gaseous phase above the growing crystal has a stoichiometric composition and the components are evaporated congruently [4, 5, 6]. The results of our experiments have indicated that the crystal growth of CdS and its analogous compounds from the gaseous phase proceeds usually in a nonstoichiometric environment [3]. A large temperature gradient causes a change in the free energy of the activation of molecules and in chemical potentials influencing the nucleation and the growth of the crystal in comparison with the case of a small temperature gradient. The vertical resistance furnace of the crystallizer covered a temperature plateau and a large temperature gradient (in the case of our arrangement it was as much as 50° C . cm^{-1}) which influenced significantly the formation of crystal seeds — nucleation and the crystal growth itself. The equipment secured high temperature stabilization in the crystallizer furnace with program control. The ampulla with cadium sulphide (Fluka AG 99.999%) was evacuated and sealed at a pressure of 5×10^{-2}—10^{-3} Pa and placed into the crystallizer temperature plateau at a temperature of 1173 K.

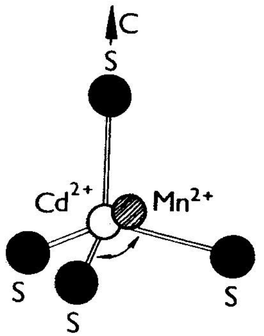

Fig. 1. The model of impurity ions Mn^{2+} incorporated into the crystal lattice of cadmium sulphide crystals.

First, the temperature in the furnace was gradually increasing up to 1473 K in order to clean the conical growth tip of the ampulla from parasitic crystallization nuclei. At a temperature of 1423 K a vertical shift mechanism was put on. The rate of the ampulla shifting in our arrangement was 0.5 mm . h^{-1} and 1 mm . h^{-1}. These discrete shift speeds were found to be advantageous [3] because the ionic radii of the impurity ions influence nucleation and the rate of the growth of cadmium sulphide crystals from the gaseous phase and the incorporation of impurities into the crystal lattice. The value of the Cd^{2+} radius

is 0.99×10^{-10} m, the Mn^{2+} ion radius is 0.91×10^{-10} m. During the growth of cadmium sulphide crystals the Mn^{2+} ions substitute the cadmium cations and incorporate very easily into the crystal lattice. The slight deformation of the CdS crystal lattice, which also occurs due to the presence of impurity ions, changes the intracrystalline field (Fig. 1). The content of impurity paramagnetic Mn^{2+} ions in CdS crystals was 0.4 mass %. CdS crystals have a wurtzite type crystal lattice with a spatial group $C_{6v}^4 - P6_3mc$. The results of the measurement of the ohmic resistance using the four-probe method are considerably influenced by the quantity of the Mn^{2+} impurity ions incorporated in the crystal lattice of cadmium sulphide. The ohmic resistance of CdS crystals in "pure state" is 10^8 Ohm . m in the dark, and in the case of doped crystals with impurity Mn^{2+} ions — the values range from 3.5×10^{-2} up to 5×10^{-2} Ohm . m at room temperature.

The spin Hamiltonian of a paramagnetic Mn^{2+} ion in its ground state $^6S_{5/2}$ provided the crystalline fields has axial symmetry (tetragonal, trigonal or hexagonal crystal lattice) is expressed as follows [7]:

$$\mathscr{H} = g \,.\, \beta \,.\, H \,.\, \mathscr{S} + D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + A \,.\, \mathscr{S} \,.\, \mathscr{I} - - \gamma \,.\, \beta_N \,.\, H \,.\, \mathscr{I} + \sum_n I_n \,.\, A_n \,.\, S; \quad (1)$$

Not all positions of the atomic nuclei of cadmium are equivalent as evident from the model in Fig. 2 analysed below. Two isotopes are present in natural cadmium $-Cd^{111}$ and Cd^{113} — with a non-zero nuclear spin $I = 1/2$, and they are approximately equal to the nuclear magnetic dipole moment. Their amounts in natural cadmium are: $Cd^{111} \sim 12.75\%$ and $Cd^{113} \sim 12.26\%$. Other isotopes of cadmium and sulphur have a zero nuclear spin and a very low half-life period due to which they do not contribute to the interaction with the electrons of the impurity paramagnetic ion Mn^{2+} incorporated in the crystal lattice which substitutes the cadmium ion (cation). The paramagnetic Mn^{2+} ion will have twelve nearest neighbouring cation Cd^{2+} as shown in Fig. 2. The twelve nearest neighbouring cations are at the same distance from the Cd^{2+} ion, which is in this case substituted by the Mn^{2+} cation. The nearest six cations are situated in the corner of the hexagonal system in the plane perpendicular to the "C" axis (direction ⟨0 0 0 1⟩). In this plane also the impurity paramagnetic Mn^{2+} ion is incorporated. The remaining six cations are present in the corners of the tetrahedron: of these, three cations are over and three below the plane of the hexagonal system. When analysing this model it is also necessary to rewrite the last expression of equation (1) as follows [8]:

$$\mathscr{H}_{SHJ} = \sum (I_H - I_T)\, A_n \,.\, \mathscr{S}, \quad (2)$$

where I_{II} represents all combinations of the nuclear spins of the Cd^{2+} cations in the hexagonal system: I_T represents the combinations of nuclear spins of Cd^{2+} cations in the tetrahedra. The summation is carried out through all posible arrangements. The absorption lines under these conditions are as follows:

$$E = A_{II} m; \quad m = 0; \quad \pm 1/2; \quad \pm 3/2; \quad \dots \pm 11/2; \quad \pm 6;$$

with relative intensities

$$I(m) = \sum_{m'=m}^{11 \text{ or } 12} \frac{w(2m')}{2^{2m'}} \frac{(2m')!}{(m'+m)!\,(m'-m)!}. \tag{3}$$

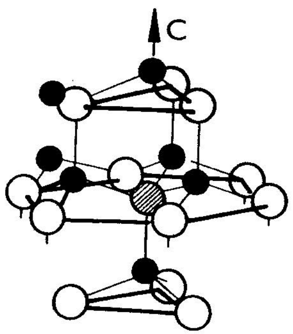

Fig. 2. The model of the crystal structure of CdS. ○ — cadmium ions; ● — sulphur ions; ⊘ — impurity Mn^{2+} ions. The thin lines represent the bond: the thick lines represent the planes in which cadmium ions are present.

Here

$$w(n) = \frac{12!}{n!\,(12-n)!} p_0^n p_E^{12-n}$$

represents the probability of the occupancy of the *n*-sites of the twelve positions with the isotopes of cadmium Cd^{111}, Cd^{113}, and the Cd^{2+} cation is substituted by the impurity Mn^{2+} ion. The particular values of this equation are as follows: $n = 2m'$, $p_0 = 1/4$; $p_E = 3/4$. It results from the numerical values that there are 25 possible combinations between the nuclear spins differring from each other. The relative intensities from the equation (3) are at the following ratio: 0.05 : 0.27 : 1.11 : 3.46 : 7.00 : 13.44 : 16.05 : 13.44 : 7.00 : 3.46 : 1.11 : 0.27 : 0.05. The relative intensities for the nine components of the superhyperfine structure experimentally verified by the EPR measurements in the CdS crystals doped by the impurity Mn^{2+} ions are: 1.6 : 3.2 : 7.4 : 12.8 : 15.8 : 12.4 : 7.4 : 3.6 : 1.8. Comparing these values with the previous ones we assume that the submitted model of the crystal lattice, verified on the basis of the superhyperfine interactions of the impurity paramagnetic M^{2+} ion with the nearest neighbourhood of the cadmium isotopes provides good results. By comparing the relative intensities achieved from the described model of a crystal lattice it is possible to

conclude that from the superhyperfine interactions measured by the EPR method also crystalline structures of some binary components can be measured using the interaction with the nuclear spins of the Cd^{111} and Cd^{113} isotopes. The model submitted illustrates the corresponding Mn^{2+} interactions with the nearest neighbourhood of the cadmium cations (see Figs. 3, 4). The superhyperfine structures measured by the EPR method are angle independent.

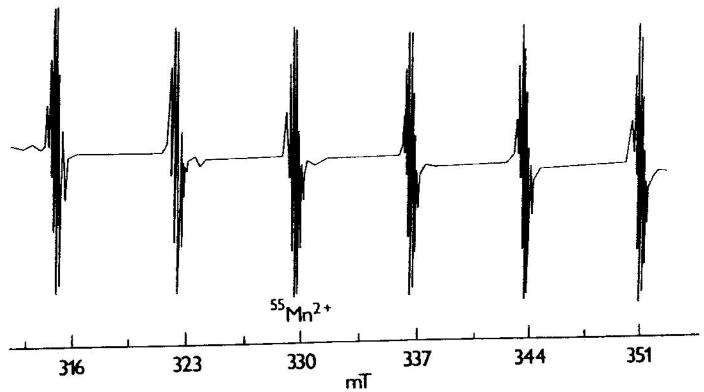

Fig. 3. Experimental spectrum of cadmium sulphide (CdS: Mn^{2+}) (0.4 mass %) at $T = 300$ K. Six major splitings arise from the nuclear and electron spins of Mn^{2+}. The nuclear spin $I = 5/2$, splittings 6.8 mT.

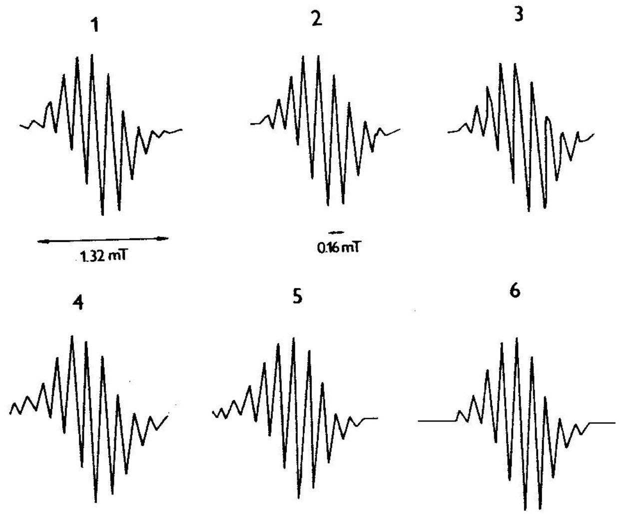

Fig. 4. Superhyperfine structure (nine components) in the crystal CdS: Mn^{2+} for transitions ($m = \pm 5/2$; $m = \pm 3/2$; $m = \pm 1/2$).

The hyperfine structure of the spectra depends on the magnetic field formed by paramagnetic electrons at cadmium isotope nuclei. If the covalent bond grows and the electrons are localized at a greater distance from the neighbouring nuclei, then the hyperfine interaction will decrease. On the other hand, the superhyperfine interactions with the nuclei of the neighbouring ions (ligands) will grow. Due to that the parameters of the spin Hamiltonian (g, A, A_n) determined from the experimental results are the criteria for the bond characteristic in the crystals [9]. With increasing bond covalence the hyperfine interaction of the Mn^{2+} paramagnetic ion decreases [10]. The value of the A in the spin Hamiltonian of Mn^{2+} impurity ions is limited by the ionicity of the bonds (at 100% ionic bond the parameter value is $A = 100 \times 10^{-4}$ cm^{-2}). It results from the analysis of the measured values that the A parameter is in linear dependence on the bond ionicity for various binary II—IV compounds (Fig. 5). In addition

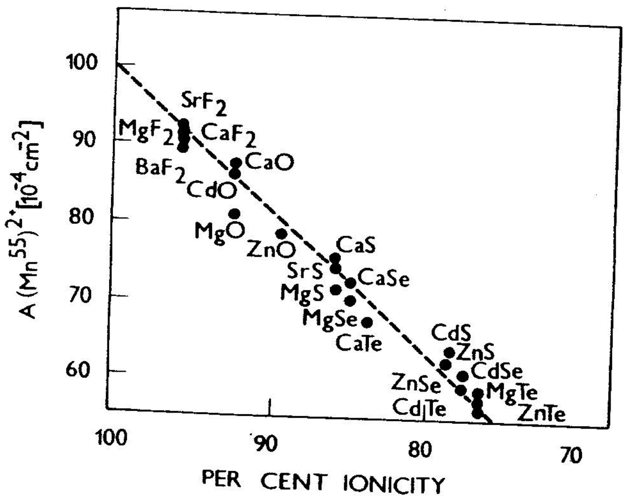

Fig. 5. The parameter A spin Hamiltonian dependence on the per cent of ionicity bonds [10].

to the ionic contribution it is possible to determine from the linear dependence for the CdS crystals also the covalent contribution of the bond character, representing in our case 20%. The g — factor value of the ground state of the impurity paramagnetic Mn^{2+} ion differs from the g-factor value of the free ion (2.0023) by a certain value of Δg. The Δg deviation is proportional to $(\lambda/\Delta E)^2$, where λ — is the spin orbital bond constant and ΔE is the energy difference between the excited ^4P state and the ground ^6S state. The Δg change causes a covalent contribution to the crystal bonds. This change is positive for the

ground state of the impurity paramagnetic $^6S_{5/2}$ ion in some compounds, and negative for cadmium sulphide in the crystalline state [10]. Due to that, the g-factor value increases if the bond ionicity decreases in the group of II—VI crystals (Fig. 6) [10].

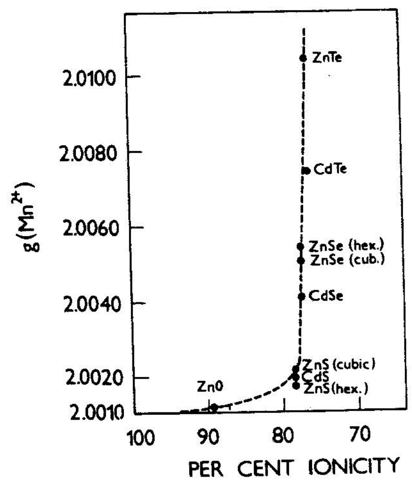

Fig. 6. The g-factor spin Hamiltonian dependence of the per cent of ionicity bonds [10].

In the table 1 calculated values of the parameters of the spin Hamiltonian impurity paramagnetic Mn^{2+} ions in the crystals of cadmium sulphide are presented.

Table 1

$H_0 = 3332.2 \pm 0.5$ mT; $f_{rez} = 9349$ MHz; $g = 2.0031 \pm 0.0005$;
$A = -66.04 \pm 0.5 \times 10^{-4}$ cm^{-2}; $A_n = 3.05 \pm 0.5 \times 10^{-4}$ cm^{-2}.

In the magnetic field is in parallel with or only slightly deviating from the "C" axis direction, then each line of the hyperfine structure of the spectrum shows a superhyperfine structure which is caused by isotropic hyperfine interaction with twelve nuclear moments of Cd^{2+} cations localized in the neighbouring positions of the paramagnetic Mn^{2+} ion environment. The superhyperfine structure of the EPR spectra is not angle dependent in the CdS spectra. It results from the analysis of superhyperfine structures that bivalent Mn^{2+} substitutes Cd^{2+} cations in the crystal lattice of cadmium sulphine. Intensities of the components of the superhyperfine structure have a shape of the Gaussian curve with identical splitting for each component (0.16 mT), and are in a very good correlation with the calculated ratios of intensities [11, 12]. The bivalent Mn^{2+}

cation was incorporated into the crystal lattice of cadmium sulphide in the course of the growth of a crystal from the gaseous phase. We have proved that the impurity bivalent paramagnetic Mn^{2+} ion influences the nucleation and the crystal growth rate.

The isotopes of the bivalent cadmium cation Cd^{111} and Cd^{113} considerably contributed to the superhyperfine interaction of 12 cadmium nuclei which are located in the nearest positions at identical distances from the paramagnetic Mn^{2+} ion. The superhyperfine interactions are identical for various orientations of the crystal in the cavity of the EPR spectrometer resonator. They are not angle-dependent.

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СВЕРХТОНКОЕ ВЗАИМОДЕЙСТВИЕ Mn^{2+} В КРИСТАЛЛАХ CdS.

Исследуемые кристаллы CdS были выращены с примесями Mn^{2+} ионов из газовой фазы методом сублимации в закрытом пространстве. С применением метода электронного парамагнитного резонанса определено сверхтонкое взаимодействие ионов с кристаллическим окружением CdS. Сверхтонкое взаимодействие поясняется с применением модели основанной по изотопах ^{111}Cd ^{113}Cd.