EPR studies of chromium ions in CdTe single crystals

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Abstract. We have studied single CdTe crystals doped with relatively high concentration of chromium. The EPR measurements were carried out at room temperature and the angular dependence of the EPR spectrum was obtained. The spectra detected at liquid nitrogen temperature indicate two types of EPR centers. Simulations of the spectra at room temperature confirm the Cr²⁺ charge state of the dopant ion at tetrahedral symmetry sites.

1. Introduction

Diluted Magnetic Semiconductors (DMSs) are of interest for study mainly due to the exchange interaction between the localised magnetic moments and the band electrons [1,2,3]. This property of DMS has potential applications in spin-electronics [4]. Most studied DMS is Cd₁₋ₓMnxTe [2]. Blinowski et al. [5] pointed out very interesting properties of Cr based DMS, namely prediction of ferromagnetism in CdTe:Cr. Moreover, CdTe:Cr shows interesting laser properties in the range from 2 nm to 3 nm [6]. In this paper we investigate CdTe:Cr bulk crystals grown from the vapour phase. Ludwig and Lorentz [7] studied Cr¹⁺ (3d⁵) ions substituted into the cadmium sites in CdTe using electron Nuclear Double Resonance (ENDOR) and EPR. Note that usually chromium ions substituting cadmium ions are expected in the Cr²⁺ valence state i.e. in the 3d⁴ configuration. However, the authors [7] determined the total spin S=5/2, g=1.9997±0.0003 as well the parameters of the cubic zero-field splitting and the hyperfine interaction with second neighbours Cd¹¹ and Cd¹³. Vallin and Watkins [8] investigated EPR spectra of Cr²⁺ (S=2) in CdTe. The Jahn-Teller coupling coefficients were determined from the changes of the fine structure of EPR spectra under uni-axial stress. The spectra observed at 4.2 K and frequency ν₀=20 GHz consist of many lines in a wide range of magnetic field. The spectra show a complex angular dependence. The spin Hamiltonian (SH) parameters D, a and F were determined from the theoretical simulations of the fine structure of EPR spectrum of Cr²⁺ in CdTe. The anisotropy of the spectra was attributed to the static Jahn-Teller distortion around Cr²⁺ ion [8]. The temperature broadening of the EPR lines was also studied. More recently the contributions from the spin-orbit coupling of Cr²⁺ ions and Te ligands were calculated using the molecular-orbital approach in [9]. The studies [9] explained the difference in the zero-field splitting parameter for Cr³⁺ in CdTe (b₁<0) and in CdS (b₂<0). The Cr³⁺ ions were studied by EPR in GaAs crystals [10] concluding that the trivalent state was predominant if the chromium concentration significantly exceeded the concentration of shallow donors in the crystal. Crystals doped during the growth process should have a higher concentration of dopant ions than those doped by diffusion. The samples used in the studies [7, 8] were bulk CdTe crystals into which the chromium ions were introduced by diffusion. In our previous paper [11] we have studies single crystals CdTe:Cr with low concentration of Cr << 1%. The angular dependence of fine structure in room temperature was
simulated by EPR-NMR programme [12]. In the present paper we investigate the samples doped by chromium during the growth process with the concentration of Cr = 5% in alloy obtained in first stage of crystal growth. Here the properties of one very broad line in the spectrum are studied.

2. Experimental

Two types of CdTe:Cr material were investigated: (i) one obtained by simple melting of the components Cd, Te, Cr (alloy), and (ii) a single crystal grown by vapour method from this alloy. The EPR spectra of CdTe:Cr samples were recorded using the X-band Bruker ESP-300 spectrometer and ELEXSYS Bruker E 500 one at room (293 K) and liquid nitrogen (77 K) temperature. The sample No. 1 was cut from the alloy containing 5% of chromium. The sample No. 2 was cleaved from the single crystals. The (110) plane of sample No. 2 was identified as the cleaved plane. The samples have the form of a rectangle of the size 3 x 2 x 1.5 mm³.

3. Cr²⁺ ion in crystal field

The electronic configuration of free Cr atom is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹. Cr atom incorporated into Al₁₁B₁₁VI crystal lattice occupy cation sites while two of the outer electrons delocalize into the conduction and valence bands. The Cr²⁺ ion in Al₁₁B₁₁VI semiconductor creates the deep impurity levels. The ground state for free Cr²⁺ ion is 5D with the orbital quantum number L=2 and the total spin S=2 yielding 25-fold degeneracy. In the crystal field of D₂d symmetry the degeneracy is partially removed: ⁵D term splits into fifteen-fold degenerate orbital triplet ⁵T₂ and tenfold degenerate orbital doublet ⁵E. The Jahn-Teller distortion leads to splitting of the ⁵T₂ ground state into fivefold degenerate ⁵B₂ orbital singlet and the ⁵E orbital doublet. The spin-orbit coupling leads to further splitting [13, 14, 15, 16, 17]. The arising energy level scheme is presented in figure 1. In external magnetic field the degeneracy of each electron spin level is removed (not presented in figure 1).

For description of the EPR spectra we employ the spin Hamiltonian with S = 2 [18]:

\[ \hat{H} = \mu_B (\mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}) + \sum_{k,q} B^q_k O^q_k (S_x, S_y, S_z) \]  

where \( \mathbf{g} \) is the gyromagnetic tensor, \( \mu_B \) is the Bohr magneton, \( \mathbf{B} \) is a magnetic field intensity, \( (S_x, S_y, S_z) \) are the spin operators, \( O^q_k \) are the Stevens operators [19, 20], and \( B^q_k \) are the fine structure parameters.

![Fig. 1. Energy level splitting for Cr²⁺ ions in the crystal field of D₂d symmetry in the Al₁₁B₁₁VI crystal (adapted from [21]).](image-url)
4. Results
Selected EPR spectra of CdTe:Cr crystals are presented in figures 2a-2d. The spectrum consists of one broad and strong component on which a few weak fine structure lines are superimposed. In this paper we study only the major intense and broad component. The effective spectroscopic g-factor and the peak-to-peak linewidth $H_{pp}$ of this line $H_{pp}$ (we denote them as $g_E$ and $H_{ppE}$) were readout from the spectrum. The way in which these parameters have been determined is sketched in figure 2a. Since the broad EPR line is strongly asymmetric the accuracy of parameters measured directly from the experimental spectrum is limited. Therefore, additionally the experimental line was fitted using the Lorenzian type curve. We were using this procedure because this type of curve describes satisfactory, in high temperature range, an experimental EPR lines of DMSs with manganium (see [22] and references therein). From the fitting we determined the corresponding parameters $g_F$ and $H_{ppF}$. The obtained values $g_E$, $H_{ppE}$ and $g_F$, $H_{ppF}$ are listed in Table 1.  

![Fig. 2. Representative EPR spectra for CdTe:Cr crystals: a) alloy sample No.1, at T = 293 K, b) sample No.1, at T = 77 K, c) single crystal sample No.2, at T = 293 K, d) sample No.2, at T = 77 K; solid lines represent experimental data, dashed lines represent Lorentzian fits to the experimental data.](image-url)
Table 1. The spectroscopic g parameters and the peak-to-peak linewidths for CdTe: Cr.

| Sample | No. 1 | T=293 (K) | T=77 (K) | No. 2 | T=293 (K) | T=77 (K) |
|--------|-------|-----------|-----------|-------|-----------|-----------|
|        |       | g_E       | g_F       | H_{ppE} (mT) | H_{ppF} (mT) | |
|        |       | 5.26±0.21 | 9.08±1.28 | 99.72±10.26 | 101.49±0.50 | |
|        |       | 5.22±0.02 | 9.46±0.02 | 101.81±20.63 | 107.68±0.24 | |
|        |       | 5.22±0.02 | 9.46±0.02 | 101.81±20.63 | 107.68±0.24 | |
|        |       | 1.65±0.02 | 2.83±0.08 | 80.20±9.47 | 162.02±12.70 | |
|        |       | 1.67±0.01 | 2.66±0.01 | 80.99±1.18 | 190.04±0.62 | |

5. Discussion and Conclusions

Our study reveals that the position of the EPR lines is independent of the orientation of the samples, whereas it depends on the crystallisation level and temperature. For the samples cut from the alloy (sample No. 1, figure 2a,b), the gyromagnetic factor g is 5.26 at T=293 K and 9.08 at T=77 K, whereas for the single crystal sample the value of g is reduced to g=1.65 and 2.83 at T=293 K and T=77 K, respectively. Such large differences in the g values are not common and may likely arise from the exchange interactions between magnetic ions for large Cr concentration. The linewidth increases with decreasing temperature. Particularly, in the case of the single crystal, the change of linewidth is significant; from 80 mT up to 162 mT. However, the same EPR behaviour was observed by Furuda et al. [2, 22] in Cd_{1-x}Mn_xTe. The strong temperature dependence of the large linewidth was interpreted in terms of the Dzyaloshinski-Moriya exchange interactions[23]. In paper [22] Lorenzian shape was attributed to that EPR measurements particularly for samples with low concentration of magnetic ions. In our case the concentration of chromium is rather high. Therefore the deviation of EPR line in figure 2 from the Lorenzian shape may be expected. This may explain the discrepancy between the experimental and fitted values in table 1. The EPR spectra of both samples at room temperature show a clear fine structure; so more pronounced for the single crystal. The angular dependence for the sample No. 2 at room temperature figure 2c [24] as well as simulation of the fine structure of the spectrum indicate the Cr^{2+} charge of the dopant ion. Importantly, the fine structure of both samples disappears at the liquid nitrogen temperature. Our previous EPR studies [11] on CdTe:Cr samples with a minor concentration of Cr ions yield results differing considerably from those obtained in the present paper. The two-component spectrum has also been observed, however, the Cr ions occurred in the Cr^{3+} state instead of Cr^{2+}.

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