
Proceedings of the XXI International Meeting on Radio and Microwave Spectroscopy
RAMIS 2005, Poznań-Będlewo, Poland, April 24–28, 2005

EPR Spectra of Cr in CdTe Crystals

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The EPR studies of CdTe:Cr were performed on X-band (9.6 GHz) spectrometer at room temperature. Single CdTe crystals were doped by chromium Cr in the synthesis process. The spectra observed were resolved into two spectra. The first one consisted of very broad line ($\Delta B = 100$ mT) and the second one showed a typical fine structure. The complete angular dependence measurements were obtained. The fine structure of Cr²⁺ or Cr³⁺ ions was assumed and simulated. It follows from the theoretical analysis of the obtained spectra that degree of ionization of the chromium Cr dopant is 3+.

PACS numbers: 75.50.Pp, 75.30.Cr

1. Introduction

Diluted magnetic semiconductors are advanced materials for magneto-electronics due to the possibility of the control of magnetic properties by modulation of the carrier density [1–3]. Cr-based diluted magnetic semiconductors are also promising materials for new optoelectronic devices e.g. tunable mid-infrared lasers (CdSe:Cr, ZnSe:Cr, CdMnTe:Cr [4]), converters of red-green into blue light [5]. The observed ferromagnetic *p*–*d* exchange interactions in zinc chalcogenides recommends them as the material for spintronics as well [2, 6, 7]. EPR investigations of the chromium in these crystals reveals this dopant in Cr²⁺ state [8, 9]. In CdTe matrix the chromium was detected in the same state Cr²⁺ [8]. In this paper we show that one can observe Cr³⁺ in CdTe by EPR studies.

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2. Experimental

The EPR studies were made on X-band (9.6 GHz) Bruker ESP-300 spectrometer at room temperature. Single CdTe crystals were doped by Cr in the synthesis process. The initial charge contained 1–4% Cr. However, the final concentration of Cr impurities measured by X-ray energy dispersive fluorescent analysis was rather smaller than 1%. The samples were cleaved along (110) plane and polished in the form of rectangle of the size $3 \times 2 \times 1.5 \text{ mm}^3$. The orientation of the sample was as in Fig. 1.

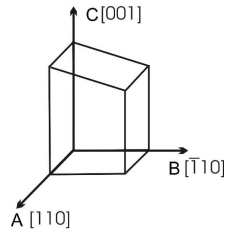


Fig. 1. Orientation of the sample, A , B , C , and $[uvw]$ are axes of reference system related to the shape of the sample and to the crystallographic system, respectively.

3. Results

The obtained representative EPR spectra are shown in Fig. 2. Each spectrum is a superposition of two component spectra. The first one consists of a broad line ($\Delta B = 100 \text{ mT}$). The second one shows a typical fine structure. The position of the line in the first component depends weakly on the orientation of the sample. Contrary, the intensity and width of this line show strong angular dependence (Fig. 2). In the second spectrum a number of groups of weak but sharp lines is

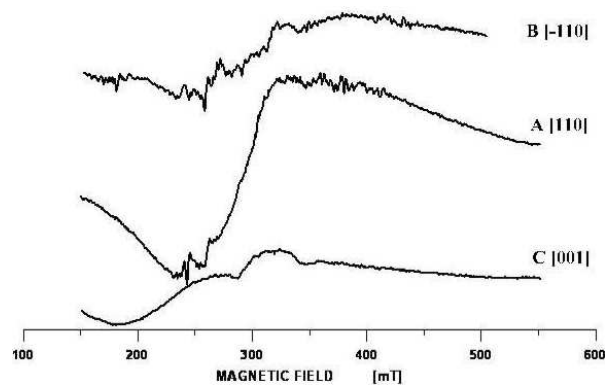


Fig. 2. Representative spectra.

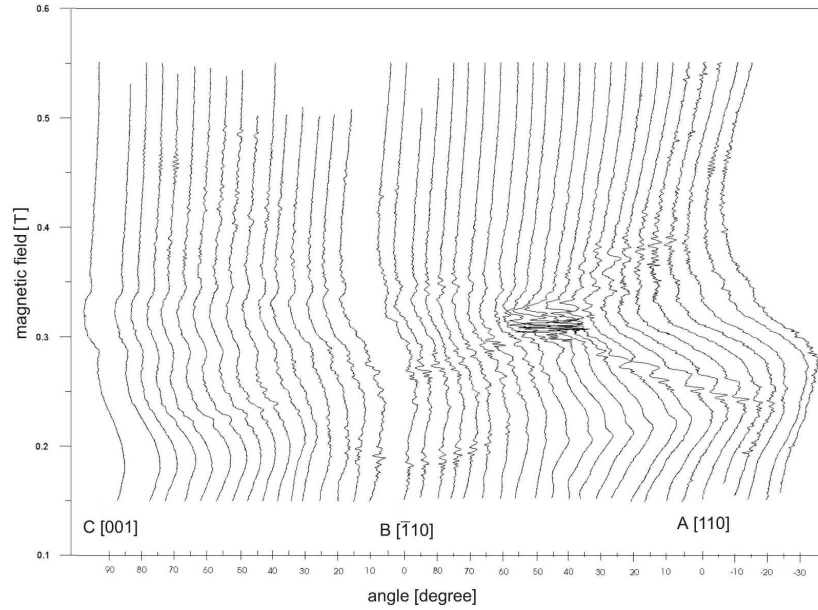


Fig. 3. Angular dependence of EPR absorption spectra for Cr in CdTe.

observed easily, there are 4–6 lines in each group. In Fig. 3 the angular dependence measurements of EPR spectra in two planes are collected.

4. Discussion

We assume that Cr ions substitute cadmium sites and our results imply that Cr ion is tetrahedrally surrounded by Te. In GaAs crystals chromium was widely used as deep acceptor to produce semi-insulating GaAs substrates. In these crystals, chromium is either in neutral Cr^{3+} ($3d^3$) [10] or in negatively charged Cr^{2+} ($3d^4$) [11] state. However, in CdTe matrix the chromium was detected by EPR and investigated as Cr^{2+} ion only [8]. Therefore, in the initial stage of the interpretation of our results we attempted to describe them based upon the properties of Cr^{2+} . Spin-Hamiltonian parameters for Cr^{2+} determined in paper [8] are listed in Table I.

TABLE I

Hamiltonian parameters for Cr^{2+} in CdTe [8].

g_{\parallel}	g_{\perp}	D [cm^{-1}]	a [cm^{-1}]	F [cm^{-1}]
1.980 ± 0.015	1.980 ± 0.015	$+0.260 \pm 0.004$	$+0.05 \pm 0.01$	-0.05 ± 0.02

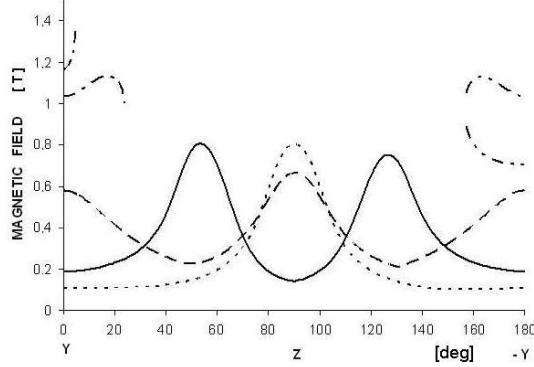


Fig. 4. Angular dependence of EPR spectra of CdTe:Cr²⁺ for parameters taken from paper [8].

The representative angular dependence of EPR spectra of CdTe:Cr²⁺ arising from the data listed in Table I are shown in Fig. 4. Some tested calculations of spin-Hamiltonian parameters for Cr²⁺ from our experimental data given in Fig. 3 yield contradictory values to those listed in Table I. Moreover, comparing those angular dependences observed by us (Fig. 3) with these obtained for Cr²⁺ (Fig. 4) we conclude that they do not arise from the same paramagnetic centres. Thus, we have presumed that the spectrum arises from Cr³⁺ centres instead of Cr²⁺ which were usually observed.

For quantitative description of the spectrum we use the spin Hamiltonian [12]:

$$\hat{H} = \beta (\mathbf{B} \cdot \hat{g} \cdot \mathbf{S}) + \sum_{k,q} B_k^q O_k^q, \quad (1)$$

where \hat{g} is the gyromagnetic tensor, β is the Bohr magneton, \mathbf{B} is a magnetic field, \mathbf{S} is spin operator, O_k^q are the Stevens operators and B_k^q are parameters of the fine structure of EPR spectrum. For Cr³⁺ ion, $k = 2$ and $D = 3B_2^0$, $E = B_2^2$.

TABLE II

Spin-Hamiltonian parameters for Cr³⁺ in CdTe.

Tensor	Matrix elements			Principal values			Direction cosines		
g	1.995	-0.379	0.103	g_x	2.521	-0.158	-0.176	-0.971	
		2.480	-0.578	g_y	2.373	0.855	-0.516	-0.457	
			2.387	g_z	1.969	-0.493	-0.838	-0.232	
D [Gs]	191.2	3.4	301.6	D_x	478.7	0.720	0.672	-0.174	
		-336.4	-122.4	D_y	-100.0	-0.100	0.348	0.932	
			145.1	D_z	-378.8	0.687	-0.653	0.318	

The spin-Hamiltonian parameters calculated from data in Fig. 3 are collected in Table II. The energy levels for Cr^{3+} versus magnetic field given by Eq. (1) are presented in Fig. 5. The vertical lines in this figure indicate the allowed magnetic dipole transitions.

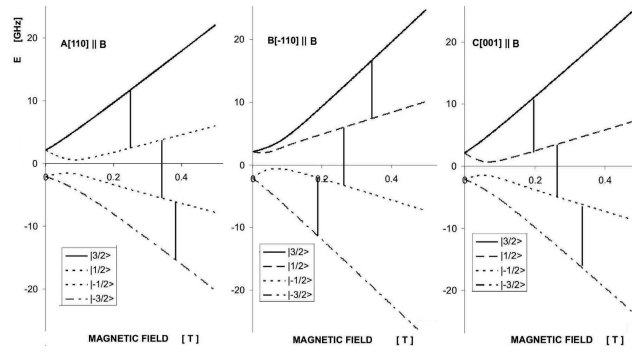


Fig. 5. Energy levels for Cr^{3+} ($S = 3/2$) versus magnetic field.

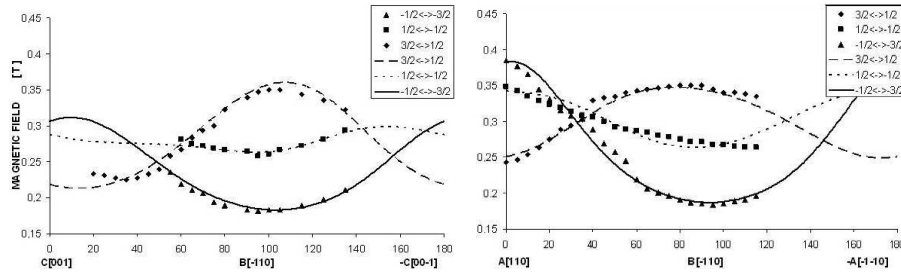


Fig. 6. Observed and computed angular dependence of Cr^{3+} EPR signals in CdTe.

A computer simulation of the spectra using parameters from Table II was done with the help of programme EPR-NMR [13]. The results are presented in Fig. 6 (solid lines) for planes AB and BC . These calculations fit to the experimental data (points in Fig. 5) very well. The results quoted in Table II indicate the great anisotropy of the spectroscopic splitting factor g . This is in opposition to the case of the Cr^{2+} in CdTe [8] where g_{\parallel} and g_{\perp} are the same, equal to 1.980 (see Table I). Such great anisotropy, however, was observed also for Cr^{3+} in the GaAs crystals mentioned above [10, 11] ($g_x = 2.367$, $g_y = 1.636$, $g_z = 5.154$).

Acknowledgments

We are grateful to Prof. J. Kuriata and to Dr. E. Lipiński for help in EPR measurements.

This work was supported by the grant No. 1 PO3B 021 27 of the State Committee for Scientific Research (Poland).

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