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HIGH-FIELD EPR OF $Zn_{1-x}Cr_xTe$

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High magnetic field electron paramagnetic resonance experiments have been performed on $Zn_{1-x}Cr_xTe$ covering the energy range 1–7 cm^{-1} in fields up to 20 T at $T = 1.2$ K. The static magnetic field was oriented along the (100), (110) and (111) crystallographic axes of the sample. Pronounced absorption lines for intra-chromium transitions have been observed for these different orientations, revealing a strong anisotropy due to a static Jahn–Teller distortion. The measured low energy level structure of the Cr^{++} ion can be described by a cubic crystal field model including this distortion of the Cr centers.

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Diluted magnetic semiconductors (DMS) or semimagnetic semiconductors (SMSC) are semiconductors (mostly II–VI) where a controlled fraction of the cations is randomly substituted by magnetic ions [1]. On the contrary to the well-known Mn, Fe and Co based DMS, the Cr based DMS are the first SMSC known so far with a ferromagnetic *p–d* exchange between the two coexisting electronic subsystems, the localized *d*-electrons of the Cr^{++} ion and the ZnTe band electrons [2]. From the magnetic point of view the Cr-SMSC have an intermediate character between that of a Brillouin-type paramagnet and a Van Vleck-type system. Moreover the Cr^{++} center in a tetrahedral crystal field undergoes a static Jahn–Teller distortion along one of the (100) axes of the crystal, which results in the existence of three types of nonequivalent Cr^{++} centers. This leads to pronounced anisotropy of the Cr^{++} ion energy level structure and magnetic properties [3].

To understand the low temperature magnetic properties of $Zn_{1-x}Cr_xTe$, we need to know the exact low energy level structure of the Cr^{++} ion. This energy diagram consists of five closely lying energy levels in the energy range between 0 and 8 cm^{-1} ($\Delta E \approx k_BT$, $T = 4.2$ K), with a complicated magnetic field dependence. A standard EPR setup typically operates at one fixed frequency between

9 and 40 GHz and at rather low magnetic fields. On the other hand, far infrared spectroscopy with higher energies ($\geq$ 5 cm^{-1}) can be used at higher magnetic fields. But in our case the most interesting energy range extends from 0 to 8 cm^{-1} in fields up to 20 T.

Therefore, high magnetic field millimeter wave electron paramagnetic resonance (EPR) experiments have been performed on the newly grown $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$. We studied two different ingots of $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ with a chromium concentration $x < 0.5\%$. The samples were grown by the modified Bridgman method. We used a millimeter wave vector network analyzer (MVNA) [4] as a source/detector for EPR experiments, which allows experiments at variable frequencies ranging from 30 to 210 GHz (1–7 cm^{-1}) in magnetic fields provided by a superconducting coil ($B \leq 18$ T) or a Bitter magnet ($B \leq 20$ T) and temperatures down to 1.2 K. With a combination of oversized wave guides and a mylar beamsplitter, high frequency radiation was coupled into a largely oversized resonant cylindrical cavity, where the sample is put at the bottom of the cavity. The heterodyne detection of the MVNA makes it possible to measure both phase and amplitude of the signal simultaneously, allowing to determine the position of the resonances more accurately.

The magnetic field up to 15 T was oriented along the (100), (110) or (111) crystallographic axes of the samples. The behavior of Cr^{++} ion energy levels in a magnetic field strongly depends on the field direction with respect to the Jahn–Teller distortion axis. There exist three types of, generally non equivalent, Cr centers (three possible distortion axes, (100), (010) or (001)). For the magnetic field along the (111) crystal axis all the centers are equivalent (the angle between the Jahn–Teller distortion axis and field direction is 54.7°). For the magnetic field $\boldsymbol{B} \parallel (110)$ direction some of the centers are distorted perpendicularly to the field, while the others are distorted at an angle of 45°. For $\boldsymbol{B} \parallel (100)$ the centers are distorted perpendicularly or parallel to the field.

Measurements of the reflected millimeter wave signal as a function of the external magnetic field show pronounced absorption lines corresponding to transitions from the ground state to the low energy excited levels of the Cr^{++} ion. The spectra have been measured for several different frequencies and the center position of the absorption lines was determined. Figure 1 shows several representative spectra for $\boldsymbol{B} \parallel (110)$ and $\boldsymbol{B} \parallel (100)$.

To describe the data we used a simple crystal field model proposed by Vallin et al. [5], also used for ZnSe [3, 6] and ZnS [7]. The Hamiltonian for d electrons of the Cr^{++} ion can be written as

$$\mathcal{H} = \mathcal{H}_{\text{CF}} + \mathcal{H}_{\text{JT}} + \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{B}}, \tag{1}$$

where $\mathcal{H}_{\text{CF}}$ represents a tetrahedral (cubic) crystal field interaction. $\mathcal{H}_{\text{JT}}$ is the Jahn–Teller term, describing a static tetragonal distortion along the (100), (010) or (001) axis. The $\mathcal{H}_{\text{SO}}$ term contains the spin–orbit interaction which yields further splittings, and $\mathcal{H}_{\text{B}}$ finally represents the magnetic field Hamiltonian giving the Zeeman splitting of the energy levels. This results in a ground state which is a singlet followed by two doublets a few cm^{-1} above the ground state. The order of these low lying energy levels for $\text{Zn}_{1-x}\text{Cr}_x\text{Te}$ is essentially different to that for $\text{Zn}_{1-x}\text{Cr}_x\text{S}$ or $\text{Zn}_{1-x}\text{Cr}_x\text{Se}$. The reason for this reversed order of the zero

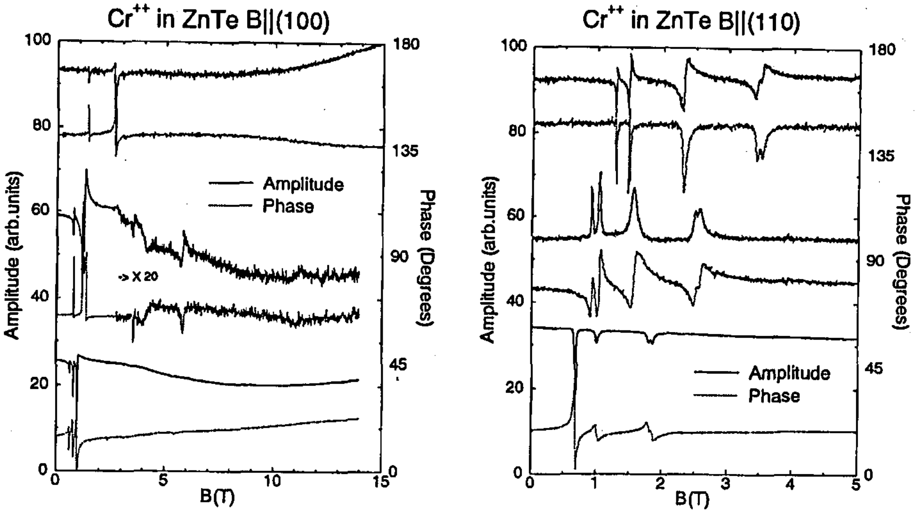

Fig. 1. Some representative MVNA absorption spectra for $\boldsymbol{B} \parallel (100)$ (left) and $\boldsymbol{B} \parallel (110)$ (right). The spectra were taken at $T = 1.2$ K for frequencies 149, 100, 89 GHz (left, top to bottom) and 138, 110, 87 GHz (right, top to bottom).

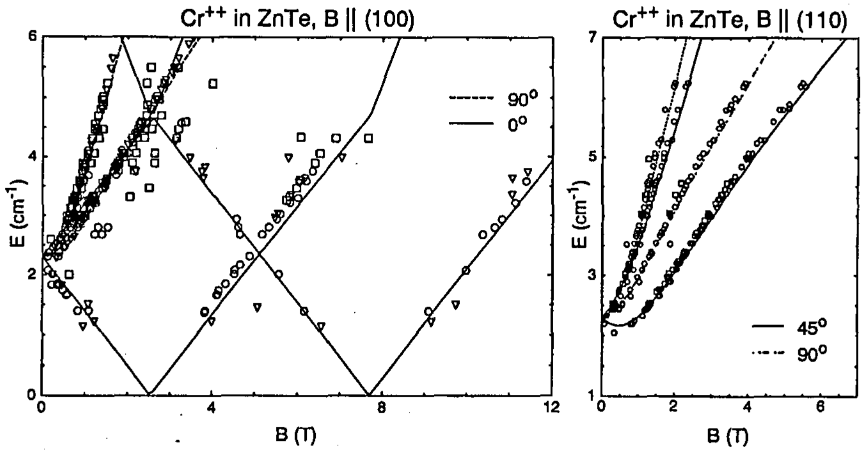

Fig. 2. Transition energy versus magnetic field for $\boldsymbol{B} \parallel (100)$ (left) and $\boldsymbol{B} \parallel (110)$ (right). □ and ▽ are data taken on sample 2642, ○ on sample 2720. The results of the model calculations (as described in the text) are plotted by solid and dashed lines.

field energy levels is a strong covalency effect present in ZnTe [8]. Therefore, different spin–orbit interaction parameters were introduced for the t and e orbital symmetries.

Figure 2 shows the transition energy versus field diagram for the magnetic field parallel to the (110) and (100) direction. The result of the calculation is shown by the solid and dashed lines and fits very well to the experimental data (points). The experimental points indeed reflect the existence of three types of nonequivalent Cr^{++} centers with different Jahn–Teller distortion axes. Especially the last resonance in the $\boldsymbol{B} \parallel (110)$ spectra, which is slightly double, reveals that there are two Cr centers distorted at an angle of 45°.

Concluding, high-field EPR showed to be a powerfull tool to study the low lying energy levels of Cr^{++} in ZnTe and that our data provide good quantitative agreement with a description of the Cr^{++} levels by the cubic crystal field model including a Jahn–Teller distortion.

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