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Optically detected magnetic resonance experiments on native defects in $ZnGeP_2$

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Abstract

In order to investigate the defects responsible for the sub-band-gap absorption in $ZnGeP_2$ optically detected magnetic resonance (ODMR) using the magnetic circular dichroism of the absorption (MCDA) as detection channel was applied. This is the first ODMR study of defects in II–IV–V_2 chalcopyrites. The experiments exhibit that three different native defects contribute to the absorption in the spectral range from 0.5 eV to the band-gap energy of about 2.0 eV. The Ge antisite defects show a dominant transition near the band edge. Zn vacancies show strong MCD above 1.6 eV and below 1 eV, and the P vacancies are detected over the complete spectral range. In combination with photoinduced EPR studies these results reveal the contributions of the different defects to the broad absorption band. Peculiarities in the MCD of the Zn-vacancies are explained in terms of long spin–lattice relaxation times.

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Keywords: Magnetic resonance; Intrinsic defects; $ZnGeP_2$; Optical properties

1. Introduction

Zinc germanium diphosphide ($ZnGeP_2$) is a ternary semiconductor with chalcopyrite structure, and has a band gap of 2.00 eV at room temperature. It is studied primarily for its potential as a nonlinear optical (NLO) material for frequency conversion applications in the mid-infrared spectral range. For NLO applications $ZnGeP_2$ is especially suited for high-power optical parametric oscillators (OPOs). Its useful properties include an intrinsic transparency range from about 0.6–11 μm, a large nonlinear optical coefficient, high thermal conductivity, and suitable birefringence for phase matching. For an efficient performance the crystals should have negligible losses at both the pump and frequency converted wavelengths [1–4]. However, the bulk crystals have a considerable defect-related absorption extending from the band gap beyond 2.5 μm. Previous electron paramagnetic resonance experiments have shown that at least three different intrinsic defects exist in the bulk crystals: the singly ionized Zn vacancy (V_{Zn}^{-}),

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the neutral Phosphorus vacancy (V_P^0), and positively charged Germanium antisite centers (Ge_{Zn}^+) [5–7]. So far, the connection to the defect-related absorption bands were obtained by comparing the EPR intensities of the different centers to the strength of the optical absorption bands [8,9] or by EPR measurements under photo excitation (photo-EPR) monitoring the dependence of the EPR intensities on the photoexcitation energy [10,11].

Our approach was to obtain a direct correlation between the absorption bands and the defect specific magnetic resonance properties of the centers by using optical detected magnetic resonance via the magnetic circular dichroism (MCD) of the absorption. This method is also called MCD–EPR [12].

2. Experimental details

The $ZnGeP_2$ bulk crystals used in this work were grown by the horizontal gradient freeze (HGF) technique. For the investigations small samples with dimensions of $2 \times 0.5 \times 3\,mm^3$ were cut along the main crystallographic directions. MCD measurements were performed at about 1.5 K in the field of a superconducting magnet capable of providing a field of up to 4 T. The measurements were performed in Faraday configuration. The light source we used was a 150 W halogen lamp dispersed by a grating monochromator. Circular polarization was produced by a combination of a linear polarizer and an electro-optic modulator operating at 50 kHz. The transmitted light was detected by a liquid nitrogen cooled germanium detector or a photomultiplier. The infrared detection limit of the setup was 1.8 μm. Using the lock-in technique, the measured MCD signal intensity is proportional to the difference between the left- and right-circular polarized transmission intensities. For the optically detected magnetic resonance a 24 GHz-setup with a cw-200 mW source was used.

3. Experimental results

Fig. 1a shows a low temperature absorption spectrum of the $ZnGeP_2$ crystals. The spectral

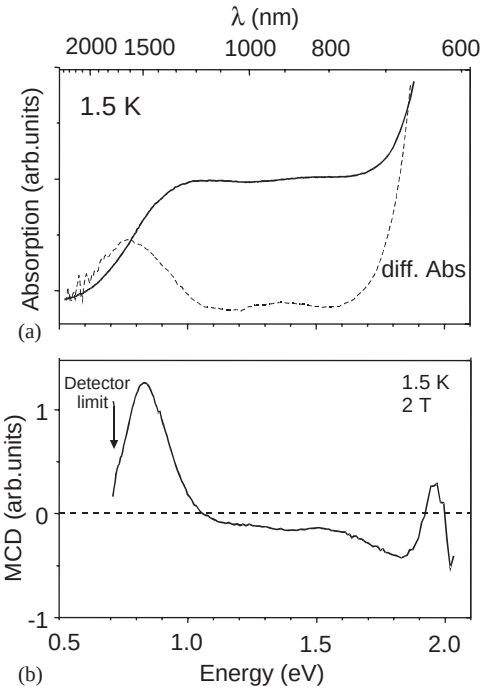

Fig. 1. Absorption spectrum (a) and (b) magnetic circular dichroism (MCD) of $ZnGeP_2$ crystals grown by the HGF technique. The dashed line in (a) shows the first derivative of the absorption spectrum.

shape of the broad sub-band-gap absorption indicates that it consists of a superposition of several absorption bands. To enhance the weak absorption structures the first derivative of the absorption is included in Fig. 1a. The MCD spectrum (Fig. 1b) shows an intense signal in the energy range below 1.0 eV. It should be noted that due to the use of the Ge-detector in this type of measurements the low-energy detection limit is 0.7 eV. Above 1 eV a rather weak MCD intensity is observed up to 1.6 eV. For higher energies the MCD shows more structure than the differential absorption. An increase to negative intensities followed by a sign reversal at about 1.9 eV is observed.

Measuring the magnetic resonance at selected energies on the MCD we obtain the following results (see Figs. 2 and 3). In the intense low-energy MCD band we find mainly the resonances originating from the Zn vacancies (upper graph in Fig. 2). Between 1.1 and 1.6 eV its intensity

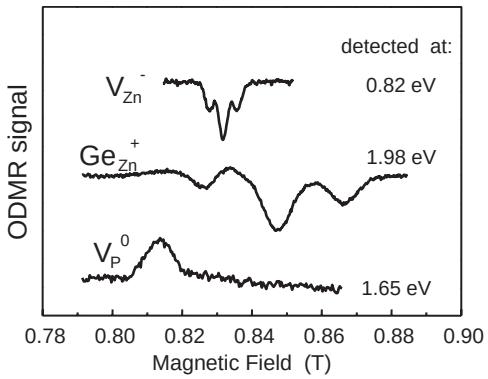

Fig. 2. Optically detected magnetic resonance spectra observed in $ZnGeP_2$. The optical detection energy is given in the figure. (24 GHz, crystal orientation: magnetic field parallel to c-axis).

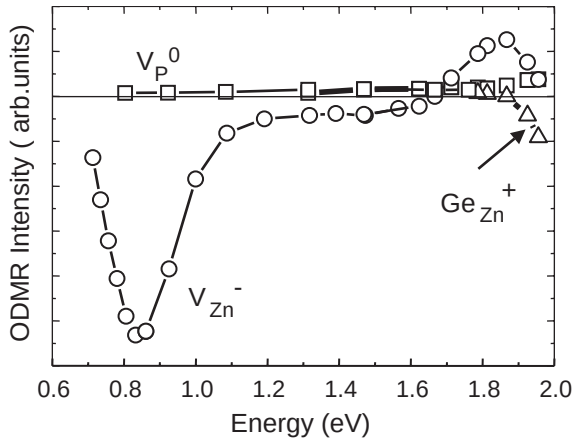

Fig. 3. Spectral dependence of the ODMR signals of the three dominant native defects observed in $ZnGeP_2$.

becomes rather weak (Fig. 3) and starts to increase again above 1.6 eV. The ODMR of the Ge-antisites is detectable only close to the band edge (>1.85 eV), while the magnetic resonance of the P-vacancy (lower graph in Fig. 2) is detected over the complete spectral range.

Discussing the nature of the optical transition we should consider the photo-EPR results obtained on the same samples [10,11]. For the Zn-vacancy the photoinduced generation and quenching of the EPR signal led to the conclusions that the $-/0$ recharging level is located 0.64 eV above the valance band (VB) and the $2-/-$ level 1.02 eV below the conduction band (CB). Consistent with these results we would ascribe the V_{Zn}^{-} – MCD detected above 1.6 eV to the $V_{Zn}^{-} \rightarrow V_{Zn}^{0} + e_{CB}^{-}$ transition. For the Ge_{Zn} centers photo-EPR gave evidence that the $+/2+$ level is located 1.7 eV above the VB. The MCD/ODMR of the Ge antisites is detected only above 1.85 eV. In this detection scheme a requirement is that the initial state of the center is the paramagnetic charge state, i.e. for the Ge_{Zn} centers the singly positive one. Thus, we would attribute the MCD above 1.85 eV to the recharging level $Ge_{Zn}^{+} + e_{VB} \rightarrow Ge_{Zn}^{0}$. For the MCD bands below 1.1 eV the results are less conclusive, presumably due to the detection limit <0.7 eV. It makes it impossible to determine the onset of the P-vacancy MCD as well as the onset of the Zn-vacancy-related MCD band below 1.1 eV.

Monitoring the magnetic field dependence of the Zn-vacancy related MCD (Fig. 4) one would expect in general the MCD intensity to increase as given by the Brillouin function for an $S=\frac{1}{2}$ system (dashed line in Fig. 4) [12]. However, two peculiarities were observed: dependent on the sweep rate (maximum 1 T/min) and direction of the magnetic field a hysteresis was observed, and at low fields (<10 mT) a "sudden" drop to zero level occurs. Obviously the hysteresis is caused by a slow relaxation of the $S=\frac{1}{2}$ system towards thermal equilibrium, i.e. the V_{Zn}^{-} ground state has a long spin–lattice relaxation time (T_1). The observation of a long T_1 for the V_{Zn}^{-} is in

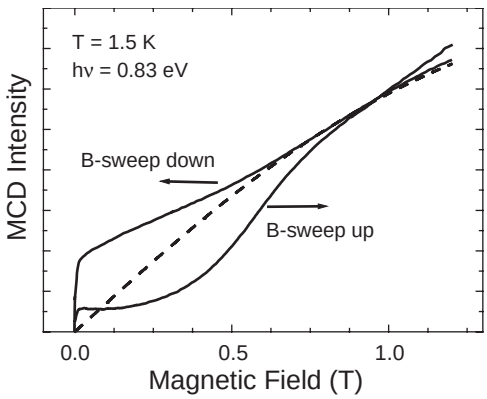

Fig. 4. Magnetic field dependence of the Zn-vacancy-related magnetic circular dichroism for sweeping the magnetic field (B) down and up. The dashed line indicates the expected behavior (Brillouin function) for this $S=\frac{1}{2}$ system.

agreement with the temperature dependence of the EPR signal [11]. To determine the magnetic field dependence of T_1 we used the fact that the scan speed of the superconducting magnet is fast compared to T_1. T_1 increased from 40 to 190 s in the field range 0.005–0.1 T and then decayed to 4 s at $B = 1$ T. The decay can be fitted by a $T_1(B) \sim B^{-1.8}$ dependence, pointing to an Raman-type relaxation process (see, for example, Ref. [13]).

The rapid change of the MCD intensity at low magnetic fields (Fig. 4) is in our opinion induced by a rapid decrease of T_1 due to level crossing of the hyperfine split Zeeman level of the V_{Zn}^{-}. The dominant hyperfine splitting of the V_{Zn}^{-} is due to the interaction with two P-neighbors and amounts to about 3.5 mT [5]. Thus, in this low field range, i.e. the Zeeman splitting is in the order of the hyperfine interaction, one has to apply the Breit–Rabi formalism for a correct level description. The state mixing opens new relaxation channels for the electron spin system.

4. Conclusions

Presenting the first MCD/ODMR study at defects in II–IV–V_2 chalcopyrites we have shown that this method is a helpful tool to study defect-related absorption in this class of nonlinear optical materials. We were able to detect the three dominant native defects in $ZnGeP_2$ and could prove that all of them contribute to the broad absorption band. The results are in good agreement to previously published photo-EPR results. However, the studies have to be extended to the infrared spectral range to complete the picture for the recharging levels of all defects in the material. For the Zn-vacancy we observe peculiarities in its ground state magnetization behavior that are explained in terms of slow spin–lattice relaxation times and level mixing.

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