Magnetic Resonance in $ZnGeP_2$ and $(Zn,Mn)GeP_2$

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Abstract.

Electron Paramagnetic (EPR) and Ferromagnetic (FMR) Resonances have been studied for the first time in the system of $(Zn,Mn)GeP_2$ ferromagnetic layer grown on undoped $ZnGeP_2$ single crystal. Strong FMR signals are registered in the wide temperature range up to room temperature. EPR and photo-EPR of intrinsic defects are observed in $ZnGeP_2$ substrate. EPR spectra characteristic of Mn^{2+} ions on Zn^{2+} sites in the bulk appear after the growth of the ferromagnetic layer on $ZnGeP_2$ crystal indicating the efficient Mn-diffusion into the bulk crystal for the annealing treatments.

Keywords: Electron paramagnetic resonance, Ferromagnetic resonance, Point defects, Chalcopyrite.

1. INTRODUCTION

Very recently ferromagnetism at room temperature has been found in $(Zn,Mn)GeP_2$ layers grown on single crystal substrates $ZnGeP_2$ [1, 2]. The hysteresis loops were measured at low temperatures and up to 350 K using SQUID technique.

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At this, no considerable variation in the lattice parameter of heterolayers was registered and close to the base material with the chalcopyrite structure was determined by X-ray diffraction.

This work reports magnetic resonance studies of the system of (Zn,Mn)GeP_2 ferromagnetic layer grown on undoped $ZnGeP_2$ single crystal substrate. Magnetic resonance spectra were measured at X-band JEOL EPR spectrometer at temperatures of 4 K to 300 K in dark and with band-gap light excitation. Several crystallographic orientations of the samples were used, and variations in EPR spectra as well as additionally the presence of a strong resonance signal were observed in the wide range of magnetic fields and with specific temperature dependences that are characteristic for ferromagnetic resonance (FMR).

2. RESULTS AND DISCUSSION

2.1. EPR in $ZnGeP_2$ substrate

Undoped $ZnGeP_2$ crystals usually have intrinsic point defects. The starting crystal was investigated at different temperatures and strong anisotropic EPR signals due to intrinsic defects were observed. They are consistent with the results of [3,4]. Figure 1 shows EPR spectra registered without light (1) and under the bandgap light excitation (2) at temperatures near 15 K and the spectrum (3) is the same like (2) but taken at 6 K to enhance the photo-EPR signal. The same spectra with the magnetic field near parallel to the [011] direction is presented in Fig. 1 (b), the top line was measured at 16 K and the bottom line was measured at 6 K under optical excitation. The spectra in Fig. 1 observed before optical excitation correspond to a zinc vacancy V_{Zn}. The structure of the defect responsible for the EPR spectrum under photo-excitation is unclear and additional EPR measurements will be done.

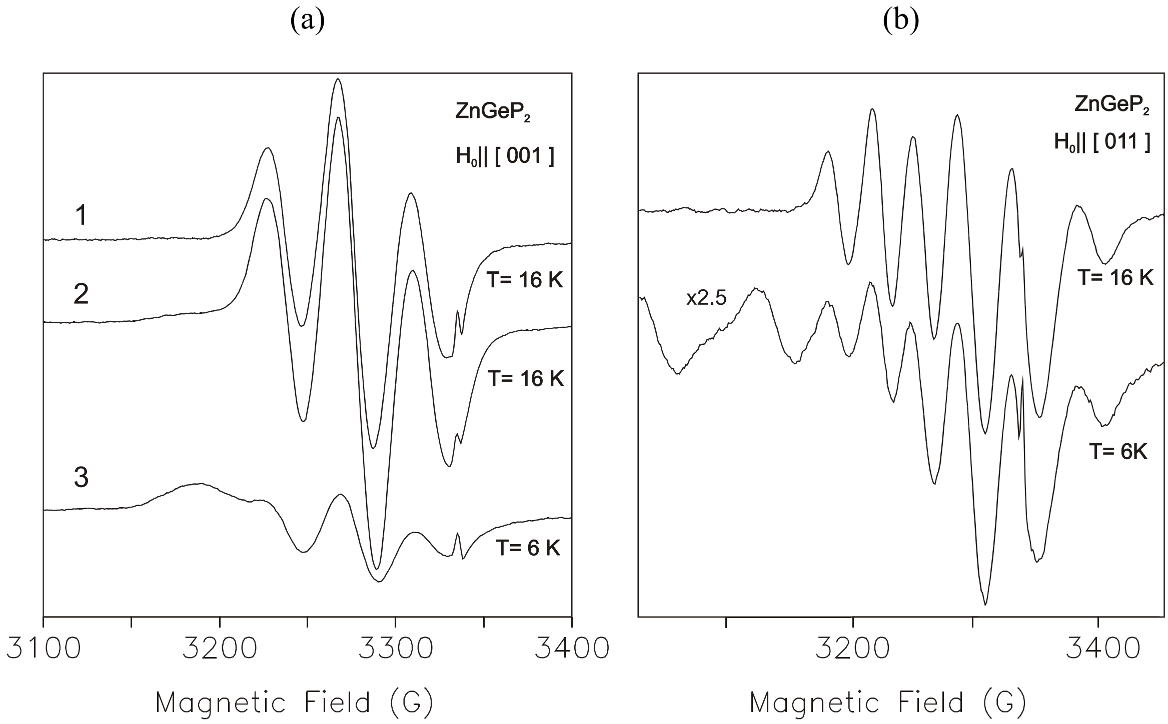

Figure 1. EPR spectra of undoped $ZnGeP_2$ in orientations $H_0 \parallel [001]$ (a), and $H_0 \parallel [011]$ (b).

2.2. EPR in $ZnGeP_2$ substrate after growth of the (Zn,Mn)GeP_2 ferromagnetic layer

EPR and photo-EPR spectra for intrinsic defects of the same type were observed in the bulk substrate after MBE growth of (Zn,Mn)GeP_2 ferromagnetic layer. In addition, Mn^{2+} centers on Zn^{2+} sites have been proved to exist according to EPR data. The typical spectrum for the orientation of the magnetic field close to the [001] axis is presented in Fig. 2. The sharp line with g=2.002 belongs to quartz. Parameters of the spectrum correspond to the data that were obtained by Baran et al. [5]. In the central part of the spectra in Fig. 2, unresolved lines of V_{Zn} overlap the 6-fold peak structure due to Mn^{2+}. The lines of V_{Zn} are not resolved with confidence because of

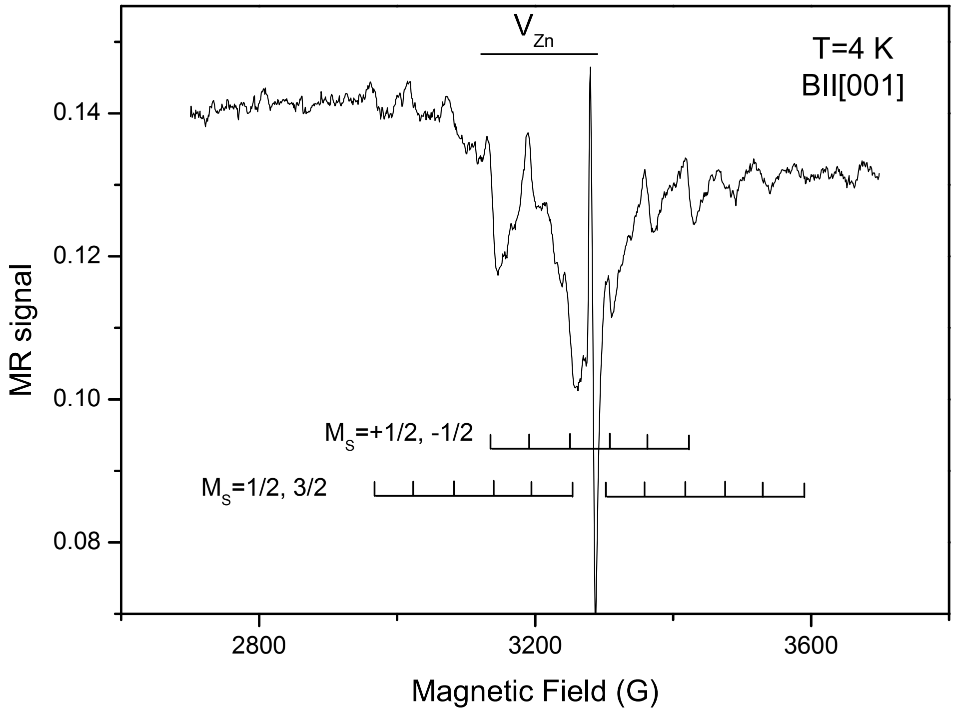

Figure 2. Magnetic resonance spectrum of Mn^{2+} ion in $ZnGeP_2$ substrate at T = 4K.

EPR signal saturation at low temperature. The area of V_{Zn} EPR signals is marked in Fig. 2. Such kind of spectrum was not observed before preparation of $(Zn,Mn)GeP_2$ ferromagnetic layer. Thus, the observation of EPR peak structure characteristic of Mn^{2+} ions in the substrate is due to Mn diffusion into the bulk occurred for the annealing treatment of the starting $ZnGeP_2$.

EPR spectra of Mn^{2+} centers were not yet studied in detail. However, one should mention that there are some evidences of more than one type of Mn-related centers present in the Mn-doped crystal.

2.3. Magnetic ordered state in (Zn,Mn)GeP₂ layer

The complicated temperature dependence was observed for the magnetic resonance in (Zn,Mn)GeP_2 layer. Fig. 3 shows a part of the magnetic resonance spectra measured at different temperatures for the magnetic field perpendicular to the

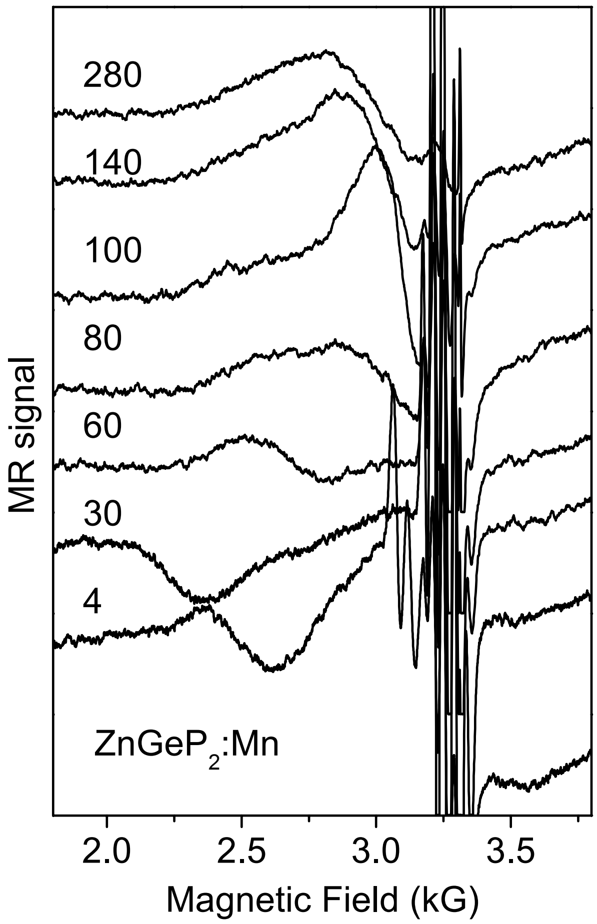

Figure 3. FMR spectra of (Zn,Mn)GeP_2 at temperatures of 4 to 280 K.

layer plane. The line-widths of these signals are much larger as compared with EPR signals and these lines were not observed in $ZnGeP_2$ substrate. EPR signals of defects in such thin layer could not be detected because of their extremally low intensity. Qualitative changes were found in magnetic resonance spectra in several temperature ranges. At low temperatures between 4 and 50 K the broadened line shifts to lower magnetic fields and splits into two lines. Then at higher temperatures the opposite behavior for the magnetic resonance line exists, and at further increasing temperature T > 100 K, the powerful line appeared in the range of 3 kG. Then the signal starts to decrease but it can be observed surely up to room temperature. Probably a different type of magnetic ordering manifests at low and high temperature ranges, that is in the line with recent studies by S. Cho [6]. We believe that the observed magnetic resonance signals are ferromagnetic resonance (FMR). One cannot exclude that at low temperature an antiferromagnetic phase exists. The orientation dependences of FMR have been observed but they were not measured and analyzed in detail.

3. CONCLUSION

The intensive FMR up to room temperature has been observed for the first time in (Zn,Mn)GeP_2 ferromagnetic layer grown on $ZnGeP_2$ single crystal substrate. Ferromagnetic resonance is a powerful instrument to reorient the spin state of ferromagnetic (Zn,Mn)GeP_2 system and could be used in devices of spintronics at room temperature. EPR spectra of Mn^{2+} ions in Zn^{2+} sites have been found in $ZnGeP_2$ substrate after the growth of ferromagnetic layer on the undoped crystal indicating the efficient Mn-diffusion into the bulk $ZnGeP_2$ crystal during the annealing treatments.

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