

# Site inequivalence for Mn<sup>2+</sup> substitution on Zn sites in ZnGeP<sub>2</sub> and ZnSiP<sub>2</sub>

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The magnetic site-inequivalence of the both Zn sites in ZnGeP<sub>2</sub> (ZnSiP<sub>2</sub>) could be resolved for Mn<sub>Zn</sub><sup>2+</sup> ( $S = \frac{5}{2}$ ) by electron paramagnetic resonance (EPR) measurements. The EPR spectra are analyzed with the generalized spin Hamilto-

nian (SH) for S<sub>4</sub> symmetry. We found that the Mn substitution on Zn site causes a strong local distortion of the free parameter  $x_f$ , which describes the positions of the anions in chalcopyrite structures with  $cla \neq 2$ .

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**1 Introduction** The ternary pnictides A<sup>II</sup>M<sup>IV</sup>X<sup>V</sup><sub>2</sub> have attracted much interest because of their nonlinear optical properties [1, 2]. However, the emphatic current interest in these compounds is mainly connected with the recent discovery of room temperature ferromagnetism (RTFM) in highly Mn-doped semiconducting CdGeP<sub>2</sub> [3], ZnGeP<sub>2</sub> [4] and ZnSnAs<sub>2</sub> [5] that enables new nonlinear magneto-optical device structures for nonlinear optics and spintronic applications.

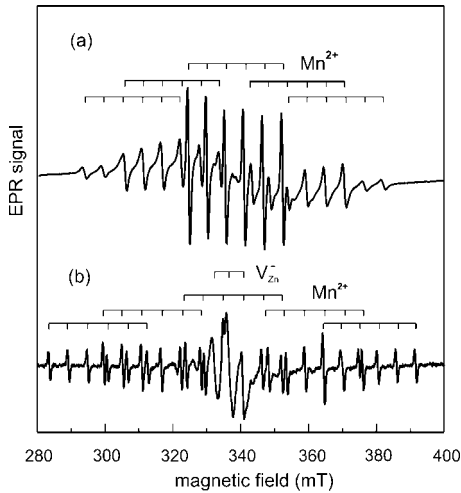
The origin of ferromagnetism in these highly Mn-doped compounds is still not settled and there have been several experimental and theoretical attempts to study this problem [6–10]. To decide between the different theoretical predictions detailed knowledge concerning the incorporation of Mn in the different charge states at the different lattice site and the Mn-induced local changes of the free parameter  $x_f$  of the chalcopyrite structure are necessary. Such data can be obtained in a unique way by systematic electron paramagnetic (EPR) investigations of these compounds with different Mn concentrations. The published results were recently summarized [11].

In this paper we present the first EPR proof of the Mn-induced local changes of the free parameter  $x_f$  for isolated Mn<sup>2+</sup> on the two magnetically inequivalent Zn sites in the tetragonal ZnGeP<sub>2</sub> structure and discuss the results together with improved data of the site inequivalence of Mn<sub>Zn</sub><sup>2+</sup> detected earlier in ZnSiP<sub>2</sub> [11, 12].

**2 Experimental details** The Mn-doped ZnGeP<sub>2</sub> bulk crystals used in this work have been grown by the horizontal gradient freeze (HGF) technique varying the Mn concentration in the melt between 0.2 and 5 mol%. For EPR studies small samples with suitable dimensions for X- and Q-band measurements were cut along the main crystallographic axes. In addition, several unintentionally Mn-doped ZnSiP<sub>2</sub> crystals [13] with low Mn concentration were studied. The EPR measurements were carried out using a Bruker ESP 300E spectrometer operating both in X- and Q-band. The sample temperatures in the range 3.9 K–300 K were achieved with Oxford Instruments continuous flow cryostats.

**3 Experimental results and discussion** Figure 1 shows the well-known EPR spectra for isolated Mn<sup>2+</sup> (3d<sup>5</sup>) on Zn site in ZnGeP<sub>2</sub> and ZnSiP<sub>2</sub>, respectively, for the magnetic field  $B$  parallel to the tetragonal crystal field  $c$ -axis [11]. Five fine structure lines are resolved, each being a sextet typical for the <sup>55</sup>Mn hyperfine (HF) structure caused by the coupling of the <sup>6</sup>A<sub>1</sub> ground state of Mn<sup>2+</sup> to the nuclear spin  $I = \frac{5}{2}$  of the natural isotope <sup>55</sup>Mn. The angular dependence of the EPR spectra can be described by a spin Hamiltonian (SH) for  $S = \frac{5}{2}$  including the fourth-order fine structure terms in tetragonal symmetry with  $z$  along the  $c$ -axis, which is shown for ZnSiP<sub>2</sub>:Mn<sup>2+</sup> in Fig. 2 rotating the magnetic field  $B$  in the (110)-plane. A similar behavior, but with smaller fine-structure splitting

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**Figure 1** Comparison of the EPR spectra of ZnGeP<sub>2</sub>:Mn<sup>2+</sup> (a) and ZnSiP<sub>2</sub>:Mn<sup>2+</sup> (b) for B || c at 80 K. The “stick” spectra present the five Mn<sup>2+</sup> fine-structure transitions ( $\Delta M = \pm 1$ ) with the six fold splitting induced by the hyperfine interaction with the Mn nuclear spin  $I = \frac{5}{2}$ . The smaller zero-field splitting and the larger line width of the Mn<sup>2+</sup> lines for ZnGeP<sub>2</sub> are evident. For ZnSiP<sub>2</sub>:Mn<sup>2+</sup> the central part of the spectrum is overlapped by the EPR spectrum of the zinc vacancy ( $V_{zn}^-$ ).

(Table 1) as well as a stronger broadening of the five fine-structure lines, is observed for ZnGeP<sub>2</sub>:Mn. In a real chalcopyrite structure with  $c/a \neq 2$  there are two inequivalent sites in the unit cell for each type of metal ion resulting from the clockwise and counterclockwise rotation of the anion tetrahedron around the  $c$ -axis by the tilting angle  $\pm \tau$ . These two magnetically nonequivalent sites for the two types of cations in II–IV–V<sub>2</sub> and I–III–VI<sub>2</sub> compounds become distinguishable for EPR centers with  $S \geq 2$ , because the fine structure lines can split into doublets via the fourth-order cubic term in the SH for special orientations [12]. For  $S = \frac{5}{2}$  spin systems the splitting is largest for the fine structure transitions  $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$  and achieves its maximum if the external magnetic field is applied perpendicular to the tetragonal  $c$ -axis. The splitting behavior is shown for weakly Mn-doped ZnSiP<sub>2</sub> and ZnGeP<sub>2</sub> in Fig. 3.

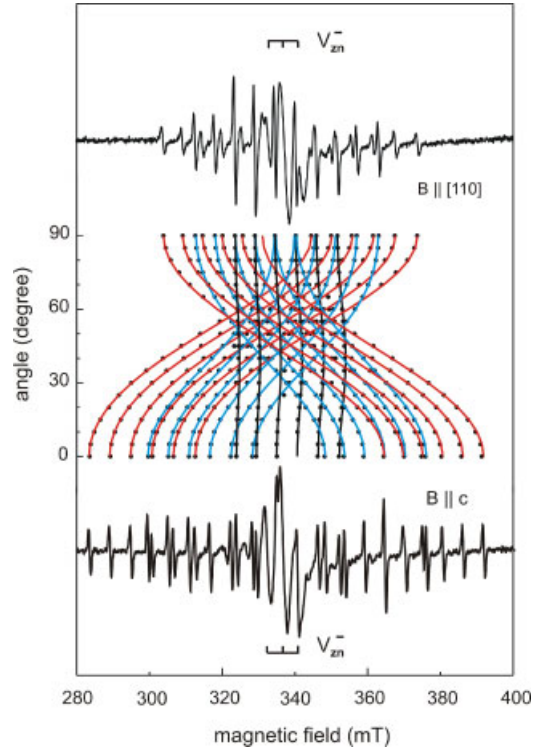
The generalized spin Hamiltonian (SH) appropriate to the Mn<sup>2+</sup> ions occupying the two magnetically nonequivalent Zn sites with the symmetry S<sub>4</sub> takes the form

$$H = \beta \mathbf{B} \hat{g} \mathbf{S} + B_{20} T_2^0 + B_{40} T_4^0 + (B_{44} + i B_{4-4}) T_4^4 + (B_{44} - i B_{4-4}) T_4^{-4} + S \hat{A} I \quad (1)$$

**Table 1** SH parameter (1) for Mn<sup>2+</sup> in ZnSiP<sub>2</sub> and ZnGeP<sub>2</sub> at  $T = 80$  K (HF constant  $A$  and fine-structure parameters  $b_m^k$  in  $10^{-4} \text{cm}^{-1}$ ).

Mn <sub>Zn</sub> <sup>2+</sup>	$g$	$b_2^0$	$b_4^0$	$b_4^4$	$b_4^{-4}$	$-A$	$ \tau_{Mn} $	$\tau_{Zn}^a$
ZnSiP <sub>2</sub>	2.003	-99.5	5.5	22.8	9.7	52.8	5.8°	1.9°
ZnGeP <sub>2</sub>	2.002	-70.2	5.5	21.81	8.8	52.8	5.5°	0.8°

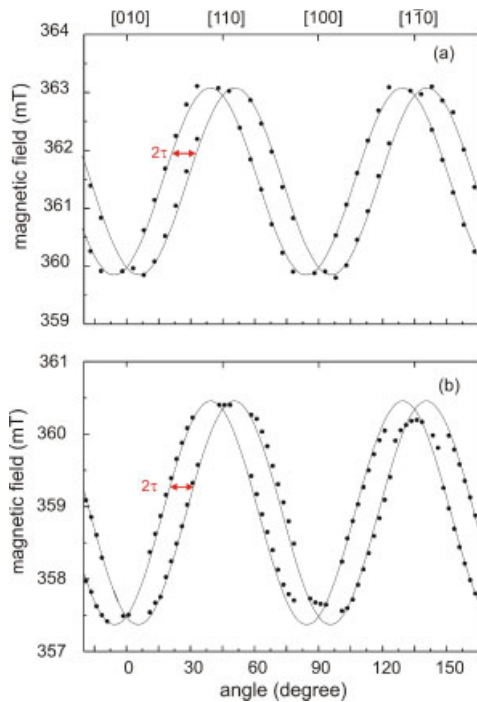
<sup>a)</sup> calculated from the data given in [15]



**Figure 2** (online colour at: www.pss-rapid.com) Angular dependence of the X-band EPR line positions of ZnSiP<sub>2</sub>:Mn<sup>2+</sup> and EPR spectra both for B || c and B || [110] at  $T = 80$  K. The magnetic field  $B$  is rotated in the (110) plane. The solid lines are calculated by exact diagonalization of SH (1) and using the parameters given in Table 1.

where  $B_{20} = \frac{2}{\sqrt{6}} b_{20}$ ,  $B_{40} = \frac{\sqrt{70}}{30} b_4^0$ ,  $B_{4\pm 4} = \frac{1}{30} b_4^{\pm 4}$ , and

$T_m^l$  are spherical tensor operators [14]; the coordinate frame  $(x, y, z)$  is given by the tetragonal unit cell. It is possible to fix the  $x$  and  $y$  directions by rotation around the fourfold rotation inversion  $z$ -axis ( $c$ -axis) by the angle  $\tau_{Mn} = \pm \frac{1}{4} \tan^{-1}(B_{4-4}/B_{44})$  so that  $B_{4-4} = 0$  and the phenomenological SH used in [12] results. However, such special choice of the  $x$  and  $y$  axes is only possible for one center orientation. A rotation around the  $c$ -axis to obtain coincidence with the second set of cubic axes introduces new terms in the SH. Line positions and line intensities were calculated by exact diagonalization of the SH matrix defined by the SH (1). The parameters of SH (1) determined from the angular dependence of the EPR spectra in (001) and (110) planes are presented in Table 1. In addition, the angle  $\tau_{Mn}$  is compared with the tilting angle  $\tau_{Zn}$  of the ZnP<sub>4</sub> tetrahedron rotation around the  $c$ -axis calculated from the free parameter  $x_f$  determined by X-ray studies [15] using the rela-



**Figure 3** (online colour at: www.pss-rapid.com) Experimental splitting (●) of the highest HF transition of the Mn<sub>Zn</sub><sup>2+</sup> fine structure lines  $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$  for ZnSiP<sub>2</sub> (a) and ZnGeP<sub>2</sub> (b) by rotation of the magnetic field  $B$  around the  $c$ -axis. The solid lines are calculated by exact diagonalization of SH (1) and using the parameters given in Table 1.

tion [12]

$$\tan \tau_{\text{Zn}} = \frac{1 - 4x_f}{1 + 4x_f} \quad (2)$$

The discrepancy between the values  $\tau_{\text{Mn}}$  and  $\tau_{\text{Zn}}$  is mainly caused by the Mn-induced local changes of the free parameters  $x_f$  at impurity site due to the local changes of the tetrahedral bonding around the Mn ions.

The value  $\tau_{\text{Mn}}$  differs distinctly not only from the  $\tau_{\text{Zn}}$  value of the undistorted lattice but also from the estimated structural parameters used for the calculation of the formation of the stable magnetic states [16].

To avoid misinterpretation it should be emphasized that from the line position of the EPR transitions the sign of  $\tau_{\text{Mn}}$  cannot be determined. This is overlooked erroneously in some attempts to correlate the zero-field parameter  $D$  and the local tilting angles  $\tau_M$  ( $M = \text{Mn}^{2+}, \text{Fe}^{3+}$ ) in II–IV–V<sub>2</sub> [17, 18] and I–III–VI<sub>2</sub> [19] semiconductors.

For Mn-concentrations higher than 1% we could confirm the formation of antiferromagnetically coupled Mn<sub>Zn</sub><sup>2+</sup>–Mn<sub>Zn</sub><sup>2+</sup> pairs in ZnGeP<sub>2</sub> suggested earlier [11]. This is evidenced by our detection of their characteristic hyperfine structure. Details are discussed elsewhere [20].

**4 Conclusion** The two non-equivalent group II and group IV sites with  $S_4$  symmetry in the II–IV–V<sub>2</sub> compounds can be distinguished by EPR for centers with  $S \geq 2$ . The determined local tilting angles  $\tau_{\text{Mn}}$  for Mn on Zn site in ZnGeP<sub>2</sub> respectively ZnSiP<sub>2</sub> differ distinctly from the angles  $\tau_{\text{Zn}}$  obtained by X-ray studies. These deviations, which are mainly caused by the local change of the free parameter  $x_f$ , can affect the formation of the stable magnetic states.

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## References

- [1] M. C. Ohmer and R. Pandey, MRS Bull. **23**, 16 (1998).
- [2] N. Dietz and F. L. Madarasz, Mater. Sci. Eng. B **97**, 182 (2003).
- [3] G. A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, and K. Sato, Jpn. J. Appl. Phys. **39**, L949 (2000).
- [4] S. Cho, S. Choi, G.-B. Cha, S. C. Hong, Y. Kim, Y.-J. Zhao, A. J. Freeman, J. B. Ketterson, B. J. Kim, Y. C. Kim, and B.-C. Choi, Phys. Rev. Lett. **88**, 257203 (2002).
- [5] S. Choi, G.-B. Cha, S. C. Hong, S. Cho, Y. Kim, J. B. Ketterson, S.-Y. Jeong, and G.-C. Yi, Solid State Commun. **122**, 15 (2002).
- [6] P. Mahadevan and A. Zunger, Phys. Rev. Lett. **88**, 47205 (2002).
- [7] Y. J. Zhao, S. Picozzi, A. Continenza, W. T. Geng, and A. J. Freeman, Phys. Rev. B **65**, 094415 (2002).
- [8] S. Cho, S. Choi, G.-B. Cha, S. C. Hong, Y. Kim, A. J. Freeman, J. B. Ketterson, Y. Park, and H. M. Park, Solid State Commun. **129**, 609 (2004).
- [9] T. Kamatani and H. Akai, Phase Transit. **76**, 401 (2003).
- [10] T. Hwang, J. H. Shim, and S. Lee, Appl. Phys. Lett. **83**(9), 1809 (2003).
- [11] W. Gehlhoff, D. Azamat, and A. Hoffmann, Mater. Sci. Semicond. Process. **6**(5–6), 379 (2003).
- [12] U. Kaufmann, A. Rüber, and J. Schneider, phys. stat. sol. (b) **74**, 169 (1976).
- [13] W. Gehlhoff, D. Azamat, A. Krtschil, A. Hoffmann, and A. Krost, Physica B **340–342**, 933 (2003).
- [14] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (World Scientific, Singapore, 1988).
- [15] H. Boudriot, E. Buhrig, H. Oettel, and H. G. Schneider, II–IV–V<sub>2</sub>-Halbleiter, in: K. Unger and H. G. Schneider (eds.), Verbindungshalbleiter (Akademische Verlagsgesellschaft, Geest & Portig K.-G., Leipzig, 1986), pp. 339–391.
- [16] Y.-J. Zhao, S. Picozzi, A. Continenza, W. T. Geng, and A. J. Freeman, Phys. Rev. B **65**, 094415 (2002).
- [17] W.-C. Zheng and S.-Y. Wu, J. Zi, Physica B **315**, 223 (2002).
- [18] W.-C. Zheng and S.-Y. Wu, Spectrochim. Acta A **58**, 1779 (2002).
- [19] W.-C. Zheng, H.-N. Dong, A. Tang, and J. Zi, Z. Naturforsch. **59a**, 100 (2004).
- [20] W. Gehlhoff, D. Azamat, and A. Hoffmann, to be published.