

## Donor centers in zinc germanium diphosphide produced by electron irradiation

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The properties of defects in p-type zinc germanium diphosphide ( $\text{ZnGeP}_2$ ) were studied by means of electron paramagnetic resonance (EPR) and photo-EPR. Besides the well-known three native defects ( $V_{\text{Zn}}$ ,  $V_{\text{P}}$ ,  $\text{Ge}_{\text{Zn}}$ ) an  $S = 1/2$  EPR spectrum is observed in electron-irradiated  $\text{ZnGeP}_2$  with an isotropic  $g = 2.0123$  and resolved hyperfine splitting from four equivalent  $I = 1/2$  neighbors. This spectrum is caused by a new center generated by the electron-irradiation and not by an existing center that is recharged as a result of the irradiation induced Fermi-level shift. It is tentatively assigned to the isolated Ge vacancy. Observation of the photoinduced recharging processes demonstrates that the location of the level  $V_{\text{Ge}}^{3-/2-}$  is at  $E_{\text{opt}} = (0.7 \pm 0.06)$  eV. An annealing of the electron-irradiated samples causes a reverse shift of the Fermi level in direction to its original position and is accompanied with a reduction of an isotropic unstructured line at  $g = 2.003$  caused by the irradiation damage.

**1. Introduction** Zinc germanium diphosphide,  $\text{ZnGeP}_2$ , is an II–IV– $V_2$  ternary chalcopyrite semiconductor and is currently the most promising optical material for nonlinear optical devices such as tunable mid-infrared optical parametric oscillator (OPO) laser systems. However, a broad absorption band in the 1–2  $\mu\text{m}$  region, which overlaps with the desirable OPO pump wavelengths, affects the performances of such OPO's up to now. This disturbing absorption is mainly attributed to photo-ionization of a deep acceptor center associated with the zinc vacancy ( $V_{\text{Zn}}$ ). A large reduction of this absorption can be obtained by high-energy electron irradiation of the crystals. This reduction is mainly caused by a metastable recharging of the  $V_{\text{Zn}}$  centers as result of the irradiation induced shift of the Fermi-level [1]. Both as-grown and annealed  $\text{ZnGeP}_2$  samples grown by the horizontal gradient freeze technique exhibit commonly a strong EPR spectrum [2] that has been identified the singly negatively charged zinc vacancy ( $V_{\text{Zn}}^-$ ) by ENDOR measurements [3, 4]. Photoinduced EPR studies have shown in addition two donor centers that have been attributed to the neutral P vacancy ( $V_{\text{P}}^0$ ) [5] and the singly charged  $\text{Ge}_{\text{Zn}}$  anti-site ( $\text{Ge}_{\text{Zn}}^+$ ) [6], respectively. Very recently, three recharging levels in the band gap of  $\text{ZnGeP}_2$  correlated with these native defects could be determined with photo-EPR using as-grown and electron-irradiated  $\text{ZnGeP}_2$  samples [7]. In the electron-irradiated samples a new center was observed [7]. However, neither its spin Hamiltonian parameters, nor level positions in the  $\text{ZnGeP}_2$  have been determined up to now.

**2. Experimental details** The  $\text{ZnGeP}_2$  crystals used in this work were grown by the gradient freezing Bridgman method. For the EPR studies small samples with suitable dimensions for X or Q-band measurements were cut along the main crystallographic directions from as-grown, post-growth annealed, and

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electron-irradiated samples. The room-temperature irradiations were performed with 2 MeV electrons to fluences in the range of  $(5-9) \times 10^{17} \text{ e/cm}^2$ . The EPR and photo-EPR measurements were carried out using a Bruker ESP 300E spectrometer operating both at the X-band ( $\nu \cong 9.5 \text{ GHz}$ ) and Q-band ( $\nu \cong 34 \text{ GHz}$ ). Temperatures in the range 3.9–300 K were achieved with Oxford Instruments continuous flow cryostats. The samples could be optically excited by monochromatic or filtered light through slits in the cavity wall of the X-band resonators or through a 0.4 mm optical fiber introduced into the Q-band cryostat [7].

**3. Experimental results and discussion** In agreement with [1, 7], for samples irradiated with high-energy (2 MeV) electrons neither the  $V_{Zn}^-$  EPR signal nor the  $V_p^0$  and  $Ge_{Zn}^+$  signals could be detected before optical excitation, if the samples are cooled down in the dark. Illumination with infrared light generates the spectra of  $V_{Zn}^-$ , and  $Ge_{Zn}^+$ . Also, the spectrum of the new center mentioned in [7] is observed. This center, described here for the first time in detail, is difficult to prove in the X-band by the strong overlapping with the residual spectra caused by the  $V_{Zn}$  and  $Ge_{Zn}$  defects as well as with an additional line above  $g = 2.003$ . The intensity of this unstructured line with a linewidth of 0.6–1.2 mT seems to be correlated with the radiation damage produced by the electron-irradiation and can be strongly reduced by thermal annealing of the samples. At temperature below 20 K and low microwave power ( $\leq 100 \text{ nW}$ ) a sharp line with a linewidth of 0.09 mT at  $g = 2.0023$  is observed. At the same time a residual spectrum of the  $V_{Zn}^-$ , but with larger linewidth is always detected. In spite of these difficulties, the existence of the new center can be unambiguously proven. Figure 1 shows the experimental and simulated spectra in the X-band at  $B \parallel c$  for a sample after the electron-irradiation. The essential feature of the new spectrum is a partially resolved anisotropic hyperfine (hf) structure with the magnetic field parallel to the tetragonal  $c$ -axis of the crystal. The observed five-line spectrum with intensities in the ratio 1:4:6:4:1 is characteristic for the interaction of a spin-1/2 center with four equivalent spin-1/2 nuclei. This spectrum can be described by the spin Hamiltonian

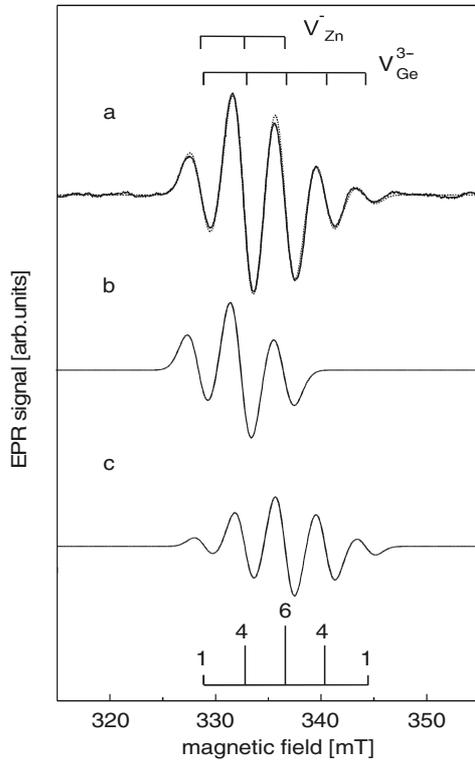
$$H = g\mu_B B \cdot S + \sum_{i=1}^4 S \cdot A_i \cdot I_i, \quad (1)$$

where the first term represents the Zeeman interaction and the second term describes a ligand hf interaction with four equivalent  $^{31}\text{P}$  neighbors ( $I = 1/2$ , natural abundance 100%). Assuming that each P nuclei interact independent with the electron spin  $S = 1/2$  and each hf interaction has axially symmetry along its  $\langle 111 \rangle$  axis, the transitions occur with energy given in first order by

$$h\nu = g\beta B + \sum_{i=1}^4 (A_{\parallel}^2 \cos^2 \theta_i + A_{\perp}^2 \sin^2 \theta_i)^{1/2} m_i, \quad (2)$$

with  $m_i = \pm 1/2$  and  $\theta_i$  the angle between  $B$  and the  $i$ -th bond direction. For an arbitrary value of the magnetic field sixteen transitions are possible and the overlapping of the different transition smears out the structure. Degeneracies occur along the high-symmetry directions and we expect a partly resolved structure. However, the strong overlapping with the zinc vacancy EPR spectrum for directions different from  $B \parallel c$  prevents its detection up to now. Therefore, only the value of the hyperfine parameters for the orientation of magnetic field parallel to the  $c$ -axis given by  $A^* = \sqrt{1/3(A_{\parallel}^2 + 2A_{\perp}^2)}$  with  $A^* = 35.7 \times 10^{-4} \text{ cm}^{-1}$  could be determined. Within experimental error the center has an isotropic  $g$  factor with value  $g = 2.0123$ .

Avoiding saturation effects by corresponding choice of temperature and microwave power, we have determined the dependence of the EPR signal intensity on the photoexcitation energy for the new center (Fig. 2). The presentation establishes in the low-energy region (0.6 – 1.1 eV) a photoinduced quenching and for the higher energy region (1.2 – 2.0 eV) an increase of the intensity of the new signal. This growth

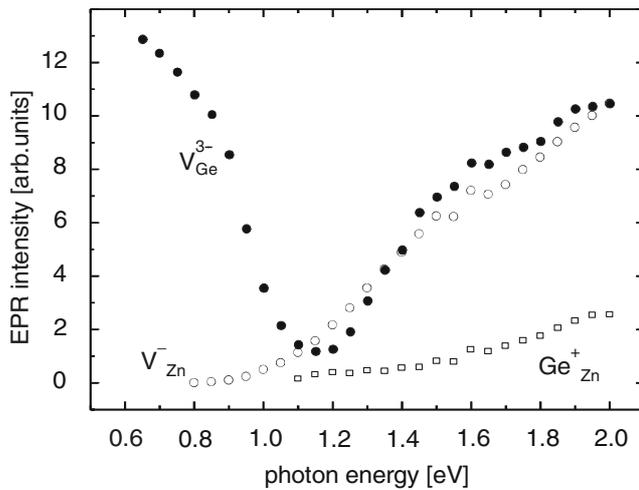


**Fig. 1** Experimental EPR spectrum of an electron irradiated ZnGeP<sub>2</sub> sample (solid line) for *B* parallel to the tetragonal axis *c* exhibiting the spectrum of the new center *c*. (*T* = 80 K,  $\nu$  = 9.48 GHz). The excellent agreement of the experimental (solid line) and simulated (dotted line) spectrum *a*) confirms that the whole spectrum is in fact produced by the overlapping lines from the zinc vacancy ( $V_{Zn}^-$ ) *b*) and the new center *c*) identified tentatively as  $V_{Ge}^{3-}$ .

is accompanied by a strong increase of the intensity of the  $V_{Zn}^-$  and  $Ge_{Zn}^+$  signal in agreement with the investigation in [7]. In the context of all the photoinduced recharging processes studied in [7] and this study, we infer that in the low-energy region the electron transfer from the new center to the conduction band exceeds the re-capture, leaving behind some centers in a non-paramagnetic state. For excitation energies higher than 1.1 eV the additional electron excitation from the doubly negatively charged zinc vacancy ( $V_{Zn}^{2-}$ ) to the conduction band causes an increase of the number of photoinduced electrons available for the re-capture by the new center. Therefore, some new centers are recharged to its paramagnetic state, inducing an increase

of the EPR signal intensity. Analyzing the spectral dependence of the observed photoinduced quenching of the EPR signal intensity in accordance with [7], we determined the optical ionization energy of the new center to  $E_{opt} = (0.7 \pm 0.06)$  eV.

Checking all available samples under optimized condition we never observed the spectrum of the new center prior to electron irradiation. Therefore, this center is unambiguously generated at least in a detectable concentration first by the electron irradiation and not by recharging of existing centers due to the Fermi-level shift caused by the electron irradiation. Taken into account the given interpretations of the previous detected native defects  $V_{Zn}$ ,  $V_P$ , and  $Ge_{Zn}$ , from the *g*-value and the hf-interaction with four



**Fig. 2** Spectral dependence of the photoinduced changes of the EPR signal intensities of an electron-irradiated ZnGeP<sub>2</sub> sample measured at 45 K in the Q-band ( $\nu$  = 34 GHz). The symbols ( $\bullet$ ,  $\circ$ ,  $\square$ ) represent the experimental values for the new center ( $V_{Ge}^{3-}$ ), the negatively charged zinc vacancy ( $V_{Zn}^-$ ), and the anti-site center  $Ge_{Zn}^+$ . The EPR intensity of the new center is multiplied by a factor 100.

phosphorus nuclei, we could assign the new defect only to the so far not observed isolated Ge vacancy ( $V_{\text{Ge}}$ ) or the Zn anti-site ( $Zn_{\text{Ge}}$ ). P on Zn or Ge site is eliminated because no large hf interaction [8] is observed. The value of the hf interaction and the strong localization of the defect wave function on the nearest neighbors exhibiting in a small linewidth, along with the sign and shift of the  $g$ -value are consistent with a vacancy center. This is in line with positron annihilation studies, which have shown that electron-irradiation produces additional vacancy-like defects in p-ZnGeP<sub>2</sub> [9]. However, further experiments are required to rule out  $Zn_{\text{Ge}}$  centers unambiguously, because the absence of a central hf in the experimental spectra can be caused by the small natural abundance of 4.1% of the Zn isotope with a nuclear spin ( $^{67}\text{Zn}$ ,  $I = 5/2$ ).

**4. Conclusions** The present EPR and photo-EPR study reveals a new spectrum not detected prior to electron irradiation of the samples. From the photo-EPR investigation we can exclude this spectrum to be caused by an existing center that is only recharged in the observed paramagnetic state as a result of the irradiation induced Fermi-level shift. Further experiments are required to determine the electronic structure and the thermal stability of this center, which is tentatively identified as germanium vacancy.

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