Extreme Reduction of the Spin-Orbit Splitting of the Deep Acceptor Ground State of Zn_S^- in Si

H. Schroth and K. Laßmann
1. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany

S. Voß and H. Bracht
Institut für Metallforschung, Universität Münster, Wilhelm-Klemm-Straße 10, 48149 Münster, Germany
(Received 30 September 1999)

Electric-dipole spin resonance of the deep acceptor Zn_S^- in Si reveals close Γ_8 and Γ_7 ground states with zero-field separation of only 0.31 meV as compared to the 43 meV of the two valence bands. With Landé's formula for the g factors of a $^2T_2$ state split by spin-orbit interaction into Γ_8 and Γ_7 this nearness can be interpreted as strong quenching of the orbital moment. The observed dependence on the Zn isotopic mass indicates a dynamic contribution of the acceptor atom to the electronic state as is expected for a Jahn-Teller effect.

PACS numbers: 76.30.Lh, 71.70.Ej

The binding energies of the Γ_8 one-hole ground states of single and double acceptors in silicon span a large, quasicontinuous scale ranging from relatively shallow (Si:B, 46 meV) to near midgap (Si:Zn_S^-, ~660 meV [1]). This is a unique situation, a challenge and check for theoretical approaches that have been quite different at the extrema of this scale [2,3]. We state here the existence of a second, countercorrelated scale, not considered previously, namely, the separation between these Γ_8 and the associated spin-orbit split-off Γ_7 states, which opens a new aspect and should be helpful for theoretical considerations.

A cornerstone to this statement is our observation, presented here, that in the case of the extremely deep Si:Zn_S^- this separation is so small (0.31 meV) that at 60 GHz and moderate magnetic fields it can be bridged by electric dipolar spin resonance (EDSR) transitions. (For comparison, this spin-orbit splitting in the case of the valence bands amounts to 42.8 meV [4].)

Taking together our EDSR data at 24, 34, and 60 GHz for Si:Zn^-, we can obtain a precise nonlinearity of the Zeeman splitting of the four Γ_8 levels consistent with the small Γ_8-Γ_7 separation. In light of this result the increasing nonlinearity of the Γ_8 Zeeman effect with increasing binding energy observed previously in EDSR of group III acceptors in Si [5] can be understood by a decreasing separation of both acceptor states. In the case of the deep Be_S^- a rather precise estimate was possible [6] for this separation (0.6 meV) which was later confirmed directly by phonon spectroscopy [7].

We regard it as an important clue to our understanding that we can describe both the reduced Γ_8-Γ_7 separation and the also observed reduction of the g factors with increasing binding energy in terms of the Landé formula by a common reduction factor k meaning an increasing quenching of the orbital momentum. For the interpretation of this quenching the system Si:Zn_S^- could again be crucial: We were able to observe an isotope effect for the spin-orbit splitting which suggests that the quenching may be due to a dynamic Jahn-Teller effect.

Doping with Zn was performed by Zn diffusion into samples of typically $5 \times 8 \times 1.5$ mm^3 at temperatures of about 1000 °C for several hours, as described in [8]. After Zn diffusion the samples were mechanically polished to remove the remains of Zn on the surface. Disks of 2–6 mm in diameter were ultrasonically cut and etched at the side walls to reduce surface-generated strain. EDSR absorption spectra between 1.8 and 10 K were recorded with the samples in the center of flat cylindrical TM_{030} reflection cavities, where the microwave *electric field* $\tilde{E}$ is maximal. These cavities are part of standard EPR microwave bridges and are positioned in the center of a horizontal NbTi-Helmholtz solenoid for static magnetic fields B up to 7 T in a plane perpendicular to $\tilde{E}$. More than 30 samples of different doping and codoping were investigated with angular variation of B in the $(1\bar{1}0)$ plane.

Typical EDSR spectra of Zn-doped samples partially compensated by P are shown in Fig. 1. A number of lines, resembling the spectra of neutral group III acceptors [5] and also of Be_S^- [6], can be attributed to singly ionized substitutional Zn. The line position depends weakly on the direction of B. Only for the narrowest lines, especially for the one labeled "1u" in Fig. 1, the anisotropy is resolvable. It can be described with $1 - 5(n_1^2 n_2^2 + n_2^2 n_3^2 + n_3^2 n_1^2)$, where the n_i's are the direction cosines of B with respect to the $\langle 100 \rangle$ axes. This anisotropy is typical for a Γ_8 state in cubic symmetry [10]. Moreover, the variation of line strengths with field direction for transitions within the Γ_8 state follows the theoretical relations given in [5] for linear coupling to the electric microwave field. At 60 GHz two additional triplet lines "α" and "β" are found which can be fitted by a superposition of lines according to the natural abundance of the three main Zn isotopes (cf. Fig. 1). In samples exclusively doped with ^{67}Zn only one line appears in the intermediate position between ^{66}Zn and ^{68}Zn. The isotope effect and the angular dependence of the spectra give evidence that the defect involves one Zn atom at a tetrahedral site either substitutional or interstitial. However, for the interstitial double donor an orbital singlet a_1

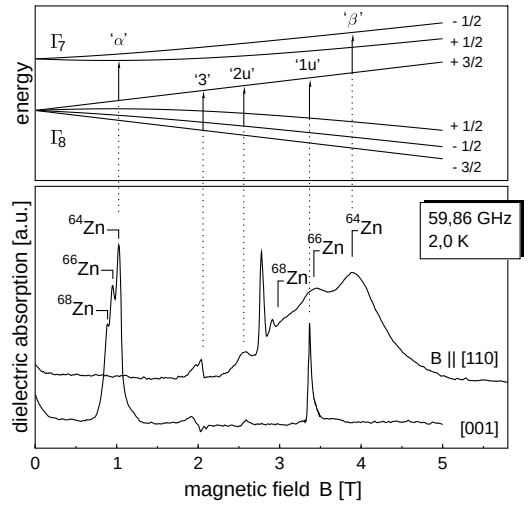

FIG. 1. EDSR spectrum of a compensated Zn-doped sample at 60 GHz. The transitions α and β to the Γ_7 state consist of triplets due to the main Zn isotopes as verified by doping with ^{67}Zn instead of natural Zn. The narrow features not marked belong to a trigonal Zn complex [9].

is expected as in the analogous case of the isoelectronic Cd [11] that cannot give rise to a Γ_8 state. Therefore the spectra are considered to be caused by *substitutional* Zn. To determine the relevant charge state, EDSR spectra were taken of a series of Zn-doped samples codoped with P or B and showing various degrees of compensation as obtained from resistivity profiles measured at room temperature. The spectra shown in Fig. 1 were observed without illumination in samples with p-type conductivity and rather high resistivities. In low-resistivity p- and n-type samples with the Fermi level near the valence and conduction bands, respectively, the samples had to be illuminated with white light to obtain the spectra. By taking into account the two acceptor levels of substitutional Zn at 319 meV [12] and at about 660 meV [1], the spectra can be attributed to $Zn_S{}^-$.

We analyze the spectra using the general form of the Zeeman matrix of two coupled Γ_8 and Γ_7 states as tabulated in [13], which is not restricted to a specific model but only reflects the transformation properties of the states involved.

$$
\begin{array}{c|cccccc}
 & |\Gamma_7,+\tfrac{1}{2}\rangle & |\Gamma_7,-\tfrac{1}{2}\rangle & |\Gamma_8,+\tfrac{3}{2}\rangle & |\Gamma_8,+\tfrac{1}{2}\rangle & |\Gamma_8,-\tfrac{1}{2}\rangle & |\Gamma_8,-\tfrac{3}{2}\rangle \\
\hline
\langle\Gamma_7,+\tfrac{1}{2}| & Z_1-\tilde{\lambda} & Z_3^* & Z_{10}^* & Z_7 & -Z_9 & 0 \\
\langle\Gamma_7,-\tfrac{1}{2}| & Z_3 & -Z_1-\tilde{\lambda} & 0 & Z_9^* & Z_7 & -Z_{10} \\
\langle\Gamma_8,+\tfrac{3}{2}| & Z_{10} & 0 & Z_2+\frac{\tilde{\lambda}}{2} & Z_6^* & 0 & Z_5^* \\
\langle\Gamma_8,+\tfrac{1}{2}| & Z_7 & Z_9 & Z_6 & Z_4+\frac{\tilde{\lambda}}{2} & Z_8^* & 0 \\
\langle\Gamma_8,-\tfrac{1}{2}| & -Z_9^* & Z_7 & 0 & Z_8 & -Z_4+\frac{\tilde{\lambda}}{2} & Z_6^* \\
\langle\Gamma_8,-\tfrac{3}{2}| & 0 & -Z_{10}^* & Z_5 & 0 & Z_6 & -Z_2+\frac{\tilde{\lambda}}{2}
\end{array}
$$

$$
\begin{aligned}
Z_1 &= 4g_{(7)}c_\phi, & Z_2 &= (12g_1' + 27g_2')c_\phi, \\
Z_3 &= -4g_{(7)}s_\phi{}^+, & Z_4 &= (4g_1' + g_2')c_\phi, \\
Z_5 &= -6g_2's_\phi{}^-, & Z_6 &= \sqrt{3}\,(4g_1' + 7g_2')s_\phi{}^+, \\
Z_7 &= 8g_{(78)}c_\phi, & Z_8 &= -(8g_1' + 20g_2')s_\phi{}^+, \\
Z_9 &= 4g_{(78)}s_\phi{}^-, & Z_{10} &= -4\sqrt{3}\,g_{(78)}s_\phi{}^-, \\
c_\phi &= \tfrac{1}{8}\mu_B B\cos\phi, & s_\phi{}^\pm &= \tfrac{1}{16}\sqrt{2}\,(1 \pm i)\mu_B B\sin\phi\,.
\end{aligned}
$$

ϕ is the angle between $[001]$ and B in the $(1\bar{1}0)$ plane. The spin-orbit coupling is included in the form $\tilde{\lambda}(\mathbf{LS})$, where $L = 1$ and $S = 1/2$ for a hole in Si. In addition, the matrix contains the four g factors of the coupled states. Thus there are five parameters to be determined experimentally. If the anisotropy g_2' can be neglected as in the case of Be^-, the simpler matrix given in [6] is obtained. On the other hand, the familiar form $g_1'\mu_B(\mathbf{BJ}) + g_2'\mu_B(B_xJ_x^3 + B_yJ_y^3 + B_zJ_z^3)$ of the Hamiltonian of an isolated Γ_8 state is obtained in the limit of infinitely large separation $|3\tilde{\lambda}/2|$ of the states Γ_8 and Γ_7. By numerical diagonalization we obtain a level splitting pattern as shown in the upper part of Fig. 1. It is the anticrossing behavior of the $\pm 1/2$ states that leads to the increased nonlinearity of the Zeeman splitting with decreasing Γ_8-Γ_7 separation. In the case of $Zn_S{}^-$ this separation is so small that, at 60 GHz, EDSR transitions α and β between both states are observable. Thus all parameters in the above energy matrix can be determined. The fit to the set of data from the three microwave bands is shown in Fig. 2. Near 60 GHz we have taken measurements at various frequencies to verify the slopes of the lines. The validity of our analysis is supported by the quality of the numerical fit. Also the angular dependence of line strengths for the transitions α and β is as expected for transitions between a Γ_8 and a Γ_7 state [14]. The assignment to transitions starting from "upper" states (u or m) has been verified by their temperature dependence.

Our results are summarized in Table I. For the three Zn isotopes we obtain the same g values but different spin-orbit splittings from our fits. It is interesting to compare the g values and the spin-orbit splitting of $Zn_S{}^-$ with those of shallower one-hole states in Si. Taking a mean isotropic $g_{(8)}$ instead of g_1' and g_2' for the Γ_8 state (this is done in Fig. 3) shows a clear monotonous dependence

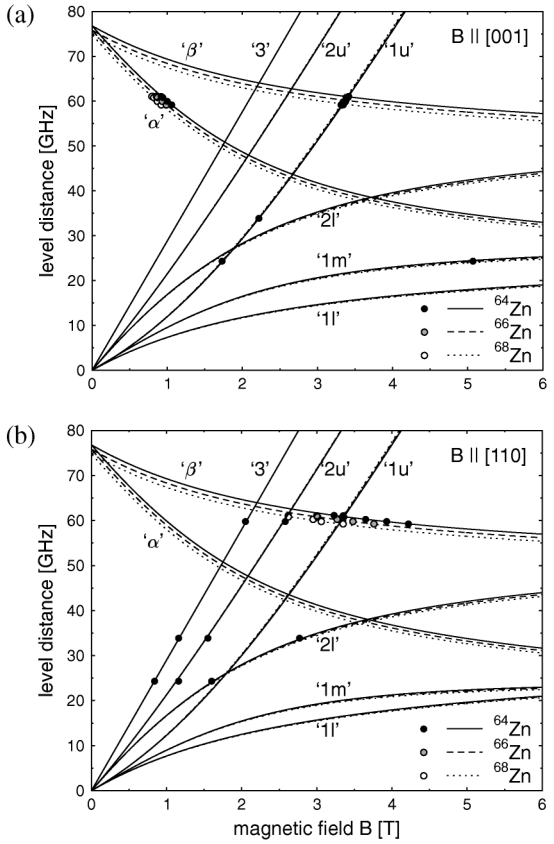

FIG. 2. Calculated fit of the level separations (lines) to the observed resonance fields of Zn_S^- in the three microwave bands (points) for the cases B ∥ [001] (a) and B ∥ [110] (b). l, m, and u represent the lower, middle, and upper transitions, respectively, within the Γ_8 quartet and the numbers in front represent Δm.

of these parameters on the binding energy (as far as experimental values exist). The strongest dependence is observed for the spin-orbit splitting, which could be determined from the EDSR data unambiguously only in the case of Zn_S^-, the value of only 0.31 meV being supported by a resonance observed under uniaxial stress in phonon spectroscopy (PS) with superconductor tunnel junctions [15]. The value of 0.6 meV estimated for Be_S^- from the nonlinear Zeeman splitting [6] has been also confirmed by PS (unpublished results by Linsenmaier, see Ref. [7]). The close proximity of the Γ_7 state is also consistent with a hitherto not explained shoulder on the high-energy side of the IR lines of $Si{:}Be_S^0$ [16,17]. This satellite is a component of the *final state* of the optical transition which

TABLE I. Parameters of Zn_S^- as determined by the fit in Fig. 2. Notice the different values of the spin-orbit splitting $|3\tilde{\lambda}/2|$ for different Zn isotopes.

g_1'	g_2'	$g_{(7)}$	$g_{(78)}$	$3\tilde{\lambda}/2$ (meV) ^{64}Zn	^{66}Zn	^{68}Zn
0.73	−0.018	−0.71	0.96	−0.318	−0.314	−0.310
±0.02	±0.005	±0.05	±0.05	±0.01	±0.01	±0.01

may be viewed as $Si{:}Be_S^-$ plus an only weakly interacting hole in an extended state. In the case of In, an excited state about 4.2 meV above the Γ_8 ground state has been observed with various techniques and has been assigned to higher vibronic levels connected with the dynamic Jahn-Teller effect (see [18], and references therein). In view of the present results we favor the alternative interpretation of this "excited" state being Γ_7: From the analysis of the nonlinearity of the Zeeman splitting of the electronic Γ_8 ground state of In previously observed by EDSR [5], we obtain for the Γ_8-Γ_7 separation 4.2 ± 0.4 meV [7]. For the shallower acceptors the Zeeman nonlinearity is too small for reasonable estimates. The spin-orbit splitting of B has been determined by Raman scattering [19–21] and IR absorption [22]; a value of 22.77 meV is given in [22]. The two data points marked with an asterisk (*) in Fig. 3 belong to the hole of the excitons bound at isoelectronic Be-Be pairs [23] and the isoelectronic A, B, C defect [23,24]. For Ga and Al we estimate values at about 14 and 15 meV, respectively, from interpolation between B and In (Fig. 3). The first Raman results appear to be in agreement with these predictions [21] and also give other confirmation of the value of 4.2 meV for In. The indicated g values of B, Al, Ga, In, and Be^- have been determined by EDSR [5,6], except for $g_{(7)}$ of B which was obtained from magneto-Raman measurements [20]. $g_{(8)}$ of Tl was taken from [25].

Neglecting the small anisotropy of the spectra, Landé's formula for a $^2T_2$ state can be applied to the coupled Γ_8 and Γ_7 states, where we allow for a reduction of the orbital moment by a factor k. We obtain the following [6]: $g_{(7)} = 4k/3 - 2/3$, $g_{(8)} = 2k/3 + 2/3$, $g_{(78)} = \sqrt{2}(2 - k)/3$, and $\tilde{\lambda} = k\lambda$. The lines in Fig. 3 are smooth interpolations to the values calculated from these expressions with the

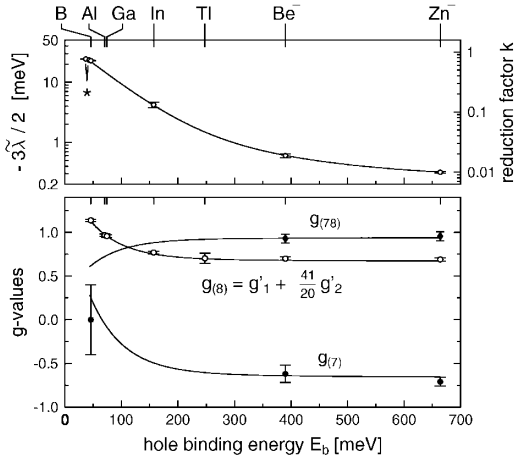

FIG. 3. Measured variation of g values and spin-orbit splitting with hole binding energy E_b in Si (points). The lines are smooth interpolations of the values calculated as a best fit to all data points from Landé's formula allowing for a reduced orbital moment by reduction factors $k(E_b)$ and a common unreduced spin-orbit splitting parameter λ as fitting parameters.

two fit parameters λ and $k(E_b)$. We obtain an increasingly quenched orbital moment with increasing binding energy (see scale on the right of Fig. 3). The reason for that could be the dynamic Jahn-Teller effect, for which the quenching is determined by the strength of the coupling to phonons (see Chap. 21 in Ref. [10]). This coupling should increase with the increased localization of the state. Also, the observed isotope effect for k in the case of Zn suggests a vibronic contribution. For coupling to Γ_5 local modes, the central Zn atom participates in the motion, so that the effective mode frequency ω should depend on the isotopic mass of Zn. Since the reduction factor for coupling to Γ_5 modes is given by $k \approx \exp(-9E_{JT}/4\hbar\omega)$ [26], a larger mass of the Zn-Si neighborhood complex leads to a smaller ω and thus a smaller k, giving a smaller spin-orbit splitting as observed (see Table I). The Jahn-Teller effect would also explain the larger g value attributed by Ginodman *et al.* to Zn_S^- [27]. Since their EPR measurements were performed under uniaxial stress, the Jahn-Teller effect is expected to be reduced by the symmetry-lowering external stress, leading to a larger k.

Interestingly, the unreduced spin-orbit splitting $|3\lambda/2|$ deduced from the fit in Fig. 3 is approximately 32 meV and thus much closer to the atomic value of Si, which is about 28 meV, than to the value of the valence band, 42.8 meV. This may reflect the localized nature of acceptor ground states in Si, which are probably described better by a t_2 dangling bond state as in the vacancy model (see [28], and references therein) than by valence band states. It must be noted though that recent calculations on the basis of valence band states have also given a reduction of the spin-orbit splitting with increasing binding energy, the latter being used as a fit parameter within a Koster-Slater ansatz [21]. (A first calculation using effective mass approximation did not specifically address the dependence on binding energy [2]. 24 meV was obtained for the spin-orbit splitting of shallow acceptors.)

However, a touchstone for any theoretical result is the understanding of the common reduction factor k for spin-orbit separation *and* g factors for the series of acceptors and also its isotope effect, at least in the case of Zn as reported here.

We are grateful to N. A. Stolwijk, A. Dörnen, and F. S. Ham for helpful discussions, to M. Cardona, T. Ruf, and J. Serrano for information on their Raman results and calculations concerning the spin-orbit splitting of acceptor states in Si prior to publication, and to W. Gehlhoff for kindly helping us with ^{67}Zn for the unambiguous identification of the isotope effect. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

[1] A. C. Wang, L. S. Lu, and C. T. Sah, Phys. Rev. B **30**, 5896 (1984).
[2] A. Baldereschi and N. O. Lipari, in *Proceedings of the ICPS13,* edited by F. G. Fumi (Tipografia Marves, Rome, 1976), p. 595.
[3] A. Zunger and U. Lindefelt, Phys. Rev. B **27**, 1191 (1983).
[4] A. K. Ramdas and S. Rodriguez, Rep. Prog. Phys. **44**, 1297 (1981).
[5] A. Köpf and K. Laßmann, Phys. Rev. Lett. **69**, 1580 (1992).
[6] H. Schroth *et al.*, Phys. Status Solidi (b) **210**, 747 (1998).
[7] H. Schroth, Ph.D. dissertation, Universität Stuttgart, 1999 [*Spinresonanz der tiefen Akzeptoren Beryllium und Zink in Silizium* (Der Andere Verlag, Osnabrück, 2000)].
[8] H. Bracht *et al.*, Phys. Rev. B **52**, 16 542 (1995).
[9] H. Schroth, K. Laßmann, and H. Bracht, in *Proceedings of the 23rd International Conference on The Physics of Semiconductors,* edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), Vol. 4, p. 2725.
[10] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Dover, New York, 1986), Chap. 18.3.
[11] A. Näser *et al.*, Phys. Status Solidi (b) **210**, 753 (1998).
[12] A. Dörnen *et al.*, Phys. Rev. B **40**, 12 005 (1989).
[13] G. F. Koster *et al., Properties of the Thirty-two Point Groups* (MIT Press, Cambridge, MA, 1963), p. 93.
[14] A. K. Bhattacharjee and S. Rodriguez, Phys. Rev. B **6**, 3836 (1972).
[15] J. Staiger, P. Groß, K. Laßmann, H. Bracht, and N. A. Stolwijk, Mater. Sci. Forum **143–147**, 675 (1994).
[16] R. E. Peale, K. Muro, and A. J. Sievers, Phys. Rev. B **41**, 5881 (1990).
[17] J. N. Heyman, A. Giesekus, and E. E. Haller, Mater. Sci. Forum **83–87**, 257 (1992).
[18] K. Laßmann, in *Festkörperprobleme/Advances in Solid State Physics,* edited by R. Helbig (Vieweg, Braunschweig, 1997), Vol. 37, p. 79.
[19] G. B. Wright and A. Mooradian, Phys. Rev. Lett. **18**, 608 (1967).
[20] J. M. Cherlow, R. L. Aggarwal, and B. Lax, Phys. Rev. B **7**, 4547 (1973).
[21] J. Serrano *et al.*, Physica (Amsterdam) **273B–274B**, 640 (1999).
[22] H. R. Chandrasekhar, A. K. Ramdas, and S. Rodriguez, Phys. Rev. B **12**, 5780 (1975).
[23] D. Labrie, T. Timusk, and M. L. W. Thewalt, Phys. Rev. Lett. **52**, 81 (1984).
[24] J. Wagner and R. Sauer, Phys. Rev. B **26**, 3502 (1982).
[25] V. A. Karasyuk *et al.*, Phys. Rev. B **54**, 10 543 (1996).
[26] F. S. Ham, Phys. Rev. **138**, A1727 (1965).
[27] V. B. Ginodman *et al.*, Sov. Phys. Semicond. **5**, 1930 (1972).
[28] G. D. Watkins, Physica (Amsterdam) **117B–118B**, 9 (1983).