Higher-order Zeeman effect of Mg-related donor complexes in silicon

S. G. Pavlov [1], D. L. Kamenskyi [2], Yu. A. Astrov [3], V. B. Shuman,[3] L. M. Portsel,[3] A. N. Lodygin [3], N. V. Abrosimov [4], H. Engelkamp [5], A. Marchese,[5] and H.-W. Hübers [1,6]

[1]*Institute of Optical Sensor Systems, German Aerospace Center (DLR), Berlin, Germany*
[2]*Experimental Physics V, Center for Electronic Correlations and Magnetism, Institute of Physics, University of Augsburg, Augsburg, Germany*
[3]*Ioffe Institute, Russian Academy of Sciences, St. Petersburg, Russia*
[4]*Leibniz-Institut für Kristallzüchtung, Berlin, Germany*
[5]*High Field Magnet Laboratory (HFML-EMFL), Radboud University, Nijmegen, The Netherlands*
[6]*Institut für Physik, Humboldt-Universität zu Berlin, Berlin, Germany*

Magnesium (Mg) atoms in interstitial positions of a silicon host lattice form double donor centers. The binding energy of the neutral Mg^0 state corresponds to midinfrared wavelengths. Due to its interstitial character, the outer orbitals of Mg atoms can form specific bonds with different trace elements in the silicon crystal. These occur as single and double donors that become detectable by infrared spectroscopy when the concentration of either Mg or the dopant coupled to it is sufficiently large. Infrared absorption spectroscopy at high magnetic fields allows us to observe the Zeeman effect of several shallow Mg-related donor complexes and neutral Mg donors, very similar to those observed for hydrogenlike centers. The quadratic Zeeman effect indicates a hydrogenlike center structure of the excited states and spatial localization of complexes with a single excess electron in its outer shell, which are formed by Mg with an impurity atom. In contrast, Mg complexes formed by bonds with two electrons are closer to substitutional double donors in silicon.

I. INTRODUCTION

Shallow impurities in semiconductors determine their electrical and optical properties, whose investigation awakens whenever new dopants or a new semiconductor quality become available. A recent technological breakthrough in silicon (Si) doping with magnesium (Mg) by a diffusion technique [1,2] provided high quality, research grade Si:Mg crystals and enabled a series of important scientific results [3–5] apparently characteristic for many interstitial impurities (X_i), forming centers alternative to those expected to be on their substitutional site (X_s).

In contrast to so called hydrogenlike (H-like) shallow impurities (group-V), with a single electron in the outermost shell of the atom, which therefore do not form covalent bonds to the host lattice atoms, magnesium (Mg, group-IIA) atoms in silicon (Si) have been shown to behave like double donor centers with a binding energy, E_{Mg}, in the neutral Mg^0 state of 107.53 meV [6]. The double donors in silicon, such as the substitutional donors from group VI, are characterized by two electrons in the outermost shell, with wave functions very different in their spatial extension [7,8]. The inner electron screens the extra ionic charge in such a way that the outer electron is in the reduced potential of the ionic nucleus [8]. From this point of view, the outer electron occurs to be in a Coulomb potential of very similar strength to those of single-electron, group-V hydrogenlike donors. As a result, infrared (IR) absorption spectra of neutral Mg^0 are very similar to those of silicon doped by group-V atoms (single donors) [6].

Optical transitions from the even-parity $1s$ ground state into the excited odd-parity p- and f-type states [9] of Mg-doped Si, which are allowed in the electric dipole approximation, have a structure similar to those of H-like donors in silicon [8]. Singly ionized Mg^+ centers and different (Mg, X) complexes reveal similar properties of their absorption spectra [10–12]. A valence electron in the outermost shell of Mg has a relatively small binding energy and tends to form bonds with impurity elements present in the Si crystal. Donor-type electrically active complexes of Mg are formed with both substitutional (X_s) and interstitial (X_i) dopants. Until now, the exact structure of such complexes is not known.

The energy spacing of experimentally observed $1s \rightarrow p$-type impurity transitions has been used for determination of the binding energy of neutral Mg centers and its complexes. These have been compared with the values obtained on the basis of the effective-mass approximation (EMA) [13]. Their binding energy is usually calculated in the same way as for the Mg^0 donor assuming EMA-like excited states, taking into account the energy spacing between specific donor transitions and their relative intensities (Fig. 1). This leads to the conclusion that Mg-related centers have EMA-like excited states and with binding energies ranging between 43 and 117 meV.

This approach, however, could be misleading in the case of centers with weakly expressed features when the number of observed lines is limited by the low concentration of the dopant or if strong interferences with other absorption occur, e.g., when overlapping with lattice absorption bands. Correc-
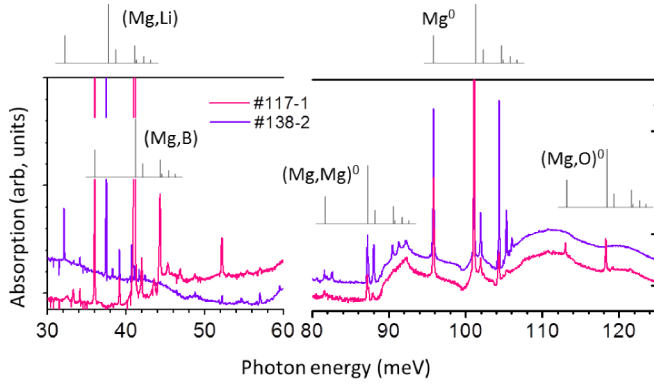
FIG. 1. Typical IR absorption spectra of Si:Mg samples in the range of magnesium-related donor intracenter transitions. Note the identic structure (depicted with insets) of impurity transitions related to single (Mg, *X*) donors (binding energy is below 50 meV) and Mg-related double donors (binding energy is above 90 meV).

tions for the binding energies of a few Mg-related complexes have been made recently using highly doped Si:Mg crystals [3]. Zeeman spectroscopy of impurity transitions provides important complementary information on the structure of the excited states. The Zeeman behavior of impurity transitions under an external magnetic field can prove the H-like structure [14]. At fields below 32 kGs ($B < 3.2$ T) the linear Zeeman effect (LZE) has been reported for Mg^0 center in $B \parallel [111]$ geometry [15]. Additionally, the spatial localization of H-like impurity center (the radius orthogonal to **B**, taken at zero field $B = 0$, ρ_0) can be determined from measurements of the quadratic Zeeman effect using the second derivative of the eigenenergy of the particular state $E(B)$ given by [16]

$$E(B) = E_0 + m\mu_B B + (e\mu_B/4\hbar)\rho_0^2 B^2, \qquad (1)$$

$$d^2E(B)\big/dB^2\big|_{B\to 0} = (e\mu_B/2\hbar)\rho_0^2, \qquad (2)$$

where $\mu_B = 0.2978$ meV/T [16] is the effective Bohr magneton for H-like donors in Si, e is the elementary charge, $\hbar$ is the reduced Plank constant, and m is the magnetic quantum number.

Donor complexes formed in overcompensated Si doped with substitutional shallow-acceptor, group III atoms, $p - \text{Si} : A_s$ have revealed a class of shallow donors (Mg_i, A_s) with binding energies between 47 and 60 meV [4] and line intensities with corresponding interstate energy intervals similar to those of H-like centers in n-Si.

While the (Mg_i^{2+}, A_s^{1-}) paired donors are evident from the charge state point of view, more complex pairings using apparently more than one outer shell electron are not well understood. Here we will briefly summarize the most important complexes following their known elemental abundances rather than their assumed electronic configuration, which remains uncertain to some extent.

A double donor complex ascribed to a (Mg, O) center with a binding energy $E_{(\text{Mg,O})}$ of 124.66 meV [8] is the most frequent one in regular Si:Mg crystals and practically unavoidable due to the large natural abundance of oxygen

in Si. Even in Si grown by the float-zone (FZ) technique, the oxygen concentration typically exceeds 10^{15}cm^{-3} [17]. Since oxygen on an interstitial site dominates in high-quality, defect/vacancy-free Si crystals [18], the (Mg_i, O_i) center is the most probable one in our samples. (Mg, O) center impurity transitions are detectable in IR absorption spectra of samples with either significant oxygen or significant Mg abundance. Neutral Mg^0 centers have a tendency to bind to oxygen on a rather long time scale (in the case of high original oxygen content in the Si crystal). This has been proven by IR spectra measured repeatedly during one year for samples kept at room temperature laboratory conditions. A (Mg, O) center shows oscillator strength and corresponding interstate energy intervals [11] similar to those of H-like centers in n-Si [9].

At moderate Mg concentrations another specific donor center becomes detectable in IR spectra, which has been recently assigned to a Mg complex Mg_{i*} paired with a different atom [3]. The isoelectronic Mg pairing to a substitutional Mg_s (Mg_i, Mg_s) has been proposed to explain the Si:Mg photoluminescence spectral features [19], but has not been confirmed in this configuration after annealing the crystal [20]. The main feature making Mg_{i*} different from multiple double chalcogen donors S_2 and Se_2 observed in Si [21] is the fine splitting (less than 1 meV) of the ground state derived from IR absorption spectroscopy [3]. The energy spacing between high odd-parity states follows, however, those of an H-like dopant.

Magnetospectroscopy of different Si:Mg samples, reported in this paper, is used as a method to resolve some of the open questions related to Si:Mg. We report on the observation of high order Zeeman effect for specific Mg-related complexes (Mg, *X*) in moderately doped (up to Mg^0 concentration of $1.56 \times 10^{15} \text{cm}^{-3}$) Si crystals. The results are compared with those for the neutral atomic Mg^0 donor. It is found that some of the centers have an H-like structure while others do not. The reasons for this are discussed.

II. EXPERIMENTAL

Concentrations of Mg centers above 10^{15}cm^{-3} are desirable for potential photonics applications of Si:Mg [5]. However, preparation of samples with such high concentrations is challenging. Our earlier attempts to dope during the growth of the Si crystal did not provide Mg^0 concentrations above 10^{14}cm^{-3} [22], because of the high volatility of Mg at Si crystal processing temperatures. The crystals used in this study were obtained by high temperature diffusion in a "sandwich" technique, for more details see Ref. [1]. As initial material, FZ grown high-purity Si crystals with a resistivity of $\approx 10^4$ $\Omega \times$ cm (sample #138-2), and boron-doped Si wafers of ≈ 25 $\Omega \times$cm resistivity were (sample #117-1) used, see Table I. Magnesium of purity 99.9995–99.9999% was used as initial material for the doping procedure. To provide the required high homogeneity of doping, both surfaces of the about 2.5-mm-thick central Si wafer were covered by Mg layers by deposition in vacuum. This Si wafer was then "sandwiched" between two other Si wafers and underwent a heating in a sealed quartz ampoule. Most of samples were kept at about $T_{\text{diff}} \sim 1200°\text{C}$ for longer than 1 h followed by rapid cooling of an ampoule with air or nitrogen gas flow at room

TABLE I. Si:Mg samples and their characteristic Mg-related centers.

Mg center type	Sample No.	Sample thickness mm	Mg^0 concentration cm^{-3}	X center concentration cm^{-3}	Binding energy meV	$\rho_0(\Delta\rho_0)$ nm	Donor type	Fig. No.
(Mg,Li)	138-2	2.0	1.5e15	$N_{Li} \sim 3.0e14$	43.78	2.36 (0.10)	H-like	1,5
(Mg,B)	117-1	1.7	7.7e14	$N_B \sim 5.2e14$	47.48	2.35 (0.21)	H-like	1,2,4
				$N_{Li} \sim 2.0e13$				
$(Mg, Mg)^0$	129-1	1.4	1.0e15	$N_B \sim 4.7e14$	94.41	2.21 (0.20)	He-like	6
	138-2	2.0	6.6e15	-				1,6
Mg^0	117-1	1.7	7.7e14	$N_B \sim 5.2e14$	107.53	2.13 (0.10)	He-like	1
	138-2	2.0	1.5e15					1,3
$(Mg, O)^0$	117-1	1.7	7.7e14	$N_O \sim 1e16$	124.60	2.15 (0.11)	He-like	1,7

temperature. The welded auxiliary Si wafers covering a doped sample were then ground off together with the original interface layer. Samples with typical flat areas 10×10 mm^2 and thickness between 0.9 and 2.1 mm were cut from the doped wafers (grown crystals). Finally, the samples were wedged to $1.5°–2°$ and the large facets were optically polished.

Low temperature (~ 5 K) IR absorption spectroscopy was used to characterize the Si:Mg samples. At low temperature electrons occupy the ground state of their impurity centers and absorption spectroscopy resolves discrete transitions of bound electrons from the ground into the excited state of the center. Only dipole-allowed transitions of electrically active donor centers were measured. Impurity absorption spectra (AS) were measured using a Bruker Vertex 80v Fourier transform IR spectrometer equipped with different detectors for the far-infrared (silicon bolometer) and the midinfrared (photoconductive MCT (Mercury-Cadmium-Telluride) and pyroelectric DLaTGS (Deuterated L-α Alanine doped TriGlycine Sulphate) detectors) covering the spectral range from 1 meV to 1 eV (1 mm to 1 μm wavelength). A globar was used as an emission source. The typical spectral resolution was between 0.085 and 0.33cm^{-1} (photon energy of 10–40 μeV). The samples were placed on the cold finger of the Janis ST-100-FTIR Supertran continuous flow cryostat equipped with diamond optical windows. Most of measurements were carried out at 5 K as determined by a temperature sensor on the cold finger nearby the sample.

Magneto-optical absorption spectra (MOAS) were taken in the High Field Magnetic Laboratory (HFML-EMFL) at Radboud University (Nijmegen, The Netherlands) using a Bruker IFS-113v Fourier transform IR spectrometer coupled to the 33 T Bitter magnet system. The MOAS were taken at fields up to 32 T with a step of 0.5–2 T. The samples were glued by FixoGum to the brass aperture inside the cryogenic dipstick of a helium heat exchange gas cryostat. The temperature was measured by a sensor located close to the sample holder and was kept at around 1.5 K. The unpolarized radiation from a globar light source was brought to the sample by a $\sim$5-m-long evacuated beam line. The absorption signal was detected by a Si bolometer with a 175-μm-thick TPX (Polymethylpentene) window located right behind the sample holder in the same cryostat. The MOAS experiments were performed in Faraday geometry: radiation propagates along the magnetic field and along the [001] Si crystal axis. Because of the long

optical path to the magnet and low IR throughput, the spectral resolution was reduced to $0.3 - 1$ cm^{-1} (photon energy 37–124 μeV) in order to increase the signal-to-noise ratio and to reduce the operation time of the magnet at high fields. A linear baseline was subtracted from each transmission spectrum. At each magnetic field 30–50 interferograms were averaged. A median three points smoothing was used to eliminate occasional sharp noise spikes in spectrum. The high homogeneity of the magnetic field in the center of a magnet enables resolution of most strong impurity absorption lines up to the largest magnetic fields (Fig. 2) of 32 T. Some reduction of the intensities with simultaneous broadening of the impurity lines occurred at B of about 24 T where the stability of field becomes slightly disturbed by cavitation in the cooling liquid streams.

III. ABSORPTION SPECTROSCOPY

The low-temperature absorption spectra of the moderately doped Si:Mg samples show features of Mg-related complexes both in the far- and in midinfrared wavelength ranges. (Mg, X) donors with atoms X from the elemental groups I to III have binding energies lower than those of neutral Mg centers, while
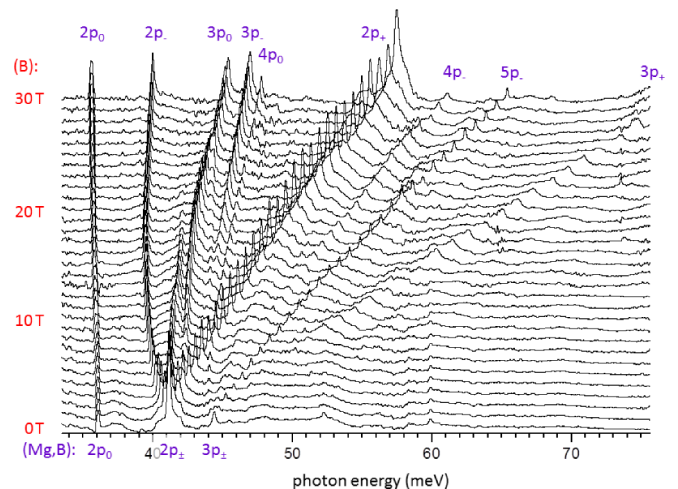

FIG. 2. Typical IR MOAS of Si:Mg in the range of magnesium-boron (Mg, B) intracenter transitions. The step of the magnetic field in the waterfall presentation is 1 T. Note the clear nonlinear Zeeman effect.
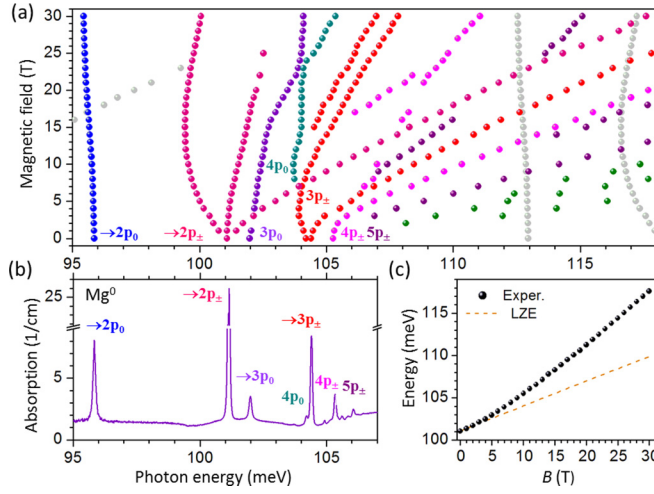
FIG. 3. MOAS (a) and AS (b) spectra of Si:Mg #138-2 sample in the range of neutral magnesium Mg^0 impurity transitions. Colored points present the peak positions of lines assigned to Mg^0 intracenter transitions, grey circles belong to other Mg-related centers. The symbols show the states where the Mg^0 transitions terminate. (c) Experimental dependence of transition $1s(A_1) \rightarrow 2p_+(B > 0)$ energy on magnetic field and LZE as from Eq. (2).

complexes with atoms X from groups larger than Si (IV) occur at higher photon energies. The strongest lines can be assigned to ground state-to-*np* excited state transitions based on their characteristic relative intensities and energy spacings.

A. Neutral Mg^0 donors

The magnetic field dependences of the intense lines [Fig. 3(a)] show Zeeman splitting, such as triple splitting for threefold degenerate triplet $np_\pm$ states, and together with energy spacing and relative line intensity data, confirms unambiguously the type of the excited state where these transitions terminate. The excited Mg^0 states with the main quantum number up to $n = 5$ (only the low-energy component $5p_-$ of the strongest transition in the $2p_\pm$ state) were resolved in the MOAS spectra. Quadratic contributions to the Zeeman effect are clearly visible at B above 3 T. Following the approach developed in Ref. [16], we have used the similarity of the wave functions and eigenenergies of the odd-parity high excited states of a H-like donor (D) to determine the radii relative to the known donor radius of the phosphorus donor in Si, using the B dependences of the corresponding impurity transitions, e.g., $1s(A_1) \rightarrow 2p_\pm$:

$$h\nu_{(P):1s \rightarrow 2p\pm}(B) - h\nu_{(D):1s \rightarrow 2p\pm}(B)$$
$$= (E_{(P):2p\pm}(B) - E_{(P):1s}(B)) - (E_{(D):2p\pm}(B) - E_{(D):1s}(B)), \quad (3)$$

where $h\nu$ is the transition photon energy. Since all H-like donors in Si have a similar structure of the odd-parity high excited states, it is common to calculate the binding energy relative to a particular state, commonly the $3p_\pm$ state [8], assigning its energy to the effective mass theoretical (EMT) value of 3.12 meV [9]. Doing so, it has been shown that most of all other odd-parity, highly excited states of H-like impurities are identical with an accuracy of better than one percent.

For such centers the relation $E_{(P):2p\pm}(B) \cong E_{(D):2p\pm}(B)$ (B) holds, as it has been shown for group-V donors in Si [16]. For such centers (D), the relative B dependences give straightaway the relative center radius, from Eqs. (1)–(3):

$$\rho_{0(P)}{}^2 - \rho_{0(D)}{}^2 = (2\hbar)(e\mu_B)d^2E(B)/dB^2(h\nu_{(D):1s \rightarrow 2p\pm}(B)$$
$$- h\nu_{(P):1s \rightarrow 2p\pm}(B))|_{B \rightarrow 0}, \quad (4)$$

using the value of the radius of phosphorus as $\rho_{0(P)} = 2.24$ nm [16].

Neutral Mg^0 (He-like double donor) transitions are known to show a structure very similar to those of group-V H-like donors (Fig. 3). The quadratic Zeeman effect (QZE) is clearly observed at fields with $B > 3T$. Assuming the validity of the formalism (4) for this specific case we obtain the ground state radius as $\rho_{Mg0} = 2.13 \pm 0.10$ nm.

B. Mg-related complexes

The transitions related to Mg complexes become detectable with increasing Mg content in the samples and with increasing concentration of particular species. For instance, in samples with the largest Mg^0 concentrations ($N_{Mg0} > 1.5e15$ cm^{-3}), some acceptor A_S related pairing is detectable even for residual acceptor abundances, and for moderate acceptor content N_A in originally *p*-type Si:A_S, (Mg, Mg) centers are clearly seen in the AS at any $N_{Mg0} > N_A$.

1. Mg, B complexes

The Si:Mg:B samples with net Mg^0 concentration $N_{Mg0} - N_B > 1e15$ cm^{-3} with the original acceptor boron $N_B \sim (2 - 5)e14$ cm^{-3} show clear sets of transitions in the far-infrared part of AS with the strongest lines having relative intensities and energy spacings similar to the EMA donors in Si [8]. The magnetic field behavior of the intense lines confirms the type of excited states, where these transitions terminate, for most of np_0, $np_\pm$ excited states [Fig. 4(a)].

The binding energy of the (Mg, B) center in Si is $E^{(Mg,B)} = 47.48$ meV [4]. In Fig. 4(c) we plot the energy difference of the transitions $1s(A_1) \rightarrow 2p_+(m = +1, B > 0)$ and $1s(A_1) \rightarrow 2p_-(m = -1, B < 0)$ of the (Mg, B) donor relative to the same transitions of the phosphorus donor in Si, $\Delta E_{\rightarrow 2p\pm}(B) = (E^{(Mg,B)}(B) - E^{(P)}(B))$ assuming (Mg, B) centers to be H-like. The small negative second derivative of this $\Delta E_{\rightarrow 2p\pm}(B)$ [Fig. 4(c)] indicates the validity of this assumption with a slightly larger transverse radius of the (Mg, B) center $\rho_{(Mg,B)} = 2.35 \pm 0.21$ nm, very similar to those of H-like donors in Si with similar binding energy [14]. Note that the radii of these centers relate as $\rho_{Mg0} < \rho_{(Mg,B)}$, while binding energies $E^{(Mg0)} > E^{(Mg,B)} > E^{(B)}$ [4,8].

2. Mg, Li complexes

Another set of transitions, which behaves similarly to a H-like donor with a binding energy of 43.87 ± 0.02 meV, could be identified in the AS and MOAS spectra [Figs. 5(a) and 5(b)] of the n-Si:Mg samples with both Li and Mg^0 concentrations exceeding 10^{14} cm^{-3}. The concentration of Li, which occurs as an interstitial donor in Si, has been estimated using the integrated absorption values of the corresponding AS and optical cross section of Li low-energy intracenter
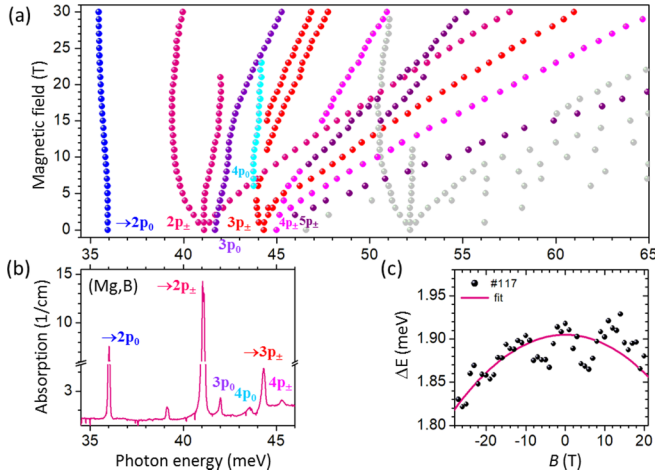
FIG. 4. MOAS (a) and AS at $B = 0T$ (b) spectra of Si:Mg:B sample #117-1 in the energy range to the (Mg, B) donor transitions. Other notations are the same as in Fig. 3. (c) Dependence of the energy difference $\Delta E_{\to 2p\pm} (B) = (E^{(Mg,B)} (B) - E^{(P)} (B))$ of the $1s(A_1) \to 2p_+(m = +1, B > 0)$ and $1s(A_1) \to 2p_-(m = -1, B < 0)$ transitions on the magnetic field for a (Mg, B) donor relative to a phosphorus donor (Si:P).

transitions, derived from the AS spectra as in Ref. [8]. It was not observed in the MOAS of the n-Si:Mg:B samples predoped either with B or with other compensating acceptors [4]. We assign this Mg-related center to a (Mg, Li) donor center. The ground state radius of the (Mg, Li) center, calculated as described above [cf. Fig. 5(c)], yields a value of $\rho_{(Mg,Li)} = 2.36 \pm 0.10$nm, which again is very similar to those of H-like donors in Si with similar binding energy [16]. Note that the radii of these interstitial centers relate as $\rho_{Mg0} < \rho_{(Mg,Li)} <$
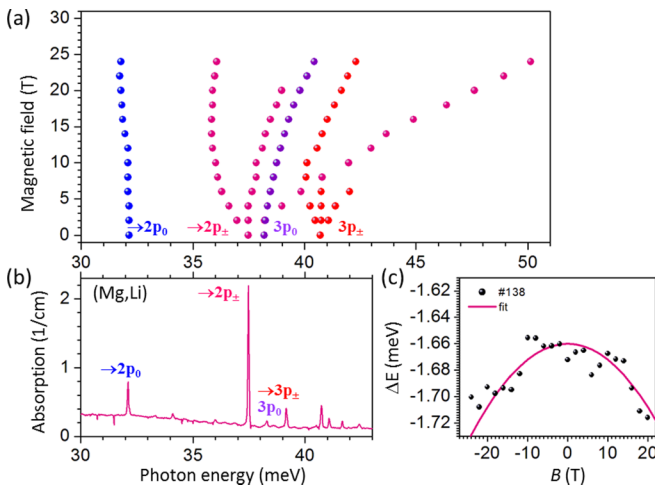

FIG. 5. MOAS (a) and AS (b) of Si:Mg #138-2 sample in the range of transitions of magnesium complex assigned preliminary to a (Mg,Li) donor. Other notations are the same as in Fig. 3. (c) Dependence of energy difference $\Delta E_{\to 2p\pm}(B) = (E^{(Mg,Li)} (B) - E^{(P)}(B))$ of $1s(A_1) \to 2p_+(m = +1, B > 0)$ and $1s(A_1) \to 2p_-(m = -1, B < 0)$ transitions for a (Mg,Li) donor relative to a phosphorus center, on magnetic field.
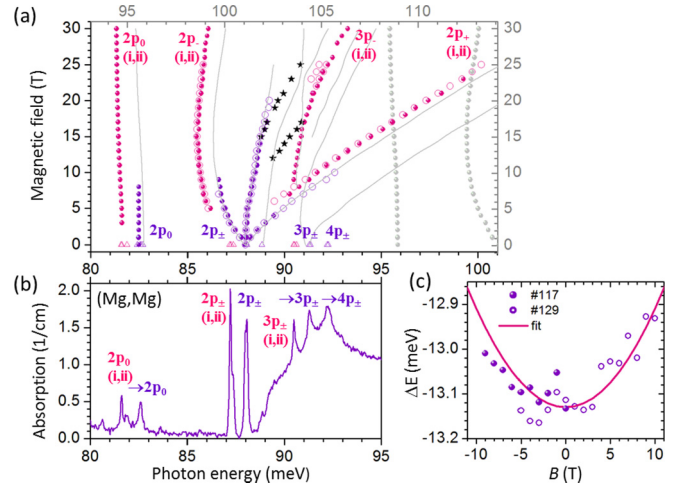

FIG. 6. (a) MOAS spectra of Si:Mg #117-1 (solid circles) and Si:Mg #129-1 (open circles) samples in the range of transitions of diatomic magnesium (Mg,Mg) donor. Notations (i,ii) indicate the transitions from thermally populated split-off-ground state. Triangles (a) shows the positions of the (Mg,Mg) transitions taken from high resolution AS spectra [3]. Stars mark the transitions which cannot be assigned to the QZE of the EMT donor. Solid grey lines are field dependences of similar transitions of Mg^0 center, the energy scale is shifted by the value of binding energy difference, energy scale for the Mg^0 center shown on the top axis of the plot (a). Other notations are the same as in Fig. 3. (b) AS spectra of Si:Mg #138-2 sample. (c) Dependence of energy difference $\Delta E_{\to 2p\pm} (B) = (E^{(Mg,Mg)} (B) - E^{(Mg0)}(B))$ of $1s(A_1) \to 2p_+(m = +1, B > 0)$ and $1s(A_1) \to 2p_-(m = -1, B < 0)$ transitions for a (Mg, Mg) donor relative to a Mg^0 center, on magnetic field.

$\rho_{(Li)}, \rho_{(Li)} = 3.31 \pm 0.05$nm [23], while the binding energies relate as $E^{(Mg0)} > E^{(Mg,Li)} > E^{(Li)}, E^{(Li)} = 33.999$ meV [8].

3. Mg, Mg donors

A series of transitions related to the (Mg, Mg) donor shows a very specific magnetic field dependence. As it was shown in Ref. [3], this center has a different symmetry than other known shallow donors in Si (T_d group), having large central cell corrections separating the ground singlet state from its doublet and triplet 1s components. A relatively small splitting of the (Mg, Mg) ground state, less than 1 meV, results in significant thermal population of the split off states even at low lattice temperature (as observed at 2 K [3]), and as a consequence, in a multiple line structure of the impurity transitions. Also the high excited states exhibit fine splitting, which is, however, not resolved in our experiments. The well spaced (Mg, Mg) lines (energy difference of 0.72 and 0.83 meV) show clear features in the Zeeman spectra [Fig. 6(a)]. The intensities of absorption lines originating from the ground state and the split-off ground state have opposite evolvement: It grows with the B field for the split-off states (high degeneracy) while it decays for the singlet ground state.

Comparison of the $E^{(Mg,Mg)}(B)$ QZE dependences with those for phosphorus (group-V, single electron, H-like donor)

and similarly with a Mg^0 center (group-IIa, double, He-like donor) gives large positive values, e.g., to Mg^0 [Fig. 6(c)]:

$$(2\hbar)/(e\mu_B)d^2E(B)/dB((E_{(Mg,Mg):2p\pm}(B) - E_{(Mg,Mg):1s}(B)) - (E_{(D):2p\pm}(B) - E_{(D):1s}(B)))|_{B\to 0}$$
$$= (\rho_{0(Mg,Mg):2p\pm}^2 - \rho_{0(Mg,Mg):1s}^2) - (\rho_{0(D):2p\pm}^2 - \rho_{0(D):1s}^2) = 9.79 \text{ nm}^2 (D \equiv Mg^0) \quad \text{and} \quad 8.801 \text{nm}^2 (D \equiv P).$$

The assumption in the frame of the EMT that the field dependences of the (Mg, Mg) donor transition in the 2p± state are equal to the same odd-parity state of a shallow donor (*D*), $E_{(Mg,Mg):2p\pm}(B) = E_{(D):2p\pm}(B)$, would lead to $\rho_{0(Mg,Mg)}^2 < 0$. Obviously, the EMT formalism for H-like donors [Eq. (3)] is not applicable anymore and cannot be used for calculation of the state localization using the QZE. This is despite the fact that the binding energies of high excited state are almost equal ($E_{2p\pm}^{(Mg,Mg)} \cong E_{2p\pm}^{(Mg0)} \cong E_{2p\pm}^{(P)} \cong 6.388 \pm 0.019$meV) and the relative level spacings still fit well (~3%) to those of the EMA donors. Using the radii relation of the H-like phosphorus donor, $\rho_{0(P):2p\pm}^2 - \rho_{0(P):1s}^2$ [16], one can roughly estimate the relation for a (Mg, Mg) center such as $\rho_{0(Mg,Mg):2p\pm}^2 - \rho_{0(Mg,Mg):1s}^2 = 167 \pm 1$ nm^2. This is only valid for the slightly extended localization of the excited state of the center since the radius of the ground state does not influence so much in their difference relation (Fig. 7).

The transitions that presumably involve overlap of (Mg, Mg) pairs with the lattice three-phonon band are hardly resolved in the Zeeman spectra and are not shown in Fig. 6(a). A few distinct lines resolved at higher field, cannot be associated with the (Mg, Mg) donor transitions at zero field.

4. Mg, O complexes

Impurity transitions of the (Mg, O) center are shown in Fig. 7. This center is very likely formed by coupling of Mg to Si-O-Si bonds of interstitial O, having two bonds replacing a Si = Si covalent bond [24]. Mg-O coupling was found to be very favorable and sometimes these centers become detectable after Mg diffusion in high purity FZ grown Si. In such a sample no characteristic O lines were detected by IR absorption spectroscopy. The QZE has mostly expressed asymmetry for different magnetic quantum numbers [Fig. 7(c)]. We assume that this is due to large contributions from the higher order Zeeman effect. We made separate estimations of the transverse radius for $m = \pm 1$. The center ground state radius derived from the QZE as described above [Fig. 7(c)] using the ρ_{Mg0} gives values for $\rho_{(Mg,O)m=+1} = 2.50 \pm 0.11$nm, $\rho_{(Mg,O)m=-1} = 2.18 \pm 0.10$nm. We assume that overestimation could infer from the above-mentioned Zeeman effect feature, and chose the smaller value to present the (Mg, O) localization in the plot in Fig. 8. Both of these radii are larger than those for the Mg^0 center, while the local vibration mode energy of oxygen in Si, the binding energies of (Mg,O) and Mg^0 center relate as $E^{(O)} > E^{(Mg,O)} > E^{(Mg0)}$, $E^{(Mg,O)} = 124.6$ meV, $E^{(Mg,O)} = 124.6$meV [8].

Specific features of the double donors: asymmetry of (Mg, O) on m_j, and specific evolution/exchange of ground state in the observed transitions of (Mg, Mg) may relate to occurrence of non-negligible contributions of high order Zeeman effect ($n > 2$ in the $\sim B^n$ field energy perturbations), including next, the third-order Zeeman effect whose contributions in
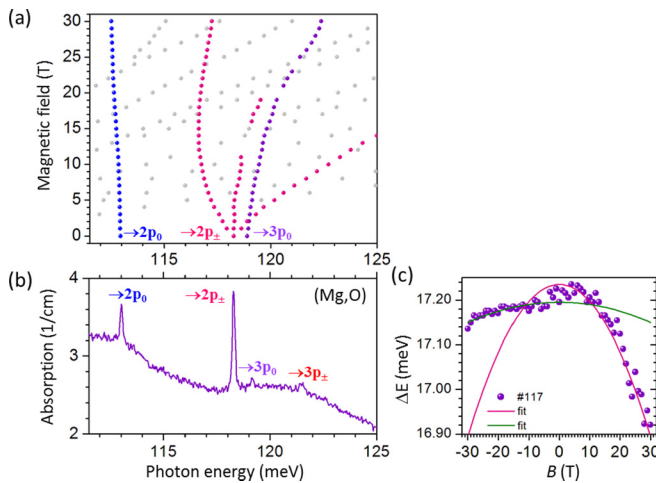

FIG. 7. (a) MOAS and (b) AS of the Si:Mg #117-1 sample in the spectral range of (Mg, O) donor transitions. Other notations are the same as in Fig. 3. (c) Dependence of the energy difference $\Delta E_{\to 2p\pm}(B) = (E^{(Mg,O)}(B) - E^{(Mg0)}(B))$ of $1s(A_1) \to 2p_+ (m = +1, B > 0)$ and $1s(A_1) \to 2p_- (m = -1, B < 0)$ transitions for a (Mg,O) donor relative to the Mg^0 center on the magnetic field.
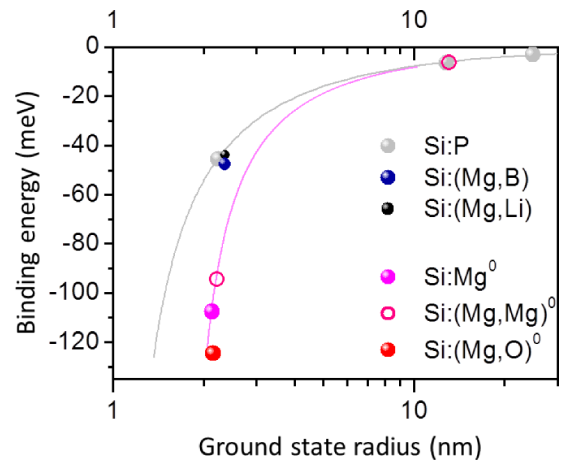

FIG. 8. State radii derived from the QZE spectra for different Mg-related complexes in comparison with a phosphorus H-like donor. The smaller of the (Mg,O) ground state radii is shown. The solid lines are approximates for single and double donors.

eigenenergies are odd in angular momentum projection. In this case evolution of impurity lines would follow the particular efficiency (expressed in factors for the B^n field, n- Zeeman effect order) of the Zeeman splitting, which is different, for instance for $2p_{3/2}$ and $2p_{1/2}$ orbitals [25] expressed in the $2p_{\pm}$ states of donors.

5. Other Mg, X complexes

There were a few more (Mg, X) shallow donors observed in the AS and MOAS. They all show a similar QZE behavior as group-V donors in Si. However, the weak line intensities in MOAS make an accurate estimate of the center's ground state radii difficult.

The ground state radii for different centers are summarized in Fig. 8. One can see that centers consisting of interstitial Mg and atoms providing a single electron to be paired with Mg_i, behave similar as the hydrogenlike phosphorus (group-V) center in Si. Pairing of Mg with atoms providing two electrons form centers with larger spatial localization of a donor state.

IV. SUMMARY

To summarize, the magneto-optical study of intracenter transitions of Mg-related complexes in Si provides important information on the structure of the state and localization of

this dopant. This can be used to distinguish between H-like and He-like, single and double donor centers. Calculations of the Mg-complex' ground state radii were made on the basis of the magnetic field dependences in the range of the quadratic Zeeman effect. Shallow impurity (Mg, X) centers, using a single outer/excess electron of atom X, either interstitial or substitutional, for forming the bond to interstitial Mg_i, behave similar to that of H-like donors. Pairing with another Mg atom (Mg, Mg) or O atom (Mg, O), forms complexes with a spatial localization more similar to those of He-like Mg double donor centers, and therefore, shares apparently two valence electrons. Our results provide valuable insight for understanding the bonding structure of Mg-related and similar interstitial impurity centers in cubic semiconductors.

[1] Yu. A. Astrov, V. B. Shuman, L. M. Portsel, A. N. Lodygin, S. G. Pavlov, N. V. Abrosimov, V. N. Shastin, and H.-W. Hübers, Diffusion doping of silicon with magnesium, Phys. Status Solidi A **214**, 1700192 (2017).

[2] V. B. Shuman, A. A. Lavrent'ev, Yu. A. Astrov, A. N. Lodygin, and L. M. Portsel, Diffusion of interstitial magnesium in dislocation-free silicon, Semiconductors **51**, 1 (2017); V. B. Shuman, Yu. A. Astrov, A. N. Lodygin, and L. M. Portsel, High-temperature diffusion of magnesium in dislocation-free silicon, *ibid.* **51**, 1031 (2017).

[3] R. J. S. Abraham, A. DeAbreu, K. J. Morse, V. B. Shuman, L. M. Portsel, A. N. Lodygin, Yu. A. Astrov, N. V. Abrosimov, S. G. Pavlov, H.-W. Hübers, S. Simmons, and M. L. W. Thewalt, Further investigations of the deep double donor magnesium in silicon, Phys. Rev. B **98**, 045202 (2018).

[4] R. J. S. Abraham, V. B. Shuman, L. M. Portsel, A. N. Lodygin, Yu. A. Astrov, N. V. Abrosimov, S. G. Pavlov, H.-W. Hübers, S. Simmons, and M. L. W. Thewalt, Shallow donor complexes formed by pairing of double-donor magnesium with group-III acceptors in silicon, Phys. Rev. B **99**, 195207 (2019).

[5] V. N. Shastin, R. Kh. Zhukavin, K. A. Kovalevsky, V. V. Tsyplenkov, V. V. Rumyantsev, D. V. Shengurov, S. G. Pavlov, V. B. Shuman, L. M. Portsel, A. N. Lodygin, Yu. A. Astrov, N. V. Abrosimov, J. M. Klopf, and H.-W. Hübers, Chemical shift and exchange interaction energy of the 1s states of magnesium donors in silicon: The possibility of stimulated emission, Semiconductors **53**, 1234 (2019).

[6] L. T. Ho and A. K. Ramdas, Excitation spectra and piezospectroscopic effects of magnesium donors in silicon, Phys. Rev. B **5**, 462 (1972).

[7] E. Janzen and H. G. Grimmeiss, The localisation of donor electrons in multivalley split 1s states for group V and VI donors in silicon, J. Phys. C **15**, 5791 (1982).

[8] B. Pajot, *Optical Absorption of Impurities and Defects in Semiconducting Crystals: I. Hydrogen-like Centres* (Springer, Berlin, 2010).

[9] R. A. Faulkner, Higher Donor Excited States for Prolate-Spheroid Conduction Bands: A Reevaluation of Silicon and Germanium, Phys. Rev. **184**, 713 (1969).

[10] L. T. Ho, Higher donor excited states for prolate-spheroid conduction bands: A reevaluation of silicon and germanium multiple neutral and singly ionized magnesium donors in silicon, Phys. B **376–377**, 154 (2006).

[11] L. T. Ho, Magnesium-oxygen complex impurities in silicon, Phys. Status Solidi C **210**, 313(1998).

[12] L. T. Ho, Infrared Absorption Spectrum of Magnesium Double Donors in Silicon, in *Proceedings of the Joint 30th International Conference on Infrared and Millimeter Waves and 13th International Conference on Terahertz Electronics*, 19–23 September, 2005 (Williamsburg, Virginia, USA, 2005), Vol. 1, pp. 170-171.

[13] A. L. Thilderkvist, M. Kleverman, and H. G. Grimmeiss, Interstitial Mg double donor in Si, Phys. Rev. B **49**, 16338 (1994).

[14] B. N. Murdin, J. Li, M. L. Y. Pang, E. T. Bowyer, K. L. Litvinenko, S. K. Clowes, H. Engelkamp, C. R. Pidgeon, I. Galbraith, N. V. Abrosimov, H. Riemann, S. G. Pavlov, H.-W. Hübers, and P. G. Murdin, Si:P as a laboratory analogue for hydrogen on high magnetic field white dwarf stars, Nat. Commun. **4**, 1469 (2013).

[15] L. T. Ho, Zeeman effect of the excitation spectrum of neutral magnesium donors in silicon, Phys. Status Solidi B **81**, K99 (1977).

[16] J. Li, N. H. Le, K.Litvinenko, S. K. Clowes, H. Engelkamp, S. G. Pavlov, H.-W. Hübers, V. B. Shuman, L. M. Portsel, A. N. Lodygin, Yu. A. Astrov, N. V. Abrosimov, C. R. Pidgeon, A. Fisher, Z. Zeng, Y.-M. Niquet, and B. N. Murdin, Radii of Rydberg states of isolated silicon donors, Phys. Rev. B **98**, 085423 (2018).

[17] R. Jakiela, A. Barcz, J. Sarnecki, and G. K. Celler, Ultrahigh sensitivity SIMS analysis of oxygen in silicon, Surf. Interface Anal. **50**, 729 (2018).

[18] P. Broqvist, A. Alkauskas, J. Godet, and A. Pasquarello, First principles investigation of defect energy levels at semiconductor-oxide interfaces: Oxygen vacancies and hydrogen interstitials in the Si–SiO2–HfO2 stack, J. Appl. Phys. **105**, 061603 (2009).

[19] R. J. S. Abraham, A. DeAbreu, K. J. Morse, V. B. Shuman, L. M. Portsel, A. N. Lodygin, Yu. A. Astrov, N. V. Abrosimov, S. G. Pavlov, H.-W. Hübers, S. Simmons, and M. L. W. Thewalt, Mg-pair isoelectronic bound exciton identified by its isotopic fingerprint in ^{28}Si, Phys. Rev. B **98**, 205203 (2018).

[20] L. M. Portsel, V. B. Shuman, A. A. Lavrent'ev, A. N. Lodygin, N. V. Abrosimov, and Yu. A. Astrov, Investigation of the magnesium impurity in silicon, Semiconductors **54**, 393 (2020).

[21] E. Janzen, R. Stedman, G. Grossmann, and H. G. Grimmeiss, High-resolution studies of sulfur- and selenium-related donor centers in silicon, Phys. Rev. B **29**, 1907 (1984).

[22] N. V. Abrosimov, N. Nötzel, H. Riemann, K. Irmscher, S. G. Pavlov, H.-W. Hübers, U. Böttger, P. M. Haas, N. Drichko, and M. Dressel, Silicon doped with lithium and magnesium from the melt for terahertz laser application, Solid State Phenom. **131-133**, 589 (2008).

[23] J. Li, K. Litvinenko, S. K. Clowes, E. Bowyer, H. Engelkamp, S. G. Pavlov, H.-W. Hübers, V. B. Shuman, L. M. Portsel, A. N. Lodygin, Yu. A. Astrov, N. V. Abrosimov, C. R. Pidgeon, and B. N. Murdin (unpublished).

[24] M. Stavola, Infrared spectrum of interstitial oxygen in silicon, Appl. Phys. Lett. **44**, 514 (1984).

[25] A. S. Varentsova, V. A. AgababaevA. M. Volchkova, D. A. Glazov, A. V. Volotka, V. M. Shabaev, and G. Plunien, Third-order Zeeman effect in highly charged ions, Nucl Instrum. Methods Phys. Res. B **408**, 80 (2017).