

Interstitial magnesium double donor in silicon

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High-resolution Fourier spectroscopy combined with perturbation techniques such as Zeeman spectroscopy and uniaxial stress have been used to study the electronic structure of the interstitial magnesium double donor in silicon. In tetrahedral interstitial positions, the two charge states Mg^0 and Mg^+ have binding energies of 107.51 and 256.68 meV, respectively. Their electronic structure can be described as a solid-state analog of the helium atom in its neutral and singly positively charged states, respectively. Interesting deviations in the binding energies of the excited states from those calculated within the effective-mass approximation (EMA) were found which have not been observed previously, to the best of our knowledge, for any similar system. These deviations are explained by a perturbation in the central-cell region that does not only affect the localized $1s(A_1)$ ground state but also the delocalized shallow-donor-like excited states. We focus especially on these deviations from EMA and the split $np_{\pm}$ states of Mg^+ and find that the local potential has a radius comparable with that for the central cell.

I. INTRODUCTION

In silicon, the group-II element magnesium gives rise to several different centers with energy levels in the band gap.¹⁻⁶ Atomic magnesium has a $[\text{Ne}]3s^2$ configuration, and the electronic behavior can tentatively be inferred by simple bonding arguments. Mg is thus expected to act as a double acceptor on a substitutional site, since two extra electrons are needed to complete the covalent bonds with the Si neighbors. On the interstitial site no bonding takes place, and a double-donor center is accordingly expected. Experimental evidence for both types of centers has been reported.¹⁻⁶ Excitation spectra of the neutral and singly positively charged versions of the double donor have been observed which enable a clear identification of the interstitial center.² The identification of the double-acceptor center is less certain, although both experimental⁶ and theoretical⁷ results have given strong evidence for its existence. In this work we focus our attention exclusively on the electronic structure of the interstitial Mg double-donor center.

Magnesium on the interstitial lattice site can exist in three different charge states: the neutral state Mg^0 and the singly positive and doubly positive charged states, Mg^+ and Mg^{2+} , respectively. The ionization energies of the neutral and singly ionized states deduced from absorption spectroscopy¹⁻³ are 107.5 and 256.7 meV, respectively.

In silicon, several double-donor systems have been studied extensively, and their energy-level structure is well understood. Examples of such systems are the single substitutional chalcogens S, Se, and Te,⁸⁻¹⁰ and, to some extent, also the Mg donor. In the case of the chalcogen double donors, two potentials with different spatial extensions have been assumed to be responsible for the bound states in the band gap. The first one is the central-cell potential, which is only effective in the central-cell region, and which almost exclusively determines the properties of the ground state. The second one is the Coulomb po-

tential, which determines the excited states. The wave functions of the excited states are delocalized. Hence in a first approximation, the excited states are generally only slightly perturbed by the central-cell potential, and this is particularly the case for the $L \geq 1$ states, having a node at the origin. The excited states are therefore expected to be well described within the effective-mass approximation (EMA), which also has been verified experimentally. When neutral, these double-donor systems form the solid-state analog of the helium atom, and one would expect that interaction between the two bound electrons will give rise to a heliumlike energy spectrum. However, it is important to note that the excitation spectra are due to optical excitation of one of the electrons in the ground state to the manifold of excited states. The final states in the transitions are thus characterized by two electrons with wave functions which are considerably different in their spatial extensions. Therefore, many-particle effects are generally small and have hitherto only been experimentally detected⁹ when the excited electron occupies one of the s states, which are the only states that have wave functions which are nonzero at the origin. The observed spectra are almost identical to that for a single donor, which implies an almost perfect screening by the inner electron remaining in the one-particle ground state. The EMA also correctly accounts for the energy-level structure of the singly ionized double donors, and in this case the binding energies for various excited states are increased by a factor of 4 ($Z=2$) compared to those for a single donor.

The silicon conduction-band minima have cylindrical symmetry and, compared to the spherical symmetric hydrogen problem, only m_L and parity remain good quantum numbers. The EMA states are labeled ns , np_0 , $np_{\pm}$, . . . , where n is the principal quantum number and states with the same $|m_L|$ are degenerate as, e.g., the $np_{\pm}$ states. Silicon has six equivalent conduction-band minima, which has the effect that all EMA states are at least sixfold degenerate. This degeneracy is partly lifted by the

valley-orbit and central-cell interactions and, e.g., in tetrahedral (T_d) symmetry all ns states are split into $ns(A_1)$, $ns(E)$, and $ns(T_2)$, which are onefold, twofold, and threefold degenerate, respectively. In the case of the chalcogens, the $1s(A_1)$ state is the ground state, whereas the $1s(E)$ and $1s(T_2)$ states are found close to the $1s$ EMA energy. In these cases, the $1s(A_1)$ state shows little or no resemblance to the EMA $1s$ state and the notation only serves as a symmetry label. Electric-dipole transitions between the states in the $1s$ manifold are EMA forbidden. However, this selection rule is relaxed when the EMA fails to describe the ground state, and the symmetry-allowed transition $1s(A_1)-1s(T_2)$ becomes visible in an excitation spectrum. Such EMA-forbidden transitions have been observed for, e.g., the chalcogens for which the $1s(A_1)-1s(T_2)$ transition give rise to one of the strongest absorption lines.^{8,10} Uniaxial-stress spectroscopy on the Mg donor² has shown that the ground state is $1s(A_1)$, and in this case the $1s(E)$ and $1s(T_2)$ states are expected to be found close to their EMA energies. No $1s(A_1)-1s(T_2)$ line has so far been observed for Mg^0 or Mg^+ . This observation forms an interesting difference between a typical chalcogen spectrum and that for Mg.

Yet another interesting feature, so far only reported for Mg^+ in silicon,² is the splitting of the $2p_{\pm}$ line into two components. In this paper we show that the effect is caused by a perturbation with an effective radius comparable to that of the central cell. It is believed that this perturbation also accounts for the marked increase of the binding energy of all p states. By considering that the s states are considerably more localized in the central-cell region compared to the p states, an even larger energy shift from the EMA values may therefore be inferred for the s states.

For a better understanding of these interesting properties, a comprehensive study of the Mg double donor has been performed, and the results presented here are discussed in detail. The investigations have been carried out by means of absorption spectroscopy. Perturbation techniques, i.e., uniaxial stress and magnetic field (Zeeman spectroscopy), have been employed in order to gain further information about the electrical properties of the Mg^0 and Mg^+ centers.

II. EXPERIMENTAL DETAILS

Mg was incorporated into the Si samples by diffusion using the sandwich technique.^{1,2} Two different float-zone silicon substrates were used: p -type boron and n -type phosphorus doped with resistivities of 14 and 40 Ω cm, respectively. The silicon substrates were polished, cleaned, and boiled in HNO_3 at 120°C for 10–25 min and then etched in HF for approximately 2 min. Magnesium was thereafter evaporated on both sides of the samples. In order to prevent the Mg from escaping into the ambient during diffusion, the Mg layers on the samples had to be covered by slices from high-purity epitaxial silicon wafers. The epitaxial wafers underwent the same cleaning procedure as the silicon samples, and Mg was evaporated onto the epitaxial side of the slices before they

were clamped to the Si samples with quartz clamps. The silicon sample, sandwiched between two slices of epitaxial wafers, were put in a quartz ampoule in a 200-mbar argon atmosphere, and the diffusion was carried out at a temperature of 1250°C from 11 to 24 h. The samples were then quenched to room temperature in diffusion pump oil. After quenching, the silicon wafers and the evaporated Mg were removed from the samples by polishing. For the stress experiments, p -type samples were used and cut into bars $2 \times 2 \times 8$ mm³ in the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions. In the Zeeman experiments both n - and p -type samples were used. The n -type samples had a somewhat different geometry, $4 \times 2 \times 8$ mm³.

The spectra were recorded with a BOMEM DA.03 Fourier-transform infrared spectrometer, and for all transmission measurements a helium-cooled Ge:Cu photoconductive detector was used. Stress measurements were performed with the samples mounted in a stress rig. Uniaxial stress was applied via a pushrod, and pressurized air onto the sample contained in a Leybold helium flow cryostat. The stress spectra were recorded at 10 K. Zeeman experiments were carried out with an Oxford superconducting spectromagnet with a split-coil magnet used in the Voigt configuration. The sample was kept in a helium bath, and the temperature was held below the λ point by pumping above the helium surface. The maximum field used was 6.1 T.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Zero-field data

The excitation spectra due to bound-to-bound transitions for both the Mg^0 and Mg^+ centers have been studied by high-resolution transmission spectroscopy. Figure

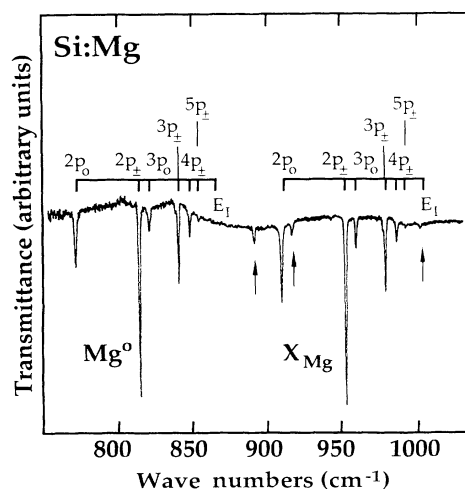


FIG. 1. The transmittance spectrum of Mg-doped silicon in the energy range 750–1050 cm⁻¹. Two series of transitions to shallow-donor-like states are observed. The labeling of the lines is according to the EMA. The series at low energy are identified as excitation of the neutral charge state of Mg. The origin of the series at higher energy is believed to be magnesium related and the arrows indicate unidentified lines (see text for details).

1 shows the absorption spectrum of magnesium-doped n -type silicon in the energy range 750–1050 cm^{-1} (93–130 meV). We readily identify two typical shallow-donor spectra for a neutral center by noting their close similarity with, e.g., that of phosphorus, regarding both the relative intensity and the energy spacings of the lines. A comparison with previous results reported by Ho and Ramdas² lead us to attribute the one at lower energy to Mg^0 . The lines have been labeled in accordance with the final state of the excited electron. The line spectrum at somewhat higher energies is labeled X_{Mg} , and is believed to be related to Mg though its constituents remain unknown.

In Table I the excitation energies for Mg^0 are listed and compared to those reported in Ref. 2. Agreement between the results in this work and those reported in Ref. 2 is excellent; only minor differences (less than 0.03 meV) are observed. When calculating the ground-state binding energy, the theoretical binding energy of one of the p states is added to the corresponding observed transition energy. The $3p_{\pm}$ state is often chosen since it gives rise to an intense line; by considering its small probability to be found in the central-cell region, its binding energy is expected to be very close to the EMA value. However, we use the $4p_{\pm}$ state for reasons which will become clear when discussing the Mg^+ spectrum. In this way we obtain a binding energy equal to 107.51 meV, in agreement with the previously reported² value of 107.50 meV. The listed EMA energies in Table I are taken from Ref. 10. The EMA predicts a ground-state binding energy of 31.27 meV,¹⁰ which is about a factor of 3 smaller compared to the value obtained here. Taking the many-particle effects into account, Ho and Ramdas² employed the analogy between Mg^0 and atomic helium, and estimated a binding energy of 56.24 meV for the Mg^0 ground state. This value is about half the experimental one and to explain this deviation additional effects have to be considered which, e.g., are caused by the central-cell potential.

The Mg^0 center should resemble a heliumlike center.

TABLE I. The experimental excitation energies E_{expt} (in meV) for Mg^0 are listed and labeled according to the final state of the excited electron; see Fig. 1. They are compared to those obtained by Ho and Ramdas (Ref. 2) labeled $E^{(a)}$. E_{EMA} is the EMA-predicted binding energies of the shallow donor states (Ref. 10). E_B is the experimental binding energy calculated by using the $4p_{\pm}$ EMA energy as reference; see text for details. The last column shows the deviations δ of the experimental energies from those predicted by the EMA.

Mg^0	E_{expt}	$E^{(a)}$	E_{EMA}	E_B	δ
$2p_0$	95.81	95.80	11.492	11.70	+0.20
$2p_{\pm}$	101.12	101.12	6.402	6.39	−0.01
$3p_0$	101.97	101.95	5.485	5.54	+0.06
$4p_0$	104.17	104.17	3.309	3.34	+0.03
$3p_{\pm}$	104.38	104.38	3.120	3.13	+0.01
$4p_{\pm}$	105.32	105.33	2.187	2.19	±0
$5p_{\pm}$	106.08	106.05	1.449	1.43	−0.02

Binding energy (Si:Mg⁰) = 107.51 meV

The ground state has the configuration $1s(A_1)^2$ and a total spin of $S=0$. Two series of excited states may thus be obtained, one series with $S=0$ and one with $S=1$. Spin is a good quantum number as long as the spin-orbit (so) interaction is too weak to mix the two series of excited states. The so interaction is expected to be weak for lighter elements, such as Mg. The electric-dipole operator cannot flip the spin, and we have to conclude that the Mg^0 spectrum is due to excitation from the $S=0$ ground state to the $S=0$ series of excited states. Disregarding the $2p_0$ states, the binding energy of the excited states for Mg^0 and X_{Mg} are in excellent agreement with the EMA values for a single donor. In the case of Mg^0 , the perfect agreement between the observed energy spacings and the EMA energies shows that the inner electron almost perfectly screens one charge from the nominal nuclear charge of two. The conclusions that could be drawn from these observations are the following: First, the remaining electron in the ground state is considerably more localized than predicted by the EMA. Second, the overlap between the two electrons is small and, hence, the exchange splitting between the $S=0$ and 1 series is negligible. It should be pointed out that if, e.g., the excited electron resides in a $ns(A_1)$ state ($n > 1$), a substantial splitting between the two series may occur. However, only excitations to p -like states have hitherto been observed. The observed binding energy for the $2p_0$ state is increased by about 0.2 meV compared to the EMA value. Although a small energy difference, it is rather large compared to energy deviations observed for the $2p_0$ state of the single substitutional chalcogen double donors, which presumably have considerably stronger central-cell potentials as shown by their larger binding energies. The origin of the increased binding energy of the $2p_0$ state will be discussed further below in conjunction with our findings for the Mg^+ center.

The relative intensities of the Mg^0 lines and that for, e.g., the shallow-donor phosphorus is very similar. This observation indicates that the electric-dipole matrix elements are similar, which at first glance would imply that the $1s(A_1)$ wave function is EMA-like. However, this would not be in line with our findings above. An obvious solution to this apparent disagreement is found by considering the large spatial extension and the node at the origin of the excited p -like states. The size of the optical matrix elements is not determined by the overlap in the central-cell region between the two electron states, but by the overlap much further out from the origin. It is therefore reasonable to assume that the $1s(A_1)$ wave function has a localized part more or less exclusively determined by the central-cell potential, and a delocalized part similar to the $1s$ EMA state. The ground-state energy would then be determined by the localized part, whereas the optical matrix elements are determined by the delocalized $1s$ EMA-like part.

The X_{Mg} lines are observed in most of our magnesium-diffused samples, although with different intensity relative to the Mg^0 lines. We therefore tentatively assign these lines as due to a Mg-related donor center. The observed transition energies are listed in Table II together with calculated and theoretical binding energies. Follow-

TABLE II. The experimental excitation energies (in meV) for the unidentified, magnesium related X_{Mg} defect. The binding energies are calculated, following the same procedure as for Mg^0 , and compared to E_{EMT} from Ref. 10. The deviations δ from theory are given in the last column.

X_{Mg}	E_{expt}	E_{EMA}	E_B	δ
$2p_0$	113.00	11.492	11.69	+0.20
$2p_{\pm}$	118.30	6.402	6.38	-0.02
$3p_0$	119.15	5.485	5.53	+0.05
$4p_0$	121.36	3.309	3.32	+0.01
$3p_{\pm}$	121.55	3.120	3.13	+0.01
$4p_{\pm}$	122.49	2.187	2.19	± 0
$5p_{\pm}$	123.23	1.449	1.45	± 0
Binding energy ($Si:X_{Mg}$) = 124.69 meV				

ing the same procedure as for Mg^0 , we obtain a binding energy of 124.69 meV for this center. Furthermore, a similar trend for the deviation δ is found for the X_{Mg} and Mg^0 centers regarding both magnitude and sign. This gives further support to our assumption of X_{Mg} being Mg related. For a detailed identification of X_{Mg} , further experimental information is needed. Diffusion experiments on samples with different background doping prior to diffusion were carried out, but no conclusive information could be obtained.

Two weak lines are found close to the $2p_0$ line of X_{Mg} , and are marked by arrows in Fig. 1. The relative intensity and the energy spacing between these two lines suggest that they are part of an additional set of donor lines. The spectral line at 892.9 cm^{-1} is then due to transitions to a $2p_{\pm}$ donor state, and the line at 918.3 cm^{-1} to transitions to a $3p_{\pm}$ state. Thus the $2p_0$ line should coincide with the $4p_{\pm}$ line of Mg^0 . These weak lines show the same relative intensity compared to the Mg^0 and X_{Mg} lines at 1.9 K and at about 10 K, which rules out the possibility of a split ground state. The lines were too weak to be studied in detail under magnetic field, but for very low fields they show a splitting similar to that for the corresponding Mg^0 and X_{Mg} lines, which gives further support to our assignment.

Figure 2 shows the high-resolution absorption spectrum of Mg^+ in the energy range $1650\text{--}2050 \text{ cm}^{-1}$ ($\approx 205\text{--}255 \text{ meV}$). This spectrum shows similar relative intensity ratios among the lines as the Mg^0 spectrum, whereas the energy spacings are about four times larger than for Mg^0 , as expected for a singly ionized donor. The lines are labeled according to the EMA. The binding energies are calculated using $4p_{\pm}$ as a reference state, and are listed in Table III together with the results of Ho and Ramdas² and the EMA (Ref. 10) ($Z=2$). A binding energy of 256.68 meV was deduced, which is about 0.2 meV larger than the value of 256.47 meV reported in Ref. 2. However, they used the $3p_{\pm}$ line as a reference state, which causes the difference in the ground-state binding energy. In Ref. 2, four additional lines were reported which the authors could not attribute to any of the shallow-donor states. We also observe these lines (indi-

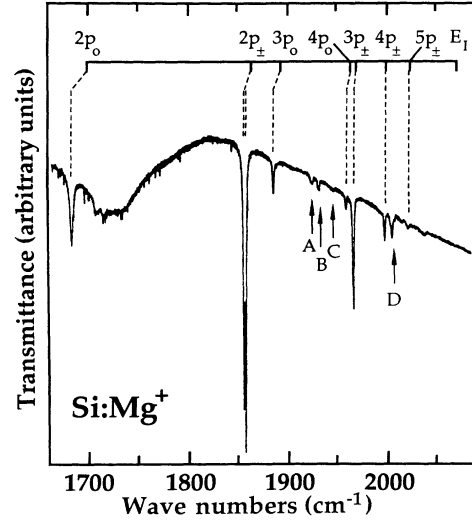


FIG. 2. The transmittance spectrum of Mg^+ in the energy range $1650\text{--}2050 \text{ cm}^{-1}$. The identification of the lines are according to the labeling scheme of the EMA. The energy spacings between the states are four times larger than those for Mg^0 , as is expected for a singly ionized donor. Four unidentified lines A, B, C, and D are observed (see text for further details).

cated by A, B, C, and D) in Fig. 2. The two lowest, A and B, at 1925.8 and 1933.2 cm^{-1} , respectively, remain unidentified while the weak line C at 1945.9 cm^{-1} is tentatively assigned to the $3d_{\pm}$ or $3d_0$ states. The fourth line D is rather strong, and observed at 2007.2 cm^{-1} , just above the $4p_{\pm}$ line. This line remains unidentified, although it is found close to the expected position of the $4f_{\pm}$ EMA line. The origin of this line will be further analyzed when discussing the stress and Zeeman data.

TABLE III. Experimental excitation energies E_{expt} (in meV) for Mg^+ . They are compared to those obtained by Ho and Ramdas (Ref. 2) labeled $E^{(a)}$. E_{EMA} are the EMA-predicted binding energies of the shallow donor states (Ref. 10). E_B is the experimental binding energy calculated by using the $4p_{\pm}$ EMA energy as reference; see text for details. The last column shows the deviations δ of the experimental energies from those predicted by the EMA. The split $np_{\pm}$ states are labeled a and b, where $np_{\pm}^a$ is the low-energy component and $np_{\pm}^b$ the high-energy component.

Mg^+	E_{expt}	$E^{(a)}$	E_{EMA}	E_B	δ
$2p_0$	208.66	208.63	45.968	48.02	+2.05
$2p_{\pm}^a$	230.25	230.22	25.608	26.43	+0.82
$2p_{\pm}^b$	230.48	230.42	25.608	26.20	+0.59
$3p_0$	233.91	233.87	21.940	22.77	+0.83
$4p_0$	243.05	243.00	13.236	13.63	+0.39
$3p_{\pm}^a$	243.98	243.99	12.480	12.70	+0.22
$3p_{\pm}^b$	244.06	243.99	12.480	12.62	+0.14
$4p_{\pm}$	247.93	247.92	8.748	8.75	± 0
$5p_{\pm}$	250.87		5.810	5.80	-0.01
Binding energy ($Si:Mg^+$) = 256.68 meV					

B. Influence of the local potential

All experimental data show that the Mg^+ center has T_d symmetry, and the splitting of the $2p_{\pm}$ line could therefore not be caused by a low-symmetry central-cell potential. The splitting was already observed in Ref. 2, and suggested to be due to a chemical splitting of the excited state, i.e., a central-cell correction. In T_d symmetry, a $p_{\pm}$ state transforms as $2T_1 + 2T_2$. One usually takes for granted that the valley-orbit and central-cell interactions are too weak to lift this twelvefold accidental orbital degeneracy sufficiently to be experimentally observed in, e.g., excitation spectroscopy. However, this is obviously not the case for Mg^+ . Transitions from the $1s(A_1)$ ground state are symmetry allowed only to final states with T_2 symmetry, and the two lines were attributed in Ref. 2 to a splitting of the $2T_2$ states into two separate T_2 components. A closer inspection reveals that the $3p_{\pm}$ line is also split into two components, although with a considerably smaller splitting compared to that for the $2p_{\pm}$ line. For this reason it is not advisable to use the $3p_{\pm}$ state as a reference state when calculating the binding energies, and therefore we choose the $4p_{\pm}$ line. In Fig. 3, the splittings of the $2p_{\pm}$ and $3p_{\pm}$ lines are presented, giving $\Delta E(2p_{\pm}) = 1.9 \text{ cm}^{-1}$ and $\Delta E(3p_{\pm}) = 0.6 \text{ cm}^{-1}$.

To gain further insight into the cause of this splitting, we first discuss a common procedure applied to the chemical splitting of s states. The central-cell potential is approximated by a Dirac delta function $A\delta(r)$, where A is the strength. This seems feasible by considering its small extension compared to the spread in the wave function. It is easily shown that a general scaling rule may be obtained which states that the influence of the local potential on the s states (e.g., the splitting between the states in an ns manifold) scales as the probability to find the electron at the origin. For hydrogenic wave functions,

the scaling rule takes the form $1/n^3$ which has proven to be valid for, e.g., the valley-orbit splitting of the chalcogen s states.¹⁰ Unfortunately, this procedure is not directly applicable for the p states, since their wave functions have vanishing amplitudes at the origin. However, it is still believed that the experimentally observed splitting is indeed due to a localized perturbation.

In the case of the $p_{\pm}$ states of Mg^+ , we have to consider a somewhat different approach. It is assumed that the local potential has a considerable constant strength within a sphere of radius R_0 and is zero for values larger than R_0 . First we employ hydrogenic wave functions ($Z=2$) and calculate the probability of finding the electron inside a sphere with radius R_0 as a function of R_0 . In Fig. 4 the probability ratios are plotted for some lower s and p states as a function of R_0 in units of the Bohr radius a_0 . The experimental value for $\Delta E(2p_{\pm})/\Delta E(3p_{\pm})$ is $1.86/0.64 = 2.91$, which is close to the calculated value of $729/256 \approx 2.85$ for $R_0 = 0$. However, this ratio is a slowly varying function of R_0 and close to the experimental value up to approximately $1.5a_0$, which makes it difficult to estimate R_0 . Nevertheless, the good agreement between the splitting and the probability ratios for R_0 , less than about $1.5a_0$, indicates that our simple model seems to be applicable and can be used to estimate the splitting of the $4p_{\pm}$ line. We find that the ratio $\Delta E(3p)/\Delta E(4p)$ is $8192/3645 \approx 2.25$ for $R_0 = 0$, and is approximately constant up to about $1a_0$. Thus the $4p_{\pm}$ line should split by approximately 0.25 cm^{-1} , which, unfortunately, is too small to be resolved.

Encouraged with our qualitative findings above, we try to apply the same procedure to estimate both the strength and the effective radius in greater detail. We assume that the splitting of the $p_{\pm}$ states has the same origin as the shift of the Mg^+ ground state from the EMA value of about 125 meV to the observed energy of 256 meV. A perturbation treatment is affected by interference effects of the true wave functions expressed as sym-

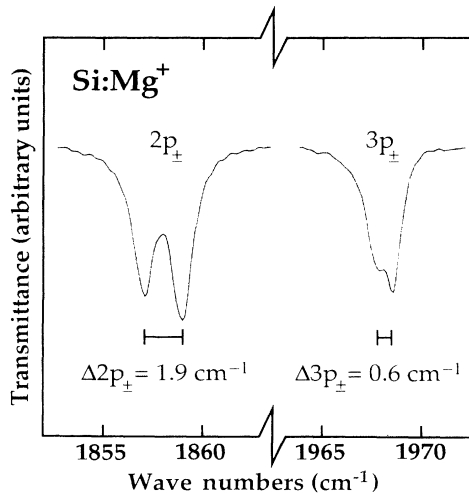


FIG. 3. An enlargement of the $2p_{\pm}$ and $3p_{\pm}$ lines in the Mg^+ spectra. The lines split due to valley-orbit and central-cell interactions. The split components are labeled a and b in Table III.

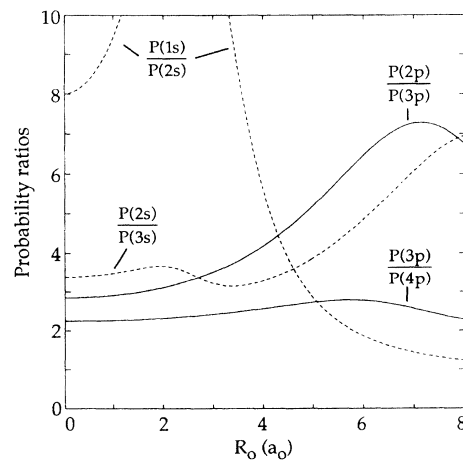


FIG. 4. The probability ratios for some lower s and p states, plotted as a function of R_0 . Hydrogenic wave functions ($Z=2$) were used in order to estimate the probability of finding the electron inside a sphere with radius R_0 as a function of R_0 .

metrized sums over the six valleys. Nevertheless, we continue our procedure in a one-valley approximation, and assume that the effective strength of the potential is identical both when considering the splitting of the $p_{\pm}$ states and the energy shift of the ground state. In this way R_0 is estimated to be about $1.1a_0$, and the constant strength to be about 300 meV. The central-cell radius is taken to be the nearest-neighbor distance (d_{NN}) which is about 2.4 Å, and $a_0(Z=2)$ is about 7 Å. Hence R_0 is about $3d_{NN}$, which is too large to be physically reasonable. The screened potential employed in the EMA calculations fails to describe the true potential close to the impurity site due to two major facts. First, the dielectric constant must approach the value of one at the origin, while in the EMA it has been assumed to be constant and equal to the static dielectric constant. Second, the core states of Mg^+ have been disregarded. In a strict treatment a pseudopotential approach would have been more appropriate, in addition to the k -dependent Coulomb potential. Both these corrections would contribute to a more localized perturbation than the constant one considered above and, hence, the effective radius would decrease.

All Mg^+ p states are considerably shifted toward lower energies compared to their corresponding EMA energies. The deviations δ for the p states of Mg^0 and Mg^+ are listed in Tables I and III, respectively. We observe that the shifts are larger for np_0 states than for $np_{\pm}$ states, thus suggesting that the np_0 states are more influenced by the local potential. This difference may be understood by noting that an increase in binding energy also corresponds to an increase in the localization in real space. In order to obtain an increased localization, the wave function must include Bloch waves not only from the conduction-band minimum but also from somewhat higher states. Two competing effects therefore have to be considered: the binding energy gained by the localization and its decrease by the inclusion of higher conduction-band states. The p_0 envelope function is directed along the prolate-shaped conduction-band valley, whereas a $p_{\pm}$ state is directed perpendicular to the valley. In order to increase their localization, a p_0 state must therefore increase the inclusion of conduction-band states along the valley, whereas a $p_{\pm}$ state must include states perpendicular to the axis. The curvature of the valley is smaller in the direction of the valley compared to that in perpendicular directions. We may thus conclude that the cost in energy when including higher states in the wave function is considerably higher for $p_{\pm}$ states than for p_0 states. The net increase in binding energy observed experimentally thus originates from two competing effects, and is accordingly larger for the np_0 states than for the $np_{\pm}$ states.

By comparing the deviations from the EMA for Mg^+ and Mg^0 , we observe that the energy shifts for Mg^0 are approximately ten times smaller than for Mg^+ . For Mg^0 the shifts are so small that only the $2p_0$ and $3p_0$ shifts are experimentally verified. The experimental ratio of the energy shifts $\delta(2p_0)/\delta(3p_0)$ for Mg^+ equals 2.48, and for Mg^0 2.62, suggesting that similar local potentials affect Mg^0 and Mg^+ . These ratios are somewhat lower than the theoretical value of 2.85, due to the fact that the

theoretical calculation is based on hydrogen p functions. In order to compare these results with experiment, we can calculate the average experimental shift of all the np functions, i.e., $\delta(np)_{ave} = [\delta(np_0) + \delta(np_{\pm}^a) + \delta(np_{\pm}^b)]/3$, where a and b label the low- and high-energy components of the split $np_{\pm}$ state, respectively. This procedure can only be carried out with some accuracy for the Mg^+ $2p$ and $3p$ states since their deviations are large enough. From this we obtain an experimental value of $\delta(2p)_{ave}/\delta(3p)_{ave} = 2.93$, in fair agreement with our theoretical calculation.

The substitutional double donors Se and S in silicon have much larger binding energies (Se^0 : 307 meV; Se^+ : 593 meV; S^0 : 318 meV; and S^+ : 614 meV) (Ref. 10) than Mg; i.e., a large influence of the local potential on the ground state $1s(A_1)$, but no major deviations for the excited p states, nor any splitting of $p_{\pm}$ states have been observed. For Mg^+ we observe an influence on all states, which according to our analysis above could be traced to an extended local potential.

It is interesting to speculate whether the local potential, which causes the shifts and splittings of the Mg lines, originates from the fact that Mg occupies an interstitial site of the lattice. It is well known that the behavior of the Coulomb potential close to the impurity site is considerably different for an interstitial defect compared to a substitutional impurity.¹¹ However, this discussion is beyond the scope of this paper.

C. Uniaxial stress

Uniaxial stress measurements have been performed on the Mg^+ charge state. The uniaxial stress behavior of EMA donor states in silicon was treated within the deformation-potential approximation (DPA), briefly outlined in the following. The overlap between p states belonging to different valleys is assumed to be small, and their response to uniaxial stress is therefore treated within the one-valley approximation, implying that all p states shift as their corresponding valley. The energy shifts relative to the common center of gravity shift δE_{cg} are then given by

$$\begin{aligned} F||[001]: \quad \delta E^{(x,y)} &= -\Delta F, \\ \delta E^{(z)} &= 2\Delta F, \\ F||[110]: \quad \delta E^{(x,y)} &= \frac{1}{2}\Delta F, \\ \delta F^{(z)} &= -\Delta F, \\ F||[111]: \quad \delta E^{(x,y,z)} &= 0, \end{aligned} \quad (1)$$

where Δ is given by $\Xi_u(s_{11}-s_{12})/3$. Ξ_u is the deformation potential for pure shear, and s_{11} and s_{12} are stiffness coefficients. F is the magnitude of the uniaxial stress, defined to be negative when compressive. Ξ_u is determined if Δ and the stiffness coefficients are known. We have used the 4.2-K values¹² $s_{11} = 7.617 \times 10^{-12}$ and $s_{12} = -2.127 \times 10^{-12}$ m²/N in our calculations.

Figure 5 shows the Mg^+ stress data obtained from absorption measurements. All p states are observed to follow their corresponding valley as expected. In Fig. 5(a), the stress results are presented for $F||\langle 111 \rangle$, and all lines shift in energy by the same amount, without any splitting.

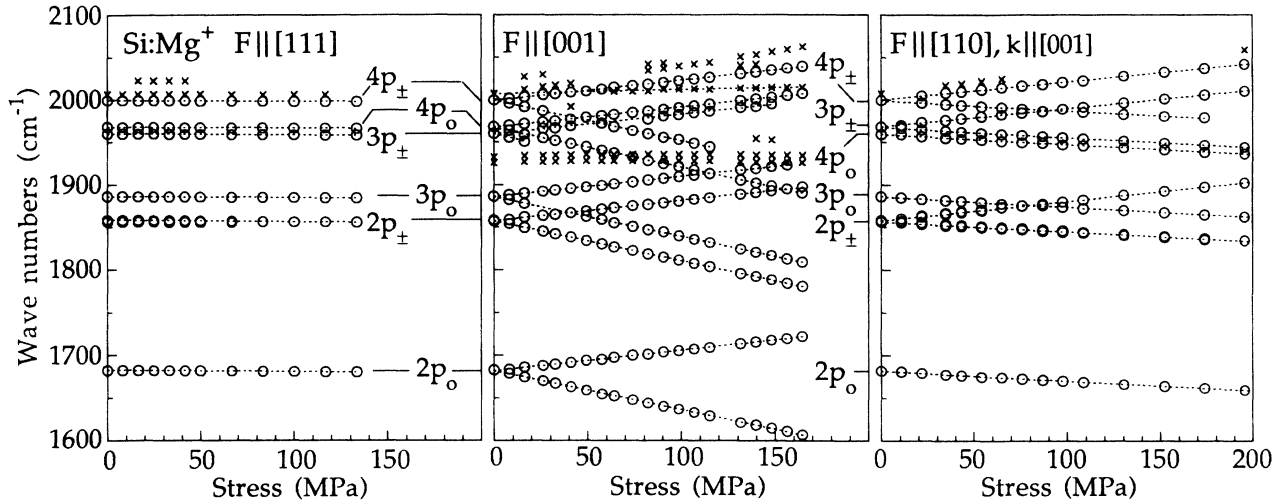


FIG. 5. The stress splitting of Mg^+ with uniaxial stress in the [111], [001], and [110] directions. Open circles are experimental data (the crosses indicate unidentified lines) and the dashed lines are a least squares fit, used to calculate Ξ_u .

This confirms the T_d position for the Mg center. Figure 5(b) shows the results for $F \parallel \langle 001 \rangle$ for which the total splitting of a p state is $|3\Delta F|$. By linear regression an average value of $0.235 \text{ cm}^{-1}/\text{MPa}$ for Δ was deduced which gives $\Xi_u = 9.0 \pm 0.2 \text{ eV}$. This value is somewhat larger than that of 8.7 eV previously reported² for Mg^0 .

In Fig. 5(c), stress data for $F \parallel \langle 110 \rangle$ are presented. A transition to an np_0 state is only possible when the electrical field has a component along the np_0 valley axis. Since the photon wave vector $\mathbf{k}$ is parallel to the z axis in these measurements, no high-energy component of np_0 could be observed (i.e., no transitions to z valleys). All $np_{\pm}$ states split by $|3\Delta F/2|$ which results in a value of $0.225 \text{ cm}^{-1}/\text{MPa}$ for Δ , and 8.59 eV for Ξ_u .

It would have been interesting to study the interaction between the two T_2 components of $2p_{\pm}$ at low stress fields, but this was not possible due to the small zero-field splitting. Unfortunately, the lowest stress available already gave rise to a stress splitting much larger than the zero-field splitting. Thus the two T_2 states had already mixed and quantized along the axis defined by the stress.

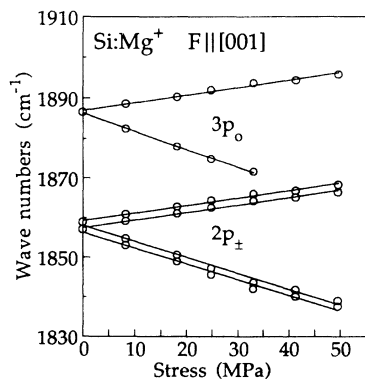


FIG. 6. An enlargement of the stress splitting of the $2p_{\pm}$ and $3p_0$ lines of Mg^+ . The stress is applied parallel to the [001] direction.

In Fig. 6, an enlargement of the stress splitting for the $2p_{\pm}$ components is presented for low stress values. For higher stress all lines broaden due to inhomogeneous stress, and the two components can no longer be resolved.

Polarization measurements are presented in Fig. 7 for $F \parallel \langle 001 \rangle$ and $F = -68 \text{ MPa}$. When the electrical vector is parallel to the z axis, i.e., $\mathbf{E} \parallel \mathbf{F}$, only transitions to the z valleys of the np_0 states are possible. For $np_{\pm}$ states, transitions to x and y valleys are allowed, i.e., the high-energy component. For $\mathbf{E} \perp \mathbf{F}$, transitions to x and y valleys are allowed for np_0 and to all valleys for $np_{\pm}$ states; see the inset in Fig. 7. All this implies that the experimental data behave exactly according to theory.

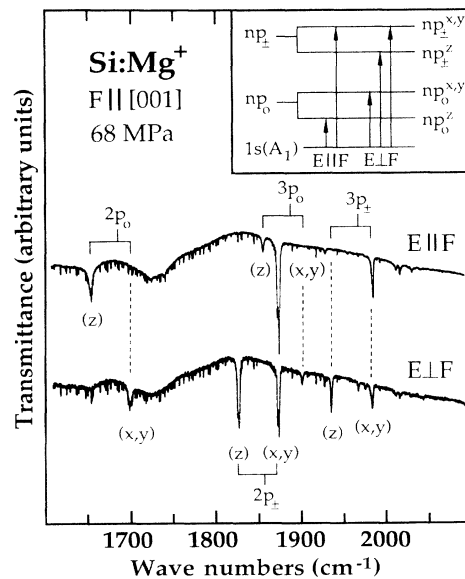


FIG. 7. Mg^+ spectra experimentally obtained with a stress of 68 MPa parallel to [001], measured with polarized light. The inset shows the allowed transitions with the electrical field parallel and perpendicular to the stress field.

The unidentified line at 2007.1 cm^{-1} is clearly observed for all three stress directions as seen in Fig. 5, marked as crosses. We observe that it does not follow the $\text{Mg}^+ p$ states under stress for $\mathbf{F} \parallel \langle 001 \rangle$ and $\mathbf{F} \parallel \langle 110 \rangle$, and therefore conclude that it is not a part of the Mg^+ excitation spectra.

D. Zeeman

The Zeeman effect for the excitation spectra of the Mg^0 and Mg^+ donors has hitherto only been studied to a minor extent. In Fig. 8 the Zeeman spectrum of Mg^0 for $\mathbf{B} \parallel \langle 001 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ is presented. The $p_{\pm}$ lines split into several components, whereas the p_0 lines show only a small shift (except for $\mathbf{B} \parallel \langle 001 \rangle$, where a small split is clearly observed). The linear Zeeman operator can be written as $H_Z = e/(2m_t)[\sqrt{\gamma}(L_x B_x + L_y B_y) + L_z B_z]$ (Ref. 13), where γ is equal to m_t/m_l , and m_t and m_l are the transverse and longitudinal effective electron masses, respectively. Here a coordinate transformation $x' = x$, $y' = y$, and $z' = z/\sqrt{\gamma}$ has been introduced which transforms the kinetic-energy term of the effective mass Hamiltonian into a spherically symmetric term, involving the transverse mass m_t . Simultaneously, this transformation implies that in the transformed coordinate system the electron moves in an effective magnetic field $(\sqrt{\gamma}B_x, \sqrt{\gamma}B_y, \sqrt{\gamma}B_z)$, where B_x , B_y , and B_z are the components of the field in the original coordinate system, corresponding to the experimentally applied field. The quantization axis z is chosen to be parallel to the longitudinal axis of the particular valley under consideration. The linear Zeeman effect is identically zero for the p_0 states ($m_L = 0$), and since L_x and L_y have the selection rule $\Delta m_L = \pm 1$, only L_z has to be considered for the $p_{\pm}$ states. Hence a $p_{\pm}$ state only splits when the magnetic field has a component along the z axis of the valley. We could therefore easily qualitatively understand the split-

ting patterns shown in Fig. 8. When $\mathbf{B} \parallel [001]$, only the $p_{\pm}$ states of the z and $-z$ valleys split (shown as full lines) whereas for the perpendicular valleys (dashed lines) no splitting occurs. The splitting is determined by $e\hbar B/m_l \cos(\theta)$, where θ is the angle between the magnetic field and the longitudinal axis of the valley. In the case of $\mathbf{B} \parallel [110]$, the $p_{\pm}$ states of the x , $-x$, y , and $-y$ valleys split by $e\hbar B/(\sqrt{2}m_t)$ (dashed lines), whereas the $p_{\pm}$ states of the z and $-z$ valleys (full lines) do not split. When $\mathbf{B} \parallel [111]$ all valleys experience the same angle to the B field, and all $p_{\pm}$ states split identically.

The L_x and L_y angular-momentum operators could be disregarded when discussing the splitting of the $p_{\pm}$ states. However, they are of importance when considering those cases where a p_+ or p_- state comes sufficiently close to a p_0 state in which they may cause an avoided crossing behavior. A prominent avoided crossing is seen for the $2p_{\pm}$ and $3p_0$ lines in Figs. 8(b) and 8(c), which will be discussed below in more detail.

A good qualitative understanding could in principle be obtained from the linear Zeeman effect. However, as is readily observed in Fig. 8, the lines show rather pronounced quadratic shifts due to the quadratic Zeeman effect. We have recently studied the quadratic Zeeman effect of shallow donors in Si within the framework of the EMA and the finite-element method (FEM).³ In that work, two different approaches were applied. In the first approach, a limited number of zero-field wave functions were numerically calculated, and the Zeeman Hamiltonian was treated as a perturbation in this basis. The results were shown to describe the lowest shallow-donor states with high accuracy, i.e., the $2p_0$, $3p_0$, and $2p_{\pm}$ states. They are therefore used when fitting the data in Fig. 8. The results are presented as full (z and $-z$ valleys) and dashed (x , $-x$, y , and $-y$ valleys) lines, and the agreement is good especially for $\mathbf{B} \parallel [001]$ and $[110]$. A small additional splitting is observed for $\mathbf{B} \parallel [111]$ which is due

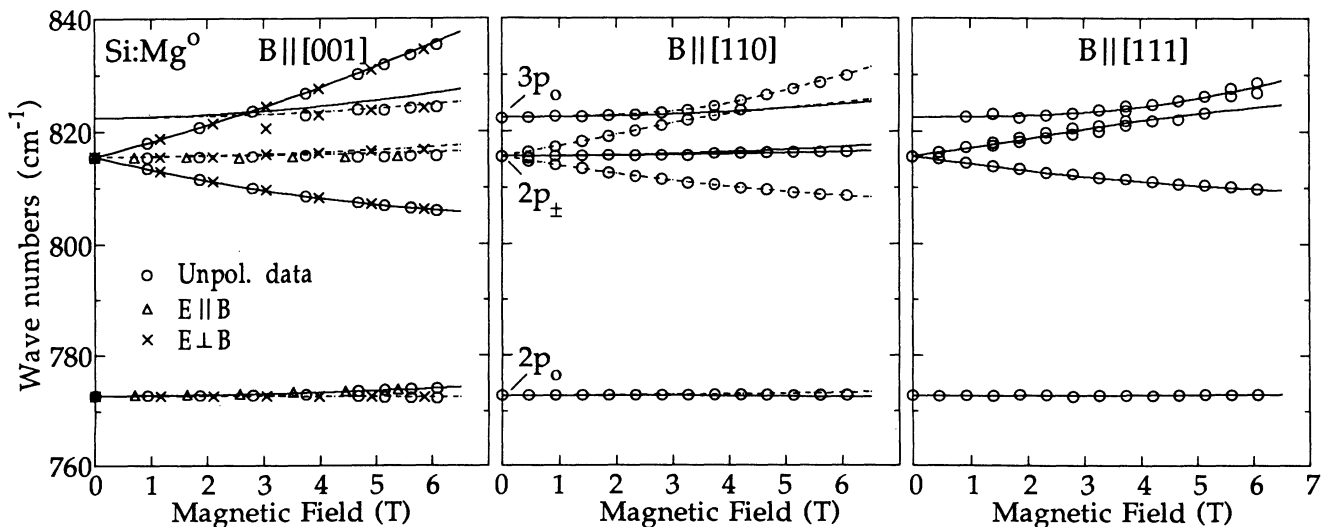


FIG. 8. Zeeman splitting of the $2p_0$, $2p_{\pm}$, and $3p_0$ states of Mg^0 with the magnetic field parallel to $[001]$, $[110]$, and $[111]$. Experimental data are shown as circles, triangles, and crosses. Dashed lines describe the calculated behavior of states at x , $-x$, y , and $-y$ valleys, while full lines describe those at z and $-z$ valleys according to Ref. 13.

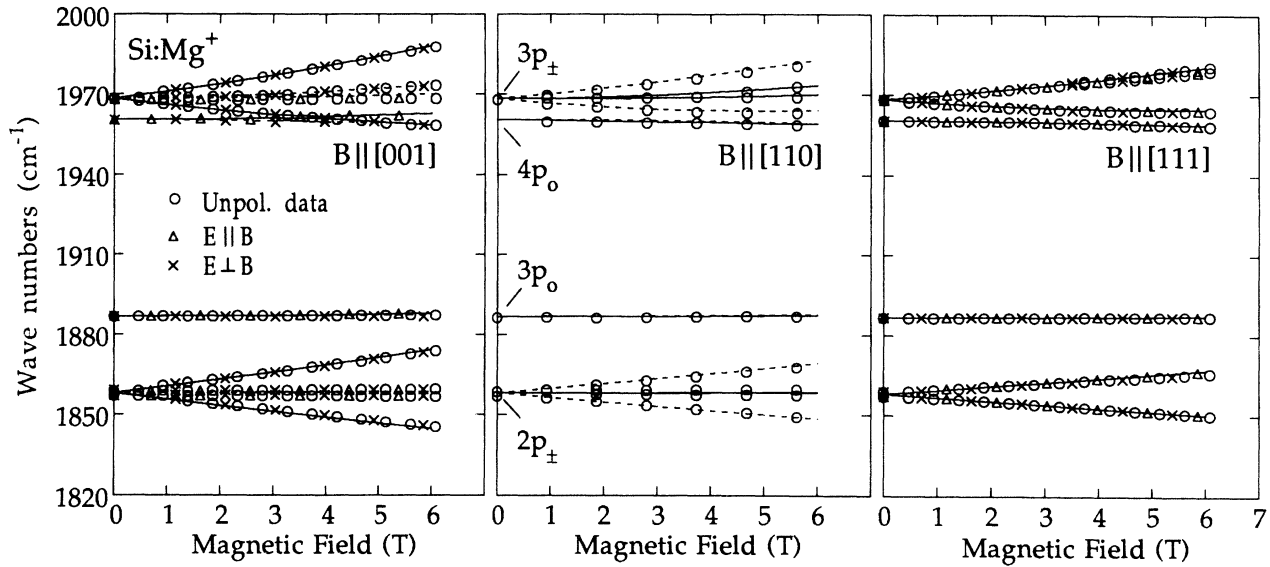


FIG. 9. Zeeman splitting of the $2p_{\pm}$, $3p_0$, $4p_0$, and $3p_{\pm}$ states of Mg^+ with $\mathbf{B}||[001]$, $[110]$, and $[111]$. Experimental data are compared to the calculated behavior explained in detail in the text. Dashed lines describe the behavior of states at x , $-x$, y , and $-y$ valleys, while full lines describe those at z and $-z$ valleys.

to a slight misalignment of the sample from the intended $[111]$ direction for the field. The second approach in Ref. 13, involving magnetic-field-dependent wave functions, had to be applied in order to describe higher excited states such as $4p_0$ and $3p_{\pm}$. Comparisons with experimental data for both Si:Mg^0 and Si:X_{Mg} are carried out in that work, and the reader is referred to Ref. 13 for further information.

The Zeeman results for the $2p_{\pm}$, $3p_0$, $4p_0$, and $3p_{\pm}$ states of Mg^+ are presented in Fig. 9 for $\mathbf{B}||[001]$, $[110]$, and $[111]$. The full and dashed lines were calculated by using the results from the FEM calculation (using zero-field wave functions) and since $Z=2$ all matrix elements describing the quadratic shifts are reduced by a factor of 4 compared to a neutral donor. It is readily seen in Fig. 9 that the quadratic shifts for Mg^+ are indeed considerably smaller compared to that for Mg^0 . However, they increase in importance for the higher states, as is seen in Fig. 10, where the Zeeman splitting of the $3p_{\pm}$ and $4p_0$ lines is presented for $\mathbf{B}||[001]$. Included in this figure, for comparison, are the splitting when quadratic terms in the Zeeman Hamiltonian has been disregarded (shown as dotted lines). Furthermore, since the energy differences between different Mg^+ states have increased by a factor of 4 compared to Mg^0 , the interaction between nearby states has been reduced by about a factor of 16. In this picture the zero-field splitting of the $2p_{\pm}$ line could not be accounted for.

A closer inspection of the Zeeman results for the interesting $2p_{\pm}$ line of Mg^+ is facilitated in Fig. 11 for $\mathbf{B}||[001]$, $[110]$, and $[111]$. As mentioned above, in T_d symmetry, a $p_{\pm}$ state transforms according to $2T_1 + 2T_2$. It is clearly observed that the two lines are due to excitation to the two T_2 states which are valley sums of the $p_{\pm}$ states belonging to the six equivalent valleys. We attribute to valley μ ($\mu = \pm x, \pm y$, or $\pm z$ relative to a right-

handed Cartesian coordinate system) two p -like states $p_i^{(\mu)}$ and $p_j^{(\mu)}$ (see Fig. 12). According to the EMA, $p_i^{(\mu)}$ equals $P_i(\mathbf{r}) \cdot u_{\mathbf{k}\mu}(\mathbf{r}) \exp(i\mathbf{k}_{\mu} \cdot \mathbf{r})$, where $P_i(\mathbf{r})$ is the envelope function and $u_{\mathbf{k}\mu}(\mathbf{r}) \exp(i\mathbf{k}_{\mu} \cdot \mathbf{r})$ is the Bloch wave of the μ 'th valley located at $\mathbf{k}_{\mu}$. As an example, in the x valley there are two orthogonal states denoted $p_y^{(x)}$ and $p_z^{(x)}$, where y and z refer to the same coordinate system defining the valleys, and not to any local coordinate system for the x valley. Furthermore, we define $p_i^{(-\mu)} = -R p_i^{(\mu)}$, where R is the operator corresponding to a 180° rotation around an axis perpendicular to μ and i . The valley sums for the T_1 and T_2 states are found by inspection of their properties under the symmetry opera-

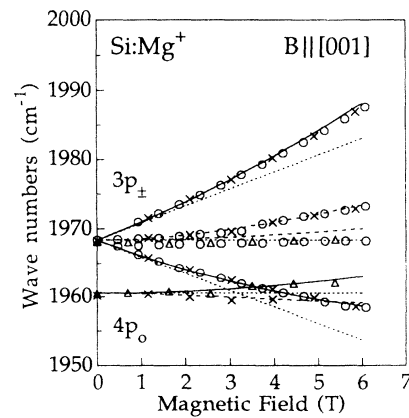


FIG. 10. An enlargement of the Zeeman splitting of the $4p_0$ and $3p_{\pm}$ states of Mg^+ for $\mathbf{B}||[001]$. The dotted lines are the calculated behavior disregarding the quadratic terms in the Zeeman Hamiltonian. Dashed and full lines describe the behavior of states at $\pm x$ and $\pm y$ valleys and $\pm z$ valleys, respectively, when quadratic Zeeman effects are included.

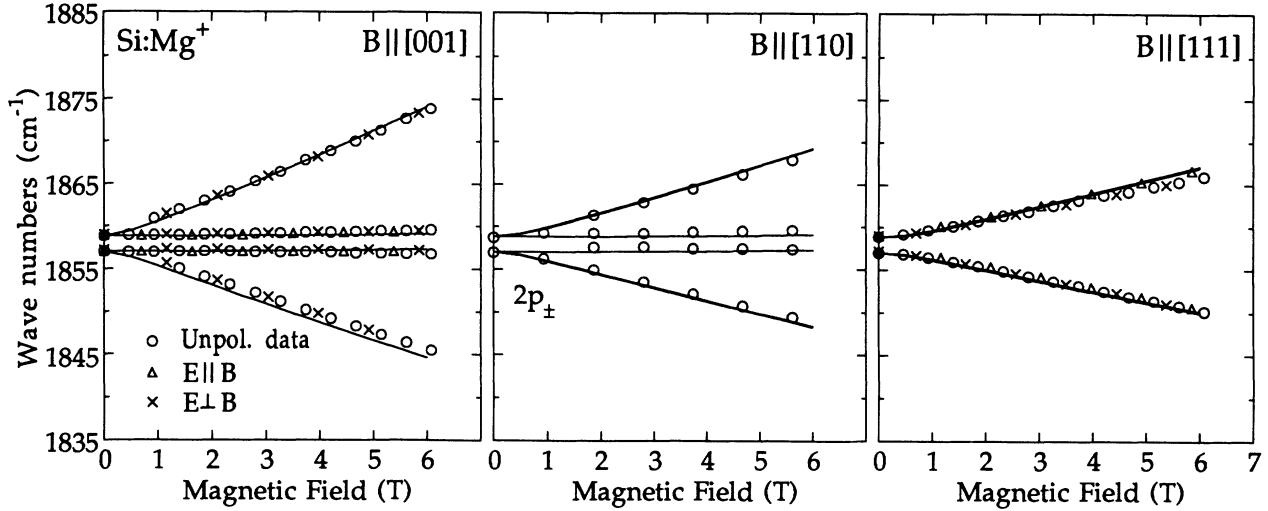


FIG. 11. The behavior of the split $2p_{\pm}$ state of Mg^{+} under magnetic field for $B||[001]$, $[110]$, and $[111]$. The full lines are the result of a calculation described in detail in the text.

tions of T_d . We denote the states as T_1^a , T_1^b , T_2^a , and T_2^b , and they are given by

$$\begin{aligned} T_x^a &= \frac{1}{2} \{ (p_x^{(y)} + p_x^{(-y)}) \pm (p_x^{(z)} + p_x^{(-z)}) \} , \\ T_x^b &= \frac{1}{2} \{ (p_z^{(y)} + p_z^{(-y)}) \pm (p_y^{(z)} + p_y^{(-z)}) \} , \end{aligned} \quad (2)$$

where the plus and minus signs give the T_2 and T_1 states, respectively. The partner states are found by cyclic permutations of the indices. A Taylor expansion reveals their behavior close to the origin. The T_2^a states are p like and, e.g., $T_{2x}^a \sim x$, whereas the T_2^b states are d like and, e.g., $T_{2x}^b \sim yz$. The zero-field positions for the two T_2 states are of course determined by the energy positions of the two lines in the $2p_{\pm}$ doublet. However, no information about the zero-field energies of the two invisible T_1 states could be extracted from the zero-field spectrum.

The orbital g values g_l for these four states could easily be calculated, and they were found to be equal to $\frac{1}{2}$ for T_2^a and T_1^a states, and $-\frac{1}{2}$ for T_2^b and T_1^b states. Furthermore, the Zeeman interaction may mix the T_2^a with the T_1^a states, and the T_2^b with the T_1^b states. This means that when the energy positions of the two T_2 states are far from those for the T_1 states only half of the normally detected Zeeman splitting for a $p_{\pm}$ line would be observed. However, when their zero-field splittings are considerably smaller than the Zeeman energy, the mixing will result in a g_l equal to 1. The results for the Mg^{+} $2p_{\pm}$ line show that the splitting is indeed characterized by $g_l=1$, and no avoided crossing behavior is observed. This is only possible when the zero-field energies of the two invisible T_1 states are sufficiently close to the two T_2 states.

The initial state in the transitions is the $1s(A_1)$ state. The relative intensities of the two $2p_{\pm}$ T_2 lines could be estimated by assuming, in a first approximation, that the EMA is applicable to describe both the ground state and the excited $2p_{\pm}$ states. In this approximation the only transitions allowed are the intravalley transitions. A

symmetry-allowed electrical-dipole matrix element is $\langle T_{2x}^a | x | 1s(A_1) \rangle$ which is proportional to $\langle 2p_x | x | 1s \rangle$ in terms of one-valley states and is certainly EMA allowed. The T_2^a line is therefore expected to be strong. In the case of the transitions to the T_2^b state, a typical symmetry-allowed matrix element is $\langle T_{2x}^b | x | 1s(A_1) \rangle$ which is proportional to the EMA-forbidden matrix element $\langle 2p_z | x | 1s \rangle$. We therefore conclude that to the extent that the EMA is applicable, only the T_2^a line should be visible. However, it should be noted that any linear combination of the T_2^a and T_2^b states that leads to correct symmetry is possible. The linear combinations for the $2p_{\pm}$ Mg^{+} state are impossible to find from group-theoretical arguments solely. However, since two lines are observed, their relative intensity ratio enables the linear combinations to be found. We define new T_2 states by

$$\begin{aligned} T_{2x}^{(1)} &= \cos(\theta) T_{2x}^a + \sin(\theta) T_{2x}^b , \\ T_{2x}^{(2)} &= -\sin(\theta) T_{2x}^a + \cos(\theta) T_{2x}^b , \end{aligned} \quad (3)$$

and correspondingly for the T_1 states. The less intense

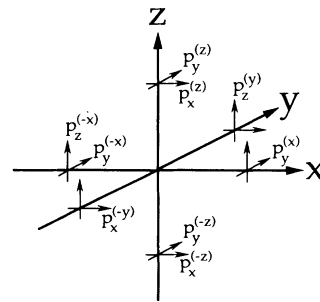


FIG. 12. The six equivalent conduction-band valleys of silicon and the attributed $p_{\pm}$ states. For clarity, only some of the states are labeled.

$2p_{\pm}$ component at lower energy is attributed to transitions to $T_2^{(1)}$, and we find from the relative intensity ratio that $\theta \approx \pm 48.5^\circ$ or $180^\circ \pm 48.5^\circ$.

The shift from its EMA energy and the splitting of the $2p_{\pm}$ state are due to a totally symmetric (T_d) potential $V(\mathbf{r})$. On the other hand, the rigid shift of the 12 accidentally degenerate states may be accounted for in the one-valley EMA approximation by a parameter Γ defined by $\Gamma = \langle p_i^{(\mu)} | V(\mathbf{r}) | p_i^{(\mu)} \rangle$. The splitting, on the other hand, has to be treated beyond this approximation, and an intervalley coupling must be assumed. Five different matrix elements describe this splitting, and the particular form of $V(\mathbf{r})$ determines their relative importance. Since we have no *a priori* information on $V(\mathbf{r})$, a detailed analysis is difficult at this stage.

In Fig. 11 the full lines result from a fitting procedure where the full Zeeman Hamiltonian has been solved. The quadratic Zeeman effect was included in the fit by only considering the first-order effect. Best intensity and polarization fits were obtained by assuming that the T_1^a and T_1^b states are mixed as for the T_2 states but with $\theta \approx 180-45^\circ$.

IV. CONCLUSIONS

A comprehensive experimental investigation of the two charge states of the interstitial magnesium double donor in silicon has been carried out by means of high-resolution Fourier-transform spectroscopy. Perturbation spectroscopy techniques such as uniaxial stress and magnetic field were used in order to gain information about the electronic structure. We find binding energies of

107.51 and 256.68 meV for Mg^0 and Mg^+ , respectively, and confirm that the double-donor system can be approximately described as a solid-state analog of the helium atom. We observe deviations in the binding energies of the excited states, from those calculated within the EMA, especially for Mg^+ , which to our knowledge have not been observed previously for any double-donor system in silicon. These deviations, together with the fact that the $np_{\pm}$ states are split, have been explained by a perturbation in the central-cell region, which cannot be described by the screened potential used in the effective-mass approximation. We find that the potential must have considerable strength within an effective radius comparable with the size of the central cell in order to affect the p states, for which the probability to find the electron close to the origin is very small. Uniaxial stress results for Mg^+ verified the donor character of the excited states and our labeling of the ground state. Zeeman spectroscopy on the Mg^0 and Mg^+ states gave valuable information about the quadratic Zeeman effect, and was found to agree with our calculations. For Mg^+ , we studied in particular the behavior of the split $2p_{\pm}$ state under magnetic field in order to find the combination of valley sums which build up the two visible T_2 components of the state.

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