Group-theoretical analysis of double acceptors in a magnetic field: 
Identification of the Si:B\(^{+}\) ground state

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A boron impurity in silicon binding an extra hole is known to have only one bound state at an energy of just below 2 meV. The nature of the Si:B\(^{+}\) ground state is, however, not well established. We qualitatively analyze the behavior in a magnetic field of isolated acceptors in a tetrahedral lattice binding two holes using group theory. Applying these results, we analyze recent measurements and conclude that the ground state of B\(^{+}\) is most compatible with a nondegenerate \(\Gamma_{1}\) state.

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I. INTRODUCTION

A neutral boron acceptor in silicon is able to weakly bind an extra hole, resulting in a positively charged ion (B\(^{+}\)). This entity is an example of a positively charged acceptor, commonly denoted by A\(^{+}\), which is the counterpart of the better known negatively charged donor D\(^{-}\). Both are related to their atomic-physics analogue, the negative hydrogen ion H\(^{-}\). The energy states associated with these ions are very shallow and spatially large. When their concentration is sufficiently high, their overlapping wave functions can form an upper Hubbard band and they play an important role in electronic transport in semiconductors at low temperatures. Since a few years, electronic states of individual dopant atoms gained renewed interest due to their prospective application in Si-based solid state quantum computing.

Neither theoretically nor experimentally much work has been done on the B\(^{+}\) state. Optical spectroscopy is difficult due to the small ionization energy [less than 2 meV (Ref. 3)]. In particular, the nature of its ground state is not well-established and to our knowledge no results have been published on the magnetic field dependence of the energy levels.

The purpose of this paper is twofold. First, we present a general group-theoretical study of the magnetic field dependence of two-hole states in tetrahedral semiconductors. To our knowledge, such an analysis has not been published before. Second, because our analysis includes all possibilities for the B\(^{+}\) ground state, it enables us to compare our results with our recently published measurements of B\(^{+}\) in a magnetic field and to draw conclusions about the nature of the B\(^{+}\) ground state.

II. BACKGROUND

The nature of the energy levels of a neutral boron acceptor (B\(^{0}\)) in silicon is well-known and the Zeeman effect in B\(^{0}\) has been studied in detail, both theoretically and experimentally. The B impurity is located at substitutional sites of the tetrahedral silicon lattice. The (one-hole) ground state is a \(1s\)-like fourfold degenerate state that belongs to the \(\Gamma_{8}\) representation of the tetrahedral double group \(T_{d}\) (for the nomenclature of representations used, see Table I). The bound hole has total angular momentum \(j = \frac{3}{2}\). The single-hole wave function is the product of a \(1s\) hydrogen-like envelope function and a band-like function. Due to spin-orbit interaction in silicon, the \(j = \frac{1}{2}\) valence band is split off by \(\sim 43\) meV,\(^{3}\) and does not need to be considered in first order. A magnetic field completely lifts the fourfold degeneracy and the lowest order Zeeman effect of the \(\Gamma_{8}\) state is linear.

As far as symmetry is concerned, the B\(^{+}\) state is similar to neutral group-II acceptors in a tetrahedral lattice, which are well-studied (e.g., Ref. 8 and references therein). Coupling two \(j = \frac{3}{2}\) \((\Gamma_{8})\) holes bound to a single nucleus gives rise to a sixfold degenerate state, because due to the Pauli-principle only the antisymmetric part of \(\Gamma_{8} \times \Gamma_{8}\) must be taken into account. This can be reduced to its components as \(\{\Gamma_{8} \times \Gamma_{8}\} = \Gamma_{1} + \Gamma_{3} + \Gamma_{5}\). Interaction between the two holes can split the state into a nondegenerate \(\Gamma_{1}\) state with total angular momentum \(J = 0\) and a fivefold \(\Gamma_{3} + \Gamma_{5}\) state carrying \(J = 2\).

Detailed quantitative calculations, which are necessary to establish the ordering and splitting of these levels, are very difficult to carry out, because of the many complicated physical effects that must be taken into account (valence band structure, crystal field, Jahn-Teller-effect, etc.). Hund’s rule, well known from atomic physics, predicts that the more symmetric \(\Gamma_{1}\) state has a higher energy than the \(\Gamma_{3} + \Gamma_{5}\) state, such that the latter is the ground state. The same conclusion was drawn from numerical calculations based on effective mass theory.\(^{9}\) However, it has been shown that a dynamic Jahn-Teller effect can provide a mechanism to reverse the ordering of the levels,\(^{10,11}\) leading to a \(\Gamma_{1}\) ground state. This has in fact been observed in several neutral double acceptors.

Very little experimental work on B\(^{+}\) has been done. The binding energy of the second hole in an isolated B\(^{+}\) state has been measured in phonon-induced conductivity measurements and photoconductivity experiments.\(^{12}\) It is slightly below 2 meV. The stress dependence has been investigated with the same techniques,\(^{12,13}\) and in one case the results were explained as evidence for a stress-induced ground state splitting.\(^{13}\) However, an interpretation of the
conductivity data is nontrivial, because only levels which are very close to either the ground state of B\(^1\) or the valence band edge can be observed with these techniques. Similar experiments in a magnetic field\(^{14}\) showed a linear increase of the binding energy, which was ascribed to Landau level formation in the valence band. In these experiments, no additional shift or splitting was resolved.

Recent transport experiments in Si resonant tunneling devices provide a way to directly observe the magnetic field dependence of the B\(^1\) state.\(^4\) These experiments showed a super linear shift of the ground state towards the valence band (Fig. 2). Neither a ground state level splitting nor bound excited states were observed.

### III. DOUBLE ACCEPTORS IN A MAGNETIC FIELD

Here, we present a group theoretical study to qualitatively analyze the magnetic field behavior of isolated acceptors binding two holes in a tetrahedral semiconductor for various possible states. This analysis is not only applicable to neutral group-II acceptors (e.g., Zn in Ge), but also to group-III acceptors binding an extra hole and singly ionized group-I acceptors (e.g., Cu\(^+\) in Ge). After this general part, we return to the specific situation of B\(^+\).

We subsequently consider various possible two-hole levels and analyze their behavior in a magnetic field using perturbation theory. All such levels transform according to single-valued representations of \(T_d\), as shown in the overview in Table II. We assume that the Coulomb force and spin-orbit interaction between the holes is sufficiently strong to split the levels into their irreducible components. Because of its possible importance for B\(^+\), we also consider the \(\Gamma_3 + \Gamma_5\) level. In all cases it is assumed that the level under consideration is well separated from neighboring levels.

Furthermore, we briefly address the analog of the central field approximation in atomic physics, where it is assumed that each of the two holes moves in the field of the negative ionized acceptor core and the averaged effective potential due to the other hole. In this approximation, the symmetry of the field in which each hole moves is unaffected by the presence of the second hole. This method is known to give a good description for some group-II acceptors in Si and Ge.\(^8\)

When a magnetic field \(\mathbf{B}\) is applied, new terms are introduced in the Hamiltonian of the holes, as given by the Zeeman-Hamiltonian

\[
\mathcal{H}_Z = -\mu_B (\mathbf{L} + 2\mathbf{S}) \cdot \mathbf{B} - \frac{1}{2} m^* \mu_B \left( r_1^2 + r_2^2 \right) B^2 \\
- \left( (\mathbf{r}_1 + \mathbf{r}_2) \cdot \mathbf{B} \right)^2,
\]

where \(m^*\) is the hole effective mass and \(\mathbf{L}\) and \(\mathbf{S}\) are the total orbital and spin angular momenta in units of \(\hbar\). The quantity

<table>
<thead>
<tr>
<th>Combination</th>
<th>Two-hole states</th>
</tr>
</thead>
<tbody>
<tr>
<td>{\Gamma_8 \times \Gamma_8}</td>
<td>\Gamma_1 + \Gamma_3 + \Gamma_5</td>
</tr>
<tr>
<td>{\Gamma_6 \times \Gamma_6} = {\Gamma_7 \times \Gamma_7}</td>
<td>\Gamma_1</td>
</tr>
<tr>
<td>\Gamma_8 \times \Gamma_8'</td>
<td>\Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5</td>
</tr>
<tr>
<td>\Gamma_6 \times \Gamma_6' = \Gamma_7 \times \Gamma_7'</td>
<td>\Gamma_1 + \Gamma_4</td>
</tr>
<tr>
<td>\Gamma_8 \times \Gamma_7 = \Gamma_6 \times \Gamma_6</td>
<td>\Gamma_3 + \Gamma_4 + \Gamma_5</td>
</tr>
<tr>
<td>\Gamma_7 \times \Gamma_6</td>
<td>\Gamma_2 + \Gamma_5</td>
</tr>
</tbody>
</table>

**TABLE II.** Overview of possible two-hole states arising from products of two single hole states and their reduction to irreducible representations of \(\tilde{T_d}\). For states originating from two equivalent single hole states (first two lines in the table), the Pauli principle allows only the antisymmetric part to be considered.

<table>
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</tr>
<tr>
<td>\Gamma_8 \times \Gamma_8'</td>
<td>\Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5</td>
</tr>
<tr>
<td>\Gamma_6 \times \Gamma_6' = \Gamma_7 \times \Gamma_7'</td>
<td>\Gamma_1 + \Gamma_4</td>
</tr>
<tr>
<td>\Gamma_8 \times \Gamma_7 = \Gamma_6 \times \Gamma_6</td>
<td>\Gamma_3 + \Gamma_4 + \Gamma_5</td>
</tr>
<tr>
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</tr>
<tr>
<td>\Gamma_7 \times \Gamma_6</td>
<td>\Gamma_2 + \Gamma_5</td>
</tr>
</tbody>
</table>

**TABLE III.** Character table for the double group \(\tilde{S}_4\) (\(\omega = e^{i\pi/8}\)).

<table>
<thead>
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<tbody>
<tr>
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<td>\Gamma_1 + \Gamma_3 + \Gamma_5</td>
</tr>
<tr>
<td>{\Gamma_6 \times \Gamma_6} = {\Gamma_7 \times \Gamma_7}</td>
<td>\Gamma_1</td>
</tr>
<tr>
<td>\Gamma_8 \times \Gamma_8'</td>
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</tr>
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</tr>
<tr>
<td>\Gamma_7 \times \Gamma_6</td>
<td>\Gamma_2 + \Gamma_5</td>
</tr>
</tbody>
</table>

085211-2
TABLE IV. Character table for the double groups \( \mathcal{C}_3 \) (top; \( \omega = e^{i\pi/3} \)) and \( \mathcal{C}_{1h} \) (bottom).

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>( E )</th>
<th>( \bar{E} )</th>
<th>( C_3 )</th>
<th>( C_3^{-1} )</th>
<th>( \bar{C}_3 )</th>
<th>( \bar{C}_3^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \Gamma_2 )</td>
<td>1</td>
<td>1</td>
<td>-( \omega )</td>
<td>( \omega^2 )</td>
<td>-( \omega )</td>
<td>( \omega^2 )</td>
</tr>
<tr>
<td>( \Gamma_3 )</td>
<td>1</td>
<td>1</td>
<td>( \omega^2 )</td>
<td>-( \omega )</td>
<td>( \omega^2 )</td>
<td>-( \omega )</td>
</tr>
<tr>
<td>( \Gamma_4 )</td>
<td>1</td>
<td>-1</td>
<td>-( \omega^2 )</td>
<td>( \omega )</td>
<td>( \omega^2 )</td>
<td>-( \omega )</td>
</tr>
<tr>
<td>( \Gamma_5 )</td>
<td>1</td>
<td>-1</td>
<td>( \omega )</td>
<td>-( \omega^2 )</td>
<td>-( \omega )</td>
<td>( \omega^2 )</td>
</tr>
<tr>
<td>( \Gamma_6 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

TABLE V. Reduction of the representations of \( T_d \) when a magnetic field is applied along a \( \langle 100 \rangle \), \( \langle 111 \rangle \), or \( \langle 110 \rangle \) direction of the tetrahedral lattice. From this table it can be deduced how the double acceptor levels split in a magnetic field.

<table>
<thead>
<tr>
<th>Direction</th>
<th>( \langle 100 \rangle )</th>
<th>( \langle 111 \rangle )</th>
<th>( \langle 110 \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>( S_4 )</td>
<td>( C_3 )</td>
<td>( C_{1h} )</td>
</tr>
<tr>
<td>( \Gamma_1 )</td>
<td>( \Gamma_1 )</td>
<td>( \Gamma_1 )</td>
<td>( \Gamma_1 )</td>
</tr>
<tr>
<td>( \Gamma_2 )</td>
<td>( \Gamma_2 )</td>
<td>( \Gamma_2 )</td>
<td>( \Gamma_2 )</td>
</tr>
<tr>
<td>( \Gamma_3 )</td>
<td>( \Gamma_1 + \Gamma_2 )</td>
<td>( \Gamma_2 + \Gamma_3 )</td>
<td>( \Gamma_1 + \Gamma_2 )</td>
</tr>
<tr>
<td>( \Gamma_4 )</td>
<td>( \Gamma_1 + \Gamma_3 + \Gamma_4 )</td>
<td>( \Gamma_1 + \Gamma_3 + \Gamma_4 )</td>
<td>( \Gamma_1 + 2\Gamma_2 )</td>
</tr>
<tr>
<td>( \Gamma_5 )</td>
<td>( \Gamma_2 + \Gamma_3 + \Gamma_4 )</td>
<td>( \Gamma_1 + \Gamma_2 + \Gamma_3 )</td>
<td>( 2\Gamma_1 + \Gamma_2 )</td>
</tr>
</tbody>
</table>

L + 2S is the total static magnetic moment of the system. Moreover, \( \mu_B \) is the Bohr magneton and \( r_i \) is the position vector of the \( i \)th hole.

The symmetry group of the Zeeman Hamiltonian \( \mathcal{H}_Z \) is \( \bar{C}_{3h} \). Unless \( \mathcal{B} \) is directed along one of the main crystallographic axes, the symmetry group of the total Hamiltonian \( \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_Z \) reduces to the trivial group. When \( \mathcal{B} \) is parallel to a \( \langle 100 \rangle \), \( \langle 111 \rangle \) or \( \langle 110 \rangle \) direction in the crystal, the symmetry group of the total Hamiltonian reduces from \( T_d \) to \( S_4 \), \( C_3 \) or \( C_{1h} \), respectively. The relevant character tables are given in Tables III and IV. Because all resulting groups are Abelian (commutative), it follows that the application of a magnetic field completely removes the degeneracy of all levels.

The way in which the \( \Gamma_i \) levels exactly split in a magnetic field is presented in Table V.

To deduce the magnetic field induced splitting of the levels, we employ first order degenerate perturbation theory. As mentioned above, it is assumed that the separation of the levels is large compared to the splitting caused by the field, so only the subspace of Hilbert space connected to the level under consideration needs to be taken into account. Given a set of basis functions \( |i \rangle \) for a particular level, we find the corresponding submatrix \( \langle i \mathcal{H}_Z | j \rangle \) of \( \mathcal{H}_Z \) and diagonalize it to obtain the splitting as a function of \( \mathcal{B} \).

Instead of trying to calculate matrix elements from \( \mathcal{H}_Z \) (after choosing a suitable set basis functions) it is much more convenient to use the well-established approach of constructing an effective Zeeman Hamiltonian. This comprises the construction of a matrix of the required size, exploiting necessary symmetries to find vanishing elements and relations between elements. The result is a matrix that usually depends on a small number of unknown phenomenological parameters, in terms of which the level splitting can be expressed. The value of these parameters cannot be determined from symmetry arguments, but their value reflects the quantitative influence of, e.g., the band structure, the Jahn-Teller effect, and the crystal field. The effective-Hamiltonian approach is especially advantageous in the present situation, where both the values of the parameters occurring in \( \mathcal{H}_Z \) and the unperturbed wave functions are not (exactly) known.

IV. LINEAR ZEEMAN EFFECT

In this section, we will investigate the first order Zeeman effect of all the double acceptor levels mentioned before.

A. \( \Gamma_i \) levels

Because \( \Gamma_4 \) occurs in neither of the antisymmetric direct products \( \{ \Gamma_i \times \Gamma_i \} \) \( (i = 1 \ldots 3) \), the effective Hamiltonian matrix \( \mathcal{H}_{\text{eff,lin}} \) vanishes identically for the three levels \( \Gamma_i \). Hence, none of these levels experiences a linear Zeeman effect.

The linear part of the effective Zeeman Hamiltonian for a \( \Gamma_4 \) or \( \Gamma_5 \) level is given by:

\[
\mathcal{H}_{\text{eff,lin}} = \mu_B \mathcal{B} (B_i J_i + B_j J_j + B_k J_k).
\]

Here, \( g \) is the gyromagnetic factor, and \( J_x, J_y, \text{ and } J_z \) are matrix representations of the components of the angular momentum operator with respect to some convenient basis. The components \( J_\alpha \ (\alpha=x,y,z) \) transform according to the \( \Gamma_4 \) representation of \( T_d \). Because \( \{ \Gamma_4 \times \Gamma_4 \} = \{ \Gamma_5 \times \Gamma_5 \} = \Gamma_4 \), the \( \Gamma_4 \) and \( \Gamma_5 \) level do have a linear Zeeman effect. Calculating the eigenvalues of the matrix \( [\mathcal{H}_{\text{eff,lin}}]_i \) \( (i=4 \text{ and } 5) \) yields:

\[
\Delta E = \begin{cases} 
+ \mu_B g B \\
0 \\
- \mu_B g B.
\end{cases}
\]

The eigenvalues are independent of the direction of the magnetic field and hence give rise to an isotropic splitting.

B. \( \Gamma_3 + \Gamma_5 \) level

The situation where the zero-field splitting of the \( \Gamma_3 + \Gamma_5 \) level is small compared to the Zeeman energy must be dealt with separately. Because \( \Gamma_3 \times \Gamma_5 = \Gamma_4 + \Gamma_5 \) contains...
\( \Gamma_4 \), there are non vanishing cross-terms in the linear effective Zeeman Hamiltonian for a \( \Gamma_3 + \Gamma_5 \) level. Therefore, such a level will have a linear Zeeman shift different from that of the individual \( \Gamma_3 \) and \( \Gamma_5 \) levels. The Hamiltonian submatrix for the \( \Gamma_3 + \Gamma_5 \) level is given by

\[
\begin{pmatrix}
0 & -\frac{\sqrt{3}}{2} a_{35} B_x & \frac{\sqrt{3}}{2} a_{35} B_y & 0 \\
-\frac{\sqrt{3}}{2} a_{35} B_x & 0 & -\frac{1}{2} a_{35} B_y & a_{35} B_z \\
-\frac{\sqrt{3}}{2} a_{35} B_y & -\frac{1}{2} a_{35} B_y & 0 & -\frac{3}{2} a_{35} B_z \\
0 & -\frac{1}{2} a_{35} B_x & -\sqrt{3} a_{35} B_y & 0 \\
\end{pmatrix}
\]

This \( 5 \times 5 \) matrix is given with respect to a basis consisting of two \( \Gamma_3 \) wave functions and three \( \Gamma_5 \)-wave functions. Only the matrix-elements connecting \( \Gamma_3 \) functions to \( \Gamma_5 \) functions are shown explicitly. This part of the matrix was derived by expressing all six possible products of \( \Gamma_1 \) and \( \Gamma_5 \) wave functions as a linear combination of \( \Gamma_4 \) and \( \Gamma_5 \) wave functions, which is possible because \( \Gamma_3 \times \Gamma_5 = \Gamma_4 + \Gamma_5 \). This procedure is simplified by using, e.g., the coupling coefficients for \( \Gamma_3 \times \Gamma_5 \) as given in Ref. 18. Application of the Wigner-Eckart orthogonality theorem and the fact that all operators occurring in the linear Zeeman Hamiltonian [Eq. (1)] transform according to the rows of \( \Gamma_4 \) complete the derivation of these matrix elements. All information about the strength of the coupling is contained in the (unknown) parameter \( a_{35} \). The upper left and bottom right parts are the same matrices as for the individual \( \Gamma_3 \) and \( \Gamma_5 \) level, respectively, as given in Sec. IV A.

From this matrix, we determine the eigenvalues for \( \mathcal{B} \) parallel to the main crystallographic directions. For \( \mathcal{B} || (100) \), so \( B_x = B, B_y = B_z = 0 \), we find

\[
\Delta E = \begin{cases} 
0 \\
\pm \frac{1}{2} \mu_B g B \\
\pm |a_{35}| B.
\end{cases}
\]

For \( \mathcal{B} || (111) \), so \( B_x = B_y = B_z = B/\sqrt{3} \), we have

\[
\Delta E = \begin{cases} 
0 \\
\pm \frac{1}{2} \mu_B g B \pm \frac{1}{2} B \sqrt{3} \mu_B g B \pm \frac{1}{2} |a_{35}| B.
\end{cases}
\]

Finally for \( \mathcal{B} || (110) \), so \( B_x = B_y = B/\sqrt{2} \) and \( B_z = 0 \), it is found that

\[
\Delta E = \begin{cases} 
0 \\
\pm \frac{1}{2} \mu_B g B \pm \frac{1}{2} \sqrt{3} \mu_B g B \pm \frac{1}{2} |a_{35}| B.
\end{cases}
\]

\( E \) is simplified by using, e.g., the coupling coefficients for \( \mathcal{H}_\text{eff,lin} \). All information about the strength of the effective Zeeman Hamiltonian contains only one term, and is straightforwardly given by

\[
\mathcal{H}_\text{eff,quad} = a_1 B^2,
\]

where \( a_1 \) is a phenomenological parameter. The simple conclusion is that a \( \Gamma_1 \) level will experience a quadratic shift, independent of the direction of the magnetic field: \( \Delta E = a_1 B^2 \). From this purely symmetry-based analysis, conclusions can be drawn neither about the magnitude of \( a_1 \) nor about its sign (that is, whether the state is diamagnetic or paramagnetic). Because \( \Gamma_3 \times \Gamma_5 = \Gamma_1 \), a similar expression holds for a \( \Gamma_2 \) level.

**V. QUADRATIC ZEEMAN EFFECT**

For some of the levels we will also give a second order approach, using the quadratic part of the effective Hamiltonian \( \mathcal{H}_\text{eff,quad} \). Note that \( \mathcal{H}_\text{eff,quad} \) contains both a second order approach to the linear part of the original \( \mathcal{H}_Z \) and a first order approach to the quadratic part of the original \( \mathcal{H}_Z \).

**A. \( \Gamma_1 \) and \( \Gamma_2 \) levels**

For the \( \Gamma_1 \) level, the effective quadratic Zeeman Hamiltonian contains only one term, and is straightforwardly given by

\[
\mathcal{H}_\text{eff,quad} = a_1 B^2,
\]

where \( a_1 \) is a phenomenological parameter. The simple conclusion is that a \( \Gamma_1 \) level will experience a quadratic shift, independent of the direction of the magnetic field: \( \Delta E = a_1 B^2 \). From this purely symmetry-based analysis, conclusions can be drawn neither about the magnitude of \( a_1 \) nor about its sign (that is, whether the state is diamagnetic or paramagnetic). Because \( \Gamma_3 \times \Gamma_5 = \Gamma_1 \), a similar expression holds for a \( \Gamma_2 \) level.

**B. \( \Gamma_3 \) level**

For a \( \Gamma_3 \) level, the effective Hamiltonian contains two unknown parameters and is given by

\[
\mathcal{H}_\text{eff,quad} = a_3 B^2 + b_3 \left(-2 \sigma_x^2 - \sigma_y^2 - \sigma_z^2 + 3 \sigma_x \right),
\]

where \( \sigma_x \) and \( \sigma_y \) are Pauli spin matrices and \( a_3 \) and \( b_3 \) are phenomenological parameters. When \( \mathcal{B} || (100) \) the eigenvalues are given by

\[
\Delta E = (a_3 \pm b_3) B^2.
\]

This is a symmetric quadratic splitting superimposed on a quadratic shift. When \( \mathcal{B} || (111) \), there is only one eigenvalue

\[
\Delta E = a_1 B^2,
\]

meaning that there is no splitting in second order and the quadratic shift is the same as for \( \mathcal{B} || (100) \). Finally, for \( \mathcal{B} || (110) \), we find the eigenvalues

\[
\Delta E = (a_3 \pm b_3) B^2.
\]
The Zeeman effect for this field direction is similar to \(B\|\langle 100\rangle\), but the splitting is twice as small.

### C. \(\Gamma_4\) and \(\Gamma_5\) levels

Because the symmetrized squares of \(\Gamma_4\) and \(\Gamma_5\) satisfy \([\Gamma_4 \times \Gamma_4] = [\Gamma_5 \times \Gamma_5]\), the results for the \(\Gamma_4\) and \(\Gamma_5\) levels are similar. For these two levels, the quadratic part of the effective Zeeman Hamiltonian has three unknown parameters \(a_i\), \(b_i\) and \(c_i\) (\(i = 4, 5\)) and is given by

\[
\mathcal{H}_{\text{eff,quad}} = a_i B^2 + b_i [3 (B_x J_x^2 + B_y J_y^2 - B_z J_z^2) - 2 B^2] + c_i [B_x J_x J_z + B_y J_y J_z + B_z J_z],
\]

where \(\{A, B\} = \frac{1}{2} (AB + BA)\) denotes the anticommutator of \(A\) and \(B\). We calculate the eigenvalues of the full quadratic Hamiltonian matrix \([\mathcal{H}_{\text{eff,lin}}, + [\mathcal{H}_{\text{eff,quad}}]\), for the three main crystallographic directions. For \(B\|\langle 100\rangle\) we have

\[
\Delta E = \begin{cases} 
\mu_B g B + (a_i + b_i) B^2 \\
(a_i - 2 b_i) B^2 \\
- \mu_B g B + (a_i + b_i) B^2.
\end{cases}
\]

For \(B\|\langle 111\rangle\) we have

\[
\Delta E = \begin{cases} 
\mu_B g B + (a_i + \frac{1}{6} c_i) B^2 \\
(a_i - \frac{1}{3} c_i) B^2 \\
- \mu_B g B + (a_i + \frac{1}{6} c_i) B^2.
\end{cases}
\]

And for \(B\|\langle 110\rangle\) we find (up to second order in \(B\))

\[
\Delta E = \begin{cases} 
\mu_B g B + (a_i + b_i + \frac{1}{8} c_i) B^2 \\
(a_i - \frac{1}{2} b_i - \frac{1}{4} c_i) B^2 \\
- \mu_B g B + (a_i + \frac{1}{4} b_i + \frac{1}{8} c_i) B^2.
\end{cases}
\]

It follows that in second order the splitting is no longer symmetric and isotropic for these levels. The Zeeman effect of the levels treated so far is schematically illustrated in Fig. 1.

### VI. CENTRAL FIELD APPROXIMATION

Finally we discuss the Zeeman effect for two-hole states in the central field approximation. In this approximation, we must start from the one-hole levels and their behavior in a magnetic field. The two-hole wave functions are antisymmetrized products of one-hole wave functions and the energy levels are obtained by examining the various ways to put the two holes in the one-hole levels.

We will present results for the case where both holes are put in a \(\Gamma_8\) level and \(B\|\langle 100\rangle\) only. Similar results for the other types of levels and other directions of the field are easily obtained in an analogous way.

---

**FIG. 1.** Schematic overview of level splitting in a magnetic field along the main crystallographic axes in several kinds of two-hole acceptor levels. The figure illustrates the qualitative aspects of the splitting. The values of the parameter have been chosen to emphasize these features.

For a magnetic field \(B\|\langle 100\rangle\), the single hole \(\Gamma_8\) ground state is split into \(\Gamma_5, \Gamma_6, \Gamma_7,\) and \(\Gamma_8\) levels of \(\bar{S}_4\). Because holes are fermions, each of these nondegenerate levels can be occupied by at most one hole. By putting each of the two holes on a different level, this gives rise to six two-hole levels \(\Gamma_5 \times \Gamma_6 = \Gamma_1, \Gamma_5 \times \Gamma_7 = \Gamma_3, \Gamma_5 \times \Gamma_8 = \Gamma_2, \Gamma_6 \times \Gamma_7 = \Gamma_2, \Gamma_6 \times \Gamma_8 = \Gamma_4,\) and \(\Gamma_7 \times \Gamma_8 = \Gamma_1,\) where all representations are of \(\bar{S}_4\).

The energy shifts of the single-hole levels have been determined experimentally. The shifts of the two-hole levels can be calculated as the sum of the shifts of the individual single hole levels from which they are composed. This results in a linear shift for each two-hole level, given by \(\mu_B g B,\) with \(g = \frac{1}{2} g_{3/2} + \frac{1}{2} g_{1/2}\) for \(\Gamma_2,\) \(g = \frac{1}{2} g_{3/2} - \frac{1}{2} g_{1/2}\) for \(\Gamma_4,\) \(g = 0\) for \(2 \Gamma_1,\) \(g = - \frac{1}{2} g_{3/2} + \frac{1}{2} g_{1/2}\) for \(\Gamma_3,\) and \(g = - \frac{1}{2} g_{3/2} - \frac{1}{2} g_{1/2}\) for \(\Gamma_2.\) The parameters \(g_{3/2}\) and \(g_{1/2}\) are the \(g\)-factors for the single hole \(j = \frac{1}{2}\) and \(\frac{3}{2}\) levels respectively. Experimental values for \(B^0\) in Si are \(g_{3/2} = 1.12\) and \(g_{1/2} = 1.04.\) In the above, a small overall shift is neglected.

### VII. APPLICATION TO \(B^+\)

Only states arising from \(\{\Gamma_8 \times \Gamma_8\}\) (see Table II) are candidates for the \(B^+\) ground state. These are \(\Gamma_1, \Gamma_3, \Gamma_5, \Gamma_3 + \Gamma_5,\) and the unsplit (central field) \(\{\Gamma_8 \times \Gamma_8\}.\) Each of these five possibilities for the \(B^+\) ground state will be compared to existing experimental data. From the previous section, we conclude that all possible ground state levels behave qualitatively differently in a magnetic field. Therefore, it is in principle possible to determine the nature of the actual ground state of \(B^+\) from the analysis of a sufficiently detailed experiment. Though this approach is hampered by the fact that the value of the parameters is not known, it is possible to draw conclusions based on the qualitative characteristics, such as linear or quadratic splitting/shift and the asymmetry of the splitting.

We refer to our recent experiments reported in Ref. 4 and
FIG. 2. Magnetic field induced shift of the \( B^+ \) ground state deduced from electrical transport measurements (Ref. 4). The angle between the magnetic field and the current is denoted by \( \theta \). The expression \( \Delta E \propto B(1+\alpha B) \) was fit to the data, yielding \( \alpha = 0.046 \ T^{-1} \).

summarize the main observations. The ground state energy shifts upwards (that is, in the direction of the valence band) and is therefore diamagnetic. The shift has both a linear and a quadratic component. The total shift amounts to 1 meV at a magnetic field of 14 T and was equal for the \( \langle 100 \rangle \) and \( \langle 110 \rangle \) directions (see Fig. 2). The width of the observed peak (full width at half maximum) increased from 1.2 meV to 1.5 meV in the same magnetic field range. Within the experimental error (\( \sim 0.2 \) meV), no splitting of the peak was detected.20

The experimentally observed super linear overall shift, independent from the direction of \( B \), best matches the behavior of a \( \Gamma_1 \) state, although this leaves the strong linear component in the measured magnetic field dependence unexplained. Therefore, we believe that the ground state of \( B^+ \) is indeed a \( \Gamma_1 \) state. This hypothesis does imply that the observed linear component in the peak shift and the peak broadening are is due to other processes (e.g., the Stark effect), as already suggested in Ref. 4.

The broadening in the observed peak is linear in the magnetic field and independent of its direction. Therefore, it cannot be explained as unresolved splitting of a \( \Gamma_3 \) level. A \( \Gamma_5 \) or \( \Gamma_3+\Gamma_5 \) ground state would give rise to linear splitting (broadening), but no overall shift would be expected in first order. Moreover, the magnitude of the splitting in a \( \Gamma_3+\Gamma_5 \) level would depend on the magnetic field direction. Therefore, these possibilities are not consistent with the experimental observations. Only when the parameter \( \alpha_3 \) (or \( \alpha_5 \)) would much larger than all other relevant parameters (that is \( \alpha_3 \approx b_3 \) or \( \alpha_5 \approx b_5,c_5,\mu_B g/|B| \)), the magnetic field dependence of the \( \Gamma_3 \) \((\Gamma_5) \) state would be similar to that of the \( \Gamma_1 \) state. In that case, \( \Gamma_3, \Gamma_5, \) and \( \Gamma_3+\Gamma_5 \) states cannot be rejected as potential ground state symmetries for \( B^+ \).

The central field approach is unlikely to yield good results for \( B^+ \), for which the wave functions of the two holes are expected to overlap considerably (due to the small nuclear charge). The peak splitting (or broadening, due to unresolved splitting) expected in this approach between the two \( \Gamma_2 \) levels would be given by \( 2\mu_B g (\frac{1}{2}g_{32}+\frac{1}{2}g_{12})B \). Assuming the \( B^0 \) values of the \( g \) factors are valid here, this would amount to 3.6 meV for \( B = 14 \) T. This is much larger than the observed 0.3 meV increase of the full width at half maximum of the measured resonance peak. Moreover, the 1-meV shift observed in the experiment is much larger than the expected overall peak shift in this approach. Therefore, the description of the \( B^+ \) ground state in the central field approximation is not consistent with the experimental observations.

In summary, magnetic field dependent measurements indicate that the \( B^+ \) ground state is a nondegenerate \( \Gamma_1 \) state. It would be interesting to have higher resolution spectroscopy data available, in order to exclude that the observed peak broadening is due to unresolved splitting. It is worth emphasizing that in our analysis, we only made use of the fact that \( B^+ \) is a double acceptor and the symmetry properties which follow from that. A knowledge of the \( B^+ \) ground state wave function would allow for obtaining quantitative information about the phenomenological parameters, which would be advantageous in the interpretation of experimental data.

VIII. CONCLUSIONS

In conclusion, we have presented a general group theoretical study of the magnetic field dependence of two-hole states of acceptors in tetrahedral semiconductors. We have used our results to analyze recent experimental observations. This analysis indicates that the \( B^+ \) ground state is most compatible with a \( \Gamma_1 \) state.

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20 In these experiments the concentration of B-impurities in the silicon was so high that they cannot be considered as fully isolated, which is proven by the increased binding energy of the second hole in the $B^+$ state. The interaction of a $B^+$ state with neighboring $B^0$ states is, however, not expected to change the nature of its ground state.