Linear Stark and Nonlinear Zeeman Coupling to the Ground State of Effective Mass Acceptors in Silicon

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It is shown by dielectric resonance absorption at 60 GHz that there is a linear coupling of the electric field to the ground state of effective mass acceptors in Si reflecting the lower T_d symmetry in the central portion of the ground state wave function. The coupling increases strongly with increasing binding energy from B to In, i.e., with decreasing Bohr radius of the acceptor. An unexpected nonlinear Zeeman splitting is observed the magnitude of which also increases from B to In. For all acceptors a central fine structure is found which correlates with the homogeneous linewidth.

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Linear coupling of an electric field to the fourfold degenerate Γ_8 acceptor ground state in silicon or germanium is forbidden within the effective mass approximation (EMA) by inversion symmetry. However, it becomes possible by the local T_d symmetry of the central cell [1, 2] and should therefore be stronger for deeper acceptors with more localized envelope functions. An experimental verification of this linear coupling can be made by measuring the strength of electric dipole resonance transitions between ground state levels split by a magnetic field. For such an experiment, high quality samples are essential: In the first EPR investigations of acceptors in Si at 10 GHz [3], the magnetic $\pm 1/2$ transition was observable only under high enough uniaxial stress to override the level mixing of the Γ_8 quartet inhomogeneously broadened by internal strains. Later, separate lines in Si:B samples could be resolved at zero stress by EPR at 10 GHz [4] and APR (acoustic paramagnetic resonance) [5]. However, the appearance of a relatively strong forbidden $\Delta m = 3$ transition showed that the random strain splitting was not small enough as compared to the magnetic field splitting at 10 GHz for an absolute determination of the strength of the electric dipolar transition. We have, therefore, designed our experiment at 60 GHz using samples with small inhomogeneous broadening according to previous ultrasonic measurements [5–8].

The interaction Hamiltonians for elastic, electric, and magnetic perturbations have been summarized in [2] on the basis of group theoretical considerations together with estimates for the coupling constants. The matrix elements for elastic and electric perturbations of the Γ_8 state with its substates with magnetic quantum numbers $m_j = 3/2,\ 1/2,\ -1/2$, and $-3/2$ (indexed 1, 2, 3, and 4, respectively) can be written as follows [5]:

$$
\begin{aligned}
&H_{11} = -H_{22} = -H_{33} = H_{44} = \Delta_1 \ , \\
&H_{12} = -H_{34} = \Delta_4 + i\Delta_5 \ , \\
&H_{13} = H_{24} = \Delta_2 + i\Delta_3 \ , \\
&H_{14} = H_{23} = 0 \ , \\
&H_{ik} = H_{ki}^{*} \ ,
\end{aligned}
$$

where the Δ_i are given by the elastic ($\underline{\varepsilon}$) and electric ($\mathbf{E}$) fields and the corresponding coupling constants:

$$
\begin{aligned}
&\Delta_{1\varepsilon} = \tfrac{1}{2}\, b' \left(2\varepsilon_{zz} - \varepsilon_{xx} - \varepsilon_{yy}\right) \ , \\
&\Delta_{1E} = \tfrac{1}{2}\, \beta' \left(2E_z^2 - E_x^2 - E_y^2\right) \ , \\
&\Delta_{2\varepsilon} = \frac{\sqrt{3}}{2}\, b' \left(\varepsilon_{yy} - \varepsilon_{xx}\right) \ , \\
&\Delta_{2E} = \frac{\sqrt{3}}{2}\, \beta' \left(E_y^2 - E_x^2\right) \ , \\
&\Delta_{3\varepsilon} = d'\varepsilon_{xy} \ , \quad \Delta_{3E} = p_{\mathrm{eff}} E_z + \delta' E_x E_y \ , \\
&\Delta_{4\varepsilon} = d'\varepsilon_{zy} \ , \quad \Delta_{4E} = p_{\mathrm{eff}} E_x + \delta' E_y E_z \ , \\
&\Delta_{5\varepsilon} = d'\varepsilon_{xz} \ , \quad \Delta_{5E} = p_{\mathrm{eff}} E_y + \delta' E_z E_x \ .
\end{aligned}
\tag{1}
$$

b' and d' are the two deformation potential constants. β' and δ' are the two coupling constants for the quadratic Stark effect and p_{eff} is the effective electric dipole moment for linear Stark coupling. p_{eff} is zero for inversion symmetry, i.e., for the acceptor ground state as calculated within the EMA. E is the externally applied electric field including the effect of a local field [9]. p_{eff} is a measure of the probability density of the state in the central cell region where the T_d symmetry is dominant. Following [2], we have taken

$$
p_{\mathrm{eff}} = \int_0^{a_{\mathrm{Si}}} F(r)^{*}\, er\, F(r)\, dV \tag{2}
$$

as a rough estimate of its magnitude. Here, e is the electron charge, a_{Si} the lattice constant of silicon, and $F(r)$ is the radial part of the envelope function. Different r dependences of $F(r)$ are obtained for the EMA Coulomb potential or, on the other hand, the δ potential which has been commonly used to approximate the case for deep impurities [10]. In both cases, the chemical shift may be accounted for by using the relation $E_B = (\hbar/a_B)^2/2m_h$ between the acceptor binding energy E_B and an effective Bohr radius a_B in the respective solutions for $F(r)$. We get $p_{\mathrm{eff,B}} = 0.9$ D and $p_{\mathrm{eff,In}} = 3$ D for the Coulomb potential. Correspondingly, we obtain $p_{\mathrm{eff,B}} = 6$ D and $p_{\mathrm{eff,In}} = 8$ D for the δ potential. From this, a chemical shift of p_{eff} larger than that of E_B could occur if there is a change from Coulomb to δ potential between the shallow

boron and the deep indium acceptor.

In a magnetic field $\mathbf{B}$, the fourfold degeneracy of the Γ_8 ground state is completely lifted. From the Hamiltonian as given in [11], one obtains for the combined splitting by a large magnetic field and small elastic and electric fields (following Yafet [12] and Neubrand [4]) as

$$E_B = \mu_B m_j |\mathbf{B}| \left\{ g_1' + g_2' \left[\frac{41}{20} + \left(m_j^2 - \frac{41}{20} \right) p(\theta) \right] \right\} + E_{B^2}(\theta) + \frac{m_j^2}{2} E_{\varepsilon,E}(\theta) \,. \quad (3)$$

The magnetic field is in the $(1\bar{1}0)$ plane with the angle θ to the [001] direction, μ_B is the Bohr magneton, g_1 and g_2 ($\ll g_1$) are the isotropic and the anisotropic part of the g factor, respectively, and $p(\theta)$ is the function

$$p(\theta) = 1 - 5\sin^2\theta + \tfrac{15}{4}\sin^4\theta. \quad (4)$$

The contribution from the quadratic Zeeman effect is given by [11]

$$E_{B^2} = \left[q_1 + (q_2 + q_3) m_j^2 \right] B^2 \quad \text{for } \mathbf{B} \parallel [001] \,, \quad (5)$$

$$E_{B^2} = \left[q_1 + q_2 m_j^2 + \frac{5}{4} q_3 \right] B^2 \quad \text{for } \mathbf{B} \parallel [111] \,. \quad (6)$$

The coupling constants q_i being proportional to $\langle r^2 \rangle$ should be larger for more extended wave functions in contrast to p_{eff}. $E_{\varepsilon,E}(\theta)$ is the additional energy shift due to small static elastic and electric fields:

$$E_{\varepsilon,E}(\theta) = -\Delta_1 \left(1 - 3\cos^2\theta\right) + \sqrt{3}\,\Delta_3 \sin^2\theta + \sqrt{3/2}\,(\Delta_4 + \Delta_5) \sin 2\theta \,. \quad (7)$$

The Δ_i are the sums of the components of elastic and electric perturbations. Random distributions of these fields will lead to an inhomogeneous broadening of the line depending on the orientation of the magnetic field. For $\mathbf{B}$ parallel to [001] we expect the smallest linewidth, and for $\mathbf{B}$ parallel to [111] the largest.

The matrix elements for phonon transitions have been calculated by Yafet [12]. His results may be extended to alternating electric fields by making use of the analogy of $\mathbf{\Delta}_\varepsilon$ and $\mathbf{\Delta}_E$. For electric dipole transitions, the components $\tilde{\Delta}_{1E}$ and $\tilde{\Delta}_{2E}$ are zero. This allows one to separate the $\Delta m = 1$ and $\Delta m = 2$ electric dipole transitions by orientation of the sample in the magnetic field. For the microwave electric field $\tilde{\mathbf{E}}$ parallel to the $[1\bar{1}0]$ direction and the magnetic field perpendicular to it with the angle θ to the [001] direction, we get

$$\begin{aligned} |\tilde{H}_{12}|^2 &= |\tilde{H}_{34}|^2 = p_{\text{eff}}^2 |\tilde{\mathbf{E}}|^2 \cos^2\theta \,, \\ |\tilde{H}_{13}|^2 &= |\tilde{H}_{24}|^2 = p_{\text{eff}}^2 |\tilde{\mathbf{E}}|^2 \sin^2\theta \,, \\ |\tilde{H}_{14}|^2 &= |\tilde{H}_{23}|^2 = 0 \,. \end{aligned} \quad (8)$$

A quadratic coupling of the alternating electric field would lead to a completely different dependence of the line intensities on angle and should occur at a magnetic field splitting larger by a factor of 2 than that for one-photon transitions. The vanishing of the $\Delta m = 1$ signal for $\theta = 0°$; i.e., $\mathbf{B}$ parallel to [110], will show that the alternating magnetic field is negligible within the sample.

The dielectric absorption was measured with the samples (vertically [110]-oriented cylinders of 2 mm diam, 1 mm thick) in the central capacitive part of a 60-GHz radial cavity (8 mm diam) operating in the second harmonic in a standard EPR microwave bridge. Care had to be taken to keep extra strains (with ensuing line broadening) due to mounting or shaping to a minimum. After sawing, the slice was ground with 9 μm Al_2O_3 and Syton polished. The cylindrical form was then obtained by ultrasonic boring. With the polished disk faces protected, 150 μm thickness of the side walls were etched off. The resulting resonance frequency deviated only by 0.5% from the calculation given in [13].

For quantitative evaluation of the line strengths, the quality factor was determined from the resonance curve optimizing the resonance and subtracting the zero line obtained when the cavity is detuned. We related the cavity losses to the loss tangent of the material by help of the above mentioned calculation of the cavity parameters and obtained the transition probability by integration stepwise for a dense enough series of magnetic field values over the lines. To determine the line position, it is sufficient to record the change in reflection of the weakly coupled cavity tuned to resonance. We do not apply magnetic field modulation; i.e., we obtained the absorption curves instead of their derivatives.

Figure 1 shows the magnetic field dependence of the absorption for a Si:B sample with orientations appropriate for both the $\Delta m = 1 (\theta = 0°)$ and the $\Delta m = 2 (\theta = 90°)$ transitions. The angular dependence of the measured line intensities shows clearly that these lines are caused by linear Stark coupling. The absence of the $\Delta m = 1$ magnetic transition $-1/2 \leftrightarrow +1/2$, that should

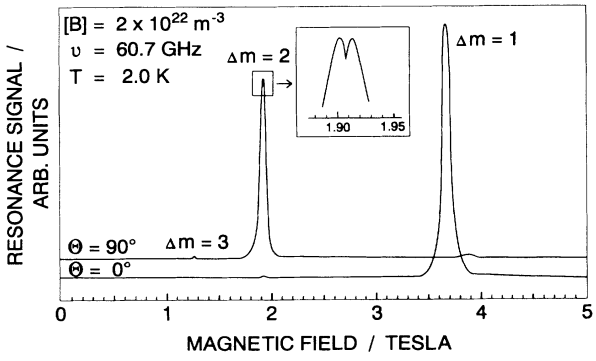

FIG. 1. Dielectric resonance absorption of a Si:B sample for two magnetic field orientations where either the $\Delta m = 1$ or 2 transitions are allowed. The weakness of the forbidden $\Delta m = 3$ line indicates that the high field situation is very well attained for this high quality sample. Inset: A magnified central portion showing a dip which is observed for all acceptors.

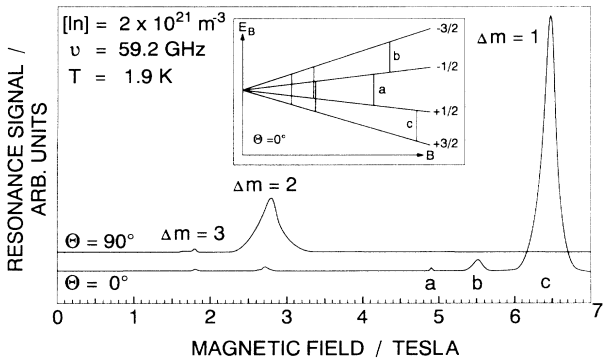

FIG. 2. Dielectric resonance absorption of a Si:In sample for two magnetic field orientations. At $\theta = 0°$ three separate lines are observable. The smallest line at 4.9 T is the forbidden $-1/2 \leftrightarrow +1/2$ transition. The other two lines correspond to the "upper" and "lower" $\pm 1/2 \leftrightarrow \pm 3/2$ transitions. Inset: A schematic of how the lines should split with additional quadratic Zeeman coupling.

appear at $|\mathbf{B}| = 4.02$ T for $\theta = 0°$ and at 3.77 T for $\theta = 90°$, indicates that the contribution due to the alternating magnetic field of the cavity is negligible. The weakness of the forbidden line $\Delta m = 3$ confirms that the selection rules for the high field case are valid; i.e., that the strength of the $\Delta m = 1$ and $\Delta m = 2$ lines correspond to the coupling in the high field limit. The angular dependences of the linewidths follow Eq. (7). This result was also observed in measurements using APR for these same crystals [6]. However, in APR the linewidth of the highest quality samples was somewhat smaller. This may be due to the fact that for the larger samples used (10 mm cubes) the residual surface strains are less effective.

The absolute values of the g_1' factors (Table I) compare well with the values given in [2] (calculated from EPR data under uniaxial stress of [3]) which confirms that these lines are due to one-quantum transitions. From the angular dependence of the line position, the relative sign of g_1' and g_2' can be obtained. We find $g_1'g_2' > 0$ for B; whereas, for Al, Ga, In we get $g_1'g_2' < 0$. This is in agreement with results of EPR at 9 GHz [4] and 20 GHz [14], as well as APR at 4 GHz [5] (it is by a misprint that $g_1'g_2' < 0$ in this reference) in the case of Si:B and also with unpublished results of APR for Si:In [15].

At higher resolution, the $\Delta m = 2$ line shows a central dip (inset of Fig. 1) for all acceptors. The linewidth is independent of intensity and does not depend on θ in contrast to the $\Delta m = 2$ line. In the measured temperature range between 1.8 and 20 K this fine structure is of the order of the natural linewidth as obtained from ultrasonic relaxation attenuation [7, 16, 17]. Its position does not move under uniaxial stress even if the $\Delta m = 2$ line is broadened and nearly split. This behavior together with the consistency of g factors obtained for this position means that this fine structure belongs to those acceptors with zero strain, i.e., with symmetric splitting of the Γ_8 quartet in magnetic field. At 24 GHz, the structure was reported to change around 4 K from a dip at lower temperatures to a peak at higher temperatures [18]. In contrast, we do not find any indication for such a change at 60 GHz between 1.8 and 20 K. This structure corresponds to the sharp central line in the EPR of Si:B at 9 GHz [4] and 20 GHz [14]. Neubrand [4] observed a change from a dip at 1.4 K to a peak at 4.2 K. The origin of this structure was not understood up to now. The discussion of similar fine structure for a $S = 1$ triplet [19] does not seem to be applicable to the Γ_8 quartet here.

In the EPR measurements [4, 14] there was also a fine structure in the central portion of the $\Delta m = 1$ line. A pronounced dip was also observed for all acceptors in our previous measurements at 24 GHz [20]. In the present measurements at 60 GHz we do not find such a fine structure. However, in the case of Si:In we observe a splitting of the $\Delta m = 1$ line (Fig. 2). From the angular dependence of the g factors and the temperature dependence of the intensities it was possible to identify these lines as the three $\Delta m = 1$ transitions: The line labeled "a" is the magnetic $-1/2 \leftrightarrow +1/2$ transition which is much smaller in intensity than the other two lines. From the temperature dependence of the line intensities we could assign the two lines labeled "b" and "c" to the "upper" and "lower" of the two possible electric $\pm 1/2 \leftrightarrow \pm 3/2$ transitions. According to Eq. (7) static uniaxial elastic or electric fields cannot be the reason for this splitting because then there should be a comparable splitting of the $\Delta m = 2$ line. The fact that this line shows only a small asymmetry indicates that the splitting increases with magnetic field. A possible cause for this could be the quadratic Zeeman effect. In the case of Si:Ga and Si:Al, we find a smaller splitting of the two electric $\Delta m = 1$ transitions, and the forbidden $+1/2 \leftrightarrow -1/2$ transition is not observable. For Si:B we got only one $\Delta m = 1$ line, but a small asymmetry of this line indicated that there might be also a quadratic Zeeman coupling. With this assumption, we evaluated the coupling constants $(q_2 + q_3)$ for the acceptors (Table I). Because of increased linewidth and smaller line intensity of the $\Delta m = 1$ line for angles $\theta \neq 0°$, it was not possible to determine all three coupling constants q_1, q_2, and q_3 separately. The constants are seen to increase from B to In inversely to the expected a_B^2 dependence for a quadratic Zeeman effect. In recent measurements at 24 GHz [18], a splitting of the $\Delta m = 1$ line due to a nonlinear Zeeman effect was also found. However, an analysis is difficult because the splitting is of the order of the inhomogeneous linewidth and we have the additional central fine structure mentioned above. As a rough estimate, we obtain a value of 2.2 for the exponent. It is planned, therefore, to check for the B^2 dependence with measurements at some intermediate frequency.

To determine the electric dipole moment p_{eff} the change in Q factor ΔQ is integrated over a whole line to include the total number of acceptors N_A. By applying

TABLE I. Coupling constants of the acceptor ground state. g factors g_1' and g_2' calculated from the angular dependence of the position of the $\Delta m = 2$ line (the sign of g_1' has been set positive), $q_2 + q_3$ from the splitting of the $\Delta m = 1$ line, p_{eff} obtained by integration of a resonance line. (Mean values for 6 In-, 6 Ga-, 4 Al-, and 9 B-doped samples with acceptor concentrations between 10^{23} and 10^{21} m^{-3}.)

	In	Ga	Al	B
g_1'	0.885	0.993	0.997	1.070
g_2'	−0.056	−0.017	−0.014	0.033
$q_2 + q_3$ (GHz/T^2)	−0.07	−0.02	−0.02	<0.01
p_{eff} (D)	0.9±0.12	0.6±0.10	0.8±0.12	0.26±0.06

the formalism developed in [13], ΔQ can be correlated to the dielectric loss which in turn is proportional to $N_A p_{\text{eff}}^2$. N_A is obtained from its standard relation to room temperature conductivity in the case of B. For Al and Ga, ir absorption of transitions between bound states together with RT conductivity have been taken. For In, Hall measurements for two samples and the empirical relation to room temperature conductivity according to [21] for the others has been used. The range of errors indicated for p_{eff} in Table I reflects the scatter in our data which is due to several reasons: (i) The difficulty of mounting the small samples exactly in the middle of the cavity. (ii) The tuning post causes a spatial variation of the resonance fields which is not included in the evaluation. (iii) The acceptor concentrations were specified only as averages over the crystals, not for the samples so that doping inhomogeneities cannot be excluded.

We found that p_{eff} increased from B to In with decreasing Bohr radius as expected if p_{eff}^2 is a measure of the probability density of the wave function in the central cell. We found also that the chemical shift is similar to that of E_B with a possible "inversion" of the trend between Al and Ga.

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