

Linear stark coupling to the ground state of effective mass acceptors

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ABSTRACT: It is shown by dielectric resonance absorption at 24 GHz and by ultrasonic resonance spectroscopy between .5 and 10 GHz that linear coupling of the electric field to the ground state of effective mass acceptors in Si exists and has a distinct chemical shift from B to In.

1. INTRODUCTION

Linear coupling of an electric field to the I_g acceptor ground state is forbidden by inversion symmetry within the Effective Mass Approximation. It becomes, however, possible by the local T_d symmetry of the central cell (Kohn 1957, Bir et al 1963) and should therefore be stronger for deeper acceptors with more localized envelope functions. We have shown by dielectric resonance absorption at 24 GHz (corresponding to electric dipole transitions between ground state levels split by a magnetic field) that there is indeed a chemical shift of the coupling strength for the acceptors B, Al, Ga, In by about a factor of 5, which is larger than the shift of the binding energies. For all the dopants the ground state splittings from internal strain fields are small enough as compared to the magnetic field splitting i.e. small overlap of the inhomogeneously broadened lines. Nevertheless, higher resonant frequencies or smaller linewidths would improve the precision of the evaluation.

The residual random splitting existing even in high quality samples means likewise an experimental difficulty if the (additional) splitting of the ground state by a static external electric field is to be observed: It is too small to be easily measurable before the breakdown field is reached. We have made use of the larger random internal electric fields in Si:B compensated by neutron transmutation to generate a broadening of the ground state splittings by these electric fields additional to the random strain fields. The electric fields can be switched off by bandgap illumination neutralizing the donor-acceptor ion pairs persistently at low temperatures. This change in the width of the splitting distribution is probed in the frequency range from 0.5 to 12 GHz by ultrasonic resonance absorption. Comparison of the measured distributions is made with Monte Carlo (MC) calculations. The analysis of the angular dependence of the linewidth in acoustic paramagnetic resonance shows that only the linear Stark coupling is effective in line broadening whereas a quadratic contribution could not be observed. The measured value for the linear coupling in the case of Si:B compares well with the value obtained by the resonance method. Other dopants could not be measured this way because appropriately compensated samples are difficult to obtain.

2. THEORETICAL CONSIDERATIONS

The interaction Hamiltonians for elastic, electric, and magnetic perturbations, have been summarized by Bir et al (1963) on the basis of group theoretical considerations together with estimates for the respective coupling constants with EMA-wavefunctions. As discussed by Zeile and Laßmann (1982) the introduction of a five-dimensional state vector Δ is useful for an evaluation not only of the splitting but also of the coupling to the elastic or electric alternating fields. The matrix elements for the elastic and electric perturbations of the Γ_8 -state with its substates with magnetic quantum numbers $m = 3/2, 1/2, -1/2, -3/2$ (indexed 1,2,3,4, respectively) are then:

$$H_{11} = -H_{22} = -H_{33} = H_{44} = \Delta_1, \quad H_{14} = H_{23} = 0, \quad H_{1k} = H_{k1}^*,$$

$$H_{12} = -H_{34} = \Delta_4 + i\Delta_5, \quad H_{13} = H_{24} = \Delta_2 + i\Delta_3,$$

where the Δ_i are given by the elastic (ϵ) and electric (E) fields and the corresponding coupling constants as follows:

$$\Delta_1\epsilon = (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})b'/2 \quad \Delta_1E = (2E_zE_z - E_xE_x - E_yE_y)B'/2$$

$$\Delta_2\epsilon = (\epsilon_{yy} - \epsilon_{xx})\sqrt{3}b'/2 \quad \Delta_2E = (E_yE_y - E_xE_x)\sqrt{3}B'/2$$

$$\Delta_3\epsilon = \epsilon_{xy}d' \quad \Delta_3E = E_xE_y\delta' + E_zp\chi$$

$$\Delta_4\epsilon = \epsilon_{yz}d' \quad \Delta_4E = E_yE_z\delta' + E_xp\chi$$

$$\Delta_5\epsilon = \epsilon_{xz}d' \quad \Delta_5E = E_xE_z\delta' + E_yp\chi$$

b' and d' are the two deformation potential constants, $B' = -(p_0^2/E_B)\beta$ and $\delta' = -(p_0^2/E_B)\delta$ the two coupling constants for the quadratic, $p\chi$ for the linear Stark effect with dipole moments $p_0 = e\langle r^2 \rangle$, and $p = e a_B$ introduced to have the dimensionless constants β , δ , and χ . The definition $a_B = \hbar/\sqrt{2} m_h E_B$ (m_h is the hole effective mass and E_B the experimentally determined binding energy.) for the Bohr-radius a_B is common to the EMA-, quantum defect, and δ -potential models (see e.g. Rynne et al 1976). The constant χ may be regarded as a characteristic of the wavefunction in the central cell and will be different for the three models. However, the wavefunctions corresponding to these models are centro-symmetric (i.e. do not reflect the local T_d -symmetry at the center) and so χ should be zero since the dipole moment $\langle r \rangle$ for these functions is zero in contrast to the constants β and δ for the quadratic Stark effect.

For any splitting due to static elastic or electric fields characterized by a splitting state vector Δ the coupling to a phonon with unit state vector Δ_ϵ the coupling is given by $\Delta_\epsilon \sin\psi$ (ψ is the angle between the five-dimensional vectors). This relation simplifies MC calculations of the resonant phonon coupling to random internal elastic or electric fields. It has been done for the strain fields from point defects or dislocations and for the electric fields from correlated and noncorrelated ion pairs (Zeile and Laßmann 1982). At 4.2 K and for the ion concentrations achieved nearest (= correlated) ion pairs will render the thermodynamically favourable configuration which therefore has been used for estimating the constant χ by comparison of MC calculations with the measured additional broadening.

The combined effect of a large magnetic field B and small electric or elastic fields on the energy of the substates E_m of Γ_8 is (Yafet 1965):

$$E_m = \mu_0(g_1' + g_2' \langle (41/20) + (m^2 - (41/20)) p(\theta) \rangle) m B + m^2 E_{\epsilon, E}(\theta) / 2$$

with $p(\theta) = 1 - 5\sin^2(\theta) + (15/4)\sin^4(\theta)$

$$\text{and } E_{\epsilon, E}(\theta) = -\Delta_1(1 - 3\cos^2(\theta)) + \sqrt{3} \langle \Delta_3 \sin^2(\theta) + (\Delta_4 + \Delta_5) \sin(2\theta) \rangle / \sqrt{2}$$

The Δ_1 are the sum of the state vector components of the elastic and electric perturbations. In the case of random distributions of these fields the various components will add to the inhomogeneous broadening of the line depending on the orientation of the magnetic field. θ is the angle between the $\langle 001 \rangle$ - or z-direction and the magnetic field in the $(1\bar{1}0)$ -plane. The influence of the linear and the quadratic Stark effect on the linewidth can be separated for $\theta = 0^\circ$ and $\theta = 55^\circ$ since

$$E(\theta = 0^\circ) = 2\Delta_1 \text{ and } E(\theta = 55^\circ) = 2(\Delta_3 + \Delta_4 + \Delta_5) / \sqrt{3}.$$

Phonon or electric dipole transitions are allowed for $m = \pm 1/2 \leftrightarrow \pm 3/2$ ($\Delta m = 1$) or $\mp 1/2 \leftrightarrow \pm 3/2$ ($\Delta m = 2$) depending on orientation whereas for $m = -1/2 \leftrightarrow +1/2$ and $-3/2 \leftrightarrow +3/2$ they are always forbidden. The matrix elements for phonon transitions have been calculated by Yafet (1965). With the unit state vector $\Delta_{\epsilon, E}$ for the elastic or electric alternating field they can be written as follows:

$$2H_{12} = -\Delta_1 \sqrt{3} \sin 2\theta + \Delta_3 \sin 2\theta + (\Delta_4 + \Delta_5) \sqrt{2} \cos 2\theta - i \langle 2\Delta_2 \sin \theta - (\Delta_5 - \Delta_4) \sqrt{2} \cos \theta \rangle$$

$$2H_{13} = +\Delta_1 \sqrt{3} \sin^2 \theta + \Delta_3 (1 + \cos^2 \theta) - (\Delta_4 + \Delta_5) (1/\sqrt{2}) \sin 2\theta - i \langle 2\Delta_2 \cos \theta + (\Delta_5 - \Delta_4) \sqrt{2} \sin \theta \rangle$$

$$H_{34} = -H_{12}, H_{24} = H_{13}, H_{14} = H_{23} = 0.$$

For electric dipole transitions the components Δ_1 and Δ_2 of the state vector are zero. This allows 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 $E //$ to the $\langle 1\bar{1}0 \rangle$ -direction and the magnetic field $B //$ to the $\langle 001 \rangle$ or the $\langle 110 \rangle$ -direction we get

$$H_{12} = i p_X E / 2, H_{13} = H_{14} = H_{23} = 0, \text{ or } H_{13} = -i p_X E / 2, H_{12} = H_{14} = H_{23} = 0,$$

respectively. The vanishing of the $\Delta m = 1$ signal for $\langle 110 \rangle$ then means that the alternating magnetic field is negligible within the sample.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The dielectric absorption was measured by positioning the samples ($\langle 110 \rangle$ -oriented cylinders of 2 mm diam., 1 mm thickness) in the capacitive part of a 24 GHz coaxial cavity in the center of a 4.5 T superconducting magnet at 4.2 K and below. Care was taken to keep extra strains and line broadening due to shaping and mounting to a minimum. The change in reflection of the weakly coupled cavity tuned to resonance was detected by a diode. To improve the signal to noise ratio we applied amplitude modulation at 1 kHz by switching the frequency of the 180 mW Gunn source from cavity resonance to a frequency far off the resonance. The modulated detector signal was integrated by a standard VSWR-meter. We do not apply magnetic field modulation i.e. we obtain the absorption curves instead of their derivatives. Thus we get the absorption strength by integration of the lines with the simplifying assumption that the electric energy of the resonator is completely stored within the sample. The magnetic field was measured with a Hall probe fixed to the outside of the cryostat. It was

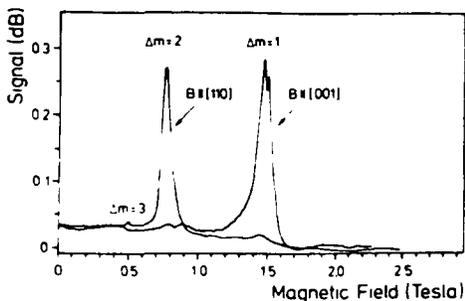


Fig.1 Dielectric resonance absorption for two orientations of a Si:B sample where either the $\Delta m = 1$ or $= 2$ transitions are allowed. $\Delta m = 3$ appears since the high field case is not attained. The central dip of the $\Delta m = 1$ line is discussed in the text. Boron concentration $C_B = 6 \times 10^{22} \text{m}^{-3}$.

calibrated at constant currents with the current/field conversion factor supplied by the manufacturer.

Fig. 1 shows the magnetic field dependence of the absorption for a Si:B sample with orientations appropriate for either the $\Delta m = 1$ or $= 2$ allowed transitions. The dip in the centre of the $\Delta m = 1$ line we find for all acceptors; it corresponds to the sharp central line in the EPR of Si:B reported by Neubrand (1978). It may be due to the additional paths in the relaxing I_8 - quartet when the upper and lower $\Delta m = 1$ transitions become equal in the centre of the line. Such a dip was not found in (pulsed) acoustic paramagnetic resonance (APR) up to 12 GHz (Zeile and Laßmann 1982 and this work) and at 24 GHz (Schulze 1984). On top of the $\Delta m = 2$ line of Fig. 2 (as well as in other cases) a weak extra peak is discernible also consistent with Neubrand's finding for the centre of the $\Delta m = 2$ line. For the orientation allowing a $\Delta m = 2$ transition the forbidden $\Delta m = 3$ transition is also seen because the high field case is not attained and has similarly been found as an asymmetric line in EPR and APR. The occurrence and the asymmetry of this line means that any transition probabilities as evaluated for the high field case must be corrected for the zero field splitting. An experimental demonstration of this has been given by Zeile and Laßmann (1982). Also the higher field $\Delta m = 1$ line contains some contribution of the forbidden $+1/2 \leftrightarrow -1/2$ transition which is resolved for an intermediate orientation as shown in Fig. 2. Thus, for an absolute evaluation of the coupling strength the resonance splitting should be larger. The relative change, however, for the different acceptor species may be estimated more reliably. (There was no systematic variation of the integrated transition probability on the small variation of linewidth of different samples with same dopant.) Some scatter in our data is due to the difficulty to mount the small samples exactly in the required orientation. Another problem was due to the fact that the cavity has some moveable parts for adapting to the sample and for tuning: This apparently lead to some mechanical instability at higher field

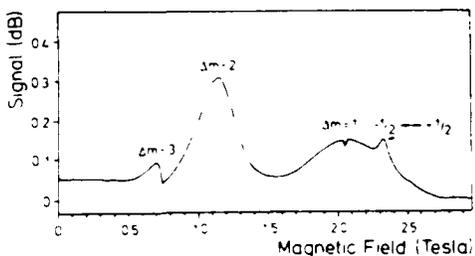


Fig.2 Dielectric resonance absorption for an intermediate orientation of a Si:In sample where in addition to both allowed the two forbidden $\Delta m = 1$ and $= 3$ transitions appear. Indium concentration $C_{In} = 3.9 \times 10^{22} \text{m}^{-3}$.

strengths with some signal drift as a consequence. With the provisos just mentioned we get for the coupling constants (dipole moments) p_x :

dopant / E_B (meV)	dipole moments p_x (Debye)	The p_x are average values of several runs for the two orientations of
In / 156	$1.0 \pm .5$	3 samples Si:In, $C_{In} = 4$ to $8 \times 10^{22} \text{ m}^{-3}$
Ga / 73	$.5 \pm .35$	1 sample Si:Ga, $C_{Ga} = 1.2 \times 10^{22} \text{ m}^{-3}$
Al / 69	$.7 \pm .4$	1 sample Si:Al, $C_{Al} = 6.9 \times 10^{22} \text{ m}^{-3}$
B / 44	$.2 \pm .15$	5 samples Si:B, $C_B = .1$ to $6 \times 10^{22} \text{ m}^{-3}$

Our g-factors compare well with those derived from the data of Feher et al (1960). The absolute value of p_x can only roughly be estimated since the cavity/sample geometry was not well enough defined. Assuming that the capacitive part of the cavity is identical with the sample volume p_x was obtained from the integrated change in Q-factor in the case of In where the signal was strong enough. For the weaker signals of Ga, Al, and B the values given are from comparison of the integrated change in cavity reflection signal to that for In. The error bars indicated contain the scatter of these latter relative values for each dopant (which were only about 20%) plus the scatter in the determination of the Q-factor in the case of In. (These absolute values have been evaluated without the consideration of the internal field due to the polarization of the silicon lattice as discussed by Mims (1976).) The scatter in the relative values is smaller: We obtain a factor of 5.1 ± 1.6 for the ratio of p_x between In and B. Since the coupling is determined by the innermost part of the wave function in the central cell it is difficult to estimate. As a guideline we have calculated $\langle |r| \rangle$ (instead of $\langle r \rangle$ which is zero for centro-symmetric wavefunctions) for the EMA and δ -potential wavefunctions (with a_B defined by the experimental binding energy as given above) over spheres of the lattice constant (as well as half the lattice constant) and obtained a ratio of 3.8 (4.9) between In and B for EMA and a factor of 1.2 (1.5) for δ -potential. In the case of a crossover (EMA for B, δ -potential for In) the ratios would be larger: 8.8 (40).

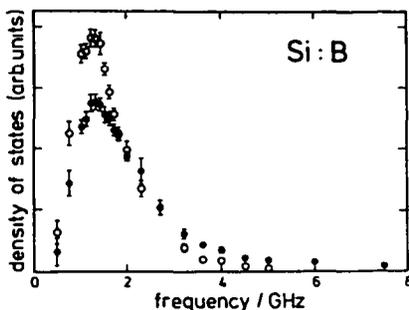


Fig.3 Splitting distributions of a Si:B sample partly compensated with P by neutron transmutation. In the neutralized (illuminated) state (o) the distribution is narrower. Electric fields from donor-acceptor pairs ($C_{da} = 1 \times 10^{21} \text{ m}^{-3}$) are responsible for the broadening in the ionized (nonilluminated) state (\bullet). Boron concentration $C_B = 5.5 \times 10^{21} \text{ m}^{-3}$.

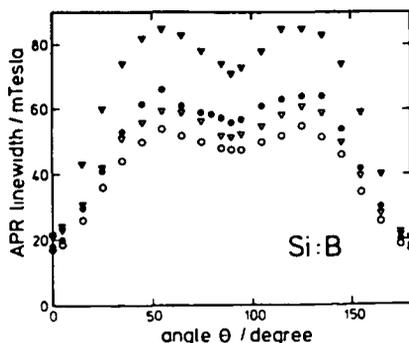


Fig.4 Angular dependence of the width of the $\Delta m = 1$ line in acoustic paramagnetic resonance at 7.5 GHz of the sample of Fig. 3 after partial (∇, ∇) and after complete (\circ, \bullet) annealing of the radiation defects (i.e. more or less ion-pairs). Since the difference between illuminated (open) and nonilluminated (filled) state is zero at 0° there is negligible contribution due to the quadratic Stark effect.

The B-doped samples ($C_B = 5.5$ and $20 \times 10^{21} \text{ m}^{-3}$) for the measurement of the influence of internal electric fields were irradiated with thermal neutrons at Harwell resulting in donor concentrations .5 and $1 \times 10^{21} \text{ m}^{-3}$. They were then annealed at several temperatures. After the final step at 750°C the splitting distribution was close to that before n-transmutation if the sample was illuminated with bandgap light at low temperatures to neutralize the donor-acceptor ion pairs, i.e. the defects were essentially healed. Without illumination, however, the distribution is broader due to the random electric fields from the ions as seen in Fig. 3. As mentioned above and described by Zeile and Laßmann (1982) these curves are obtained by measuring the resonance attenuation of ultrasound in the corresponding frequency range. To distinguish between quadratic and linear Stark effect measurement of the APR is helpful: The linewidth for certain directions of the magnetic field does not contain a contribution of the linear coupling. In Fig.4 this is the 0° direction. From comparison of the angular dependence of the linewidth with and without illumination we find that the quadratic coupling has no measurable effect so that the broadening of the distribution is solely due to the linear coupling. From comparison with MC-calculations we derive $p_x = (0.26 \pm 0.13)$ Debye which compares quite well with the result of the resonance method. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We are obliged to many colleagues for the supply of samples: W. Zulehner, Wacker Chemitronic (Si:B,Al,Ga); J.S. Blakemore, then at Florida Atlantic Univ. (Si:In); M. Vilain, LETI, Grenoble (Si:In); N.W. Crick, Harwell (neutron transmutation) and L. Challis, Nottingham, for arranging this possibility.

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