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A CALCULATION OF VALENCE BAND MASSES, EXCITON AND ACCEPTOR ENERGIES AND THE GROUND STATE PROPERTIES OF THE ELECTRON–HOLE LIQUID IN CUBIC SiC

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The Luttinger parameters of cubic SiC are determined by using a modified Lawaetz approach, including the hole–phonon coupling for small spin–orbit interaction:

$\gamma_1^* = 2.817, \quad \gamma_2^* = 0.508, \quad \gamma_3^* = 0.860, \quad \kappa^* = -0.41.$

Revised ground state calculations of the electron–hole liquid, including the nonparabolic valence band dispersion, for conflicting theories of the electron–phonon interaction, yield a good agreement between the ϵ_0^*-approximation and experiment. The calculated ground state binding energy of the free exciton and of the point-charge acceptor are 26.7 and 179 meV respectively. These calculations yield a revised value of the band gap energy $E_g = 2.416$ eV.

SiC RECENTLY FOUND increasing attention due to a number of reasons. An electron–hole liquid (EHL), stable up to high temperatures [1–3] of 40–70 K was discovered. Multiple bond excitons [4] were observed. Technological progress led to the production of comparatively efficient light emitting diodes [5] for the blue part of the spectrum.

The optical and electonic properties of SiC can only be understood in detail and compared with theoretical predictions if the electronic band structure – in particular the masses and the dispersion of the bands close to the valence band maximum and the conduction band minimum – is known. The values of the conduction band masses $m_l = 0.647m_0$, $m_t = 0.24m_0$ and the location of the c.b. minimum at the X-point of the Brillouin zone are well established for the cubic polytype 3C–SiC from experiment [6]. No experimental determination of the valence band masses of 3C–SiC or of any other polytype exists.

In this letter, a derivation of the Luttinger parameters for 3C–SiC is presented. Polaron effects [7] and the size of the spin–orbit splitting [8] are taken into account.

Energy levels of the free exciton and the effective mass acceptor are calculated for the first time, based on these parameters, giving a revised value of the fundamental band gap. The ground state energy and the density of the EHL are sensitive functions of the kinetic energies of electrons and holes. A revised calculation of these quantities is presented for two conflicting theories [9, 10] of the electron–phonon interaction and compared with experiment. The experimental results are found to be in agreement with only one of the predictions – in contrast to earlier results.

A five–level $\mathbf{k}\cdot\mathbf{p}$ analysis was successfully used by Lawaetz [11] to compute the effective masses for a number of semiconductors – excluding SiC. The basic parameters in his momentum matrix elements were obtained from the experimental valence band parameters for Ge. We adopt the same procedure here. However, the Si valence band parameters $\gamma_1 = 4.285$, $\gamma_2 = 0.339$, $\gamma_3 = 1.446$ and $\kappa = -0.42$ are used by us for the derivation of the momentum matrix elements. The Si parameters are known from quantum cyclotron resonance experiments [12] with the same accuracy as the Ge parameters and Si has an overall band structure which is more similar to the SiC band structure than the Ge band structure. The energies $E'_{0h} = 5.21$ eV, $E'_0 = 7.1$ eV and

Table 1. Comparison of experimental and theoretical parameters of the EHL *in cubic* SiC. *The theoretical* and *experimental values refer to a non-parabolic valence band and a spin–orbit splitting of* 10 meV. E_B *is the binding energy of the* EHL *with respect to the lowest exciton state.* E_{TOT} *is the ground state energy with* $E_{TOT} = E_B + E_X$, *where* $E_X = 26.7$ meV *is the exciton binding energy, determined in this paper,* n *is the density and* E_F *is the Fermi energy.* K.S. corr. *is the correction term of the exchange interaction proposed by Keldysh and Silin to account for electron–phonon interaction*

	E_B (meV)	E_{TOT} (meV)	n (10^{18} cm^{-3})	E_F (meV)
Experiment	17 ±3	44 ±4	10.1 ± 1.7	40 ±5
Theory, no K.–S. corr.	15.2	42.0	9.9	39.5
Theory, with K.–S. corr.	22.0	48.8	12.6	46.7

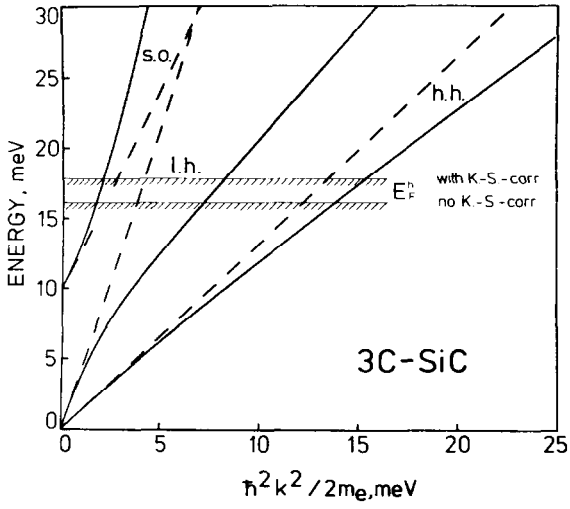

Fig. 1. Valence band dispersion curves for cubic SiC. Solid lines are solutions of the 6 x 6 valence band Hamiltonian, dashed lines are the bands which result if coupling with the spin–orbit split-off bands is neglected. The results for a spherical average over 190 directions are given (see [8]). The straight lines are the hole Fermi energies in the EHL calculated for two conflicting theories of the electron–phonon interaction. K.–S. corr. means Keldysh–Silin correction.

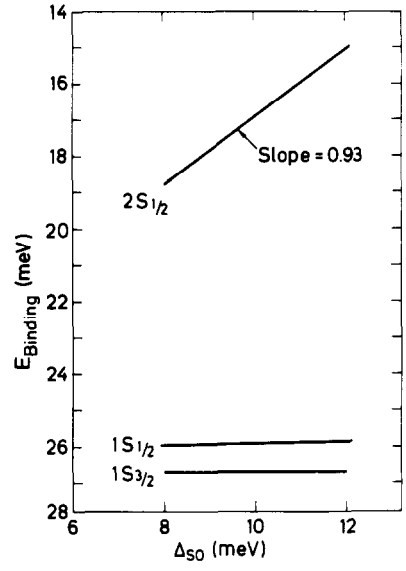

Fig. 2. Binding energies of the three lowest exciton states computed (see text) as a function of the valence band spin–orbit splitting Δ_{so}.

$C = 3.85$ eV are taken from van Vechten's theory [13] and $E_0 = 6$ eV is taken from experiment [14]. The remaining input parameters to our calculations are the lattice constants of Si and SiC: $a_{Si} = 5.43$ Å and $a_{SiC} = 4.35$ Å. For the definition and discussion of the above energies we refer to [11] and [13].

The resulting Luttinger parameters of SiC are:

$$\gamma_1 = 3.27, \quad \gamma_2 = 0.66, \quad \gamma_3 = 1.07, \quad \kappa = -0.25.$$

The coupling of the holes to longitudinal optical phonons – the Fröhlich coupling – is already pronounced in SiC and leads to a renormalization of the effective masses and of the Luttinger parameters. Trebin and Rössler [7] extended the concept of Fröhlich to the case of degenerate bands including intra- *and* inter-band hole–LO phonon scattering. Numerical solutions are given for the limiting cases of infinite and zero spin–orbit coupling Δ_{so}. We adopt the solutions for zero spin–orbit coupling since

$$\Delta_{so} = 10\,\text{meV}\ [8] \quad \text{and} \quad \hbar\omega_{LO}(\Gamma) = 120.5\,\text{meV}.$$

The renormalized Luttinger parameters are:

$$\gamma_1^* = 2.817, \quad \gamma_2^* = 0.508, \quad \gamma_3^* = 0.860,$$

$$\kappa^* = -0.41.$$

The results given here are based on improved values of energies E'_{0h}, E'_0, E_0 and C as compared to [2]. The mass renormalization for zero spin–orbit splitting is also larger than for the case of infinite spin–orbit splitting assumed in [2]. The results given here compare well with and improve considerably, an estimate of Beni *et al.* [10] based on a numerical evaluation of the band structure calculation of Hemstreet and Fong [15] who used the empirical pseudo-potential method.

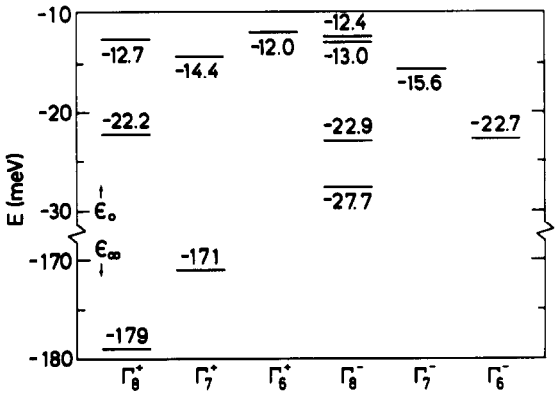

Fig. 3. Calculated spectrum of point-charge acceptors. Notice the break in the binding energy scale. The two lowest states (Γ_8^+ and Γ_7^+) were computed assuming high-frequency screening with ϵ_∞, all others with ϵ_0.

A strong interaction of the light hole and heavy hole bands with the spin–orbit split valence band results from the small spin–orbit splitting. Consequently, all three bands have a strongly nonparabolic dispersion [8]. In Fig. 1 the parabolic and nonparabolic dispersion curves of the three bands are compared with each other. An angular average over 190 directions [8] is shown. In particular, the light hole mass, but also the heavy hole mass is strongly increased at low energies. Thus the total number of hole states available below a certain fixed energy of, for example, 15 or 20 meV is correspondingly increased by about 40% and the stability of the EHL in 3C–SiC is also expected to increase. A recalculation of the ground state properties of the EHL in 3C–SiC is of considerable general interest, as will be discussed now.

SiC is the most polar of all semiconductors ($\alpha_{\text{electron}} = 0.31$) in which an EHL has been observed and its properties unambiguously assessed. Therefore, it is an ideal test material for conflicting theories [9, 10] of the EHL in polar semiconductors.

Beni *et al.* [10] recently proposed to calculate the ground states properties of the EHL in SiC in the framework of the ϵ_0^*-approximation, where the electron–phonon interaction is readily taken into account by using ϵ_0 and polaron masses. Keldysh and Silin [9] proposed a further correction to the exchange interaction E_{exch} by a zeroth order term of $1 + [(\epsilon_0 - \epsilon_\infty)/3\epsilon_\infty]$. Bimberg *et al.* [2] compared the results of ground state calculations based on both theories using the most recent conduction band and parabolic valence band parameters with the experimental results. The experimentally determined density $n = (9.2 \pm 1.7) \times 10^{18}\,\text{cm}^{-3}$ was found to lie between the two theoretical estimates of 7.4×10^{18} and $12.8 \times 10^{18}\,\text{cm}^{-3}$ without and with Keldysh–Silin correction, respectively.

The ground state calculations of the EHL in cubic SiC were modified by us to take into account the newly determined valence band parameters and the valence band non-parabolicity. Since the number of states available in the non-parabolic valence bands up to the Fermi energy (shown by the horizontal lines in Fig. 1) is 40% larger than in the parabolic case, a stabilization of the EHL leading to larger (theoretical) e–h-densities is expected for both alternatives. Table 1 compares the results of the modified ground state calculations with the experimental results. The value of the experimentally determined density had also to be revised to a slightly larger value to account for the modified valence band parameters which enter the line shape fit. The experimental ground state energy E_{TOT} was calculated from $E_{\text{TOT}} = E_B + E_X$, where E_B, the binding energy relative to the lowest exciton state was taken from the experiment [2] and the exciton binding energy $E_X = 26.7$ meV will be derived below.

The experimental results and the theoretical results calculated on the basis of the ϵ_0^*-approximation are surprisingly close to each other. Reinecke and Bimberg [16] found a similar agreement between the experimentally determined critical temperature and a theoretical one, derived on the basis of a modified plasma approach and the ϵ_0^*-approximation. Nevertheless, this excellent agreement between experiment and results calculated on the basis of the ϵ_0^*-approximation should not be regarded as ultimate conclusive evidence but as an indication in favour of this theoretical model, because assumptions on the band structure independence of $E_{\text{exch}} + E_{\text{cor}}$, the sum of exchange and correlation energies, entered the calculations, as was discussed elsewhere [17].

The calculation of the exciton binding energy follows the tensor-operator approach to the effective-mass equation for the indirect-gap case [18], recently extended to cover the small spin–orbit splitting limit, and successfully applied to Si [19]. The results are shown in Fig. 2, as a function of the valence band spin–orbit splitting Δ_{so}. We notice a very small anisotropy splitting of the $1S$ ground state, equal to 0.8 meV, and independent of Δ_{so}. We also notice the linear dependence of the $1S_{3/2} - 2S_{1/2}$ separation on Δ_{so}. Wavelength modulation experiments [8], while unable to resolve the very small anisotropy splitting of the ground state, indicate a 10 meV $1S_{3/2} - 2S_{1/2}$ separation, which, with the help of Fig. 2, determines the value $\Delta_{so} = 10.2$ meV. The theoretical value of the ground state binding energy, 27.6 meV, together with the experimental results of [8], yields a revised value of the energy gap, $E_g = 2.416 \pm 0.001$ eV.

The effective-mass prediction for the point-charge acceptor can also be calculated with the method of Baldereschi and Lipari [20]. As the binding energy (see below) exceeds the optical phonon energy, the

high-frequency value of the dielectric function was used, $\epsilon_\infty = 6.52$, rather than the static value $\epsilon_0 = 9.72$ used in the exciton calculations. The result of the calculation for the $1S$ ground state is $E_A = 179$ meV, a rather large energy, which points to possible failure of some of the approximations used in our procedure. In particular, the central-cell amplitude of the acceptor state is so large that a position (or momentum) dependent screening function $\epsilon(r)$ should replace the constant value adopted here. Also, the polaron correction to the effective-mass parameters is adequate only in the limit $E_i(\mathbf{k}) \ll \hbar\omega_{LO}$, where $E_i(\mathbf{k})$ is the kinetic energy of a hole in the ith valence band. The acceptor wavefunction, however, mixes Bloch states up to $E_i(k) \sim E_A > \hbar\omega_{LO}$, so that intermediate (between bare and polaron-corrected) parameter values should be introduced. In fact, experimental information on the Al acceptor [21], indicates a somewhat larger binding energy, $E_A = 206$ meV.

In Figure 3 the lowest acceptor states are shown, classified according to their symmetry character. Parity labels appear because, due to the neglect of k-linear terms in the band dispersion, the acceptor Hamiltonian has inversion symmetry. It is interesting to notice the low-lying Γ_7^+ state, which is only 8 meV above the ground state, and to which the same caveats apply. The higher excited states are much shallower, and their eigenvalues were computed with the static value of the dielectric function. Their accuracy is expected to be very good, and it is hoped that this theoretical spectrum shall provide a useful guideline for experimental investigations.

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