Band-gap shifts in heavily doped n-type GaAs

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(Received 16 December 1985)

We present theoretical results for the band-gap shifts in heavily doped n-type GaAs. We find that the bands are far from being shifted rigidly. The states at the band edges are shifted more than the states with Fermi momentum. Consequently, the band-gap narrowing deduced from absorption experiments is strongly underestimated. Our results are compared to those from experiments on photoluminescence, cathodoluminescence, and diode-injection luminescence and from absorption measurements. Agreement is found with all the experimental results and we give a new explanation for the position of the luminescence peak in the diode-injection experiments and its shift with varying forward bias voltage.

The fact that the bands in heavily doped semiconductors are shifted in energy due to the presence of the ionized dopant ions and released charge carriers is a well-known fact.[1-4] However, it was until recently that theoretical efforts were made to determine these shifts quantitatively, taking all effects into account in a realistic way.[5-11] The results of Refs. 5, 6, and 8 have found strong experimental support in recent publications.[12,13] We refer to Refs. 1 and 2 for a more extensive list of references to earlier experimental and theoretical works and to Refs. 5—11 for the up-to-date theory.

Let us introduce our notation and simultaneously make a brief recapitulation of the various contributions to the band shifts. We assume n-type GaAs as the semiconductor, but similar shifts occur also in p-type semiconductors. In heavily doped GaAs we are faced with a system of interacting charged particles—donor electrons and donor ions. Let us first neglect all interactions. In the absence of interactions the electrons constitute a noninteracting free-electron gas and occupy the states at the bottom of the conduction band for wave numbers up to k_F, the Fermi wave number. The bands are unshifted so far. Let E_g denote the unperturbed band gap. We introduce $E_{g,1}$, $E_{g,2}$, and $E_{g,3}$. $E_{g,1}$ is the distance in energy from the bottom of the conduction band to the top of the valence band, and equals E_g so far. $E_{g,1}$ is the lower threshold for luminescence. With $E_{g,2}$ we mean the energy distance between a state with wave number k_F in the conduction band and the top of the valence band. This energy is the lower absorption threshold if diagonal transitions are allowed. Finally, $E_{g,3}$ denotes the difference in energy between states at k_F in the conduction band and in the valence band (in the heavy-hole band). This energy is the lower threshold for absorption if only vertical transitions (momentum conserving) are allowed, and the upper threshold for luminescence. The band-gap shifts are defined as

$$\Delta E_{g,i} = E_{g,i} - E_g, \quad i = 1,2,3 \; . \tag{1}$$

When no interactions are present $\Delta E_{g,3}$ equals the so-called Burstein-Moss shift.

Now let us turn on the interaction but still not allow the electrons to correlate. If the ions are distributed at random (this is what we assume) the energy of the different electron states will not change and all band-gap shifts are unchanged (we assume that the electron-ion interaction is given by a pure Coulomb potential). If on the other hand the ions were forming a donor superlattice, all electron states, both in the conduction and valence band, would be shifted the same amount, the Madelung energy. This shift would give no contribution to the band-gap shifts.

We now remove all restrictions and allow the electrons to correlate. The electrons avoid each other for two different reasons. Electrons with the same spin avoid each other for statistical reasons, and all electrons independently of relative spin directions avoid each other because of the Coulomb repulsion. Thus, effectively each electron is surrounded by an exchange and correlation hole. This lowers the energy of the electron, i.e., the conduction band is shifted downwards. Furthermore, the electron density will relax around the impurities, causing an enhancement around each impurity. This further lowers the electron energies and causes the conduction band to shift downwards.

Even though there are no donor electrons in the valence band, this band will be shifted in energy. The reason is the following. All experiments measuring the band-gap shifts involve a hole in the valence band and an electron in the conduction band. In the absorption experiments such electron-hole pairs are created, and in the luminescence experiments the electron-hole pairs are annihilated. The hole is attracted by the donor electrons and tends to be surrounded by an enhancement in the electron density. This reduces the energy of the hole. The hole is repelled by the positively charged donor ions and has a tendency to avoid them, which causes a further reduction of its energy. Thus even less energy is needed to create an electron-hole pair or is released when a pair is annihilated. In other words, the valence band is shifted upwards in energy. This can be regarded in an alternate way. The presence of the hole is really the absence of an electron in the valence band. When the valence band is full the valence electrons

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have no possibility of correlating with the donor electrons or donor ions (except via virtual transitions across the band gap; these transitions are the origin of the background screening constant). When an electron is removed from the valence band a new channel is opened up and the rest of the valence-band electrons can, through virtual transitions to the empty state, correlate with the donor ions and donor electrons and thereby lower their energy. The valence-band electrons avoid the donor electrons not because of the statistics in this case, but only because of the Coulomb repulsion. Furthermore, these electrons are, because of the Coulomb attraction, piling up around each donor ion. Thus this new freedom lowers the energy of the system and hence the energy needed to excite an electron from the valence band into the conduction band.

To summarize, the band gaps are reduced due to four negative self-energy shifts. The shift downwards of the conduction band can be split into $\Sigma^{c,e}$ and $\Sigma^{c,i}$, caused by electron-electron and electron-ion interactions, respectively. In a similar way the shift upwards of the valence band causes the band gaps to change by the two contributions $\Sigma^{v,e}$ and $\Sigma^{v,i}$. All these four Σ's are negative and tend to reduce the band gaps. All the states in each band need not, however, be shifted the same amount (rigid-band shifts). In Si and Ge the bands are to a good approximation shifted rigidly.[5,6] In Ref. 8 we found that when all electrons, in the piezoexperiments on Ge, were transferred to one valley, the states at the bottom of the band were shifted more than the states further up in the band. This causes "stretching" of the density of states. In the one-valley configuration the screening from the donor electrons is less effective and hence the electron-impurity interaction, tending to "stretch" the density of states, is more important. Thus in GaAs, which is a one-valley semiconductor, the deviations from rigid-band shifts can be expected and are found below.

We performed the calculation within the same formalism and with the same approximations as in Refs. 5, 6, 8, and 11. GaAs is a polar semiconductor, but the polar coupling is so weak that it can be neglected. The polaron energy is only 2.5 meV for a polaron in the conduction band and 5.4 meV for a polaron in the valence band. We have actually made a calculation including the polar coupling. The effect of this coupling increases with donor density but involves only the electron-electron interaction contribution to the self-energies. The total effect on the band-gap shifts is never larger than 1% and can be neglected (it tends to reduce the band gaps). Here we present the results of the so-called ϵ_0 approximation which drastically simplifies the computations. We used the following set of data, obtained from Ref. 14. The background-screening constant was chosen to be 13.0, the electron effective mass 0.0665, and the hole masses 0.45 and 0.082, respectively. The coupling between the valence bands was taken into account the same way as in Refs. 5 and 6. This more accurate treatment of the valence bands, instead of replacing them by one band with one effective mass, is rather important if one wants quantitative results. In Refs. 5 and 6 only the self-energy shifts at the top of the valence band were needed. Here we also needed the shifts at Fermi momentum, which are more complicated. The derivation of these shifts is the only extension of the theory in Refs. 5 and 6.

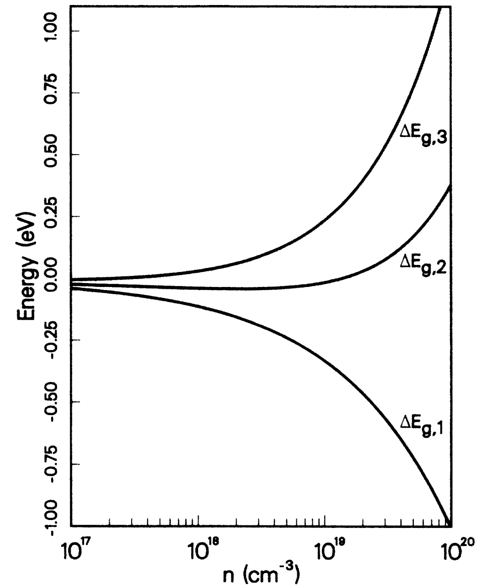

FIG. 1. The various band-gap shifts, defined in the text, as functions of donor concentration.

The various band-gap shifts as functions of donor concentration are shown in Fig. 1. To be noted is that the difference between $\Delta E_{g,3}$ and $\Delta E_{g,1}$ is much larger than the Burstein-Moss shift because of the stretching of the density of states. The difference in size of the self-energy shifts for states with Fermi momentum and states at the

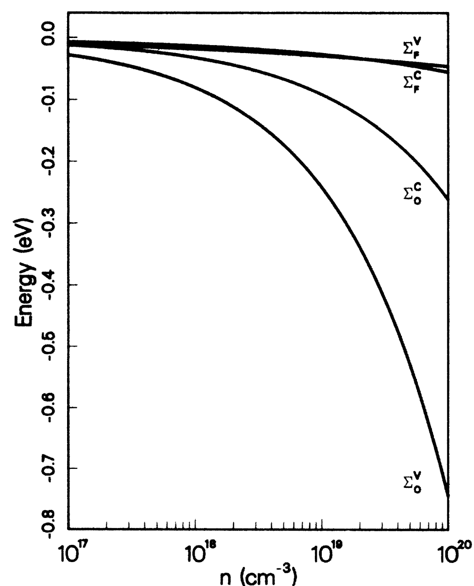

FIG. 2. The self-energy shifts for electrons, superscript c, and holes, superscript v, in states with zero momentum, subscript 0, and Fermi momentum, subscript F, as functions of donor density.

band edges is clearly seen in Fig. 2, where the total self-energy shifts for different states are shown. The superscripts c and v denote the conduction and valence bands, respectively, and the subscripts F and 0 represents Fermi momentum and zero momentum, respectively. The state at the top of the valence band is shifted most dramatically. The dominating contribution comes from the electron-ion interaction as can be seen in Fig. 3, where the different contributions to the self-energy shifts have been separated out. The electron-ion contribution is much larger for the valence band than for the conduction band. This is because of the relatively much larger effective mass. To be noted also is that the electron-electron interaction gives a contribution to the "band stretching" in the conduction band. The exchange part of this interaction tends to expand the band, and the correlation part tends to compress it. The exchange part is independent of the effective mass, while the correlation part decreases with decreasing mass. In the conduction band of GaAs the effective mass is extremely small, and the correlation part is too weak to compensate the stretching caused by the exchange part.

Now let us turn to the experimental comparison. In order to compare our results to experiments at different temperatures we subtracted the unperturbed band-gap values from the experimental energies. At 4.2, 20, 77, and 300 K, we used the values 1.518, 1.521, 1.512, and 1.426 eV, respectively, all obtained from Ref. 14.

The results from photoluminescence (PL) and cathodoluminescence (CL) experiments are very similar. In these experiments high-energy holes are created in the valence band, in the first experiment by photoexcitation and in the second by electron-beam bombardment. The holes start to thermalize. They cannot recombine with the electrons in the conduction band until they reach the states with Fermi momentum, if only vertical transitions are allowed. Thus, the upper threshold for the luminescence line is given by $\Delta E_{g,3}$. Depending on the relative sizes of the recombination and thermalization rates the lower edge can vary, but can never be lower than $\Delta E_{g,1}$. If the thermalization rate is large enough some holes are collected at the top of the valence band before they recombine. If this is the case the luminescence peak extends between $\Delta E_{g,3}$ and $\Delta E_{g,1}$ and there is a second peak close to $\Delta E_{g,1}$. This is also what is found in Fig. 2 of Ref. 15. In that paper, however, the extra, much weaker peak was interpreted as caused by recombination from a deep level. The authors also mention that the size of this low-energy peak grows with decreasing donor density, which is to be expected if its origin is what we believe it to be. At lower donor density the Fermi momentum is smaller and hence the probability is larger for the hole to reach the top of the valence band before recombination. What we need for a systematic comparison between the theoretical and experimental results are the full luminescence peaks, preferably with expanded intensity scale at the lower edge. Unfortunately, most experimental papers give only the peak positions and sometimes also the width. In Fig. 4 we have plotted the experimental peaks that we have found in literature. The upper curve is our $\Delta E_{g,3}$ and the lower our $\Delta E_{g,1}$. P, E, and D denote experimental peaks from PL, CL (electron beam excitation), and diode injection, respectively. The correlation between the upper edges of the P and E peaks and our $\Delta E_{g,3}$ is obvious. Also to be noted is the similarity between the results from these two experi-

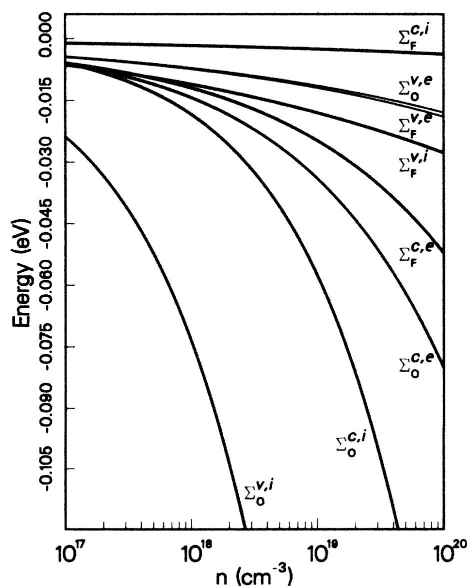

FIG. 3. The self-energy shifts of Fig. 2 have been split into their two components—the electron-electron interaction part, index e, and the electron-ion part, index i.

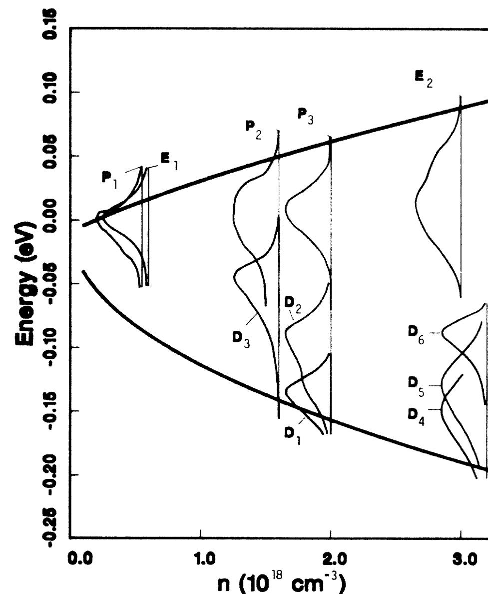

FIG. 4. The upper and lower curves are $\Delta E_{g,3}$ and $\Delta E_{g,1}$, respectively. The peaks are from various experimental papers, specified in the text. P, E, and D denotes photoluminescence cathodoluminescence (electron beam excitations) and diode-injection luminescence experiments, respectively. All peaks lie down flat and have been normalized to have the same intensity amplitude.

ments. We further notice that there is no indication of nonvertical transitions. We can also conclude that the recombination rate is larger than the thermalization rate. The PL peaks are from Ref. 16 and the CL results from Ref. 17, both measurements performed at 77 K. We will return to the D peaks later. There are more experimental results on PL in Refs. 16 and 18 and on CL in Refs. 19 and 20 but no full peaks are given, just the peak positions. In Refs. 15 and 21 both the peak positions and the widths for PL and CL, respectively, are given and these data are shown in Fig. 5. Solid and open circles denote the peak positions in PL and CL, respectively. The lengths of the bars, centered at the peak position are twice the experimental full width at half maximum. Assuming triangular peak shapes the bar edges represent the peak thresholds. The upper bar edges are then to be compared to the upper curve, representing the theoretical upper threshold, $\Delta E_{g,3}$. The lower curve represents our $\Delta E_{g,1}$.

In the diode experiments holes are injected at the top of the valence band. They get there through tunneling from the p side of the diode. By increasing the applied voltage in the forward direction, across the diode, holes of higher energies are injected. At low injection rate the peak from the luminescence should be close to $\Delta E_{g,1}$, which is its lower threshold. At higher injection level (larger applied voltage) the peak position should move to higher energies. This is exactly what is found in the experiments. One further finds that the intensity of the peak increases drastically with increased injection level, but the intensity at the lower threshold remains almost constant. We have denoted the experimental diode-injection luminescence peaks with D in Fig. 4. D_1 and D_2 are from Ref. 22 at 4.2 K and are peaks at low and high injection levels, respectively. D_3 is a luminescence peak from Ref. 16, measured at 77 K and high injection level. The peaks D_4, D_5, and D_6 are from Ref. 23 and were measured at 20 K and with increasing injection level. Plotted this way, with a linear intensity scale and with all peaks normalized to the same peak value, it looks as though the lower peak threshold shifts upwards with injection level. This is, however, not the case as is shown in Fig. 6, where the peaks D_4, D_5, and D_6 are replotted in a logarithmic plot and are not normalized. The low-energy intensity is the same for all three peaks. This is even more clearly seen in the original Fig. 1 of Ref. 23, where a large number of peaks at varying injection levels are shown. The same behavior was reported in Ref. 16 and the lower threshold for peak D_3 is near $\Delta E_{g,1}$.

Two models have previously been proposed for the explanation of the unexpected low energy of the peak threshold in the diode experiments. In the so-called "diagonal tunneling" model[22,24] one assumes that an electron in the conduction band on the n side recombines with a hole in the valence band on the p side of the p-n junction. The second model, the so-called "band-filling" model[23,24] proposed by Nelson *et al.*,[23] assumes electron tunneling from the conduction band of the n side to an impurity band below the conduction-band edge on the p side. The luminescence then is due to recombination on the p side. These models are no longer needed to explain the experimental data. Our proposal is that the luminescence is due to vertical recombination between holes at the top of the valence band and electrons in the conduction band, both carriers from the n side of the diode.

To conclude the experimental comparison we show in Fig. 7 those experimental points from Fig. 3 of Ref. 18 valid for n-type GaAs. The points represent the energy, for various donor concentrations, at which the absorption

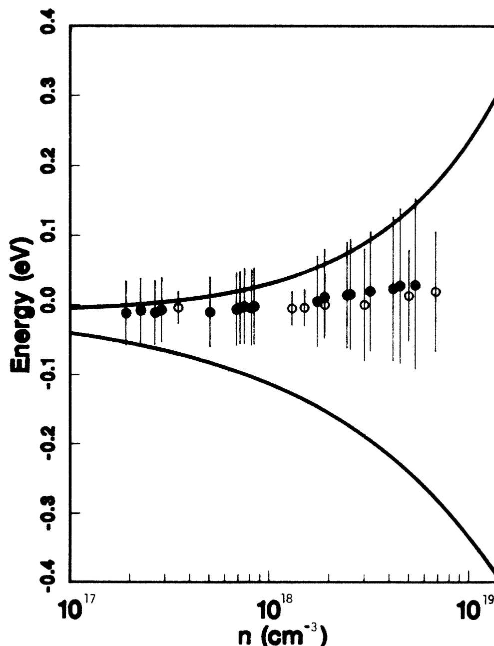

FIG. 5. Two set of experimental data, one from PL experiments (Ref. 15), solid circles, and one from CL experiments (Ref. 21), open circles. The bars indicate a rough estimate of the peak extensions. The upper and lower curves are $\Delta E_{g,3}$ and $\Delta E_{g,1}$, respectively.

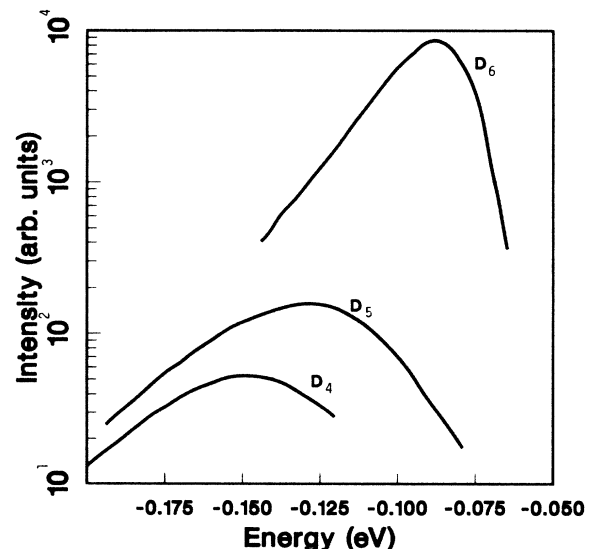

FIG. 6. The experimental luminescence peaks from the diode-injection experiments at the density 3.2×10^{18} cm^{-3}, shown in Fig. 4. Here we have not normalized the peaks and they are given in a logarithmic scale.

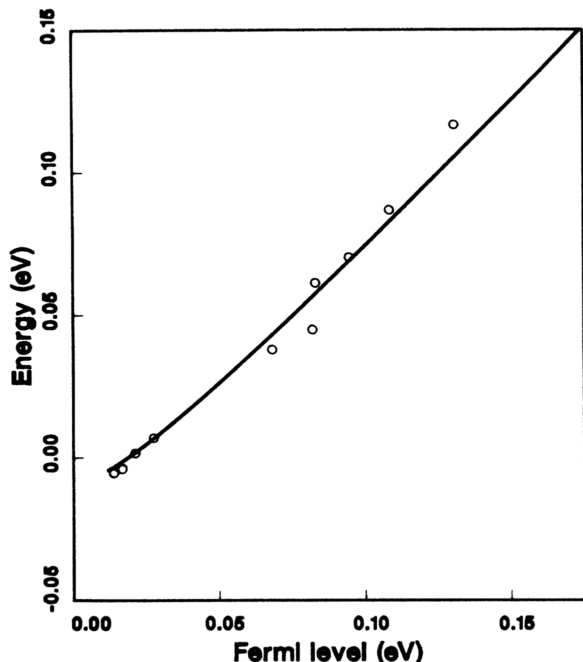

FIG. 7. The circles are experimental estimates of the absorption thresholds for n-type GaAs as a function of density (expressed as Fermi energy), taken from Fig. 3 of Ref. 18. The curve is our $\Delta E_{g,3}$, the ideal absorption threshold.

coefficient equals the constant value 300 cm^{-1}. The donor concentration is expressed in terms of the Fermi energy or Fermi level. The curve is our $\Delta E_{g,3}$, which is the ideal lower absorption threshold. The good agreement between the theoretical curve and the experimental points should not be taken too seriously, as the value 300 cm^{-1}, as far as we understand, was chosen rather arbitrarily, but it is interesting to note the correlation.

To summarize, we found large band shifts, especially for states near the band edges. The band shifts for states with Fermi momentum were checked against the energy position of the upper luminescence threshold in photoluminescence and cathodoluminescence experiments and good agreement was found. These shifts were also tested against the experimental absorption threshold and the agreement was excellent (but the experimental estimates contained some arbitrariness). The shifts for states near the band edges were compared to the position of the lower luminescence threshold in diode-injection experiments, and here also the agreement was good. The large shifts of these states explained the unexpected low luminescence thresholds in the diode experiments.

This research was supported by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05 840R21400 with Martin Marietta Energy Systems, Inc. and the University of Tennessee. Support from the Swedish Natural Science Research Council is also acknowledged.

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