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Two-Electron Band-to-Band Transitions in Solids*

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In highly excited Si and Ge there appears an emission band at about $h\nu = 2E_g$, which is explained by two-electron radiative transitions across the band gap. The dependence on energy, temperature, and excitation intensity is measured and compared with theoretical calculations. The weak temperature dependence, the quadratic dependence on the injection current, and the energy dependence agree with the theoretical consideration. A transition coefficient of about 10^{-61} cm^9 sec^{-1} is found, in agreement with a rough theoretical estimate. The line shape indicates that, at least at room temperature, the two-electron transitions are phonon assisted. This leads also to the conclusion that the Auger recombination in Si must be phonon assisted, in contradiction to former considerations.

GENERAL

In previous papers the appearance of radiative two-electron transitions across the band gap was established.[1,2] Emission bands were observed in Si and Ge at an energy of about $h\nu = 2E_g$. In this paper we report further experimental results and give a more detailed examination of this effect.

Radiative two-electron transitions are well known in atomic physics in absorption, for example, as preionization. Heisenberg[3] has pointed out that the change of the angular momentum of the single particles in an electric-dipole transition is in first approximation $\Delta l_1 = \pm 1$, $\Delta l_2 = \pm 2$ or 0. In every case, the total change of angular momentum is $\Delta L = \pm 1$, if spin-orbit coupling is neglected.

In contrast to the atomic situation, in a solid both electrons may have the same initial state and the same final state, since l is no longer a good quantum number. For example, in the octahedral group O, transitions from Γ_{15} and Γ_{25} to all states may occur. Therefore, transitions between valence band and conduction band may occur with twice the energy of the one-electron transiton. Because of the strong absorption due to one-electron transitions at the energy of twice the band gap, the expected transitions can only be observed in emission.

Since energy doubling may also occur due to nonlinear optical effects, a material with inversion symmetry has to be chosen. In this case, electric-dipole transitions are not possible at the Γ point of the Brillouin zone because of the parity selection rule. In the k space away from the Γ point this selection rule does not hold. Therefore, an indirect-gap material has to be used. An additional advantage of an indirect-gap material is that in these materials the one-electron transitions near the band gap are not possible without other perturbation because of the momentum conservation, whereas the two-electron transitions are allowed if both electrons have opposite momentum in the indirect extrema. From these points of view and from experimental considerations, we have chosen indirect-gap semiconductors with inversion symmetry, namely, Si and Ge.

The line shape of the expected emission spectrum is calculated under the following assumptions. Because of the small relative change of energy and momentum transfer over the whole linewidth, we have assumed the transition matrix elements to be constant, i. e., we have calculated the line shape

only from the phase-space integration over the two initial states and the two final states. The distribution function of the occupied conduction-band states and the empty valence-band states is assumed to be a Boltzmann distribution with lattice temperature, which is well fulfilled under our experimental conditions. The dependence of the energy on the momentum components is assumed to be quadratic. The phase-space integration is to be carried out in the range between the energy values E and $E+dE$ under the condition of momentum conservation,

$$J(E)\,dE = \int\int\int\int_E^{E+dE} e^{-E/kT}\,\delta\left(\sum k_i\right) d^3k_1\,d^3k_2\,d^3k_3\,d^3k_4 .$$

This integration is evaluated in the Appendix. It leads to a line shape of the form

$$J(E) = (E - 2E_g)^{3.5}\, e^{(2E_g - E)/kT},$$

with $E \geq 2E_g$. This line shape is indicated in Fig. 1 in the case of Si.

In the one-particle picture the transition is to be treated in second-order perturbation theory, one perturbation-Hamiltonian operator being the Coulomb interaction between the carriers and the other being the dipole interaction with the radiation field. As usual, the interaction with the other electrons is taken into account by an effective dielectric constant in the electron-hole picture.

In Si the initial state is a Slater determinant of two conduction-band electrons Δ_{1c}; the final state is that of two valence-band electrons at Γ_{25}^{+}. The intermediate state is composed of one Γ_{25}^{+} valence-band electron and any Γ_c^{-} conduction-band electron. The resonance determinator ΔE is of the order of 0.5 eV for the Γ_{2c}^{-} or Γ_{15c}^{-} state.[4] The transition probability W is given by

$$W = (2\pi/\hbar)\left|\sum_{\Gamma_c^-} \langle \Gamma_{25v}^{+} \mid er \mid \Gamma_c^{-} \rangle \times \langle \Gamma_c^{-}, \Gamma_{25v}^{+} \mid e^2/\epsilon r_{12} \mid \Delta_{1c}, \Delta_{1c} \rangle / \Delta E \right|^2 g(E)\,dE.$$

In this perturbation treatment the part of the electron-electron interaction is the same as in the case of Auger transitions. These transitions are treated theoretically by Beattie and Landsberg.[5] These authors come to the conclusion that the matrix element of the Coulomb interaction is proportional to $(\Delta k)^{-2}$, where Δk is the transferred momentum. Even though direct Auger transitions in Si are possible without an additional activation energy,[6] there are experimental indications that, corresponding to the large momentum transfer, the Auger transitions in Si may be phonon assisted.[7] For this reason we have also considered the possibility that the momentum is not transferred in the electron collision but that momentum conservation is fulfilled by participation of two phonons. If these phonons are the same as in the one-electron radiative transition, the corresponding line shape of two-electron transitions is expected to be the same as in the case of frequency doubling due to nonlinear optical effects, namely, to be a convolution integral of the radiation intensity of the one-electron transition. This convolution integral obtained from experimental results[8] is also indicated in Fig. 1.

To get a rough estimate of the expected transition coefficient of the two-electron transitions, we have approximated the transition probability by a product of the Auger-transition probability C and the probability B for radiative transitions. This calculation neglects interference effects within the matrix element caused by different intermediate states Γ_c, and it neglects the difference between the intermediate state implied in the two-electron transition and the real state implied in the single transitions. But it is reasonable to assume that these neglections give no more uncertainty than one order of magnitude.

The transition coefficient in this approximation is

$$P = \hbar^2 BC(\Delta E)^{-2}\tau^{-1}/2\pi,$$

where $\tau = 10^{-13}$ sec is the collision time of the electrons. The transition coefficient for the Auger process is found to be $C = 5\times10^{-30} - 2\times10^{-34}$ cm^6 sec^{-1}.[9,10] If one assumes that these values correspond to a direct Auger process, as considered by those authors, it has to be multiplied by the transition coefficient for direct radiative processes $B = 2\times10^{-11}$ cm^3 sec^{-1}.[11] This would lead to a two-electron transition coefficient of $P = 5\times10^{-57} - 5\times10^{-61}$ cm^9 sec^{-1} in the case of direct transitions. In the case of phonon-assisted transitions, the multiplication with the transition coefficient for indirect radiative transitions[11] $B' = 4\times10^{-15}$ cm^3 sec^{-1} would lead to $P' = 10^{-60} - 10^{-64}$ cm^9 sec^{-1}. If the experiments indicate that the two-electron transition is phonon assisted, this would be a strong argument for the assumption that the Auger effect in Si is also phonon assisted. This is because in this case the transition probability for the direct Auger effect must be lower by more than three orders of magnitude than the indirect one.

EXPERIMENTAL

The samples were excited by a GaAs injection laser in the case of Si and by direct carrier injection via a p-n junction in both Si and Ge. In the case of laser excitation high-purity 4000-Ω cm B-doped Si from Wacker Chemie was used. It was excited by an RCA laser diode with 23-W peak power. In the case of carrier injection via a p-n

junction into Si, cylinders of about 0.2-mm length and diameter from n-type as well as p-type material were taken with a majority-carrier density of about 10^{15} cm^{-3}. The carriers were injected from the top of the cylinder via a diffused p-n junction. On the back side these samples were mounted on a copper heat sink, whose temperature was controlled, and which was used as an Ohmic contact. The temperature difference between Si and Cu was estimated to be less than 10 K. The luminescence was observed from the side of the cylinder. In the case of Ge, a little slice of n-type material of about 10^{15}-cm^{-3} carrier density also mounted on a Cu heat sink was used. The injection was carried out via an alloyed p-n junction of area about 10^{-7} m^2. The luminescence was observed from the front of the slide. In this case, the sample temperature was estimated to be about 100 K, when the Cu was cooled by liquid nitrogen. The injection current densities were of the order of 10^4 A cm^{-2} in both materials.

In all cases the excitation was carried out in the form of pulses of a few microseconds duration with a duty cycle of 10^{-2} or less. In a completely metal-enclosed cryostat system the luminescence radiation was focused to the entrance of a Zeiss double-prism monochromator *MM* 12 or a 0.75-m Spex grating monochromator in connection with a Schott filter BG 18 in one case (full triangles in Fig. 1). The luminescence radiation was detected by an EMI 6256A photomultiplier with S-11 response cooled to about 250 K in the case of Si and by an EMI 9684B photomultiplier with S-1 response cooled to about 80 K in the case of Ge.

The measurements were taken using a "digital-boxcar-integration" method: The signal was taken as a pulse sequence from the multiplier. During the excitation the signal pulses were counted in one counter. Between the excitation pulses the dark count rate was registered by another counter. The exact agreement of the count time of both counters was reached by digital setting of the gate times from the same clock. Every measuring point in the spectral measurements corresponds to a total integration time of a whole day, i.e., an effective measuring time of 15 min in the case of a duty cycle of 10^{-2}. With this method we have reached a measuring sensitivity of 10^{-19} W.

All spectral values are corrected for the spectral response of the detection system and for reabsorption by multiplying with the absorption coefficient obtained by Dash and Newman.[12]

RESULTS AND DISCUSSION

Figure 1 shows the energy dependence of the high-energy luminescence from Si. As mentioned, the expected curve of direct two-electron transitions (full line), as well as that of two-phonon-assisted two-electron transitions, is also given this figure. The values of E_g are taken from Long.[13] From the fact that the spectrum is independent of the excitation mechanism and independent of the material type, we conclude that this high-energy luminescence is an intrinsic effect.

The following known effects can be excluded as a source of this radiation. Frequency doubling due to nonlinear optical effects, which may also lead to a spectrum as indicated by the dashed line, is excluded because of the inversion symmetry of

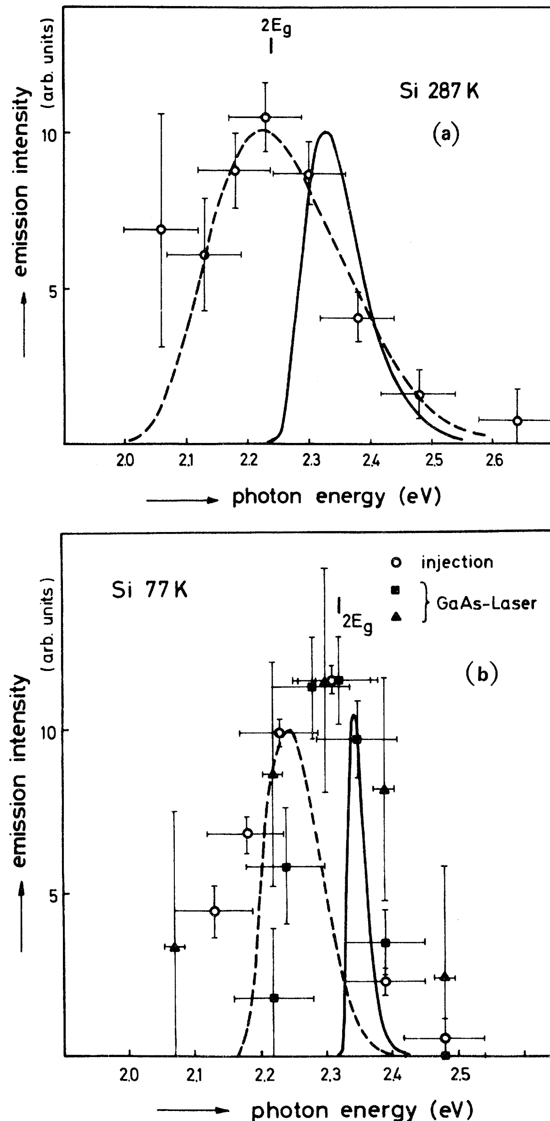

FIG. 1. Energy dependence of the $2E_g$ emission band from Si; (a) room temperature, (b) liquid-nitrogen temperature. Experimental values from excitation due to injection (open circles) and from laser excitation are given. The solid line gives the theoretical values for direct two-electron transitions; the dashed line gives values for phonon-assisted transitions (no absolute values).

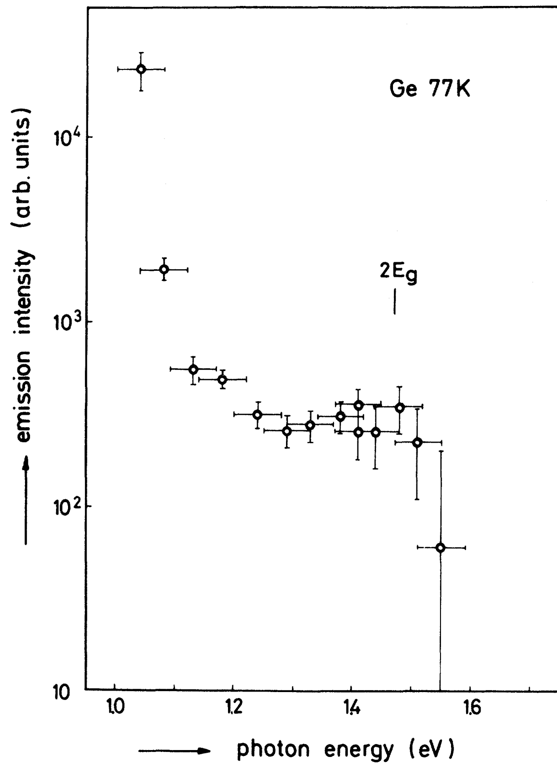

FIG. 2. Energy dependence of the high-energy luminescence from Ge excited by carrier injection.

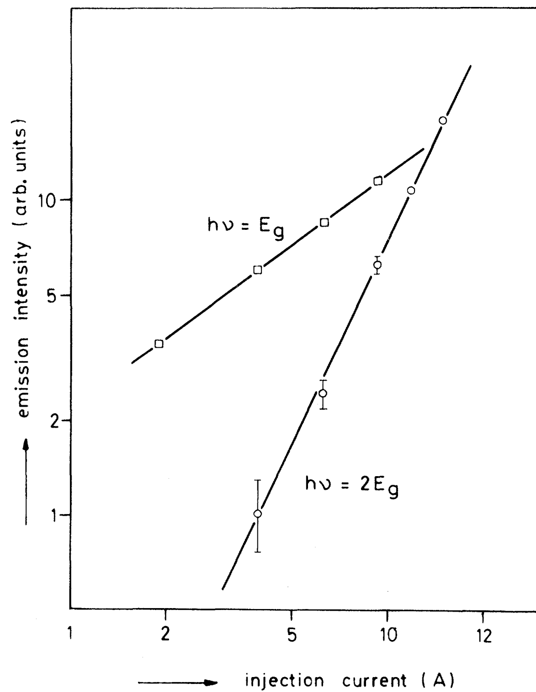

FIG. 3. Dependence of the integrated emission intensity on the injection current in the case of Si excited by injection at room temperature.

Si. Perhaps it may appear on account of impurities which destroy the inversion symmetry,[14] but this possibility is easily ruled out from quantitative considerations; even if one takes the strongest lowest-order nonlinear optical coefficient of the III-V compounds, i.e., that of InSb,[15,16] one obtains an expected value of at least seven orders of magnitude lower than the observed intensity. We have proven this argument also experimentally; in the case of laser excitation, we have compared the ratio between the E_g laser intensity and its frequency-doubled $2E_g$ intensity with the ratio between the E_g emission and the $2E_g$ emission from Si. These ratios disagreed by nine orders of magnitude, i.e., the $h\nu = 2E_g$ intensity from Si is far too high to be explained by any nonlinear optical effect. High-energy luminescence from nonequilibrium carriers as known in the case of high electric fields[17] and in the case of band-to-band Auger recombination[18] is, aside from other reasons, excluded since in these cases there should appear no maximum at the energy of $2E_g$.

To show, that it is a general effect independent of the band structure of Si, we have reproduced it in Ge. Figure 2 shows the energy dependence of the high-energy luminescence of Ge. There appears also a peak at the energy of $2E_g$. Toward lower energies there appears a broad continuum, which we explain as originated by nonequilibrium Auger particles. This intensity should decrease monotonically toward $2E_g$, as indicated from GaAs measurements.[19] The low-energy increase may be explained by thermalization of Auger holes in the split-off valence band as argued in a previous paper[18] in the case of room temperature, where this effect covers a possible $h\nu = 2E_g$ emission from Ge.

In the case of Si excited by injection, we have also investigated the dependence of the intensity of the whole $2E_g$ emission band on the injection cur-

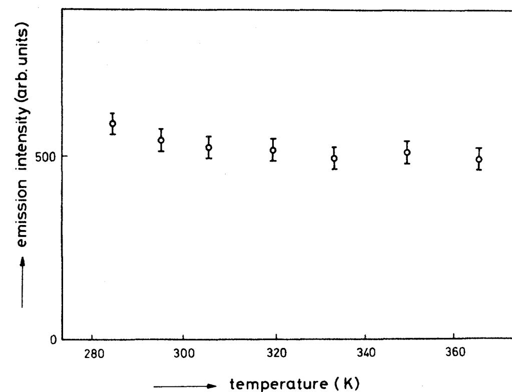

FIG. 4. Dependence of the integrated emission intensity on the temperature in the case of Si excited by a constant injection current.

rent as well as on the temperature. These results are shown in Figs. 3 and 4. As is to be expected for two-electron transitions, the intensity increases nearly quadratically (the exponent is 2.1) with the injection current, and it depends weakly on the temperature.

In Fig. 1(a) the dashed line agrees well with the experimental data, whereas the full line does not agree. Therefore we conclude that the two-electron transitions at room-temperature in Si are phonon assisted. This leads also to the conclusion that the Auger recombination in Si is phonon assisted, as discussed above, and not a direct one, as considered so far.[9,20] In Fig. 1(b) the agreement with both theoretical curves is poor. This may be caused by the low accuracy of the measured values. However, in all experiments there appeared the same line shape. We propose to explain this line shape by participation of both effects. This explanation is not in contradiction to the room-temperature data since, from phase-space integration, it is to be expected that the direct process decreases with increasing temperature according to $J \propto T^{-3/2}$, if the carrier densities are constant. On the other hand, the phonon-assisted process increases because of the increasing phonon density (in this case the phase-space integration is temperature independent). We hope to get a final conclusion from He-temperature experiments, which are in progress.

From the absolute intensity, the calculated carrier density, the sample geometry, and from reabsorption data, we have calculated an experimental transition coefficient. In the case of Si, we get a value of $P = 10^{-61}$ cm^9 sec^{-1} with laser excitation and of $P = 10^{-62}$ cm^9 sec^{-1} with injection. Both values are uncertain within two orders of magnitude because of the strong dependence on the carrier-concentration calculation. The actual value should lie at $P = 10^{-61}$ cm^9 sec^{-1} within one order of magnitude. Since the Auger recombination in Si must be phonon assisted, our theoretical calculation holds only in the case of the phonon-assisted process. With this calculation our experimental value agrees well. In the case of Ge, we get a value of $P = 10^{-62}$ cm^9 sec^{-1} with an uncertainty of two orders of magnitude.

APPENDIX

The phase-space integration is carried out in the vicinity of the band extrema. It is assumed that the dependence of the energy on the momentum is quadratic.

Because only the line shape will be estimated, we neglect constant factors:

$$J(E)\,dE \propto \int\int\int\int_E^{E+dE} e^{-(E-2E_g)/kT}\, d^3k_1\, d^3k_2\, d^3k_3\, d^3k_4 ,$$

with the boundary condition $k_1 + k_2 = k_3 + k_4$. The integration range in the k space is determined by the assumed energy-momentum dependence

$$E' = E - 2E_g = \tfrac{1}{2}\hbar^2 \sum_{l=1}^{4} \sum_{i,j=1}^{3} (k_{li} - k_{li0})(k_{lj} - k_{lj0})/m^*_{lij} ,$$

where l indicates the particle state, i, j label the coordinates, and k_{li0} are the positions of the extrema. There exists a linear transformation

$$q_{mj} = \sum_{l,i} c_{mjli}(k_{li} - k_{li0}) ,$$

which transforms the boundary condition into $q_{4j} = 0$ and the energy-momentum dependence into

$$E' = \sum_{m,j} q_{mj}^2 .$$

The integral is only changed by a constant factor:

$$J(E)\,dE \propto \int\int\int\int_{E'}^{E'+dE} e^{-E'/kT} d^3q_1 d^3q_2 d^3q_3 d^3q_4\, \delta(q_{4j}) .$$

By the δ function one integration does not take place. Transformation to polar coordinates and integration over the angles leads to

$$J(E)\,dE \propto e^{-E'/kT} \int\int\int_{E'}^{E'+dE} r_1^2 r_2^2 r_3^2\, dr_1\, dr_2\, dr_3 ,$$

with $E' = r_1^2 + r_2^2 + r_3^2$. One integration is infinitesimal:

$$r_3 = (E' - r_1^2 - r_2^2)^{1/2} ,$$
$$dr_3 = \tfrac{1}{2}(E' - r_1^2 - r_2^2)^{-1/2} dE .$$

There remains a double integration over the region of real argument

$$J(E) \propto e^{-E'/kT} \times \int_{r_1=0}^{r=E} \int_{r_2=0}^{r_2=(E'-r_1^2)^{1/2}} r_1^2 r_2^2 (E' - r_1^2 - r_2^2)^{1/2} dr_1\, dr_2 ,$$

which leads to

$$J(E) \propto E'^{7/2} e^{-E'/kT}$$

or

$$J(E) \propto (E - 2E_g)^{7/2} e^{-(E-2E_g)/kT} ,$$

with $E \geq 2E_g$. If one considers the carrier densities n, p to be temperature independent, an additional temperature dependence of the form of T^{-6} appears:

$$J(E) \propto n^2 p^2 T^{-6} (E - 2E_g)^{7/2} e^{-(E-2E_g)/kT} .$$

The integral intensity of the emission band then depends in the following form on the temperature:

$$J = \int_{2E_g}^{\infty} J(E)\,dE \propto n^2 p^2 T^{-3/2} .$$

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High-Field Scattering Mechanisms in *n*-Germanium at 300 °K

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The hot-electron characteristic of n-germanium at room temperature is theoretically derived taking into account the effects of the ⟨100⟩ valleys and the nonparabolicity of the ⟨111⟩ valleys. It is shown that the experimental results may be explained by theory only when both these effects are included.

I. INTRODUCTION

The electron drift velocity in n-type germanium at high fields is experimentally found to be almost field independent.[1] But early hot-electron theories[2-5] considering only parabolic ⟨111⟩ valleys fail to give a field-independent velocity when the energy loss through both the acoustic and the optic phonons are taken into account. The velocity becomes field independent only if the energy loss through the acoustic phonons is neglected. However, even then the calculated values of the electron temperature are too high, and the value of the deformation-potential constant for optic scattering, required to fit the experimental values of the drift velocity, is lower than that obtained from the analysis of low-field results. It was shown by the present authors in an earlier paper[6] that if the effect of the ⟨100⟩ valleys are included in the usual simple theory, the velocity becomes field independent even when the energy loss through the acoustic phonons is taken into account. The electron temperature is also found to be reasonable, but the value of the optical-deformation-potential constant which gives fit between theory and experiment is almost unaltered. In this paper the alterations in these results caused by the incorporation of the nonparabolicity in the ⟨111⟩ valleys and the associated overlap corrections are discussed.

II. METHOD OF ANALYSIS

High-field-conductivity characteristics considering the nonparabolicity of the ⟨111⟩ valleys have been recently obtained by Dumke.[7] In this analysis, the effect of the nonclassical excitation of the acoustic phonons was also considered and the symmetric part of the distribution function was obtained by the Levinson method.[8] However, on detailed computation we find that the nonclassical excitation of the acoustic phonons has negligible effect. The distribution function obtained by Dumke[7] from his detailed analysis is also almost Maxwellian at room temperature. The small deviation at low energies is unlikely to affect the results significantly. The analysis may, therefore, be much simplified by assuming a Maxwellian distribution function with an electron temperature determined by the energy-balance condition. The equations giving the momentum relaxation time and the electron temperature for the nonparabolic ⟨111⟩ bands assuming a Maxwellian distribution function and classical excitation of acoustic phonons are given in the following: