Two-Electron Transitions in the Condensed Phase of Nonequilibrium Carriers in Si†

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Two-electron transitions are observed in Si at liquid-He temperature for high excitation levels. A broad emission line appears at an energy of $h\nu = 2.28$ eV with a linewidth of about 20 meV. The experimental line shape agrees well with a theoretical calculation obtained from the model of electron-hole drops proposed by Pokrovsky, Kaminsky, and Svistunova.

In 1966 Haynes[1] observed a new photon emission line in pure Si at liquid-He temperature. He attributed this line to the decay of an excitonic molecule. The line shift relative to the free-exciton line and the linewidth are explained by the ionization of the second exciton. Pokrovsky and Svistunova[2] observed a similar line in Ge, and they attributed this line to a condensed phase of nonequilibrium carriers. Such a condensation was proposed by Keldysh.[3] From the line shapes, Pokrovsky, Kaminsky, and Svistunova[4] (PKS) determined the carrier densities in the condensate to be 2.6×10^{-17} cm^{-3} in the case of Ge and 3.7×10^{18} cm^{-3} in the case of Si.

There are many arguments of the reaction kinetic type for [2,4-6] and against[7-9] the PKS model. Since these arguments are contradictory, no final conclusion can be reached therefrom. There are only two nonreaction kinetic experiments which support the PKS model in the case of Ge, namely, the appearance of electrical pulses in a diode structure[10,11] and the scattering of infrared light.[12] The scattering experiment could not be reproduced.[13] In CuCl and CuBr excitonic molecules were identified.[14-16] In the case of Si, no experimental evidence for either model is known.

In this paper we report about radiative two-electron transitions in highly excited Si at liquid-He temperature, which give experimental evidence for the PKS model.[4]

Two-electron radiative transitions from band to band were reported in previous papers.[17] These transitions seem to be suitable to distinguish between both models: In a two-electron transition a biexciton can be completely annihilated, emitting a single photon. No phonon is needed for momentum conservation because the two electrons may have opposite momentum. Therefore, because of the two-electron transition a sharp emission line is to be expected at an energy of $h\nu = 2(h\nu_0 + \hbar\omega) - E_M = 2.310$ eV, where $h\nu_0$ is the energy of the indirect one-electron transition of the free exciton, $\hbar\omega$ is the energy of the phonon participating in this transition, and E_M is the binding energy of the biexciton, which may be neglected in the case of Si.[18] In the case of the PKS model, a broad emission band should appear at an energy of $h\nu = 2(h\nu' + \hbar\omega) = 2.280$ eV with a half-width of about 20 meV. $h\nu'$ is the energy of the new emission line observed by Haynes.[1]

In our experiment we have excited a slice of pure Si (p type, 4000 Ω cm at room temperature) by a pulsed GaAs laser. The sample was immersed in liquid He, which was pumped slightly below the λ point. The emitted radiation passed through a 0.75-m Spex monochromator and through a BG 18 filter and was detected by an EMI 6256-Å photomultiplier with S 11 characteristic. The registration was carried out in an automatic cycle using the "digital-boxcar-integration" method reported previously.[17] Every filling of the He Dewar took 24 h, and in this time we registrated the whole spectrum. Because of the low

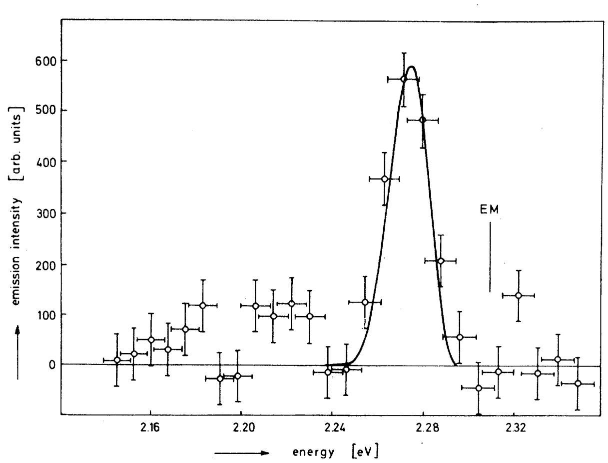

FIG. 1. High-energy luminescence spectrum of Si at a temperature of about 2 K. EM indicates the total energy of an excitonic molecule. The curve is calculated from the model of nonequilibrium carrier condensation proposed by Pokrovsky, Kaminsky, and Svistunova.

signal-to-noise ratio we added the results of thirty experimental runs.

Figure 1 shows the spectrum we obtained after adding. A broad emission line appears at an energy of 2.28 eV with a half-width of about 20 meV. In the figure *EM* denotes the position of the sharp emission line to be expected from the biexciton model. To compare our results with the PKS model, we used it to calculate a theoretical emission line. Because of the small screening length within the drops, we have assumed that momentum conservation is only fulfilled between the band valleys, but not within a valley. In this case the theoretical calculation is reduced to a convolution integration of the one-electron transition line shape $J(h\nu_1)$ calculated in Ref. 4. If one corrects the line position for the phonon assistance in the one-electron transition, one obtains for the zero-phonon, two-electron transition line shape

$$J(h\nu_2)=\iint J(h\nu_1)J(h\nu_1{}')\times\delta(h\nu_2-h\nu_1-h\nu_1{}'-2\hbar\omega)\,d\nu_1\,d\nu_1{}'.$$

The result of this calculation is given in the figure (solid line). The agreement with our experimental results is very good, and we conclude therefrom that the PKS model is correct in the case of Si. From the fact that the single-particle energy calculation holds, we furthermore conclude that particle pairing can be neglected, which may be considered similar to the case of superconductivity.[19]

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