[9]The parameters derived from the most recent set of phase shifts *do* follow this general trend [M. J. G. Lee, Phys. Rev. B 4, 673 (1971)].

[10]Since the bottom of the free-electron-like band falls in the vicinity of V_{MT}, the range of κ usually includes $[(n_0+n_1)9\pi/4]^{1/3}/S_{WS}$.

Motion of Electron-Hole Drops in Pure Ge

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We study the motion of electron-hole drops in pure Ge at 2°K. An analysis of their luminescence by a time- and space-resolved technique yields their diffusion coefficient (150 cm^2/sec) and their lifetime (40 μsec). We also measure the formation time (0.1–0.7 μsec) of drops containing about 10^6 electron-hole pairs. A discussion of these new results is given.

Between approximately 10 and 70°K, the luminescence spectrum of pure germanium exhibits only emission lines due to the phonon-assisted decay of free excitons.[1,2] Below 10°K, new radiation peaks arise and grow rapidly when the temperature is further decreased.[3,4] Their maxima all fall about 5 meV below the LA, TO, and TA phonon replicas of the free exciton. Similar data have been obtained[5] in Si at low temperature and have been interpreted in terms of the recombination of excitonic molecules which were predicted by Lampert[6] in 1958. It has also been proposed[4,7] that one interpret the new emission lines observed in pure Ge as arising from the radiative annihilation of excitonic molecules. However, following an idea of Keldysh,[8] Pokrovskii and co-workers[3,9,10] have suggested explaining these results by the condensation of excitons into electron-hole drops (hereafter called EHD). In fact, it is now quite clear[11-13] that EHD are responsible for the low-energy emission lines observed in pure Ge at low temperature.

We wish to report here some new experiments performed in Ge to investigate the motion of EHD and the formation time of drops containing approximately 10^6 electron-hole pairs. To our knowledge, these measurements provide the first determination of the diffusion constant of EHD and they also yield the first data obtained on their time of formation.

Motion of EHD.—In these experiments, the light emitted by a pulsed GaAs laser was focused onto a 50-Ω-cm Ge sample at 2°K so that the excitation spot was a thin horizontal line whose width was less than 50 μm. The pulse length was 1.5 μsec with a fall time smaller than 0.1 μsec and the repetition rate was 300 cps; the peak power of the laser used was approximately 10 W. The recombination light emitted from the irradiated face of the Ge sample was sent onto a rapid detector by means of a very good elliptic mirror. During the experiment, the positions of the GaAs laser and of the sample were left unchanged, but the detector, which was a Ge photodiode with a fall time of 0.2 μsec, could be displaced in a vertical plane. It was therefore possible to observe the light emitted at a distance x from the exciting spot. With this apparatus, we were able to separate entirely the light coming from two points separated vertically by 100 μm on the sample. Besides, the photodiode was followed by a boxcar integrator to analyze the detected signals as a function of time.

As shown for example in Ref. 10, the only radiation which can be observed in Ge at 2°K is due to the EHD. Figure 1 represents the measured luminescence decays of the EHD at 2°K for different points of the sample. These results can be explained quite well by a diffusion of the EHD with a total lifetime $\tau \sim 40$ μsec and a duffusion constant $D \sim 150$ cm^2/sec. This interpretation is supported by the variation with x of the time delay t_M corresponding to the maximum of the different curves given in Fig. 1. Indeed, from Fig. 2 it can be seen that t_M varies as x^2. Let us add that Pokrovsky, Kaminsky, and Svistunova failed[10]

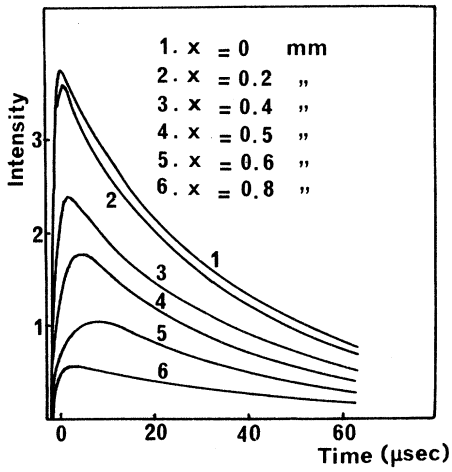

FIG. 1. EHD luminescence decay curves for different points x of the sample at 2°K. The time origin corresponds to the maximum of curve $x=0$. The results obtained for $x=0.8$ mm are perturbed by light emitted at $x=0$. This parasite light is not absorbed and is reflected on the sample boundaries before emerging from some points of the sample.

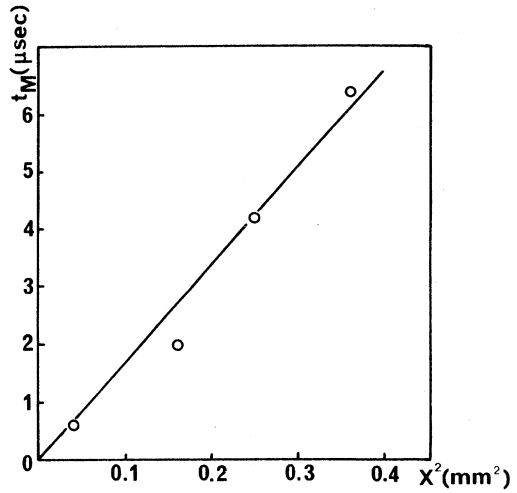

FIG. 2. Time delay t_M of the maximum of the different curves shown in Fig. 1 as a function of x^2; t_M is measured with respect to the maximum of curve $x=0$ in Fig. 1.

to measure the EHD diffusion constant, but the result that we got is consistent with the limit value of D that they could reach. It must be noted that the 40-μsec lifetime is obtained only in large samples having a thickness greater than 2 mm. In thinner samples we find $\tau \sim 10$ μsec,[4] and we believe that this is due to surface effects. In addition, the radiative lifetime has also been measured as described in Ref. 7 and found equal to 80 μsec. The ratio of this lifetime to the radiative lifetime of free excitons is therefore[7] near 16. If n_c is the density of electron-hole pairs in a drop and $\Phi(r)$ the wave function of the relative electron-hole motion of the free exciton, the value of this ratio is readily explained since it is equal to $n_c/|\Phi(r=0)|^2$ with[9] $n_c \sim 2.5\times10^{17}$ cm^{-3} and $|\Phi(r=0)|^2 \sim 10^{16}$ cm^{-3}. Besides, our results show that the quantum efficiency of the EHD radiative recombination is 50%, but this is smaller than the data given in Ref. 9, i.e., 80–100%. However, our value is consistent with the abrupt decrease of the efficiency which is observed when a uniaxial stress is applied.[14] This effect is related to a decrease of n_c due to the modification of the band structure. It is thought that the nonradiative recombination mechanism could be an Auger process, since n_c is fairly large.

The result obtained for D seems difficult to explain if one considers the large mean mass M of the EHD which contains[12] $\sim 10^6$ electron-hole pairs. If one assumes that the mean kinetic energy E_c of an EHD is kT, the collision time of EHD is $\tau_c \sim 5\times10^{-4}$ sec at 2°K, according to the formula $D=\tau_c E_c/M$. Obviously, this value of τ_c is meaningless. On the other hand, Bagaev *et al.*[15] have proposed that the interaction of an EHD with phonons should be quite low, because of the Fermi degeneracy in such a drop. Accordingly, one could assume that the EHD have a straight-line motion, but this is in contradiction with the x^2 variation law of t_M. To obtain a satisfactory value of τ_c from our experiments, it is necessary to suppose that E_c is much greater than kT. Remembering that the EHD are in fact "energy drops" and that at least 50% of their energy decays nonradiatively, one can assume that a part of this energy is converted into kinetic energy of the whole drop. However, it is now difficult to propose a specific mechanism for that energy conversion. It can be noticed that another kind of excitation of the whole drop, namely plasma oscillations, is characterized by an effective temperature of ~ 15°K[16] when the lattice temperature is near 2°K. It is therefore not unreasonable to assume that E_c is much greater than kT in the case of these EHD.

Time of formation.—To determine the formation time t_f of EHD we have performed experiments whose principle is similar to those described in Refs. 11 and 12. The n region of a Ge photodiode was excited at 2°K with a pulsed GaAs laser whose peak power was ~ 10 W. The pulse

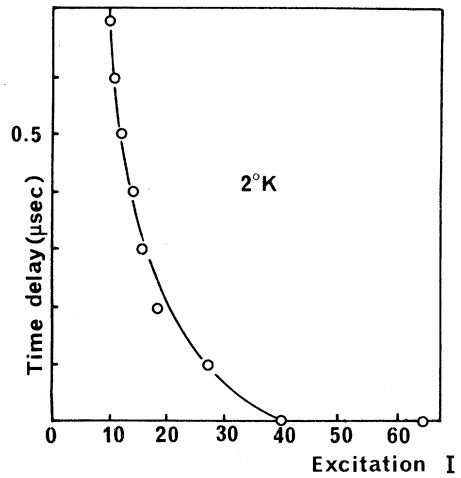

FIG. 3. Time delay between the excitation light pulse and the appearance of the first EHD as a function of the excitation peak power in arbitrary units. That power corresponds approximately to 10 W for $I=65$.

length was 30 nsec with a fall time equal to 20 nsec and the repetition rate was 100 cps. The photodiode, which was mounted in a coaxial structure, was loaded with a 50-Ω resistance, and we have observed the fluctuations of the photovoltaic current in that resistance by use of a rapid and sensitive oscilloscope.

These fluctuations are analogous to those of a photomulitplier and are due to the desctruction of EHD in the electric field of the junction.[11,12] We have measured, as a function of the excitation I, the time delay between the end of the top of the exciting light pulse and the appearance of the first EHD which could be detected; these drops correspond approximately to 10^6 electron-hole pairs. Figure 3 represents the time delay, which is obviously equal to t_f, versus the excitation; from $I=40$ to $I=65$, t_f was too small to be measured with our apparatus. In addition, it must be noticed that the delays which have been determined are certainly not perturbed by the transit time of the EHD or of the free excitons across the n region of the photodiode. Indeed, the width w of that region is 20 μm so that the time required to cross it is of the order of $w^2/4D$, i.e., ~6.5 nsec.

These data show that the formation time of EHD is quite short and does not alter the interpretation of the results represented in Fig. 1. Besides, the order of magnitude of t_f seems in agreement with the idea that a free exciton reaching the surface of a drop will condense in that drop with a probability near unity. Indeed, a crude calculation of the growing rate R of EHD can be performed in that model. If N is the number of electron-hole pairs in a drop whose radius is r, R can be written

$$R=\frac{dN}{dt}=\frac{N}{t_f}=\frac{4\pi r^2 n_{ex} v_{ex}}{3},$$

where n_{ex} is the density of created excitons whose thermal speed is v_{ex}. In our experiments, n_{ex} can be estimated to be about 10^{15} cm^{-3}; with $r\sim 1$ μm,[12] $N\sim 10^6$, and $v_{ex}\sim 8\times 10^5$ cm/sec, we thus find $t_f\sim 0.03$ μsec. This value is rather satisfying, but further investigations are necessary to improve the model that we propose.

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Lack of Photoemission Evidence for Tailing of Density of States into Energy Gap of Amorphous Si

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A photoemission study of amorphous Si for $5.5 \leq \hbar\omega \leq 11.7$ eV has been made with emphasis placed on checking an earlier report of photoemission evidence for a tailing of the density of states into the energy gap. A comparison of photoelectron energy distribution curves from amorphous Si with those of Au and crystallized Si yielded no evidence for tailing of the density of states. It is concluded that the large tailing of the density of states previously reported is not an intrinsic property of amorphous Si but probably a result of the different sample preparation. In both our amorphous and crystallized Si films the Fermi level is located 0.28 ± 0.05 eV above the valence band maximum at the surface.

Much of the experimental and theoretical work on amorphous materials has been centered around the postulate that the lack of long-range order results in the loss of sharp band edges because the density of states has a tail of localized states into the energy gap.[1,2] In a previous Letter,[3] Peterson, Dinan, and Fischer (PDF) interpreted their photoemission data from amorphous Si in terms of an exponential tailing of the density of states into the energy gap. Our photoemission data provide no evidence for such tailing and in fact allow us to place an upper limit of 3×10^{19} states/cm^3 eV on the number of states in the energy gap. Previous studies of Ge combining both optical absorption and photoemission measurements similarly found no evidence for a tail of localized states in the gap.[4] Optical-absorption and photoconductivity measurements[5] are more sensitive to states in the gap; the importance of this work is not just in setting an upper bound but in showing that it is possible to prepare samples which do not show the large tailing effects previously observed by photoemission.

The essence of the present work is a comparison of photoelectron energy distribution curves (EDC's) from amorphous Si with those of Au and crystallized Si films keeping factors which affect experimental resolution, such as the analyzer geometry and collector surface, as nearly identical as possible. To this end, all films were formed and measured in the same apparatus and ultrahigh vacuum was maintained without interruption throughout a series of experiments, such as comparison of EDC's from amorphous and annealed films or EDC's from Au and amorphous Si films.

The amorphous Si films, about 1000 Å thick, were electron-gun evaporated from both 100-Ω-cm n-type and 1000-Ω-cm p-type crystals onto polished Si single crystals [1000-Ω-cm (111) n type], and subsequently onto annealed polycrystalline Si films, and polycrystalline Au films. The source-to-substrate distance was 48 cm. The base pressure was less than 1×10^{-11} Torr and the pressure during evaporation less than 5×10^{-9} Torr at the typical evaporation rate of 2 Å/sec.[6] Similar results were obtained from samples prepared and measured on the different substrates at room temperature and on substrates maintained at temperatures as low as 100°K.

The EDC's were measured over a photon energy range $5.5 \leq \hbar\omega \leq 11.7$ eV using a spherical retarding field energy analyzer.[7,8] The EDC's were obtained by taking the derivative of the current-voltage curve using a previously described ac technique.[9,10]

Evidence for disorder-induced tailing of the density of states of amorphous Si into the gap might be first sought by comparing the high-en-