Decay Kinetics of Electron-Hole–Drop and Free-Exciton Luminescence in Ge: Evidence for Large Drops*

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(Received 11 March 1974)

Following pulsed laser excitation of Ge, we observe both the free-exciton (FE) and electron-hole–drop (EHD) luminescence decay. The kinetics are in excellent agreement with exact numerical solutions of the rate equations of Pokrovskii and Hensel, Philips, and Rice, yielding EHD and FE total lifetimes 35.6 ± 0.5 and 7.7 ± 0.5 μsec, respectively, the EHD radiative enhancement factor $\rho = 5.1$, and values of the thermionic emission and backflow coefficients. The data suggest the production of EHD of diameter ~ 0.4 mm.

At low temperatures and high excitation, electrons and holes (e-h) in Ge are known to form free excitons (FE) and electron-hole drops (EHD).[1,2] A rate-equation model for the decay of the EHD-FE system has been proposed by Pokrovskii,[1] and extended by Hensel, Phillips, and Rice[3] to interpret their observation of cyclotron resonance of Auger electrons from the EHD decay. In this paper we report the *direct* observation of the decay kinetics of the 709-meV EHD luminescence intensity I_{709} at temperatures $1.8\ \mathrm{K} \leq T \leq 4.2\ \mathrm{K}$, as well as the *concurrent* 714-meV FE luminescence I_{714} for $T \geq 3.8$ K. Our data are fitted by the above model with excellent results, yielding experimental values of several important parameters of the system.

The rate equations used for the EHD and FE are[3]

$$\dot{\nu} = -\nu/\tau_0 - \alpha\nu^{2/3} + \beta T^{1/2}\nu^{2/3}N_x/V, \quad (1)$$

$$\dot{N} = -N_x/\tau_x + N_d\alpha\nu^{2/3} - N_d\beta T^{1/2}\nu^{2/3}N_x/V. \quad (2)$$

Here N_d and N_x are the number of EHD and FE in the effective volume V accessible to the FE,[4] and ν is the number of e-h pairs in any one drop. The bulk lifetimes, assumed independent of T, of the EHD and FE are τ_0 and τ_x, respectively, and the coefficients α[5] and β[6] describe the thermionic emission ("evaporation") and backflow of the FE. To explain our data we also must assume N_d to be constant.[3] Neglecting backflow,[3] Eq. (1) has approximate solutions[7] $\nu \propto \exp(-t/\tau_0)$ at low T, and $\nu^{1/3} \propto (1 - t/t_c)$ at $T \lesssim 4$ K, where the cutoff time $t_c \propto \nu_0^{1/3}$.

Our experiments are performed on a p-Ge crystal (impurities $\lesssim 10^{10}\ \mathrm{cm}^{-3}$) of dimensions $8.5 \times 8.5 \times 2.0\ \mathrm{mm}^3$, optically polished and etched. A GaAs laser pulse of peak power 41 W and duration 80 nsec is focused on the sample immersed in liquid He. The luminescence is collected from the back face of the crystal, analyzed by a monochromator, and detected by a photodiode of rise time ~ 1 μsec. The amplified signal is averaged over $\sim 10^5$ pulses by a variable-delay sampling gate of width 1 μsec. We are able to observe a dynamic range in signal of over 2 orders of magnitude.

Each laser pulse, absorbed by the Ge in a layer $\lesssim 1$ μm thick of area $A \sim 2.6 \times 10^{-3}\ \mathrm{cm}^2$, produces $N_{e\text{-}h}{}^0 = 8.23 \times 10^{12}$ e-h pairs which relax extremely rapidly to the indirect band gap edge. Such a high initial carrier density forms FE very rapidly ($\lesssim 10^{-9}$ sec[8]), and possibly condenses directly into EHD; the risetime of the signals is that of our detector, implying that the formation time of the EHD under such conditions is $\lesssim 1$ μsec. During this time, the EHD and FE phases tend to equilibrate rapidly because of the large FE density (n_x) and the large EHD surface area. Thus we expect from Eq. (1) the form $N_{x0}/V = \alpha/\beta T^{1/2}$ for the "initial" FE density used in solving the rate equations. In addition, the EHD phase tends to coalesce into one roughly spherical drop in order to lower its surface energy.[9] Several microseconds after excitation, we take the effective volume to be $V = \frac{4}{3}\pi L_x{}^3 = 5.16 \times 10^{-3}\ \mathrm{cm}^3$, using the FE diffusion length $L_x = (D\tau_x)^{1/2}$, $D = 1500\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$,[1] independent of T, and $\tau_x = 7.7$ μsec.

The EHD luminescence decay, Fig. 1, is strikingly nonexponential at all but the lowest T. At 1.8 K the evaporation and backflow terms in Eq. (1) are small compared to ν/τ_0, and the signal decays exponentially; but as T increases, these terms grow exponentially, and at 4.2 K dominate the shape of the curve. At all T investigated we observe a finite cutoff time τ_c, shown clearly in Fig. 2, where $I_{709}{}^{1/3} \propto \nu^{1/3}$. Our data fall much faster near t_c than predicted by the approximate solutions above, indicating the importance of including the backflow term. Numerical solutions

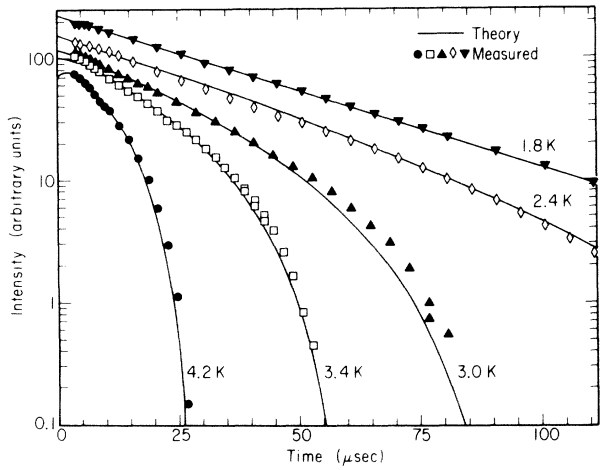

FIG. 1. EHD luminescence I_{709} following pulsed laser excitation. In this and the following figures the theoretical curves are simultaneous solutions of Eqs. (1) and (2) fitted to our data, and the intensity units are identical.

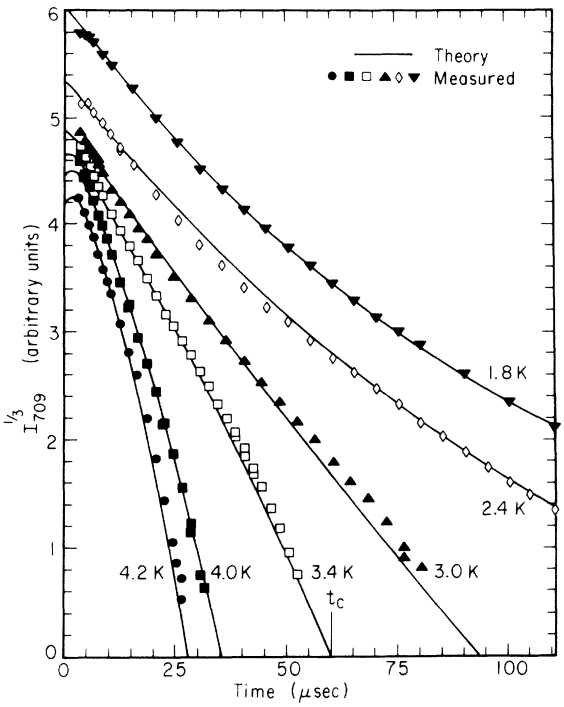

FIG. 2. Cube root of the EHD luminescence intensity following pulsed laser excitation. The finite cutoff time t_c is indicated for the data at 3.4 K.

to the coupled equations assuming a single initial drop size have the observed behavior and display finite t_c for all T. The sharpness of the cutoff, Fig. 2, allows us to place an upper limit on the standard deviation of a possible Gaussian distribution in initial EHD radius (R_0) of 15%, limited only by our signal-to-noise ratio.

The decay of the FE liminescence is shown in Fig. 3 at 3.8 K together with the EHD signal. During the time the EHD is observable, the FE decays slowly, indicating that N_x is being supported by evaporation of EHD. Once the EHD signal has vanished, the FE luminescence decays exponentially with time constant τ_x. It is interesting to note that although $\tau_0 \gg \tau_x$, Table I, the data of Fig. 3 could be taken to mean $\tau_x \gg \tau_0$ were the detailed kinetics not both understood and observed over a wide dynamic range.

We made a least-squares fit to all our data for both I_{709} and I_{714} for all T at once with computer-generated numerical solutions of Eqs. (1) and (2), taking $I_{709} = G_d N_d \nu/\tau_0^r$ and $I_{714} = G_x N_x/\tau_x^r$; G_d and G_x are instrumental constants, and τ_0^r and τ_x^r are radiative lifetimes. The initial values ν_0 and N_{x0} are taken to be $\nu_0(T) = \nu_4 f(T)$, where $\nu_4 = \nu_0$ at 4.2 K, and $f(T)$ is found by extrapolating the data to $t = 0$; and $N_{x0}(T) = C T^{3/2} \exp(-\varphi/k_B T) \propto \alpha/\beta T^{1/2}$ as above, which agrees well with our extrapolated FE data. The T-independent parameters fitted are τ_0, τ_x, φ, $\alpha/[T^2 \exp(-\varphi/k_B T)\nu_4^{1/3}]$, $\beta C/V\nu_4^{1/3}$, and $N_d \nu_4/C$. Our calculated results for I_{709} and I_{714}, scaled to fit the data, are shown in Figs. 1–3. The agreement found between theory and experiment is excellent over the entire range of intensity and T observed.

In order to obtain separately the parameters α, β, ν_0, and C, we use the values of $N_{e\text{-}h}{}^0$ and V given above and the condition $N_{e\text{-}h}{}^0 = N_d \nu_0(T)$

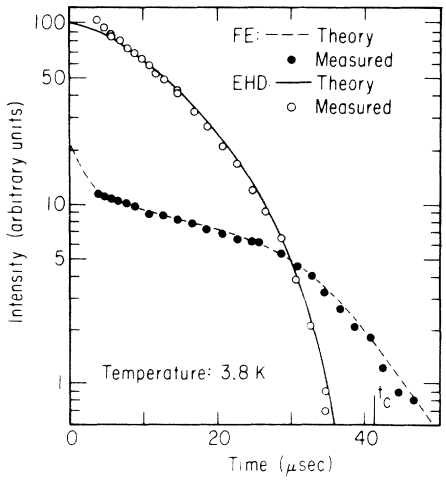

FIG. 3. Concurrent FE and EHD luminescence decay following pulsed laser excitation.

TABLE I. FE and EHD parameters for Ge.

Parameter	This work	Other measurements and theory
τ_0 (μsec)	35.6 ± 0.5	40 ± 5 (Ref. 3)
		40 (Ref. 2)
τ_x (μsec)	7.7 ± 0.5	8 (Ref. 1)
		7 ± 0.4 (Ref. 10)
α(4.2 K) (10^9 sec^{-1})	3.4 ± 0.5	4.79 (Ref. 5)
β (10^{-6} cm^3 sec^{-1} K$^{-1/2}$)	~ 2.8	3.60 (Ref. 6)
ν_0(4.2 K) (10^{12})	3.5 ± 0.7	
R_0(4.2 K) (10^{-2} cm)	1.6 ± 0.1	
R_0(1.8 K) (10^{-2} cm)	2.1 ± 0.2	
N_{x0}(4.2 K)/V (10^{14} cm^{-3})	~ 9.1	6.48 = $\alpha/\beta T^{1/2}$
τ_x^r/τ_0^r	6.5 ± 1.5	16 (Ref. 2)

$+N_{x0}(T)$. We also take $N_d = 1$, for the following reasons: (a) The e-h density created by each laser pulse is greater than that of the EHD phase. (b) Neither the data nor the fit shows evidence for a distribution in R_0, or for variation of N_d with time; these facts seem incompatible with the production of more than one drop. (c) The deviation of the experimental from the theoretical values of α and β, Table I, is a minimum for $N_d = 1$, increasing monotonically with N_d.

Table I lists several of the parameters derived from our least-squares fit. Our values of τ_0 and τ_x agree well with those of other workers[1-3,10] and we believe they are accurate under our experimental conditions. For $N_d = 1$ the agreement found between the experimental and theoretical values of $\alpha(T)$ and β is quite good, considering the limitations of the model. These are the first published experimental values of α and β; our theoretical expression[5] for α also differs significantly from those previously used.[1,3] For the initial drop radius we calculate $R_0 \simeq 0.21$ mm at 1.8 K; previously reported[1,3] values are $R \sim 1$–10 μm. Our large value of R_0 is a consequence of the high level of excitation used. Recent experiments here on EHD dimensional resonances[11] and luminescence[12] suggest the existence of EHD of this size and larger. The experimental values $N_{x0}(T)$ agree surprisingly well with the equilibrium theory above, confirming our assumption that the newly formed EHD-FE system tends to equilibrium in a time of the order of microseconds. We also find

$$\frac{\tau_x^r}{\tau_0^r} = \frac{G_x}{G_d}\frac{N_x}{N_d\nu}\frac{I_{709}}{I_{714}} = 6.5 \pm 1.5$$

for 3.8 K $\leq T \leq$ 4.2 K. We use the experimental values of I_{709}/I_{714} and the values of $N_x/N_d\nu$ from our fit, both at 10.5 μsec (e.g., see Fig. 3). We determine G_x/G_d by folding the slit function of our monochromator with the experimentally known line shapes.[13] The knowledge of the ratio τ_x^r/τ_0^r enables us to calculate the EHD radiative enhancement factor $\rho = (\tau_x^r/\tau_0^r)[|\psi_x(0)|^2/n_0]$. Using the value[2] 0.78 for the bracketed term, we find $\rho = 5.1$. This number is to be compared to the theoretical values[14] 1.79, neglecting multiple e-h scattering, and 2.33, including this effect. Finally, our fitted value $\varphi = 13$ K is lower than other thermodynamic values[13,15] by about 4 K. This discrepancy can be explained by sample heating, which we estimate to be ~0.3 K at 2.4 K and ~0.06 K at 4.2 K, from the energy absorbed per pulse and the heat capacity of the Ge sample. If we use these estimates, the corrected value becomes $\varphi \sim 17$ K.

This experiment, to our knowledge, is the first to resolve the decay kinetics of the lunimescence from EHD and FE over a wide dynamic range. In doing so, it both confirms the rate-equation model of Pokrovskii and Hensel, Phillips, and Rice, and yields unambiguous values of τ_0 and τ_x The value of ρ obtained provides a measure of the importance of e-h scattering in the theory of the EHD. The data also show that EHD can exist with radii much larger than previously measured. Our experimental results clearly contradict the predictions of the biexciton model,[10] and offer strong evidence for the existence of EHD.

We would like to thank W. L. Hansen and E. E. Haller for providing the Ge crystals used, and R. S. Markiewicz and Bernard J. Feldman for

helpful discussions.

*Work supported in part by U.S. Atomic Energy Commission.

†Postdoctoral Fellow of the Schweizerischer Nationalfonds.

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[4]We have fitted by equations using the spatial dependence of the FE density $n_x \propto \exp(-r/L)/r$, and find the homogeneous model of Eqs. (1) and (2) more satisfactory.

[5]Here $\alpha = (g8\pi^2 m^* k_B^2/h^3)(3/4\pi n_0)^{2/3} T^2 \exp(-\varphi/k_B T)$, from the Richardson-Dushman expression. For an e-h pair we use the degeneracy $g=16$, the optical mass $m^* = 0.19 m_0$, the density $n_0 = 2.16 \times 10^{17}$ cm^{-3} and the thermodynamic value $\varphi = 17$ K [see P. Vashishta, P. Bhattacharyya, and K. S. Singwi, Phys. Rev. Lett. 30, 1248 (1973)].

[6]Here $\beta = 4\pi(k_B/2\pi m_d^*)^{1/2}(3/4\pi n_0)^{2/3}$, where for FE the density-of-states mass $m_d^* = 0.335 m_0$ [see T. K. Lo, B. J. Feldman, and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973)].

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Experimental Evidence for Split Interstitials in Copper*

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(Received 21 January 1974)

The magnitudes, anisotropy, and temperature dependences of the three independent elastic constants of copper irradiated below 4 K with thermal neutrons provide evidence for the ⟨100⟩ split configuration of free interstitials and thermally excited resonance modes, and lead to a model for the configuration of the I_C close-pair defect.

Much is known about interstitials in copper as a result of intensive research over the past two decades.[1] However, very little is known about the geometry of the interstitial. Calculations for the free interstitial, beginning with the work of Huntington and Seitz,[2] favor[1] the ⟨100⟩ split interstitial geometry over the ⟨110⟩ split configuration (crowdion), or the interstitial located at the bcc position. Recently, Ehrhart and Schilling[3] have excluded the crowdion configuration for Al from measurements of diffuse x-ray scattering. No models have yet been firmly established for the close-pair configurations.

Also recently, Dederichs, Lehmann, and Scholz[4] have found by means of a computer simulation of a copper lattice that a ⟨100⟩ split interstitial should have two resonance modes of frequency of about $\omega_m/7$, where ω_m is the maximum lattice