Further comments on the luminescence line shape of the free exciton in germanium*

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The free-exciton luminescence line shape in germanium has been measured as a function of crystal temperature and free-exciton density. In order to fit these data, the theory includes nonparabolicity effects, collision broadening, and Gaussian broadening. From this fit, the bottom of the free-exciton band is at 712.8 ± 0.1 meV and the electron-hole droplet binding energy is 1.9 ± 0.2 meV.

The luminescence line shape of the free exciton (FE) in germanium was first carefully measured and analyzed by Benoît à la Guillaume and Voos[1] in order to accurately determine the binding energy of the electron-hole-droplet (EHD) liquid with respect to the FE gas. The experiment was repeated by Lo,[2] Thomas *et al.*,[3,4] and Martin.[5] Even though these various measured line shapes largely agreed with one another, there were some striking differences in their theoretical analyses which led to differences in their calculated binding energies. This paper reports measurements of the FE line shape as a function of the FE density and crystal temperature which sheds more light on these various theoretical analyses and gives an improved determination of the EHD binding energy.

The theoretical line shape $I_1(h\nu)$ is proportional to the product of the FE density of states $D(h\nu)$ and the probability of an exciton being in that state, the Boltzmann factor. From Elliott's analysis of allowed indirect transitions from a parabolic band[6]

$$D_E(h\nu) \propto (h\nu - E_0)^{1/2}, \quad E_0 = E_G - \hbar\omega - E_x, \qquad (1)$$

where E_G is the indirect band gap, $\hbar\omega$ is the phonon energy, and E_x is the FE binding energy. Using Eq. (1) Benoît à la Guillaume and Voos found that $I_1(h\nu)$ was too narrow and had to be Gaussian broadened in order to agree with the experimental line shape.

Frova *et al.*[7] measured the absorption coefficient $\alpha(h\nu)$ which is proportional to $D(h\nu)$, and they found that α was different from Eq. (1) because of strong nonparabolicity of the exciton bands. Using α and a temperature-dependent collision broadening, Thomas *et al.*[4] found excellent agreement between theoretical and experimental line shapes.

In order to explain our observed data, we have had to include nonparabolicity, Gaussian broadening, and pressure broadening. We start with the theoretical line shape $I_1(h\nu)$ given by

$$I_1(h\nu) = C\alpha(h\nu)\exp(-h\nu/kT),$$

where C is a constant. We use $\alpha = D_E$ for $0 \le h\nu - E_0 \le 0.3$ meV and the experimental values of α from Ref. 4 for $h\nu - E_0 \ge 0.3$ meV. These values of α are almost identical to the theoretical values calculated by Altarelli.[8] I_1 is collision broadened by a Lorentz function

$$I_2(h\nu) = \int I_1(h\nu') \frac{\Gamma}{(h\nu - h\nu')^2 + (\frac{1}{2}\Gamma)^2}\, d(h\nu').$$

Then I_2 is convoluted with a Gaussian function

$$I_3(h\nu) = \int I_2(h\nu') \times \exp\left(-\frac{(4\ln 2)(h\nu' - h\nu)^2}{\delta^2}\right) d(h\nu').$$

Finally, I_3 is folded into the experimentally determined slit function $S(h\nu)$,

$$I_4(h\nu) = \int I_3(h\nu') S(h\nu - h\nu')\, d(h\nu'), \qquad (2)$$

which is fitted to the experimental spectra by varying C, Γ, and δ.

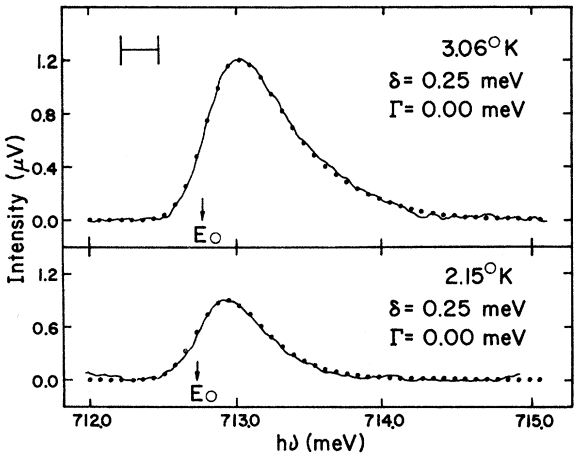

FIG. 1. Experimental (solid line) and theoretical (dotted line) line shapes of the free-exciton luminescence at 3.06 and 2.15 °K with incident laser intensities of 0.014 and 0.070 W/mm^2, respectively. The intensity scale is in units of photovoltage across a germanium photodiode, which is proportional to photons per second per unit wavelength interval.

The experiments were performed on very-high-purity p-type Ge with an impurity concentration of $\sim 10^{11}$ cm^{-3}. The samples were optically polished, etched in CP-4 solution ($HF:CH_3COOH:HNO_3:Br_2$ in the approximate ratios 50:50:80:1), mounted on a copper flange, and immersed in liquid helium. An unfocused argon-ion laser beam (5145 Å) was directed onto one face of the sample, and the luminescence was collected from the opposite face and analyzed by a Jarrell-Ash $\frac{1}{4}$-m monochromator with a grating of 590 grooves/mm blazed at 1.3 μm.

The LA-phonon-assisted FE luminescence spectra at 2.15 and 3.06 °K are shown in Fig. 1. Fitting Eq. (2) to the data gives the dotted lines in Fig. 1. Because of the low temperature of 2.15 °K and the low laser power at 3.06 °K, the FE densities are very low for both of these spectra; no collision broadening is expected and Γ is set equal to zero. Further evidence that $\Gamma = 0$ is the fact that a decrease in the laser power by a factor of 2 produces no change in the line shapes. The FE luminescence line shapes are shown at very low FE density and at very high saturated density at 4.23 °K in Fig. 2. Again fitting Eq. (2) to the data gives the dotted lines in Fig. 2.

The observed broadening of the spectra at 4.23 °K gives convincing evidence for collision broadening which was first observed by Thomas *et al.*[4] by density modulated absorption measurements. The observed broadening is not due to thermal heating because heating would shift the line to higher energies which is not observed. The highest value of Γ measured at 4.23 °K is 0.15 ± 0.04 meV which is in reasonable agreement with the value of 0.20 ± 0.04 meV of Thomas *et al.*[4]

The observed Gaussian broadening is temperature independent and its halfwidth is equal to 0.25 ± 0.05 meV, in reasonable agreement with the value of 0.31 meV of Benoît à la Guillaume and Voos. Benoît à la Guillaume and Voos suggested that the Gaussian broadening is due to the LA phonon's short lifetime. To check this idea, we compared the LA-phonon-assisted bound excitation line shape (712 meV) to the no-phonon bound exciton line shape (739 meV) in a germanium crystal doped with 10^{14}-cm^{-3} Ga. There were no differences in these two line shapes. There was also

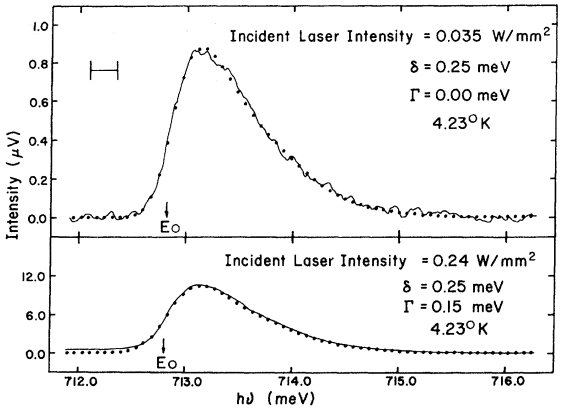

FIG. 2. Experimental (solid line) and theoretical (dotted line) line shapes of the free exciton luminescence at 4.23 °K at very low and very high, saturated free exciton densities.

no broadening observed in the LA-phonon-assisted absorption,[7] further evidence against phonon broadening. The source of this Gaussian broadening is unknown. Two possible, but unlikely, answers are further instrumental broadening or phonon dispersion.

By fitting Eq. (2) to the data, E_0, the bottom of the FE band, is found to be independent of temperature and equal to 712.8 ± 0.1 meV. It should be mentioned that the uncertainty of the source of the Gaussian broadening has not been included in this error bar. The EHD binding energy ϕ is equal to $E_0 - \mu$, where μ is the chemical potential of the EHD liquid. By fitting the EHD line shape to the standard theory,[2] we found $\mu = 710.9 \pm 0.1$ meV at 1.61 °K. This gives us an EHD binding energy of 1.9 ± 0.2 meV, which is in excellent agreement with previous spectroscopic determinations of ϕ: Benoît à la Guillaume and Voos,[1] 2.0 meV; Lo,[2] 2.06 ± 0.15 meV; Thomas *et al.*,[4] 1.8 ± 0.2 meV; and Martin,[5] 2.25 ± 0.15 meV.

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