Radiation of exciton molecules in uniaxially compressed germanium

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For the conditions of strong uniaxial compression of germanium along a nonsymmetrical crystallographic direction, close ($\sim 5°$) to the $\langle 001\rangle$ axis, the radiation of exciton molecules (EM) has been observed and their binding energy has been estimated to be $\Delta_M = 0.15 \mp 0.1$ meV.

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Up to now efforts have been unsuccessful with respect to a reliable observation of the radiative decay of exciton molecules (the bound state of two excitons) in Ge crystals, despite interesting and intensive searches in this direction, such as in Refs. 1–3. The major difficulty here lies in the fact that the partial fraction of EM in the nonequilibrium electron-hole (*e-h*) gas at low temperatures is small because of the low binding energy[4] $\Delta_M = 0.03$ R (R is the exciton Rydberg) compared with the binding energy ϕ of the electron-hole fluid (EHF). (In unstrained Ge[5] $\phi \sim 0.5$ R). The partial pressure of the EM gas relative to the excitons can be increased by removing the degeneracy in the hole and electron bands by means of a uniaxial strain. In this case the stability of the EHF is reduced significantly,[6] whereas the EM binding energy is less sensitive to the degree of band degeneracy. It was precisely for the conditions of uniaxial compression of Si (along the $\langle 100\rangle$ axis), when $\phi \approx 0.15$ R, that radiative EM decay had previously been successfully observed.[7]

Maximum removal of degeneracy in Ge is realized for compression along the $\langle 111\rangle$ axis. In this case, however,[8] $\phi \sim 0.28$ R and the EM radiation line could not be identified in the spectra. We note that an EHF in Ge can be obtained with an even lower binding energy if the compression is done along a nonsymmetrical direction, close to the $\langle 100\rangle$ axis. In this case the electron and hole bands are also nondegenerate, and the effective mass of the density of hole states is 8% less than with Ge compressed along the $\langle 111\rangle$ axis. Under these conditions it is possible to reduce the stability of the EHF to values of $\phi \approx 0.18$ R and to observe in the spectra the EM line, comparable in intensity to the radiation line of free excitons.

We investigated Ge crystals, compressed along the $\langle 111\rangle$ axis and the $\langle 1,1,16\rangle$ axis, making a 5° angle with the $\langle 001\rangle$ direction. The concentration of shallow impurities in the series of crystals studied amounted to 10^{10}–10^{13} cm^{-3}. The method of uniaxial compression of the crystals, which had dimensions of $3\times3\times10$ mm^3, was described earlier.[7] The nonequilibrium *e-h* pairs were excited with argon ($\lambda = 0.5145$ μm) or YAG-Nd^{3+} ($\lambda = 1.06\,\mu$m) lasers with up to 2 W power. A double monochromator with a 600-line/mm grating and an 8-Å/mm dispersion in the operating region was used as the spectral instrument. The radiation was detected with a cooled Ge-Cu

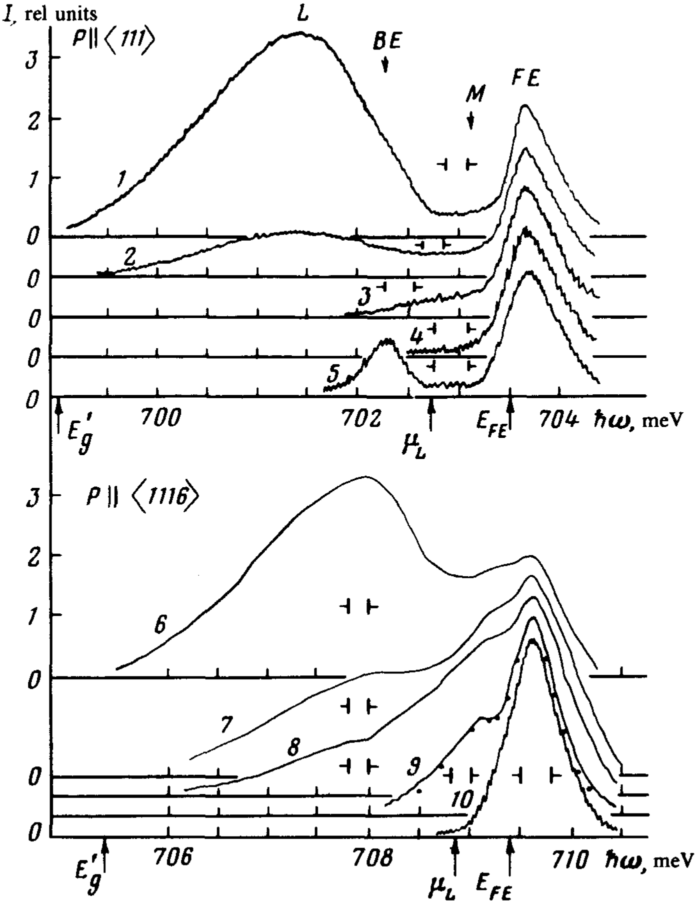

FIG. 1. Radiation spectra (LA-components) of germanium, compressed along the ⟨111⟩ (~13 kgf/mm^2) and ⟨1,1,16⟩ (~20 kgf/mm^2) axes for $T = 1.8$ K and different excitation densities P. The spectra 1–10 refer to pumping levels of 5,1,0.3,0.03,0.03,50,20,8,2,0.03 W/cm^2. Spectra 1–4, 6–10 are for pure crystals with $N_i = N_D + N_A < 5\times10^{11}$ cm^{-3}, spectrum 5 is for crystal with $N_i = 5\times10^{12}$ cm^{-3}. The locations of the renormalized gap E_g', chemical potential μ_L in the EHF and of the exciton level E_{FE} are shown by arrows. The points along curve 9 show the contour of the exciton and EM radiation lines in ⟨100⟩ Si for the same kT/R (i.e., for $T = 9$ K) and I_M/I_{FE} ratios; the energy scale in this case has been reduced by a factor of R(Si)/R(Ge)≈4.8.

bolometer in the synchronous detection mode of operation. The spectra were recorded with a resolution of 0.2–0.3 meV.

Figure 1 shows the radiation spectra of Ge crystals, compressed along the ⟨111⟩ and ⟨1,1,16⟩ axes, recorded for different pumpings and $T = 1.8$ K. At low excitation levels ($P \leqslant 30$ mW/cm^2) only the line of the free excitons *FE* (curves 4 and 10) is visible in the radiation spectra of pure crystals ($N_i < 10^{11}$ cm^{-3}), while the line of the bound excitons BE (curve 5) is also observed in crystals with $N_i = 5\times10^{12}$ cm^{-3}. With an increase in pumping to 0.2–0.5 W/cm^2 a "red" wing appears on the *FE* line (curve 3).

With a further increase in the excitation in ⟨111⟩ Ge the "red" wing of the *FE* line is not increased, but the radiation line of the EHF with $\phi = 0.8$ meV ≈ 0.28 R grows at its low-frequency edge. In the ⟨1,1,16⟩ Ge, the "red" wing of the *FE* line continues to grow at these same pumpings and becomes a fairly well resolved *M* line (curves 9,8,7). Only for $P > 10$ W/cm^2 does the radiation line appear for the EHF with a binding energy that is 1.5 times less than in the ⟨111⟩ Ge, namely: $\phi \approx 0.5$ meV $= 0.18$ R. The density of the gas phase in the ⟨1,1,16⟩ Ge close to the condensation threshold in the EHF at 1.8 K amounts to $1\text{–}2 \times 10^{15}$ cm^{-3} ($r_s \sim 3$), which is an order of magnitude higher than in the ⟨111⟩ Ge. On the basis of the following results, we attribute the observed emission line *M* to the radiative decay of the exciton molecules (EM→exciton + phonon + photon).

1. The shape of this line does not change with an increase in pumping and its width Γ agrees well with that expected for indirect annihilation of the EM, namely: $\Gamma \sim \frac{\mu}{m} R \approx 0.5$ meV (μ, m are the reduced and translation masses of the exciton).[7]

2. The *M* line appears in the spectra of the pure crystals at high excitation densities and its intensity increases superlinearly with respect to the intensity of the *FE* line: $I_M \sim I_{FE}^{1.6\text{–}1.8}$. The deviation of the exponent from two is due partially to an increase of the diffusion depth of the excitons and molecules with an increase in the excitation power. In addition, judging from the violet edge of the exciton radiation line, the temperature of the excitons increased by 0.3–0.5 K at higher pumpings, compared with the bath temperature.

3. For fixed pumping, the *M* line disappears from the spectrum with an increase in temperature (Fig. 2). Under thermodynamic equilibrium conditions, the ratio of the densities of molecules and excitons is equal to

$$n_M / n_{FE}^2 \sim (kT)^{-3/2} \exp\left(\frac{\Delta_M}{kT}\right). \tag{1}$$

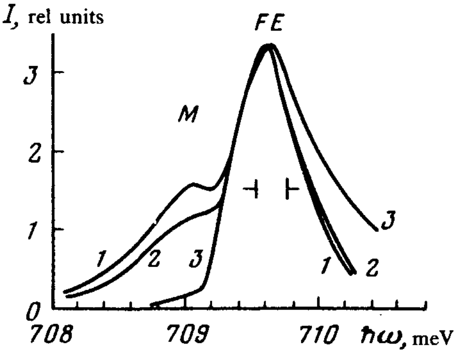

FIG. 2. Radiation spectra of ⟨1,1,16⟩ Ge for $P = 2$ W/cm^2 and different temperatures T: 1—1.8 K,2—2.1 K, 3—4.2 K.

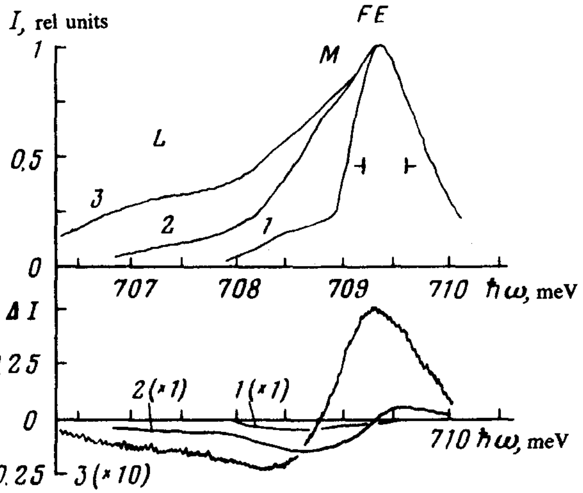

FIG. 3. Radiation spectra of ⟨1,1,16⟩ Ge $I(\hbar,\omega)$ for different P (W/cm^2): 1–0.5, 2–6, 3–15, and their change $\Delta I(\hbar\omega)$ upon application of electric field E (V/cm) = : 1,2—60,3—20.

The ratio $I_M(kT)^{3/2}/I_{FE}^2$ in the 1.8–3 K region decreased slightly with an increase in temperature. Estimates of Δ_M from the formula (1) gave a value of $\Delta_M = 0.15 \pm 0.1$ meV, which does not contradict the theoretical calculation $^4\Delta_M \sim 0.03$ R$\approx$0.09 meV.

4. Studies of the spectra when impact ionization is present also confirm the molecular origin of the *M* line. Due to the action of a weak electric field free carriers acquire kinetic energy, and upon collisions with bound states they break them. It is seen from Fig. 3, where the differential spectrum is shown, that at low excitation densities, when the EHF line is still absent in the spectra (curve 1), it is the intensity of the *M* line that is primarily reduced in the electric fields. At higher pumpings, when the *L* line is present in the spectrum (curves 2 and 3), the electric field also causes a breakup of the EHF drops, so that the density of excitons is increased somewhat and, consequently, the intensity I_{FE} also. The intensity of the *M* line decreases under these conditions. Such behavior of the spectra serves as a strong argument against interpreting the *M* line in terms of exciton-exciton (electron) collisions or an *e-h* plasma.

Finally, we compared the shape of the *M* line with the contour of the radiation line of the exciton molecule in ⟨100⟩ Si. The exciton and molecular spectra, recorded for identical I_M/I_{FE} and kT/R ratios, were compared. The result of this comparison is shown by the points in Fig. 1 (curve 9) for the experimental contour in the ⟨1,1,16⟩ Ge, measured at $T = 2$ K. The observed good agreement of the spectra for Ge and Si confirms the identical origin of the *M* line. Let us emphasize that no fitting parameters were used in this comparison.

In conclusion it should be noted that the radiative decay processes of exciton trions (bound states of an exciton with an electron or hole) can make their own contribution in the spectral region of interest to us. Under equilibrium conditions, for $T \lesssim 2$ K, the concentration of trions should be significantly lower than that of exciton molecules. Moreover, in trion radiation, particles—electron or hole—lighter than the exciton take part in the emission processes. Therefore the line of indirect trion annihilation, in principle, should be wider than for the exciton molecule.

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[1] G. A. Thomas and T. M. Rice, Solid State Commun. **23**, 359 (1977).

[2] G. A. Thomas, J. B. Mock, and M. Capizzi, Phys. Rev. **B18**, 4250 (1979).

[3] A. E. Zhidkov and Ya. E. Pokrovskii, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 499 (1979) [JETP Lett. **30**, 468 (1979)].

[4] W. F. Brinkman, T. M. Rice, and B. Bell, Phys. Rev. **B8**, 1570 (1973).

[5] J. C. Hensel, T. G. Phillips, and G. A. Thomas, Solid State Phys. **32**, 27 (1977).

[6] V. S. Bagaev, T. I. Galkina, O. V. Gogolin, and L. V. Keldysh, Pis'ma Zh. Eksp. Teor. Fiz. **10**, 304 (1969) [JETP Lett. **10**, 192 (1969)].

[7] V. D. Kulakovskii and V. B. Timofeev, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 248 (1977) [JETP Lett. **25**, 228 (1977)].

[8] B. J. Feldman, H.-h, Chou, and G. K. Wong, Solid State Commun. **24**, 521 (1977).