Excitons and excitonic molecules in uniaxially deformed germanium in a magnetic field

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(Submitted 29 January 1981)
Zh. Eksp. Teor. Fiz. **81**, 684–695 (August 1981)

The magnetic properties of indirect excitons and of excitonic molecules are investigated using the radiative-recombination spectra of uniaxially compressed germanium crystals placed in a magnetic field. It is established that the diamagnetic susceptibility of the excitonic molecules is $\chi_M \approx 2.7\chi_{FE}$ (χ_{FE} is the susceptibility of the free excitons). The g factors of the electron and of the hole in the indirect exciton are estimated from the Zeeman-splitting spectra for germanium compressed along the ⟨001⟩ and ⟨111⟩ axes. Instability of the excitonic molecules to decay into spin-oriented excitons is observed in a magnetic field. The role of the paramagnetic and diamagnetic contributions to the decrease of the stability of the excitonic molecules in a magnetic field is analyzed.

PACS numbers: 75.20.En, 71.35. + z, 71.70.Ej, 75.30.Cr

§1. INTRODUCTION

Excitonic molecules (or biexcitons) recently observed in radiative-recombination spectra of uniaxially deformed silicon[1,2] and germanium[3] spectra have exceedingly small characteristic binding energies (on the order of several degrees). As a result, the excitonic molecules in these crystals serve as a convenient model for experimental investigations of the molecular properties in a magnetic field. Thus, for example, the strongest magnetic field in which the energy of the paramagnetic splitting of the corresponding spin states of the electron and hole and of the diamagnetic shift of the exciton begin to exceed the exitonic-molecule energy has the readily attainable values $H \sim 8$ T for Si and $H \sim 1$ T for Ge. In the case of the hydrogen molecule this situation arises in astronomically strong magnetic fields ($\sim 10^4$ and 10^6 T, respectively).

From this point of view, Ge and Si differ not only in values of the excitonic-molecule binding energy, but have also substantially different ratios of the liftime τ_l and the spin relaxation time τ_s. In Si, where $\tau_s > \tau_l$, there is no equilibrium between excitons in different spin states, so that paramagnetic splitting has no effect on the stability of the excitonic molecule in a magnetic field. It was found in our earlier experiments[4] that in uniaxially compressed Si the ratio of the intensities of the exciton and excitonic-molecule emission lines has a weak dependence on the magnetic field up to $H \sim 8$ T. This led to the conclusion that the diamagnetic susceptibility of an excitonic molecule is close to two exciton susceptibilities.

In Ge, where $\tau_s < \tau_l$, the influence of the paramagnetic splitting on the stability of the excitonic molecule can no longer be neglected. In an investigation of the emission spectra of Ge uniaxially compressed along an axis close to ⟨001⟩, at $T = 1.5$–2 K, we have observed that the excitonic-molecule emission line disappears from the spectrum at $H > 1.5$ T. A detailed analysis of this phenomenon shows that decrease of the stability of the excitonic molecule in a magnetic field receives a diamagnetic as well as a paramagnetic contribution, and these contributions can be experimentally separated. The present paper is devoted to the group of questions outlined above.

In §3 are reported new experiments that confirm the molecular origin of the M line observed in the emission spectra of Ge, as well as the results of measurements, more accurate than in Ref. 3, of the binding energy Δ of the excitonic molecules in the absence of a magnetic field. In §4 are presented the results of an investigation of the paramagnetic and diamagnetic properties of indirect excitons in Ge compressed along the axes ⟨001⟩ and ⟨111⟩. The stabilization of an excitonic molecule in a magnetic field is investigated in §5.

§2. EXPERIMENTAL TECHNIQUE AND CRYSTALS

All the investigated samples were pure germanium with less than 10^{12} cm^{-3} electrically active impurities and with an approximate dislocation density 10 cm^{-2}. To lift the orbital degeneracy of the electron (hole) spectrum we used uniaxial compression of the Ge crystal along the ⟨111⟩ axis and along an axis close to ⟨001⟩ (the direction ⟨1,1,16⟩). The samples were rectangular parallelepipeds measuring $10 \times 3 \times 3$ mm, which were polished first mechanically and then electrically. The crystal uniaxial compression technique was described before.[5] The apparatus for the production of the uniaxial pressure was placed together with the sample inside a superconducting solenoid and were situated in superfluid helium at $T = 1.5$–2.2 K. All the magneto-piezoelectric investigations were made in the Voigt geometry. The nonequilibrium carriers were excited by a cw aluminum-yttrium garnet laser ($\lambda = 1.064$ μm) of 6 W power. The spectral instrument was a double monochromator with a 600 line/mm grating and with an approximate linear dispersion 8 Å/mm in the operating region. The recombination radiation was detected by a Ge(Cu) photoresistor cooled to $T \sim 100$ K and then registered with a lock-in amplifier. In investigations of the nonlinear dependence of the emission spectra on the pump, a registration technique differential with respect to intensity was used, using approximately 10% modulation of the exciting-light power density.

 0038-5646/81/080366-06$02.40

§3. EMISSION OF EXCITONIC MOLECULES IN THE ABSENCE OF A MAGNETIC FIELD

In undeformed Ge crystals, the partial fraction of the exitonic molecules in the nonequilibrium e–h gas is extremely low at $T<4$ K. The reason is the unusually low dissociation energy of the excitonic molecules, $\Delta \sim 0.05R$ (R is the exciton Rydberg) compared with the binding energy of the electron-hole liquid (EHL) $\varphi \sim 0.5R$.[6] The situation changes radically under conditions of strong uniaxial compression of the Ge along a direction close to the ⟨001⟩ axis. Under these conditions, owing to the total lifting of the orbital degeneracy in the electron and hole bands and the decrease of the effective mass of the state density for the holes, the EHL binding energy decreases to values $\varphi \sim \Delta$. The gas density near the phase boundary in the EHL therefore increases substantially, and with it the partial fraction of the exitonic molecules. Under these conditions a new and sufficiently well resolved M line was observed in the spectra, comparable in intensity with the free-exciton line FE, which we have attributed to the excitonic-molecule emission on the basis of an analysis of the spectrum shape and its dependence on the temperature, the pump, and the applied electric field.[3] We present here new results that confirm the molecular origin of this line.

Under conditions of thermodynamic equilibrium, the densities of the excitons n_{FE} and of the excitonic molecules n_M are connected by the relation

$$n_M = n_{FE}^2 \left(\frac{4\pi\hbar^2}{m_{FE}kT}\right)^{3/2} \frac{\nu_M}{\nu_{FE}^2} \exp\left(\frac{\Delta}{kT}\right), \qquad (1)$$

where ν_M and ν_{FE} are the statistical weights of the excitonic molecules and of the free excitons, and m_{FE} is the translational mass of the exciton. In accord with (1), the intensity of the excitonic-molecule emission line should vary quadratically with the exciton emission intensity: $I_M \sim I_{FE}^2$. For an experimental verification of this relation (which should hold also in the absence of detailed balance in the gas phase) it is important that the exciton temperature remain constant when the exciting-light power is varied. The power-law exponent n can be determined with highest accuracy by using a differential (with respect to intensity) spectrum measurement procedure. The value of n is determined directly from the intensity ratios I_M/I_{FE} measured in the differential and integral spectra:

$$n = \frac{(I_M/I_{FE})_{\text{diff}}}{(I_M/I_{FE})_{\text{int}}}. \qquad (2)$$

Figure 1 shows plots of the differential (with 13% intensity modulation—curve 1′) and summary (curve 1) spectra of the lines M and FE. The exponent n obtained in this manner turned out to equal 1.9 ± 0.1, as expected for a bimolecular process.

The emission of the excitons and excitonic molecules in Ge is indirect in character and is accompanied by emission of a phonon that carries away momentum in accord with the conservation law. It is of great interest to compare the excitonic-molecule emission spectra with the LA and TA photon emission, which correspond in accord with the symmetry laws to transitions that

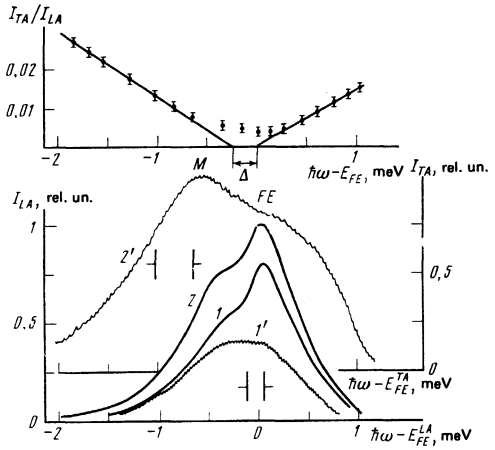

FIG. 1. Emission spectra of excitons and excitonic molecules in Ge⟨1, 1, 16⟩ at $T = 1.8$ K in a zero magnetic field with emission of LA and TA photons. The LA spectra 1 and 1′ were recorded with a 13% modulation of the intensity of the exciting light at $W \approx 20$ W/cm² (1—integrated, 2—differential, magnification 6×). The TA (2′) and LA (2) spectra were recorded at $W \approx 25$ W/cm². The intensity ratio of the TA and LA components is shown in the upper part of the figure (the TA spectrum is shown with a magnification 42×).

are allowed and forbidden in zeroth order in **k**. For the forbidden transitions, there appears in the matrix element an additional factor proportional to the modulus of the quasimomentum **k**. In the case of the exciton-phonon spectrum, the intensities of the forbidden (TA) and allowed (LA) components satisfy the relation

$$I_{FE}^{TA}(E) \sim E I_{FE}^{LA}(E), \qquad (3)$$

where $E \sim k^2$ is reckoned from the low-frequency boundary of the spectrum ($E = 0$ corresponds to the emission of an exciton at rest). In the case of radiative decay of an excitonic molecule (excitonic molecule → photon + phonon + exciton), **k** corresponds to the quasimomentum of the recoil of the particle produced in the transition (to the exciton). For the emission intensities of excitonic molecules in the allowed and forbidden spectra, $I_M^{LA}(E)$ and $I_M^{TA}(E)$, relation (3) should also hold, but here the energy E is reckoned from the high-frequency boundary of the spectrum ($E = 0$ corresponds to a recoil exciton at rest). Figure 1 shows the emission spectra of the excitons and excitonic molecules with emission of LA and TA phonons, measured at the same optical pumping (~5 W/cm²) (curves 2 and 2′, respectively). We point out that the emission intensity in the TA component is smaller by a factor of almost 200 than in LA. Therefore the quality of the TA-component plot is worse than that of LA. In the upper half of Fig. 1 is shown the intensity ratio I^{TA}/I^{LA}. It is seen that from the line M the relation (3) is satisfied with sufficient accuracy. This allows us, in particular, to exclude completely a possible interpretation of the M line as the result of emission in an electron-hole plasma. In the latter case the emission probability should increase when the high-frequency limit of the spectrum is approached, in contrast to the experimental results.

We note that if good plots are obtained of both the LA and the TA components of the spectrum, the measure-

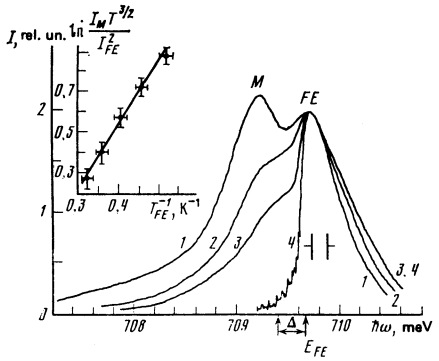

FIG. 2. Emission spectra of excitons and excitonic molecules in Ge⟨1, 1, 16⟩: 1–3) $W = 25$ W/cm^2; $T_b = 1.47$ (1), 1.74 (2), 2.10 K (3); 4) $W = 3$ W/cm^2 and $T = 2.1$ K. The inset shows a plot of $\ln(I_M T_{FE}^{3/2}/I_{FE}^2)$ vs $1/T_{FE}$, from which the binding energy of the excitonic molecule was determined.

ment of the ratio of the intensities of the M and FE lines uncovers a possibility of estimating in experiment the binding energy of the excitonic molecule (see the upper part of Fig. 1). Approximating the linear TA and LA component intensity ratio up to the crossing of the energy scale, we can find the corresponding boundaries of the excitonic-molecule and exciton spectra, and hence also the binding energy Δ. In our experiments we obtained for Δ the estimate $0.1 < \Delta < 0.4$ meV. The accuracy of this method of estimating Δ is sensitive to the temperature and decreases with increase of the latter.

The binding energy Δ in uniaxially deformed Ge can be determined with higher accuracy by the thermodynamic method. Within the framework of this method, which presupposes quasi-equilibrium between the components of the gas phase, the value of Δ is determined by comparing the intensities of the emission lines M and FE measured at different temperatures [see Eq. (1)]. Figure 2 shows the emission spectra of the excitons and excitonic molecules measured at constant optical pumping (~25 W/cm^2) in the bath temperature interval $T_B = 1.45$–2.2 K. The temperature T_{FE} of the exciton subsystem, determined from the halfwidth of the exciton emission line ($\delta = 1.8kT$) changed in this case from 1.9 to 3 K. The error in the determination of T_{FE} by this method is connected with the broadening of the exciton emission line on account of the dispersion of the phonons, of their finite lifetime, as well as of the inhomogeneity of the deformation. Judging from the fact that the difference $T_{FE} - T_B$ decreased monotonically with decreasing excitation power and amounted to ~0.3 K at $W \sim 0.4$ W, we estimate the error in the obtained values of T_{FE} at 0.1–0.2 K. The inset of Fig. 2 shows the temperature dependence of the intensity ratio of the lines M and FE plotted in the coordinates $\ln(I_M T_{FE}^{3/2}/I_{FE}^2)$ and $1/T_{FE}$. It is seen that the experimental dependence is well described by expression (1). It was found from this expression that $\Delta = 0.27 \pm 0.06$ meV. This is higher than the result of variational calculations, according to which $\Delta \sim 0.003\,R$ or ~0.1 meV for Ge.[7,8]

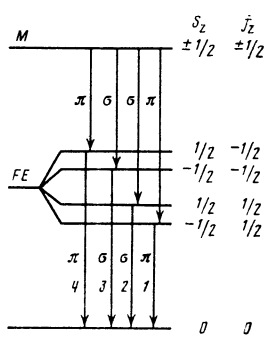

FIG. 3. Level-splitting scheme of excitons and excitonic molecules in a magnetic field.

§4. ELECTRON AND HOLE g FACTORS IN AN INDIRECT EXCITON AND DIAMAGNETIC SHIFT IN EXCITON SPECTRUM

We consider first the properties of an indirect exciton in uniaxially deformed Ge in a magnetic field. In a weak magnetic field, when the cyclotron frequency $\omega_c = eH/\mu_{FE}\,c < R/\hbar$, the exciton energy can be expressed in the form

$$E_{FE}(s_z, j_z, H) = E_{FE}^0 + (s_z g_e + j_z g_h)\,\mu H + {}^1/_2 \chi_{FE} H^2. \quad (4)$$

Here μ_{FE} is the reduced mass of the exciton, μ is the Bohr magneton, s_z (j_z) and $g_{e,h}$ are respectively the projections of the electron (hole) spins on the magnetic field direction and their g factors, and χ_{FE} is the diamagnetic susceptibility. In undeformed Ge the contributions to the diamagnetic susceptibility come from excitons that contain electrons in four valleys equivalent in energy but with different orientations of the principal axes of the ellipsoids. This is the cause of the large large anisotropy of the diamagnetic shift in undeformed Ge when H is parallel to ⟨100⟩.[9] Under conditions of strong compression of the Ge crystals along the ⟨111⟩ axis and along an axis close to ⟨001⟩, there remain excitons with electrons in the nearest split-off valley and holes with identical $|j_z|$.

a. Zeeman splitting. The ground state of the indirect exciton in uniaxially compressed Ge is split in a magnetic field into four levels (Fig. 3). The intensities of the Zeeman components (1–4) in the emission spectrum depend on the matrix element of the transition, as well as on the population of the corresponding spin states. The selection rules for transitions (1–4) with LA-phonon emission are listed in Table I, where the following symbols are used: u_z is the displacement amplitude, e_i are the polarization vectors, λ and η are constants. Figure 4 shows the exciton emission spectra with LA-phonon emission in Ge uniaxially compressed along an

TABLE I. Selection rules for indirect transitions in germanium with LA-phonon emission.[9]

s_z	j_z = 1/2	j_z = −1/2
1/2	$\frac{1}{\sqrt{6}}\eta e_+ u_z$	$-\sqrt{\frac{2}{3}}\lambda e_z u_z$
−1/2	$\sqrt{\frac{2}{3}}\lambda e_z u_z$	$\frac{1}{\sqrt{6}}\eta e_- u_z$

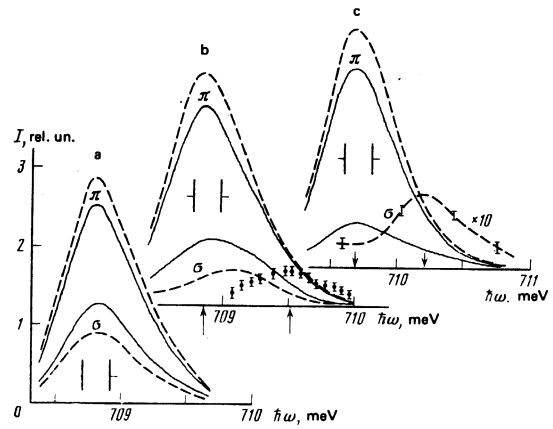

FIG. 4. Emission spectra of indirect exciton in Ge⟨1, 1, 16⟩ in fields H = 0 (a), 1.8 (b) and 4.7 T (c). Solid lines—experiment, dashed curves—contours of spectra, corrected for depolarization in accord with Eq. (5) (γ = 0.17). The contribution to the π component from the recombination of the excitons in the upper spin state at H = 1.8 T is shown by the points (with magnification 3$^{\times}$). The distance between the arrows on spectra b corresponds to $(|g_e| + |g_h|1)\,\mu H$, and on specta c it is equal to $g_e\mu H$.

axis close to ⟨001⟩. The spectra were recorded in the Voigt geometry (H⊥k at H ∥ P) in the polarizations π ($E \parallel H$) and σ(E⊥H). It is seen from the figure that the intensities of the components 2–4, which corresponds to emission of excitons in spin-excited states, decreases rapidly with increasing magnetic field. In fields $H \geqslant 5$ T the π component of the spectrum coincides fully with the emission spectrum in a zero field. We call attention to the presence of depolarization of the radiation from the crystal, owing to the multiple reflections inside the sample. As a result, the experimentally measured π and σ components ($I^e_{\pi,\sigma}$) contain contributions from the component with the other polarization

$$I^e_{\pi(\sigma)} = (1-\gamma)I_{\pi(\sigma)} + \gamma I_{\sigma(\pi)}. \qquad (5)$$

The depolarization coefficient γ was determined experimentally from the ratio I^e_σ/I^e_π for the component 1 in fields $H > 5$ T, when $g_{e,h}\,\mu H$ exceeds 2 kT as well as the spectral width of the gap. Under these conditions I^e_σ/I^e_π was independent of H, since the emission line should be fully polarized under these conditions, $I^e_\sigma/I^e_\pi = \gamma/1-\gamma$. The depolarization coefficient was usually small, 0.15–0.25, so that the π and σ components could be reliably enough separated with the aid of (5) (dashed curves of Fig. 4). It follows from the selection rules (Table I) that at H = 0 we have $I_\sigma/I_\pi = (1/4)\eta^2/\lambda^2$, and $\eta = \lambda$ if only transitions through the nearest band Γ_2' are taken into account.[9] Experiment yielded $I_\sigma/I_\pi \sim 1/3$ (Fig. 4). It follows therefore that $\eta > \lambda$ ($\eta \approx 1.2\lambda$), i.e., transitions through the L_3' band must also be taken into consideration.[9] In fields $H > 3$ T the π and σ components correspond to transitions from the lowest and first-excited states, the energy interval between which is determined by the smaller of the g factors (g_e or g_h). This interval turned out to be 1.7 ±0.2 in Ge ⟨001⟩ (Fig.4) and 1.0 ±0.2 in Ge ⟨111⟩.

The second g factor can be obtained from an analysis of the form of the emission spectrum measured in one polarization, since the matrix elements for the transitions 1 and 4 (2 and 3) coincide (see Table I and Fig. 3). If the exciton system is in equilibrium, the intensity distribution in the spectrum is given by

$$I_{\pi,\sigma}(E) \sim (E^{1/2} + [E - |g_e \pm g_h|\mu H]^{1/2}) \exp(-E/kT), \qquad (6)$$

where E is reckoned from the low-frequency edge of the exciton component 1 (2). It follows from this expresion that the components 3 (4) do not appear in the spectrum in the form of separate lines. We have chosen for the analysis the intense π component, because it is not distorted much by the contribution from the weak component on account of the presence of depolarization. The contribution made to the π component by recombination of excitons in the upper spin state 4 can be separated in fields H = 1.5–2.5 T. In stronger fields ($H > 5$ T) this state is practically unpopulated and the emission spectrum agrees, within the limit of experimental error, with the spectrum at H = 0. At H = 1.5–2.5 T the contribution made to the π component by emission from the excited state is the difference between the emission contours, normalized at the maxima, at $H \neq 0$ and H = 0. This contribution is shown by the points in Fig. 4 for H = 1.8 T. The obtained summary g factor in Ge ⟨001⟩ at $P \sim 25$–35 kgf/mm^2 turned out to be 6 ±1.

The smallest g factor agrees with the free-electron values known for Ge, namely g_e = 1.57 at H ∥ ⟨100⟩ and 0.9 at H ∥ ⟨111⟩.[10] It is natural to ascribe the second g factor obtained by us ($|g|$ = 4.5 ±1) to the hole in the exciton. From polarization measurements (the component 1 has π polarization) it follows that the g factors of the electrons and holes in an indirect exciton in uniaxially deformed Ge have opposite signs, just as in the case of the free electrons and holes in these crystals. It must be noted, however, that the obtained value of the g factor for the hole is substantially larger than the hole g factor in an indirect exciton in undeformed Ge (g_h = −1.6—Ref. 9) and is the less than the g factor of a free hole in strongly compressed Ge along the ⟨001⟩ axis (g_h = −6.8—Ref. 11).

b. *Diamagnetic shift.* In addition to the paramagnetic splitting, the exciton emission spectrum experiences in a magnetic field a strong diamagnetic shift. For the analysis that follows it is convenient to represent the dependence of the shift $E_{FE}(s_z, j_z, H) - E_{FE}(H=0)$ in the spectrum on the magnetic field strength in terms of the coordinates $\delta E_{FE}/H$ and H. When account is taken of only the first terms in the expansion in H [Eq. (3)] the plot of $\delta E_{FE}/H$ in the region of weak magnetic fields should be approximated by a straight line whose slope yields the diamagnetic susceptibility and the intercept with the ordinate axis yields the total g factor of the electron and hole, namely $(1/2)(|g_e| + |g_h|)\mu$. Experimental plots of $\delta E_{FE}(H)/H$ measured for Ge compressed along ⟨001⟩ ($P \sim 25$ kgf/mm^2) and ⟨111⟩ ($P \sim 18$ kgf/mm^2) are shown in Fig. 5.[1)] We note that at these strains one can neglect the nonparabolicity of the hole band all the way to quasimomenta $k \sim a_B^{-1}$ (a_B is the Bohr radius of the exciton).[11] It is seen from Fig. 5 that in magnetic fields H = 1–1.5 T, when $\hbar\omega_c \sim R/2$, a deviation of the experimental plot from linearity is already distinctly observed.

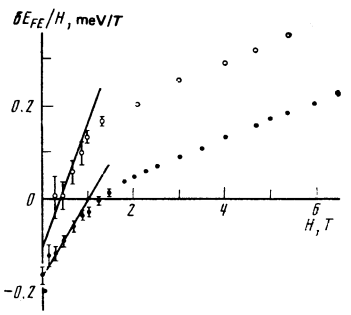

FIG. 5. Experimental plots of the exciton emission line shift vs. the magnetic field at H||P|| ⟨1,1,16⟩ (●) and H|| P|| ⟨111⟩ (○). The solid lines show the diamagnetic shift calculated for excitons in these cases in Ref. 12.

We consider now the dependence of the diamagnetic shift in very weak fields, $H \lesssim 1$ T. This region is of interest because it is possible to calculate here the diamagnetic susceptibility with sufficient accuracy within the framework of perturbation theory, allowing for the anisotropy of the electron and hole mass spectra.[12] It is well known that the Hamiltonian of an electron with an isotropic spectrum, moving in a central field (without allowance for the spin motion), contains a correction to the ground-state energy, in the form $(e^2/8mc^2) \times [\mathbf{H}\times\mathbf{r}]^2$. The situation is different with excitons in a semiconductor with anisotropic electron and hole masses. Owing to the mass-spectrum anisotropy, the correction, quadratic in the magnetic field, to the exciton energy appears not only in first-order perturbation theory (Langevin diamagnetism), but also in second order, from the Hamiltonian term linear in H (Ref. 12) (van Vleck orbital paramagnetism). Calculations performed for uniaxially compressed Ge ⟨111⟩ and Ge ⟨001⟩ (Ref. 12) have demonstrated that in both cases the contribution to the susceptibility from the orbital paramagnetism is numerically small (<2.5%). The diamagnetic (Langevin) correction to the energy of an indirect exciton in Ge at H ∥ P turned out to be 0.27 meV/T^2 for P ∥ ⟨111⟩ and 0.18 meV/T^2 for P ∥ ⟨001⟩. The straight lines in Fig. 5 correspond to these calculations. It is seen that in weak fields, $H < 1$ T, the calculation describes satisfactorily the experimental $\delta E_{FE}(H)$ dependence. It is also possible to determine from this the sum of the moduli of the g factors of the electrons and holes in an exciton. These turned out to be $|g_e| + |g_h| = 5.5 \pm 0.5$ for Ge ⟨001⟩ (in agreement with the values obtained above) and $|g_e| + |g_h| = 5 \pm 0.5$ for Ge ⟨111⟩.

§5. EXCITONIC MOLECULE IN A MAGNETIC FIELD

The investigation of the effect of a magnetic field on the emission spectrum of an excitonic molecule in Ge is extremely interesting because of the rapid spin relaxation of the electrons and holes compared with the lifetime of the excitons in the excitonic molecule. As a result it is possible to distinguish experimentally in Ge, unlike in Si, between the triplet and singlet excitons and to separate the contributions made to the excitonic-molecule dissociation by the paramagnetic splitting and by the diamagnetic susceptibility.

It is natural to expect, in analogy with the hydrogen molecule, that in the ground state the resultant spin of the excitonic molecule is zero. The energy of such a singlet biexciton in a magnetic field is

$$E_M(H) = E_M(0) + \delta E_M, \tag{7}$$

where $\delta E_M \sim (1/2)\chi_M H^2$ in the case of weak magnetic fields (χ_M is the diamagnetic susceptibility of the excitonic molecule). It follows from (4) and (7) that the binding energy of the excitonic molecule in a magnetic field is

$$\Delta_M(H) = 2E_{FE}(-1/2, 1/2, H) - E_M(H) = \Delta - (|g_e| + |g_h|)\mu H + 1/2 H^2 \delta\chi, \tag{8}$$

where $\delta\chi = 2\chi_{FE} - \chi_M$. The question of the diamagnetic susceptibility of an excitonic molecule in weak magnetic fields was considered theoretically in Ref. 13, where it was shown that $\chi_M/2\chi_{FE} < 1.9$, and also with the excitonic molecule in Si as the example, where a ratio $\chi_M/2\chi_{FE} < 1.5$ was obtained.[4]

Owing to the paramagnetic splitting the excitonic molecules cease to be stable even at $\delta\chi = 0$ (the binding energy becomes zero) in a field $H = H_{cr} = \Delta/(|g_e| + |g_h|) \times \mu$. In uniaxially compressed germanium $H_{cr} \sim 1.5$ T. It must be borne in mind, however, that at $T \neq 0$ the singlet excitonic molecules can exist even at $H > H_{cr}$ because of the finite population of the spin-excited states of the excitons. At thermodynamic equilibrium it is easy to obtain from the condition that the chemical potentials be equal, $2\mu_{FE} = \mu_M$, the following relation for the excitonic-molecule and exciton densities:

$$F(H) = \frac{n_M(H)}{n_{FE}^2(H)} \Big/ \frac{n_M(0)}{n_{FE}^2(0)} = \exp\frac{1/2\, H^2\delta\chi}{kT} f(g_e, g_h, H, T), \tag{9}$$

where the densities of the excitonic molecules and of the excitons, $n_M(0)$ and $n_{FE}(0)$ at $H = 0$ are connected by Eq. (1), and the function f, which describes the decrease of the fraction of excitonic molecules in the gas phase

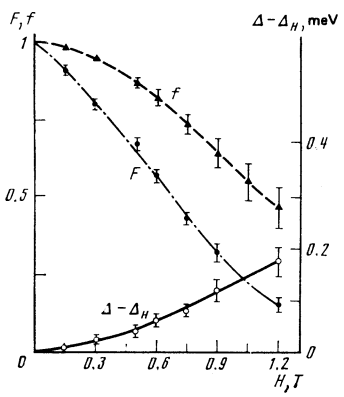

FIG. 6. Change of the ratio of the emission line intensities of the excitons and excitonic molecules, I_M/I^2_{FE} in α magnetic field, obtained in experiment (curve F) and calculated without allowance for the diamagnetic shifts for the exciton and the exciton and the exitonic molecule, using the g factors obtained from the Zeeman-splitting spectra (curve f). In the lower part is shown the change of the excitonic-molecule binding energy $(\Delta - \Delta_H)$ obtained from the ratio of these functions and due to the difference between the diamagnetic shifts of the exciton and of the molecule.

because of the paramagnetic splitting, is equal to

$$f=\frac{1}{4}\left[\operatorname{ch}\frac{(g_e+g_h)\mu H}{2kT}+\operatorname{ch}\frac{(g_e-g_h)\mu H}{2kT}\right]. \quad (10)$$

For Ge ⟨001⟩ the function $f(H)$ shown in Fig. 6 was calculated using $g_e = 1.6$ and $g_h = 4.5 \pm 1$. As seen from (9), from the deviation of the experimental $F(h)$ from the function $f(H)$ we can estimate $\delta\chi$ and then, knowing χ_{FE}, we can estimate also the ratios of the diamagnetic susceptibilities of the excitons and the exitonic molecules.

The effect of the magnetic field on the emission spectra of excitonic molecules and excitons is illustrated in Fig. 7, which shows the change of the emission spectrum of Ge ⟨100⟩ at a fixed excitation density at $H = 0$, 0.4, 0.8, and 1.2 T. It is seen from the figure that the excitonic-molecule emission line vanishes from the spectrum with increasing magnetic field, while the emission intensity of the excitons increases at the same time. The integrated intensity of these lines remains practically unchanged in this case. It is thus clearly seen that with increasing magnetic field the stability of the excitonic molecules in Ge decreases rapidly, and this is accompanied by a decrease in the excitonic-molecule density and by an increase of the exciton density. The constancy of the integrated intensity agrees with the very small difference between the quantum yields for the excitonic molecules and for the excitons (~15%).

The ratio

$$F(H)=\frac{I_M(H)}{I_{FE}^2(H)}\Big/\frac{I_M(0)}{I_{FE}^2(0)}$$

measured at $T = 1.8$ K is shown in Fig. 6. As seen from a comparison of the functions $f(H)$ and $F(H)$, the experimentally observed decrease of the intensity of the excitonic-molecule emission line intensity cannot be described solely in terms of the contribution from the paramagnetic (linear in H) terms, and it must be assumed that $\chi_M > 2\chi_{FE}$. The change $\Delta_H - \Delta$ is shown in Fig. 6. It follows from it that $\chi_M = (2.7 \pm 0.5)\chi_{FE}$. This result agrees with the results of an investigation of χ_M in compressed silicon[4] as well as with the χ_M calculated in Ref. 13.

§6. CONCLUSION

In our opinion, the most interesting result of this paper is the observation of the destruction of the excitonic molecules in uniaxially deformed germanium in a magnetic field. The observed instability is due to the fact that the spin-oriented excitons cannot form, in accord with the Pauli principle, a stable molecular state. The analysis has been carried out in a magnetic-field range such that the cyclotron energy is lower than the exciton Rydberg so that the excitons are not yet fully diamagnetic. Practically complete spin orientation of the exciton takes place under conditions of rapid spin relaxation, when the paramagnetic splitting in the exciton exceeds substantially the thermal energy. For Ge, this situation is realized under uniaxial compression along a direction close to ⟨001⟩, in magnetic fields $H \sim 1.5$ T and $T = 1.45$ K. The gas of the spin-oriented excitons in uniaxially deformed germanium is a most convenient

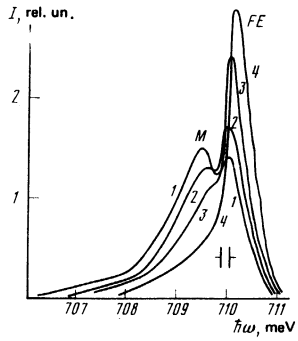

FIG. 7. Effect of the magnetic field on the exciton and biexciton emission spectra; $T = 1.5$ K; $H = 0$ (1) 0.4, (2), 0.8 (3). and 1.2 T (4).

model object for the study of the statistical properties of excitons of high density. If it turns out for certain directions of uniaxial deformation in Ge (e.g., dilatation along a direction close to ⟨001⟩) in a magnetic field that not only the excitonic molecules but also the electron-hole liquid is unstable because of the complete spin orientation of the carriers, then under these conditions one could expect Bose-Einstein condensation in the exciton gas when the critical parameters (density and temperature) are reached. In addition, a spin-oriented exciton gas is convenient also for the study of ionization collapse of excitons.

In conclusion, the authors thank T.G. Tratas and V.M. Édel'shteĭn for interesting opinions and discussions.

[1)] The energy of the exciton term was determined by measuring the low-frequency edge of the exciton-phonon spectrum, where the emission intensity was half the maximum value.

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Translated by J. G. Adashko