[1)]The authors thank T. M. Perekalina for providing the specimen.

[2)]Noticeable anisotropy in the basal plane occurs only at temperatures below 200 Å.[1]

[3)]To eliminate the crude errors in a determination of $\partial K_1/\partial T$ and $\partial K_2/\partial T$ by a graphical method, we approximated the $K_1(T)$ and $K_2(T)$ curves analytically.


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# Low-temperature photoluminescence of gallium arsenide


V. V. Stopachinskiĭ

*P. N. Lebedev Physics Institute, USSR Academy of Sciences*



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The emission spectra of gallium arsenide with different contents of impurities were investigated in a wide range of excitation levels. It is shown that the dominant recombination channel of the free excitons is captured by shallow donors and acceptors followed by very rapid annihilation of the exciton-impurity complexes. When the excitation density increases to $n_{cr} \sim 10^{15}$ cm$^{-3}$, the free-carrier gas condenses into electron-hole drops with equilibrium density $n_0 \sim 10^{16}$ cm$^{-3}$.



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## 1. INTRODUCTION

A rather large number of various collective effects in semiconductors are presently discussed in the literature. One of the most interesting manifestations of collective interactions should be taken to be the condensation of excitons into electron-hole drops (EHD). This phenomenon has been investigated in sufficient detail in the indirect semiconductors Ge and Si, and most experiments have been explained not only qualitatively but also quantitatively.

In semiconductors with direct allowed transitions, the possibility of condensation of excitons or of free carriers is denied by most workers, because of the short lifetime of the gas phase ($\tau \sim 10^{-9}$ sec). To explain the observed emission spectra at high excitation levels in straight-band semiconductors it is therefore customary to resort to the so-called collective radiative processes, such as inelastic exciton–exciton collisions (the $P$ band),[1] inelastic collisions of biexcitons,[2] etc. In addition, the contribution of the radiation of the electron-hole plasma,[3] i.e., of interband recombination with allowance for the change of the width of the forbidden band as a result of the collective interactions, is also considered.

The short lifetimes of the free excitons in semiconductors with direct allowed transitions notwithstanding, one can apparently not exclude the possibility of experimental observation of EHD. It can be shown[4] that EHD with equilibrium density $n_0$ and radius $R$ should be produced at $n_{av} \gtrsim n_0 R/3\tau_0 v_{av}$, where $n_{av}$ is the average density of the condensing gas, $v_{av}$ is the average thermal velocity, and $\tau_0$ is the lifetime. Estimates show that in gallium arsenide (GaAs) at $n_{av} \sim 10^{15}$ cm$^{-3}$ there can exist EHD with radius $R \sim 10^{-4}$ cm and equilibrium density $n_0 \sim 10^{16}$ cm$^{-3}$ [5] at $\tau_0 \sim 10^{-9}$ sec. It should be noted here that $n_{av} \sim 10^{15}$ cm$^{-3}$ seems to exclude completely a contribution of free excitons to the condensed phase, since there can be no free excitons in GaAs at these densities. What should be condensed in this case are the free carriers, as is indeed confirmed by experiment.[6,7]

## 2. FEATURES OF RADIATIVE RECOMBINATION IN GaAs

One of the most important characteristics of optical transitions in solids is the oscillator strength $f_i$ for processes in which light is absorbed, or the radiative lifetime $\tau_i$ in the case of emission. If we disregard the dispersion of the dielectric constant, then $\tau_i = 3m_0c^3/2e^2n\omega_i^2 f_i$, where $m_0$ is the mass of the free electron, $n$ is the refractive index, and $\omega_i$ is the frequency of the light.

Using the known expression for the oscillator strength[8] in the case of direct allowed transitions, we can estimate the radiative lifetime of the free excitons $\tau_{ex} \sim 5 \cdot 10^{-5}$ sec in GaAs.

However, if the crystal contains impurities (shallow donors and acceptors), then the free excitons can become bound to form exciton-impurity complexes.[9]



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Rashba and Gurgenishvili[10] have shown that exciton-impurity complexes should correspond to giant oscillator strengths and to associated short radiative-recombination times $\tau_i \sim 10^{-9}$ sec. If the exciton is weakly coupled with the center, then the oscillator strength in the deuteron approximation is[11]

$$f_i=8\left(\frac{\mu}{M}\frac{E_{ex}}{E_i}\right)^{1/2}\frac{\pi a_{ex}^3}{\Omega_0}f_{ex},$$

where $\Omega_0$ is the unit-cell volume, $\mu$ is the reduced mass of the electron and hole, $M$ is the exciton mass, $a_{ex}=\varepsilon\hbar^2/\mu e^2$ is the Bohr radius of the exciton, $E_{ex}=\mu e^4/2\hbar^2\varepsilon^2$ is the exciton Rydberg number, and $E_i$ is the exciton binding energy at the center. (In the deuteron approximation the wave function is determined completely by the binding energy

$$\Psi_i(\mathbf{r}_e,\mathbf{r}_h)=\Phi_{ex}(\mathbf{r})\varphi_i(\mathbf{R}),\quad \varphi_i(R)=\left(\frac{\alpha}{2\pi}\right)^{1/2}\frac{e^{-\alpha R}}{R},$$

where $\alpha=(2mE_i)^{1/2}$, $\hbar=1$). For GaAs we obtain $f_i/f_{ex}=\tau_{ex}/\tau_i \gtrsim 10^5$, and $\tau_i \sim 10^{-9}$ sec. The experimental data on the measurement of the radiative lifetimes of the exciton-impurity complexes in GaAs agree well with the theoretical calculations.[12]

Such small radiative lifetimes of the exciton-impurity complexes ensure a very effective radiative recombination channel for the free excitons at moderate impurity concentration ($N_D+N_A \gtrsim 10^{14}$ cm$^{-3}$). This channel is practically impossible to saturate when the excitation density is increased to $n_{av} \sim 10^{15}$ cm$^{-3}$, when the crystal can no longer contain any excitons, since each impurity can capture the free excitons many times, because of the small values of $\tau_i$. As a result, the possibility of an experimental observation of collective radiative processes such as inelastic exciton–exciton collisions, etc. is doubtful if the concentration of the impurities is $\sim 10^{14}$ cm$^{-3}$ and higher. For pure GaAs samples ($N_D+N_A \sim 10^{12}$ cm$^{-3}$), however, it is necessary to examine in greater detail the concentration dependences of the probabilities of the capture of free excitons by the impurity, and, e.g., of the inelastic exciton–exciton collisions.

It should also be noted that certain possibilities for observing collective radiative processes appear at temperatures $kT \gtrsim E_i$.

## 3. EXPERIMENTAL PROCEDURE

The characteristics of the samples used to study the recombination-radiation spectra are listed in Table I. The samples FK-1, Fk-2, and FK-3 had ohmic contacts obtained by fusing-in indium. The dark current-voltage characteristics were analogous to those given by Bagaev *et al.*[7] The breakdown fields for shallow donors were $E_{D_0} \sim 3$ V/cm. The exciton impact ionization, which leads to the vanishing of the exciton components of the emission spectrum, took place in fields $E \lesssim 2$ V/cm, and the breakdown field depended on the excitation intensity. The measurements were performed both with stationary excitation (He–Ne laser, 10 mW) and with pulsed excitation. In the latter case, a copper-vapor laser was used ($\lambda = 5105$ Å). The excitation pulse duration was $\tau_p \sim 10$ nsec, the maximum pulse power was $P_p = 5$ kW, and the repetition frequency was $\omega = 5$ kHz.

Table I.

| Parameters | Sample | | | | |
|---|---|---|---|---|---|
| | A-1 | A-2 | FK-3 | FK-1 | FK-2 |
| $(N_D-N_A)\cdot 10^{-11}$ cm$^{-3}$ | 5.6 | 5.6 | $2\cdot 10^2$ | $8\cdot 10^2$ | $6\cdot 10^3$ |
| $\mu_{77K}\cdot 10^{-3}$, cm$^2$/V·sec | — | — | 110 | 145 | 105 |
| $d$, $\mu$ | 10 | 10 | 20 | 25 | 20 |

In the case of stationary excitation, the signal was registered in standard fashion, using a photomultiplier (FÉU-79), a narrow-band amplifier with synchronous detector (PAR Model 186A Synchro-Het Lock-in Amplifier), and an automatic recorder (KSP-4). The high repetition frequency of the excitation pulses has made it possible to use a system with double strobing to register the pulsed signals. The first strobing was with a type S-1-39 or S-1-53 stroboscopic oscilloscope. The broadened pulses were then amplified and fed to a strobe-integrator, with the aid of which it was possible to record the emission spectrum at any instant of time, and also to analyze the waveform of the radiation pulse. Such pulse-signal registration schemes combine the good time resolution of stroboscopic oscilloscopes with the high sensitivity of systems of relatively low frequency, which are used after the time conversion. However, the time resolution of our registration system was on the whole limited by the characteristic times of the photomultipliers (18 ÉLU-FK, 14 ÉLU-FK, FÉU-83) used for the time measurements.

Since the excitation pulse duration was comparable in our case with the recombination times, a correct quantitative analysis of the various aspects of the kinetics is difficult. We therefore draw only qualitative conclusions from the time characteristics.

The sensitivity of the registration system can be greatly increased in the case of pulsed excitation by measuring the amplitude of the pulses broadened by the strobing oscilloscope with a narrow-band amplifier with synchronous detection. It becomes impossible in this case, to be sure, to obtain information on the waveform of the radiation pulse.

## 4. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

We have investigated the spectra of the spontaneous emission of "pure" epitaxial GaAs films. The spontaneous luminescence regime was reached by sharp focusing of the exciting-laser beam. The absence of stimulated emission was monitored against the dependences of the radiation intensity on the excitation intensity $J$ on $I$ and on the linear dimension $l$ of the pumped region at constant $I$. The spectra width of the DFS-12 monochromator slit did not exceed 0.2 meV in all the experiments.

Figure 1 shows the emission spectrum of sample FK-3, obtained by excitation with an He–Ne laser ($I = 1$ W/cm$^2$). This is not the purest sample, but its emission

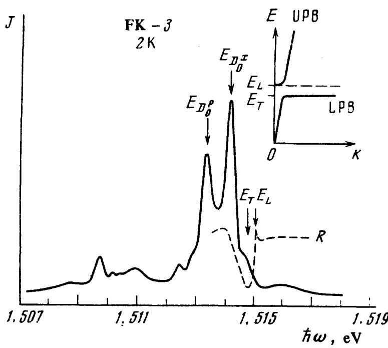


FIG. 1. Emission spectrum of sample FK-3 ($N_D - N_A = 2 \cdot 10^{13}$ cm$^{-3}$) at 2 °K ($I = 1$ W/cm$^2$); dashed curve—reflection $R$ spectrum obtained in[14]. In the upper right corner is shown the energy spectrum of the polariton: UPB—upper polariton branch, LPB—lower polariton branch.

contains all the principal components of the spectrum. The universally accepted point of view concerning the individual emission lines in the spectrum of Fig. 1 reduces to the following. The emission line width $\hbar\omega_{max} = 1.5141$ eV is due to recombination of an exciton bound with a neutral donor ($D_0^x$). The radiative transition of a free hole to a neutral donor is accompanied by emission width $\hbar\omega_{max} = 1.5133$ eV ($D_0^p$). The recombination of an exciton bound with a neutral acceptor leads to the appearance of lines near 1.5123 eV. The relatively weak emission lines in the region 1.508–1.512 eV are due to the so-called two-electron transitions,[15] in which the neutral donor goes over into an excited state ($n = 2$). However, the model proposed by Rossi *et al.*[15] has been experimentally confirmed only for the line $\hbar\omega_{max} = 1.5097$ eV. Another interpretation is therefore possible for the other lines. In particular, the emission band with $\hbar\omega_{max} \sim 1.511$ eV, which is shifted towards the long-wave side relative to the free exciton by an amount $E_{ex}$, can be attributed to inelastic exciton–exciton collisions ($P$ band), since the intensity of this band depends quadratically on the free-exciton intensity ($\hbar\omega_{max} \sim 1.5157$ eV), as is seen from Fig. 2.

Nonetheless, this interpretation does not correspond to reality, since samples with small impurity contents (samples A-1 and A-2) do not emit at all in the entire region $\hbar\omega = 1.508$–$1.512$ eV, thus indicating that this emission is of impurity origin. By way of a working hypothesis we can propose that the $P$ band ($\hbar\omega_{max} \sim 1.511$ eV) is due to inelastic collisions of free excitons with exciton-impurity complexes (exciton on a neutral donor). This mechanism explains both the observed dependences of the intensity of this band, as well as its energy position. In addition, the probability of such a process can be larger than in the case of inelastic exciton–exciton collisions, since the orbit of the exciton coupled to the impurity is larger than the Bohr radius of the exciton.

What remained unexplained in the emission spectrum shown in Fig. 1 were the two shortest-wavelength lines. In the earlier papers (see, e.g.,[15]), the emission with $\hbar\omega_{max} \sim 1.5157$ eV was attributed to the free exciton, and the line width $\hbar\omega_{max} \sim 1.5147$ eV was connected with the emission of a complicated exciton-impurity complex that contains a neutral donor. Sell *et al.*[14], however, have reviewed the interpretation of the emission spectrum in the phonon energy region $\hbar\omega \sim 1.5145$–$1.5160$ eV. The justification for this review were the results of experiments on the reflection spectra of pure epitaxial GaAs films at low temperatures. A typical reflection spectrum obtained by them[14] is shown in Fig. 1 (dashed curve $R$). A theoretical analysis of this spectrum has made it possible to determine the energies of the transverse and longitudinal excitons in GaAs. Thus, for example, the transverse-exciton energy $E_T$ should correspond to a minimum of the reflection spectrum, and the energy position of the spike coincides with the longitudinal exciton $E_L$. Taking this circumstance into account, it is practically impossible to explain the observed emission spectrum of the free exciton, inasmuch as to interpret the energy position of the emission-line maximum it is necessary to assume too large an effective temperature of the exciton gas. Sell *et al.*[14] have assumed therefore that the emission in the energy region $\hbar\omega \sim 1.5145$–$1.5160$ eV must be explained with spatial-dispersion taken into account.

In this case the line with $\hbar\omega \sim 1.5157$ eV can be attributed to emission from the upper polariton branch (UPB), and the emission from the lower polariton branch (LPB) leads to the appearance of the line with $\hbar\omega_{max} \sim 1.5147$ eV. It should be noted that there is still no exact quantitative theory of radiative recombination with allowance for spatial dispersion, but the singularities of the emission spectrum can be qualitatively quite well explained by taking into account the specifics of the energy spectrum of the UPB and LPB. In particular, it becomes understandable why the UPB emission is shifted towards the short-wave side relative to the position of the spike in the reflection spectrum. The point is that the effective exciton temperature, which, as a rule, is somewhat higher than the lattice temperature at moderate excitation levels, should lead to large shifts of the UPB emission maximum in comparison with the LPB maximum.

Thus, the energy position of the UPB emission maximum is determined by the excitation intensity, which specifies $T_{eff}$ for the excitons. This conclusion was confirmed by the results of experiments shown in Figs. 3 and 4. These figures show the emission spectra of sample A-2 with impurity concentration $N_D - N_A = 5.6 \cdot 10^{11}$ cm$^{-3}$, obtained at different excitation levels $I$ in

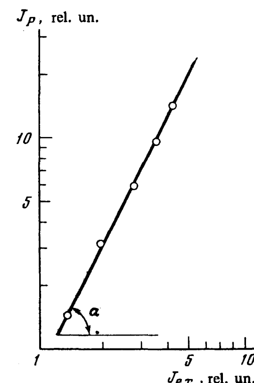


FIG. 2. Dependence of the $R$-band intensity ($\hbar\omega_{max} \sim 1.511$ eV) on the exciton intensity ($\hbar\omega_{max} \sim 1.5157$ eV) for the sample FK-3 in the excitation-level $I \sim 1$—$10$ W/cm$^2$, $\tan\alpha = 2$.

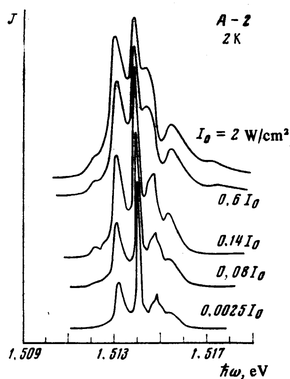


FIG. 3. Emission spectra of sample A-2 ($N_D - N_A = 5.6 \cdot 10^{11}$ cm$^{-3}$) at 2 °K as a function of the excitation level. $I_0 = 2$ W/cm$^2$.

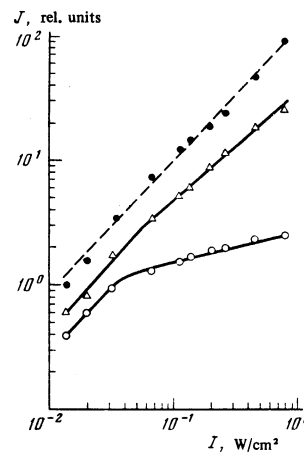


FIG. 5. Plots of the intensities of the different components of the spectrum on the excitation intensity: ●—integral of UPB radiation, Δ—intensity of $D_0^b$ radiation, o—intensity of $D_0^x$ radiation.

the interval from 0.005 to 700 W/cm$^2$ (He–Ne laser). In contrast to the lower-impurity samples, the relative contribution of the emission of the free excitons from this crystal is noticeably larger, and it can be seen from Fig. 5 that the growth of the intensity of the exciton-impurity complex $D_0^x$ is substantially slowed down at $I \gtrsim 0.05$ W/cm$^2$. The excitation level $I \approx 0.05$ W/cm$^2$ should apparently correspond to the average density of the generated electron-hole pairs $n_{av} \sim N_D - N_A = 5.6 \cdot 10^{11}$ cm$^{-3}$. By the same token, recognizing that the integrated intensity of the UPB radiation depends linearly on the excitation level not only in the interval indicated in Fig. 5, but also at much higher densities, we can estimate the exciton concentration (or the concentration of the electron-hole pairs) in the entire range of employed excitation levels. Thus, for example, the EHD emission ($\hbar\omega_{max} \sim 1.5123$ eV) first observed by Bagaev *et al.*[6] occurs at $n_{av} \sim 10^{15}$ cm$^{-3}$, i.e., at densities such that there can no longer be any free excitons in the sample.

A distinguishing feature of the emission spectra of the purest samples (Figs. 3 and 4) is also the presence of a weak emission band due to interband recombination. This band becomes noticeable at $I \gtrsim 2$ W/cm$^2$. With increasing excitation level it shifts towards the long-wave side, gradually coalescing with the UPB radiation. This circumstance can be interpreted as a Mott transition in the exciton system. Of course, the emission spectrum must not have any exciton components in this case. Time measurements performed on sample A-2 at the corresponding pulse-excitation densities have shown that the weak exciton luminescence bands that are seen in the spectrum are delayed 10–15 nsec relative to the excitation pulse and therefore correspond to much lower $n_{av}$.

One other important distinguishing feature of the emission of the purest samples is that it is possible to trace the formation of the emission band of the condensed phase. As seen from Fig. 4, the energy position of this band initially coincides with $D_0^b$. The emission maximum shifts next to the long-wave side with increasing excitation level, and at $I \gtrsim 0.7$ kW/cm$^2$ its energy position, as well as the shape of the emission band, cease to depend on $n_{av}$ in the sample up to values $n_{av} \sim 10^{16}$ cm$^{-3}$.

For crystals with impurity contents $N_D - N_A > 10^{13}$ cm$^{-3}$ it is practically impossible to register the initial stage of the onset of EHD, for in this case the dominant factor in the spectra is still the radiation of the exciton-impurity complexes, which apparently is produced in the interior of the sample on the tail of the diffusion distribution. Only in electric fields strong enough to break down not only the free excitons but also the shallow donors is it possible to suppress this recombination channel and to observe the EHD emission band.

The results of experiments with an electric field are shown in Fig. 6. The excitation in these experiments was produced with a copper-vapor laser. The spectra were recorded at the instant when the excitation pulse

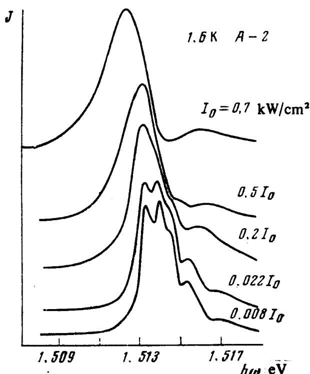


FIG. 4. Emission spectra of sample A-2 ($N_D - N_A = 5.6 \cdot 10^{11}$ cm$^{-3}$) at 1.6 °K as a function of the excitation level. $I_0 = 0.7$ kW/cm$^2$.

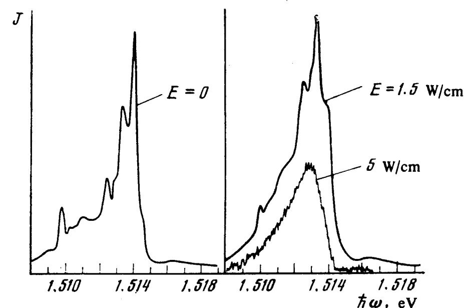


FIG. 6. Emission spectra of sample FK-3 ($N_D - N_A = 2 \cdot 10^{13}$ cm$^{-3}$) as functions of the electric field intensity of $T = 2$ °K and $I = 800$ W/cm$^2$. The sensitivity of the recording system at $E = 5$ V/cm has been increased by twenty times.

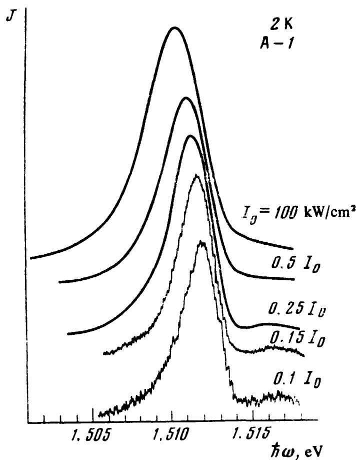


FIG. 7. Emission spectra of sample A-1 ($N_D - N_A = 5.6\cdot 10^{11}$ cm$^{-3}$) as functions of the excitation level. $I_0 = 100$ kW/cm$^2$.

was a maximum. If the monochromator slit is used to cut out of the spectrum one exciton-impurity complex or another (for example, $D_0^x$) and the waveform of the radiation pulse is recorded, then the maximum of this pulse is delayed relative to the excitation maximum. The time delay depends on the excitation level and increases with increasing $I$. This experiment indicates that in the case of small delays the radiation of the exciton-impurity complexes is indeed produced in the interior of the sample and moves closer to the surface as the concentration of the free carriers decreases with time; the increased intensity is attributed to the lower losses to reabsorption.

By measuring the dependence of the delay of the exciton-impurity complex emission maximum on the excitation level, we can estimate the lifetime $\tau_{eh}$ of the electron-hole plasma from the formula

$$\tau_{eh} = \frac{t_2 - t_1}{\ln(I_2/I_1)},$$

where $t_1$ and $t_2$ are the delays of the radiation at excitation intensities $I_1$ and $I_2$, respectively. For the sample FK-3 we obtain $\tau_{\perp} \sim 4\cdot 10^{-9}$ sec. Thus, the probability of interband recombination at electron and hole density $n_0 \sim 10^{16}$ cm$^{-3}$ turns out to be less than the probability of the radiative decay of the exciton-impurity complexes, for which $\tau_i \lesssim 10^{-9}$ sec.[12] It is precisely this circumstance which explains the tremendous contribution made by the radiation of complexes from the interior of the sample, where the excitation density is much lower than on the surface.

## 5. PRINCIPAL CONCLUSIONS

From among all collective effects occurring in various semiconductors and discussed in the literature what takes place at low temperatures in GaAs is a phase transition of the gas–liquid type with EHD formation. However, in contrast to Ge or Si, it is not the excitons which are condensed in GaAs, but the gas of free carriers, a fact most clearly confirmed in experiments with an electric field. The difference between the condensation mechanism in GaAs, on the one hand, and in the Ge and Si on the other, is due to the specific features of the radiative recombination in semiconductors with allowed direct transitions. Since the effective free-exciton lifetimes, which are determined by capture on impurity states and by the existence of a nonradiative recombination channel, are small enough ($\sim 10^{-9}$ sec), it follows that the critical density $n_{cr}$ is determined in final analysis not by the phase diagram but by kinetic relations of the type[4] $n_{cr} \gtrsim n_0 R / 3\tau_0 v_{av}$. As a result, $n_{cr}$ turns out to be of the order of $10^{15}$ cm$^{-3}$, which is much higher than the density corresponding to the Mott transition for free excitons in GaAs. Thus, the excitation-densities at which EHD can exist in GaAs lie in a rather narrow interval, from $n_{av} \sim 10^{15}$ cm$^{-3}$ to $n_{av} = n_0 \sim 10^{16}$ cm$^{-3}$. When the excitation level is increased further ($I > 10$ kW/cm$^2$), the emission spectra must be determined by recombination processes of the electron-hole plasma, whose temperature can differ noticeably from the lattice temperature.[1] This is precisely how one must interpret the emission spectra of sample A-1, which are shown in Fig. 7.

It must also be emphasized that to explain the entire aggregate of the experimental data obtained both with the purest samples and with samples of lower purity there is no need to resort to any collective radiative processes. Moreover, it must be concluded that so long as excitons can exist in the crystal, the capture of free excitons by impurities in GaAs at low temperatures, followed by a very rapid annihilation of the exciton-impurity complexes, is the dominant recombination channel.

It is not unlikely that the last conclusion is valid also for other semiconductors with direct allowed transitions, since the samples A-1 and A-2 used in the present study are the purest ones, if the "purity" criterion for all the materials is taken to be, for example, the average distance between impurity atoms, measured in units of the Bohr radius of the free exciton.

In conclusion the author thanks V. S. Bagaev, L. V. Keldysh, and V. B. Timofeev for extremely useful discussion of the results.

[1)]When explaining the experimental data obtained with epitaxial GaAs films of thickness $d \sim (20-30)\ \mu$ at very high excitation levels ($I \sim 1$ MW/cm$^2$), one must apparently take into account also the contribution that the substrate can make to the recombination of the free carriers. It is easy to show that at $I = 1$ MW/cm$^2$ the electron-hole plasma fills, as a result of expansion at Fermi velocity, the entire volume of a film $20\mu$ thick in $10^{-9}$ sec. In this case the substrate, which is usually made of compensated GaAs, can lead not only to the appearance of a powerful nonradiative-recombination channel, but also distort appreciably the observed emission spectra. For example, as shown by our experiment, an emission band due to recombination on donor acceptor pairs in the substrate material can appear in the region $\hbar\omega \sim 1.49$ eV; this can be easily verified by exciting the sample from the substrate side.

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# A model for a phase transition due to nonlinear resonance of lattice vibrations

G. M. Zaslavskiĭ, V. F. Shabanov, K. S. Aleksandrov, and I. P. Aleksandrova

*L. V. Kirenskiĭ Institute of Physics, Siberian Division, USSR Academy of Sciences*
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It is shown that a structural transition in a crystal can be due to a nonlinear resonance "capture" of different lattice vibration modes. The condition for capture is $\alpha > \epsilon$ ($\alpha$ is a dimensionless anharmonicity parameter and $\epsilon$ is a dimensionless coupling constant for the modes). A phase transition model is constructed on the basis of new experimental data for the group of isomorphous crystals of the triglycinsulfate type. It is shown that a coherent state of the orientational vibrations of the heavy-atom groups is formed below the transition point, and the thermodynamic characteristics of this state are found. The connection between the dynamical approach developed and the models for the ferroelectric type of ordering is discussed.

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## INTRODUCTION

Structural lattice instability is one of the mechanisms that can lead to a phase transition of the ferroelectric type. From the dynamical point of view, such a transition may be accompanied by the appearance of the so-called "soft mode," whose frequency tends to zero as $T \to T_c$.[1] However, the dynamical approach allows us to look at the problem of instability of lattice structures from a somewhat more general point of view. Indeed, if the variation of some parameter (e.g., the temperature) leads to a situation in which some characteristic frequencies of the system turn out to be close (i.e., in resonance), then the structure of the system should also be reconstructed, and the soft mode corresponds to the particular case of such a resonance.

In[2] the possibility was discussed of the occurrence of a structural phase transition because of a resonance-type instability arising as a result of the interaction of certain types of degrees of freedom of the lattice. The present paper is devoted to a detailed analysis of this question. Underlying it are a number of experimental data on the analysis of the spectra of the Raman scattering (RS) of low-frequency optical lattice vibrations in the vicinity of a ferroelectric phase transition. These data have now been obtained for the family of isomorphous crystals of the TGS group (triglycinsulfate, triglycinselenate, triglycinfluoroberyllate),[3] for ammonium fluoroberyllate (AFB),[4] dihydrate of sodium ammonium selenate,[5] etc. It is customarily assumed that the phase transition occurring in the enumerated crystals is of the order-disorder type.[1] The RS data allow us, however, to obtain a more detailed picture of the phase transition. The reason for this consists, on the one hand, in the fact that there can exist in complex lattices individual structural atomic groups which are relatively weakly coupled to the remaining lattice and which execute motions almost independent of the other groups. Therefore, it may turn out to be possible to indicate that atomic group whose critical behavior determines (primarily) the phase transition. Thus, in all the above-enumerated crystals the isotopic substitution of hydrogen by deuterium does not lead to a significant change in the Curie temperature. This leads to the conclusion that the ordering is undergone by the relatively heavy elements: the glycine ions in TGS or the tetrahedral groups in the other crystals. On the other hand, the width of the line and its intensity in the RS spectra

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