Temperature-modulated photoluminescence of GaP:N

M. Gál

Research Institute for Technical Physics of the Hungarian Academy of Sciences, H-1325 Budapest, P.O. Box 76, Hungary

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We have measured the temperature-modulated photoluminescence of excitons bound to isolated nitrogen and also to nitrogen pairs of different separations. It is shown that temperature modulation can reveal further evidence on the recombination mechanism of bound excitons. The line-shape study of the temperature-modulated spectra indicates the existence of a second-order resonant transition from the $J = 2$ state of the bound exciton. Samples heavily doped with nitrogen show temperature-dependent transfer of excitons from one type of nitrogen pair to another.

I. INTRODUCTION

Excitons bound to N substituting for P in GaP have been investigated extensively both by experiment and theory.[1-10] Different spectroscopic techniques have been used first to identify and later to study the binding of the isoelectronic trap, its excited states, the energy transfer between these states, etc.[11-13] Besides the normal luminescence and absorption measurements,[4-7] several techniques utilizing external perturbations, such as magneto- and piezo-spectroscopy have been used,[2] among other methods,[14,15] to gain further information on the nature and symmetry of the binding centers induced by nitrogen.

We have used temperature-modulated photoluminescence (TMP) to study the recombination mechanism of excitons bound to nitrogen in GaP.

Temperature modulation is a technique fruitfully used in other branches of optical spectroscopy.[16] In the present study we show that it can be successfully applied to photoluminescence, increasing its resolution and yielding further information on the thermal effects influencing radiative recombination. GaP, doped with nitrogen at high concentrations, shows a series of emission lines from excitons bound to isolated nitrogen and nitrogen pairs, labeled NN_i, $i = 1, 2, \ldots$ in order of increasing separation and decreasing binding energy.[4] The $1S$ state of the exciton bound to an isolated nitrogen is split by exchange interaction into a $J = 1$ (A line) and a $J = 2$ (B line) level, about 0.9 meV apart. The uniaxial "crystal-field" splitting of an NN_i pair produces further splittings which, however, are usually small relative to the exchange splittings. No-phonon radiative transitions from the $J = 2$ level to the ground state of the crystal are forbidden, but at the lowest temperatures the B-line emission is observed due to various symmetry-breaking effects.[4]

Our TMP measurements were performed between 8 and 13 K. The low-temperature limit was set by sample heating caused by the temperature modulation, while the 13-K limit was chosen to exclude nonradiative and other thermally activated processes.

II. EXPERIMENTAL

A. Temperature modulation and measurement

The temperature modulation was achieved by so-called indirect heating.[16] The sample was mounted on a heater, the temperature of which was modulated. The heater was a 1000 Å thick Cr layer evaporated on a silicon crystal. Si was used since at low temperatures it is an insulator with high thermal conductivity. The resistance of the Cr layer was approximately 1 kΩ at liquid-He temperatures, and it dissipated 2 mW at the modulating frequency of 15 Hz.

The Si slice was mounted on the cold finger of the He cryostat with silver paste, while the samples were pressed on the heater with a layer of silicone vacuum grease between. The temperature of the specimen was measured by an Allen-Bradley carbon resistor mounted next to the sample. To be able to detect the amplitude of the temperature oscillations, the resistor was ground and polished to a thickness of 30 μm. After being polished it was calibrated to a precision Ge thermometer, between 4.2 and 25 K. The absolute temperature value was accurate to ± 0.1 K; the reproducibility was ± 0.01 K. The amplitude of the modulating voltage was set to read $\Delta T = 0.5$ K at every temperature.

B. Optical and electrical

The optical arrangement was analogous to a conventional photoluminescence setup. The luminescence was excited by the 488-nm line of an argon ion laser that was chopped mechanically at 1 kHz. The laser power was attenuated to about 5 mW and slightly defocused on the sample. The

luminescence emission was collected from the ex-
cited face to the specimen and focused on the en-
trance slit of the monochromator. The monochro-
mator was a modified Zeiss PGS-2 model with a
1200 lines per mm grating blazed at 5600 Å. It
was driven by a stepping motor at 0.46 Å per
step. The energy resolution of the monochromator
was 0.1 meV in the range of interest and was lim-
ited by the signal-to-noise ratio of the modulated
signal.

The radiation was detected by an EMI 9558 pho-
tomultiplier and rectified by two lock-in systems.
One of the lock-in's was in phase with the refer-
ence signal from the chopper; the other with the
current passing through the heater. At every po-
sition of the stepping motor the lock-in signals
were measured and stored digitally by a Schlum-
berger data acquisition system on punched paper
tape and a listing. The number of measurements
at each point could be preprogrammed. We gen-
erally used four measurements for each channel
at every step. The paper tape was then processed
by a desk top calculator which, after averaging,
plotted the luminescence (L), the modulated lumi-
nescence (ΔL), and their ratio ($\Delta L/L$) on an X-Y
recorder using linear interpolation between the
measured points. The ratio $\Delta L/L$ can be approx-
imated by $(1/L)(\partial L/\partial T)\Delta T$ and thus it is propor-
tional to the temperature derivative of the loga-
rithm of the luminescence intensity.

C. Crystals

Most of the measurements were performed on
epitaxial layers grown on GaP substrates by liq-
uid-phase epitaxy. The nitrogen concentration
varied between 6×10^{16} and 2×10^{18} cm^{-3}. Some of
the more heavily doped layers ($[N] = 2 \times 10^{18} - 1 \times 10^{19}$
cm^{-3}) were vapor-phase epitaxial layers. The
samples, usually 10–50 μm thick, were either
intentionally doped or undoped crystals of n or p
type. The dopants were Te or S for the n-type
layers ($[N_D] \approx 10^{18}$ cm^{-3}) or Zn for the p-type layers
($[N_A] \approx 10^{18}$ cm^{-3}). The luminescence of some of
the epitaxial layers showed varying amount of line
broadening, even at 1.8 K, which was found inde-
pendent of crystal mounting and was probably due
to the internal strain caused by the epitaxial
growth.

III. RESULTS AND DISCUSSION

A. Lightly doped crystals

For samples with nitrogen concentration below
10^{18} N/cm^3 the exciton tunneling from one type of
nitrogen pair to another is not important.[11] A typ-
ical spectrum of a lightly doped crystal ($[N] = 8
\times 10^{16}$ cm^{-3}) at 10 K is shown on Fig. 1 showing the
A-B structure and its first and second optical
phonon replicas. It can be seen that one-to-one
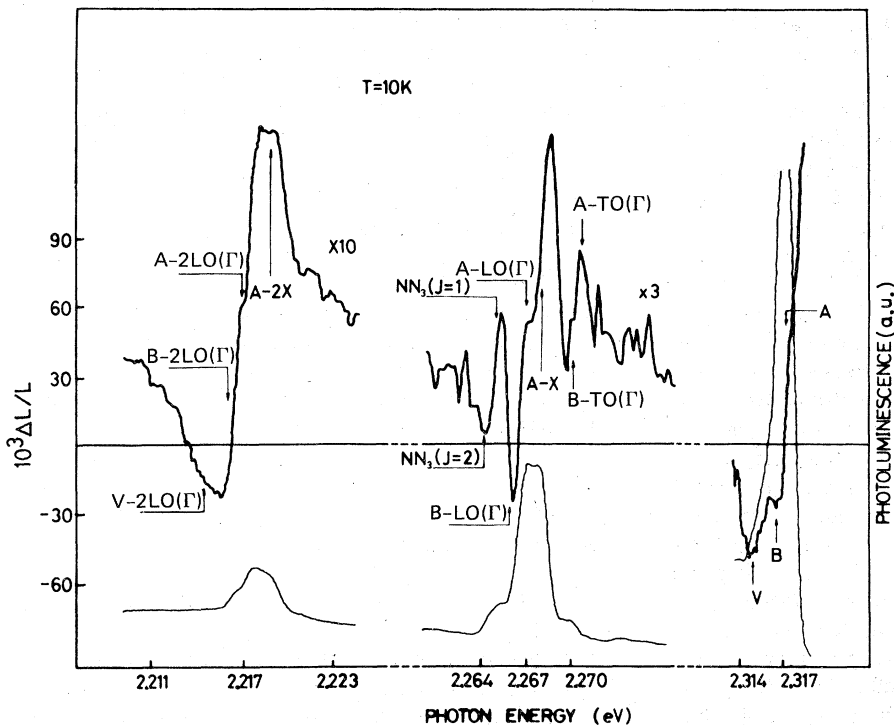correspondence does not exist between the peaks

FIG. 1. Temperature-
modulated photolumines-
cence and photoluminescence
spectra at 10 K of excitons
bound to isolated nitrogen
and its first and second op-
tical phonon replicas. Ni-
trogen concentration 8 $\times 10^{16}$
cm^{-3}.

of the two types of spectra. The change in sign between the A and B lines is responsible for the high resolution at the one-phonon replica. The change in sign between the A and B lines was described in a previous work,[17] where the temperature-induced change ΔL (and not the relative change) was recorded as a function of wavelength. This change in sign is expected, since it is known that thermal equilibrium is established rapidly (~10^{-11} sec) between the A and B levels. Thus the population can be determined by the Boltzmann factor and level degeneracies.[6] Raising the temperature by ΔT will increase the exciton population of the A state, making $\Delta L/L > 0$, at the expense of excitons in the B state ($\Delta L/L < 0$). This effect can be evaluated by calculating $\Delta L/L$ for the respective transitions. For the A and B states, the luminescence intensity, in first order, can be written in the following form[18]:

$$L(\omega, T) = CN(T)f(T)G(\omega, T), \qquad (1)$$

where C is a temperature-independent term, $N(T)$ is the number of excitons taking part in the emission, $f(T)$ is the radiative transition probability, and $G(\omega, T)$ is the line-shape function which can be approximated by a Lorentzian or a Gaussian curve.[19] For the $\Delta L/L$ derivative signal we get, by substituting (1) into $(1/L)(\partial L/\partial T)\Delta T$, the following expression:

$$\frac{\Delta L}{L} = \left(\frac{1}{N}\frac{dN}{dT} + \frac{1}{f}\frac{df}{dT} + \frac{1}{G}\frac{dG}{dT} \right)\Delta T \qquad (2)$$

It can be shown[17] that in equilibrium, at 10 K, using $N_B/N_A = \frac{5}{3}\exp(0.87/kT)$, the dominant term comes from $(1/N)(dN/dT)$. At 10 K, using $\Delta T = 0.5$K, the calculated value of $\Delta L/L$ for the A line is 4.64×10^{-2}, while the measured value was $3.9 \times 10^{-2} \pm 5\%$. For the B line, these values were -1.16×10^{-2} the calculated value and $-0.9 \times 10^{-2} \pm 10\%$ the measured value. We believe the poor agreement between the measured and calculated values is due to the uncertainty of the ΔT values. As was described in Sec. II A, $\Delta T = 0.5$ K was measured by a calibrated carbon resistor mounted next to the samples. It does not necessarily mean, however, that the GaP samples of different mass and thermal conductivity experience the same temperature oscillations. In fact, the samples are expected to have a lower ΔT value due to their greater mass and lower thermal conductivity with respect to the carbon resistor.[20] Using $\Delta T = 0.4$ K instead of $\Delta T = 0.5$ K, the agreement is within the experimental error. The best fit of ΔT for the different samples was found to be inversely proportional to the sample size, in agreement with the expectations. We also found a slight temperature dependence of ΔT, which can be due to the

temperature dependence of the thermal conductivity of GaP.[21]

In addition to the forbidden transition, the excitons in state B can recombine by making a virtual transition to state A and absorbing or emitting a phonon.[22] This path will be important when the absorbed phonon energy is close to the A-B energy separation, that is for long-wavelength acoustical phonons. This second-order, resonant process has been investigated in oxygen-doped ZnTe,[22] and good agreement was found between theory and experiment. In N-doped GaP, Merz et al.[9] have observed a band (labeled V in Ref. 9) which was attributed to the transition from the B state involving a phonon emission and a virtual transition to the A state. This band peaked at slightly lower energy from the B line than the A-B splitting since the phonon density of states in GaP is very small at low phonon energies.[23] Since long-wavelength acoustical phonons are involved in this process, it is probable that this term will have an important contribution to the temperature derivative spectrum at low temperature. Sturge et al. have recently shown[13] that the radiative efficiency of excitons bound to nitrogen in GaP is close to 100% at low temperatures. Thus, nonradiative effects or thermally activated processes do not play an important role at 10 K. We have calculated the effect of the second-order transitions on the TMP signal. The transitions with phonon absorption are expected to affect only the high-energy side of the A line due to the phonon density of states as mentioned above, while the transitions with phonon emission are expected to appear at energies 1-2 meV lower than the B line.

The second-order terms can be written formally in the same way as the first-order term,

$$L^+ = CN_B(T)f(T)^+ G(\theta_q, \omega, T)^+ \qquad (3)$$

for phonon absorption and

$$L^- = CN_B(T)f(T)^- G(\theta_q, \omega, T)^- \qquad (4)$$

for phonon emission, where $N_B(T)$ represents the number of excitons in B state and $G^{\pm}$, the lineshape function. In the Appendix it is shown that for the second-order terms $\Delta L/L$ can be approximated by the following expressions:

$$\frac{\Delta L^+}{L} = \left(\frac{1}{N_B}\frac{dN_B}{dT} + \frac{1}{n_q}\frac{dn_q}{dT} \right)\Delta T \qquad (5)$$

for phonon absorption, and

$$\frac{\Delta L^-}{L} = \left(\frac{1}{N_B}\frac{dN_B}{dT} + \frac{1}{n_q+1}\frac{dn_q}{dT} \right)\Delta T \qquad (6)$$

for phonon emission, where $n(\theta_q)$ is the phonon occupation number.

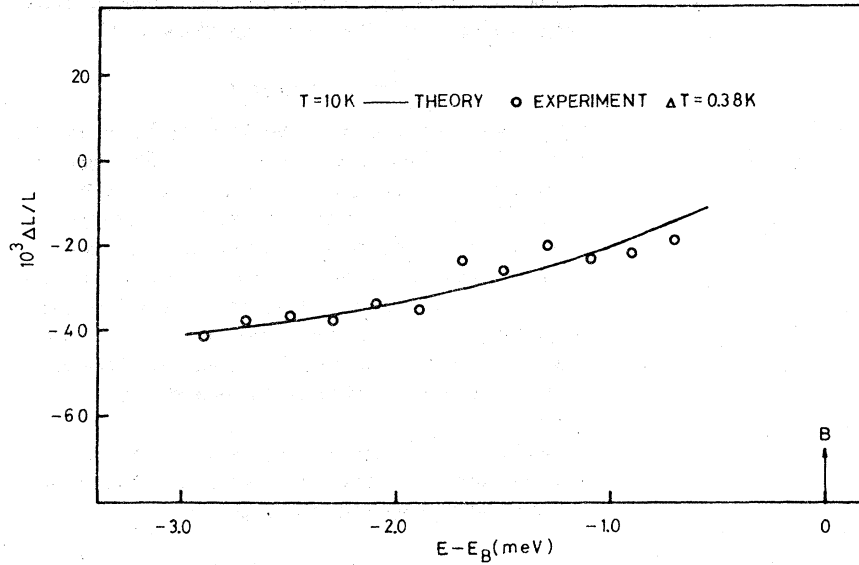In Figs. 2 and 3 we have plotted as a function of

FIG. 2. Calculated TMP spectrum for second-order transition with phonon absorption and the experimental points in sample with $[N] = 8 \times 10^{16}$ cm^{-3}.

energy Eqs. (5) and (6), respectively, together with the measured points representing the temperature-induced relative change in the photoluminescence intensity.

The parameter ΔT was again chosen to give the best fit, and, similar to the first-order transition, $\Delta T < 0.5$ K. In the example shown, $\Delta T = 0.38 K$. We believe that these experimental results substantiate the model developed by Dietz,

Thomas, and Hopfield[22] on the second-order radiative transitions of excitons bound to isoelectronic impurities.

According to the model used, other isoelectronic impurities should behave similarly, independent, for example, of their concentration. In fact, for the nitrogen pair lines we have found very similar line shapes with some modifications resulting from the crystal-field splitting and the temperature-dependent transfer between the pair lines (to be
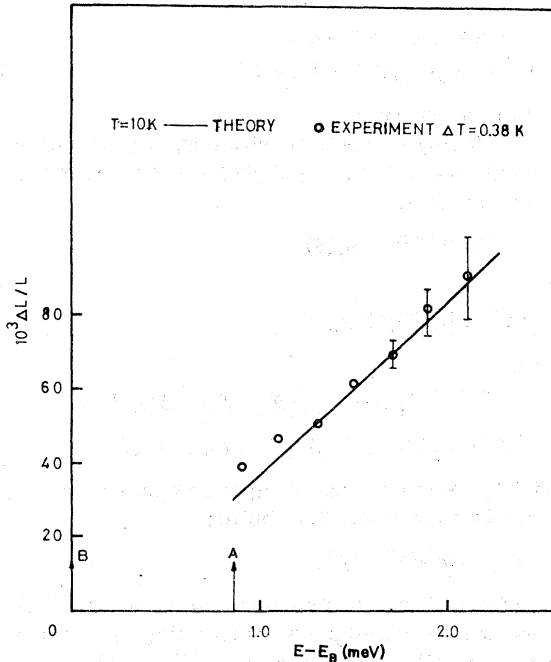

FIG. 3. Calculated TMP spectrum for second-order transition with phonon emission and experimental points in the same sample as Fig. 2.
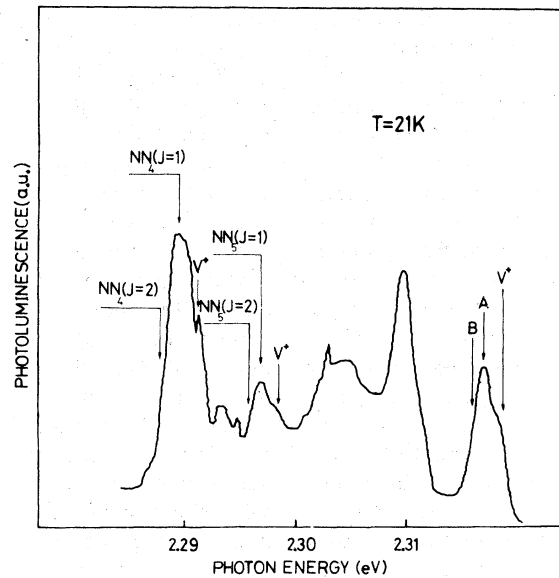

FIG. 4. Photoluminescence spectrum of sample with $[N] = 9 \times 10^{17}$ cm^{-3} at $T = 21$ K showing the asymetrical broadening of some of the nitrogen lines. It is interpreted to be due to a new line, labeled V^+, derived from the $J = 2$ state of the bound exciton at $T > 20$ K temperatures.

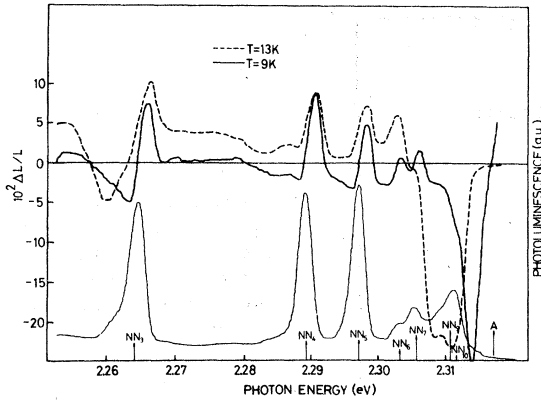FIG. 5. TMP and photoluminescence spectra of a sample doped heavily with nitrogen, $[N] = 3 \times 10^{18}$ cm^{-3}, showing the effect of temperature on the TMP spectrum.

described below). The model seems also to be confirmed by the fact that at higher temperature ($T > 20$ K) the nitrogen lines are asymmetrically broadened towards higher energy in the luminescence spectra (Fig. 4), indicating the existence of the second-order resonant transition of the excitons in B state by a phonon absorption (labeled V^+ on Fig. 4).

B. Heavily doped crystals

In heavily doped crystals ($[N] > 10^{18}$ cm^{-3}) exciton tunneling from one type of nitrogen trap to another is of great importance.[11] For these concentrations, one has to take into account the temperature dependence of the energy transfer process. In Fig. 5 the spectra of a heavily doped ($[N] = 3 \times 10^{18}$ cm^{-3}) crystal are shown at $T = 9$ K and $T = 13$ K. It can be seen that at higher temperatures the derivative signal is positive for the lower-energy lines because of the exciton transfer from higher-energy states. In fact, even at 9 K the line shape of the isolated nitrogen-exciton is modified with respect to the lightly doped case. These results indicate a temperature-dependent energy transfer (even at 9 K) between the pairs. This additional temperature dependence can be explained by phonon-assisted tunneling of excitons through the excited states of the pairs, with phonons of energy comparable to the thermal energy.[24] This effect can compensate for the thermalization of excitons from the B state in the low-energy levels resulting in a positive $\Delta L/L$ signal and reducing the number of excitons in the higher-energy lines, thus making $\Delta L/L < 0$.

Quantitative calculations are very difficult to make since the number of excitons in the different pair traps have to be determined from kinetics rather than simple energy calculations. Owing to

the above band-gap excitation, such kinetics cannot be determined from our experiments.[12]

IV. CONCLUSIONS

In this work we have shown that the temperature-modulation technique can be successfully used in photoluminescence spectroscopy. The results indicate that, besides thermalization, second-order effects have to be included in order to explain the observed temperature dependence of the radiative recombination from the A and B levels. A model including second-order resonant transitions, proposed by Dietz, Thomas, and Hopfield, gives good agreement with the experimental results.

Results on crystals heavily doped with N show temperature-dependent transfer of excitons from one type of nitrogen pair to another.

APPENDIX

The expressions governing the luminescence intensity due to the second-order transitions are[18]

$$L^+ = CN_B(T)f(T)^+G(\theta_q, \omega, T)^+ \qquad (7)$$

for phonon absorption and

$$L^- = CN_B(T)f(T)^-G(\theta_q, \omega, T)^- \qquad (8)$$

for phonon emission.

Considering interaction with only one type of acoustical phonon, $f(T)^+$ and $f(T)^-$ can be written in the following form:

$$f(T)^+ = |\langle H^{(2)} \rangle^+|^2 n_q(\theta)$$

and

$$f(T)^- = |\langle H^{(2)} \rangle^-|^2 (n_q + 1),$$

where

$$\langle H^{(2)} \rangle^+ = (H'_{BA} H''_{AO})/[E_A - E_B - E(\theta_q)],$$

$$\langle H^{(2)} \rangle^- = (H'_{BA} H''_{AO})/[E_A - E_B + E(\theta_q)],$$

and $n(\theta_q)$ is the phonon occupation number described by the Bose distribution

$$n(\theta_q) = (e^{\theta_q/kT} - 1)^{-1}.$$

The effect of this second-order term on the TMP signal can be evaluated by calculating the temperature derivative of the terms in (7) and (8), respectively. The term df/dT can be written as the sum of two terms,

$$\frac{df}{dT} = |\langle H^{(2)} \rangle|^2 \frac{dn_q}{dT} + n_q \frac{d}{dT} |\langle H^{(2)} \rangle|^2.$$

Since at low temperatures the bound exciton states are basically temperature independent, we can suppose that for long-wavelength acoustical phonons $(1/H)(dH/dT)$ can be neglected relative to $(1/n_q)(dn_q/dT)$. As in the first-order case let us suppose that $(1/G)(dG/dT) \ll (1/N)(dN/dT)$. Under

these assumptions, the results can be summarized as follows:

$$\frac{\Delta L^+}{L} = \left(\frac{1}{N_B} \frac{dN_B}{dT} + \frac{1}{n_q} \frac{dn_q}{dT} \right) \Delta T ,$$

and

$$\frac{\Delta L^-}{L} = \left(\frac{1}{N_B} \frac{dN_B}{dT} + \frac{1}{n_q + 1} \frac{dn_q}{dT} \right) \Delta T .$$

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