Optical investigations of the undulation spectrum of GaP:N:Zn

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The undulation spectrum occurs in the luminescence of GaP when it is doped with the isoelectronic trap, nitrogen, and an acceptor—in the present case Zn. A broad emission band is observed which extends about 20 meV below the nitrogen bound-exciton energy E^A and contains regular undulations. We show that the luminescence originates from the decay of excitons bound to N-Zn pairs of up to 50-Å separation, and that the undulatory behavior is a result of averaging the numbers of equivalent sites in the pair-separation shells. The N-Zn interaction is investigated by time-resolved resonant excitation and temperature-dependent measurements. The 1.6-K decay lifetime of the luminescence decreases sharply with luminescence energy from ~ 1 μsec at E^A to about 50 nsec at the low-energy limit of the undulation spectrum. The splitting of the exciton energy levels increases up to 5 meV as the N-Zn separation decreases and the dominant interaction is thought to be an internal Stark effect. Spatial energy transfer by tunneling of excitons is important and determines the temperature-dependent nonradiative recombination.

I. INTRODUCTION

In GaP, luminescence studies are a valuable tool for investigating impurity states. The reason is that in many cases the radiative recombination involves very sharp zero-phonon lines which allow accurate analysis. Both isolated defects and a wide variety of complex centers have been investigated in this way; examples of the former are neutral acceptors,[1] neutral donors,[2] and the N and Bi isoelectronic impurities,[3,4] and of the latter, N-N pairs,[3] donor-acceptor pairs,[5] and Zn-O, Cd-O,[6] and Li_2O complexes.[7]

One particular feature of the luminescence that escaped adequate explanation for several years was the undulation spectrum,[8,9] seen in GaP:N when the material also contained acceptors. The interesting aspect of this emission was its apparent dissimilarity to other luminescence spectra of GaP. Instead of a series of sharp zero-phonon lines, the spectrum consists of a broad band with a regular periodic undulation, from which its name derives. Two explanations for this behavior have been suggested—first, that there is an interference effect between the wave functions of nitrogen and the acceptor,[8] and second, that the exciton decay excited rotational levels of the hole on the acceptor.[9] However, the present authors have recently shown[10] that neither model is correct. The spectrum is in fact similar to other GaP spectra, being formed from the decay of bound excitons. The binding site consists of a nitrogen atom and an acceptor, and the many individual emission lines from various N-to-acceptor pair-separation shells overlap to form the broad spectrum. The undulations are merely the result of averaging the numbers of equivalent sites per shell.

In this paper we discuss in detail the experiments which lead to this identification of the undulation spectrum, and investigate further the behavior of excitons bound to N-acceptor pairs. Several experimental techniques are employed, including temperature-dependent (Sec. III B), and time-resolved measurements (Sec. III D), below-band-gap resonant excitation, and excitation spectra measurements (Sec. III C). From these experiments the origin of the undulation spectrum is discussed in Sec. IV A. A model description of the spectral shape is developed in Sec. IV B and found to be in essential agreement with observation. In Sec. IV C we consider the splitting of the energy levels of excitons bound to N-Zn pairs and in Sec. IV D discuss the role of spatial energy transfer of excitons.

II. EXPERIMENTAL

A. Measurement apparatus

For measurement of the luminescence, GaP samples were usually immersed in liquid He pumped below the λ point; however for temperature-dependent properties an evaporation crysotat was used instead. The emission was detected by a 1-m monochromator, and an RCA 31034A photomultiplier. Photon counting techniques were employed and the spectra were recorded in a multichannel analyzer. Above-band-gap excitation was provided by the 4880-Å line of an argon laser, with a cavity dumper incorporated for lifetime measurements. For below-band-gap excitation, including measurement of excitation spectra, a dye laser operating with sodium fluorescein was used. The wavelength could be continuously scanned from 5330 to 5700 Å with a resolution of 0.3 Å. At a fixed wavelength the resolution could be improved to 0.15 Å. The dye laser was modified to include a cavity dumper for time-resolved resonant measurements and a

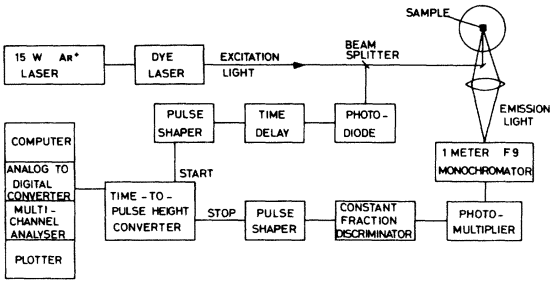

FIG. 1. Schematic diagram of luminescence measuring apparatus for time-resolved measurements.

pulse width of about 15 nsec was obtained. Excitation intensities were in the range 0.1–10 W/cm^2 for *cw* operation, with similar average intensities for pulsed measurements. A schematic diagram of the apparatus, illustrating time-resolved measurements with the dye laser, is shown in Fig. 1.

B. Crystals

Undulation spectra are observed in samples containing both nitrogen and an acceptor. Measurement on many samples containing different acceptors (e.g., Zn, C, Mg, Cd) in varying concentrations have been reported, and consistent reproducible behavior is observed.[8-11] In this study we have concentrated on two vapor-grown Zn-doped samples, which were obtained from Bell Laboratories. These contain 10^{18} and 2×10^{17} cm^{-3} Zn acceptors (sample KH912 and KH913, respectively), and a smaller amount of nitrogen, about 10^{17} cm^{-3}. Nitrogen concentrations in GaP are usually found from the absorption strength of the *A* line,[12] but in undulation samples this may be unreliable because of the pairing effect of acceptors. The concentration can also be estimated if NN pair lines are present.[3] In neither sample are these observed (see Fig. 2) from which we conclude that the concentration is indeed less than 2×10^{17} cm^{-3}.

III. RESULTS

A. Luminescence spectra

In Fig. 2 we show the 1.6-K luminescence spectra of the two Zn-doped samples, and for comparison one sample, W49, containing 4×10^{17} cm^{-3} nitrogen, but a much lower acceptor concentration. In each case the *A* line at 2.317 eV is present which originates from the decay of excitons bound to isolated N atoms, and is the higher-energy ($J=1$) component of the exciton.[3] The $J=2$, *B* line, although forbidden, usually dominates the lower temperature emission because of thermalization. This is observed in sample W49, but in KH912 and KH913 the undulation spectrum apparently replaces

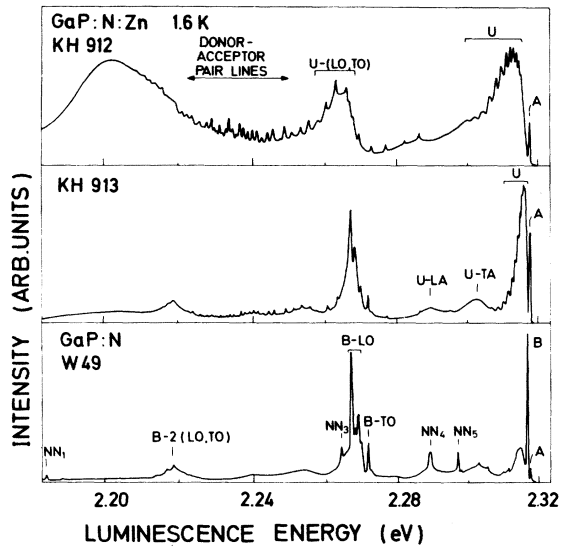

FIG. 2. Luminescence spectra of three doped GaP samples. KH912 and KH913 are used for the detailed investigation of the undulation spectra. W49 contains 4×10^{17} N/cm^3 and a smaller acceptor concentration. The spectrum is shown for comparison of the spectral features.

the *B* line and extends 20–30 meV to lower energy. Phonon replicas of the undulations are also observed which are broad because of the width of the undulation spectrum. However we can distinguish TA, LA, and a group of optical-phonon replicas, from a comparison with the sidebands of the *A* and *B* lines of sample W49 and from the known phonon energies of GaP.[12,13] Donor-acceptor pair lines[5] are also seen in samples KH912 and KH913, particularly in the former. By comparing the position and relative strengths of the lines with known Zn-S spectra,[5] we conclude that sulphur donors are present. In none of the samples is there any discernable emission from excitons bound to neutral acceptors. For Zn this emission has a zero-phonon line lying about 5 meV above the *A* line.[1]

The undulation spectra are shown on an expanded scale in Fig. 3. The shape of the envelope is concentration dependent but the position of the undulation peaks are identical in the two samples. The numbering of the peaks is the same as that used by Hopfield *et al.*[8] Complex fine structure is observed, particularly in the lightly doped samples KH913, up to peak $n=9$, and in the complete spectrum about 100 separate features can be distinguished. These are the individual zero-phonon lines of excitons bound to N-Zn pairs of different separations.[10] The fine structure is much less pronounced in sample KH912 showing up as slightly distorted undulations. The high concentration of acceptors increases the line broadening of the exciton emission lines, as discussed in Sec. IV B.

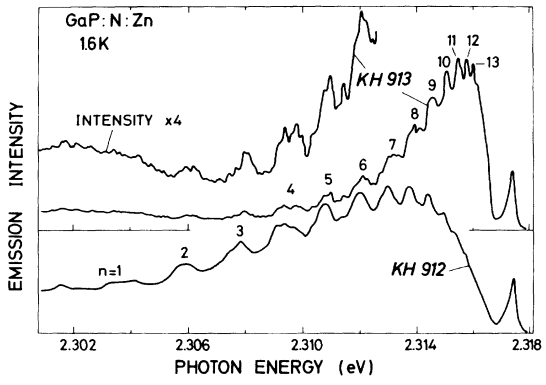

FIG. 3. Detailed undulation spectra. KH913 contains fewer acceptors than KH912. The numbering of the undulations is the same as in Ref. 8.

B. Temperature dependence

As the temperature is increased, the shape and position of the undulation peaks are unchanged, but the maximum of the envelope moves to lower energy as shown in Fig. 4 for KH912, and similar data are found for KH913. The strong temperature dependence is indicative of a nonradiative transition[14] which is determined by a thermally activated process. From the data the activation energy $W(E)$, can be found since the quenching rate P_{nr} is given by

$$P_{nr} = \omega_{nr} e^{-W(E)/kT} . \quad (1)$$

Here E is the emission energy and ω_{nr} is the quenching rate extrapolated to high temperature. The luminescence intensity $I(T,E)$ is therefore given by

$$I(0,E)/I(T,E) - 1 = \omega_{nr} \tau(E) e^{-W(E)/kT} , \quad (2)$$

where $I(0,E)$ and $\tau(E)$ are the luminescence intensity and lifetime, both measured at $T \to 0$ K.

In Fig. 5(a), $I(0,E)/I(T,E) - 1$ is plotted against I/T for various values of E. A family of straight lines results which have different $W(E)$. In the inset graph in Fig. 4 we plot $W(E)$ against $E^A - E$, and by so doing find that $W(E)$ equals the energy difference between the A line and the luminescence energy. We therefore conclude that excitation to E^A is the rate-determining process in the thermal quenching of the undulation spectrum.

The value of $\omega_{nr}\tau(E)$ can also be obtained from the data by applying Eq. (2). Using values of $\tau(E)$ given in Sec. III D we find $\omega_{nr} \sim 10^9 - 10^{10}$ sec^{-1}.

At higher temperatures (above 20 K) the thermal quenching is dominated by a larger activation energy as shown in Fig. 5(a). This may result from excitation to the free-exciton level, but the data are not sufficiently accurate for a detailed analysis of the activation energy.

Although the thermal quenching of the undulation spectrum involves excitation to E^A, the full emission intensity is apparently not transferred to this energy. In sample KH913 there is an increase of intensity at E^A for temperatures up to 5 K, but this only accounts for a small fraction of the emission that is quenched from the undulation spectrum, and above this temperature the intensity at E^A decreases. In sample KH912, no such increase is observed; the intensity at E^A decreases monotonically with increasing temperature. The behavior of the A line above 6 K is shown in Fig. 5(b) for the two samples KH912 and KH913 and also for a sam-

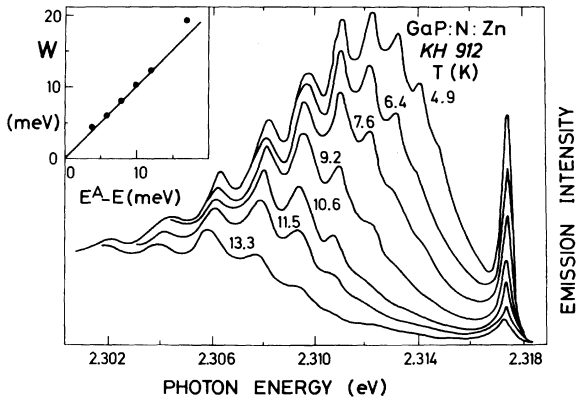

FIG. 4. Variation of the undulation spectra with temperature. Inset is a plot of the activation energy of nonradiative recombination versus energy below E^A (see text).

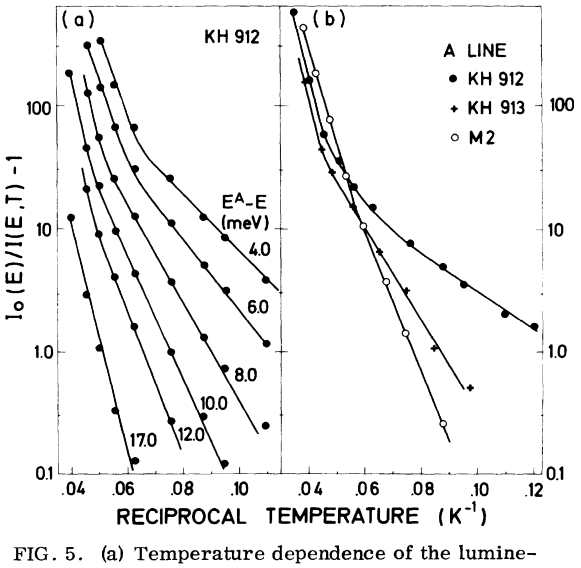

FIG. 5. (a) Temperature dependence of the luminescence intensity at various emission energies (E) within the undulation spectrum. (b) Temperature dependence of the A line intensity of three GaP:N samples; M2 contains under 10^{17} N/cm^2 and acceptors are not detectable.

ple with a low concentration of acceptors where no undulations are observed. Up to 20 K the temperature dependence is different for each sample, but above this a common quenching curve with an activation energy of 21 meV is observed.

Since the quenched excitation energy does not appear as radiative decay at E^A, we conclude that the energy must be transported through the crystal by a transfer process involving A line or weakly perturbed excitons until it reaches a nonradiative recombination center.[15] Furthermore this transfer involves no significant activation energy since otherwise this would appear in the quenching data of Fig. 5(a). A feasible mechanism for this transfer is exciton tunneling. This process has been investigated in GaP:N and is known to occur over distances greater than 100 Å,[16] and is therefore applicable to the impurity levels of our samples. The nonradiative processes and the influence of exciton transfer are discussed in greater detail in Sec. IV C.

C. Resonant excitation

In this section we discuss two resonant excitation experiments giving information both about higher-energy states of the excitons bound to N-Zn pairs which form the undulation spectrum, and about the energy-transfer process mentioned in Sec. III B. The first measurement is that of the excitation spectrum, which is obtained by selecting an emission energy E and varying the excitation energy E^x, in the range $E<E^x<E_g$, where E_g is the band-gap energy. Examples of excitation spectra for various emission energies are shown in Fig. 6. A strong peak is observed at energy E^A, independent of E, and further features appear below E^A whose positions vary with E. Peaks may occur in the excitation spectrum by one of two general mechanisms:

(i) Absorption into higher-energy states of the radiating exciton. (At the temperature of our experiments, 1.6 K, thermal excitation will be sufficiently weak that radiative decay will be predominately from the lowest-energy component of a group of levels.) In particular these higher states may be the various multiplet levels due to different spin configurations of the component particles. Alternatively they may correspond to the higher-energy orbital eigenfunctions (rydberg series). In the excitation spectrum these mechanisms are characterized by features that vary with E, since they are directly related to the radiating center. Structure of this type in the spectra of Fig. 6 is therefore attributed to such processes. The data are replotted in Fig. 7 to show more clearly the evolution of the levels. In this figure the radiating

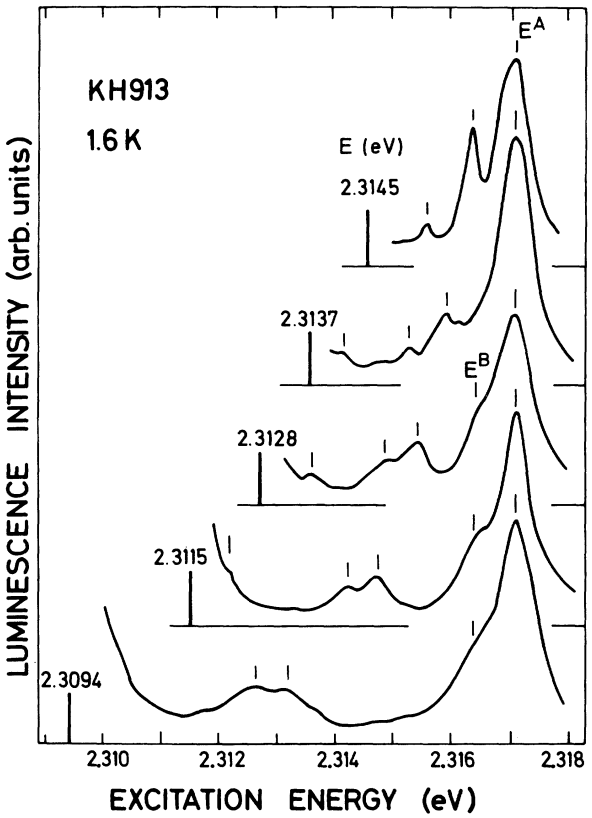

FIG. 6. Excitation spectra of samples KH913. Vertical lines indicate the luminescence energy E. The peaks marked E^A and E^B correspond to absorption at the A and B excitons; other structure corresponds to higher-energy states of the observed exciton.

lowest-energy level is plotted along the diagonal line and the higher-energy levels are given by points vertically above. The different exciton ground-state energies E correspond to different N-Zn separations R, and the lower horizontal scale in Fig. 7 is obtained from the experimentally determined $E(R)$ relation described in Sec. IV B. In Fig. 7 we have traced only the three dominant peaks in the excitation spectrum. Other weaker features are observed, but are not sufficiently well resolved for analysis. At low emission energy the peaks broaden and overlap, as indicated by the error bars in Fig. 7.

(ii) As an alternative to absorption into higher-energy states of the observed radiating center, a peak may occur in the excitation spectrum corresponding to absorption into any other center in the crystal. However this only contributes to the spectrum if an energy-transfer process exists to move the excitation from one center to another. With this mechanism, the position of the peak is independent of E. We therefore attribute the peak

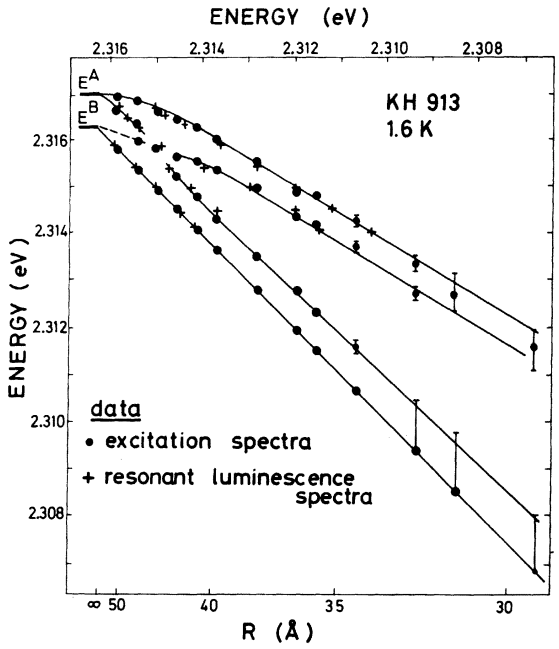

FIG. 7. Energy levels of excitons bound to N-Zn pairs as deduced from excitation spectra and resonant excitation spectra. The levels of a multiplet are denoted by points separated vertically while excitons originating from different N-Zn pairs are separated horizontally. The N-Zn separation R is obtained from the analysis of Sec. IV B.

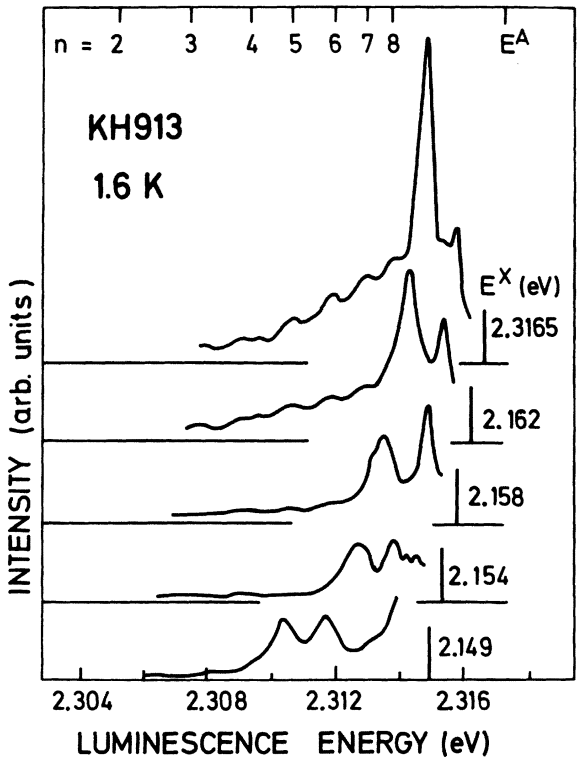

FIG. 8. Resonant luminscence spectra for various excitation energies E^x (indicated by vertical lines). The upper horizontal scale gives the usual position of undulation peaks.

at E^A in the excitation spectrum to this process, the centers in question being isolated nitrogen atoms. This assignment supports the conclusion of Sec. III B, that transfer via levels at E^A is particularly efficient. A further, weak, peak at 2.321–2.322 eV was also observed in the excitation spectra, which we attribute to similar absorption into exciton states bound to isolated Zn acceptors.[1]

An alternative resonant excitation experiment is the measurement of luminescence spectra for a specific below-band-gap excitation energy. Figures 8 and 9 show examples of these "resonant luminescence spectra." The information contained in these measurements is identical to that in the excitation spectra, but it is useful to perform both experiments, as the data are displayed differently. In Fig. 8 we see that the spectra comprise a background on top of which there are superimposed sharp peaks. In Fig. 9, where the sharp structure has been omitted, the background is seen to be just the regular undulation spectrum as observed with above-band-gap excitation. The position of the undulation peaks is independent of excitation energy except that no emission at higher energy than E^x is ever observed. The over-all intensity of this background varies greatly with E^x; it is very strong at $E^x = E^A$ but decreases rapidly at lower excitation energy. We attribute the presence of this background to the transfer process discussed above. The transfer rate should depend little on the final state, provided it is lower in energy than E^x, and therefore we expect to observe the undulation spectrum essentially unchanged. Furthermore, the maximum strength of the signal occurring at $E^x = E^A$ clearly corresponds to the peak at E^A in the excita-

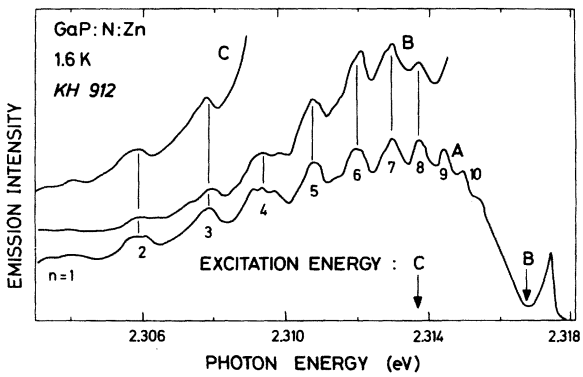

FIG. 9. Comparison of the luminescence spectra with above-gap excitation (A) and with excitation below E^A (B,C) showing the presence of undulations in both cases. For clarity the sharp structure of the type seen in Fig. 8 has been omitted.

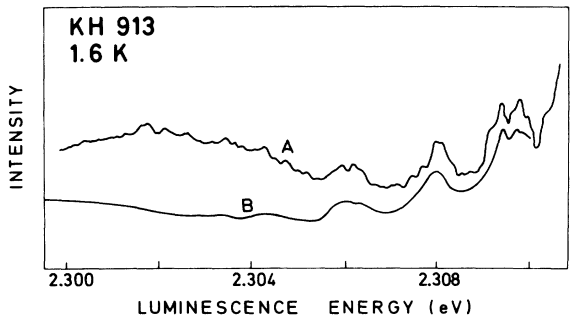

FIG. 10. Comparison of the luminescence spectra with above-gap excitation (A) and with excitation below E^A(B; E^x = 2.314 eV), showing the reduction of the TA phonon replica near 2.302 eV.

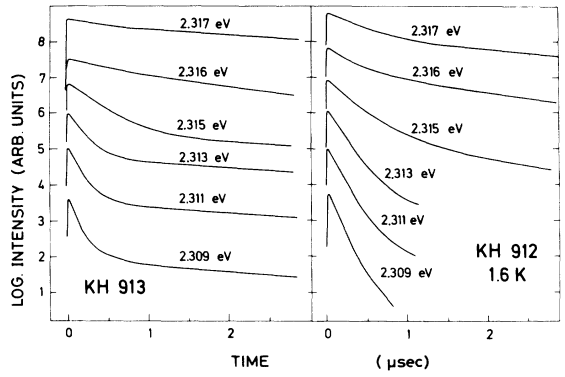

FIG. 11. Examples of luminescence decay of the two undulation samples for above-gap excitation.

tion spectrum.

The sharp peaks in the resonant luminescence spectrum (Fig. 8) originate from the higher-energy states of the radiating exciton. These peaks are replotted in Fig. 7 and are in agreement with the excitation spectra data. The various values of E^x are plotted on the diagonal line and the positions of the peaks in the spectra are given by points plotted horizontally. Note that the spectra have to be normalized to the luminescence spectrum obtained with above-gap excitation, so that the data are not influenced by the changing density of states of N-Zn pairs.

Finally we use resonant excitation to establish that the broad peak in the undulation spectrum of KH913 near 2.302 eV (Fig. 3) is indeed a phonon replica of the upper part of the undulation spectrum as suggested in Sec. III A. This is important as some features of the time-resolved measurements (Sec. III D), and deviations from the model spectral shape (Sec. IV B), are attributed to the presence of this replica. We expect that if excitation is sufficiently lower in energy than E^A, the upper part of the undulation spectrum will not be excited and so the phonon replica will be correspondingly weaker. In Fig. 10 spectra from above-band-gap and resonant excitation are compared. The different shape of the spectrum in the region near 2.302 eV confirms the presence of the TA replica.

D. Decay lifetime

Typical 1.6-K decay curves for both samples with above-band-gap excitation are shown in Fig. 11. The lifetime τ decrease monotonically with energy from about 1–2 μsec at E^A to ~60 nsec at the low energy end of the undulation spectrum. The change in τ is found to be continuous, rather than stepwise, from accurate investigation of the decay at closely spaced energy intervals; the upper limit on the energy range of constant τ is 0.2 meV. This observation is significant for the identification of the undulation spectrum as it indicates that different emission energies arise from unrelated decay processes.[10]

Below 2.314 eV the decay of KH912 is exponential over at least two decades of intensity. KH913 has the same τ for the initial decay, but also a larger time-constant component, evident at longer times. This presumably originates from the TA phonon replica of the high-energy part of the undulation spectrum, which will be much less evident in KH912 because it has a different shaped spectrum (Fig. 3). Above 2.314 eV the decay of KH913 tends to become exponential, but KH912 has a faster initial slope. This is a further consequence of energy transfer to lower-energy levels and is more pronounced in KH912 because of the higher density of available sites for transfer.

Values of τ are plotted against energy in Fig. 12 and are virtually identical for both samples. In the energy range 2.314–2.317 eV, where the initial

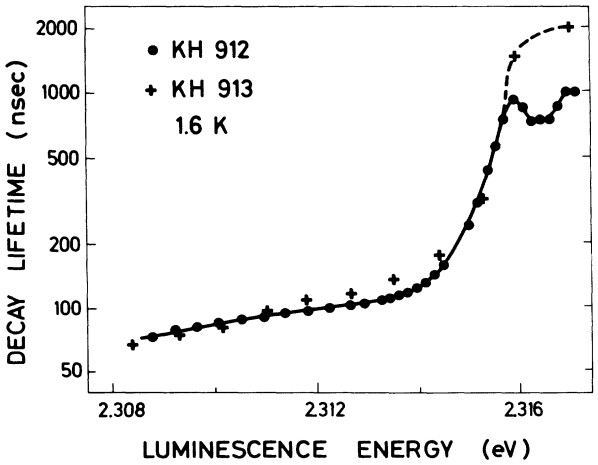

FIG. 12. Decay time vs luminescence energy, deduced from data as in Fig. 11.

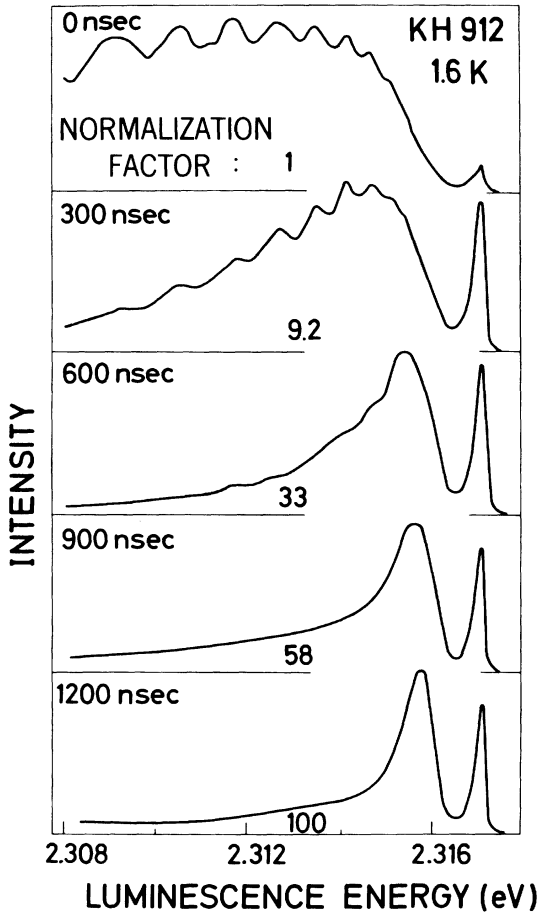

FIG. 13. Luminescence spectra at various times after the end of the excitation pulse, illustrating the fast decay at low energy compared to that near E^A. The normalization factor relates the peak intensities of the different spectra.

decay is dominated by transfer effects in KH912, τ is taken from the slope at longer times. The overall effect of the decay can be seen in the time-resolved spectra shown in Fig. 13. At short times the emission strength lies in the undulations with the low-energy region enhanced since here τ is small. At longer times the emission strength moves to higher energy and eventually only two fairly sharp peaks remain, roughly at the energy of the A and B lines.

As the temperature is increased, τ decreases rapidly, and is constant over an increasing range of energy below E^A. This is consistant with the temperature-dependent measurements of Sec. III B; in the energy range over which thermalization with the A line occurs, τ must be constant, and the strong nonradiative recombination will decrease τ.

IV. DISCUSSION

In Sec. IV A the identification of the undulation spectra as the decay of excitons bound to N-Zn pairs is discussed, but the arguments of the authors' previous publication[10] are not repeated in full. Having established that a new type of pair spectrum is involved, the remainder of the discussion is aimed at a description of the effect of the N-Zn interaction on the bound exciton. Just as in donor-acceptor pair spectra, the relation between emission energy and pair separation is of central importance, and is deduced empirically from the experimental data in Sec. IV B. No theoretical basis for this relation has yet been found chiefly because there is as yet no good theoretical description of the nitrogen isoelectronic impurity. However, using the empirical relation, we construct in Sec. IV B a model description of the detailed spectrum, including the effect of varying the acceptor concentration, and find good agreement with the data except for the energy range within a few meV of E^A. The origin of this discrepancy is identified as the energy-transfer process mentioned in Secs. III B–III D. This process is considered in Sec. IV D, and despite the complexity of the transfer behavior, a feasible over-all description encompassing all the relevant experimental data is given.

The higher-energy levels of the bound exciton are considered in Sec. IV C. We suggest an explanation for the much larger observed splitting of the exciton bound to an N-Zn pair compared to the $E^A - E^B$ splitting.

A. Origin of undulations

The conclusion from the above experimental data is that the undulation spectrum is made up of zero-phonon lines of excitons bound to N-acceptor pairs. The reasoning behind this conclusion and the reason for rejecting the other suggested interpretations of these spectra have been discussed elsewhere[10] and are summarized here. First, the resonant excitation experiment establishes that a perturbation of the initial state of the exciton is involved rather than a final-state effect as suggested by Morgan *et al.*[9] Second, the lifetime data indicate that each energy corresponds to an exciton bound to a different N-acceptor pair with the exciton energy depending on the N-to-acceptor separation R. Finally it was found that this model, that the spectra are formed from a series of pair lines which overlap because they are close together, can explain the appearance of apparently regular undulations. This is demonstrated in Fig. 14(b) which plots the number of equivalent sites for the N-acceptor shells versus R, where the discrete lines for each shell have

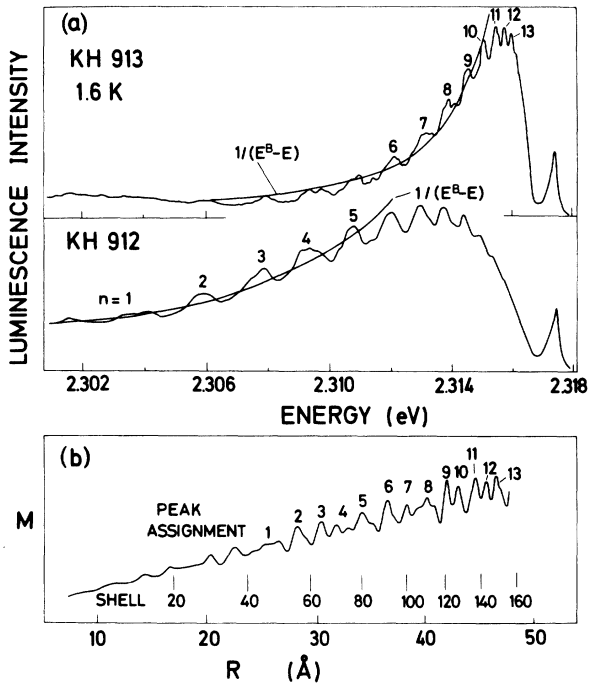

FIG. 14. (a) Undulation spectra of Fig. 3 repeated and compared to the predicted envelope shape $1/(E^B-E)$. (b) Model calculation of undulation peaks as described in the text. The peak assignment results from a detailed comparison of the peak shape of both experiment and the model.

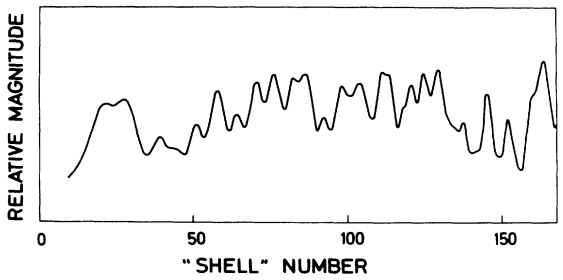

FIG. 15. Similar model calculation of the undulation peaks as in Fig. 13(b), except that computer generated random numbers replace the calculated equivalent site numbers.

been broadened by replacing them by Gaussians. It was demonstrated that not only did this procedure produce regular undulations of about the correct magnitude, but that there existed a good correspondence between the shape of the peaks so formed, and the observed spectra. Thus an attempt to assign the undulation peaks to the N-acceptor shell numbers is possible. In sample KH913 the spectral broadening is less and therefore the discrete lines corresponding to each shell appear. Unfortunately the lines are never sufficiently clear to identify each unambiguously, but it is apparent that approximately the same number of lines are present as required by the assignment to the shell numbers. In the low-energy region where the lines are further apart in energy and therefore potentially easy to identify the spectrum overlaps with the TA phonon replica.

A number of possible fits between the undulation peaks and those of the model calculation were attempted. The identification shown in Fig. 14 was found to be the best and is the same as that suggested previously.[10] Reasonable agreement is obtained between the detailed features of the undulations and of the model.

In the previous paper it was questioned whether or not the undulatory behavior in the averaged number of equivalent sites had its origin in the symmetry of the GaP lattice. It was remarked that a surprising property of random number was an apparent periodicity.[17] This effect is recognized as being responsible for other undulatory phenomena—in particular the population of artic foxes,[18] and the effect known as magnetization ripple,[19] the latter phenomena resulting from experimental data having an appearance remarkably similar to the undulation spectra. In Fig. 15 we show a series of computer generated random numbers broadened by the same procedure as for the calculation in Fig. 14. It is seen that undulations occur with comparable shape and frequency to those in the model spectrum, with the exception that the background level fluctuates more. It appears therefore that the undulations can be explained by this random behavior and are not a peculiar effect of the GaP symmetry. However, the reason for the smoother envelope is a result of the physical situation since the close packing of atoms in GaP ensures that the average of the equivalent site numbers is a smoother function of separation than it would be if the numbers were purely random.

B. Spectral shape

In the model of Fig. 14(b) no attempt is made to specify the relation $E(R)$ between the exciton energy and the N-to-acceptor separation R, because no theoretical description for this interaction is reported in the literature. The nitrogen trap is neutral and therefore we cannot use the familiar $E(R)$ expression applicable to donor-acceptor pairs. Instead we use the assignment of the peaks to plot $E(R)$ and this is shown in Fig. 16. A reasonably accurate analytic function to describe the data is

$$\Delta = E^B - E(R) = E_0 e^{-\beta R^3}, \tag{3}$$

where $E_0 = 0.022$ eV, $\beta = 3.2\times10^{19}$ cm^{-3}, and Δ is the energy difference between the emission energy and

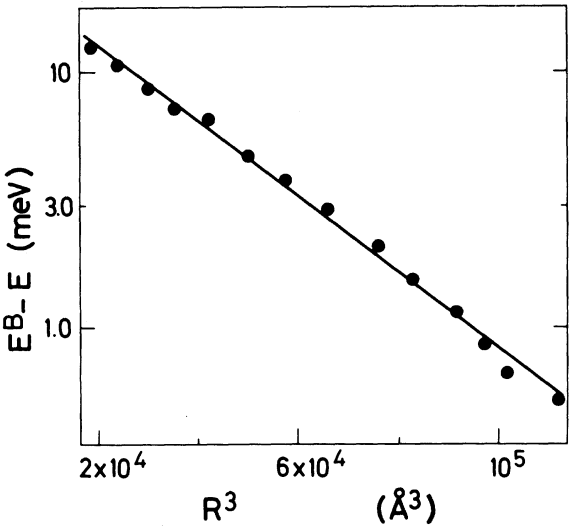

FIG. 16. Logarithmic plot of the exciton energy measured from E^B vs R^3, demonstrating the empirical energy-separation relation of Eq. (3).

the B line position. This relation is different from the expression $\Delta \sim e^{-\alpha R}$ suggested by Hopfield *et al.*,[8] which does not give a good fit to the data. A theoretical calculation of $E(R)$ will be complicated by the splitting of the exciton levels, which is a significant fraction of Δ (see Fig. 7). Hopfield's formula might apply to the "center of gravity" of the exciton multiplet, but the empirical relation (3) is only for the lowest-energy component which dominates the emission. Also Hopfield's formula was only intended for the situation when R is significantly greater than the exciton radius, which is not generally the case here.

Using Eq. (3) the shape of the envelope of the undulation spectrum can be derived from the probability $P(R)$ of finding an N-Zn pair with a certain separation. In the continuum approximation, which is sufficient to describe the envelope (as distinct from the undulation peaks),

$$P(R) = 4\pi R^2 N_{\mathrm{Zn}} e^{-4\pi R^3 N_{\mathrm{Zn}}/3}, \tag{4}$$

where N_{Zn} is the acceptor concentration. The density of states in energy, which should give the spectral line shape, is given by

$$P(\Delta) = (4\pi N_{\mathrm{Zn}}/3\beta\Delta)\,(\Delta/E_0)^{4\pi N_{\mathrm{Zn}}/3\beta}, \tag{5}$$

which simplifies to

$$P(\Delta) = 4\pi N_{\mathrm{Zn}}/3\beta\Delta \tag{6}$$

if $N_{\mathrm{Zn}} < 10^{18}\,\mathrm{cm}^{-3}$. This expression is compared to the envelope of the undulation spectra of the two samples in Fig. 14. The agreement at low energies is good except where the spectrum is influenced by the TA phonon replica. At high energy the spectra deviate strongly from the model—more so for the higher-doped sample. This is a consequence of energy transfer from the higher-energy levels with the result that the emission intensity is less than expected from the density of states. In KH912 there are more available sites for transfer than in KH913 and therefore the quenching of the high-energy emission will be correspondingly greater, as observed.

In the model spectrum of Fig. 14(b), the line broadening of the individual exciton lines was introduced in an arbitrary manner. However we can account for the broadening, and, with the help of Eq. (3), can quantitatively justify our model in the following way. It is apparent from a comparison between the spectra in Fig. 3 together with data from other undulation samples,[8,9,11] that the line broadening of the individual N-Zn bound excitons is primarily a function of acceptor concentration. We suppose therefore that the mechanism is the presence of a second acceptor which exerts an influence on exciton energy in the same way as does the first. This second acceptor will be randomly distributed, giving a range of exciton energies, and thus a broadened line. By definition the N-to-second-acceptor distance R_2 must be greater than R which denotes the nearest acceptor. The distribution function for R_2 is therefore

$$F(R_2) = 4\pi R_2^2 N_{\mathrm{Zn}} \exp(-\tfrac{4}{3}\pi R_2^3 N_{\mathrm{Zn}} + \tfrac{4}{3}\pi R^3 N_{\mathrm{Zn}}). \tag{7}$$

The mean value $\bar{R}_2$ is given by

$$\bar{R}_2^3 = R^3 + (2\pi N_{\mathrm{Zn}})^{-1}. \tag{8}$$

The line broadening $\sigma(E)$ of the exciton line can therefore be approximated as the interaction energy of the second acceptor at $\bar{R}_2$. If we assume the interaction energy has the same functional form as for the first acceptor, then

$$\sigma(E) = A\, e^{-\beta \bar{R}_2^3} = \Delta e^{-\beta/2\pi N_{\mathrm{Zn}}}. \tag{9}$$

In the model calculation of the effect of line broadening on the discrete exciton lines, we assumed σ to be constant in shell number (see Fig. 14 and Ref. 10). The shell number increases as R^2,[5] and using Eq. (3) we find that this model is equivalent to a dependence on Δ given by

$$\sigma(E) \sim \Delta(\ln\Delta)^{2/3}. \tag{10}$$

This has virtually the same energy dependence as the prediction of Eq. (9), since $(\ln\Delta)^{2/3}$ varies slowly with energy, and therefore justifies our assumption. For sample KH912 the magnitude of σ is given reasonably well by Eq. (9) for $N_{\mathrm{Zn}} \sim 10^{18}$ cm^{-3}. The lower acceptor concentration of KH913 implies a very much smaller broadening because

of the $e^{-\beta/2\pi N_{Zn}}$ term, and certainly the features are very much sharper in this sample. However the linewidth is about 0.1 meV and therefore probably limited by other more common broadening mechanisms, such as internal stress, etc.

We point out that the type of line broadening analyzed above maybe quite common. In particular, in GaP:N, where NN pair lines are observed in luminescence, there is often a low-energy tail to the emission lines which approximates to a $1/E$ behavior. This is probably due to a third N atom approaching the pair, or alternatively due to accidental acceptors by the same mechanism as for the undulation spectrum.

Summarizing the arguments of this section, we began by choosing the best assignment of specific N-Zn separations to the peaks of the undulation spectrum. This gave an empirical $E(R)$ relation [Eq. (3)] from which we could derive the envelope shape of the spectrum and the line broadening. The fact that both are in adequate agreement with experiment is good evidence that our initial assignment is correct since this is a necessary condition for a proper description of these features.

C. Levels of the exciton bound to an N-Zn pair

Figure 7 shows the various energy levels of excitons whose ground state forms the undulation spectrum. When the N-Zn separation is small (<40 Å) there are two groups of levels well separated in energy. As R increases the levels converge steadily to the A and B lines. This convergence indicates that the levels originate from different spin configurations of the exciton, rather than from the states of a rydberg series.

The exciton bound to an isolated N atom has two spin states, due to the coupling between the $j=\frac{1}{2}$ electron and the $j=\frac{3}{2}$ hole. These are the $J=1$ allowed A line, and $J=2$ forbidden B line. The splitting is about 0.8 meV with the B line lying lowest.[3] The presence of a neutral acceptor may influence these levels in a variety of ways. First, the hole on the acceptor may couple with the hole on the exciton. This situation is similar to that analyzed by Schmidt *et al.*[20] for excitons bound to neutral acceptors in GaAs. Three levels, approximately equally spaced, are expected, in order of increasing energy, $J=\frac{5}{2}$, $J=\frac{3}{2}$ and $J=\frac{1}{2}$. The final state of the exciton recombination is a $J=\frac{3}{2}$ hole on the acceptor and so the transitions are allowed, in contrast to the B line. Alternatively the presence of the acceptor gives the center axial symmetry which will split the exciton levels. The details of the splitting depend on the orientation of the N and Zn atoms which changes randomly with the different N-Zn shells.

The magnitude of the splittings due to both these mechanisms depends on the size of the crystal field and therefore should be comparable to crystal-field effects in other shallow bound-exciton states. For example excitons bound to neutral Zn acceptors,[1] are split by ~1 meV.[1] Excitons bound to N-N pairs,[3] where there is axial symmetry, are also split by about 1 meV, hardly more than the $E^A - E^B$ splitting. In the present case at small values of R, the splitting reaches 5 meV (Fig. 7). This much larger value suggests that neither of these two mechanisms is dominant although both effects must occur to some extent.

Two other mechanisms could account for the splitting. First, there may be a stress field set up by the presence of the acceptor in the lattice. A problem with this is that the stress should also split the final state of radiative transition which is just a hole on the acceptor. In this case two radiative transitions of different energy occur with no thermalization between them. This conflicts with our model for the undulation spectrum which requires only one transition energy for each N-Zn pair. The alternative is an internal Stark effect splitting due to the nuclear charge on the acceptor. Such an effect can occur because the exciton wave function is not centrally symmetrical about the acceptor. In this case the final state is not split as the hole wave function is symmetrical about the acceptor atom. A rough estimate of the uniform field required to split the exciton by 5 meV is 10^3–10^4 V/cm.[21] The field of a unit point charge in GaP at a distance of 40 Å is about 10^6 V/cm; clearly the electric field is sufficient. However it is difficult to give an accurate calculation of the splitting as the field is highly nonuniform. We consider the Stark effect to be the likely origin of the splitting.

When the change in binding energy due to the acceptor is larger than the $E^A - E^B$ splitting, the acceptor interaction dominates the levels and the $J=1$ and $J=2$ character is lost. Instead the interaction causes the optical transition from the lowest-energy state to be allowed. Therefore we expect a rapid transition from the observed long lifetime of the A and B excitons (1 μsec at 1.6 K, determined by $A-B$ thermalization), to a much shorter lifetime characteristic of an allowed transition. It is seen from Fig. 12 that this is precisely what happens, with the rapid change in τ occurring about 1 meV below E^B. The low-energy limit of τ is approximately 60 nsec. Experiments[22] have shown that the A line in GaP has a radiative lifetime of 40 nsec, and therefore the observed values are just what is expected for an allowed transition.

The presence of the acceptor also makes Auger recombination possible, and this may contribute to τ. Excitons bound to Zn acceptors have a lifetime of 110 nsec which is determined by Auger recom-

bination.[1] The shorter lifetimes found here suggest that radiative recombination is dominant.

D. Energy transfer

It has been suggested several times in the preceding discussion that an energy-transfer mechanism is required to interpret some details of the behavior of the undulation spectrum. Specific effects attributed to this process are the thermal quenching of the emission (Sec. III B), the peak at E^A in the excitation spectrum (Sec. III C), the fast initial decay of time-resolved luminescence (Sec. III D), and the discrepancy between the calculated and observed envelope shape of the spectrum (Sec. IV B). In this section we attempt to account for these effects in a mutually consistant way and provide a qualitative description of the transfer.

Further evidence for the occurrence of exciton transfer comes from a comparison between absorption and luminescence measurements. We have shown in Sec. IV B that in the energy range within a few meV of E^B the observed spectrum does not follow the calculated density of states. In sample KH912, assuming a random distribution of acceptors, we estimate that 75% of the exciton levels occur within 1 meV of E^B, but in contrast only 5% of the emission is in this energy range. The optical absorption is also proportional to the density of state but is uninfluenced by energy transfer. Both Morgan *et al.*[6] and Sturge[23] find, in contrast to the emission, that most of the absorption strength lies near E^A with only a weak tail in the region of the undulation spectrum.[24] This is therefore in general agreement with the calculated density of states. The different shape of the luminescence spectrum must be a consequence of transfer which reduces the exciton population below that given by the density of states.

Transfer is also predicted to occur from a comparison with similar effects in GaP:N.[16] It is found that strong quenching of the A line occurs when the density of available sites for transfer exceeds about 10^{17} cm^{-3}, and this condition is fulfilled in our undulation samples. In GaP:N, the mechanism was identified as exciton tunneling and presumably the same is true in this case. The transfer rate p, between two nearest-neighbor sites separated by a distance D is given by

$$p = \omega_0 e^{-2\alpha D}, \tag{11}$$

where ω_0 is of order 10^{12}–10^{13} sec^{-1}, α is a tunneling parameter expected to be about 40 Å^{-1}, and we assume that the final-state energy is no more than kT above the initial state (and may of course be lower in energy).

In principle it is possible to measure the rate of transfer by observing the slow onset of luminescence from the lower level when the upper level is excited resonantly.[16] This was attempted for excitation at E^A but the transfer rate is so fast (>10^8 sec^{-1}) that the delayed luminescence rise time was barely detectable. This fast transfer rate is confirmed by the temperature quenching experiments illustrated in Fig. 5 which gave a value 10^9–10^{10} sec^{-1} for the quenching rate parameter ω_{nr} of Eq. (2). This parameter is clearly of the same order as the transfer rate. In view of this rapid transfer it is perhaps surprising that the luminescence near E^A decays rather slowly. The reason for this must be the distribution of sites. The radiating excitons occupy the small fraction of sites that have nearest neighbors sufficiently far away that no transfer occurs. The decay of these excitons is governed by the radiative lifetime. As seen in Fig. 11 the decay is in fact nonexponential, indicative of the effects of transfer,[16] but the majority of the excitons in fact tunnel away in a time much less than the time resolution of our apparatus and are not detected.

Experiment shows that the nonradiative transition of the undulation spectrum is by excitation to E^A followed by a rapid movement of the exciton through the crystal. The question arises as why excitation is not to the lower-energy B line since transfer should be equally fast as at the A line. A possible explanation is that the density of states near E^A is greater than near E^B. For a nonradiative transition, the exciton has to escape completely from the initial site and so a multiple transfer process, rather than a single hop, is required. For this to be efficient there must be sufficient density of states in an energy range kT, otherwise multiple transfer would be thermally activated and much slower. If the density of states at E^A is greater than at E^B, then only by excitation to E^A will the exciton be able to escape from the initial site.

There is some experimental evidence that this condition occurs. First, at long times after excitation, two peaks remain in the time-resolved spectra, near E^A and E^B (Fig. 13). These are the $J=1$ and $J=2$ lines of weakly perturbed excitons, and it is seen that the B line is broader than the A line. Second, the intensity of the A and B lines are related, and at 1.6 K about 90% of the intensity should be in the B component (see Fig. 2, samples W49). In the undulation samples there is a sharp peak at E^A but no correspondingly larger peak at E^B. This can be explained if the intensity is spread over a larger energy range at E^B, since the integrated intensity at E^A is in fact much less than it is near E^B.

Finally it is seen in Fig. 7 that the uppermost

exciton level approaches E^A asymptotically. This means that all the N-Zn pairs with $R > 50$ Å have a component very close to E^A, whilst the corresponding levels near E^B are more extended in energy. Thus the density of states is greater near E^A.

V. SUMMARY

The undulation spectrum of GaP is shown to originate from the decay of excitons bound to a nitrogen isoelectronic trap and an acceptor. In the present experiments the acceptor is Zn. The exciton binding energy is a function of N-Zn separation with an interaction observable for values less than about 50 Å. In the limit of small N-Zn separation the exciton binding energy is reduced by about 22 meV below the A line. The individual pair lines are not clearly distinguishable because of the relatively weak interaction, but instead overlap to give the characteristic regular undulations.

The hole on the acceptor influences the spin states of the exciton in such a way that the lowest energy transitions become optically allowed. This is in contrast to the nitrogen bound exciton whose lowest level is forbidden. This effect causes a rapid decrease in observed lifetime at emission energies just below E^B. The exciton spin multiplet structure is obtained from excitation spectra measurements and is thought to be dominated by an internal Stark effect. The splitting is in fact a significant fraction of the increase in binding energy due to the pairing.

A relation $E(R)$ between exciton binding energy and N-Zn separation has been determined empirically. A model description of the spectrum is developed from the observed $E(R)$ and is in general agreement with experiment. Discrepancies from the model can be explained by exciton energy transfer by tunneling.

The undulation spectrum is quenched when the temperature is increased above 4 K, with the emission intensity decreasing most at high energy. The rate-limiting process in the quenching is identified as excitation to E^A and the energy-transfer process is an important mechanism in determining the subsequent nonradiative transition.

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