Undulation Spectra of GaP:N

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(Received 19 May 1975)

Undulation spectra are observed in the luminescence of GaP:N codoped with an acceptor. New experimental data prove that the luminescence is a series of zero-phonon lines of excitons bound to N-acceptor pairs. The undulatory behavior originates from the averaged number of equivalent sites for different N-to-acceptor shells. Calculations show that this number has an approximately periodic fluctuation with the maxima separated by about 9 shells.

Undulation spectra were first observed in the luminescence of GaP:N by Thomas.[1] These spectra occur in a 25-meV energy range immediately below the A and B lines, which are excitons bound to the nitrogen isoelectronic impurity in GaP.[2] Undulations appear whenever the material contains acceptors, and have been observed with Zn, C, Mg, and Cd.[3] The spectra of two Zn-doped samples are shown in Fig. 1(a).

Much conflicting discussion surrounds the explanation of the undulatory behavior, although it is generally agreed that the luminescence is the decay of excitons bound to N atoms, perturbed by a nearby acceptor. The first model was given by Hopfield, Kukimoto, and Dean[3] who proposed that an interference effect between the exciton wave function on the nitrogen and acceptor atoms modulates the radiative transition probability. However, Morgan, Lorenz, and Onton[4] found this model incapable of explaining the magnitude of the undulations, the discrepancy being a factor of 20; they proposed instead that the exciton decay excited rotational levels of the acceptor with each undulation peak corresponding to separate rotor levels.

Both these groups of authors were aware of fine structure in the spectra but were impressed by the need to explain the overall regularity of the undulations. In contrast, Henry and Sturge[5] found that the undulations comprised many sharp lines that tended to overlap when there was sufficient broadening, giving a smooth envelope. Our experiments confirm this result, as shown in Fig. 1(a). Henry and Sturge[5] proposed zero-phonon lines of excitons bound to N-acceptor pairs, with each undulation corresponding to one specific N-to-acceptor separation ($R_{N\text{-}A}$). They surmised that both initial and final states would be split, yielding a complex multiplet structure seen at high resolution and giving broad undulations when the linewidth was increased.

We have carried out a series of detailed investigations of undulation samples containing Zn acceptors which resolve the uncertainty surrounding the explanation of these spectra. These experiments will be reported in full elsewhere[6]; the most significant results are summarized below.

(1) The decay lifetime decreases monotonically from 200 nsec, at the high-energy limit, to ~70 nsec, at the low-energy limit. Below 2.314 eV, the decay is exponential over at least two decades in intensity I; above, it becomes progressively more nonexponential.

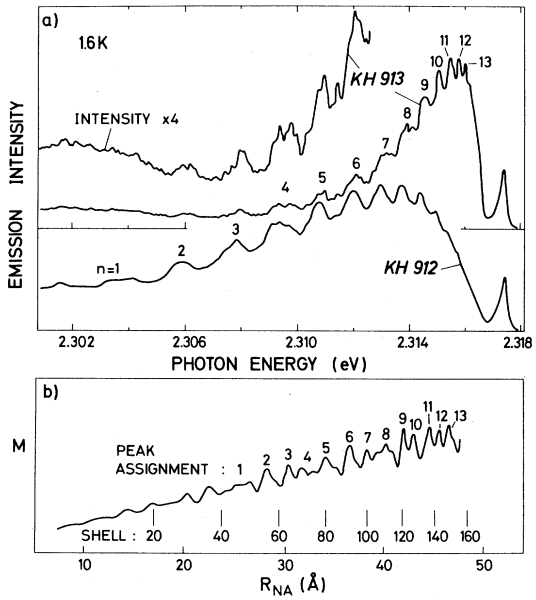

FIG. 1. (a) Luminescence spectra of Zn-doped GaP:N with undulations numbered as in Ref. 3. Fine structure is observed in sample KH913, which has the lower Zn-doping level. (b) The averaged number of equivalent sites M versus N-to-acceoptor separation $R_{N\text{-}A}$.

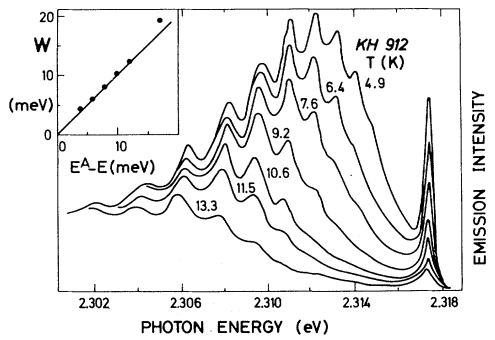

FIG. 2. The undulation spectra at various temperatures. Inset is a plot of the activation energy of thermal quenching W against the energy difference between the A line and the observed emission, $E^A - E$.

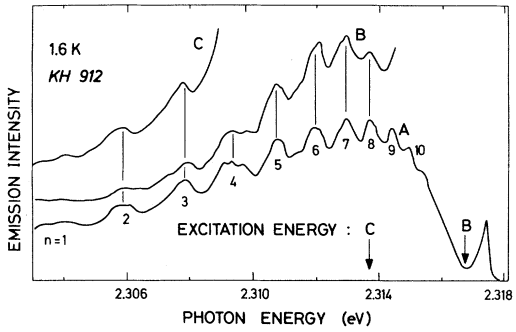

FIG. 3. Undulation spectra observed with different excitation energies $h\nu_{ex}$: curve A, $h\nu_{ex} = 2.540$ eV (greater than band gap); curve B, $h\nu = 2.3167$ eV; curve C, $h\nu = 2.3136$ eV. The intensity scales for the three curves differ.

(2) Raising the temperature quenches the higher-energy undulations first, as shown in Fig. 2, but there is no change in the shape or position of the peaks. The activation energy for the nonradiative transition is found from a plot of $[I(T \to 0)/I(T)] - 1$ versus $1/T$ at various points on the spectra, and equals the energy difference between the A-line energy E^A and the emission energy (Fig. 2, inset).

(3) Undulations can be excited even when the excitation energy is significantly below E^A; examples are given in Fig. 3. The undulations clearly occur at the same energy as with above-gap excitation. Further conclusive identification are the identical decay lifetimes to those with above-gap excitation. In addition the emission is linear in excitation intensity, thus ruling out two-photon and two-step absorption processes.

A fundamental difference between the model of Morgan, Lorenz, and Onton[4] compared with those of Hopfield, Kukimoto, and Dean[3] and Henry and Sturge[5] is that the former requires an essentially unperturbed initial state, the A and B lines, and an excited final state, the acceptor rotor levels, while the latter propose that the acceptor lowers the bound-exciton energy. Our experiments show decisively that Morgan's model is inapplicable. Excitation of undulations well below E^A is incompatible with an unperturbed initial state. It is also difficult to explain the lifetime and temperature-dependence data with this model.

Clearly the emission energy is the initial-state energy of a bound exciton, and this conclusion is supported by the thermal-quenching experiments. The data in Fig. 2 indicate that the rate-determining process in the competing nonradiative transition is excitation of the exciton to E^A, although the subsequent recombination process is not yet clear. From the decrease of τ with energy, we further conclude that there is no significant thermalization or relaxation between exciton states corresponding to different emission energies in the spectrum; otherwise τ would either be constant or increase at lower energy or the decay would be nonexponential. Thus the spectrum cannot originate from different levels of the same exciton; instead each energy corresponds to excitons bound to distinct N-acceptor pairs, with different energies corresponding to different $R_{N\text{-}A}$. The sharpness of the line structure in the spectra (~ 0.1 meV) together with the energies involved complete the identification of the luminescence as the zero-phonon lines of excitons bound to N-acceptor pairs.

It remains to discuss the origin of the undulatory behavior of the bound-exciton energy. Objections to the Hopfield-Kukimoto-Dean model have been given above. Several difficulties arise in the explanation of the Henry and Sturge model.[5] Firstly, the total emission intensity of the undulation should be proportional to the number of equivalent sites in the corresponding N-to-acceptor separation shell. This number varies discontinuously but no equivalent variations are observed in the spectra. Secondly, if the fine structure is due to multiplet behavior, then, unless the splitting is in the final state, thermalization should occur. Experimentally (Fig. 2), increasing T does not change the shape of the undulations

and this contrasts with the complete thermalization that is found in the multiplets of both N-N pairs[2] and donor-acceptor pairs[7] in GaP. Finally, the lifetime data set an upper limit on the energy width of a multiplet since all components of a single exciton must have the same τ. This restricts the width to <0.4 meV which is only one fifth of the undulation separation at the low-energy end of the spectrum.

We are led therefore to the conclusion that it is the fine structure, rather than each complete undulation peak, that corresponds to different shells in the pair separation. Thus each undulation would correspond to the smearing out of several shells giving an apparently smooth and regular modulation. It is shown here that such a modulation can result from an unexpected behavior in the numbers of equivalent sites in the shells. We evaluated these numbers for the first 170 shells of the "type-II" variety[7] (N and Zn occupy P and Ga sites, respectively). Since the exciton energy will be a smooth function of $R_{N\text{-}A}$, a plot of the equivalent site number against $R_{N\text{-}A}$ should represent the form of the emission spectrum, apart from this smooth energy scaling function. To simulate the line broadening of the spectrum the discrete lines for each shell were replaced by Gaussians. One example of this procedure, with a broadening corresponding to about twice the shell separation, is shown in Fig. 1(b). It is seen that the random behavior of the discrete shells is replaced by at least fifteen regular-looking "undulations," with a period of approximately nine shells. The depth of the undulations is approximately 20%, in rough agreement with observation, and the precise broadening required to obtain the undulations is not critical.

A possible assignment of the peaks on the basis of the shape of the observed spectrum is shown in Fig. 1(b). The features used are the characteristic shape of peak $n=1$ and the small peak between $n=5$ and $n=6$. Note also that the two other peaks that least resemble smooth undulations in the model spectrum ($n=4$ and $n=8$) correspond to peaks in the experiment that are the most distorted [Fig. 1(a)]. Furthermore, between peaks $n=1$ and $n=6$ there should be 45 shells [Fig. 1(b)]. In fact about forty distinct features occur between these two peaks in the fine structure of sample KH913 in Fig. 1(a).

A complete fit of the data requires the dependence of exciton energy and line broadening on $R_{N\text{-}A}$, and neither has been theoretically evaluated. In particular the line broadening is clearly determined by the acceptor concentration rather than by well-understood mechanisms, such as temperature, instrumental resolution, or strain. Thus it is difficult to justify physically our choice of a broadening parameter. However the fact that this straightforward model for the undulations can explain not only the general shape, but also much of the detail of the spectra, argues strongly for its acceptance.

Finally, having established that the series of equivalent site numbers will produce undulations when suitably broadened, it is of interest to ask whether the phenomenon has a physical origin arising from the symmetry of the GaP lattice. In this context we note that a series of random numbers can display apparent periodicity—the "arctic fox effect"—and this is the explanation of other undulatory phenomenon in physics.[8] We suspect that this is also the origin of the present undulations since we are unable to find an explanation from the symmetry of GaP, but a final determination awaits a more detailed study of this point.

We thank Dr. Henry and Dr. Sturge for supplying the samples used in this investigation and for making available preprints of their work on the subject. We are also grateful to Professor Queisser and Dr. Morgan for useful discussions, and to W. Heniz for technical assistance.

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