

## Observation of nonradiative energy transfer in the excitation of $\text{Nd}^{3+}$ luminescence in GaP

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(Received 25 September 1989; revised manuscript received 12 February 1990)

We have carried out luminescence-excitation measurements on a  $\text{Nd}^{3+}$  complex in GaP in the range 1.5–2.2 eV to determine the mechanisms by which the *internal*  $\text{Nd}^{3+}$  luminescence is generated. At low temperatures we observe transitions into the  $^4S_{3/2}$  and  $^4F_{7/2}$  excited states of  $\text{Nd}^{3+}$  and two broad excitation bands whose integrated intensities are orders of magnitude greater than that of the  $\text{Nd}^{3+}$  excited states. These broadbands demonstrate for the first time that nonradiative energy transfer from external states is the dominant low-temperature mechanism for the excitation of  $\text{Nd}^{3+}$  luminescence in GaP. Reasonable assignments have been made for the origin of the broadbands on the basis of similar work carried out on rare-earth-doped II-VI semiconductors.

The incorporation of rare-earth (RE) ions into III-V semiconductor hosts in the hope of obtaining efficient luminescent centers has generated a considerable amount of research activity in the recent past. The characteristic sharp-line  $4f$  luminescence transitions are observed using optical and electrical excitation.<sup>1–3</sup> The mechanisms by which the internal luminescence occurs within the  $4f$  shell of the rare-earth ions have been documented for the II-VI semiconductors<sup>4</sup> but as yet a detailed picture has not emerged for the III-V semiconductors. Knowledge of the excitation mechanisms should help in maximizing the luminescence properties and in turn lead to practical applications of RE-doped III-V systems.

The system studied is GaP:Te implanted with Nd ions at room temperature with an energy of 350 keV to a dose of  $1 \times 10^{13} \text{ cm}^{-2}$ . The area of the sample was  $6 \text{ mm}^2$  and so we estimate that there are  $\sim 5 \times 10^{11}$  Nd ions in this sample. The sample was annealed at  $850^\circ\text{C}$  for 2 h and the characteristic  $\text{Nd}^{3+}$  luminescence was subsequently observed though it is not clear what fraction of the total implanted Nd ions participate in the luminescence. The experiments were carried out in an optical cryostat at pumped liquid-helium temperatures ( $\sim 1.6 \text{ K}$ ). Excitation spectra were recorded by illuminating the GaP: $\text{Nd}^{3+}$  sample with a dye laser (with R6G, DCM, or LD700 dyes) pumped by an  $\text{Ar}^+$  laser and monitoring the resulting  $\text{Nd}^{3+}$  luminescence as the dye laser was scanned. The luminescence signals were detected by a liquid- $\text{N}_2$ -cooled North-Coast (model EO-817L) Ge detector.

Under the above annealing conditions a Nd complex labeled "A" in Ref. 5 dominates the  $\text{Nd}^{3+}$  luminescence. Three internal luminescence transitions from the  $^4F_{3/2}$  level to the  $^4I_{9/2}$ ,  $^4I_{11/2}$ , and  $^4I_{13/2}$  levels of  $\text{Nd}^{3+}$  are observed. This sample was chosen for our study of  $\text{Nd}^{3+}$  excitation mechanisms as it allowed us to conduct measurements on a single Nd complex in GaP.

The low-temperature spectrum showing the  $^4F_{3/2} \rightarrow ^4I_{9/2}$  luminescence transition of the A complex using above band-gap excitation is given in Fig. 1. The spectrum consists of five lines which according to group theory shows that the Nd ion is at a site of lower than the  $T_d$  symmetry of the substitutional or the interstitial lattice

sites in GaP. The shielding of the  $4f$  shell by the outer  $5s$  and  $5p$  shells results in an extremely weak interaction with the lattice and so the reduction of the symmetry cannot come about because of any interaction with lattice vibrations, e.g., a Jahn-Teller distortion. The Nd ion is therefore part of a defect complex. As with many other RE-doped systems the microscopic nature of the Nd-complex has not yet been established.<sup>4,5</sup>

The excitation spectra obtained by monitoring the five luminescence lines of the  $^4F_{3/2} \rightarrow ^4I_{9/2}$  transition are shown in Figs. 2 and 3. The spectrum in Fig. 2 was taken with LD700 and DCM dyes and was normalized by keeping a constant 25 mW of excitation power on the sample.

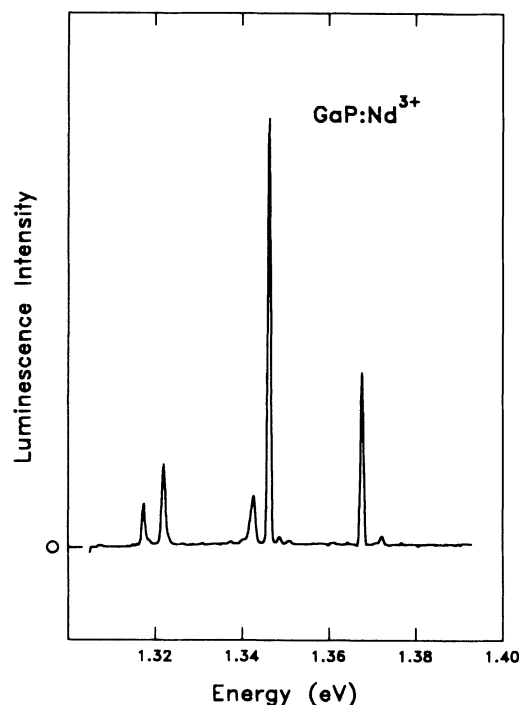


FIG. 1. The  $^4F_{3/2} \rightarrow ^4I_{9/2}$  luminescence transition at  $T=1.6 \text{ K}$  using above band-gap excitation at 2.71 eV.

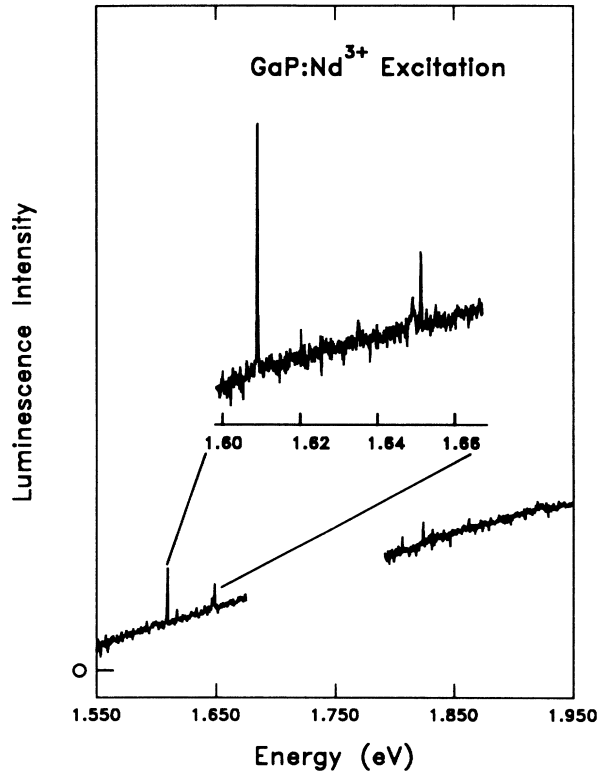


FIG. 2. Excitation spectrum of the  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  luminescence transition in the region 1.55–1.95 eV at  $T=1.6$  K. The laser power was maintained at 25 mW.

We did not have an efficient dye in the blank region of Fig. 2. The spectrum consists of a broadband with some sharp lines in the 1.60–1.66-eV region superimposed on it. In the inset in Fig. 2 the energy region of the sharp lines is shown in greater detail. By comparison with other  $\text{Nd}^{3+}$  systems these sharp lines are assigned to transitions from the lowest level of  ${}^4I_{9/2}$  to some of the crystal-field split levels within the  ${}^4S_{3/2}$  and  ${}^4F_{7/2}$  states.<sup>6</sup> The spectrum in Fig. 3 consists of a zero-phonon line at 2.076 eV with a structured sideband to higher energy. The broad excitation bands of Figs. 2 and 3 are clearly not internal sharp-line  $\text{Nd}^{3+}$  4*f* transitions but they nevertheless dominate over the internal excitation spectrum shown in the inset of Fig. 2. Identical excitation spectra were found for the  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  and  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$   $\text{Nd}^{3+}$  luminescence transitions. No luminescence bands corresponding to these broad excitation bands were observed.

In a review of 4*f* luminescence in II-VI semiconductors Boyn<sup>4</sup> classified the mechanisms for the generation of the internal  $\text{RE}^{3+}$  luminescence: (a) direct excitation into excited states within the 4*f* shell, (b) excitation by nonradiative transfer from broadbands with energies ranging from above the luminescence transition to near the band-gap energy  $E_g$  showing strong spectral overlap with the transitions in (a) above, and (c) excitation from broadbands in the region around  $E_g$  due to generation followed by capture of free excitons. The direct excitation into the  ${}^4S_{3/2}$  and  ${}^4F_{7/2}$  levels contributes very little intensity to the overall excitation spectrum (Fig. 2). This results from

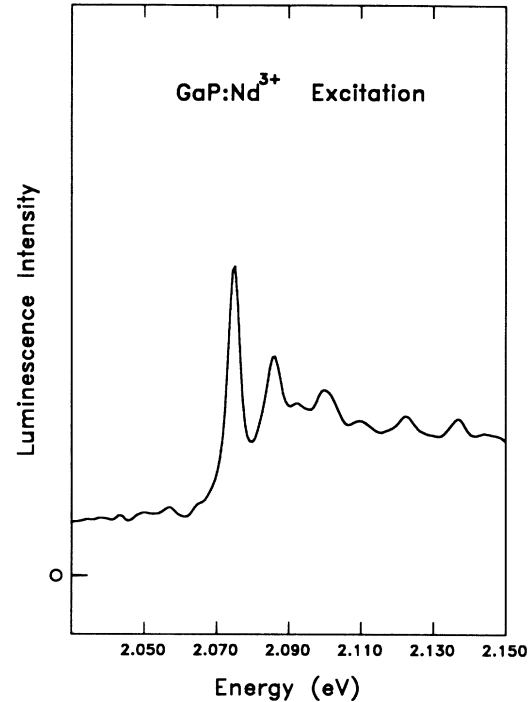


FIG. 3. Excitation spectrum of the  ${}^4F_{3/2} \rightarrow {}^4I_{9/2}$  luminescence transition in the region 2.03–2.15 eV at  $T=1.6$  K. The laser power was maintained at 10 mW.

the small oscillator strength of these internal transitions. It is unlikely that direct energy transfer [mechanism (c) above] would occur from an exciton into the 4*f* shell at very low temperatures because of the lack of spectral overlap of the exciton and rare-earth energy levels and so the main effect of the excitons on the  $\text{Nd}^{3+}$  luminescence is by capture into impurity states with subsequent energy transfer into the 4*f* shell. Therefore, mechanism (c) contributes to mechanism (b). As we did not have a dye laser that operated in the region of the band-gap energy ( $\sim 2.3$  eV) we cannot check on (c) directly. We have already seen that excitation using an  $\text{Ar}^+$  laser at 2.71 eV gives rise to  $\text{Nd}^{3+}$  luminescence as shown in Fig. 1.

The energy positions of the broadbands of Figs. 2 and 3 show that they belong to mechanism (b) above. We write for the ratio of the efficiency of the internal 4*f* excitation to the external excitation

$$R = n(f_f/f_e), \quad (1)$$

where  $R$  is the ratio of the intensities of the internal 4*f*-4*f* lines to the broadband,  $n$  is the efficiency of the deexcitation of the external state by the Nd ion, and  $f_e$  and  $f_f$  are the oscillator strengths of the external and 4*f*-4*f* internal transitions, respectively.<sup>7</sup> No luminescence was observed from the broadbands so we conclude (at least at low temperature) that  $n=1$ . Then, taking the value of  $R=1.1 \times 10^{-3}$  from Fig. 2 and using  $f_f=1 \times 10^{-7}$  (Ref. 8) we find  $f_e \sim 1 \times 10^{-4}$ . This number is a lower estimate for  $f_e$  since we did not observe the low-energy tail of the band in Fig. 2 but gives an order-of-magnitude estimate. The value of  $f_e$  is in the range for donor-acceptor pair transi-

tions in semiconductors. The position of this band relative to the luminescent  ${}^4F_{3/2}$  levels along with the value of  $f_e$  are very similar to results in II-VI semiconductors, e.g., the  $\text{Tm}^{3+}$  center in  $\text{ZnS}$ .<sup>7</sup> The electrical behavior of the RE ions in III-V semiconductors has not yet been established<sup>3</sup> but there is some suggestion that they behave as acceptors.<sup>9</sup> The transition in Fig. 2 is therefore assigned to donor-acceptor pair transitions with the Nd complex as part of the pair. The spectral overlap of this band with the  ${}^4S_{3/2}$  and  ${}^4F_{7/2}$   $\text{Nd}^{3+}$  levels provides the path for the nonradiative energy transfer.<sup>10</sup>

Similarly the  $f_e$  of the band in Fig. 3 is estimated to be 0.1. This is evidently a much stronger transition than that of Fig. 2. The sideband structure in the band does not follow the energy-level scheme for donors or acceptors in GaP and is not characteristic of bound-exciton transitions on common impurities in GaP.<sup>11</sup> The structure above the line at 2.076 eV is therefore most likely to be vibrational. This band has only been observed in  $\text{GaP:Nd}^{3+}$  and so we assign it to a Nd-related defect. On the basis of the large oscillator strength, the transition in Fig. 3 can be reasonably assigned to a transition between "external states" of the  $\text{Nd}^{3+}$  complex.<sup>7</sup> These external states could arise from the complexing of the  $\text{Nd}^{3+}$  ion into a close donor-acceptor pair, for example.<sup>4</sup> Another possibility for this band is that it is due to a center remote from the Nd ion but as the spectrum in Fig. 3 has not been observed before

in GaP we discount this possibility. Again spectral overlap with some  $\text{Nd}^{3+}$  excited states such as  ${}^2G_{7/2}$  (Ref. 12) provides the path for the energy transfer.<sup>10</sup>

In conclusion, our excitation experiments demonstrate that nonradiative energy transfer is the dominant mechanism in the excitation of *internal*  $\text{Nd}^{3+}$  luminescence in GaP at low temperatures. On the basis of order-of-magnitude estimates for the broadband oscillator strengths we have made assignments for the bands to distant donor-acceptor and "external-states" transitions involving the  $\text{Nd}^{3+}$  complex directly. These results show a striking similarity to the work carried out on RE ions in II-VI materials. Experiments such as optically detected magnetic resonance should help greatly in identifying the nature of the energy-transferring species because of their sensitivity to spin-dependent energy transfer.<sup>13</sup> Temperature-dependent lifetime measurements on the  $\text{Nd}^{3+}$  complex are now under way to obtain more insight into the energy-transfer mechanism. Further experiments with a range of  $\text{GaP:Nd}^{3+}$  samples would also be helpful to determine if the excitation spectra in this study are sample dependent.

The interest of H.-J. Queisser in this work is gratefully appreciated as are discussions with J. Schneider, J. Weber, and G. Brunthaler. The technical assistance of W. Heinz is much appreciated.

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<sup>12</sup>This assignment is based on the Dieke diagram for  $\text{Nd}^{3+}$ , G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Wiley, New York, 1968).

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