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'Similarity law' in the phonon spectrum of bound exciton luminescence in GaP:N

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Abstract. A low temperature spectrum with periodically repeated phonon structures, induced by the localised vibration model in nitrogen doped GaP has been observed. Experiments and analysis show that all of the phonon sidebands from nitrogen-bound exciton luminescence come from multi-phonon optical transition processes described by Huang–Rhys' theory.

1. Introduction

Much work has been done on the optical properties of isoelectronic bound excitons in GaP:N. At the same time, much attention has been paid to the properties of their many phonon sidebands. Evstropov *et al* (1976), Chang *et al* (1980a, b), and Zheng and Zhang (1986) have investigated the exciton–phonon coupling in this system. Snyder *et al* (1984, 1985) made a theoretical calculation of the spectral shapes of the phonon sidebands. Recently, Zhang *et al* (1988) have studied the phonon sideband structures of NN_i pair centres by selective excitation. Chang *et al* (1980a, b) suggested that due to the strong coupling of the bound exciton with phonons, there exists an 'exciton-LO phonon' complex, also known as a 'dressed exciton' (Balkanski 1981). Evstropov *et al* (1976) and Zheng and Zhang (1986) suggested that all phonon sidebands come from the multi-phonon process described by Huang–Rhys' theory (the so called CC process), so the strength of the exciton–phonon coupling could be described by Huang–Rhys factor S. This has been strongly supported by the selective excitation spectra of Zhang *et al* (1988), but Snyder *et al* (1984, 1985) argued that while the LO phonon sideband was due to a CC process, the TA and LA phonon sidebands were derived from the $k \neq 0$ components of the bound exciton wavefunction (the so called MC process). They made a theoretical calculation of the line shapes of TA and LA phonon sidebands based on the bound exciton wavefunction. Although the calculated line shapes were similar to the experimental results, it should be noted that they did not estimate the strength of such an indirect transition relative to a zero-phonon transition. Also, for NN_i pair centres, it seems that it would be impossible to get good results from such a calculation since the binding energies of pair centres may be much larger than that of an isolated N centre.

In this work we report a very interesting experimental result, that is, the luminescence of the NN_1 pair centre shows a periodically repeated phonon spectrum with the period

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of the local vibration mode $h\nu_{loc}$. To our knowledge, such a phonon sideband structure has never been reported in impurity spectra of III–V semiconductors, but it has been observed in a different material, KBr–O_2^- (Rebane 1970). Our analysis confirms that all phonon sidebands of bound exciton luminescence in GaP : N come from the CC process.

2. Experimental procedure and results

2.1. Experimental procedure

The experimental system for this work was the same as that used previously (Zheng and Zhang, 1986). The excitation source was a CW Ar^+ laser. The power used was about 50 mW. The photoluminescence was detected by a system composed of a GDM-1000 double grating monochromator, a cooled C31034-02 photomultiplier, and a PAR124A lock-in. The emission below 17500 cm^{-1} (2.1697 eV) was taken from the first-order spectrum of the spectrometer. In this region the spectrometer has a rather flat response. Above 17500 cm^{-1}, the emission was taken from the second order. In all of these experiments, the resolution was 0.1–0.2 meV.

Four epitaxial nitrogen doped GaP samples with different nitrogen concentrations were used. The concentrations, measured by optical absorption (Lightowlers *et al* 1974), were 1.0×10^{19} cm^{-3}, 2.4×10^{18} cm^{-3}, 2.0×10^{18} cm^{-3} and 2.2×10^{18} cm^{-3} for samples G_1-Y, SG-1, HG-1 and HG-2, respectively.

2.2. Results

Figure 1 is a typical emission spectrum of the NN_1 pair centre. All the samples we used showed the same spectrum as in figure 1 except for tiny variations in relative intensity (less than 3%). The most important feature of figure 1 is that the phonon sideband of the local vibration mode periodically repeats the total spectrum of one phonon replicas below the zero-phonon line. In other words, the phonon sidebands on the low energy side of the zero-phonon line are periodically repeated with a period equal to $h\nu_{loc}$, the energy of the local mode. The intensity of the first-order local phonon band is comparable with that of the LO phonon band, and the second-order local phonon band is clearly seen in the spectrum. So three periods can be observed in the spectrum. Along with the periodically repeated structures, there are other combinations of phonon sidebands. For example, in the second period, there is a 2LO phonon band with three components: $2LO^{\Gamma}$, LO^{Γ} + X and 2X. These three lines also existed in the emission spectrum of an isolated N centre in a lightly doped sample (Thomas *et al* 1963), but the local mode band was unobservable. In the third period, two other combination bands, LOC + LO + TA and LOC + 2LO are observable. The phonon energies and the relative intensities of the periodic structures are listed in table 1. The relative intensities have been calibrated to the spectral response. The phonon energies agree very well with the results of Thomas *et al* (1963) and Koteles and Datars (1976). For other centres, only the NN_3 pair's local mode phonon line can be seen clearly, but the coupling strength is weaker than that of the NN_1 pair. For this reason, and also because of the overlap with the NN_1 pair's spectrum, the second or higher order phonon sidebands from the NN_3 pair are usually unobservable except for the second order LO phonon band (Faulkner and Dean 1970, Zheng and Zhang 1986).

According to Huang–Rhys' theory, when there exists a local mode $h\nu_{loc}$, and $h\nu_{loc} > h\nu_q$ (crystal mode), multi-phonon emission processes occur, such that $h\nu =$

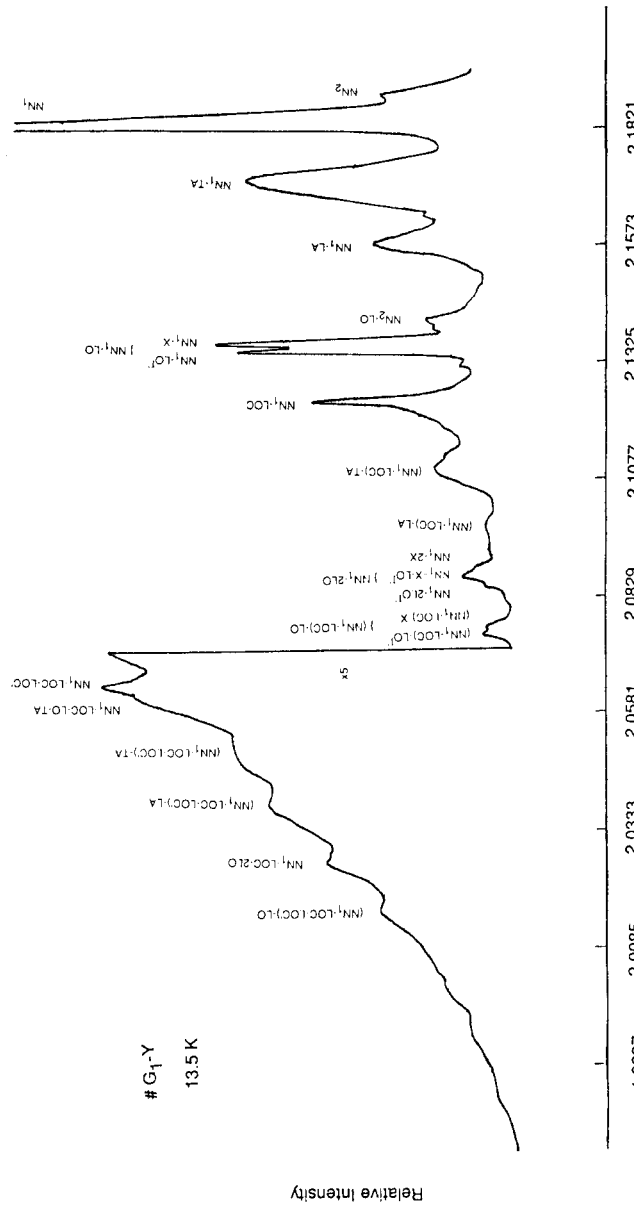

Figure 1. Photoluminescence spectrum of NN_1 pair centre in GaP:N.

Table 1. Phonon energies (meV) and relative intensities in each period (the relative intensities were normalised to the zero phonon or local phonon line in each period, data in brackets are the error of measurement).

Period	Zero or LOC	TA	LA	X	LO^{Γ}	LOC
1		13.3 (0.2)	27.5 (0.2)	48.4 (0.1)	50.1 (0.1)	61.2 (0.1)
	1	0.168	0.105	0.164	0.160	0.116
2		14.3 (0.6)	27.0 (0.6)	48.4 (0.1)	50.1 (0.1)	60.1 (0.1)
	1	0.533	0.371	0.335	0.342	0.260
3		14.5 (0.6)	24.8 (0.6)	47.9 (0.6)		—
	1	0.701	0.605	0.422		—

$W_{if} - h\nu_q - nh\nu_{loc}$. Here n local phonons and one crystal phonon are emitted along with the zero-phonon emission of energy W_{if}. These multi-phonon processes will show a similarly repeated phonon spectrum with a period of $h\nu_{loc}$, obeying the so-called 'similarity law' (Rebane 1970):

$$F(h\nu) = C_0 F_B(h\nu) + C_1 F_B(h\nu - h\nu_{loc}) + C_2 F(h\nu - 2h\nu_{loc}) + \ldots.$$

Here $F_B(h\nu)$ stands for the basic spectral shape composed of the zero-phonon line and the first-order band phonon lines, and $C_n = (S_{loc}^n)/n!$. In theory, the repetition is not only in component but also in relative intensity. Nevertheless, because of the overlap effect discussed below, the relative intensities in the real spectrum more or less depart from what is expected from the theory, especially for acoustic phonon bands. In fact LO phonons can also induce a repeated structure, but with a smaller period ($h\nu_{LO} < h\nu_{loc}$), and only 2LO, LOC + 2LO and LOC + LO + TA are observable. The other components actually overlap with the components induced by the local mode, which leads to the departure from theory of relative intensities and phonon energies in table 1. For example, the first-order local phonon band shows an asymmetric broadening in its low energy side, and in the second period, the position and relative intensity of the TA phonon band is changed. Actually, the TA and LA 'phonon sidebands' of the LO phonon band should be responsible for these effects. Since the S factor of the LO phonon is considerably large, in the third period the influence from the LO phonon is quite significant, especially on the relative intensity. For example, the LOC + LO + TA band has a significant influence on 2LOC + TA, as well as 3LO on 2LOC + LA. The slight difference between the first- and the second-order local mode energies indicates that there may be a non-linear coupling effect.

3. Discussion and conclusions

In impurity involved optical transitions in semiconductors, there are two kinds of possibly existing phonon related processes, i.e. the CC process and the MC process (Vink *et al* 1974, Monemar and Samuelson 1976). If the Hamiltonians H_e, H_{el} and H_{er} describe the pure electronic part, the electron–phonon interaction, and the external electromagnetic field, respectively, then one can consider that H_{el} and H_{er} are two perturbations to H_e.

Two different ways to treat these two perturbations lead to either multi-phonon optical transitions (CC) or phonon assisted optical transitions (MC):

(i) $\{H_e: \Phi_j^0\} \xrightarrow{H_{el}} \{\Phi_j\} \qquad \{\Phi_i\} \xrightarrow{H_{er}} \{\Phi_f\}$ CC

(ii) $\{H_e: \Phi_i^0\} \xrightarrow{H_{el}+H_{er}} \{H_e: \Phi_f^0\}$ MC.

We can say that the CC process is the transition between two coupling states Φ_i and Φ_f, and the MC process is the transition between two non-coupling states Φ_i^0 and Φ_f^0. In fact they are just two different approximations to real optical transition processes. In real situations, both of these two processes are possible, and which one is dominant depends on the relative magnitudes of H_{el} and H_{er}. Usually deep or localised centres have a strong lattice relaxation which is a key factor in determining the strength of the electron–phonon interaction. So, in general, the CC process is dominant when impurities are deep or localised centres, such as deep D-A pairs in GaP (Vink *et al* 1974, Monemar and Samuelson, 1976), GaP:N and GaP:Bi. Likewise, the MC process is dominant when impurities are shallow centres (shallow donors, shallow acceptors or other non-localised centres), such as shallow D-A pairs in GaP (Vink *et al* 1974), neutral bound excitons on GaP:S and GaP:Zn (Dean *et al* 1967, 1971).

In GaP, recombinations of neutral donor, S, bound excitons and isoelectronic impurity, N, bound excitons are typical MC and CC processes, respectively. In its emission and absorption spectra, the neutral donor, S, bound exciton showed a strong zero-phonon line and weak LA^X, TA^X and TO^X phonon replicas (Dean 1967, Dean *et al* 1971). Since S is a non-localised centre, these phonon replicas are actually similar to the indirect transition of an X point exciton. For the case of the isoelectronic centre, N, the CC process should contribute significantly since N is a very localised centre. We will now give arguments and analysis to show that in the case of GaP:N, all observable phonon sidebands indeed come from the CC process. First, the 'similarity law' in phonon sideband structure is the most direct evidence for a CC process, because the intensities of multi-phonon lines will decrease with increasing order by factors of the Huang–Rhys factor S in CC processes, but by several orders of magnitude in MC processes. Secondly, we should consider the relative strength between CC and MC processes. For the neutral donor, S, bound exciton, the intensities of the LA^X, TA^X and TO^X phonons, which participated in the MC process, were less than 1% of that of the zero-phonon line S^0 (Dean *et al* 1971). For the nitrogen bound exciton, its zero-phonon transition probability is two orders of magnitude larger than that of S^0 (Dean 1970), and its phonon sidebands usually have intensities greater than 10% of that of the zero-phonon line. So, if we attributed a phonon sideband in GaP:N to an MC process, then its transition probability would be at least three orders of magnitude larger for an N centre than for an S donor. This seems scarcely possible because an MC process is very similar to the indirect transition from the band edge states, although it depends on each specific impurity in detail. Thirdly, in the theoretical calculation based on an indirect transition model by Snyder *et al* (1984, 1985), the line shapes of the TA and LA phonon sidebands were quite sensitive to the electron binding energy, and to make the calculated line shapes close to the experimental they had to choose 10 meV for the binding energy. Indeed, 10 meV might be correct for the electron binding energy of an isolated N centre. However, according to the studies of Zheng and Zhang (1986) and Zhang *et al* (1988), the phonon sideband structures for NN_1 and NN_3 pairs are almost the same as that of an isolated N centre, but their electron binding energies are much larger, 120 meV and 41 meV (Cohen and Sturge 1977), respectively. When using the model of Snyder *et al*, one could not expect to get a line

shape comparable to the experimental result. Fourthly, when calculating the radiative decay lifetime by a detailed balance relation, Sturge *et al* (1977) included TA and LA phonon sidebands in the CC process, and their calculation agreed well with experimental results.

In summary, the most important results and conclusions of this work are the following:

For an NN_1 pair centre, the bound exciton has quite a strong interaction with the local vibration mode, which has been shown by the 'similarity law' in its phonon spectrum.

All phonon sidebands of the bound exciton luminescence in GaP:N come from Huang–Rhys' multi-phonon optical transition (i.e. a CC process).

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