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A THEORETICAL STUDY OF PRESSURE BEHAVIOURS OF N AND NN_i TRAPS IN GaP

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We find that the changes of curvatures of the conduction band minima have a crucial influence on the pressure behavious of N and NN_i traps in GaP. The results calculated with a simple model representing such pressure variations of the conduction band show very good agreement with the experiments.

Recently, ZHAO Xue-shu et al. in this laboratory have investigated the photoluminescence of N and NN_i traps in GaP under hydrostatic pressure up to 70 kbar[1]. B.Gil et al. have carried out similar studies at lower temperatures(5K)[2]. Their experimental results on the pressure shifts of the bound exciton lines are reproduced in fig.1.

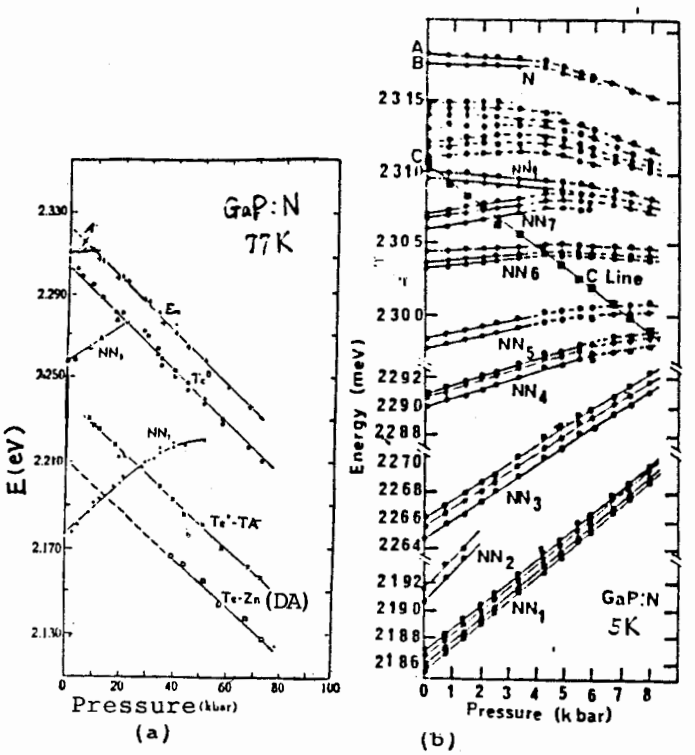

Fig.1 The pressure dependence of the levels of N and NN_i observed by (a) ZHAO Xue-shu et al., (b) B.Gil et al..

As all these excitons lie close to the conduction band, they should be predominently determined by the conduction band states. Morever, they are close to the X minima, which have very large densities of states. Thus it had seemed hard to understand their very different pressure behaviours from the X minima, which have a negative pressure coefficient.

A correct theoretical explanation must account for the following distinct features of the experimental results:

(i) Practically in all cases the exciton level shifts toward higher energy with increasing pressure.

(ii) The deeper is the exciton level, the greater is the pressure coefficient. (NN_2 is an exception whose coefficient is greater than that

of NN_1).

(iii) At higher pressures, the exciton level-pressure relation becomes visibly nonlinear, showing a decrease of pressure coefficient with increasing pressure.

Our investigations have shown that these features in fact follow naturelly from certain changes of the conduction band structure with pressure. The pressure variation of the conduction band of GaP is schematically represented in fig.2. Γ edge shifts upwards at a rate of 10.7meV/kbar and X shifts downwards at a rate of 1.5meV/kbar. It is clear from fig.2 that the curvature of Γ valley should decrease and that of X valley should increase with pressure, as has been found in alloying effect and some other experiments.[3,4] The curvature increases in the case of X valley signifies that the higher up states will shift upwards, despite the minus pressure coefficient of the X band edge. For a level deeper in the gap, the wave function is constituted more of the higher states and the level is hence expected to go up with pressure. But a shallower level will depend relatively more on states closer to the band edge and its pressure coefficient should thus be smaller. Furthermore, if we follow a given level, as it goes up and becomes shallower, the pressure coefficient should be accordingly reduced. This will show up as a nonlinear behaviour at high pressure, as observed in experiments.

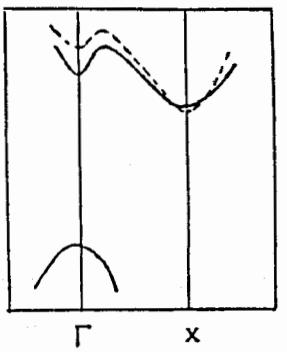

Fig.2 The conduction band of GaP under pressure(dash curve).

The above changes of the conduction band structure with pressure can be somewhat crudely described in terms of the changes of the effective masses. In fact, we have been able to account for the experimental results fairly satisfactorily on this basis, using the Koster-Slater model for the bound state problem:

$$VG(R_0, R_0, E)=1 , \tag{1a}$$

$$G(R_0,R_0,E)=\frac{\Omega}{(2\pi)^3}\int \frac{d^3k}{E-E_c(\vec{k})} . \tag{1b}$$

The Green's function is in Wannier representation. $E_c(\vec{k})$ is the conduction band energy as a function of $\vec{k}$ and V is the on-site impurity potential. (1a) and (1b) determine the bound level E. For a defect pair separated by R_m, we have

$$V(G(R_0,R_0,E)\pm G(R_m.R_0,E))=1 , \tag{2a}$$

$$G(R_m,R_0,E)=\frac{\Omega}{(2\pi)^3}\int \frac{e^{i\vec{k}\cdot\vec{R}_m}}{E-E(\vec{k})}\, d^3k . \tag{2b}$$

The pressure dependence of the bound level E is thus determined completely by the structure of the conduction band $E(\vec{k})$ if we neglect the change of V with pressure. For the construction of $E(\vec{k})$, we have followed Kleiman's procedure[5] by subdividing the BZ into subzones arround Γ, X, L valleys and introducing corresponding effective mass expression for $E(\vec{k})$(parabolic band model). In this model, the pressure dependence of the band structure is simply described by the shifts of the band edge and the changes of the corresponding effective masses. The important parameters used in our calculation are listed in table 1. E_j refers to the energy position of the edge of j valley (relative to the top of the valence band), and $\frac{dE_j}{dP}$ its pressure coefficient. We have neglected the change of m_L under pressure. $\frac{dm_\Gamma}{dP}$ is taken directly from the experimental results for GaAs[3] and $\frac{dm_X}{dP}$ is deduced from the experimental fact that the level bound to single N does not change with pressure at very low pressures(1kbar).

Table 1. The important parameters in our calculations, P(kbar), E(meV)

$E_X=2,332+\frac{dE_X}{dP}P$, $\frac{dE_X}{dP}=-1.5$
$E_\Gamma=2,874+\frac{dE_\Gamma}{dP}P$, $\frac{dE_\Gamma}{dP}=10.7$
$E_L=2,732+\frac{dE_L}{dP}P$, $\frac{dE_L}{dP}=4.0$
$m_X=m_X^0+\frac{dm_X}{dP}P$, $\frac{dm_X}{dP}=-0.0035m_X^0$, $m_X^0=0.36m_e$
$m_\Gamma=m_\Gamma^0+\frac{dm_\Gamma}{dP}P$, $\frac{dm_\Gamma}{dP}=0.007m_\Gamma^0$, $m_\Gamma^0=0.12m_e$
$m_L=m_L^0$, $m_L^0=0.299m_e$

As can be seen in fig.3b, the calculated pressure dependences of the levels associated with N and NN_i in GaP (solid curve) agree very well with the experimental results(dashed curve). Fig.3a shows in particular the calculated results(solid curve) compared with the experimental results(dash curve and dark spot) of Zhao et al., reproducing quite well the observed nonlinear behaviour of NN_1. In table 2 we give the calculated pressure coefficients of N and NN_i traps under low pressure and corresponding experiment values.

Table 2. The pressure coefficients(meV/kbar) of N and NN_i at low pressure

	NN_1	NN_2	NN_3	NN_4	NN_5	NN_6	NN_7	NN_8	NN_9	N
Theory	2.33	1.50	1.12	0.44	0.35	-0.35	0.07	-0.17	-0.11	~0.
Experiment	1.67	2.06	1.26	0.66	0.45	0.19	0.35	/	-0.15	~0.

In the calculation we noticed that the shallower the level,the better is the agreement (including single N). This is easy to understand. For energies close to the band edge, the Green's function is mainly determined by the lower states just above the band edge, which are reasonably

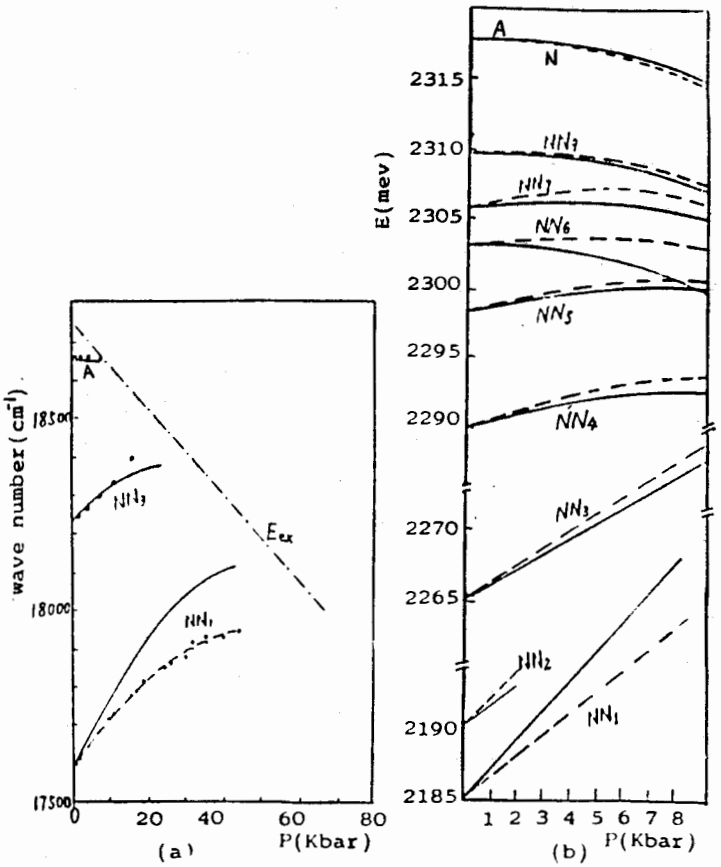

Fig.3 The calculated pressure behaviours of N and NN_i (soild curve) compared with (a) the experimental results of ZHAO Xue-shu et al.[1] (dashed curve and dark spot), (b) the experimental results of B.Gil et al.(dashed curve)[2].

well described by the simple parabolic band model; whereas for energies deeper in the gap, the Green's function depends on more widely spread states in the band, which are bound to show larger deviations from the simple model.

In summary, we have made a theoretical study on the pressure behaviours of N and NN_i traps in GaP. Our major conclusion is that the changes of the curvatures of the energy valleys have a crucial influence on the pressure behaviours of these isoelectronic traps, and that such effects can be satisfactorily described in terms of pressure-dependent effective masses associated with the X and Γ valleys.

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