Nitrogen states in Ga(As,P) and the Koster-Slater model*

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Recent photoluminescence data in Ga(As,P):N as a function of P fraction, x, indicates the existence of three states associated with isolated nitrogen impurities for $x \lesssim 0.47$. For $x \gtrsim 0.47$, however, only one state has been measured with photoluminescence. This state, N_X, has been described by a Koster-Slater model in recent work and the numerical agreement between the predictions of these calculations and the data was thought to support the model. We show that the model is extremely sensitive to parameters used in calculations and that such numerical agreement does not justify the model. The only support for the Koster-Slater model is the observation of a single state. Recent electromodulation data indicate the existence of two states.

I. INTRODUCTION

The isoelectronic-impurity nitrogen in III-V mixed-crystal alloys [particularly Ga(As, P)] has been studied intensively because of fundamental scientific and practical aspects of its optical properties[1]: it is strongly luminescent even in indirect-semiconductor host crystals.[1,2] This property, combined with the development of high-quality vapor-phase epitaxial Ga(As, P) crystals and the ease of fabrication of p-n junctions, has made possible the commercial production of yellow Ga(As, P):N light-emitting diodes,[1] for example. More fundamentally, nitrogen has been thought[1,2] to be a classic instance of short-range impurity (as opposed to the common hydrogenic donors and acceptors in semiconductors).

Recent experimental data,[3-10] however, indicate that the nitrogen potential in Ga(As, P) is more complicated than in the simple short-range (i.e., Koster-Slater[11]) model considered in previous work.[2,12-18] Instead of the single state predicted by the Koster-Slater model,[2,11-18] there are *three* states observed[3-10] which can be associated with isolated nitrogen centers [i.e., N_X, N_Γ, and N'_Γ displayed in Fig. 1 (Refs. 10 and 19)]. The energy of the lowest, N_X, decreases monotonically with decreasing mole fraction of P, x (i.e., $x=1.0$ corresponds to GaP), and is associated with the X-conduction-band minimum, as indicated by pressure measurements.[5] The next-higher state N_Γ follows the Γ minimum for $x \lesssim 0.42$, bends over for $x \simeq 0.42$, and then follows the X minimum for $x \gtrsim 0.42$ (Ref. 5) until $x \simeq 0.47$; there has been no observation of N_Γ for $x > 0.47$. Measurement of the highest state N'_Γ has been recently reported[10] and its characteristics are displayed in Fig. 1 (Refs. 10 and 19) (in this context, it is interesting to note that this observation[10] was preceded by the theoretical prediction[6,20] of N'_Γ).

These data are in agreement with a new theory[6,8,20] in which the nitrogen potential is described by a mixture of a long-range potential (V_l) and the usual[2,12-18] short-range potential (V_s). This theory predicts three states, as exhibited in Fig. 2. They are produced by hybridizing the usual short-range state[2,11-18] [which corresponds to $V_l = 0$ in Fig. 2(a)] and long-range states associated with the Γ and X minima [which correspond to $V_s = 0$ in Fig. 2(a)]. From Fig. 2(b), it is clear that all the general features[10,19] of N_Γ, N'_Γ, and N_X in Fig. 1 for $x \lesssim 0.47$ are described well by the three hybridized states predicted by this theory (the details are reported elsewhere[6,20]).

In the composition range $0.47 \lesssim x$, however, only one state has been observed[3-8,10] (i.e., N_X in Fig. 1). A possible explanation is that N_Γ is higher in energy in this composition range than has been supposed[6,20] [i.e., than is illustrated in Fig. 2(b)] and, therefore, has escaped observation. Recent data[21,22] from electromodulation spectroscopy, in

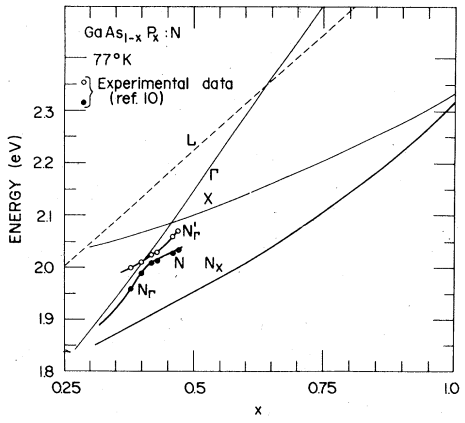

FIG. 1. Photoluminescence data indicating the concentration dependence of Γ, L, X, and the peaks associated with electronic states of isolated nitrogen impurities in Ga(As, P) (after Refs. 10 and 19).

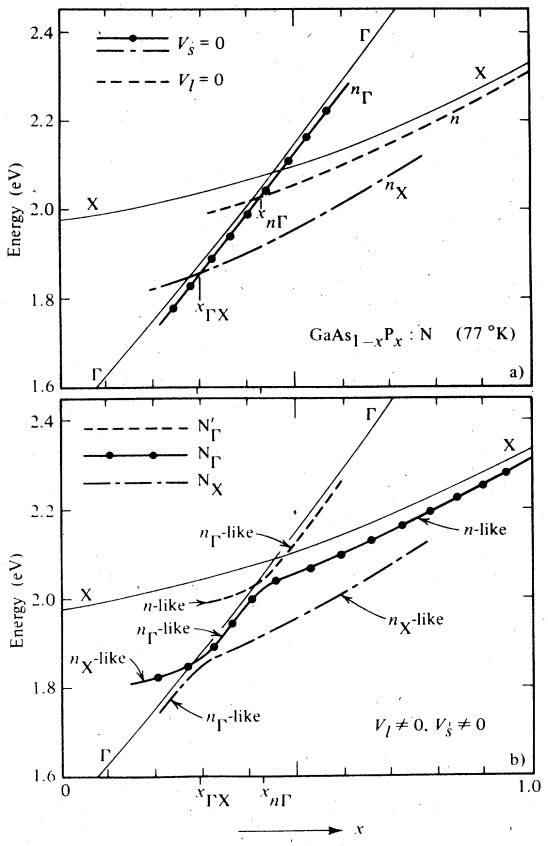

FIG. 2. (a) Schematic illustration of composition dependence of the energies of bound states in Ga(As, P) associated with the Γ (n_Γ) and X (n_X) conduction-band minima which are produced by the long-range potential (V_l) in the absence of the short-range isoelectronic potential (V_s). Also displayed is the energy of the state n produced by V_s (in the Koster-Slater approximation) when $V_l = 0$, which is the subject of previous work (Refs. 12–18). In this figure, the effects of L are neglected (after Ref. 6). (b) Schematic illustration of states resulting from the combined potential $V_s + V_l$ (where V_s is treated within the Koster-Slater approximation). In the region where the energies of the n and n_Γ states (i.e., $x \simeq x_{n\Gamma}$) and the n_Γ and n_X states (i.e., $x \simeq x_{\Gamma X}$) cross, a splitting into two branches occurs. Effects of L are neglected (after Ref. 6).

fact, suggest the presence of two states.

If, however, we interpret the observation[3-8,10] of only N_X for $x \gtrsim 0.47$ as meaning that there is only one state present at these compositions, it is attractive to attribute[23-25] N_X to a Koster-Slater type of potential.[2,12-18] Within this model, the decreasing energy of N_X with decreasing x could then quite plausibly be associated with increasing strains and increasing proportion of As,[13,14,23] which would be reflected in an increasing Koster-Slater-potential parameter.[13,14,23]

Another possible contributing factor (within the Koster-Slater model) to the decrease in the energy of N_X stems from the recent important discovery[24,25] that L (Ref. 26) in GaAs lies 170 ± 30 meV below X, in contrast to traditional beliefs.[24,25] This discovery[24,25] led to a reinterpretation of previous results in GaAs which had been used to support a model in which L was ignored.[24,25] These new results for L were used to extrapolate a possible x dependence of the energy of L in Ga(As, P).[24,25] The energy of N_X was calculated within a putative two-level version of the Koster-Slater model and the resulting good agreement between theory and experiment was thought to demonstrate "conclusively the importance of the L_6^C wave-function components in the isoelectronic trap."[24,25]

In this paper, we demonstrate that the energy of the Koster-Slater state is, indeed, sensitive to the presence of L (although the two-level model[24,25] is not a very accurate representation of the solution of the Koster-Slater model[11]). But, the energy is also extremely sensitive to the model used to represent the conduction band. Therefore, given the uncertainties in the band structure (or density of states) as well as in the value of the energy of L (Refs. 24 and 25) and combining this with the reasonable assumption that the Koster-Slater parameter depends upon x, it seems that a good agreement[23-25] between experimental energies and the Koster-Slater model cannot be used to conclude anything meaningful about either the validity of the model or the importance of any contributing factor such as L (Refs. 24 and 25) (although the effect of L must be considered in future calculations).

It seems, therefore, that the strongest support for the Koster-Slater-model (as opposed to the Kleiman model[6,8,20]) description of N_X in Ga(As, P) for $x \gtrsim 0.47$ is just the fact that only one state is observed[3-8,10] in photoluminescence. It is difficult, however, to reconcile this model with the experimental data for $x \lesssim 0.47$ (which the Kleiman theory describes well[6,8,20]). In addition, the effects of L and increasing As content further complicate interpretations within this model. In the Kleiman theory,[6,20] on the other hand, N_X is derived from X by a long-range potential (so that its energy is relatively insensitive to band structure—that is, the position of L), whereas N_Γ corresponds to a Koster-Slater state (which may explain the uncertainty in its energy for $x \gtrsim 0.47$ and the apparent discrepancy between theory and experiment in that region). Furthermore, recent electromodulation data[21,22] seem to indicate two states rather than one.

II. KOSTER-SLATER MODEL AND N_X

In the one-band one-site Koster-Slater model,[11-18] the potential V is assumed to be so localized at a site $\vec{R}_0$ that its matrix elements between Wannier states $|\vec{R}_n, s\rangle$ associated with lattice site $\vec{R}_n$ and band s are given by the following equation:

$$\langle \vec{R}_m, t | V | \vec{R}_n, s\rangle = V_0 \delta_{mn} \delta_{m0} \delta_{st} \delta_{sc} , \tag{1a}$$

where V_0 is the Koster-Slater[11] parameter and c denotes the band to which V couples (i.e., the lowest conduction band in our system). Equation (1a) requires that the matrix elements between Bloch states $|\vec{k}, s\rangle$ associated with momentum $\vec{k}$ and band s be constant and independent of momentum

$$\langle \vec{k}', t | V | \vec{k}, s\rangle = (V_0/N) \delta_{st} \delta_{sc} , \tag{1b}$$

where we assume N unit cells in the host crystal.

The Wannier and Bloch-state representations lead to two exact equations for the energy eigenvalue of the impurity state (i.e., E_{N_X} in our problem)

$$V_0 G(0, E_{N_X}) = 1 , \tag{2a}$$

and, equivalently, in the Bloch representation,

$$\det | S - E_{N_X} I | = 0 . \tag{2b}$$

In Eq. (2a), G is the one-electron Green's function of the host crystal in the Wannier representation

$$\begin{aligned} G(0,E) &\equiv \frac{1}{N} \sum_{\vec{k}} \frac{1}{E - E_c(\vec{k}) + i\delta} \\ &= \int_{-\infty}^{\infty} dt \, \frac{\rho_c(t)}{E - t + i\delta} , \end{aligned} \tag{2c}$$

where E_c and ρ_c are the conduction-band dispersion relation and density of states, respectively, and $\delta \to 0^+$.

In Eq. (2b), the $N \times N$ matrix S has elements

$$S_{\vec{k}\vec{k}'} = E_c(\vec{k}) \delta_{\vec{k}\vec{k}'} + V_0/N$$

and I denotes the corresponding $N \times N$ identity matrix. Since both L and X have high, approximately equal, masses and densities of states,[24] Eq. (2b) was approximated by a two-level model[24,25]

$$\det \begin{vmatrix} E_L(x) - E_{N_X} & U_1 \\ U_1 & E_X(x) - E_{N_X} \end{vmatrix} = 0 \tag{3a}$$

where E_L and E_X denote the x-dependent energies of L and X, respectively, and U_1 is a potential parameter (not equivalent to V_0) which is to be determined from experiment.

From the forms of Eqs. (2), which involve all momenta, neither the accuracy of a two-level model, in general, nor the derivation of Eq. (3a) according to a specific approximation, in particular, is clear. Leaving aside the question of the accuracy of a two-level model for the moment, we can show that a different equation from Eq. (3a) is a logical consequence of the assumption that the masses and densities of states at L and X (assumed equal) dominate. According to this assumption,

$$\rho_c(t) \simeq \rho_X(t - E_X) + \rho_L(t - E_L) ,$$

$$\rho_L(t) \simeq \rho_X(t) \simeq C\delta(t) ,$$

where ρ_L (ρ_X) is the density of states associated with L (X) and C represents the number of states in either L or X. Inserting these expressions into Eqs. (2a) and (2c), we can easily derive

$$\begin{vmatrix} E_L(x) - E_{N_X} + U_2 & U_2 \\ U_2 & E_X(x) - E_{N_X} + U_2 \end{vmatrix} = 0 , \tag{3b}$$

$$U_2 \equiv V_0 C . \tag{3c}$$

Equation (3b) is a two-level approximation consistent with the full Koster-Slater model[11] in Eqs. (2). Moreover, the potential parameter U_2, in Eq. (3b) is explicitly related to the Koster-Slater parameter V_0, in contrast to U_1 in Eq. (3a).

The question of the accuracy of two-level models leads us naturally to calculations within the Koster-Slater model. In the numerical calculations which follow, we choose the following values for the conduction-band minima[24,25]:

$$E_\Gamma(x) = 1.508 + 1.192x + 0.174x^2 , \tag{4a}$$

$$E_X(x) = 1.971 + 0.159x + 0.202x^2 , \tag{4b}$$

$$E_L(x) = 1.802 + 0.77x + 0.16x^2 . \tag{4c}$$

These values differ from those preferred by other workers,[1] but suffice for our purposes. In order to study the influence of L on the band structure, we specify G by two different models used in previous work[13-14,20] (we consider only states in the gap, so that $\mathrm{Im}(G) \propto \rho_c = 0$ at these energies). One model[20] is

$$\mathrm{Re}[G(0,E)] = \Lambda_\Gamma(E) + 3\Lambda_X(E) + 4\Lambda_L(E) , \tag{5a}$$

$$\Lambda_i(E) = -\left(\frac{m_i \Omega}{\pi^2 \hbar^2}\right) k_i \left[1 - |r_i| \tan^{-1}\left(\frac{1}{|r_i|}\right)\right] , \tag{5b}$$

$$r_i \equiv S_i/k_i , \quad S_i^2 = 2m_i(E - E_i/\hbar^2 . \tag{5c}$$

In Eqs. (5), the unit cell volume $\Omega = \frac{1}{4}[d(x)]^3$, where $d(x)$ is the lattice constant in Å, $d(x) = 5.65 - 0.20x$. From fitting to empirical pseudopotential densities of states, as in previous work,[13,14] we find $k_\Gamma = 1.397/d(x)$, $k_X = 3.797/d(x)$, and $k_L = 2.595/d(x)$. In addition, we set $m_\Gamma/m_0 = 0.068$

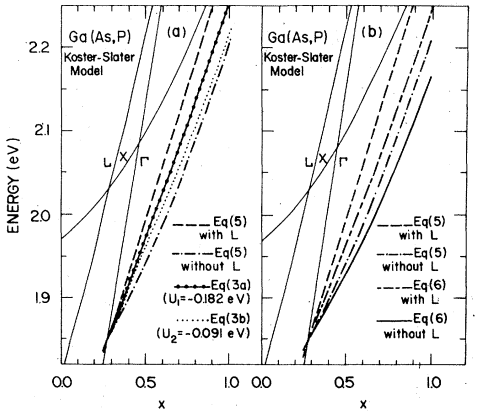

FIG. 3. (a) Comparison of composition-dependent energy calculations for N_X in Ga(As, P) within the Koster-Slater approximation for two-level models [i.e., Eqs. (3)] and the full calculations using the model of Eqs. (5) with and without L. The parameters U_1 and U_2 and V_0 in Eqs. (2) and (3) were determined by setting E_{N_X} =1.848 eV for $E_L = E_X$. The intrinsic uncertainty of the two-level models is illustrated. Energies of the Γ, L and X minima are indicated. (b) Comparison of full Koster-Slater model calculations for two different models of the density of states [i.e., Eqs. (5) and (6)]. The potential parameters were determined by setting E_{N_X} =1.848 eV for $E_L = E_X$. The effects of including L and the sensitivity to band density of states are indicated.

$+0.052x$ and $m_X = m_L = 0.35 m_0$ (where m_0 is the free-electron mass).

Another model[13,14] is given by

$$\mathrm{Re}[G(0,E)] = R_\Gamma(E) + R_X(E) + R_L(E), \tag{6a}$$

$$R_i(E) = \pi C_i \Delta_i [u_i + (u_i^2 - 1)^{1/2}], \tag{6b}$$

$$u_i \equiv (E - E_i - \Delta_1)/\Delta_1 . \tag{6c}$$

The parameters for this model corresponding to the same band-structure calculation[13,14] are $C_\Gamma = 0.0115$ eV^{-2}, $\Delta_\Gamma = 0.8$ eV, $C_L = 0.1070$ eV^{-2}, $\Delta_L = 1.325$ eV, $C_X = 0.1838$ eV^{-2}, and $\Delta_X = 1.55$ eV. Neither of the models in Eqs. (5) or (6) is *a priori* more correct.

In Fig. 3, we illustrate the results of these computations, where we normalize E_{N_X} to the experimental energy at $x = 0.28$ (i.e., when $E_L = E_X$) as in previous work.[24,25] From comparing the two-level-model[24,25] descriptions [i.e., Eqs. (3)] with more rigorous results using the model Green's function in Eqs. (5), we reach two important conclusions. One is that the two-level-model energies deviate considerably from each other, indicating the intrinsic uncertainties in such models. The other conclusion is that these differ markedly from the results of a more rigorous solution of the Koster-Slater model. In fact, the two-level curves in Fig. 3(a) are closer to the results produced from neglecting L than to those including L. It is clear, therefore, that agreement between the two-level models and experiment cannot yield any information concerning the effect of L upon N_X.[24,25]

In Fig. 3(b), we compare the energies calculated using the Green's-function models in Eqs. (5) and (6). This figure clearly shows the sensitivity of the results to the model used to describe the density of states [see Eq. (2c)]. Indeed, using Eqs. (5) without L and Eqs. (6) with L yields energies whose difference is less than that between energies calculated with and without L in either model.

It is, therefore, clear that good agreement between a Koster-Slater-model calculation and experimental data must be considered as having little physical significance.[24,25] The only support for a Koster-Slater-model description of N_X in Ga(As, P) is, therefore, the experimental observation of only N_X in the region $x \gtrsim 0.47$. Recent electromodulation data[21,22] indicate the presence of two states in this region, lending support to the Kleiman model.[6,20]

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[26]We use the symbols Γ, X, and L as shorthand for Γ_6^c, X_6^c, and L_6^c, respectively.