Phonon sidebands of excitons bound to isoelectronic impurities in semiconductors

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The configuration coordinate (CC) and momentum conservation (MC) models have been widely used to explain the phonon sidebands of impurity spectra in semiconductors. In this paper, the distinction between the CC and MC models is discussed. We conclude that the MC model only applies to shallow Coulombic impurities; in other cases, such as isoelectronic traps, the CC model is more appropriate. We show that the Huang-Rhys parameters for bulk phonon modes coupling to a bound electron or exciton can be calculated from the bound-state wave function in k space if the phonon-induced intervalley and intravalley electron scattering processes of the pure crystal are known. We study in detail the phonon sidebands of nitrogen-bound excitons in GaP, giving the selection rules for electron-phonon coupling in the CC model, and showing that their strength can be well accounted for by the CC model. The apparently anomalous "X" peak of the LO-phonon sideband in GaP:N is shown to be associated with intervalley scattering in the conduction band. The MC model, which has been used in an attempt to explain the phonon sidebands of GaP:N in some previous work, is shown to be inapplicable to this case.

I. INTRODUCTION

It has been known for a long time that impurity spectra in semiconductors may show two kinds of phonon sidebands (PS's) which can be interpreted by either the "configuration coordinate" (CC) or the "momentum conservation" (MC) models.[1] The CC model[2] is a simplified version of the multiphonon optical transition theory proposed by Huang and Rhys[3] and Pekar[4] about 40 years ago. The MC model, on the other hand, is a natural extension to impurity spectra[5] of the theory of indirect transitions in a perfect semiconductor.[6] These two models have been used to explain the PS's in many impurity associated spectra, but the relationship between them has not been adequately discussed. For this discussion, we first need to know if these two models correspond to two coexisting mechanisms of electron-phonon interactions or if they are just two different approximations to describe the interactions. In the former case, they could be taken as two independent processes, and the total transition cross section of the PS's would be the sum of the contribution from the two processes,[7] or in other words, the two models could be combined to explain the observed PS's.[8] But the problem is not that simple since, as has been pointed out before[9] and will be discussed in further detail in this paper, they are, in fact, two different approximations to the same basic method for calculating the phonon-assisted optical transition probabilities involving an impurity. Therefore, the two models must be combined with caution.

While the PS's of excitons bound to shallow Coulombic impurities (donors and acceptors), have been interpreted in terms of the MC model,[1] the PS's of excitons bound to nitrogen and other isolectronic impurities in GaP have been consistently interpreted in terms of the CC model.[10–14] However, Snyder and coworkers[5] and Dai *et al.*[8] have argued that all the PS's of the isolated N-bound exciton except the LO(Γ) peak should also be interpreted by the MC model. They showed that they could account for the spectral shape of the PS's in this model, but did not discuss its absolute intensity. Hong, Zhang, and Dou[15] have also applied the MC model in an attempt to account for an apparently anomalous temperature dependent of the PS's.[16–18] However, this anomaly has been shown to be an experimental artifact.[13,14,19,20] In Ref. 8 it was argued that the CC model can be applied only to LO(Γ) phonons, which couple to the exciton via the Fröhlich interaction. Other phonon features could not be explained by the CC model because "the k-dependent effects of both the impurity wave function and the phonon energy are not included in the model."[8] This is incorrect: such effects have been included in the CC model, for instance by Stoneham.[21] In this paper we will formulate the CC model in a way that includes such k-dependent effects. The model accounts semiquantitatively for all the PS's, including the so-called "X" sideband whose interpretation has been controversial. We will also show that the MC model accounts quantitatively for the PS intensity of excitons bound to Coulombic impurities, but fails by many orders of magnitude to account for that of excitons bound to isoelectronic traps such as nitrogen.

In Sec. II of this paper, we will discuss the distinction between the CC and the MC models, how they are related, and how they differ in their predictions of the optical transition rate for the PS's and for the no-phonon (NP) line. We show how for bulk-mode phonons the Huang-Rhys parameters S, which represent the strength of the exciton-phonon coupling and determine the intensities of the PS's in the CC model, relate to the intravalley and intervalley electron-phonon scattering processes of the in-

trinsic semiconductor. Based on these scattering processes, an (in principle) accurate way of calculating the S parameters is given. In Sec. III, we apply our calculations to excitons bound to an isoelectronic trap, using the Hopfield-Thomas-Lynch (HTL) model,[22] as developed recently by one of us,[23] to model the exciton state, and show that while the MC model cannot explain the observed intensities of the PS's of nitrogen-bound excitons in GaP, the CC model does. Symmetry selection rules for the phonons which can be involved in the optical transition are also discussed. Section IV gives a summary of the work.

II. FORMALISM

In a crystal which contains an impurity, within the Born-Oppenheimer approximation, the wave function for the system has the form

$$\Psi_{jn}=\Phi_j(\mathbf{x},\mathbf{Q})\chi_{jn}(\mathbf{Q}) , \tag{1}$$

where $\Phi_j(\mathbf{x},\mathbf{Q})$ and $\chi_{jn}(\mathbf{Q})$ are the electronic part and the phonon part, and $\mathbf{x}$ and $\mathbf{Q}$ are coordinates of electrons and lattice ions, respectively.

For the optical transitions with phonon participation, there are two basic approximations, i.e., the CC and the MC models, in calculating the transition rates.

In the CC model, we first consider the electron-phonon interaction H_{EL} to the uncoupled states of the total system $\{\Phi_j^0\chi_n^0\}$, and obtain the coupled states $\{\Phi_j\chi_{jn}\}$. In general, both the electron states Φ_j and the phonon states χ_{jn} are modified from the uncoupled states. However, here we will adopt the Condon approximation, in which the electronic state is unaffected by the phonon interaction so that the optical transition is between two coupled states $\Phi_i^0\chi_{in}$ (subscript i stands for the initial state) and $\Phi_f^0\chi_{fn'}$ (f stands for the final state).

In the MC model, the optical transition rate is usually calculated by applying second-order time-dependent perturbation between the initial state $\Phi_i^0\chi_n^0$ and the final state $\Phi_f^0\chi_{n'}^0$. This is, in fact, equivalent to another procedure:[2] first apply H_{EL} to the electronic parts $\{\Phi_j^0\}$ of the uncoupled states $\{\Phi_j^0\chi_n^0\}$ to yield coupled states $\{\Phi_j\chi_n^0\}$ (note that the phonon parts are unchanged); and then consider the optical transition between the initial state $\Phi_i\chi_n^0$ and the final state $\Phi_f\chi_{n'}^0$.

The CC and the MC models, as used here, both assume linear electron-phonon coupling, but differ as follows: the CC model considers the electron-phonon interaction to infinite-order perturbation in the phonon states, but only to zeroth-order perturbation in the electron states (the Condon approximation). The MC model treats the electron-phonon interaction as a perturbation in the electron states, but not in the phonon states. In this sense, they are two distinct mechanisms. However, in principle, the CC model can go beyond the Condon approximation by taking into account the effect of the electron-phonon interaction on the electron wave functions, as, for example, in the theory of multiphonon nonradiative transitions.[24] If this is done, there will be an MC-like contribution in the optical transition matrix element; but this is a higher-order effect. We are not going to pursue this extension in this paper, but we must point out that such an extension might in fact be necessary to explain some fine structure in the observed spectra, such as the very weak sharp peak at the TA(X) phonon energy riding on the broad PS's in the excitation spectrum of GaP:N.[25] In either model, we may have the same mechanisms of electron-phonon interaction [Fröhlich (polar), deformation potential, piezoelectric].

A. CC model

According to the theory of Huang-Rhys and Pekar,[3,4,24] with linear electron-phonon interaction, the optical transition rate for the NP line is

$$F_{\mathrm{CC}}(W_{\mathrm{if}})=(2\pi/\hbar)|M_{\mathrm{if}}|^2e^{-S} , \tag{2}$$

where W_{if} is the separation of the electronic states in the relaxed lattice; i.e., the transition energy of the NP line, $M_{\mathrm{if}}=\langle\Phi_f^0|H_{ER}|\Phi_i^0\rangle$ is the transition matrix element in the Condon approximation, and H_{ER} is the interaction of the electrons with the external electromagnetic field. For the transition emitting one phonon $\hbar\omega_q$, the corresponding transition rate is

$$F_{\mathrm{CC}}(W_{\mathrm{if}}-\hbar\omega_q)=(2\pi/\hbar)|M_{\mathrm{if}}|^2e^{-S}S_q \tag{3}$$

where $S=\Sigma_qS_q$. S_q is the so-called Huang-Rhys parameter for the vibration mode $\hbar\omega_q$ and is defined as

$$S_q=[1/(\hbar\omega_q)^2]|\langle\Phi_f^0|U_q|\Phi_f^0\rangle-\langle\Phi_i^0|U_q|\Phi_i^0\rangle|^2 , \tag{4}$$

where U_q is the potential energy of the electron-phonon interaction.

In general, the PS structure is determined by the density of states of the phonons $g(\omega)$ and the spectrum of S_q. For an explicit calculation of S_q, we must be able to calculate the matrix elements $\langle\Phi_j^0|U_q|\Phi_j^0\rangle$ for both initial and final states, which requires the knowledge of the impurity state wave function and of the electron-phonon interaction. The selection rules for the possible phonon modes involved in the PS's are determined by whether $\langle\Phi_f^0|U_q|\Phi_f^0\rangle-\langle\Phi_i^0|U_q|\Phi_i^0\rangle$ is nonzero. Up to this point, we have talked about transitions of the total system, and the transition rates are given in terms of many-electron quantities. In most cases, however, they can be calculated in terms of one-electron quantities, as we do in this paper.

Now we are going to apply the theory to an exciton bound to an isoelectronic (i.e., electrically neutral) impurity. To do so we use the HTL model[22] of the exciton. In this model the impurity is assumed to exert a short-range attractive potential on one type of carrier: in the case of nitrogen in GaP this is the electron. The electron bound by this potential produces an attractive Coulomb field for the hole, which thus occupies an acceptorlike state. This model has been shown to account quantitatively for the energy-level structure of excitons bound to nitrogen pairs in GaP,[23,25] and has been used to obtain the wave function of the exciton bound to isolated nitrogen.[23]

The electron bound state in the HTL model can be generally represented by a sum of Bloch states φ_{nk},[26]

$$\varphi_i^0=\Sigma_{nk}a_{nk}\varphi_{nk} . \tag{5}$$

If the acceptorlike bound exciton state is taken as the initial state, and the ground state of the crystal as the final state, we have

$$M_{\rm if}=\Sigma_{nk}\,A_k a_{nk}\langle\varphi_{vk}|H_{er}|\varphi_{nk}\rangle\ , \tag{6}$$

$$S_q=[1/(\hbar\omega_q)^2]|\langle\varphi_i^0|u_q|\varphi_i^0\rangle -\Sigma_k|A_k|^2\langle\varphi_{vk}|u_q|\varphi_{vk}\rangle|^2\ , \tag{7a}$$

or in k space

$$S_q=[1/(\hbar\omega_q)^2]|\Sigma_{n'n}\Sigma_k a^*_{n'k+q}a_{nk}\langle\varphi_{n'k+q}|u_q|\varphi_{nk}\rangle -\Sigma_k|A_k|^2\langle\varphi_{vk}|u_q|\varphi_{vk}\rangle|^2\ , \tag{7b}$$

where A_k is the Fourier transform of the envelope function $F(r)$ for the hole motion,[23] φ_{vk} is the valence-band state, H_{er} and u_q are the one-electron operators corresponding to H_{ER} and U_q for many electrons.

From Eq. (7) we can see how the electron and the hole of a bound exciton contribute to the exciton-phonon coupling. Because the matrix element $\langle\varphi_{vk}|u_q|\varphi_{vk}\rangle$ is zero unless $q=0$, the hole contribution is negligible for a deep impurity center[27,28] and S_q is only determined by the electron bound state. Equation (7) has taken into account the Coulomb correlation between electron and hole, so it is more general than the well-known result[29,30] where the Coulomb correlation is neglected.

If we use the one-band approximation for the electron bound state, and neglect the contribution from the hole, we have

$$S_q=[1/(\hbar\omega_q)^2]|\Sigma_k a^*_{k+q}a_k\langle\varphi_{ck+q}|u_q|\varphi_{ck}\rangle|^2\ . \tag{8}$$

In practice, in order to calculate the Huang-Rhys parameter S_q, we need to know the detailed wave function, given by a_{nk}, as well as all the scattering matrix elements $\langle\varphi_{n'k+q}|u_q|\varphi_{nk}\rangle$. Therefore the shape of the PS's are not only determined by the density of states (DOS) of the phonons,[1] but also by the electronic wave function and the scattering matrix elements. For interaction with a bulk mode, u_q is the same as in the perfect crystal, since the change of bulk modes induced by introducing a finite number of impurities is vanishingly small.[31] For a local or quasilocal mode, however, u_q is determined by each specific impurity center. In the above theory, u_q is not limited to any specific interaction mechanism.

B. MC model

In the MC model, $H_P=H_{EL}+H_{ER}$ is taken as the perturbation to the uncoupled state $\{\Phi_j^0\chi_n^0\}$. The first-order perturbation theory gives the transition rate of the NP line

$$F_{\rm MC}(W_{\rm if}^0)=(2\pi/\hbar)|M_{\rm if}|^2\ , \tag{9}$$

where $W_{\rm if}^0$ is the separation of the uncoupled electronic states, and the matrix element $M_{\rm if}$ is the same as that in the CC model. The most obvious difference between (9) and (2) is the exponential factor e^{-S}. They are equivalent only when $S\ll 1$ (very weak lattice relaxation). Also, the NP line energy is different. The CC model includes the lattice relaxation and gives a polaron correction, while the MC does not. This is important in determining the position of the NP line, because not only the Fröhlich interaction but also the other interactions (e.g., deformation potential) contribute to the polaron correction.[30] While the correction due to the Fröhlich interaction is not very much different for band-edge states and bound states, that due to the deformation interaction can be very different and can affect the binding energy significantly.

The second-order perturbation gives the transition rate of the one-phonon transition between the acceptorlike bound exciton state and the ground state (see the Appendix),

$$F_{\rm MC}(E-\hbar\omega_q)=\frac{2\pi}{\hbar}|M_{cv}|^2\left|\sum_k A_{\rm ex}(k)\right|^2\left|\sum_k A^*_{\rm ex}(k)A_k\sum_n a_{nq+k}\frac{\langle\varphi_{ck}|u_q|\varphi_{nq+k}\rangle}{E_{\rm ex}-E-\hbar\omega_q}\right|^2\ , \tag{10}$$

where $M_{cv}=\langle\varphi_{v0}|H_{er}|\varphi_{c0}\rangle$, E is the bound exciton state, $E_{\rm ex}$ is the ground state of the free exciton at Γ associated with the first conduction band, and $A_{\rm ex}(k)$ is the Fourier transform of the envelope function $F_{\rm ex}(r)$ for the free exciton. We have assumed that the Γ state is the only significant intermediate state. For phonons with a wave vector near the conduction-band minimum k_0, the transition rate given by (10) cannot exceed the transition rate of the indirect excitons, and will not greatly change from one kind of impurity to another.

In calculating the transition rate of a PS microscopically, the MC model only considers the scattering processes between the $\mathbf{k}=\mathbf{q}$ point and Γ. The CC model includes the contribution from scattering between two general points $\mathbf{k}$ and $\mathbf{k}'$, as long as $\mathbf{k}'-\mathbf{k}=\mathbf{q}$ and the process is allowed by the symmetry selection rules. For the MC model, the weaker the localization of an impurity state (i.e., the more concentrated in k space), the greater the ratio of the PS to the NP line in an indirect-gap semiconductor. For the CC model, the tendency is the other way: the more localized the state, the stronger the lattice relaxation will usually be, and thus the stronger the PS becomes. On the other hand, for the limiting case of a very delocalized state $a_{\mathbf{k}}\sim\delta_{\mathbf{k},\mathbf{k}0}$, the transition rates of the NP and the PS are zero in the CC model (within the Condon approximation) because a_Γ is zero, while in the MC model, they are nonzero for the PS as a_q is not zero. In the CC model, the NP line and all the PS's have the same matrix element $M_{\rm if}$, and the total transition rate is distributed among the NP line and the PS's. In the MC model, the NP line and the PS's are independent, since PS's are possible regardless whether or not the NP line appears, as long as $a_{\mathbf{q}}$ and the scattering matrix element $\langle\varphi_{c0}|u_q|\varphi_{cq}\rangle$ are not zero.

From the above argument we conclude that in the case of impurity-involved optical transitions, the MC model is only applicable for very delocalized impurity states, where $S_q \ll 1$ for all the vibration modes $\hbar\omega_q$.

A concrete calculation of S_q is rather difficult. Ridley[32] did a simplified calculation for some materials which shows how S depends on the degree of localization of the impurity states. In the next section, we will calculate S_q for the PS's of the A line in GaP:N.[33,34]

III. THE PS's OF N-BOUND EXCITONS IN GaP

A. Is the MC model applicable to GaP:N?

The phonon sidebands of N-bound excitons have been measured several times since the first investigation of GaP:N (Ref. 33) and are shown in Fig. 1 (Ref. 11) (this spectrum is taken at 4.2 K, where A-line emission is predominant). Those PS's which are believed to be associated with bulk modes are labeled LO(Γ), X, TO(Γ), LA, and TA. TA and LA are broadbands, while LO(Γ), X, and TO(Γ) are sharp, TO(Γ) being very weak. Comparing the PS spectrum to the phonon DOS,[35] we find that all the PS peaks are close to, if not exactly at, the peaks of the DOS. The relative intensities, however, are quite different from the DOS. Furthermore, not all the peaks of the DOS show as peaks in the spectrum. The X band at 48.4±0.1 meV (Ref. 13) is close to a DOS peak at about 48.6 meV,[35] and the LA band at 26.7±0.4 meV (Ref. 13) is close to a DOS peak at about 27 meV.[35] The TA band at 13.3±0.2 meV (Ref. 13) is slightly higher than the nearest DOS peak at about 11.4 meV,[35] but the DOS corresponding to this PS peak is still quite large. The same bulk phonons are seen for both isolated N and NN_i pair centers.[13,14] A local mode sideband has also been observed for most NN_i pair centers.[34]

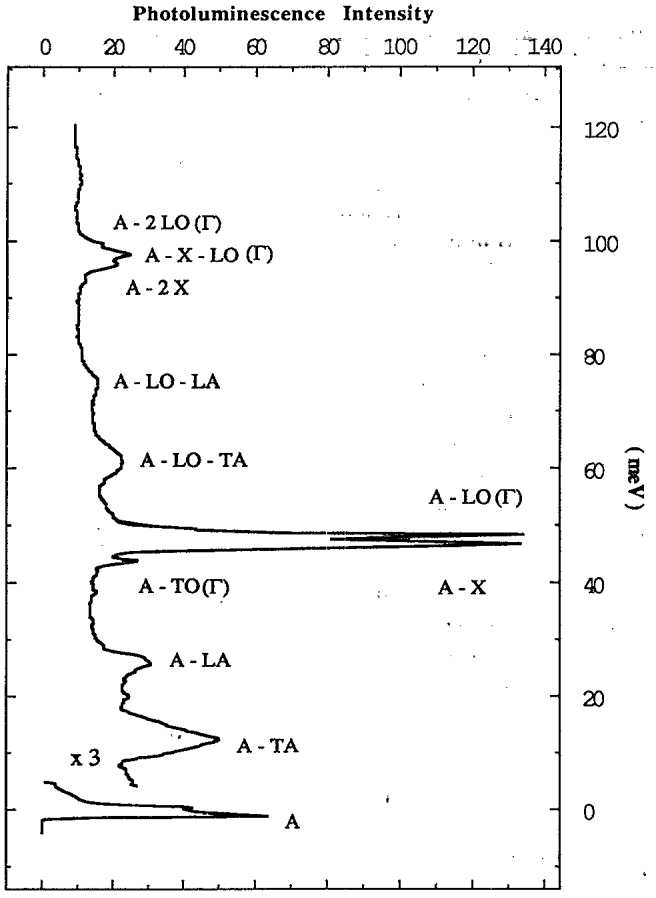

FIG. 1. Photoluminescence spectrum of the isolated nitrogen-bound exciton in GaP (T=4.2 K, A line at 2.317 eV. Excitation: 2.328 eV, $[N]=10^{16}$ cm^{-3}) (Ref. 11).

As we have already discussed in Sec. II, the MC model should be only applicable to very delocalized impurity states. For the localized impurity states associated with nitrogen in GaP, in some key aspects, the MC model cannot be consistent with the experimental results for the following reasons, some of which have been mentioned before.[9]

(1) The PS's of excitons bound to neutral shallow donors and acceptors (A^0X and D^0X) provide good examples of MC transitions.[36,37] In the first row of Table I, we give the spontaneous emission probabilities (in order of magnitude) of the NP lines of A^0X, D^0X, and N-bound excitons in GaP, obtained from the absorption strength of the NP line through the Einstein relations.[11,36–39] In the second row we give the spontaneous emission probabilities for the PS of each exciton, obtained from that of the NP by measuring the relative contributions to the photoluminescence intensity, and also an estimated result for the indirect free exciton which is taken from a calculated value for Si.[40] The probabilities are all in the order of 10^3–10^4 sec^{-1}, except for the N-bound exciton which is higher by a factor of over 10^3. A numerical estimate based on the MC model, made in the Appendix, shows that the predicted spontaneous emission probability for the PS of the N-bound exciton is of the order of 10^4 sec^{-1}.

(2) The "X" band at 48.4 meV (Ref. 13) cannot be identified with the MC LO phonon at the X point,[8,15] whose energy is 46.6±0.2 meV.[37,41] Furthermore, coupling to the LO(X) phonon is forbidden by symmetry selection rules which we will discuss later. Even if we take into account the fact that the conduction-band minimum is not exactly at X (Ref. 42) so that the MC phonon is on the Δ_1 line,[35] the energies do not agree, since the dispersion along Δ_1 near X is very small.

(3) In the MC model calculation, the line shape of the TA and LA PS's is quite sensitive to the electron binding energy.[5] The "near-resonant effect" for some components a_k of the bound electron wave function is important in the explanation of Dai *et al.* of the strong A-

TABLE I. Spontaneous emission probabilities of NP and total PS for A^0X, D^0X, and N-bound excitons in GaP, and the indirect free exciton in Si (in sec^{-1}).

	A^0X	D^0X	N-bound exciton	Indirect free exciton
NP	$\sim 10^3$	$\sim 10^5$	9.8×10^6	
PS	$\sim 10^4$	$\sim 10^3$	1.1×10^7	5×10^3

LO(X) band (i.e., the X band) in terms of the small electron binding energy (<10 meV) of the A line.[8] However, all NN_i pair centers have almost the same PS structure,[13,14] while their electron binding energies are very different, being as large as 125 meV for NN_1,[25] so the near-resonant effect cannot be of any importance in these cases.

(4) In GaAs:N under pressure, a similar doublet structure of the LO PS was observed for NN_1 (Ref. 43) and isolated N (Ref. 44) centers, with a PS/NP ratio comparable to that in GaP, even in the pressure range where the band structure is direct. In this case, the Γ-X mixing is very strong and the MC model would require the NP line to be strongly enhanced relative to the PS's.

B. CC model in GaP:N

The symmetry selection rules for phonons involved in the CC model are mainly determined by the matrix element $\langle \varphi_i^0 | u_q | \varphi_i^0 \rangle$ in Eq. (7) for a localized bound state. For an A_1 symmetry state of P-site impurity in GaP, only LA(X), LO(L), and LA(L) phonons are allowed if only phonons at X and L points are considered.[32] However, phonons elsewhere in the Brillouin zone are allowed[45] (Table II). These phonons could make a significant contribution to bound electron-phonon coupling for a deep impurity state since its wave function is well extended in k space. Also, when the conduction-band minima are not located at the zone boundary, as in GaP,[42] particular phonons, not precisely at a symmetry point, could be important. From Eq. (48) we can see that an intervalley or intravalley scattering which connect points $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$ with large electron wave-function amplitudes of $a_{\mathbf{k}}$ and $a_{\mathbf{k}+\mathbf{q}}$ will give a large contribution to the coupling constant $S_{\mathbf{q}}$. For the N-bound exciton the wave function of the bound electron is 80–90 % in the vicinity of X, the remainder being near L, with less than 1% near Γ.[23,46] Hence $X-X$ and $X-L$ scattering will be dominant, while the contribution from $X-\Gamma$ or $L-\Gamma$ scattering will be negligible. In contrast, in the MC model only $X-\Gamma$ scattering is considered.

The origin of the "X" PS's at 48.4 meV in GaP:N has been unclear since the earliest studies. Here we will discuss a few possible origins of this PS. Our general conclusion is that while the PS at 50.1 meV labeled LO(Γ) comes from small-q LO phonons coupled by the Fröhlich interaction, "X" includes contributions from the entire LO-phonon branch, and, like the TA and LA PS's (considered below), is due to deformation potential interaction.

From Table II, the LO(L) and LA(L) phonons are allowed for an A_1 state. If we consider the selection rules for deformation potential scattering,[47,48] the LO(L) and LA(L) phonons can be coupled by intervalley scattering between the X_1 and L_1 conduction-band states. LA(X) is allowed and LO(X) is forbidden both by the A_1 impurity symmetry and by the selection rules for intervalley scattering between two nonequivalent X_1 points belonging to two "stars". In GaAs,[47] on the other hand, LO(X) is allowed, and LA(X) forbidden, since $M_{\mathrm{As}} > M_{\mathrm{Ga}} > M_P$. However, coupling to an LO(Σ) phonon, which can connect two nonequivalent valleys on Δ_1, is allowed under both selection rules. This could be important because of the spread of the wave function in k space, and the conduction-band minima are not precisely at X but at $(0,0,1-\delta)$ points on the Δ line,[1] with $\delta=0.08$, which we call "$\Delta\delta$." A phonon connecting two such minima (the so-called f process[49,50]) has a wave vector $\mathbf{q}=(1-\delta,1-\delta,0)$ which is equivalent to $(\delta,\delta,1)$, i.e., a phonon with Σ_1 symmetry and $\mathbf{q}$ 6.45° off [001]. The phonon energy at that point is about 47.8 meV (Ref. 35) which is only 0.6 meV from that of the X band. However, the peak position could be mainly determined by the DOS of the phonons. Also, the X band is close to the energy of the LO(L) phonon, and it is likely that both $\Delta\delta-\Delta\delta$ and $\Delta\delta-L$ intervalley scattering contribute to it. $\Delta\delta-\Delta\delta$ scattering is favored by the electron wave function, but near $(\delta,\delta,1)$ the phonon DOS is relatively low, so that $\Delta\delta-L$ scattering is favored by the DOS. Note that the $\Delta\delta-\Delta\delta$ scattering matrix element is not zero even though it is zero between exact X points, and the matrix elements may increase rather fast when leaving the critical points.[51]

Another type of possible scattering between two X valleys is the so-called g process,[49,50] which is allowed and requires phonons on Δ with $\mathbf{q}$ near $(0,0,0.16)$. However such near zone-center LO phonons are not appreciably shifted from LO(Γ) at 50.1 meV, so the contribution of these phonons would be indistinguishable from the LO(Γ) band. As neither the phonon energies at general $\mathbf{k}$ points nor the deformation potential constants for two general points are available, we are not able to make a more quantitative judgment at the present stage.

For the LA PS, the f process $\Delta\delta-\Delta\delta$ scattering by a $(\delta,\delta,1)$ LA phonon would give a peak at $\sim$30 meV which is not observed.[35] The peak of the LA PS at 26.7 ± 0.4 meV (Ref. 13) agrees with the LA(L) phonon 26.7 ± 0.1 meV.[52] From the electron wave function,[23] the intervalley scattering matrix elements,[53] and the phonon DOS,[35] the contribution of $\Delta\delta-\Delta\delta$ scattering to the LA PS's should be an order of magnitude larger than that of $X-L$ scattering by L phonons. The fact that this is not the case remains to be explained, as does the fact that the LA PS is much weaker than TA and X PS's, when the overlapping contribution of two TA phonons is subtracted.[12] In general, LA PS's associated with localized impurities in GaP have lower energies than the 31.7 meV LA(X) phonon, which appears in shallow impurity spectra.[36,37] For example, in the spectra of donor-acceptor (D-A) pairs involving deep impurities the LA PS are all in the range 27.7–29.5 meV.[54] For the TA PS of the A line, which peaks at 13.3 meV,[13] Table II show that TA

TABLE II. Symmetry allowed bulk phonons in coupling to a P site. A_1 electron bound state for CC model in GaP (the origin of coordinates is assumed at P site) (Refs. 27 and 45).

	Γ	L	X	Δ	Λ	Σ
LO		L_1		Δ_1	Λ_1	Σ_1
TO						Σ_1
LA		L_1	X_1	Δ_1	Λ_1	Σ_1
TA						Σ_1

phonons from high symmetry points and lines are forbidden except those from the Σ_1 branch. The fact that this slightly exceeds the TA(X) phonon energy (13.0±0.1 meV (Ref. 37) again suggests that $\Delta\delta-\Delta\delta$ scattering is important.

The situation in GaAs:N under hydrostatic pressure is very similar to that in GaP:N. All the main features, LO(Γ), X, TO(Γ), LA and TA, appear in the spectra for the isolated N center[43] and the NN_i centers.[42] The phonon energy for the X band is 33.5±0.2 meV at atmospheric pressure. This is close to a peak in the DOS of the GaAs phonons[35] at 33.7 meV which appears to correspond to a maximum in the LO(Σ) branch. Again the f process intervalley scattering between nonequivalent X valleys apparently makes a significant contribution to the exciton-phonon coupling.

The Huang-Rhys parameter can be calculated either by using (7a) where a bound-state wave function in real space is used, or using (7b) where the wave function in k space is used. Some calculations have been done for various types of bound electron wave functions in real space: billiard-ball-like,[32] hydrogenic, "δ function," quantum defect and Gaussian,[21] or spherical square well.[55] The so-called "δ-function-type" is actually an approximation to the spherical square well, obtained by ignoring the contribution to the coupling of the wave function within the well (there is no bound state for a true δ-function potential in three dimensions). There are some disadvantages in using a real-space bound-state wave function. For example, one has to use a single effective mass in all these wave functions, which is not a good approximation when one has a deep impurity state with its wave function well extended in k space. On the other hand, to perform the calculation in k space is usually more difficult because one needs to know the detailed properties of the electron bound state a_{nk} and all the scattering matrix elements $\langle \varphi_{n'k+q}|u_q|\varphi_{nk}\rangle$.

We will consider two kinds of electron-phonon interactions: Fröhlich and deformation potential, and then apply them to the N-bound exciton in GaP. For the Fröhlich interaction, we will calculate the S parameter two ways: in real space and k space. For the deformation potential, we will work only in real space.

For the Fröhlich interaction, we have[56]

$$u_q = i(\hbar\omega_{\rm LO}/q)\left[\frac{\hbar}{2m^*\omega_{\rm LO}}\right]^{1/4}\sqrt{4\pi\alpha/V}\,\exp(i\mathbf{q}\cdot\mathbf{r})\ , \tag{11}$$

where α is the Fröhlich constant, m^* is the effective mass, and V is the crystal volume. From (7a) we then have

$$S_q = \left[\frac{2\pi e^2}{\hbar\omega_{\rm LO}V}\right](1/\varepsilon_\infty - 1/\varepsilon_0)F(\mathbf{q})/q^2\ , \tag{12}$$

where $F(\mathbf{q})$ is defined as

$$F(\mathbf{q}) = |\langle \varphi_i^0|\exp(i\mathbf{q}\cdot\mathbf{r})|\varphi_i^0\rangle|^2\ . \tag{13}$$

We take the real-space wave function as the δ-function type[21]

$$\varphi_i^0 = (\beta/2\pi)^{1/2}\exp(-\beta r)/r\ , \tag{14}$$

where $\beta=(2m^*E)^{1/2}/\hbar$, E is the electron binding energy. $F(q)$ is given explicitly as

$$F_r(q) = [\pi/2 - \arctan(2\beta/q)]^2(2\beta/q)^2\ . \tag{15}$$

If the k-space electron wave function is used, since only modes with small q are important for the Fröhlich interaction, $F(q)$ is approximately given by

$$F_k(\mathbf{q}) = |s(\mathbf{q})|^2\ , \tag{16}$$

where $s(\mathbf{q})=\Sigma_{\mathbf{k}}a^*_{\mathbf{k}}a_{\mathbf{k}-\mathbf{q}}$, which is roughly the Fourier transform of the bound electron probability density $|\varphi_i^0|^2$.[23] $s(q)$ was calculated in Ref. 23 by using a Koster-Slater one-band one-site model[57] and in this case it depends only on $|\mathbf{q}|$.

The contribution from all LO phonons is

$$S \equiv \sum_{\mathbf{q}} s_q = \left[\frac{e^2}{\pi\hbar\omega_\Gamma}\right](1/\varepsilon_\infty - 1/\varepsilon_0)\int_0^Q F(q)\,dq\ , \tag{17}$$

where $F(q)$ is given by $F_r(q)$ or $F_k(q)$. $Q=(6\pi^2N/V)^{1/3}$ (=1.14 Å^{-1} for GaP) is taken as the cutoff wave vector. Only contributions from small q are important in (17).

Introducing a bound-polaron radius r_0, so that

$$S = \frac{e^2}{2\varepsilon r_0\hbar\omega_{\rm LO}}\ , \tag{18}$$

where r_0 is defined as

$$r_0^{-1} = 2/\pi\int_0^Q F(q)\,dq \tag{19}$$

and $1/\varepsilon = 1/\varepsilon_\infty - 1/\varepsilon_0$. For GaP, $\varepsilon_\infty=9.04$, $\varepsilon_0=11.1$;[32] m^* in β takes the average value for the X valley, $m^*=0.365m_0$;[58] $\hbar\omega_{\rm LO}$ takes its Γ point value of 50.1 meV.[13]

We have calculated S for the Fröhlich interaction for different electron binding energies by using $F_r(q)$ or $F_k(q)$ in (17), as shown in Fig. 2. For example, if the electron binding energy for an isolated N-bound exciton is taken as 6 meV,[23] we obtain an S parameter of 0.195 or 0.175, respectively, which agrees well with the experimental value for the LO(Γ) sideband of 0.20±0.02.[11,59] This good agreement supports the result for the electron wave function obtained in Ref. 23. The corresponding bound polaron radius given by (19) is 15 or 17 Å, which is about the same as the polaron radius for a conduction-band state at X point defined by[56] $r_p=(\hbar/2m^*\omega_{\rm LO})^{1/2}\sim 14.5$ Å, since the bound electron wave function is, in fact, mostly concentrated in the X valleys.

For a deformation potential interaction, we have[60]

$$u_q = [\hbar/(2NM\omega_q)]^{1/2}D_q\exp(i\mathbf{q}\cdot\mathbf{r})\ , \tag{20}$$

where D_q is the deformation potential, N is the total number of unit cells, and M is the total mass in the unit cell. To perform the calculation in real space, we have

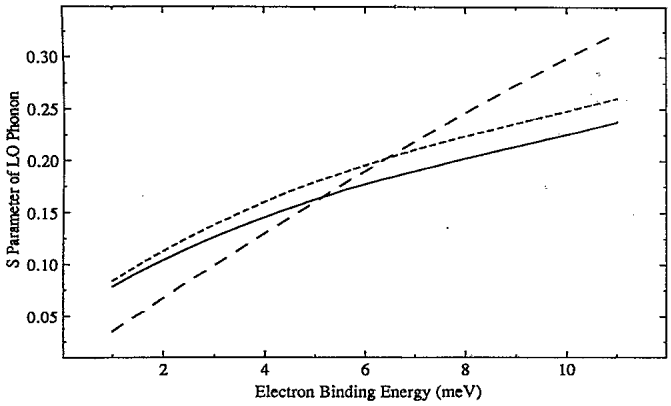

FIG. 2. Calculated Huang-Rhys parameters of LO-phonon sidebands vs the electron binding energy for the isolated nitrogen bound exciton in GaP. Full line: Fröhlich interaction, k-space wave function. Dotted line: Fröhlich interaction, real-space wave function. Dashed line: deformation-potential interaction, real-space wave function.

$$S_q=\frac{\hbar|D_q|^2}{(2NM\omega_q)(\hbar\omega_q)^2}F(\mathbf{q}) . \tag{21}$$

If a δ-function type wave function is used, $F(\mathbf{q})$ is the same $F_r(q)$ given by (15). Using the k-space wave function, we have

$$S_q=\frac{\hbar}{(2NM\omega_q)(\hbar\omega_q)^2}\left|\sum_{\mathbf{k}} a^*_{\mathbf{k}+\mathbf{q}}a_{\mathbf{k}}D(\mathbf{q},\mathbf{k})\right|^2 , \tag{22}$$

where $\langle \mathbf{k}+\mathbf{q}|u_{\mathbf{q}}|\mathbf{k}\rangle=[\hbar/(2NM\omega_q)]^{1/2}D(\mathbf{q},\mathbf{k})$, and $D(\mathbf{q},\mathbf{k})$ is the deformation-potential constant defined in Ref. 53.

In principle, (22) is more accurate than (21). However, it is much more difficult to do the calculation in k space for deformation-potential interaction than for the Fröhlich interaction, because the summation over k space in (22) includes both intervalley and intravalley scattering processes and the small-$\mathbf{q}$ approximation cannot be made. To evaluate $D(\mathbf{q},\mathbf{k})$ for each scattering process is also very tedious. Here we will estimate S for LO, LA, and TA PS's, using the real-space wave function. From (21), we have

$$S\approx\frac{|D|^2\Omega}{4\pi^2M\hbar\omega_0^3}\int_0^Q F(q)q^2dq , \tag{23}$$

where Ω is the volume of unit cell, and we have assumed an average value $|D|^2\omega_0^{-3}$ for $|D_q|^2\ \omega_q^{-3}$. D is an "effective" deformation-potential constant and ω_0 is the peak frequency of the PS. The approximation is expected to be rough, especially for acoustic phonons. The peak energies for X, LA, and TA sidebands are 48.4, 26.7, and 13.3 meV, respectively.[13] We choose $D_{\mathrm{LO}}=6.5$ eV/Å, $D_{\mathrm{LA}}=1$ eV/Å, and $D_{\mathrm{TA}}=1$ eV/Å, which are typical values of deformation-potential constants in III-V semiconductors.[53] The calculated result for LO or X PS is shown in Fig. 2 for the range of possible binding energies. Specifically, for a 6-meV binding energy, we have $S(X)\approx0.19$, $S(\mathrm{LA})\approx0.03$ and $S(\mathrm{TA})\approx0.22$. These values are in reasonable agreement with experiment.[11–13]

The above calculation assumes that the f process $\Delta\delta-\Delta\delta$ intervalley scattering dominates, since the wave function (14) is for a single valley and we have given m^* its X valley value. For the reasons discussed above this approximation might not be valid for all the PS's, but the results indicate that the CC model does give the correct order of magnitude for the transition rates of the PS's.

C. Discussion

Based on some general arguments and comparisons among different impurities, we have shown that in the MC model the PS transition rate of an impurity bound exciton is limited to the corresponding intrinsic indirect transition rate, and the model cannot account for the observed PS of localized excitons. It is not surprising that the MC (Refs. 5 and 8) model gave a spectral shape of the PS in reasonable agreement with the experimental results for GaP:N because this shape is mainly determined by the DOS of the phonons (in Refs. 5 and 8 the overall PS/NP ratio was scaled to fit the experimental data).

In the MC model, the absolute transition rate of the PS will not change very much for different impurity centers, but the ratio of PS to NP can change by orders of magnitude, since the ratio of PS to NP is directly related to the ratio $|a_X|^2/|a_\Gamma|^2$ and a_Γ is strongly dependent on the impurity. On the other hand, in the CC model, $|a_X|^2/|a_\Gamma|^2$ may change without significantly affecting the S parameters and hence the PS/NP ratio, so long as the contribution to the bound-state wave function from valleys with large density of states, usually X valleys, does not change much. This explains qualitatively why the S parameters do not vary significantly from the isolated N center to the NN_1 pair center.

Although the application of the MC model is done in the one-band approximation, the PS transition rate will not change by orders of magnitude if the multiband model is used, even if the contribution from the higher conduction bands is of the same order of the magnitude, as can be seen from expression (10). In fact, as pointed out in Ref. 8, the contribution from higher conduction bands is negligible because the transitions involving the higher conduction bands are very weak and the major contribution to the impurity wave function comes from the lowest conduction band. On the other hand, the NP transition rate, and hence the PS/NP ratio, depends on a_Γ, which will change a lot if the multiband model is used. In the multiband model a_Γ is larger than in the one-band model,[8,26] thus increasing the discrepancy between the MC model and experiment.

Contrary to the suggestion of Ref. 15, neither CC nor MC models predict that the ratio of PS's to the NP line will change significantly with temperature ($T<150$ K for GaP:N), apart from the effect of phonon occupation number.[20]

IV. SUMMARY

We have clarified the distinction between the CC and MC models in describing impurity-related optical transitions and the relationship between them. We conclude

that the MC model can only be used for shallow Coulombic impurities, otherwise the CC model is a better approximation. In the CC model, Huang-Rhys parameters for bulk phonon modes coupling to a bound electron or exciton can be calculated in terms of the bound-state wave function in k space and the phonon-induced intervalley and intravalley electron scattering processes of the intrinsic crystal.

We have studied in detail the PS's of nitrogen-bound excitons in GaP and their selection rules, and calculated the Huang-Rhys parameters, within the CC model. We account for the position and strength of the four main features of the PS's: LO(Γ) is due to the Fröhlich interaction and its calculated S parameter agrees well with the experimental results; X, LA, and TA are all due to the deformation-potential interaction, and their estimated S parameters are also in agreement with experimental results. We have shown that the MC model, which has been used in an attempt to explain the PS of nitrogen-bound excitons in some previous work, is inapplicable to this case.

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APPENDIX

In the MC model, the PS transition rate can be calculated by second-order perturbation theory, i.e.,

$$F_{\mathrm{MC}}(W_{\mathrm{if}}^0-\hbar\omega_q)=\frac{2\pi}{\hbar}\left|\sum_j\left[\frac{M_{j(m+1),f(m+1)}\mathcal{M}_{im,j(m+1)}}{W_{ji}^0-\hbar\omega_q}+\frac{\mathcal{M}_{jm,f(m+1)}M_{im,jm}}{W_{fj}^0-\hbar\omega_q}\right]\right|^2, \tag{A1}$$

where

$$M_{jm,j'm'}=\langle\Phi_{j'}^0\chi_{m'}^0|H_{ER}|\Phi_j^0\chi_m^0\rangle,$$
$$\mathcal{M}_{jm,j'm'}=\langle\Phi_{j'}^0\chi_{m'}^0|H_{EL}|\Phi_j^0\chi_m^0\rangle.$$

If a bound exciton state with energy level $E=W_{if}^0$ is considered, only the first term in (A1) is important, since the second term tends to have a much larger denominator. Then we have

$$F_{\mathrm{MC}}(E=\hbar\omega_q)=\frac{2\pi}{\hbar}\left|\sum_j\frac{\langle\Phi_f^0|H_{ER}|\Phi_j^0\rangle\langle\Phi_j^0|U_q|\Phi_j^0\rangle}{W_{ji}^0-\hbar\omega_q}\right|^2. \tag{A2}$$

In this case, we choose a free-exciton state Φ_j^0 as the intermediate state, where $j=(m,\mathbf{k}_{\mathrm{ex}})$ and m is the quantum number of the exciton states. It can be shown that the ground state of the Γ free exciton is the most effective intermediate state. Therefore, we get Eq. (10) in the main text for the transition rate or, correspondingly, the spontaneous emission probability[61] is given as

$$W_{\mathrm{MC}}(E-\hbar\omega_q)=\frac{2\alpha(E-\hbar\omega_q)E_p}{3\hbar c^2m}\left|\sum_k A_{\mathrm{ex}}(k)\right|^2\left|\sum_k A_{\mathrm{ex}}^*(k)A_k\sum_n a_{nq+k}\frac{\langle\varphi_{ck}|u_q|\varphi_{nq+k}\rangle}{E_{\mathrm{ex}}-E-\hbar\omega_q}\right|^2, \tag{A3}$$

where m is free-electron mass, α is the fine-structure constant, E_p is the energy constant associated with the momentum matrix element between the conduction band and the valence band, and all the other parameters are defined in the main text. Using the one-band approximation, and assuming that a_{q+k} and $\langle\varphi_{ck}|u_q|\varphi_{q+k}\rangle$ are relatively slow varying functions of k compared to $A_{\mathrm{ex}}(k)$ and A_k, for q near the conduction-band minimum, we have approximately

$$W_{\mathrm{MC}}(E-\hbar\omega_q)=\frac{2\alpha(E-\hbar\omega_q)E_p}{3\hbar c^2m}\left|\sum_k A_{\mathrm{ex}}(k)\right|^2\left|\sum_k A_{\mathrm{ex}}^*(k)A_k\right|^2\left|a_q\frac{\langle\varphi_{c0}|u_q|\varphi_q\rangle}{E_{\mathrm{ex}}-E-\hbar\omega_q}\right|^2. \tag{A4}$$

We want to estimate the W_{MC} for the isolated nitrogen center (A line) in GaP:N. For simplicity, we only consider the LO phonons. The total spontaneous emission probability W_{MC} is the summation of (A4) over all modes, and it is given approximately as

$$W_{\mathrm{MC}}\approx\frac{\alpha(E-\hbar\omega_0)E_p}{6\hbar c^2m}\left[\frac{a}{a_{\mathrm{ex}}}\right]^3\xi^2C_X\left[\frac{\hbar}{2M\omega_0}\right]\times\frac{|D(\mathbf{q}_0)|^2}{(E_{\mathrm{ex}}-E-\hbar\omega_0)^2}, \tag{A5}$$

where C_X is the summation of $|a_q|^2$ in X valleys, $\xi=\Sigma_k A_{\mathrm{ex}}^*(k)A_k$, a is the lattice constant, a_{ex} is the radius of the free exciton, $D(\mathbf{q}_0)$ is the deformation potential for $\mathbf{k}=\mathbf{q}_0$ to $\mathbf{k}=0$ intervalley scattering process as used in (22), and ω_0 is the frequency of the LO phonon. For the A line, $C_X=0.94$ and $\xi=0.63$.[23] $a_{\mathrm{ex}}=72.6$ Å [the direct free-exciton binding energy is about 9 meV (Ref. 62)] and $E_p=22.3$ eV. $\hbar/(2M\omega_0)=8.3\times10^{-3}$ Å^2 and $D(\mathbf{q}_0)=4$ eV/Å.[53] With these values, we get $W_{\mathrm{MC}}(\mathrm{LO})\sim1.5\times10^4$ sec^{-1}. This value is two orders smaller than the experimental result, but of the same order as that for shallow impurities, which is what we ex-

pected for the MC model. For the ratio of PS/NP, the one-band model gives a value a factor of 10 smaller than experiment, and may be overestimated due to the inaccuracy of a_Γ. In fact, with a_Γ from the one-band model, the oscillator strength of the A line is about one order smaller than the experimental result. By considering this, the ratio will be of the order of 1×10^{-3}, which again gives the spontaneous emission probability of MC PS in the order of 1×10^{4} ($\sec^{-1}$). If a_Γ from the multiband model is used, we should expect that the ratio is in the order of 1×10^{-5} since a_Γ is about three orders larger than the one-band model.[8,26]

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