

Model for phonon-assisted indirect recombination at impurity sites in semiconductors: A test of impurity wave-function theories

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A new method for studying the wave functions associated with defect levels is presented. The method is based on a model that includes the role of intrinsic lattice phonons in indirect electron-hole recombination at impurity sites in semiconductors; the model contains information about the impurity-phonon matrix elements and the intrinsic phonon dispersion relations as well. In particular, it can be used in conjunction with experimental data as a test of the accuracy of impurity wave-function models. As an illustration, an application to the acoustic-phonon sidebands in the low-temperature luminescence spectrum of the N-bound exciton in GaP is described wherein the method is used to test the Koster-Slater one-band one-site approximation for the electron wave function.

The need for accurate theoretical descriptions of localized traps, and with it the need for experimental verification of the models, is widely recognized.¹ To date, the application of luminescence spectra to this problem has been primarily limited to the comparison of calculated energy levels with those inferred from the direct, no-phonon transitions. However, some of the same spectra contain further information in the phonon sidebands, related to the defect wave functions. The considerable information implicitly contained in such spectra strongly encourage the consideration of models that describe in detail the interactions responsible for the phonon sidebands.

In this paper, we consider indirect radiative transitions (at $T=0$ K) involving an impurity level in the forbidden energy gap of a semiconductor, and present an expression for the resulting line shape of the associated phonon sideband. It is shown that the derived phonon sideband line shape is a sensitive function of the impurity wave function, and hence can be used as a test of impurity wave-function models.² We also show that these spectra can provide information about the electron-phonon matrix elements and the phonon density of states and dispersion relations.

We emphasize that the phonon sidebands in luminescence spectra due to impurities in indirect-band-gap semiconductors such as GaP may contain contributions from both direct and indirect electronic transitions. Direct transitions and electron-phonon coupling within the configuration coordinate (CC) model have been studied extensively.¹ On the other hand, indirect transitions, in which a carrier is scattered from one part of the Brillouin zone to another by emission or absorption of a phonon with the appropriate wave vector while simultaneously emitting or absorbing a photon, have not received as much attention. While some impurity-related luminescence features have been recognized as being due to indirect transitions,³ to our knowledge no quantitative analysis of the line shapes has thus far been given.

From a perturbation-theory approach, the fundamental distinction between indirect and direct transitions is in the order of the electron-hole interaction. Direct transitions are described by first-order time-dependent perturbation theory, while indirect transitions are a second-order effect. For a band-to-band indirect transition, aided by emission of a phonon with wave vector \mathbf{Q} , the transition rate is⁴⁻⁶

$$I = \frac{2\pi}{\hbar} \delta(h\nu - E_G + h\nu_\alpha(\mathbf{Q})) \left| \sum_i \left[\frac{\langle \phi_{\nu,\mathbf{k}} | H_p | \phi_{i,\mathbf{k}} \rangle \langle \phi_{i,\mathbf{k}} | H_\alpha(\mathbf{Q}) | \phi_{C,\mathbf{k}'} \rangle}{E_c(\mathbf{k}') - E_i(\mathbf{k}) - h\nu_\alpha(\mathbf{Q})} + \frac{\langle \phi_{\nu,\mathbf{k}} | H_\alpha(\mathbf{Q}) | \phi_{i,\mathbf{k}} \rangle \langle \phi_{i,\mathbf{k}} | H_p | \phi_{C,\mathbf{k}'} \rangle}{E_V(\mathbf{k}) - E_i(\mathbf{k}') + h\nu_\alpha(\mathbf{Q})} \right] \right|^2, \quad (1)$$

where $\phi_{\nu,\mathbf{k}}$ and $\phi_{C,\mathbf{k}'}$ are the initial and final states in the valence and conduction bands, respectively. The sum over i includes in principle all electronic bands and $\phi_{i,\mathbf{k}}$ and $\phi_{i,\mathbf{k}'}$ are intermediate scattering states. The quantity $\langle H_p \rangle$ is the matrix element for a direct optical transition (the photon wave vector is assumed negligible) and $\langle H_\alpha \rangle$ is the matrix element due to scattering emission or absorption of a phonon from branch α . Finally, $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$, and $h\nu_\alpha(\mathbf{Q})$ is the cor-

responding phonon energy.

It is straightforward to generalize Eq. (1) to the case of transitions involving one or two impurity levels. Upon expanding the localized wave function(s) in terms of perfect-crystal band states one obtains¹

$$\psi_{\text{imp}}(r) = \sum_{n,\mathbf{k}} A_n(\mathbf{k}) \phi_{n\mathbf{k}}(r), \quad (2)$$

where $\phi_{n\mathbf{k}}(r)$ is the Bloch wave function for band n and

wave vector \mathbf{k} . The luminescence spectrum due to indirect transitions between, for example, an impurity electron level and a free or weakly bound hole level is⁷

$$L(h\nu) = \frac{2\pi}{\hbar} \sum_{\alpha} \sum_{\mathbf{k}} \delta(h\nu - E_{np} + h\nu_{\alpha}(\mathbf{k})) \left| \sum_n A_n(\mathbf{k}) \sum_i \left(\frac{\langle \phi_{\nu,0} | H_p | \phi_{i,0} \rangle \langle \phi_{i,0} | H_{\alpha}(\mathbf{k}) | \phi_{n,\mathbf{k}} \rangle}{E_e - E_i(0) - h\nu_{\alpha}(\mathbf{k})} + \frac{\langle \phi_{\nu,0} | H_{\alpha}(\mathbf{k}) | \phi_{i,\mathbf{k}} \rangle \langle \phi_{i,\mathbf{k}} | H_p | \phi_{n,\mathbf{k}} \rangle}{E_h - E_i(\mathbf{k}) + h\nu_{\alpha}(\mathbf{k})} \right) \right|^2, \quad (3)$$

where E_{np} the no-phonon energy, is the difference between the bound-electron and hole energies, $E_e - E_h$. In Eq. (3) we sum over lattice vibrational modes only. Although a sum over the impurity-related modes should also be included, the luminescence features due to a localized mode are often distinguishable from those due to lattice modes. It is thus usually practical to ignore the sidebands due to such local modes, at least in the application of Eq. (3). Quasilocalized impurity modes, which are resonant with the lattice phonon bands, typically appear where the intrinsic phonon density of states is low, making it possible to distinguish them from the lattice modes as well. No quasilocalized modes have been identified in the GaP:N spectra which are considered here.

The spectrum calculated from Eq. (3) depends critically on several factors, including the bound-electron wave function, which is represented by the coefficients $A_n(\mathbf{k})$. These must be calculated according to a wave-function model, and inserted into Eq. (3) along with expressions for the matrix elements, phonon energies, and band energies. The calculated line shape can then be compared with the measured spectrum, thus providing a test for the impurity wave function. The other critical factors in Eq. (3) are the phonon dispersion relations and the k dependence of the matrix elements. Lattice-dynamical models which accurately reproduce neutron scattering data are available for most materials of interest.⁸ Furthermore, optical matrix elements can be calculated⁶ using Bloch functions obtained from pseudopotential⁹ or other types of empirical band-structure calculations.¹⁰ However, the perturbation $H_{\alpha}(\mathbf{k})$ corresponding to creation or absorption of a phonon is not well known. In this paper a simple model for $H_{\alpha}(\mathbf{k})$ is used, and the relative strengths of the LA and TA scattering are adjusted to obtain the best fit to the measured luminescence spectrum. It is seen below that, even without detailed knowledge of these matrix elements, Eq. (3) provides a sensitive test for the accuracy of impurity wave-function models.

This method is not limited to the case of recombination between a bound electron and a free hole; it is general, and may be applied to other radiative transitions involving defect levels. However, in some cases the indirect-transition spectrum is too weak to measure. Another practical consideration is that the formalism does not include configuration coordinate (CC) interactions,^{11,12} which also produce phonon sidebands that may overlap with the indirect-transition spectrum. In practice, it will therefore be necessary either to deconvolve the CC contribution from the measured spectrum,^{11,12} or to study spectra in which the overlap of CC and indirect-transition sidebands is not significant. Whether any deconvolution method is accurate enough to remove all CC interactions without distorting the indirect-transition spectrum, particularly when the CC coupling is strong, is not clear. Apart from the CC interaction, any mechanism which broadens the no-phonon line (such as the Coulomb interaction in donor-acceptor recombina-

tion,¹³ or broadening due to alloying¹⁴) also broadens the phonon sideband features. Thus, for the present we limit ourselves to a discussion of spectra due to bound excitons which include GaP:N (luminescence¹⁵) and GaP:O (absorption spectrum due to creation of an exciton bound to neutral oxygen.¹⁶).

A further application for consideration is to the impurity potential, $V(\mathbf{r})$. In the Koster-Slater defect model the wave function is insensitive to the detailed form of the potential,¹⁷ so that knowledge of the $A_n(\mathbf{k})$ does not guarantee knowledge of $V(\mathbf{r})$. However, the phonon scattering matrix elements in Eq. (3) contain additional information about the potential. Instead of assuming a simple k dependence for the matrix elements, as we do in our illustration below, they could be calculated in the rigid-ion approximation, where the phonon scattering potential is⁶

$$H_{\alpha}(\mathbf{k}) = \sum_{j,\beta} \nabla V(\mathbf{r} - \mathbf{R}_{j\beta}) \cdot \delta \mathbf{R}_{j\beta}(\mathbf{k}) \quad (4)$$

Here the $\delta \mathbf{R}_{j\beta}$ are the displacements of the atoms from their equilibrium positions. The procedure in this case would be to assume a form for the potential $V(\mathbf{r})$, calculate the phonon scattering matrix elements and $A_n(\mathbf{k})$, and then adjust the potential to obtain the best fit of the calculated indirect spectrum to the measured spectrum. A more complete discussion will be published elsewhere.

The nitrogen-bound exciton state in GaP (Ref. 15) was selected as a test case for our indirect-transition model. Although it is a shallow level, the impurity potential is highly localized, as in the case of a deep level. Furthermore, this defect state has been extensively studied, and several theoretical models for the wave function are available.¹⁷⁻²⁰ Presented here are the results for the Koster-Slater¹⁷ model for the electron wave function. Clearly, the method is not limited to this type of wave function, and can be applied to any model wave function.

We are not concerned here with the no-phonon line or the LO- Γ phonon replicas, which are unambiguously due to direct recombination and CC interaction, respectively. We consider only those parts of the spectrum which may contain a significant contribution from indirect transitions. It is shown below that the acoustic-phonon sidebands can be fit moderately well with the measured indirect-transition spectrum given by Eq. (3), using reasonable models for the electron wave function, phonon dispersion relations, band structure, and matrix elements.

In the Koster-Slater model a simple form is chosen for the highly localized impurity potential and only one band is used in the expansion of the electron wave function [Eq. (2)]. The resulting k -space coefficients of the wave function are

$$A(\mathbf{k}) = N/[E_e - E_c(\mathbf{k})] \quad (5)$$

where $E_c(\mathbf{k})$ is the lowest conduction-band energy at wave vector \mathbf{k} , and N is the normalization factor. It is assumed

that the hole is weakly bound by a Coulomb potential, so that in k space the hole state is localized at $\mathbf{k}=\mathbf{0}$. Thus, Eq. (3) may be used.

The GaP phonon-dispersion relations used in these calculations are obtained using the second-neighbor ionic model developed by Banerjee and Varshni,²¹ with one modification. The dynamical matrix consists of a short-range force-constant part and a long-range Coulomb part; the latter part mainly affects the optic phonons. However, the line shapes of the optic-phonon sidebands in the luminescence spectrum are narrow because of the small dispersion in the optic branches, and consequently are not very sensitive to changes in the wave function. They are not included in this calculation, and the Coulomb interaction in the phonon model is neglected. In principle, however, the optic-phonon branches can be included.

The optical matrix elements are assumed to be constant functions of \mathbf{k} , and the following k dependence is assumed for both the TA and LA phonon scattering matrix elements.

$$\langle H_{\alpha}(\mathbf{k}) \rangle = C_{\alpha} [\sin(|k|r_s) - |k|r_s \cos(|k|r_s)] / |k|^2,$$

where r_s is the radius of the Wigner-Seitz cell. This expression has been used to describe LA phonon scattering of electrons in metals;²² it is flat at the zone edge, and drops smoothly to zero at the zone center. The C_{α} are relative strengths for LA and TA phonon scattering, scaled to fit the relative heights of the LA and TA peaks in the measured spectrum. Finally, the semiempirical sp^3s^* tight-binding model of Vogl, Hjalmarson, and Dow¹⁰ is used to obtain the electronic band structure needed to calculate the wavefunction coefficients in Eq. (5) and the energy denominators in Eq. (3). Because of the energy differences in denominators in Eq. (3), the lowest conduction band at $k=0$ is the dominant intermediate scattering state, and only this state is included in the sum over i . The electronic binding energy is treated as an adjustable parameter. The sum over the Brillouin zone, which is necessary to evaluate the spectrum of Eq. (3), has been done numerically using a technique for evaluating generalized densities of states developed originally by Lehmann and Taut²³ and later modified by Hjalmarson.²⁴

The results are shown in Fig. 1. Assuming an electron binding energy of 10 meV, and including only the LA and uppermost TA phonon branches, one obtains the spectrum shown in Fig. 1(a). The relative electron-phonon scattering strengths chosen are $C_{LA}/C_{TA}=0.35$. The positions and widths of the LA and TA peaks are approximately the same as those in the measured acoustic-phonon sideband, which is shown in Fig. 1(b). In Figs. 1(c) and 1(d) the sensitivity of the spectral shape to change in the charge density is demonstrated. The calculated charge density is changed by varying the electron binding energy in Eq. (5). It is clear that the spectral line shape is very sensitive to the spread in k space of the electron charge density, and therefore to the degree of localization of the wave function in real space.

In summary, a general formalism for the contribution of indirect transitions to impurity-related luminescence in a semiconductor has been derived. Specifically, the formalism provides a relationship between the impurity charge density in k space and the phonon sidebands in the luminescence spectrum. Using the relation to test the Koster-Slater model for the nitrogen-bound exciton wave function in GaP, we

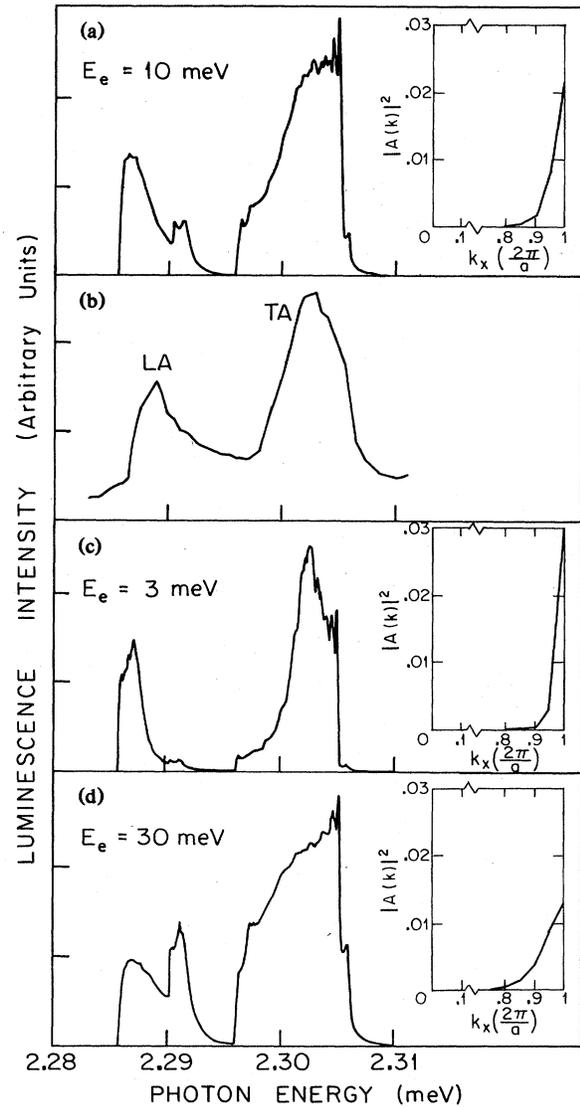


FIG. 1. Acoustic-phonon sidebands in GaP:N luminescence. (a) (top) Sidebands calculated from Eq. (3) using electron binding energy of 10 meV. (b) Typical low-temperature spectrum measured by one of us (M.A.G.), shown for comparison. No-phonon line (not shown) is at 2.316 eV. (c) and (d) (bottom) Sidebands calculated using binding energies of 3 and 30 meV, respectively. Insets show corresponding Koster-Slater electron charge densities along k_x . Intensity scales for (a)–(d) are not equivalent. The peak that is a strong function of the trap depth in (a) and (d) increases as a result of delocalization of the wave function in k space.

find that the shape of the calculated acoustic-phonon sideband is sensitive to the electron charge density spread in k space. We also find that the Koster-Slater model fits the luminescence data moderately well when an electron binding energy of about 10 meV is used. Beyond these specific results, the indirect-transition formalism promises to provide a new and general method for obtaining information about deep level wave functions and potentials from measured spectra.

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