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Radiative and nonradiative recombination of bound excitons in GaP:N. IV. Formation of phonon sidebands of bound excitons

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Due to the energy-band structure of GaP:N, we propose that the phonon sidebands of the excitons bound to isoelectronic traps consist of two components: phonon-assisted indirect transition and direct transition with phonon emission (multiphonon process). Thus, the phonon sidebands have some special features, such as the line shape with double-peak structure and the anomalous temperature behavior different from that of zero-phonon emissions. We calculate the LO-phonon sideband of excitons bound to NN_1 based upon the two-component model, explain its double-peak structure and anomalous temperature behavior observed in experiment, and propose possible physical mechanisms of the fixed activation energies of the LO-phonon sidebands of bound excitons and the bound-exciton tunneling from deep nitrogen traps to shallow ones.

I. INTRODUCTION

The isoelectronic-trap material GaP:N has been thoroughly studied and found to have many applications. However, there are several problems concerning basic properties that remain yet unsolved. Among them are the luminescence line shape and the anomalous temperature behavior of the LO-phonon sidebands of the excitons bound to nitrogen and nitrogen-pair traps. These problems are of great importance in investigating transition mechanisms in semiconductor materials because of their direct connection with bound-exciton transition processes, the bound-exciton wave function, and intrinsic phonon processes.

In the low-temperature luminescence spectra of GaP:N, all the acoustic- and optical-phonon sidebands of bound excitons are well resolved. The longitudinal-optical-phonon sidebands show a narrow double-peak structure, while the acoustic-phonon sidebands have broader profiles.[1] This double-peak structure of the LO-phonon sidebands was observed early in the study of GaP:N and remains without explanation. On the other hand, according to the multiphonon transition theory, it seems that the LO-phonon sidebands of bound excitons should have the same temperature behavior as that of their corresponding zero-phonon emissions. However, it has been found in experiment that this is not true.[2] The integrated intensity ratio between the LO-phonon sideband and zero-phonon emission depends on temperature strongly. This suggests that the LO-phonon sidebands of the bound excitons in GaP:N do not merely come from the multiphonon transition at the Γ point in **K** space.[3] Based on the above-mentioned experimental results and the fact that the wave functions of bound excitons distribute in all **K** space with a maximum at the X point, we propose that the bound-exciton transitions have two paths: direct transition at the Γ point and indirect transition with momentum-conserving phonon emission at all other points in **K** space, as we shall discuss below. The multiphonon process of the direct transition gives the normal phonon sidebands (replica) of bound excitons which follow multiphonon process theory. The indirect transition gives a set of phonon sidebands superimposed on the phonon sidebands (replica) of the direct transition. Thus, the total phonon sidebands of bound excitons have some special properties such as a double-peak line shape and temperature behavior different from that of zero-phonon emissions.

Considering the distribution of the bound-exciton wave function in all **K** space, Snyder *et al.* developed a perturbation method to calculate the line shape of TA- and LA-phonon sidebands of the excitons bound to isolated nitrogen to test the accuracy of the bound-exciton wave function by comparing with experimental luminescence spectra.[4] They did not study the LO-phonon sideband because they believed it comes merely from the multiphonon process of the direct transition at the Γ point and because of its relatively too narrow profile to test the accuracy of the wave function. In the following sections, we develop the perturbation method to calculate the LO-phonon sideband of NN_1 excitons to explain the double-peak structure and anomalous temperature behavior. We also propose the physical mechanisms of the fixed activation energies of the LO-phonon sidebands of bound excitons and the bound-exciton tunneling from the deepest trap to shallower ones. The good agreement between the experimental and the calculated LO-phonon sideband proves that the bound-exciton decay mechanism of the multiphonon transition and the indirect transition with momentum-conserving phonon emission is valid.

II. THEORY

The III-V compound gallium phosphide is a material with indirect energy-band gap. Nitrogen-related isoelectronic defects introduce a series of deep levels in the band gap of crystalline GaP. All the deep levels are not really deep in the band gap, with bound energy ranging from 20 meV (isolated-nitrogen trap) to 140 meV (NN_1 trap),[1,5] but they possess the character of deep levels because of their highly restricted wave function in real space. The wave-function restriction in real space causes the wave-function dispersion in **K** space. The maximum probabilities (the square of wave function) of bound excitons appear at the X point, Γ point, and other boundary points in **K** space, while the first maximum appears at the X point.[6-8] The most obvious properties of a material with such a quasidirect band gap and wave-function distribution is that the material acts as an indirect band-gap material as well as a direct band-gap material. In **K** space, direct transition can occur at the Γ point and indirect transition between the X point (and all other points except Γ) and Γ point. This is true for all the nitrogen-pair traps and the isolated-nitrogen trap in GaP:N. The problems we are interested in come from this point. While the direct transition of bound excitons makes GaP:N an efficient light-emitting-diode (LED) material, the multiphonon process accompanying the direct transition and the indirect transition with momentum-conserving phonon emission produce complex phonon sidebands which are both indirect-transition-like and direct-transition-like and of which the line shapes are sensitive to the intrinsic phonon dispersion relation and density of states.

One component of the LO-phonon sideband of NN_1 excitons, the indirect transition with momentum-conserving phonon emission, can be depicted with second-order perturbation theory which gives the luminescence of indirect transition as follows:[4,9]

$$L_{\mathrm{MC}}(h\nu)=\frac{2\pi}{\hbar}\sum_{\alpha,\mathbf{K}}\delta(h\nu-E_{np}+h\nu_\alpha(\mathbf{K}))\times\left|\sum_n A_n(\mathbf{K})\sum_i\left[\frac{\langle 0|H_{\mathrm{p}}|\phi_{i,0}\rangle\langle\phi_{i,0}|H_\alpha(\mathbf{K})|\phi_{n,\mathbf{K}}\rangle}{E_e-E_i(0)-h\nu_\alpha(\mathbf{K})}+\frac{\langle 0|H_\alpha(\mathbf{K})|\phi_{i,\mathbf{K}}\rangle\langle\phi_{i,\mathbf{K}}|H_{\mathrm{p}}|\phi_{n,\mathbf{K}}\rangle}{E_h-E_i(\mathbf{K})+h\nu_\alpha(\mathbf{K})}\right]\right|^2 . \quad (1)$$

Here MC denotes the momentum-conserving phonon-associated luminescence. E_{np} is the energy gap between the impurity level and the top of valence band. The δ function represents energy conservation. The wave function of the bound excitons can be expanded in Bloch states of a perfect crystal:

$$\psi_{\mathbf{K}}=\sum_n A_n(\mathbf{K})|\phi_{n,\mathbf{K}}\rangle , \quad (2)$$

where n denotes the energy bands of the perfect crystal and **K** is the wave vector. The final state of bound-exciton transition is $|0\rangle$. i denotes the intermediate scattering states, H_{p} and $H_\alpha(K)$ represent the electron transition Hamiltonian and the scattering Hamiltonian of the αth branch phonon with wave vector **K**, respectively. The physical processes involved in this formula are schematically presented in Fig. 1. A bound exciton includes an electron tightly bound to a nitrogen trap and a hole relatively loosely bound to the bound-electron–trap complex.[10] The tightly bound electron contributes to the wave-function dispersion of the bound exciton in **K** space, while the wave function of the hole part concentrates mostly at the Γ point.[7] Although the total wave function is expressed with Eq. (2), the real transition can be viewed as the transition between a hole with $\mathbf{K}=0$ and an electron with nonzero momentum **K**. Considering the selection rules of the indirect transition,[4] there may be two transition paths: either the hole is scattered to an intermediate state by a phonon with wave vector **K** and then gives off emission through the direct combination with an electron at point X (path 1), or the electron is scattered to an intermediate state at the Γ point by a phonon with wave vector **K** and then gives off emission through the direct combination with a hole at the Γ point (path 2). In these paths, the intermediate state energy plays an important role, which determines the energy denominator. Only the lowest conduction band and the highest valence band are important as intermediate states, while the others give a much larger energy denominator and subsequently a much smaller contribution to L_{MC}.

To calculate L_{MC}, the energy-band structure of crystal GaP, the bound-exciton wave function, the dispersion relation of the LO phonon, and the LO-phonon density of states are needed. There is much work on the energy-band structure of GaP; we take Cohen and Bergstresser's results[11] in our calculation. We use Dai's semiempirical method to get the NN_1 exciton wave function in **K** space.[12] This method can give the wave function with much ease but with an accuracy similar to that derived from a first-principles calculation.[8] Banerjee and Varshni's dispersion relation of the LO phonon and LO-phonon density of states, which come from a next-nearest

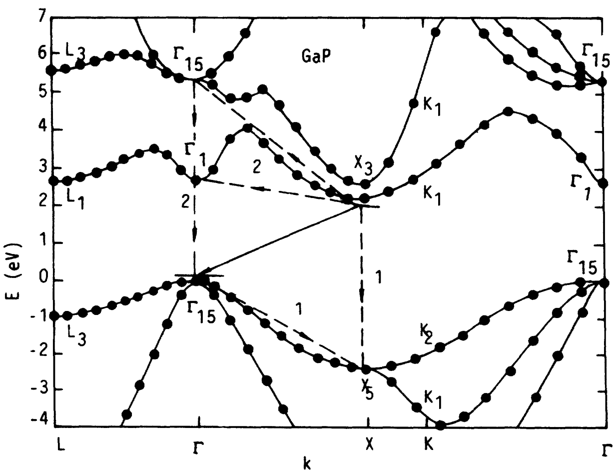

FIG. 1. Schematic diagram of the indirect-transition processes of bound excitons in GaP:N.

rigid-ion model,[13,14] are employed.

This part of the contribution to the LO-phonon sideband originates from the indirect transition with momentum-conserving phonon emission. We call it the MC contribution. The other part which contributes to the phonon sideband comes from the multiphonon process, which is well described with the configuration-coordinate (CC) model;[15] we call it the CC contribution. It has been a long time since these two parts have been studied separately in some semiconductors with deep level defects,[16] but it was not so in GaP:N. In GaP:N, it was assumed that the phonon sidebands of bound excitons originate from only the multiphonon process. As mentioned above, this is only one component of the sidebands.

With the configuration-coordinate model, the CC contribution can be described as

$$P_{if} = |M_{if}|^2 e^{-s} \frac{S^m}{m!} \ . \qquad (3)$$

M_{if} is the matrix element of the transition between the initial state and the final state. S is the well-known Huang-Rhys factor. It is assumed that temperature is 0 K, at which all vibration states are in the ground state. As to the LO phonon, when the temperature is below 10 K, $h\omega_{\mathrm{LO}}/kT \ll 1$, Eq. (3) can be approximately used in describing the LO-phonon sideband of low-temperature luminescence spectra. Because only one-phonon sidebands are important, as we can see in low-temperature spectra, m equals 1. The CC contribution can be simply represented by a Lorentz function with a maximum of P_{if}. While multiphonon transition occurs at the Γ point in **K** space, the LO phonons involved are those at the Γ point. The LO phonons involved at different points in **K** space with different energies cause the phonon sidebands to broaden and determine the sideband line shape.

III. RESULTS AND DISCUSSION

The calculated LO-phonon sideband of NN_1 bound excitons is shown in Fig. 2, along with the sideband from the low-temperature luminescence spectrum. The two peaks of the calculated sideband are given strengths similar to those in the experimental spectrum by adjusting the relative contribution of the MC component and the CC component. For simplicity, we take a Lorentz function as the CC contribution; the MC contribution is calculated only considering the LO phonons in the $\Gamma-X$ direction. This will not change the line shape much but makes it much easier to calculate, for the LO-phonon dispersion relations in other directions have the same tendency as that in the $\Gamma-X$ direction except with a small difference in their slopes.[17]

The CC interaction between bound excitons and the crystal lattice may not produce the double-peak structure in the LO-phonon sideband of bound excitons. The highly localized wave function at the X point contributes to the LO-phonon sidebands by indirect transition and makes the sidebands appear a maximum near the X point. Because of the LO-phonon density of states and the contribution of other boundary points in **K** space, the maximum does not exactly appear at the X point. The localized wave function near the Γ point and the large direct transition probability contribute to the sidebands by indirect transitions and multiphonon processes, respectively, and produce another maximum at the Γ point. Strictly speaking, the scattering matrix element and the energy of intermediate states also influence the sideband line shape, but they do not cause significant change. Thus, the LO-phonon sidebands of bound excitons appear as two peaks chiefly corresponding to the wave-function distribution in **K** space. For acoustic phonons, the sidebands show some complicated structure due to their dispersion relation.[4]

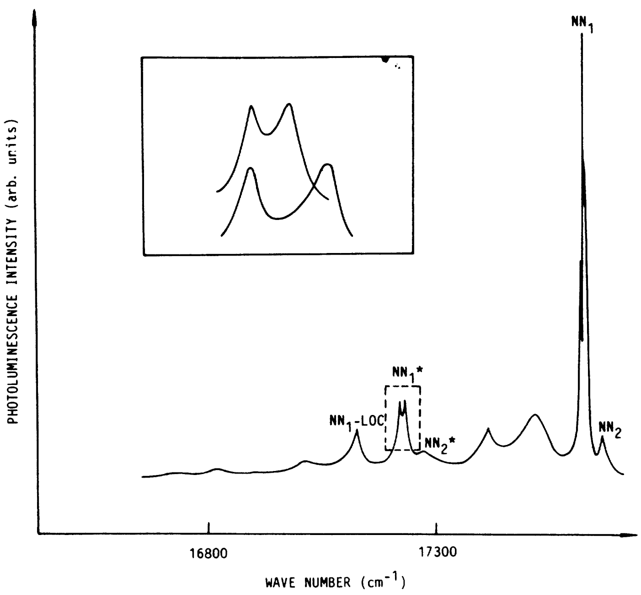

FIG. 2. Comparison of the calculated LO-phonon sideband of NN_1 excitons with experimental luminescence spectrum. In the inset, the upper curve is the experimental LO-phonon sideband. The lower one is calculated results. The peak separation of the calculated curve is larger than that of the experimental one. This deviation may be reduced heavily when taking into account all important factors in determining the LO-phonon sideband.

The anomalous temperature behavior cannot be explained without considering the MC contribution of the LO-phonon sidebands. According to the multiphonon transition theory which has been supported by many experiments, without the MC contribution, the LO-phonon sidebands should have the same temperature behavior as their corresponding zero-phonon emission, that is, the ratio between the integrated intensities of them should be a constant when the temperature changes. In fact, the ratio is strongly temperature dependent.[2] This can be understood by taking into account the temperature-dependent factors in the MC contribution of the LO-phonon sidebands. Because the indirect transition probability is different at different points in **K** space considering the energy of intermediate states which determines the energy denominator in Eq. (1) and the LO-phonon density of states, the wave-function distribution in **K** space determines not only the sideband line shape but also the sideband intensity. Thus, the change of the wave-function distribution will cause the change in the LO-phonon sideband intensity. There are two ways in which temperature affects the wave-function distribution. First, as the energy-band structure of the host crystal changes with temperature,[18] the bound-exciton wave-function also changes. The deeper the trap is, the less the influence. So the sideband intensity changes with temperature, and the change becomes less obvious for deeper traps. This trend is the same as the experimental results.[2] Second, when the temperature rises, the kinetic energy of bound excitons increases. The real-space localization of the bound excitons decreases when this happens, and the bound-exciton wave function becomes more strongly localized in **K** space. When the localization in **K** space increases, first the indirect transition may become strong, then when the wave function concentrates too near the X point and the Γ point where the LO-phonon density of states decreases to zero, the indirect transition will decrease. This causes the ratio between the integrated intensities of the sideband and zero-phonon emission to have the same trend as observed in experiment. We also believe that the change of the wave-function distribution of bound excitons with temperature plays a role in the temperature behavior of zero-phonon emission of bound excitons which comes merely from the direct transition at the Γ point. The change of the energy-band structure itself also affects the indirect-transition intensity. When the energy band changes with temperature, the energy of intermediate states E_i changes. From Eq. (1), the indirect-transition intensity L_{MC} will change with temperature, too. Finally, it is obvious that the change with temperature in the number and the distribution in **K** space of LO phonons will cause the change in L_{MC}.

We may conclude from this that the ratio between the intensities of the LO-phonon sidebands and their corresponding zero-phonon emission of bound excitons are practically temperature dependent. The accurate comparison with experimental results needs further investigation considering all the temperature-dependent factors. This is a much more complex task.

While different nitrogen traps have their own activation energies of thermal quenching, most LO-phonon sidebands of different traps have a fixed activation energy as discussed in paper I. The fixed activation energy can also be understood with our two-component model of the bound-exciton transition. The bound excitons at points other than Γ in **K** space transit through the intermediate states at the Γ point, i.e., by indirect transition, to produce LO-phonon sidebands. Bound excitons in such intermediate states can be scattered back to their original states by the LO phonon. When the temperature raises to a certain degree corresponding to the energy of the LO phonon, this process gradually dominates the equilibrium. To those traps with binding energy larger than the energy of the LO phonon, their LO-phonon sidebands appear as thermal quenching with a fixed activation energy (50 ± 10 meV) determined by the energy of the LO phonon (50 meV at the Γ point, about 46 meV at the X point). There is another problem worth discussing. In a separate paper (paper III), we have investigated the phenomena of bound-exciton transfer to a shallower nitrogen trap with phonon assistance under the high-density selective excitation. Here, we can explain this with the above-mentioned indirect-transition process. In indirect-transition processes, there is an intermediate state involved at which the conservation of momentum is valid while the conservation of energy is invalid. When a shallower nitrogen trap acts as the intermediate state of the indirect transition of a deeper trap and the energy difference between them is compensated by a set of phonons, the intermediate state may become a real excited state. So the tunneling process of an exciton bound to a deeper trap to a shallower one is completed.

In summary, there exist direct transitions as well as indirect transitions in the isoelectronic-trap material GaP:N. With this assumption, in principle we can interpret the luminescence properties of the phonon sidebands of bound excitons and the physical mechanism of bound-exciton tunneling processes.

Note added. We began this work shortly after one of the authors (X.Y.Z.) proposed the basic thought developed in the present paper (Ref. 3). After we finished the main part of our work, we received a copy of the paper by Dai *et al.* [Phys. Rev. B **37**, 1205 (1988)]. The paper by Dai *et al.* is based on a similar idea that indirect transition plays an important role in determining the line shape of phonon sidebands, but there is much significant difference in interpretation between our paper and the one by Dai *et al.*

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