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THEORY OF DONOR- AND ACCEPTOR- BOUND PHONONS

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The theory of impurity-phonon binding first proposed by Dean, Manchon, and Hopfield is reformulated and generalized. It is shown that each impurity polarization is associated with bound phonon state. Effects of higher excited states, band-structure effect on acceptor-bound phonons, and phonon-dispersion effect are analyzed.

I. Introduction

In n-type GaP, Dean, Manchon, and Hopfield [1] found a new Raman-active mode between TO and LO phonons, and attributed it to an LO phonon bound by donor dielectric effect. In contrast to usual mass-defect local modes [2], this donor-bound LO phonon shows no systematics for substituent masses and is observable only at low temperatures ($k_BT <<$ donor binding energy). The microscopic mechanism of this binding [1] is closely related to Toyozawa and Hermanson's exciton-phonon complex [3], but the simplicity of the impurity-phonon complex permits closed expression for binding energies and wavefunctions without any adjustable parameters. The calculated binding energy, however, is about 2/3 of the experimentally observed values [1].

The binding of impurity and phonon is also found for acceptors [4, 5]. Especially interesting is the case of ZnTe doped with Li [5], where i) one observes two peaks between TO and LO phonons and ii) the calculated binding energy is less than a half of observed value in poor agreement with experiment.

It is the purpose of this communication to show that i) inclusion of phonon dispersion (neglected by Dean et al.) improves the theoretical binding energy and explains the width of bound phonon peaks, and that ii) in case of acceptor-bound phonons, valence-band structure is responsible for the appearance of doublet and also for deeper binding energies than donor-phonon bound states.

II. Theory of Impurity-Phonon Binding

The theory of impurity-phonon binding [1] consists in expanding the bound phonon wavefunction ϕ in terms of crystal phonon states

ϕ_k , $\phi = \Sigma_k \phi_k c_k$, and the requirement that ϕ be an eigenfunction of the total Hamiltonian including electron-phonon coupling gives an equation for the coefficients c_k

$$(E - \hbar\omega_k)\ c_k = \sum_{k'} T_{kk'}\ c_{k'}. \qquad (1)$$

The kernel of this integral equation $T_{kk'}$ is the scattering matrix, which to the second order in electron-lattice interaction reduces to

$$T_{kk'} = \sum_j \frac{\langle 0|V_k\ e^{-ik.r}|j\rangle \langle j|V_{k'}\ e^{ik'.r}|0\rangle}{\hbar\omega_{k'} + E_o - E_j} + \frac{\langle 0|V_{k'}\ e^{ik'.r}|j\rangle \langle j|V_k\ e^{-ik.r}|0\rangle}{\hbar\omega_k - E_o + E_j} . \qquad (2)$$

Here V_k is the Fröhlich coupling $\propto k^{-1}$, and 0 and j are impurity ground and excited states, respectively. Equation (1) is in general not easy to solve. Dean et al. [1] neglect phonon dispersion by putting $\omega_k = \omega_{LO}$ = const, ii) take only one intermediate state j in (2), and iii) use hydrogen model for impurity wavefunctions to obtain explicit forms for $T_{kk'}$.

In this paper we generalize their method in various ways in order to go beyond these simplifications. We shall later consider phonon dispersion effect, and let us for the moment concentrate on the effect of higher excited states and of non-hydrogen-like impurity states. We first convert the integral equation (1) into an eigenvalue problem. This can be easily done by writing down an equation for $\chi_j = \Sigma_k V_k c_k$, instead of an equation for c_k (1). The result is (i, j = impurity states)

$$(E - \hbar\omega_{LO})\ \chi_j = \sum_j S_{ij}\ \chi_j , \qquad (3)$$

with

$$S_{ij} \propto \sum_k k^{-2}\ \langle i|e^{ik.r}|0\rangle \langle 0|e^{-ik.r}|j\rangle$$

$$= (4\pi)^{-1} \langle 0,i|1/r|j,0\rangle , \qquad (4)$$

which is nothing but an exchange integral.

Equations (3) and (4) are our principal result : The bound phonon problem (1) is now shown to be equivalent to the problem of fictitious helium atom bound uniquely by exchange interactions. From this analogy, without explicit calculation, we can tell immediately that *each impurity state is associated with a bound phonon state*.

Effect of higher excited states is easily calculated for donor-bound phonons by using hydrogen-like wave functions for 0, i and j in eqs. (3)-(4) and diagonalizing a 2 x 2 (or bigger) matrix S_{ij}. The result for GaP is only to improve the binding energy by 2 %, contrary to general belief [1, 4].

In case of acceptors, degenerate valence band structure results in more complicated impurity states than donors. Baldereschi and Lipari's spherical model [6] is a convenient way of classifying acceptor states. According to them, 2p hydrogenic state splits into a triplet $2p_{1/2}$, $2p_{3/2}$ and $2p_{5/2}$. Our argument above shows that acceptor-bound phonons can also be classified according to this scheme. Thus in ZnTe:Li, deeper bound phonon is associated with $2p_{3/2}$ while shallower phonon is associated with $2p_{5/2}$. The bound phonon associated with $2p_{1/2}$ should be too close to crystal LO phonon to be observed.

Baldereschi and Lipari's method is further important in quantitatively calculating acceptor states. They show that acceptor binding energy is larger than in hydrogen model due to shrinkage of acceptor wavefunctions which increases average potential energy $\langle j|1/r|j\rangle$. In our case of acceptor-bound phonons, this shrinkage of impurity wavefunction increases the exchange interaction (4) because of increase of wavefunction overlaps. In case of ZnTe:Li, preliminary estimate shows that binding energy is 1.7 times that in hydrogen model.

Finally we briefly mention phonon dispersion effect. It is intuitively evident that since phonon energy decreases when one goes away from the Γ point where $\omega_k = \omega_{LO}$, this dispersion pushes down the impurity-phonon bound states, and hence results in deeper binding energy. Also since the bound state is degenerate with LO phonon continuum, bound phonon can decay into crystal phonons to obtain width. In case of n-GaP, this dispersion effect improves theoretical binding energy by about 15 %.

In summary, we have shown that i) dielectric effect of donors or acceptors can trap phonons and each impurity polarization (or excitation) is associated with bound phonon state ; ii) band-structure effect on acceptors, giving rise to shrinkage of acceptor wavefunctions, deepens the phonon binding ; and finally iii) phonon dispersion pushes down the bound states and broadens it.

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