

# Phonon Broadening of Impurity Lines

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The theory of line broadening given by Lax is found not to apply to shallow impurities in Ge and Si. Observed broadening may be instrumental at low temperatures and may be due to lifetime broadening through phonon interaction at nitrogen temperature. Calculations suggest that *p*-type spin resonance in germanium and silicon may be observable.

## I. INTRODUCTION AND CONCLUSIONS

CALCULATIONS by Lax and Burstein<sup>1</sup> have suggested that the width of impurity levels in silicon is due to the simultaneous emission or absorption of one or more phonons accompanying the change of state of the electron. We find that due to the weakness of the electron-phonon interaction in germanium and silicon the dominant optically induced transition is purely electronic without any change of phonon occupation number.

Burstein<sup>1</sup> and Newman<sup>2</sup> have reported measurements on B and In in silicon, respectively, which show a significant increase in line broadening by 77°K. Hrostowski<sup>3</sup> showed that there is a lower excited state about  $4 \times 10^{-3}$  eV below the states observed by Burstein and Newman both for B and In. The observed broadening may be a lifetime effect due to a transition into this lower state by emitting a phonon.

It has been suggested that the broadening mechanism of Lax and Burstein rules out the observability of spin resonance in *p*-type germanium and silicon.<sup>4</sup> Present calculations show that this is not the case. However, significant lifetime broadening due to phonon emission does occur. Calculations suggest that this broadening will not be sufficient to obliterate the line. Broadening due to strains or other imperfections may obscure the resonance as suggested by Kohn<sup>4</sup> in all but very pure and strain free samples.

If the lifetime theory of broadening is correct, the predicted low-temperature line width of the lowest excited state is considerably smaller than the experimental measurements, particularly for indium in silicon where a two phonon transition may be required. The low-temperature line widths appear to be limited by instrumental resolving power.

## II. CALCULATION

We write the total wave function of the system, impurity electron plus phonons, as a product function in

the spirit of the Born-Oppenheimer approximation

$$\Psi = \phi_{el} \prod_q x_q. \quad (1)$$

The optical absorption is proportional to the square of the momentum matrix element of  $\Psi$  between the two electronic levels under consideration

$$|\langle \psi_a | p_{el} | \psi_b \rangle|^2 = |\langle \phi_a | p_{el} | \phi_b \rangle|^2 \prod_q |\langle x_q^a | x_q^b \rangle|^2. \quad (2)$$

The electron-phonon interaction couples the states  $\Psi_i$  and  $\Psi_j$  with the matrix elements

$$\begin{aligned} \langle i | H_I | j \rangle &= a_q^\dagger \alpha_{ij}^*(q) + a_q \alpha_{ij}(q), \\ \alpha_{ij}(q) &= i |\hbar q / 2\rho V v|^{1/2} Z \int \phi_i^* e^{iq \cdot r} \phi_j dr, \end{aligned} \quad (3)$$

$q$  is the phonon wave vector,  $V$  the volume,  $\rho$  the density,  $v$  the sound velocity, and  $Z$  the deformation potential constant. When  $i$  and  $j$  are different, the electron-phonon interaction allows transitions between  $i$  and  $j$  with emission or absorption of phonons. This effect will be treated subsequently as a lifetime broadening. When  $i=j$ , the electron-phonon interaction displaces the center of oscillation of the phonons, by different amounts for  $i=a$  and  $i=b$ . The matrix element of Eq. (2) will then give an overlap between states of different phonon occupation numbers. In other words, phonons may be emitted or absorbed simultaneously with the electronic excitation. This is the broadening mechanism suggested by Lax.<sup>1</sup> However, there is also a matrix element for no change of phonon occupation which, for weak coupling, outweighs the totality of those transitions in which the occupation numbers change.

### a. $\alpha_{ij}=0$ , $i=j$

The Hamiltonian of a given phonon oscillator is

$$H = \hbar \omega_q (a_q^\dagger a_q + \frac{1}{2}) + \alpha_{ii}^* a_q^\dagger + \alpha_{ii} a_q. \quad (4)$$

The transformation to the displaced oscillator is

$$\begin{aligned} H' &= e^{iS} H e^{-iS}; \quad \psi' = e^{iS} \psi, \\ S(q) &= [-i \alpha_{ii}^*(q) a_q^\dagger + i \alpha_{ii}(q) a_q] / \hbar \omega_q, \\ H' &= \hbar \omega_q (a_q^\dagger a_q + \frac{1}{2}) - |\alpha_{ii}(q)|^2 / \hbar \omega_q. \end{aligned} \quad (5)$$

The overlap integral may be evaluated by expanding the exponential  $e^{iS}$ . Only zero and one phonon terms need be kept at this point. Higher terms vanish in the limit of

<sup>1</sup> M. Lax and E. Burstein, Phys. Rev. **97**, 39 (1955).

<sup>2</sup> R. Newman, Phys. Rev. **99**, 465 (1955).

<sup>3</sup> H. J. Hrostowski and R. H. Kaiser, J. Phys. Chem. Solids **4**, 148 (1958).

<sup>4</sup> W. Kohn, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 257.

infinite volume when we are dealing with *nonlocalized* modes. It should be emphasized that we are justified in neglecting two and more phonons in a *single* mode. The

case of two or more phonons in different modes does not vanish for infinite volume and is here treated rigorously. The overlap integral may be evaluated as

$$|\langle e^{iS_a x_{n'}} | e^{iS_b x_n} \rangle|^2 = \begin{cases} \exp[-(2n_q+1)|(\alpha_{aa}(q)-\alpha_{bb}(q))/\hbar\omega_q|^2] & n'=n, \\ |(\alpha_{aa}(q)-\alpha_{bb}(q))/\hbar\omega_q|^2 \begin{cases} n_q \\ n_q+1 \end{cases} & n'=n-1, \\ |(\alpha_{aa}(q)-\alpha_{bb}(q))/\hbar\omega_q|^2 \begin{cases} n_q \\ n_q+1 \end{cases} & n'=n+1. \end{cases} \quad (6)$$

Substituting Eq. (6) in Eq. (2) gives

$$|\langle \psi_a | p_{e1} | \psi_b \rangle|^2 = \begin{cases} |M_{e1}|^2 e^{-\gamma_{ab}} & \text{no phonons} \\ |M_{e1}|^2 e^{-\gamma_{ab}} |(\alpha_{aa}(q)-\alpha_{bb}(q))/\hbar\omega_q|^2 \begin{cases} n_q & \text{absorption} \\ n_q+1 & \text{emission} \end{cases} & \text{one phonon} \\ |M_{e1}|^2 e^{-\gamma_{ab}} \left| \frac{(\alpha_{aa}(q)-\alpha_{bb}(q))}{\hbar\omega_q} \right|^2 \left| \frac{(\alpha_{aa}(q')-\alpha_{bb}(q'))}{\hbar\omega_{q'}} \right|^2 \begin{cases} n_q \\ n_q+1 \end{cases} \begin{cases} n_{q'} \\ n_{q'}+1 \end{cases} & \text{two phonons,} \end{cases} \quad (7)$$

$$\gamma_{ab} = \sum_q |(\alpha_{aa}(q)-\alpha_{bb}(q))/\hbar\omega_q|^2 (2n_q+1), \quad (8)$$

$$M_{e1} = \langle \phi_a | p_{e1} | \phi_b \rangle.$$

If we sum over all one phonon, two phonon, etc., possibilities we obtain

$$\sum_{q_1, q_2, \dots, q_n} |\langle \psi_a | p_{e1} | \psi_b \rangle|^2 = |M_{e1}|^2 \gamma_{ab}^n e^{-\gamma_{ab}} / n! \quad n \text{ phonons,} \quad (9)$$

$$\sum_n |M_{e1}|^2 \gamma_{ab}^n e^{-\gamma_{ab}} / n! = |M_{e1}|^2. \quad (10)$$

The fraction of the line strength in the no phonon transitions then depends on the constant,  $\gamma$ , which is proportional to the strength of the electron-phonon interaction. For weak interaction, the no phonon line is dominant; for strong interaction it is exponentially small. Although the above results are valid for strong coupling [for nonlocalized modes and neglecting  $\alpha_{ij}$  in Eq. (3) with  $i \neq j$ ], the convergence will be slow and Lax's moment method<sup>1</sup> would be more suitable for studying line shape.

Our approach has assumed the phonons to be independent. This is true when we ignore the terms  $i \neq j$  in Eq. (3) and is analogous to the neglect of recoil in the polaron problem.

### b. Hydrogenic Model

Using a simple hydrogenic ground state

$$\phi = (\pi\beta^3)^{-1/2} e^{-r/\beta}, \quad (11)$$

and ignoring the oscillator displacement in the excited state, we obtain for  $T=0^\circ\text{K}$

$$\gamma = -Z^2/6\pi^2\hbar\beta^2v^3\rho. \quad (12)$$

Taking  $Z=15$  ev for silicon and germanium gives  $\gamma=0.15$  silicon;  $\gamma=0.05$  germanium. A more accurate calculation using better wave functions, shear deforma-

tion, and transverse modes gives similar results. Values are not quoted since the deformation constants are not well known. It appears that for  $n$  and  $p$  germanium, the observed line is a no phonon line. The one phonon line might be observable as a broad tail, especially for silicon at higher temperatures.

### c. Lifetime; $\alpha_{ij} \neq 0, i \neq j$

If we now consider the  $i \neq j$  components of the phonon interaction in Eq. (3) we get a lifetime broadening equal to  $\hbar w$ , full width at half-maximum, where  $w$  is the transition probability. Standard perturbation theory gives

$$\hbar w_{ij} = \frac{E^3 Z^2}{2\pi\hbar^3 \rho v^5 [1 + (E/E_0)^2]^4} \frac{(\beta_i + \beta_j)^3}{2^3 (\beta_i \beta_j)^{3/2}} \begin{cases} n & \text{absorption} \\ n+1 & \text{emission} \end{cases}, \quad (13)$$

$$E_0 = (\beta_i + \beta_j)\hbar v / \beta_i \beta_j.$$

We have rather arbitrarily taken the wave functions of states  $i$  and  $j$  as 1s functions with Bohr radius  $\beta$ .  $n$  is the number of phonons in a mode of energy  $E$ .

To estimate the lifetime broadening of the  $B$  line observed by Burstein we note that the binding energy of the excited state is 0.011 ev. Another excited state lies  $4 \times 10^{-3}$  ev below it. We take

$$\begin{aligned} \beta_i &= \beta_j; & e^2/2\kappa\beta &= 0.011 \text{ ev}; & \beta &= 53 \text{ \AA}; \\ E &= 4 \times 10^{-3} \text{ ev}; & Z &= 15 \text{ ev}; & v &= \text{long. vel.}, \end{aligned}$$

and compute

$$E_0 = 2.1 \times 10^{-3} \text{ ev}; \quad \hbar w = 2.7 \times 10^{-5} (n+1) \text{ ev} = 6 \times 10^{-5} \text{ ev} \quad \text{at } 77^\circ\text{K}.$$

The experimental broadening is at least  $10^{-3}$  ev at  $77^\circ\text{K}$  even if the low-temperature breadth is assumed to be instrumental. The calculation is extremely sensitive to the value of  $\beta$  when  $E \geq E_0$ . If  $\beta$  had been taken a factor of 2 smaller, the broadening would have been 30 times greater, sufficient to agree with experiment. Correct wave functions are needed for a conclusive calculation. Another possible explanation for the disagreement might be the occurrence of a state not seen in optical transitions at the most favorable energy for broadening,  $E \simeq E_0$ .

At  $T=0^\circ\text{K}$  the lowest excited state is lifetime broadened only by transitions to the ground state. Equation (13) gives  $\hbar\omega \simeq 3 \times 10^{-6}$  ev for this broadening in  $B$  doped silicon. If the theory can be trusted to give *relative* values correctly the width would be  $\sim 5 \times 10^{-5}$  ev on multiplying by 16 as suggested by the above calculation. It seems possible, therefore, that measured low-temperature line widths are limited by instrumental resolving power for the lowest excited state transition.

#### d. $p$ -Type Spin Resonance

A more accurate calculation of lifetime broadening appropriate to the  $p$ -type spin resonance problem has been carried out using a 4-fold degenerate wave function for  $p$ -type germanium of the form

$$\phi_{m=+\frac{3}{2}} = (\pi\beta^3)^{-\frac{1}{2}} \begin{bmatrix} e^{-r/\beta} \\ 0 \\ 0 \\ 0 \end{bmatrix}. \quad (14)$$

The phonon interaction was taken from Ehrenreich's<sup>5</sup> deformable ion model with  $C_1 = +6.6$  ev,  $C_4 = +13.3$  ev,  $\delta = 0.7$ .

The effective deformation potentials for transitions between the 4 magnetic levels are given by

<sup>5</sup> H. Ehrenreich and A. W. Overhauser, Phys. Rev. **104**, 649 (1956).

$$\begin{aligned} (a) \quad Z_{\frac{3}{2}, \frac{1}{2} \text{ long}}^2 &= (8/45) \left( \frac{2}{5}C_1 + \frac{\delta}{2}C_4 \right)^2, \\ (b) \quad Z_{\frac{3}{2}, \frac{1}{2} \text{ trans}}^2 &= (4/15) \left( \frac{2}{5}C_1 + \frac{\delta}{2}C_4 \right)^2, \\ (c) \quad Z_{\frac{3}{2}, -\frac{1}{2} \text{ long}}^2 &= (4/45) \left[ \left( \frac{2C_1}{5} \right)^2 + \left( \frac{2}{5}C_1 + \frac{\delta}{2}C_4 \right)^2 \right], \quad (15) \\ (d) \quad Z_{\frac{3}{2}, -\frac{1}{2} \text{ trans}}^2 &= (2/15) \left[ \left( \frac{2C_1}{5} \right)^2 + \left( \frac{2}{5}C_1 + \frac{\delta}{2}C_4 \right)^2 \right], \\ (e) \quad Z_{\frac{3}{2}, -\frac{3}{2}}^2 &= Z_{\frac{1}{2}, -\frac{3}{2}}^2 = 0. \end{aligned}$$

The values of  $Z^2$  for transitions between levels of given  $m_J$  are the same as those for which the signs of both  $m_J$  values are reversed. The zero result in (15 e) is a consequence of time reversal symmetry.

Using Ehrenreich's values we compute  $Z^2$

$$(a) \ 9.5(\text{ev})^2; \ (b) \ 14.2(\text{ev})^2; \ (c) \ 5.4(\text{ev})^2; \ (d) \ 8.0(\text{ev})^2.$$

For a magnetic field splitting of  $10^{-4}$  ev the broadening due to the  $(\frac{3}{2}, -\frac{1}{2})$  transition is  $4 \times 10^{-7}$  ev. Additional broadening from the  $(n+1)$  factor in Eq. (13) begins at about  $1^\circ\text{K}$ .

The pairs of states  $(\frac{3}{2}, -\frac{3}{2})$  and  $(\frac{1}{2}, -\frac{1}{2})$  are time reversal or Kramers' doublets. No strain interactions occur between members of a doublet but linear combinations of the doublets due to strain may occur which gives a broadening due to the change in  $g$  value.

It should be noted that because of the small value of  $E$  in this case, the results are independent of the value of  $\beta$ . The main uncertainty lies in the determination of  $Z$ . The value of  $Z$  is very sensitive to the relative sign of  $C_1$  and  $C_4$ . We have taken the signs to be the same, which gives the largest value of  $Z$ . Unless the values of  $C$  are badly in error, a  $p$ -type resonance may be observable in strain free samples.