

Phonon coupling and photoionisation cross-sections in semiconductors

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Abstract. The coupling to lattice vibrations affects the photoionisation spectra of defects in semiconductors. This is especially important for deep defects. The effects are characterised mainly by a Huang–Rhys factor S_0 and by a spectral moment. These are calculated for a variety of electron–photon coupling mechanisms as a function of the observable ionisation energy E_1 rather than the unobservable effective radius used by previous workers. For Fröhlich coupling a good approximation for the Huang–Rhys factor is $S_0(x)/S_0(0) = x/\sqrt{[(5+x)/6]}$ with $x = E_1/(\text{effective Ryd for a purely hydrogenic centre})$.

1. Introduction

It is well known that optical transitions between bound states of defects in solids usually involve the absorption or emission of phonons. Despite this, it is almost universally assumed that photoionisation does not involve phonons other than the momentum-conserving phonon for indirect gap materials. This belief is a consequence of theoretical complexity, experimental uncertainties and the relatively small electron–photon coupling in semiconductors rather than a demonstrated result. The present note gives some estimates of the degree of phonon participation in a form which should prove convenient in the analysis of the properties of deep defects as well as shallow ones.

Almost two decades ago, Hopfield (1958) demonstrated the relation between the radial extent of a Gaussian bound-state wavefunction and the mean number of phonons emitted in the transition. This useful result has two drawbacks: defect wavefunctions are not accurately represented by Gaussians, nor are their spatial distributions measured directly. Instead, the photoionisation threshold E_1 and something about the type of binding potential (eg Coulombic, isovalent, etc) might be known, with the associated implications for the wavefunction. Thus the two key properties calculated will be expressed in terms of E_1 for certain standard situations. These properties are the Huang–Rhys factor S_0 , the mean number of phonons emitted at zero temperature, and the first moment relative to the transition energy with no phonon emission. If $S_{0\alpha}$ is the Huang–Rhys factor for mode α , then the first moment μ_1 is

$$\mu_1 = \sum_{\alpha} S_{0\alpha} \hbar\omega_{\alpha}. \quad (1)$$

The various $S_{0\alpha}$ can be calculated in terms of the wavefunction of the defect electron and the electron–lattice coupling. For simplicity, continuum models of the lattice and electron–lattice coupling will be used, paralleling work by Duke and Mahan (1965) on analogous

properties. The generalisation to other cases is not very different in principle and most aspects are discussed by Stoneham (1975, § 3.6).

2. Expressions for $S_{0\mathbf{k}}$

We assume an isotropic elastic continuum of density ρ and sound velocity v , with dielectric constants ϵ_∞ and ϵ_0 . The longitudinal optic phonons are assumed to be dispersionless and of energy $\hbar\omega_0$; the acoustic phonons are taken to belong to a threefold degenerate branch of energy $\hbar k/v$ for wavevector k . The cut-off wavevector is taken as $Q = (6\pi^2 N)^{1/3}$ where N is the number of atoms per unit volume.

The general expression for $S_{0\mathbf{k}}$ involves an electron–lattice coupling coefficient $V_{\mathbf{k}}$ and $M_{\mathbf{k}}$, which depends on the change in charge density in the transition:

$$S_{0\mathbf{k}} = |V_{\mathbf{k}}|^2 |M_{\mathbf{k}}|^2 \quad (2)$$

$$M_{\mathbf{k}} = \int d^3 r [\rho_i(r) - \rho_f(r)] \exp(-i\mathbf{k} \cdot r). \quad (3)$$

Here the charge densities ρ_i and ρ_f refer to the initial and final states; if the final unbound state can be regarded as constant in space, $M_{\mathbf{k}}$ may be written

$$M_{\mathbf{k}} = \int d^3 r |\psi_i(r)|^2 \exp(-i\mathbf{k} \cdot r) \quad (4)$$

in terms of the bound-state wavefunction. The electron–lattice coupling terms can be written in the form

$$|V_{\mathbf{k}}|^2 = f(k)/\Omega_c \quad (5)$$

where Ω_c is the crystal volume and $k = |\mathbf{k}|$. The important point about continuum forms of $V_{\mathbf{k}}$ is that they depend solely on the properties of the host material. Indeed, for present purposes only the qualitative dependence on k is needed. These dependences are given by Duke and Mahan:

$$\text{Fröhlich coupling to LO phonons} \quad f(k) = A_F k^{-2} \quad (6a)$$

$$\text{Deformation potential coupling to acoustic phonon} \quad f(k) = A_D k^{-1} \quad (6b)$$

$$\text{Piezoelectric coupling to acoustic phonons, with screening} \quad f(k) = A_P/[k^3(1 + k^2/\kappa^2)^2]. \quad (6c)$$

The materials constants A_F , A_D and A_P can be derived from the Duke–Mahan paper, e.g. $A_F = 2\pi(e^2/\hbar m_0)(\epsilon_\infty^{-1} - \epsilon_0^{-1})$. The screening wavevector is κ .

The effects of phonon coupling are now determined by equations (2), (4), (5) and (6) in terms of materials properties and the Fourier transform of the ground-state charge density. We now relate this Fourier transform to E_1 and the known features of the defect and examine the observable consequences.

3. Expressions for $M(\mathbf{k})$

The $M(k)$ are Fourier transforms of the charge density, not of the defect wavefunction. They have some general properties which are worth mentioning. First, normalisation

of $\psi_i(r)$ ensures

$$M(0) = \int d^3r |\psi_i(r)|^2 = 1. \tag{7}$$

Secondly, if $F_i(k)$ is the Fourier transform of $\psi_i(r)$, then the convolution theorem gives us

$$M(\mathbf{k}) = (1/2\pi)^3 \int d^3\mathbf{k}' F^*(\mathbf{k}') F(\mathbf{k}' - \mathbf{k}). \tag{8}$$

This expression is useful for shallow defects with short-range potentials in hosts with non-parabolic bands $E_B(\mathbf{k})$, for which $F(\mathbf{k}) \sim [E_i + E_B(\mathbf{k})]^{-1}$ (see e.g. Stoneham 1975, equation (5.2.22)). Thirdly, for small \mathbf{k}

$$|M(\mathbf{k})|^2 \simeq 1 - \sum_x B_x k_x^2 \tag{9}$$

can be written for wavefunctions of definite parity. Here, omitting a numerical factor which depends solely on the angular part of $\psi_i(r)$, one finds $B_x \sim \langle r_x^2 \rangle$, i.e. B_x depends on the 'moment of inertia' of the charge. For s functions the B_x are all the same, with

$$M(k) = (1/k) \int dr r |\psi_i|^2 \sin kr / \int dr r^2 |\psi_i|^2 \tag{10a}$$

$$B = \int dr. r^4 |\psi_i(r)|^2 / \int dr. r^2 |\psi_i(r)|^2. \tag{10b}$$

Equation (9) is a convenient simple approximation. Since $|M|^2$ is positive definite, the equation must be modified when $\sum_x B_x k_x^2 > 1$. In practice it usually suffices to set $|M|^2 = 0$ in that regime, so that relatively weak coupling to phonons with wavelengths much shorter than the orbital radius is ignored.

Table 1.

Wavefunction type	Form of radial wavefunction (unnormalised)	$M(k)$	Relationship between E_1 and a	Value of B
Hydrogenic 1s	$\exp(-r/a)$	$[1 + (ka/2)^2]^{-2}$	$E_1 \equiv E_H = (m^*/m_0)/\epsilon_0^2 \text{ Ry}$ $a = (m_0/m^*)\epsilon_0 \text{ au}$	a^2
Delta function	$r^{-1} \exp(-r/\bar{a})$	$\frac{\tan^{-1}(k\bar{a}/2)}{(k\bar{a}/2)}$	$E_1 = \hbar^2/2m^*\bar{a}^2$ $\bar{a} = (\hbar^2/2m^*E_1)^{1/2}$ $\bar{a} = a(E_H/E_1)^{1/2}$	0
Quantum defect	$r^{\nu-1} \exp(-r/va)$	$\frac{\sin[2\nu \tan^{-1}(\frac{1}{2}kva)]}{v^2 ka [1 + (\frac{1}{2}kva)^2]^\nu}$	$E_1 = E_H/v^2$; a and E_H related as for hydrogenic function	$a^2 v^2 [\frac{1}{6}(1 + 5v^2)]$
Gaussian 1s	$\exp(-r^2/a^2)$	$\exp(-a^2 k^2/8)$	No simple prescription	$\frac{1}{2}a^2$

Specific expressions for $M(k)$ can be obtained in quite a few cases. Only s states will be discussed, although other examples are simply found. The most useful are listed in table 1. Some comments are necessary. First, the quantum defect method (e.g. Bebb 1969) gives a wavefunction which interpolates between the hydrogenic ($\nu = 1$) and delta function ($\nu \rightarrow 0$) forms. However, the delta function limit is automatically deep, for $E_1 = E_H/v^2$ with E_H given by host properties. Thus E_1 and ν cannot be varied separately. The delta function can be defined separately, of course, and this is done in table 1.

Secondly, there is no satisfactory way of defining E_1 for Gaussian wavefunctions; they correspond to potentials $V(r) \sim r^2$ without unbound states. Thirdly the values of the orbital radius a for which the shortest wavelength is determined by the zone boundary Q rather than B of equation (10) can be found. This is achieved by writing $BQ^2 = 1$. For the quantum defect method, for example, this gives

$$Q^2 a^2 = 6/[v_0^2(1 + 5v_0^2)] \tag{11}$$

and defines a value of v_0 ; for deeper, more delta function-like defects the zone boundary provides the cut-off. For most III–V and II–VI hosts Qa is in the range 10–50, so that the zone boundary is relatively unimportant for all but the deepest defects. We return to this point in §6. Finally, E_H and a are properties of the host alone. Thus the quantum defect prescription gives

$$B_{\text{eff}} = \frac{1}{6}a^2(E_H/E_V)[1 + 5(E_H/E_V)] \tag{12}$$

so that B_{eff} decreases monotonically with E_V .

5. Observable effects

We consider only effects at zero temperature. It is useful to recall that, if a photoionisation cross section $G_0(E - E_V)$ is observed without phonon cooperation, then emission of a single phonon of energy E_x and fractional intensity S_{0x} gives an extra component in the cross section of $S_{0x}G_0(E - E_V - E_x)$ with a corresponding reduction in the original component. We shall not discuss momentum-conserving phonons here.

There are three main factors of interest.

(i) The Huang–Rhys factor S_0 :

$$S_0 = \sum_k S_{0k} \rightarrow \sum_{\text{branches}} (1/2\pi^2) \int dk k^2 f(k) |M(k)|^2 \dots \tag{13}$$

which is a measure of the degree of phonon cooperation. When S_0 is appreciable, any structures in $G(E - E_V)$ reflecting critical points in the conduction band are likely to be negligible.

(ii) The first moment μ_1 :

$$\mu_1 = \sum_k S_{0k} \hbar\omega_k \rightarrow \sum_{\text{branches}} (1/2\pi^2) \int dk k^2 f(k) |M(k)|^2 \hbar\omega_k \dots \tag{14}$$

If the photoionisation cross section has the standard form with a broad maximum, the peak E_{max} is shifted by μ_1 relative to the threshold. A direct fit of the quantum defect lineshape in this case would suggest a potential more like a delta function than appropriate.

(iii) The precise form of S_{0k} as a function of the phonon energy affects the threshold of photoionisation and the slope of the cross section. For weak coupling

$$G(E - E_V) = (1 - S_0)G_0(E - E_V) + \sum_k S_{0k}G_0(E - E_V - \hbar\omega_k) \tag{15}$$

with only one-phonon processes. Coupling to optical phonons only shows at energies exceeding $\hbar\omega_0$ above threshold in our model. Coupling to acoustic phonons shows at threshold and is especially significant for piezoelectric coupling, where $|V_k|^2$ has a peak related to the screening. Whether the threshold is significantly affected or not depends

also on how close to the threshold experiments are carried out. The main effect is a curvature of $G(E - E_1)$ whose character tends to suggest a higher threshold than the true one.

6. Results

The results can be summarised in two parts: firstly, the dependence on E_1 that is expected from the approximation of equation (10) to $|M(k)|^2$ and secondly, the accuracy of the approximation based on equation (9). The qualitative dependence on E_1 follows from equation (12) and dimensional analysis of the integrals in S_0 and μ_1 unless $BQ^2 > 1$, when the conclusions are more complex. There are also complications when there is piezoelectric coupling, when S_0 has a logarithmic singularity involving phonons with wavevector $k \sim 3\kappa$, i.e. with wavelength comparable with the screening length. As discussed by Duke and Mahan (1965), the observable consequences depend on the precise details of both piezoelectric and deformation-potential coupling. Since these vary from case to case, generalisations will not be attempted here, except to note that more than S_0 and μ_1 will be needed to give a useful description of threshold behaviour.

Table 2.

Type of coupling	S_0	μ_1	Comment
Fröhlich	$A_p/3\pi^2\sqrt{B}$	$A_F\hbar\omega_0/3\pi^2\sqrt{B}$	Only one frequency; all moments vary as $1/\sqrt{B}$
Deformation potential	$(3A_D/B)/8\pi^2$	$[A_D/B](\hbar\nu/\sqrt{B})/5\pi^2$	Most important phonon energies $\sim \hbar\nu/\sqrt{B}$.
Piezoelectric (screened)	Roughly $-\frac{3A_p}{2\pi^2 X^2} \ln(3\sqrt{X})$	Roughly $(3/2^2)A_p(\hbar\nu/\sqrt{B})$	$X \equiv B\kappa^2$. S_{0k} has a peak of order κ^{-1} at $k \sim 3\kappa$. Higher moments are well behaved.

Table 2 gives the approximate results. For pure Fröhlich coupling S_0 and μ_1 (and indeed all higher moments) vary as $B_{\text{eff}}^{-1/2}$. For deformation potential coupling $S_0 \sim B_{\text{eff}}^{-1}$ and $\mu_N \sim B_{\text{eff}}^{-1-(N/2)}$. Piezoelectric coupling gives $S_0 \sim X^{-2} \ln(3X^{1/2})$ and $\mu_1 \sim B_{\text{eff}}^{-1/2}$ with $X \equiv B_{\text{eff}}\kappa^2$. In all cases the value of S_0 increases as E_1 rises, with a saturation at large E_1 . This can be seen from equation (12) where $B_{\text{eff}}^{-1/2}$ varies roughly linearly with (E_V/E_H) when $E_1 \sim E_H$, yet varies as $(E_V/E_H)^{1/2}$ for deeper centres; there is, in any case, an upper bound when $|M(k)|^2 \simeq 1$ throughout the zone.

The remaining results are conveniently summarised in figure 1. For reference, (E_V/E_H) can range up to 50 or 100 in the III-V semiconductors, although clearly the bandgap puts an upper bound on E_1 . In the III-V compounds, the product Qa tends to lie in the range 10-50, i.e. the Bohr radius for a hydrogenic defect is much larger than the lattice spacing. The results show the expected dependence of S_0 on ionisation energy, which is intermediate between $E_1^{0.5}$ and $E_1^{1.0}$. No simple power law fits well. However, the approximation (9) works well qualitatively. When scaled to agree with the numerical results in the hydrogenic limit, very satisfactory agreement is obtained for deeper centres (curve D). The expression here is

$$S_0 \sim (E_V/E_H)/[1/6(5 + E_V/E_H)]^{1/2}.$$

Obviously, more exact results can be obtained by interpolation.

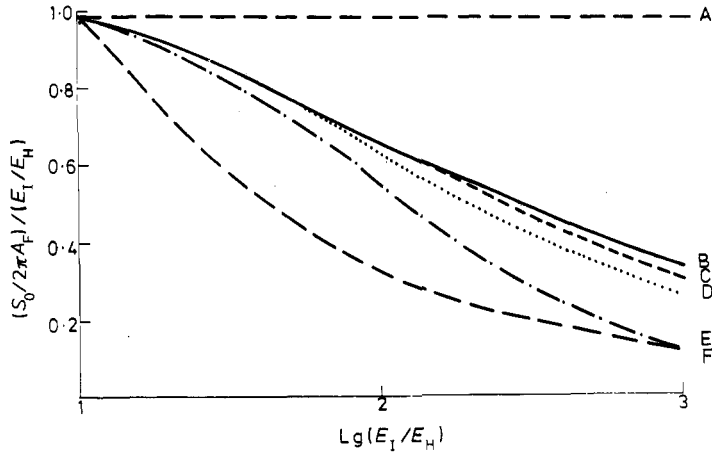


Figure 1. S_0 in units $(A_F E_I / 2\pi E_H a)$ as a function of E_I/E_H . Curve A limiting case, $S_0 \propto E_I$; curve B exact, $Qa = \infty$; curve C exact, $Qa = 100$; curve D approximate, $Qa = \infty$; curve E exact, $Qa = 10$; curve F limiting case, $S_0 \propto E_I^{1/2}$. Exact means that numerical integration was used without the approximation of $M(k)$; for the approximate curve, equations (9) and (12) were used but the curve was scaled to fit the exact curve in the hydrogenic limit.

Finally, we return to equation (11) and the circumstances in which the shortest-wavelength phonons of importance are determined by $BQ^2 = 1$ rather than by $k = Q$. For the zone boundary to be relatively unimportant (i.e. S_0 negligibly dependent on Q), equation (11) gives $\nu_0 = 0.22$ for $Qa = 10$ and $\nu_0 = 0.024$ for $Qa = 100$. Values listed in the Appendix show these estimates of ν_0 are slightly optimistic for Fröhlich coupling. A significant dependence on Q appears around $\nu = 0.4$ for $Qa = 10$ and $\nu = 0.1$ for $Qa = 100$.

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Appendix. Values of integrals appearing in S_0

The values listed here are of the integral

$$\int_0^Q dk k^2 f_i(k) |M_k|^2$$

using equations (6) and table 1. The integrals were evaluated numerically and are in units of the appropriate power of a .

Table A1.

Wavefunction or type of potential	Fröhlich coupling, with $f_1(k)$			Deformation potential ($Qa = \infty$) with $f_2(k)$	Piezoelectric coupling ($Qa = \infty$) with $f_3(k)$		
	$Qa = \infty$	$Qa = 100$	$Qa = 10$		$Ka = 0.2$	$Ka = 0.1$	$Ka = 0.01$
Delta-function	4.355				2.099	2.772	5.065
Quantum defect							
$\nu = 0.1$	31.790	27.707	9.351		4.161	4.853	7.156
$\nu = 0.2$	12.585	12.409	7.628		3.298	3.989	6.290
$\nu = 0.4$	4.480	4.479	4.171	222.39	2.345	3.028	5.326
$\nu = 0.6$	2.333	2.333	2.318	16.112	1.753	2.420	4.710
$\nu = 0.8$	1.441	1.441	1.440	2.880	1.330	1.973	4.251
Hydrogenic							
$\nu = 1.0$	0.98175	0.98175	0.98175	0.7854	1.012	1.624	3.882

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