

ENERGY STATES OF A ONE-DIMENSIONAL CRYSTAL WITH VACANT LATTICE SITES

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ABSTRACT

In this present paper, the effect of regularly spaced vacant sites (in an otherwise perfect one-dimensional crystal) on the electronic energy states has been investigated. The crystal model has been idealized by setting a δ -potential barrier at each occupied lattice point. Use has been made of the calculated energy levels in determining the percentage changes in electrical conductivity and low-frequency limit (ν_f) of fundamental absorption band.

INTRODUCTION

It is well known from the work of Kronig and Penny (1931) that many of the results about the energy states of a real three-dimensional crystal may be obtained from a hypothetical one-dimensional crystal. This is particularly true in the case of long wavelength limit of fundamental absorption band and the variation of electrical conductivity with temperature. In a three-dimensional crystal, the difficulty arises because the lattice gives symmetry along planes. The potential due to the lattice contributes, in addition to this, another symmetry of approximately spherical in nature. The latter type of symmetry is due to atomic or ionic sites. This necessitates a matching of plane and spherical waves over a large number of boundaries distributed according to the lattice (Slater, 1953*a* and 1953*b*). It is very difficult to incorporate the effect of lattice imperfections in such a three-dimensional representation. However, in some cases of regular imperfections, a one-dimensional representation can be utilized with profit. In this paper, we give the shift of long wavelength limit of fundamental absorption band (ν_f) and the change of electrical conductivity with vacancy concentration for a one-dimensional crystal. The method is based on a straightforward perturbation theory with the use of a δ -function potential at each lattice point.

THE UNPERTURBED PROBLEM

We take the unperturbed energy states and wave functions as corresponding to the perfect crystal. Figure 1 shows the idealized square type potential in such a

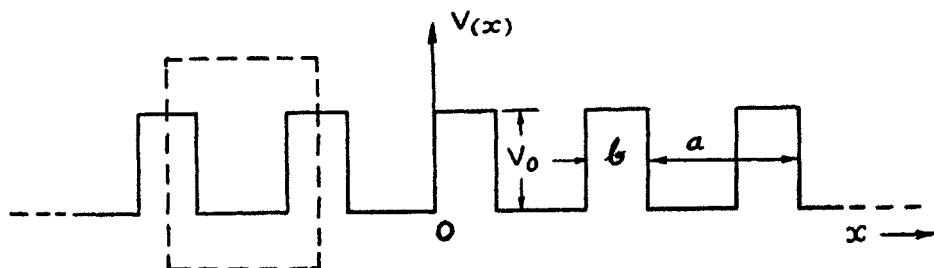


FIG. 1. Idealized potential in a perfect one-dimensional crystal.

case according to Kronig and Penny (1931). The part shown with dotted rectangle represents a typical unit cell with lattice constant equal to a . V_0 is the height and b is the width of the potential hump. The situation can be further idealized by supposing that $b \rightarrow 0$ and $V_0 \rightarrow \infty$ with $V_0 b = A = \text{constant}$. This reduces the potential to a number of δ -functions of strength A spaced regularly at distance a .

The eigenvalue equation for unperturbed electronic energy can be simply written as (Kittel, 1954)

$$\theta \frac{\sin \phi}{\phi} + \cos \phi = \cos \lambda, \quad \dots \dots \dots (1)$$

where $\theta = maA/\hbar^2$, $m = \text{mass of the electron}$; $\hbar = \text{Planck's constant}/2\pi$, $\phi = \alpha a$, $\alpha = \sqrt{(2mW)/\hbar}$, $W = \text{electronic energy}$, $\lambda = ak$, $k = 2\pi g/Na$, $N = \text{total number of lattice points in the crystal}$ and $g = 0, 1, 2, 3, \dots, N-1$.

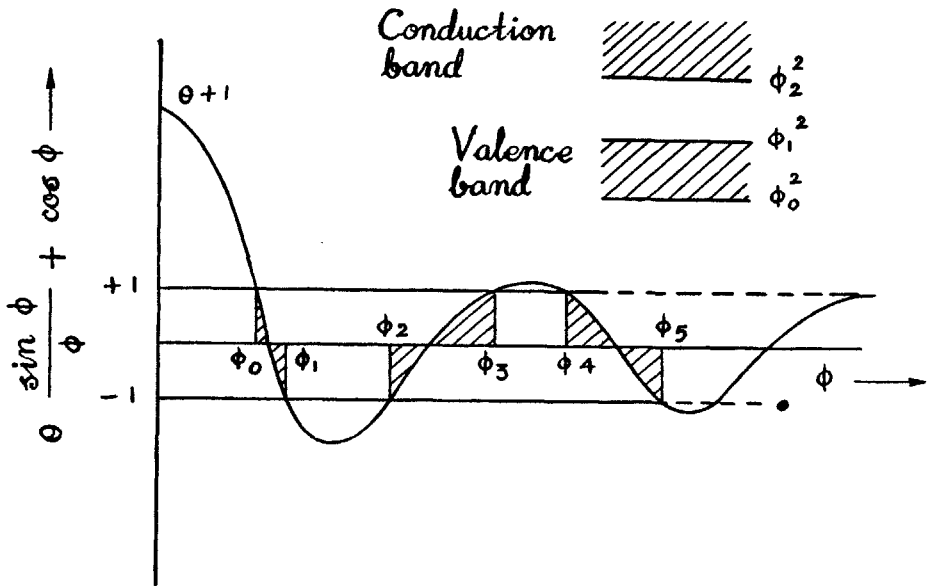


FIG. 2. Allowed energy states of the ideal crystal (Kramers, 1935).

In Figure 2, the allowed electronic energy values are given by values of ϕ within the shaded region. The minimum permissible energy is

$$W_0 = \hbar^2 \phi_0^2 / (2ma^2).$$

Energy at the top of the valence band is

$$W_1 = \hbar^2 \phi_1^2 / (2ma^2), \quad \dots \dots \dots (2)$$

and that at the bottom of the conduction band is

$$W_2 = \hbar^2 \phi_2^2 / (2ma^2). \quad \dots \dots \dots (3)$$

The unperturbed value of ν_f is given by

$$\nu_f^{(0)} = (W_2 - W_1)/\hbar = \hbar(\phi_2^2 - \phi_1^2) / (8\pi^2 ma^2). \quad \dots \dots (4)$$

From the graph of Figure 2, $\phi_1 = \pi$. Let $\phi_2 = \pi(1+\delta)$. If the crystal has a band gap of n electron-volts, it is easily seen that

$$\pi\delta \approx (0.3n)/2\pi.$$

For most semiconductors n is between 0.2 and 2.0 so that $\pi\delta$ is small compared to unity. Substituting the value of ϕ_2 in equation (1) and equating the right hand side to -1 , we get

$$\delta \doteq \left\{ -1 + \sqrt{1 + \frac{8\theta}{\pi^2}(1+\theta/3)} \right\} / \{2(1+\theta/3)\} \quad \dots \quad (5a)$$

Better approximation to the root by the Newton-Raphson method gives a correction

$$\Delta\delta = \frac{-4.05878^4(1+0.2\theta\delta)}{\{\theta - \delta(\theta + 9.8696) - \delta^2(3.9348\theta + 4.9348) + \delta^3(3.9348\theta + 21.170)\}} \quad (5b)$$

Generally both θ and δ are small compared to unity, so that the correction given by equation (5b) is usually insignificant. By substituting the values of ϕ_1 and ϕ_2 in equation (4), we have

$$v_f^{(0)} = \{h\delta(2+\delta)\} / \{8ma^2\}, \quad \dots \quad (6)$$

where δ is given by equation (5a).

The wave function of the electron in the assumed perfect lattice is a plane wave with constants characteristic to each unit cell, viz.

$$\psi_n(x) = A_n e^{i\alpha x} + B_n e^{-i\alpha x}, \quad \dots \quad (7)$$

where x is the distance measured from the origin (Figure 1), and A_n and B_n are constants for a particular cell, say the n th, at which the value of the wave function is sought. By Floquet's theorem, these are related to the constants of the cell containing the origin as

$$A_n = A_0 e^{\{-ina\alpha + 2\pi in/N\}}; \quad \dots \quad (8a)$$

and

$$B_n = B_0 e^{\{ina\alpha + 2\pi in/N\}}. \quad \dots \quad (8b)$$

Normalization of the unperturbed wave function gives

$$\sum_{n=0}^{N-1} \int_{na}^{(n+1)a} \psi_n^*(x) \psi_n(x) dx = 1,$$

which by equation (7) reduces to

$$\sum_{n=0}^{N-1} A_n^2 \int_{na}^{(n+1)a} \left[1 + \frac{B_n^2}{A_n^2} + \frac{B_n}{A_n} e^{-2i\alpha x} + \frac{B_n^*}{A_n} e^{2i\alpha x} \right] dx = 1 \quad \dots \quad (9a)$$

Now

$$\frac{B_n}{A_n} = \frac{B_0}{A_0} e^{2ina\alpha} = \frac{B_0}{A_0} e^{2in\phi} \quad \dots \quad (9b)$$

and the continuity of the wave function gives

$$\frac{B_0}{A_0} = - \frac{[1 - e^{i(\alpha-h)a}]}{[1 - e^{-i(\alpha+h)a}]} = - \frac{[1 - e^{i(\phi-\lambda)}]}{[1 - e^{-i(\phi+\lambda)}]} \quad \dots \quad (9c)$$

Hence by equations (9a), (9b) and (9c), we obtain

$$\sum_{n=0}^{N-1} A_n^2 \left[\left(1 + \frac{\sin^2 \frac{\lambda - \phi}{2}}{\sin^2 \frac{\lambda + \phi}{2}} \right) a - 2(\sin \phi / \alpha) \cdot \frac{\sin \frac{\lambda - \phi}{2}}{\sin \frac{\lambda + \phi}{2}} \right] = 1.$$

Again, from (8a), $A_n^2 = A_0^2$. Therefore,

$$A_0 = (1/\sqrt{N}) \cdot \{1/\sqrt{f(\phi, \lambda)}\}, \quad \dots \dots \dots (10a)$$

where

$$f(\phi, \lambda) = a \left[1 + \frac{\sin^2 \frac{\lambda - \phi}{2}}{\sin^2 \frac{\lambda + \phi}{2}} - 2(\sin \phi / \alpha) \cdot \frac{\sin \frac{\lambda - \phi}{2}}{\sin \frac{\lambda + \phi}{2}} \right]. \quad \dots \dots (10b)$$

THE PERTURBED ENERGY STATES

The perturbed potential in a crystal with vacant lattice sites can be represented as in Figure 3. This corresponds to the potential of a perfect crystal with a negative potential at each vacancy of height $-V$ and width 2ζ such that

$$2V\zeta = A.$$

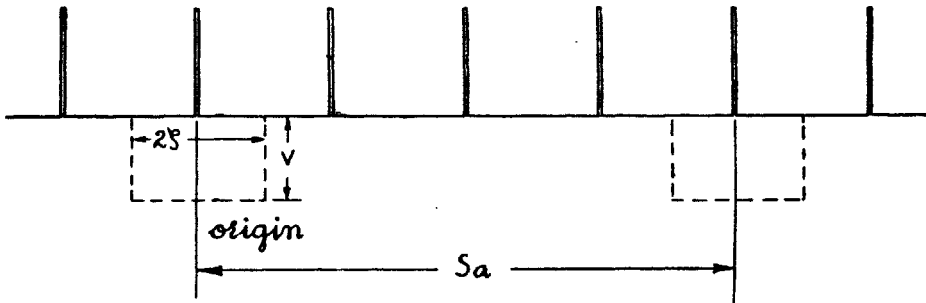


FIG. 3. Idealized potential for vacancy in a one-dimensional crystal.

Let the concentration of vacancies be $1/S$, supposed regular. Then the matrix element of the perturbing potential becomes

$$\begin{aligned} (\phi | V_{\text{perturbing}} | \phi') &= -V \sum_{p=0}^{N/S} \int_{Spa}^{S(p+1)a} (A_{\phi, Sp}^* e^{-i\alpha x} + B_{\phi, Sp}^* e^{i\alpha x})(A_{\phi', Sp} e^{i\alpha' x} + B_{\phi', Sp} e^{-i\alpha' x}) dx \\ &- V \sum_{p=0}^{N/S} \int_{S(p-1)a}^{Spa} (A_{\phi, Sp-1}^* e^{-i\alpha x} + B_{\phi, Sp-1}^* e^{i\alpha x})(A_{\phi', Sp-1} e^{i\alpha' x} + B_{\phi', Sp-1} e^{-i\alpha' x}) dx \end{aligned}$$

Substituting the values of A 's and B 's from equations (8), (9) and (10), we then have

$$(\phi | V_{\text{perturbing}} | \phi') = - \frac{V}{S\sqrt{\{f(\phi, \lambda)f(\phi', \lambda')\}}} \cdot F,$$

where the factor F is given by

$$\begin{aligned}
 F = & \left[\left\{ \frac{e^{i(\alpha' - \alpha)\zeta} - 1}{i(\alpha' - \alpha)} \right\} \left\{ 1 + e^{i(\alpha' - \alpha)(a - \zeta)} \right\} \right. \\
 & - \frac{(e^{-ika} - e^{-i\alpha a})(e^{i(\alpha + \alpha')\zeta} - 1)(1 + e^{i(\alpha + \alpha')(a - \zeta)})}{i(e^{-ika} - e^{i\alpha a})(\alpha + \alpha')} \\
 & - \frac{(e^{ik'a} - e^{i\alpha'a})(e^{-i(\alpha + \alpha')\zeta} - 1)(1 + e^{-i(\alpha + \alpha')(a - \zeta)})}{\{e^{ik'a} - e^{-i\alpha'a}\} \{-i(\alpha + \alpha')\}} \\
 & \left. + \frac{(e^{-ika} - e^{-i\alpha a})(e^{ik'a} - e^{i\alpha'a})(e^{i(\alpha - \alpha')\zeta} - 1)(1 + e^{i(\alpha - \alpha')(a - \zeta)})}{(e^{-ika} - e^{i\alpha a})(e^{ik'a} - e^{i\alpha'a})(i(\alpha - \alpha'))} \right].
 \end{aligned}$$

In the limiting case of a δ -perturbing potential with $\zeta \rightarrow 0$, $V \rightarrow \infty$ but $2V\zeta = A = \text{constant}$, we have

$$\begin{aligned}
 & (\phi | V_{\text{perturbing}} | \phi') \\
 & = - \frac{A}{2S\sqrt{\{f(\phi, \lambda)f(\phi', \lambda')\}}} \left[(1 + e^{i(\phi' - \phi)}) - \frac{(1 - e^{i(\lambda - \phi)}) \cdot (1 + e^{i(\phi + \phi')})}{(1 - e^{i(\lambda + \phi)})} \right. \\
 & - \frac{(1 - e^{-i(\lambda' - \phi')})(1 + e^{-i(\phi + \phi')})}{(1 - e^{-i(\lambda' + \phi')})} \\
 & \left. + \frac{(1 + e^{i(\lambda - \phi)})(1 - e^{-i(\lambda' - \phi')})(1 + e^{i(\phi - \phi')})}{(1 - e^{i(\lambda + \phi)})(1 - e^{-i(\lambda' + \phi')})} \right]. \quad \dots \quad \dots \quad \dots \quad (11a)
 \end{aligned}$$

From equation (11a), we get the diagonal term, after algebraic simplification, as

$$(\phi | V_{\text{perturbing}} | \phi) = - \frac{A}{Sf(\phi, \lambda)} \cdot \frac{\sin^2 \phi}{\sin^2 \frac{\lambda + \phi}{2}} \quad \dots \quad \dots \quad (11b)$$

Therefore, the first order corrected energy is

$$W^{(1)} = W - \frac{A}{Sf(\phi, \lambda)} \cdot \frac{\sin^2 \phi}{\sin^2 \frac{\lambda + \phi}{2}} = \frac{\hbar^2 \phi^2}{2ma^2} - \frac{A}{Sf(\phi, \lambda)} \cdot \frac{\sin^2 \phi}{\sin^2 \frac{\lambda + \phi}{2}} \quad \dots \quad (12)$$

It can be shown that higher order energy corrections are usually negligible. From equation (12) it follows that the effect of vacancy is always to lower the energy level. It is possible, however, that a level higher than another may actually become lower due to perturbation. There will also be levels that are undisturbed. One such is at the top of the valence band ($\phi_1 = \lambda_1 = \pi$), where the value of the fraction

$$\left\{ \sin^2 \phi \right\} / \left\{ \sin^2 \frac{\lambda + \phi}{2} \right\}$$

is given by

$$\lim_{\substack{\xi \rightarrow 0 \\ \epsilon \rightarrow 0}} \left\{ \sin^2 (\pi + \xi) \right\} / \left\{ \sin^2 \left(\pi + \frac{\xi + \epsilon}{2} \right) \right\}, \quad \dots \quad \dots \quad (13a)$$

where ξ denotes a small change in ϕ near π due to a small change ϵ in λ near π . ξ and ϵ are related through the eigenvalue equation (1), viz.

$$\theta \frac{\sin(\pi + \xi)}{(\pi + \xi)} + \cos(\pi + \xi) = \cos(\pi + \epsilon). \quad \dots \quad (13b)$$

Expanding both sides of equation (13b), it can be shown that ξ is a second order infinitesimal in ϵ and hence the limit of expression (13a) is zero. However, $f(\phi_1, \lambda_1) \neq 0$ so that the energy at the top of valence band is unchanged due to perturbation, viz.

$$W_1^{(1)} = (\hbar^2 \pi^2) / (2ma^2). \quad \dots \quad (14a)$$

At the bottom of the conduction band, we have

$$\frac{\sin^2 \phi_2}{\sin^2 \frac{\phi_2 + \lambda_2}{2}} = \frac{\sin^2 \pi(1 + \delta)}{\sin^2 \frac{\pi(1 + \delta) + \pi}{2}} \doteq 4(1 - \pi^2 \delta^2 / 4). \quad \dots \quad (14b)$$

Again from equation (10b),

$$f(\phi_2, \lambda_2) = a \left[2 + \frac{2 \sin \pi \delta}{\pi(1 + \delta)} \right] \doteq 2a(1 + \delta - \delta^2 - 0.6449\delta^3). \quad \dots \quad (14c)$$

Substituting equations (14b) and (14c) in equation (12) and simplifying, we get the first order corrected energy at the bottom of conduction band as

$$W_2^{(1)} \doteq \frac{\hbar^2 \pi^2 (1 + \delta)^2}{2ma^2} - \frac{2A}{Sa} (1 - \delta - 0.468\delta^2 + 0.113\delta^3). \quad \dots \quad (14d)$$

The perturbed band gap $E = W_2^{(1)} - W_1^{(1)}$ and ν_f are obtained from (14a) and (14d) respectively as follows :

$$E = \hbar^2 \delta (2 + \delta) / (8ma^2) - 2A(1 - \delta - 0.468\delta^2 + 0.113\delta^3) / Sa \quad \dots \quad (15a)$$

and

$$\begin{aligned} \nu_f &= \frac{W_2^{(1)} - W_1^{(1)}}{\hbar} = \hbar \delta (2 + \delta) / (8ma^2) - 2A(1 - \delta - 0.468\delta^2 + 0.113\delta^3) / Sa\hbar \\ &= \nu_f^{(0)} - 2A(1 - \delta - 0.468\delta^2 + 0.113\delta^3) / Sa\hbar. \quad \dots \quad (15b) \end{aligned}$$

Hence the long wavelength limit of the fundamental absorption band shifts to the longer wavelength side. Since δ is small, the percentage shift is given approximately by

$$200A / Sa\hbar \nu_f^{(0)} \% \approx 200\theta / \pi^2 S \delta \% \approx (100/S) \% \quad \dots \quad (16)$$

which is obtained from equations (1), (5a) and (6).

The electrical conductivity of a semi-conductor at an absolute temperature T is given by a formula of the type

$$\sigma_T = \sigma e^{-E/kT}, \quad \dots \quad (17a)$$

where σ is a certain constant, E = band gap, and k = Boltzmann's constant.

If the band gap decreases by an amount ΔE due to vacancy, the percentage increase in conductivity is given by

$$100 \Delta \sigma_T / \sigma_T \% = 100(e^{\Delta E/kT} - 1) \% \quad \dots \quad (17b)$$

Now from equation (16) $\Delta E/E = \Delta \nu_f/\nu_f \approx 1/S$, so that $\Delta E \approx E/S$. The percentage increase in conductivity can, therefore, be put as $\approx 100(e^{E/SkT} - 1) \%$ or approximately by $100 E/SkT \%$ unless the temperature is very low or the vacancy concentration is very high.

DISCUSSION

The fractional change in ν_f equal to $1/S$ is a result that is expected semi-classically, the reason being that this indicates the fractional fall of average potential throughout the lattice.

For a vacancy of 1 in 10^4 atoms, the value of ν_f decreases by about $(1/100) \%$, which is near the limit of accuracy of an ordinary good optical spectroscope. Vacancies rarer than this will be difficult to detect optically although the range will be extended if the ν_f of the crystal falls in red or infra-red region.

The electrical conductivity change is much more due to the exponential nature of variation. Most semi-conductors have E value between 0.2 and 2.0 electron-volts, so that the percentage increase of conductivity at room temperature is between $(800/S) \%$ and $(8000/S) \%$. With a vacancy concentration of 1 in 10^4 , this comes out as between 0.08 % to 0.8 %, a change that can be precisely measured by accurate electrical methods. At lower temperature, the percentage increase will be more.

The percentage shift in ν_f is the same for all crystals having the same vacancy concentration. The percentage change in electrical conductivity, on the other hand, depends on E and S both. Knowing the value of E from fundamental absorption data, S can be calculated from the increase in electrical conductivity.

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