Disordered One-Dimensional Crystals

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A mathematical method is developed which gives fairly generally the density of eigenstates for one-dimensional disordered systems. The method is applied first to a disordered linear chain of elastically coupled masses. The results for the energy spectrum are closely related to those obtained by Dyson.

Then we consider the electronic energy-states in a one-dimensional disordered crystal, represented by a series of δ-function potentials of different strengths, randomly distributed.

We solve the resulting functional equation explicitly in that case which corresponds to a uniform crystal with a small amount of impurities; that is, we find the shape of the impurity bands.

I. INTRODUCTION

THE energy levels of an electron in a pure crystal can be computed in principle if the crystal potential is known. In this paper we will study the case in which the crystal consists of different atoms, randomly distributed.

We restrict our considerations to a one-dimensional crystal model and hope that this gives in some respects a qualitatively correct description of real three-dimensional crystals.

We shall use a general mathematical method which also applies to similar problems. One of these is the determination of the eigenfrequencies of a linear chain which consists of elastically coupled atoms with randomly varying masses. This problem is interesting in itself and most suitable for demonstrating the mathematical method involved. Therefore, we will consider it first.

II. FREQUENCY SPECTRUM OF A DISORDERED CHAIN

(a) Description of the Model

Suppose that we have an alloy containing i different kinds of atoms $A^1, \cdots, A^i$ with the masses $m^1, \cdots, m^i$. Let p^j be the fraction of atoms A^j, $\sum p^j = 1$. As a one-dimensional model of this crystal we choose a chain of elastically coupled masses $m_1, m_2, m_3, \cdots$, where the nth mass m_n can assume the values $m^1, \cdots, m^i$ with the probabilities $p^1, \cdots, p^i$. Suppose for the present that these probabilities are independent of the nature of the atoms which occupy the neighboring places $(n-1)$ and $(n+1)$. (The case where a correlation between neighboring atoms exists will be discussed in Appendix II.) Furthermore we will assume that the forces between all neighboring atoms can be described by the same elastic constant k.

Now consider such a chain of many, say N, atoms and assume as the boundary conditions that the chain is fixed at the points which correspond to the place numbers $n=0$ and $n=N+1$. Then the equation of

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motion for this chain may be written as

$$m_n \ddot{u}_n = k(u_{n+1} + u_{n-1} - 2u_n) \text{ for } n = 1, 2, \cdots N, \quad \text{(II, 1a)}$$

$$u_0 = u_{N+1} = 0. \quad \text{(II, 1b)}$$

Here $u_1 \cdots u_N$ are the displacements of the masses $m_1 \cdots m_N$ from their equilibrium position and $u_0 = u_{N+1} = 0$ are merely introduced to establish the validity of (II, 1a) also for $n=1$ and $n=N$.

With $M_n \equiv m_n/k$, $M^j = m^j/k$ and $\ddot{u}_n = -\omega^2 u_n$, Eq. (II, 1) gives

$$u_n(2 - M_n \omega^2) = u_{n+1} + u_{n-1} \text{ for } n = 1, 2, \cdots N, \quad \text{(II, 2)}$$
$$u_0 = u_{N+1} = 0.$$

The secular equation for the eigenvalues ω_ν^2 of ω^2 can now be written as

$$\begin{vmatrix} 2 - M_1\omega^2 & -1 & & & \\ -1 & 2 - M_2\omega^2 & -1 & & \\ & -1 & 2 - M_3\omega^2 & -1 & \\ & & & -1 & 2 - M_N\omega^2 \end{vmatrix} = 0.$$

We could try to determine the possible eigenvalues ω_ν^2 from this equation and then by averaging over all possible chains find the mean distribution of the eigenvalues. This way, however, is mathematically difficult. We have found a different method which seems considerably simpler.

(b) New Formulation of the Eigenvalue Problem

We write Eq. (II, 2) in matrix form:

$$\begin{pmatrix} u_n \\ u_{n+1} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 2 - M_n\omega^2 \end{pmatrix} \begin{pmatrix} u_{n-1} \\ u_n \end{pmatrix}$$

$$\text{for } n = 1, 2, \cdots N, \quad \text{(II, 3)}$$
$$u_0 = u_{N+1} = 0.$$

From this it follows that

$$\begin{pmatrix} u_N \\ u_{N+1} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -1 & 2 - M_N\omega^2 \end{pmatrix} \cdots$$

$$\times \begin{pmatrix} 0 & 1 \\ -1 & 2 - M_1\omega^2 \end{pmatrix} \begin{pmatrix} u_0 \\ u_1 \end{pmatrix}. \quad \text{(II, 4)}$$

Now instead of considering $u_0=0$ and $u_{N+1}=0$ as fixed numbers in Eq. (II, 4) for ω^2, we fix only $u_0=0$. Then with $u_0=0$ and $u_1=\cos\omega t$, Eq. (II, 4) gives $u_{N+1}=u_{N+1}(\omega^2)\cos\omega t$ as a function of ω^2 and t, and whenever $u_{N+1}(\omega^2)=0$, then both the boundary conditions are satisfied and $\omega^2=\omega_\nu^2$ is an eigenvalue of our problem.

To study the ω^2 dependence of $u_{N+1}(\omega^2)$, we look at the two-dimensional vectors

$$\mathbf{v}_n(\omega^2)\equiv\begin{pmatrix}u_{n-1}\\u_n\end{pmatrix}\qquad(\text{II, 5})$$

in an x-y plane; $\mathbf{v}=\begin{pmatrix}x\\y\end{pmatrix}$. These vectors have a remarkable property: With increasing ω^2 the vector $\mathbf{v}_n(\omega^2)$ rotates uniformly in the positive direction around the zero point in the x-y plane, i.e., if $\varphi_n/2$ is the angle between the positive x-direction and the vector $\mathbf{v}_n$, then $\varphi_n(\omega^2)$ increases monotonically with ω^2.

To prove this we define

$$z_n(\omega^2)=u_{n-1}/u_n=\tan(\varphi_n/2).\qquad(\text{II, 6})$$

Then (3) implies

$$z_{n+1}=1/(2-M_n\omega^2-z_n)\quad\text{for}\quad n=1, 2, \cdots N.\qquad(\text{II, 7})$$

with the boundary condition

$$z_1=0,\quad z_{N+1}=\infty.\qquad(\text{II, 8})$$

Equations (II, 6) and (II, 7) establish a continuous connection between φ_n and φ_{n+1}. We shall make this connection unique by requiring in accordance with (II, 6) and (II, 7) that

$$\varphi_n=2\pi h+\pi\quad\text{implies}\quad\varphi_{n+1}=2\pi h+2\pi.\qquad(\text{II, 9})$$

(Here and in the following, h is any integer.)

If we furthermore put $\varphi_1=0$ (in accordance with the boundary condition $u_0=0$) then $\varphi_n=\varphi_n(\omega^2)$ is a well-defined function of ω^2. The second boundary condition $u_{N+1}=0$ is satisfied whenever

$$\varphi_{N+1}(\omega^2)=\pi+2\pi h\quad(\text{boundary condition}).\qquad(\text{II, 10})$$

Now from (II, 6) and (II, 7) it follows that

$$\left(\frac{\partial\varphi_{n+1}}{\partial\varphi_n}\right)_{\text{for constant }\omega^2}=z_{n+1}^2\left(\frac{1+z_n^2}{1+z_{n+1}^2}\right)\geq 0,$$

$$\left(\frac{\partial\varphi_{n+1}}{\partial\omega^2}\right)_{\text{for constant }\varphi_n}=2M_n\left(\frac{z_{n+1}^2}{1+z_{n+1}^2}\right)\geq 0.$$

Therefore with $\varphi_1=0$ the functions $\varphi_2(\omega^2)$, $\varphi_3(\omega^2)$, $\cdots$ are monotonic nondecreasing functions of ω^2.

Let now ω^2 increase from ω_a^2 to ω_b^2. Then $\varphi_{N+1}(\omega^2)$ increases monotonically from $\varphi(\omega_a^2)$ to $\varphi(\omega_b^2)$ and whenever in this region $\varphi_{N+1}(\omega^2)=\pi+2\pi h$, then both the boundary conditions are satisfied and $\omega^2=\omega_\nu^2$ is an eigenvalue. Therefore the number of eigenvalues in the interval $\omega_a^2<\omega^2<\omega_b^2$ is (with an error smaller than

unity) given by

$$\frac{1}{2\pi}[\varphi_{N+1}(\omega_b^2)-\varphi_{N+1}(\omega_a^2)]$$
$$\equiv N[M(\omega_b^2)-M(\omega_a^2)],\qquad(\text{II, 11})$$

where $M(\omega^2)$ is defined as

$$M(\omega^2)\equiv(1/N)\times\{\text{number of eigenvalues }\omega_\nu^2$$
$$\text{with }\omega_\nu^2<\omega^2\}.\qquad(\text{II, 12})$$

Then[1]

$$M(\omega^2)=(1/2\pi N)\varphi_{N+1}(\omega^2)+\text{const}.\qquad(\text{II, 13})$$

(c) Chains with Randomly Distributed Atoms

So far we have discussed only one chain with a specified distribution of the masses $M^1, \cdots M^i$ over the places $(1), \cdots (N)$. Now we consider a large number of such chains with different random distributions of the masses. For each of these chains the vector

$$\mathbf{v}_n(\omega^2)=\begin{pmatrix}0 & 1\\-1 & 2-M_{n-1}\omega^2\end{pmatrix}\cdots\begin{pmatrix}0 & 1\\-1 & 2-M_1\omega^2\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix}$$

is a different function of ω^2.

Let us describe the probability distribution of the vector $\mathbf{v}_n(\omega^2)=\begin{pmatrix}u_{n-1}\\u_n\end{pmatrix}$ over the different directions in in the x-y plane by means of a distribution function for $z_n=u_{n-1}/u_n$. We define:

$$w_n[z]dz$$
$$\equiv\frac{\text{No. of chains for which }z<z_n(\omega^2)<z+dz}{\text{total number of chains}}.\qquad(\text{II, 14})$$

Then we can easily obtain a relationship between the distribution functions $w_n[z]$ and $w_{n+1}[z]$ for z_n and z_{n+1}:

If in all chains the nth place were occupied by the same mass $M_n=M^i$, then z_{n+1} would be a definite function of z_n:

$$z_{n+1}=1/(2-M^i\omega^2-z_n);\quad z_n=2-M^i\omega^2-(1/z_{n+1}).$$

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[1] If all the masses are equal, $M_n=M$, then

$$\mathbf{v}_{N+1}=\begin{pmatrix}0 & 1\\-1 & 2\alpha\end{pmatrix}^N\begin{pmatrix}0\\1\end{pmatrix},\quad\text{with}\quad\alpha=1-M\omega^2/2.$$

The eigenvalues of the matrix $\begin{pmatrix}0 & 1\\-1 & 2\alpha\end{pmatrix}$ are $\lambda_{1,2}=\alpha\pm(\alpha^2-1)^{\frac{1}{2}}$. If these eigenvalues are real, i.e., $|\alpha|>1$ or $M\omega^2>4$, then for increasing n, $\mathbf{v}_n$ converges to an eigenvector of the matrix. This eigenvector does not satisfy the second boundary condition and therefore no eigenvibrations can exist in this region. If $|\alpha|<1$, however, then $\lambda_{1,2}=e^{\pm i\beta/2}$ with real β, and

$$\begin{pmatrix}0 & 1\\-1 & 2\alpha\end{pmatrix}^N\begin{pmatrix}0\\1\end{pmatrix}=\mathbf{a}\cos(N\beta/2)+\mathbf{b}\sin(N\beta/2),$$

where $\mathbf{a}$ and $\mathbf{b}$ can be expressed by the eigenvectors of the matrix and depend slowly (compared with $N\cdot\beta$) on β. Therefore $\varphi_{N+1}(\omega^2)\approx N\cdot\beta$ and

$$M(\omega^2)=\frac{\beta}{2\pi}+\text{const}=-\frac{1}{\pi}\arcsin\left\{1-\frac{M\omega^2}{2}\right\}+\frac{1}{2}.$$

Therefore, in this special case, the probability of finding z_{n+1} in an interval dz_{n+1} must be equal to the probability of finding z_n in the corresponding interval, i.e.,

$$w_{n+1}[z_{n+1}]dz_{n+1}=w_n[z_n]dz_n,$$

or

$$w_{n+1}[z]=\frac{1}{z^2}w_n[2-M^i\omega^2-\tfrac{1}{2}].$$

Since actually the nth place can be occupied by all masses $M^1\cdots M^i$ with the probabilities $p^1\cdots p^i$, the actual relationship between $w_{n+1}[z]$ and $w_n[z]$ is

$$w_{n+1}[z]=\sum_j p^j\cdot\frac{1}{z^2}w_n\left[2-M^i\omega^2-\frac{1}{z}\right]. \quad (II, 15)$$

According to the boundary condition $z_1=0$ for all chains, we have

$$w_1[z]=\delta(z). \quad (II, 15a)$$

With this the functions $w_n[z]$ are completely determined.

If for large n the functions $w_n[z]$ approach a function $w[z]$, then $w[z]$ must satisfy

(a) $\quad w[z]=\sum_j p^j(1/z^2)w[2-M^i\omega^2-(1/z)],$

(b) $\quad w[z]\geq 0,$ $\quad\quad\quad\quad\quad\quad (II, 16)$

(c) $\quad\displaystyle\int_{-\infty}^{\infty}w[z]dz=1.$

(The relations (b) and (c) follow from the definition of $w_n[z]$ as a probability density.)

We shall see, however, in Appendix I that $w[z]$ may become an extremely singular function. (We shall give there an example where $w[z]$ is not continuous in any interval of the real axis.)

Therefore it is convenient to introduce

$$W_n[z]=\int_0^z w_n[z']dz'. \quad (II, 17)$$

Here we consider $W_n[z]$ as a many-valued function of z. (This convention is necessary in order to obtain the simple Eq. (II, 18) for $W_n[z]$.) The main branch $\tilde W_n[z]$ of $W_n[z]$ is obtained by integrating $\int_0^z w[z']dz'$ on the direct way without touching infinity (suppose $z\neq\infty$). The other branches are obtained by adding or subtracting $\int_0^\infty w_n[z]dz+\int_{-\infty}^0 w_n[z]dz=1$ several times. We see that $\tilde W_n[0]=0$ and that for all branches $W_n[0]$ in an integer.

Now Eq. (II, 15) can be written as

$$W_{n+1}[z]=\sum_j p^j W_n[2-M^i\omega^2-(1/z)]$$
$$-\tilde W_n[-\infty]. \quad (II, 18)$$

Here the same branch of W_n has to be taken for all values of j. Then $W_{n+1}[0]=W_n[-\infty]-\tilde W_n[-\infty]$ is

an integer and therefore one branch of W_{n+1}, namely $\tilde W_{n+1}$ vanishes at $z=0$ in agreement with $W_{n+1}[z]=\int_0^z w_{n+1}[z']dz'$. Instead of (II, 15a), we can write

$$W_1[z]=\quad\tfrac{1}{2}\quad\text{for}\quad z>0$$
$$0\quad\text{for}\quad z=0\quad\quad (II, 18a)$$
$$-\tfrac{1}{2}\quad\quad\quad z<0.$$

Then the functions $W_n[z]$ are completely determined by (II, 18) and (II, 18a). Now it can be shown (see Appendix I) that

$$\lim_{n\to\infty}\frac{W_1[z]+W_2[x]+\cdots+W_n[z]}{n}=W[z]\quad (II, 19)$$

exists (II, 19) and that $W[z]$ is a continuous function. This function satisfies the relations:

(a) $\quad W[z]=\sum_j p^j W[2-M^i\omega^2-(1/z)]-\tilde W[-\infty],$

(b) $\quad W[z]$ is a monotonic nondecreasing

function of z, $\quad (II, 20)$

(c) $\quad \tilde W[\infty]-\tilde W[-\infty]=1;\quad \tilde W[0]=0.$

[The relations (b) and (c) are satisfied already by each $W_n[z]$ and (a) follows from (II, 18) and (II, 19).] It can be shown (see Appendix I) that $W[z]$ is uniquely determined by (II, 20).

Differentiating (II, 20), we obtain with $w[z]=(d/dz)\times W[z]$ Eqs. (II, 16) for $w[z]$, provided that $W[z]$ is a differentiable function. In cases where $W[z]$ may not be differentiable, we shall sometimes say "$w[z]$ is given by Eq. (II, 16)," as synonymous to "$W[z]=\int_0^z w[z']dz'$ is given by Eq. (II, 20)."

By means of (II, 18), (II, 18a), and (II, 19) the function $\tilde W[z]$ can be calculated by iteration.[2] This iteration method can be assumed to converge quite well except in some limiting cases. In Sec. IV we shall give an approximate explicit expression for $W[z]$ in such a limiting case.

As a last step we have to express $M(\omega^2)$ of Eq. (12) by means of the distribution functions $w[z]=w[z,\omega^2]$, or $W[z]=W[z,\omega^2]$ (it is convenient to indicate the ω^2 dependence explicitly).

Let us consider for a specified chain the numbers

$$\varphi_{N+1}(\omega^2)>\varphi_N(\omega^2)>\cdots>\varphi_2(\omega^2)>\varphi_1(\omega^2)=0. \quad (II, 21)$$

Write $\varphi_{N+1}(\omega^2)=2\pi H+\epsilon$, where $0\leq\epsilon<2\pi$ and H is a large integer (we assume that N is very large). Now compare with (II, 21) the numbers

$$\varphi_{N+1}(\omega^2)\geq 2\pi H>2\pi(H-1)>\cdots$$
$$>4\pi>2\pi>\varphi_1(\omega^2)=0. \quad (II, 22)$$

Since $2\pi>\varphi_{n+1}-\varphi_n>0$ [this is seen from (II, 6), (II, 7), (II, 9)], it must occur for H different values of n that φ_n and φ_{n+1} include an integral multiple of 2π, i.e., that $\varphi_{n+1}\geq 2\pi h>\varphi_n$. From (II, 6), (II, 7), and (II, 9)

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[2] In Sec. IV(b) a different iteration method for $w[z]$ is developed.

it is seen that the latter condition is satisfied if and only if $-\pi \leq \varphi_n - 2\pi h < 0$ or if $-\infty \leq z_n < 0$. Therefore H is equal to the number of z_n's with negative sign in the series $z_N, z_{N-1}, \cdots z_1 = 0$. On the other hand—averaging over many chains—this number is given by

$$N \int_{-\infty}^{0} w[z]dz = -N\tilde{W}[-\infty].$$

Therefore, for large N,

$$(1/2\pi N)\bar{\varphi}_{N+1} = \bar{H}/N = -\tilde{W}[-\infty]$$

and with (13) we obtain the final result for $M(\omega^2)$ as defined in (II, 12):

$$\bar{M}(\omega^2) = -\tilde{W}[-\infty, \omega^2]. \qquad (II, 23)$$

[The additive constant in (II, 13) is seen to be zero by checking (II, 23) for $\omega^2 = 0$. Then $z_{n+1} = 1/(2 - z_n)$ and $z_n \to 1$ for $n \to \infty$. Therefore $\int_{-\infty}^{0} w_n[z_n]dz_n = -W_n[-\infty, \omega^2] \to 0$. On the other hand, (II, 12) gives $M(\omega^2) = 0$ for $\omega^2 = 0$.]

(d) Summary

We define

$$F[\alpha^1, \cdots \alpha^i; p^1, \cdots p^i] = \int_{-\infty}^{0} w[z]dx, \qquad (II, 24)$$

where $w[z]$ is uniquely determined by

$$w[z] = \sum_i p^i \frac{1}{z^2} w[2\alpha^i - (1/z)],$$

$$w[z] \geq 0, \qquad (II, 25)$$

$$\int_{-\infty}^{\infty} w[z]dz = 1.$$

Now the relative number of eigenvalues with $\omega_\nu^2 < \omega^2$ for a long random chain is

$$\bar{M}(\omega^2) = F[\alpha^1, \cdots \alpha^i; p^1, \cdots p^i], \qquad (II, 26)$$

with $\alpha^j = 1 - M^j\omega^2/2$. Here p^j is the fraction of atoms with mass M^j.

Similar results were obtained for the first time by Dyson.[3] Dyson's results, though equivalent, are slightly more complicated mathematically. In particular the relationship (II, 26) is much simpler than Dyson's expression for the distribution function.

III. ELECTRONIC ENERGY LEVELS IN ONE-DIMENSIONAL DISORDERED POTENTIALS

In this section, we consider the electronic energy levels in one-dimensional models of a disordered crystal consisting of different atoms $A^1, \cdots A^i$. We restrict ourselves to models which satisfy the following conditions:

[3] F. J. Dyson, Phys. Rev. **92**, 1331 (1953).

1. The atoms $A_1, A_2, \cdots A_N$ in the one-dimensional model shall be equidistant; let the nth atom A_n lie at $x = nl$.

2. The atom A_n can be any one of the $A^1, \cdots A^i$. Considering many systems, we assume that the probability of A_n being an A^j is p^j, independent of the neighboring atoms. (The more general case where correlations between neighboring atoms exist is discussed in Appendix II.)

3. The potential $V(x)$ in the interval $(n - \frac{1}{2})l < x < (n + \frac{1}{2})l$ shall be determined completely by the nth atom, $V(x) = U^j(x - n \cdot l)$ in $(n - \frac{1}{2})l < x < (n + \frac{1}{2})l$, if $A_n = A^j$.

The general method for calculating the density of electronic energy states will be described in (c). As a preliminary we shall consider in (a) and (b) two special potential types for which the results can be stated more explicitly. Here the crystal potential is represented by a succession of equidistant δ functions of different strengths:

$$V(x) = \sum_n (\hbar^2/2m) V_n \cdot \delta(x - n \cdot l).$$

Here V_n characterizes the potential of the nth atom and can assume the values $V^1, \cdots V^i$ corresponding to the different atoms $A^1, \cdots A^i$. Now we consider separately the cases

(a) $V_n > 0$ for all n,

(b) $V_n < 0$ for all n.

We shall prove that the density of eigenstates in these cases can be expressed by the function $F[\alpha^1 \cdots \alpha^i; p^1 \cdots p^i]$ of Eq. (II, 24).

(a) $V(x) = \Sigma_n (\hbar^2/2m) V_n \delta(x - nl)$; $V_n > 0$

We write the wave function in the interval $(n-1)l < x < nl$ as $\psi = A_n e^{ikx_n} + B_n e^{-ikx_n}$, with $x_n = x - l(n - \frac{1}{2})$ where $k = [(2m/\hbar^2)E]^{\frac{1}{2}}$ and E is the energy. Then $\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix}$ and $\begin{pmatrix} A_n \\ B_n \end{pmatrix}$ are connected by the relationship

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = \begin{bmatrix} \left(1 + \dfrac{V_n}{2ik}\right)e^{ikl} & \dfrac{V_n}{2ik} \\ -\dfrac{V_n}{2ik} & \left(1 - \dfrac{V_n}{2ik}\right)e^{-ikl} \end{bmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix}$$

$$\equiv \mathfrak{M}_n \begin{pmatrix} A_n \\ B_n \end{pmatrix}. \qquad (III, 1a)[4]$$

Assuming as boundary conditions the vanishing of $\psi(x)$ at $x = l/2$ and $x = (N + \frac{1}{2})l$ these boundary condi-

[4] If all the potentials are equal: $V_n = V_0, \mathfrak{M}_n = \mathfrak{M}_0$, then the regions in which eigenstates exist are given by $|\lambda_{1,2}| = 1$, where $\lambda_{1,2}$ are the eigenvalues of $\mathfrak{M}_0$: $|\mathfrak{M}_0 - \lambda_{1,2}| = \lambda_{1,2}^2 - 2\lambda_{1,2}[\cos kl + (V_0/2k) \sin kl] + 1 = 0$. $|\lambda_{1,2}| = 1$ is equivalent to $|\cos kl + (V_0/2k) \times \sin kl| < 1$.

tions can be written as

$$A_1 + B_1 = 0,$$
$$A_{N+1} + B_{N+1} = 0.$$

(III, 1b)

Now we introduce

$$\tau_n = -iA_n/B_n.$$

(III, 2)

Then (III, 1) can be written as

$$\tau_{n+1} = (c_n\tau_n + 1)/(\tau_n + c_n^*), \quad \text{where}$$
$$c_n = i[1 + (2ik/V_n)]e^{ikl} \quad \text{(III, 3a)}$$

$$\tau_1 = \tau_{N+1} = i \quad \text{(boundary conditions).} \quad \text{(III, 3b)}$$

To solve this boundary problem we define with $\tau_1 = i$ and Eq. (III, 3a) the functions of k: $\tau_1 = i$, $\tau_2(k)$, $\cdots \tau_{N+1}(k)$. Then the k values of the electronic eigenstates are given by $\tau_{N+1}(k) = i$. From (III, 3a) with $\tau_1 = i$ it is seen by induction that $|\tau_n| = 1$ for all n values. Therefore we can introduce angles φ_n by

$$\tau_n = e^{i\varphi_n}.$$

(III, 4)

The continuous relation between φ_n and φ_{n+1} given by (III, 3a) and (III, 4) can be made unique by the auxiliary requirement that

$$\varphi_n = \tfrac{1}{2}\pi - kl + 2\pi h_0 \quad \text{shall imply}$$
$$\varphi_{n+1} = \tfrac{1}{2}\pi + kl + 2\pi h_0, \quad \text{(III, 5)}$$

with the same integer h_0 in both expressions. If furthermore we put $\varphi_1 = \pi/2$ (in accordance with the boundary condition $\tau_1 = i$), then $\varphi_n = \varphi_n(k)$ is a well-defined function of k (for given V_n's); and whenever $\varphi_{N+1} = \tfrac{1}{2}\pi + 2\pi h$, then $\psi(x)$ vanishes at $x = (N + \tfrac{1}{2})l$ and both the boundary conditions are satisfied. From (III, 3), (III, 4), and (III, 5) with $V_n > 0$ it follows by a short calculation that $\varphi_n(k)$ is a monotonically nondecreasing function of k. Therefore in an interval $k_1 < k < k_2$ the boundary condition $\varphi_{N+1}(k) = \tfrac{1}{2}\pi + 2\pi h$ is satisfied (with an error smaller than 1) $[\varphi_{N+1}(k_2) - \varphi_{N+1}(k_1)]/2\pi$ times, i.e., the number of eigenstates in the interval $k_1 < k < k_2$ is

$$N[M(k_2) - M(k_1)] = [\varphi_{N+1}(k_2) - \varphi_{N+1}(k_1)]/2\pi \quad \text{(III, 6)}$$

with

$$M(k') \equiv (1/N) \times \{\text{No. of eigenstates with } k < k'\}$$
$$= [\varphi_{N+1}(k')/2\pi] + \text{const.} \quad \text{(III, 7)}$$

Suppose now that we have many random chains of δ potentials, where V_n can assume the values $V^1, \cdots V^i$ with the probabilities $p^1, \cdots p^i$. We look at φ_n (for a specified large n) in many such chains. We define $w(\varphi)d\varphi$ as the probability that φ_n lies in any one of the intervals

$$2\pi h + \varphi < \varphi_n < 2\pi h + \varphi + d\varphi,$$

with $h = 0$ or ± 1 or $\pm 2 \cdots$. For this function $w(\varphi)$ we can easily derive a functional equation. In order to write this equation most conveniently, we must express φ_n as a function of φ_{n+1}. We shall write

$$\varphi_n = \varphi_{n+1} - D^i(\varphi_{n+1}), \quad \text{provided that } A_n = A^i. \quad \text{(III, 8)}$$

From (III, 3a), (III, 4), and (III, 5) we could easily derive an explicit expression for the so defined functions $D^i(\varphi)$. We shall need, however, in the following only two properties of the functions $D^i(\varphi)$ which are easily verified:

$$D^i(\varphi + 2\pi) = D^i(\varphi),$$
$$D^i(\tfrac{1}{2}\pi + kl) = 2kl.$$

(III, 9)

Assuming now that $w(\varphi)$ is the distribution function for φ_n as well as for φ_{n+1} (for large enough n), we obtain by the same reasoning as in Sec. II for $w(\varphi)$:

$$w(\varphi)d\varphi = \sum_j p^j w(\varphi - D^j(\varphi))d(\varphi - D^j(\varphi)). \quad \text{(III, 10)}$$

It is convenient to introduce

$$W(\varphi) = \int_{\frac{1}{2}\pi + kl}^{\varphi} w(\varphi')d\varphi', \quad \text{(III, 11)}$$

where $w(\varphi)$ is considered as a periodic function, $w(\varphi + 2\pi) = w(\varphi)$ [this follows from the above definition of $w(\varphi)$]. Then $W(\varphi)$ is a single-valued function defined for all real values of φ and satisfies the relations:

(a) $W(\varphi) = \sum_j p^j W(\varphi - D^j(\varphi)) - W(\tfrac{1}{2}\pi - kl),$

(b) $W(\varphi + 2\pi) = W(\varphi) + 1,$

(c) $W(\tfrac{1}{2}\pi + kl) = 0,$

(III, 12)

(d) $W(\varphi)$ is a monotonically nondecreasing

function of φ.

[(III, 12)(a) is obtained from (III, 10) by integration; note that $\varphi = \tfrac{1}{2}\pi + kl$ implies that $\varphi - D^j(\varphi) = \tfrac{1}{2}\pi - kl$ and that $W(\tfrac{1}{2}\pi + kl) = 0$. (III, 12)(b) and (d) follow from the definition of $w(\varphi)$ as a probability density and (III, 12)(c) follows from (III, 11).]

In order to express $M(k)$ of Eq. (III, 7) by means of $W(\varphi)$, we shall use a method different from that applied in II but more generally applicable. From (III, 7) we have

$$2\pi N M(k) + \text{const} = \varphi_{N+1}(k)$$
$$= [\varphi_{N+1}(k) - \varphi_N(k)] + [\varphi_N(k) - \varphi_{N-1}(k)]$$
$$+ \cdots + [\varphi_2(k) - \varphi_1(k)]. \quad \text{(III, 13)}$$

We see that $2\pi M(k) + \text{const}$ equals the average value over different chains of $\varphi_{n+1}(k) - \varphi_n(k)$ (for large enough n). This average value can be written as

$$\langle \varphi_{n+1} - \varphi_n \rangle_{\text{Av}}$$
$$= \sum_i p^i \int (\varphi_{n+1} - \varphi_n)_j w(\varphi_n) d\varphi_n. \quad \text{(III, 14)}$$

Here the subscript j indicates that φ_n and φ_{n+1} are related by $\varphi_n = \varphi_{n+1} - D^j(\varphi_{n+1})$ as in Eq. (III, 8), i.e., $(\varphi_{n+1} - \varphi_n)_j$ equals $(\varphi_{n+1} - \varphi_n)$ provided that $V_n = V^j$.

Integration by parts gives from (III, 14)

$$\langle \varphi_{n+1}-\varphi_n\rangle_{\text{Av}}=\sum_j p^j(\varphi_{n+1}-\varphi_n)_jW(\varphi_n)\Big|_{\frac{1}{2}\pi-kl}^{\frac{1}{2}\pi-kl+2\pi}$$

$$-\sum_j p^j\int_{\frac{1}{2}\pi-kl}^{\frac{1}{2}\pi-kl+2\pi}\left(\frac{d\varphi_{n+1}}{d\varphi_n}-1\right)_jW(\varphi_n)d\varphi_n$$

$$=2kl+\int_{\frac{1}{2}\pi-kl}^{\frac{1}{2}\pi-kl+2\pi}W(\varphi_n)d\varphi_n$$

$$-\int_{\frac{1}{2}\pi+kl}^{\frac{1}{2}\pi+kl+2\pi}\sum_j p^jW(\varphi_{n+1}-D^j(\varphi_{n+1}))d\varphi_{n+1}.$$

[We could have integrated in (III, 14) over any interval of length 2π. The present choice of the limits of integration is convenient because at these limits $(\varphi_{n+1}-\varphi_n)_j$ $=2kl$, independent of j.]

By means of the functional Eq. (III, 12a) for $W(\varphi)$, the last integral can be written as $-\int\{W(\varphi)+W(\frac{1}{2}\pi-kl)\}d\varphi$, and we finally obtain

$$(1/2\pi)\langle\varphi_{n+1}-\varphi_n\rangle_{\text{Av}}=-W(\tfrac{1}{2}\pi-kl)=M(k). \quad \text{(III, 15)}$$

[Note that the additive constant in (III, 13) vanishes because for $k\to 0$ $W(\frac{1}{2}\pi-kl)\to W(\frac{1}{2}\pi+kl)=0$.] With this result our problem is reduced to finding $W(\varphi)$ from (III, 12). We could calculate $W(\varphi)$ directly from (III, 12) by an iteration method. We shall see now, however, that $W(\varphi)$ is closely related to $W[z]$ in (II, 20) and that consequently $M(k)$ can be expressed by means of $F[\alpha^1\cdots\alpha^i; p^1\cdots p^i]$ of (II, 24). We define

$$z_n=\frac{1-ie^{i(-\varphi_n+kl)}}{1-ie^{i(-\varphi_n-kl)}}=\frac{\cos kl-\sin\varphi_n}{1-\sin(kl+\varphi_n)}. \quad \text{(III, 16)}$$

Then (III, 3) and (III, 4) imply

(a) $z_{n+1}=1/(2\alpha_n-z_n)$ with

$$\alpha_n=\cos kl+(V_n/2k)\sin kl. \quad \text{(III, 17)}$$

(b) $z_1=z_{N+1}=-1$ (boundary conditions).

For a better understanding of the transformation (III, 16) note that $\varphi'=\frac{1}{2}\pi-kl$ and $\varphi''=\frac{1}{2}\pi+kl$ are transformed into $z'=\infty$ and $z''=0$. Therefore $z_n=\infty$ implies that $z_{n+1}=0$ because $\varphi_n=\varphi'$ implies that $\varphi_{n+1}=\varphi''$. It follows that the relation between z_{n+1} and z_n must have the form $z_{n+1}=c/(b-z_n)$ and furthermore c can be made unity. From (III, 17) we can draw a simple interesting conclusion: Consider a region where none of the pure A^j crystals $(j=1, 2,\cdots i)$ has an energy level, i.e., a region where $|\alpha^j|=|\cos kl+(V^j/2k)\sin kl|>1$ for all j.[4] Now for a mixed crystal we obtain from (III, 17a) with $z_1=-1$ successively $|z_2|<1$, $|z_3|<1$, $\cdots|z_{N+1}|$ <1, because $|\alpha_n|>1$. Therefore the second boundary condition $z_{N+1}=-1$ cannot be satisfied. That means that in this region the mixed crystal has no electronic states either.

This result was conjectured first by Saxon and Hutner and proved subsequently by Luttinger.[5]

Let us now define $w[z]$ by $w[z]|dz|=|w(\varphi)d\varphi|$ where z and φ are connected by Eq. (III, 16). (Note that $d\varphi/dz>0$ if $0<kl<\pi$ and $d\varphi/dz<0$ for $\pi<kl<2\pi$). Then Eq. (III, 10) gives for $w[z]$:

$$w[z]=\sum_j p^jw\left[2\alpha^j-\frac{1}{z}\right]\cdot\frac{1}{z^2}, \quad \text{with} \quad \alpha^j=\cos kl+\frac{V^j}{2k}\sin kl;$$

furthermore

$$\int_{-\infty}^{\infty}w[z]dx=1 \quad \text{and} \quad w[z]\geq 0.$$

The same function $w[z]$ which is uniquely determined by these relations, occurred in (II, 25), only with a different meaning of the α^j's. To express $M(k)$ in terms of $w[z]$, we write $kl=2\pi h+\delta$ with $0\leq\delta<2\pi$. Then Eq. (III, 15) with $W(kl)=0$ gives

$$M(k)=W(\tfrac{1}{2}\pi+2\pi h+\delta)-W(\tfrac{1}{2}\pi-2\pi h-\delta)$$

$$=2h+W(\tfrac{1}{2}\pi+\delta)-W(\tfrac{1}{2}\pi-\delta)$$

$$=2h+\int_{\frac{1}{2}\pi-\delta}^{\frac{1}{2}\pi+\delta}w(\varphi)d\varphi$$

$$=\begin{cases}2h+\int_{-\infty}^{0}w[z]dz & \text{for} \quad 0\leq\delta\leq\pi \\[2mm] 2h+1+\int_{0}^{\infty}w[z]dz & \text{for} \quad \pi\leq\delta<2\pi.\end{cases}$$

Therefore we have the final result: If $kl=2\pi h+\delta$ (i.e., we are in the region of the $(2h+1)$th and $(2h+2)$th band), then

$$M(k)$$

$$=\begin{cases}2h+F[\alpha^1\cdots\alpha^i; p^1\cdots p^i] & \text{for } 0\leq\delta\leq\pi \\[2mm] 2h+2-F[\alpha^1\cdots\alpha^i; p^1\cdots p^i] & \text{for } \pi\leq\delta<2\pi.\end{cases} \quad \text{(III, 18)}$$

Here $F[\ ]$ is defined as in (II, 24) and $\alpha^j=\cos kl+(V^j/2k)\sin kl$.

(b) $V(x)=-\sum_n(\hbar^2/2m)V_n\delta(x-nl); \quad V_n>0$

A single one-dimensional potential hole $V(x)$ $=-(\hbar^2/2m)V_0\delta(x)$ with $V_0>0$ has exactly one bound electron state with the binding energy $(\hbar^2/2m)(V_0^2/4)$. Therefore we expect that for the crystal potential considered there exist states with negative total energy. We shall consider here these states only. Then the wave function in the interval $(n-1)l<x<nl$ can be written as

$$\psi(x)=A_ne^{ikx_n}+B_ne^{-ikx_n}, \quad \text{with} \quad x_n=x-l(n-\tfrac{1}{2}).$$

[5] J. M. Luttinger, Philips Research Repts. 6, 303 (1951).

Here k is real and $E = -(\hbar^2/2m)k^2$ is the total energy. The relation between $\begin{pmatrix} A_n \\ B_n \end{pmatrix}$ and $\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix}$ is easily found:

$$\begin{pmatrix} A_{n+1} \\ B_{n+1} \end{pmatrix} = \begin{bmatrix} \left(1 - \dfrac{V_n}{2k}\right)e^{kl} & -\dfrac{V_n}{2k} \\ \dfrac{V_n}{2k} & \left(1 + \dfrac{V_n}{2k}\right)e^{-kl} \end{bmatrix} \begin{pmatrix} A_n \\ B_n \end{pmatrix}$$

$$\equiv \mathfrak{M}_n \begin{pmatrix} A_n \\ B_n \end{pmatrix}. \quad \text{(III, 19a)}$$

The boundary conditions $\psi = 0$ at $x = l/2$ and $x = (N + \frac{1}{2})l$ can be written as

$$A_1 + B_1 = 0,$$
$$A_{N+1} + B_{N+1} = 0. \quad \text{(III, 19b)}$$

If all potentials are equal, $V_n = V_0$, $\mathfrak{M}_n = \mathfrak{M}_0$, then the regions in which eigenstates exist are given by $|\lambda_{1,2}| = 1$ or $|\alpha_0(k)| = |-\cosh(kl) + (V_0/2k)\sinh(kl)| < 1$, where $\lambda_{1,2}$ are the eigenvalues of $\mathfrak{M}_0$. In the case where $|\alpha_0(0)| > 1$ or $V_0 l > 4$, no eigenstates with $k \approx 0$ are possible; i.e., the energy of all states is negative, and we have a band with N bound states which correspond for very large values of $V_0 l$ to the bound states of N single potential holes. For $V_0 l < 4$ however, the energy band will be broadened so as to include some states with positive energy. Therefore the number of states with negative energy, which we are considering here, will be smaller than N.

In the following, we shall assume that $lV_n < 6$ for all n. This is a very weak assumption [e.g., for $l = 10^{-8}$ cm it means that the binding energy in a single potential hole, $|E_b| = (\hbar^2/2m)(V_0^2/4)$ is smaller than $(\hbar^2/8ml^2) \times 36 = 28$ ev]. However, it simplifies the following considerations since it implies that $d\alpha_n(k)/dk < 0$ (for all n and k values), where $\alpha_n = -\cosh(kl) + (V_n/2k)\sinh(kl)$. Now we apply to (III, 19) the transformation

$$z_n = -(A_n e^{-kl} + B_n)/(A_n + B_n e^{-kl}). \quad \text{(III, 20)}$$

This gives

$$z_{n+1} = 1/(2\alpha_n - z_n), \quad \text{with}$$
$$\alpha_n = -\cosh(kl) + (V_n/2k)\sinh(kl), \quad \text{(III, 21a)}$$

$$z_1 = z_{N+1} = 1 \quad \text{(boundary conditions)}. \quad \text{(III, 21b)}$$

If we put $z_1 = 1$, then by (III, 21a) $z_2(k), z_3(k), \cdots z_{N+1}(k)$ are functions of k and $z_{N+1}(k) = 1$ is the condition for an eigenstate. Furthermore the $z_n(k)$ are monotonically nondecreasing functions of k for $V_n l < 6$ (because then $d\alpha_n/dk < 0$). It follows then as in (II) that the number of eigenvalues in an interval $k_1 < k < k_2$ is given by $N[M(k_2) - M(k_1)]$, where

$$M(k) = F[\alpha^1 \cdots \alpha^i; p^1 \cdots p^i] + \text{const}, \quad \text{with}$$
$$\alpha^j = -\cosh(kl) + (V^j/2k)\sinh(kl). \quad \text{(III, 22)}$$

(c) General Method

Now we develop the general method for calculating the density of electronic energy levels in a potential which satisfies the conditions 1–3.[6] In the interval $(n - \frac{1}{2})l < x < (n + \frac{1}{2})l$ the wave function $\psi(x)$ is determined by the values of $\psi(x)$ and $\psi'(x)$ at one point. The values of $\psi(x), \psi'(x)$ at the ends of the interval are related by

$$\begin{pmatrix} \psi(x) \\ \psi'(x) \end{pmatrix}_{x=(n+\frac{1}{2})l} = \mathfrak{M}_n(k) \begin{pmatrix} \psi(x) \\ \psi'(x) \end{pmatrix}_{x=(n-\frac{1}{2})l}. \quad \text{(III, 23)}$$

Here the matrix $\mathfrak{M}_n(k)$ is determined by the potential in the nth interval. Since we assumed this potential to depend on the nature of the nth atom only, we can write

$$\mathfrak{M}_n(k) = \mathfrak{M}^i(k) \quad \text{provided that} \quad A_n = A^i.$$

The matrices $\mathfrak{M}^1(k), \cdots \mathfrak{M}^i(k)$ shall be assumed known. They depend on the electron energy. k shall be any parameter which characterizes this energy. If we proceed from one cell to the next, then $\psi(x), \psi'(x)$ change continuously with x. Therefore

$$\begin{pmatrix} \psi(x) \\ \psi'(x) \end{pmatrix}_{x=(N+\frac{1}{2})l}$$
$$= \mathfrak{M}_N(k)\mathfrak{M}_{N-1}(k) \cdots \mathfrak{M}_1(k) \begin{pmatrix} \psi(x) \\ \psi'(x) \end{pmatrix}_{x=l/2}. \quad \text{(III, 24)}$$

We can assume that $\psi(x)$ is real and therefore define φ_n by

$$\tan(\tfrac{1}{2}\varphi_n) = \frac{\psi(x)}{\psi'(x)}\bigg|_{x=(n-\frac{1}{2})l}. \quad \text{(III, 25)}$$

Then (III, 23) and (III, 25) imply a relationship between φ_n and φ_{n+1}. This relationship can be made unique by an auxiliary requirement [see Eq. (III, 5)]. We write the so-defined unique connection between φ_n and φ_{n+1} as

$$\varphi_n = \varphi_{n+1} - \Delta^i(\varphi_{n+1}) \quad \text{provided that} \quad A_n = A^i. \quad \text{(III, 26)}$$

The functions $\Delta^i(\varphi)$ can be computed from the matrices $\mathfrak{M}^i$ and are periodic: $\Delta^i(\varphi + 2\pi) = \Delta^i(\varphi)$. As our boundary conditions we shall assume $\psi(x) = 0$ at $x = l/2$ and $x = (N + \frac{1}{2})l$ or, in terms of φ,

$$\varphi_1 = 0, \quad \varphi_{N+1} = 2\pi h.$$

If we define by (III, 26) with $\varphi_1 = 0$ functions $\varphi_1 = 0$, $\varphi_2(k), \cdots \varphi_{N+1}(k)$, then the eigenstates of the systems are given by $\varphi_{N+1}(k) = 2\pi h$. Considering now many random systems, we describe the probability distribution of φ_n by a density function $w(\varphi)$. This function

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[6] In this section we shall omit some proofs which are obtained by the same reasoning as the corresponding proofs in (II) or (IIIa).

satisfies [see Eq. (III, 10)]

$$w(\varphi)d\varphi = \sum_j p^i w(\varphi - \Delta^j(\varphi))d(\varphi - \Delta^j(\varphi)),$$

$$w(\varphi) \geq 0,$$

$$\int_0^{2\pi} w(\varphi)d\varphi = 1, \tag{III, 27}$$

$$w(\varphi + 2\pi) = (\varphi).$$

For $W(\varphi) = \int_d^\varphi w(\varphi')d\varphi'$, where d is an arbitrary constant, we obtain

$$\begin{aligned}
&W(\varphi) = \sum_j p^i W(\varphi - \Delta^j(\varphi)) + C(k), \\
&W(\varphi) \text{ is monotonic in } \varphi, \\
&W(\varphi + 2\pi) = W(\varphi) + 1, \\
&W(d) = 0.
\end{aligned} \tag{III, 28}$$

The relations (III, 28) determine the function $W(\varphi)$ and the constant $C(k)$ (for fixed k) uniquely. Furthermore $W(\varphi)$ and $C(k)$ can be calculated from (III, 28) by an iteration method. We note that $C(k)$ is independent of the choice of d and that $C(k)$ can be written as

$$C(k) = \sum_j p^i \int_{-\Delta^j(0)}^0 w(\varphi)d\varphi. \tag{III, 29}$$

In order to find the mean value of $\varphi_{N+1}(k)$, we write

$$\bar\varphi_{N+1}(k) = N\langle \varphi_{n+1} - \varphi_n \rangle_{\text{Av}}$$

$$= N \sum_j \int p^i(\varphi_{n+1} - \varphi_n)_j w(\varphi_n)d\varphi_n \quad \text{(for large } N \text{ and } n\text{)}.$$

The subscript j indicates that φ_{n+1} and φ_n are related by $\varphi_n = \varphi_{n+1} - \Delta^j(\varphi_{n+1})$. Integration by parts gives, with (III, 28), the result

$$\frac{1}{2\pi N}\bar\varphi_{N+1}(k) = C(k). \tag{III, 30}$$

Let us assume first that for all possible chains $\varphi_{N+1}(k)$ increases with k monotonically. Then for k increasing from k_1 to k_2, $\varphi_{N+1}(k)$ increases from $\varphi_{N+1}(k_1)$ to $\varphi_{N+1}(k_2)$ monotonically. Hence in this interval the boundary condition $\varphi_{N+1}(k) = 2\pi h$ is satisfied $(1/2\pi) \times \{\varphi_{N+1}(k_2) - \varphi_{N+1}(k_1)\}$ times and therefore the average number of eigenvalues in $k_1 < k < k_2$ is

$$\frac{1}{2\pi}\{\bar\varphi_{N+1}(k_2) - \bar\varphi_{N+1}(k_1)\} = N\{C(k_2) - C(k_1)\}.$$

This condition that $\varphi_{N+1}(k)$ is monotonic in k for all possible chains was satisfied in the special cases considered in II, III(a), and III(b), and there we used this property of $\varphi_{N+1}(k)$ for obtaining the results. Now we shall extend our theory to cases where this condition is not satisfied, i.e., where the functions $\varphi_{N+1}(k)$ for the individual chains need not be monotonic. In these

cases we can determine $(1/2\pi N)\bar\varphi_{N+1}(k) = C(k)$ as before, but now $C(k)$ also need not be monotonic. Assuming however that $C(k)$ is a smooth function of k, we can divide the k-values into intervals in each of which $C(k)$ is monotonic.

Let us consider such an interval $k_1 < k < k_2$ where the function $C(k)$ is monotonic, assume for example that $C(k)$ increases with k in (k_1, k_2). Now there may be chains for which $\varphi_{N+1}(k)$ does not increase with k in (k_1, k_2). We shall show however that the fraction of these chains goes to zero when N and the number of chains compared approach infinity.

Let N, m, s be large numbers such that $ms = N+1$ and write $\varphi_{N+1}(k)$ as a sum of s terms:

$$\begin{aligned}
\varphi_{N+1}(k) &= (\varphi_m - \varphi_1) + (\varphi_{2m} - \varphi_m) + \cdots \\
&\quad + (\varphi_{(\nu+1)m} - \varphi_{\nu m}) + \cdots + (\varphi_{sm} - \varphi_{(s-1)m}) \\
&= t_1 + t_2 + \cdots + t_{\nu+1} + \cdots + t_s.
\end{aligned}$$

Averaging over all chains, we obtain

$$t_{\nu+1} = \langle \varphi_{(\nu+1)m} - \varphi_{\nu m} \rangle_{\text{Av}} = mC(k), \quad \text{independent of } \nu.$$

Consider now for a moment those of the chains only for which $\varphi_{\nu m}$ (for one specified ν) lies in a certain small interval. Then for these chains the numbers $\varphi_{\nu m}, \varphi_{\nu m+1}, \varphi_{\nu m+2}, \cdots$ will soon approach the probability distribution given by $w(\varphi)$, independent of the value of $\varphi_{\nu m}$; i.e., almost all of the $\varphi_{\nu m}, \varphi_{\nu m+1}, \varphi_{\nu m+2}, \cdots \varphi_{\nu m+m}$ are (for large n) distributed according to $w(\varphi)$. Therefore the average of $(\varphi_{(\nu+1)m} - \varphi_{\nu m})$ taken over the restricted class of chains with specified $\varphi_{\nu m}$ will also be $mC(k)$, independent of the value of $\varphi_{\nu m}$. Now in the sum

$$\frac{d}{dk}\varphi_{N+1}(k) = \frac{d}{dk}(\varphi_m - \varphi_1) + \cdots + \frac{d}{dk}(\varphi_{sm} - \varphi_{(s-1)m})$$

$$= t_1' + \cdots + t_s',$$

averaging over all chains again, each term has a positive average value and the average value $t_{\nu+1}'$ is independent of t_ν'. Therefore, for large s, the fraction of chains for which the sum in negative approaches zero, i.e., for almost all chains $\varphi_{N+1}(k)$ increases with k and we have the final result:

In a region $k_1 < k < k_2$ where the mean value $\bar\varphi_{N+1}(k) = 2\pi NC(k)$ is a monotonic function of k, there the number of eigenvalues is given by

$$N|C(k_2) - C(k_1)| = (1/2\pi)|\bar\varphi_{N+1}(k_2) - \bar\varphi_{N+1}(k_1)|.$$

There may be chains for which $\varphi_{N+1}(k)$ has not the monotonic character of $\bar\varphi_{N+1}(k)$ but the fraction of these chains goes to zero and hence they can be neglected.

IV. IMPURITY BANDS

Introduction

Suppose that we have a crystal of A atoms with a small amount of B-atoms. Then in an energy region

where the pure A crystal has no allowed electronic states, there may occur an "impurity band" of electron states due to the B atoms. Impurity bands can occur also in the frequency spectrum of an elastic chain: Suppose the chain consists of atoms A with mass M and a small number of atoms B with a lighter mass m. Then above the frequency limit of the pure M chain, there appears a band of frequencies due to the masses m.

If the B atoms in the crystal are far apart from each other, then the impurity band will be very narrow and for increasing concentration of the B atoms the width of the impurity band will increase.

By means of the general methods developed in the previous sections, it is possible in principle to calculate the density of eigenstates everywhere and in particular in the impurity band. But the iteration method used in II and III, though always convergent, converges sufficiently quickly only so long as the fraction q of B atoms is not too small.

In this section, however, we shall consider the case where the concentration of B atoms is very small. Therefore we have to apply here a different method. We shall approach the problem first, in (a), by a simple approximate method. Later, in (b), we shall develop a more accurate theory based on the general results of Secs. II and III.

It will be sufficient to consider for the present the impurity bands of the elastic chain only. The generalization to electron impurity bands is then straightforward.

(a) Approximate Method

Here we calculate the impurity bands in an over-simplified model of the elastic chain. We cannot expect this calculation to give quantitatively good results. The reasons for considering this model however are: (1) Since we obtain explicit results here, we can check the validity of an approximation method which becomes essential in (b). (2) Our over-simplified model can also be applied to three-dimensional problems. It is therefore interesting to check the usefulness of this model by comparison with the more realistic model of (b).

Assume that we have a chain of elastically coupled masses M (fraction p) with a small number of lighter masses m (fraction q). Then each m-mass in the chain will generally be embedded in many M-masses and will therefore in first approximation behave like a mass m when embedded in an infinite chain of M masses. In a second approximation which will be studied here, we take into account not only one mass m but also the next nearest m mass, neglecting all other m-masses in the chain.

Suppose that the two m masses considered are separated by s M masses. Then for calculating the frequencies due to these two m masses we consider them in our simplified model as embedded in an infinite chain of M masses, and again separated by s M masses.

Now we shall calculate the eigenfrequencies due to

the two m masses for such a system. Then, by averaging over these systems with the correct statistical weight for all possible s values, we shall obtain an approximate expression for the energy spectrum of a disordered chain.

Looking at one m mass in a random chain, the probability that the next m mass in one direction of the chain is separated by s M masses is clearly $P_1(s) = qp^s$ $(s = 0, 1, 2, \cdots)$. Likewise the probability that the next m mass in the other direction is separated by s M masses is $P_2(s) = qp^s$. Therefore the probability that the next m mass in one or the other direction is separated by s m masses becomes $P(s) = P_1(s)P_2(>s) + P_2(s)P_1(>s) + P_1(s)P_2(s)$, or

$$P(s) = 2qp^{2s+1} + q^2p^{2s} \quad (\approx 2qp^{2s} \text{ for } q \ll p). \quad \text{(IV, 1)}$$

Now we consider a chain consisting successively of: K_0 masses M, 1 mass m, s masses M, 1 mass m, K masses M, where K is very large. As in II, let u_n be the displacement of the nth mass and define

$$\mathbf{v}_n = \begin{pmatrix} u_{n-1} \\ u_n \end{pmatrix}; \quad T_\alpha = \begin{pmatrix} 0 & 1 \\ -1 & 2\alpha \end{pmatrix}; \quad T_\beta = \begin{pmatrix} 0 & 1 \\ -1 & 2\beta \end{pmatrix},$$

$$\text{with} \quad 2\alpha = 2 - M\omega^2, \quad 2\beta = 2 - m\omega^2. \quad \text{(IV, 2)}$$

Now the displacement vectors $\mathbf{v}_1$ and $\mathbf{v}_{2K+s+3} = \mathbf{v}_{end}$ at the beginning and the end of the chain are related by

$$\mathbf{v}_{end} = T_\alpha{}^K T_\beta T_\alpha{}^s T_\beta T_\alpha{}^K \mathbf{v}_1. \quad \text{(IV, 3)}$$

We want to calculate the eigenfrequencies due to the two m masses above the frequency limit of the pure M chain. In this region T_α has real eigenvalues:

$$T_\alpha \mathbf{v}' = \lambda' \mathbf{v}', \quad T_\alpha \mathbf{v}'' = \lambda'' \mathbf{v}'', \quad \text{(IV, 4)}$$

with

$$\lambda' = \alpha + (\alpha^2 - 1)^{\frac{1}{2}}, \quad \lambda'' = \alpha - (\alpha^2 - 1)^{\frac{1}{2}}, \quad \lambda'' < -1 < \lambda' < 0,$$

$$\mathbf{v}' = \begin{pmatrix} 1 \\ \lambda' \end{pmatrix}, \quad \mathbf{v}'' = \begin{pmatrix} 1 \\ \lambda'' \end{pmatrix}.$$

If now the m masses vibrate with a frequency above the frequency limit of the M chain, then the amplitude of the M masses must decrease exponentially towards the ends of the chain, i.e.,

$$\left. \begin{array}{r} T_\alpha{}^n \mathbf{v}_{K+s+3} \\[4pt] T_\alpha{}^{-n} \mathbf{v}_{K+1} \end{array} \right\} \to 0 \text{ for large } n.$$

This is possible only if

$$\mathbf{v}_{K+s+3} = \mathbf{v}' \times \text{const},$$
$$\mathbf{v}_{K+1} = \mathbf{v}'' \times \text{const}.$$

Therefore the eigenfrequencies are given by the relation

$$\mathbf{v}' = T_\beta T_\alpha{}^s T_\beta \mathbf{v}'' \times \text{const}, \quad \text{(IV, 5)}$$

with

$$S=\begin{pmatrix}1 & -\lambda' \\ 1 & -\lambda''\end{pmatrix}; \quad Sv'=\begin{pmatrix}1 \\ 0\end{pmatrix}\times\text{const}; \quad Sv''=\begin{pmatrix}0 \\ 1\end{pmatrix}\times\text{const};$$

$$ST_{\alpha}S^{-1}=\begin{pmatrix}\lambda'^2 & 0 \\ 0 & 1\end{pmatrix}\times\text{const}.$$

We obtain from (IV, 5)

$$\begin{pmatrix}1 \\ 0\end{pmatrix}=ST_{\beta}S^{-1}\begin{pmatrix}\lambda'^{2s} & 0 \\ 0 & 1\end{pmatrix}ST_{\beta}S^{-1}\begin{pmatrix}0 \\ 1\end{pmatrix}\times\text{const},$$

and inserting

$$ST_{\beta}S^{-1}=\begin{pmatrix}(B+1)\lambda'^2 & -\lambda'^2 \\ 1 & B-1\end{pmatrix}\times\text{const},$$

$$\text{with}\quad B=\frac{(\alpha^2-1)^{\frac{1}{2}}}{\beta-\alpha},\quad (IV, 6)$$

we finally obtain as conditions for the eigenfrequencies:

$$(1-B)^2=\lambda'^{2(s+1)}$$

or

$$B=\frac{(\alpha^2-1)^{\frac{1}{2}}}{\beta-\alpha}=1\pm|\lambda'|^{s+1}. \quad \text{(Note that } |\lambda'|<1.) \quad (IV, 7)$$

It is easily seen that this equation [where α, β, and λ' are given by (IV, 2) and (IV, 4)] determines exactly two eigenfrequencies $\omega_s{}^+$ and $\omega_s{}^-$ above the limit frequency of the M chain, provided that $m<\frac{1}{2}M$. For $M>m>\frac{1}{2}M$ two such solutions exist only if s is large enough. (Consider as an illustration the case $s=0$ where the two m masses are neighbors. If $m<\frac{1}{2}M$, then two vibrations exist where the masses m swing against each other or in phase. In the latter case the effective swinging mass is $2m$ and therefore this type of localized vibration in the chain is possible only for $2m<M$.)

When we average now over all possible values of s, the density of eigenfrequencies in the impurity band can be written as

$$\mu(\omega^2)=\frac{1}{2}\sum_s P(s)\{\delta(\omega^2-\omega_s{}^{+2})+\delta(\omega^2-\omega_s{}^{-2})\}, \quad (IV, 8)$$

where

$$\mu(\omega^2)d\omega^2=\frac{\text{No. of frequencies in } d\omega^2}{\text{No. of } m \text{ masses in the chain}}.$$

Here we have assumed that either $m<M/2$ and hence for each s two frequencies $\omega_s{}^{\pm}$ (above the frequency limit of the pure M-chain) exist, or that we consider only large s values. If $m<M/2$ is satisfied, then $\mu(\omega^2)=0$ beneath the frequency limit of the M chain and $\int_0^\infty \mu(\omega^2)d\omega^2=1$ [since $\sum P(s)=1$] i.e., the number of frequencies in the impurity band equals the number of m masses. For large values of s, i.e., if the two m masses

are far apart, $\omega_s{}^+$ and $\omega_s{}^-$ approach, according to (IV, 7), a frequency $\bar{\omega}$, given by $B=1$ or

$$\bar{\omega}^2=\frac{4}{M}\frac{1}{\vartheta(2-\vartheta)}, \quad \text{with} \quad \vartheta=\frac{m}{M}. \quad (IV, 9)$$

This frequency $\bar{\omega}$ is therefore the resonance frequency of a single mass m in a long chain of masses M. [The frequency limit of the pure M chain is given by $\omega^2=(4/M)<\bar{\omega}^2$.]

If the concentration q of the m masses decreases then the probability of finding two m masses close to each other (e.g., $s<10$) decrease with q^2. Now only two m masses close to each other can give a frequency much different from $\bar{\omega}$. Therefore, for low impurity concentration q, almost all frequencies lie near to $\bar{\omega}$.

Let us consider this case, where frequencies much different from $\bar{\omega}$ can be neglected, in more detail. The relation (IV, 6) can be written near $\omega=\bar{\omega}$ as

$$B-1=\left(\frac{\vartheta(1-\vartheta/2)}{(1-\vartheta)^2}\right)\left(\frac{\omega^2-\bar{\omega}^2}{\bar{\omega}^2}\right), \quad (IV, 10)$$

with $\bar{\omega}^2$ and ϑ from (9). Using $c=B-1$ as our new coordinate, the eigenfrequencies are determined [see Eq. (IV, 7)] by

$$c=B-1=\pm|\lambda'|^{s+1}. \quad (IV, 11)$$

Therefore the density of frequencies $\mu[c]=\mu(\omega^2)d\omega^2/dc$ is given by

$$\mu[c]=\frac{1}{2}\sum_{s=0}^{\infty}P(s)\{\delta(c-|\lambda'|^{s+1})+\delta(c+|\lambda'|^{s+1})\}$$

$$=\sum_{s=1}^{\infty}qp^{2s}\{\delta(c-|\lambda'|^s)+\delta(c+|\lambda'|^s)\}. \quad (IV, 12)$$

This function $\mu[c]$ is highly singular at $c\approx0$ (note that $|\lambda'|<1$ and that therefore the δ functions accumulate around $c=0$). In a real chain these δ functions will be smeared out a little by the interactions between more than two masses which we have neglected here. Therefore it is reasonable to replace $\mu[c]$ for $c\approx0$ by a smoothed function $\bar{\mu}[c]$. In order to determine $\mu[c]$ we form $\int\mu[c]dc$, replace this by a smoother function, and differentiate again: If $c=|\lambda'|^{s_0}$, where s_0 is a positive integer, then

$$\int_0^{c+0}\mu[c']dc'=\sum_{s=s_0}^{\infty}qp^{2s}=\frac{1}{2}p^{2s_0}=\frac{1}{2}|c|^{4\epsilon},$$

with

$$\epsilon=\ln p/2\ln|\lambda'|=q\left/2\ln\left|\frac{2-\vartheta}{\vartheta}\right|\right.. \quad (IV, 13)$$

[Here $\lambda'=\alpha+(\alpha^2-1)^{\frac{1}{2}}$ has been replaced by its value at $\omega=\bar{\omega}$: $\lambda'=-\vartheta/(2-\vartheta)$.] Therefore the most natural

way of smoothing $\int_0^c \mu(c')dc'$ is to replace it by

$$\int_0^c \bar{\mu}[c']dc' = \tfrac{1}{2}|c|^{4\epsilon} \quad \text{for} \quad c > 0.$$

This gives

$$\bar{\mu}[c] = 2\epsilon|c|^{4\epsilon-1}.$$

The same result is obtained by replacing the s summation in (IV, 12) by an integration. This is justified if besides $p \approx 1$ also $|\lambda'| \approx 1$ is satisfied. A simple calculation gives

$$\int_{s=1}^{\infty} ds\, qp^{2s}\{\delta(c-|\lambda'|^s)+\delta(c+|\lambda'|^s)\} = 2\epsilon|c|^{4\epsilon-1}$$

$$(\text{if } |c| < |\lambda'|),$$

with ϵ as in (IV, 13). This replacement of the sum by an integral can be described quasi-physically as follows: Actually the numbers s of M atoms between two nearest m atoms is an integer, occurring with the probability $P(s) = 2qp^{2s}$ (for $p \approx 1$). We calculate, however, *as if* s could assume any positive value with the probability density $2qp^{2s}$. This procedure is justified mathematically only if $|\lambda'| \approx 1$. In our example it gives good results, however, also if this condition is not satisfied since even then the result agrees with the preceding smoothing method. The procedure of replacing s by a continuous parameter will be used again in (b). We shall assume there also that the condition $|\lambda'| \approx 1$ is not so essential for the result.

Concluding our discussion of the simplified model—in which we take into account only the interaction between two nearest masses m at a time—we see that the density of eigenfrequencies in the impurity band can be described by

$$\mu[c] \approx \bar{\mu}[c] = 2\epsilon|c|^{4\epsilon-1}, \quad (\text{IV, 14})$$

with

$$c = \frac{\vartheta(1-\vartheta/2)}{(1-\vartheta)^2}\frac{\omega^2-\bar{\omega}^2}{\bar{\omega}^2}, \quad \epsilon = \frac{q}{2\ln|(2-\vartheta)/\vartheta|}, \quad \vartheta = \frac{m}{M},$$

provided that the following conditions are satisfied: (1) q must be small enough such that almost all eigenfrequencies lie near $\bar{\omega}$; (2) ω must lie near to $\bar{\omega}$ such that the approximation (IV, 10) is valid and that $\mu(c)$ can be replaced by $\bar{\mu}[c]$.

The previous theory could be improved by considering the vibrations of 3, 4, 5 $\cdots$ masses m in a chain of masses M. This way of approach to the problem is troublesome, however. Therefore we shall use in the next part (b) a different method based on the results of Secs. II and III. We shall obtain there a better expression for $\mu[c]$, which is different from (IV, 14).

(b) *More Accurate Method*

In order to calculate the impurity bands of an M chain containing some lighter masses m (fraction $q \ll 1$)

we begin here—according to the general theory of Secs. II and III—by calculating the distribution function $w[z]$. Equations (II, 16a) and (II, 20a) for $w[z]$ and $W[z]$ read now

(a) $\quad w[z] = \dfrac{p}{z^2}w\left[2\alpha-\dfrac{1}{z}\right] + \dfrac{q}{z^2}w\left[2\beta-\dfrac{1}{z}\right],$

(IV, 15)

(b) $\quad W[z] = pW\left[2\alpha-\dfrac{1}{z}\right] + qW\left[2\beta-\dfrac{1}{z}\right] + \text{const},$

where p and q are the fractions of M- and m-masses in the chain and α, β are given by (IV, 2). We are considering a region above the frequency limit of the M chain, i.e., $\alpha < -1$. Furthermore we can assume $-1 < \beta < +1$, since for $\alpha < -1$ an $\beta < -1$ no eigenfrequencies exist.

It is convenient to introduce

$$x = (z-\lambda')/(z-\lambda''),$$
$$w(x)dx = w[z]dz; \quad W(x) = W[z], \quad (\text{IV, 16})$$

where λ', λ'' are defined as in (IV, 4). Then $w(x)$ is determined by [see (IV, 15a) and (II, 16)]:

(a) $\quad w(x) = p\lambda''^2 w(\lambda''^2 x) + q\dfrac{\partial T_\beta^{-1}(x)}{\partial x}w[T_\beta^{-1}(x)],$

(b) $\quad w(x) \geq 0,$ (IV, 17)

(c) $\quad \displaystyle\int_{-\infty}^{\infty} w(x)dx = 1.$

with

$$T_\beta^{-1}(x) = \frac{x(B-1)+\lambda'^2}{-x+(B+1)\lambda'^2}; \quad B = \frac{(\alpha^2-1)^{\frac{1}{2}}}{\beta-\alpha}. \quad (\text{IV, 18})$$

Before we go into details it is important to obtain a qualitative idea of the behavior of $w(x)$: As before, let u_n be the displacement of the nth mass and define the numbers

$$x_n = (z_n-\lambda')/(z_n-\lambda''),$$

where

$$z_n = u_{n-1}/u_n.$$

Then the relationship between x_{n+1} and x_n is

$$x_{n+1} = T_\alpha(x_n) = \lambda'^2 x_n,$$

or

$$x_{n+1} = T_\beta(x_n) = [(B+1)\lambda'^2 x_n - \lambda'^2]/[x_n+(B-1)],$$

depending on whether the nth mass is M or m. Now $w(x)dx$ is the probability that x_n (for large n) lies in the interval $(x, x+dx)$, when we compare either many chains at the same n or many different n-values at one long random chain. In the case of a pure M chain ($q=0$), the relation between x_{n+1} and x_n is always $x_{n+1} = \lambda'^2 x_n$; and since $\lambda'^2 < 1$, x_n will go to zero for $n \to \infty$. Therefore we have $w(x) = \delta(x)$ for $q=0$.

For very small values of q one might assume $w(x)$ to differ only slightly from $\delta(x)$ because in the series $x_1, x_2, x_3, \cdots$ the relation between successive x values is mostly $x_{n+1} = \lambda'^2 x_n$, which tend to push x to zero. Only the transformation $x_{n+1} = T_\beta(x_n)$, which occurs with the small probability q, may push x out of the neighborhood of zero again. But this effect of a transformation T_β will generally be canceled by the many following transformations T_α.

This argument fails, however, if $T_\beta(0) \approx \infty$. Here again many of the x_n's will be near to zero, but a transformation T_β now pushes these x_n's near to infinity. An x_n near enough to infinity, however, cannot be transformed into the neighborhood of zero, even by as many as $1/q$ successive transformations T_α.

Hence in this case the x_n's accumulate around $x = \infty$ as well as around $x = 0$ and $w(x)$ differs from zero appreciably at $x \approx 0$ *and* $x \approx \infty$. We see that even a small number of lighter masses m in a chain of masses M may change $w(x)$ considerably if the "resonance condition" $T_\beta(0) = \infty$ is satisfied. From (IV, 18) it follows that $T_\beta(0) = \infty$ or $T_\beta^{-1}(\infty) = 0$ is equivalent to $B = 1$. Therefore $T_\beta(0) = \infty$ means [see part (a)] that ω equals the resonance frequency of a single m mass in an M chain. [The same result can be obtained easily without referring to part (a).]

We return to Eqs. (IV, 15). In deriving these equations in Sec. II we obtained an iteration method for $W[z]$. Now we derive Eq. (IV, 15) once more in order to obtain a new and here more useful iteration method.

Considering a chain of M and m masses, let us define the numbers z_n as before. Then for a particular chain

$$z_{n+1} = 1/(2\alpha - z_n) \equiv T_\alpha[z_n], \quad 2\alpha = 2 - M\omega^2$$

or

$$z_{n+1} = 1/(2\beta - z_n) \equiv T_\beta[z_n], \quad 2\beta = 2 - m\omega^2$$

according to whether the nth mass M_n is M or m. Assume that $M_n = m$ for $n = s_1, s_2, \cdots (s_{n+1} > s_n)$ and that all other places are occupied by masses M. Now consider among the z_n's only $z_{s_1}, z_{s_2}, \cdots$ and write for convenience $z_{s_n} \equiv z_{(n)}$. Then

$$z_{(n+1)} = T_\alpha^{(s_{n+1} - s_n - 1)} T_\beta[z_{(n)}].$$

Let $w_{(n)}[z]$ be the distribution function for $z_{(n)}$ if we average over many chains.

Assuming for a moment that in all chains there would be the same number $s = (s_{n+1} - s_n - 1)$ of M masses between the nth m mass and the $(n+1)$th m mass, we would obtain

$$z_{(n+1)} = T_\alpha^s T_\beta[z_{(n)}],$$

and consequently, for

$$W_{(n)}[z] = \int_0^z w_{(n)}[z']dz':$$

we obtain

$$W_{(n+1)}[z] = W_{(n)}[T_\beta^{-1} T_\alpha^{-s}[z]] + \text{const}.$$

Since it occurs, however, with the probability $P'(s) = qp^s$ that the nth and $(n+1)$th m masses are separated by s M masses, we obtain

$$W_{(n+1)}[z] = \sum_{s=0}^{\infty} qp^s W_{(n)}[T_\beta^{-1} T_\alpha^{-s}[z]]$$
$$+ \text{const}. \quad (\text{IV}, 19)$$

This gives a new iteration method for $W[z]$, since again

$$\lim_{n \to \infty} (W_{(1)}[z] + W_{(2)}[z] + \cdots + W_{(n)}[z]) \times \frac{1}{n} = W[z].$$

[This can be proved in the same way as (II,19).] It is easily verified that the equation

$$W[z] = \sum_{s=0}^{\infty} qp^s W[T_\beta^{-1} T_\alpha^{-s}[z]] + \text{const}$$

is equivalent to

$$W[z] = pW[T_\alpha^{-1}[z]] + qW[T_\beta^{-1}[z]] + \text{const},$$

which is Eq. (15b). Introducing x and $W(x)$ as in (IV, 16), we can write (IV, 19) as

$$W_{(n+1)}(x) = \sum_{s=0}^{\infty} qp^s W_{(n)}(T_\beta^{-1}(\lambda''^{2s}x)) + \text{const}. \quad (\text{IV}, 20)$$

So far our equations are quite general. Now we assume that q is very small. Then the number s of M masses between successive m masses is mostly very large, since the probability for a certain value s is $P'(s) = qp^s$. Here we make the following approximation: We calculate *as if* s could assume any positive value with the probability density qp^s. This is equivalent to replacing the s-summation in (IV, 20) by an integration. [This is mathematically justified if, besides $p \approx 1$, also $|\lambda''| \approx 1$. We may assume, however, as explained in (a), that the requirement $|\lambda''| \approx 1$ is not very important for the result.] Then we obtain for $W(x)$, from (IV, 20),

$$W(x) = \int_0^{\infty} qp^s W(T_\beta^{-1}(\lambda''^{2s}x))ds + \text{const}; \quad (\text{IV}, 21)$$

and, differentiating, we get

$$w(x) = \int_0^{\infty} qp^s w(T_\beta^{-1}(\lambda''^{2s}x)) \frac{dT_\beta^{-1}(\lambda''^{2s}x)}{dx} ds,$$

or, with

$$\tau = \lambda''^{2s}x, \quad \epsilon = q/\ln\lambda''^2,$$

$$w(x) = \int_x^{(+\infty)x} \frac{1}{\epsilon} \frac{1}{\tau} \left|\frac{x}{\tau}\right|^{\epsilon-1} w(T_\beta^{-1}(\tau)) \frac{dT_\beta^{-1}(\tau)}{d\tau} d\tau.$$

The last equation can be written as

$$w(x)=\int_{-\infty}^{\infty} L(\tau,x)\frac{dT_\beta^{-1}(\tau)}{d\tau}w(T_\beta^{-1}(\tau))d\tau \qquad (\text{IV, 22})$$

$$=\int_{-\infty}^{\infty} L(T_\beta(\tau'),x)w(\tau')d\tau',$$

with

$$L(\tau,x)=\epsilon|x|^{\epsilon-1}/|\tau|^\epsilon \quad \text{for}$$
$$\qquad\qquad 0<x<\tau \quad \text{and} \quad \tau<x<0 \qquad (\text{IV, 22'})$$
$$=0 \quad \text{otherwise.}$$

We want to solve Eq. (IV, 22) for $w(x)$ under the assumption that q is very small and that the frequency considered lies near the resonance frequency of a single m mass in an M chain (i.e., $B\approx 1$). In order to do this we note:

1. For any function $g(\tau)$ which vanishes in a neighborhood of $\tau=0$, we obtain from (IV, 22')

$$\int_{-\infty}^{\infty} L(\tau,x)g(\tau)d\tau=\begin{Bmatrix} c_1|x|^{\epsilon-1} & \text{for} & x>0 \\ c_2|x|^{\epsilon-1} & \text{for} & x<0 \end{Bmatrix} \text{ near } x=0,$$

where c_1 and c_2 are constants.

2. We have seen that $w(x)$ is very small except near $x=0$ and $x=\infty$. Therefore, in (22), $[dT_\beta^{-1}(\tau)/d\tau]\times w(T_\beta^{-1}(\tau))$ is very small near $\tau=0$. [From (IV, 18), with $B\approx 1$, it is seen that $T_\beta^{-1}(0)$ is neither near to 0 nor near to ∞.]

Looking now at $w(x)$ on the left of Eq. (IV, 22), we see that $w(x)$ near $x=0$ must be almost equal to a function $\Delta(x)$ defined as

$$\Delta(x)=aq|x|^{\epsilon-1} \quad \text{for} \quad 0<x<1$$
$$=bq|x|^{\epsilon-1} \quad \text{for} \quad -1<x<0 \qquad (\text{IV, 23})$$
$$=0 \qquad\qquad \text{otherwise,}$$

where a and b are constants. Inserting into both sides of (IV, 22) such a function $w(x)$ with

$$w(x)=\Delta(x) \quad \text{for} \quad -1<x<1,$$
$$=0 \qquad \text{except near } x=0 \text{ and } x=\infty,$$

where we note that $\Delta(x)$ is very small for $x\rightarrow\pm 1$, we obtain from (IV, 22) near $x=0$:

$$\Delta(x)=\int_{-1}^{1} L(T_\beta(x'),x)\Delta(x')dx'$$
$$+\int_{x'\approx\infty} L(T_\beta(x'),x)w(x')dx',$$

or

$$\Delta(x)=\int_{-1}^{1} L(T_\beta(x'),x)\Delta(x')dx'+dL(T_\beta(\infty),x), \qquad (\text{IV, 24})$$

with

$$d=\int_{x'\approx\infty} w(x')dx'.$$

[Here we used that $L(x_0,x)$ depends very slowly on x_0 near $x_0=T_\beta(\infty)$.]

Now the constants a, b, and d can be determined as follows: from $\int_{-\infty}^{\infty} w(x)dx=1=\int_{-1}^{1}\Delta(x)dx+d$, it follows that

$$(a+b)\ln\lambda''^2+d=1. \qquad (\text{IV, 25})$$

Two further relations between a, b, and d are obtained from (IV, 24) by comparing both sides for $x>0$ and $x<0$. These three equations for a, b, and d give us, after a short calculation[7]:

$$\frac{1}{a}=2\ln\lambda''^2+\mathcal{g}_3-\mathcal{g}_2-\frac{\mathcal{g}_1\mathcal{g}_3}{\ln\lambda''^2} \quad \text{if} \quad B<1, \qquad (\text{IV, 26a})$$

$$\frac{1}{a}=2\ln\lambda''^2+\mathcal{g}_2\frac{\ln\lambda''^2-\mathcal{g}_3}{\ln\lambda''^2-\mathcal{g}_2} \quad \text{if} \quad B>1, \qquad (\text{IV, 26b})$$

$$\mathcal{g}_1=q\int_0^1 |(x+|c|)|^\epsilon|x|^{\epsilon-1}dx\approx\tfrac{1}{2}\ln\lambda''^2(1+|c|^{2\epsilon}),$$

$$\mathcal{g}_2=q\int_{-|c|}^0 |(x+|c|)|^\epsilon|x|^{\epsilon-1}dx\approx\ln\lambda''^2|c|^{2\epsilon},$$

$$\mathcal{g}_3=q\int_{-1}^{-|c|} |(x+|c|)|^\epsilon|x|^{\epsilon-1}dx\approx\tfrac{1}{2}\ln\lambda''^2(1-|c|^{2\epsilon}),$$

where $|c|=|B-1|$. (The approximate expressions for the integrals can be used since $q\ll 1$.)

As the last step in our calculation, we show that $M(\omega^2)$ of Eq. (II, 12) can be expressed by the constant a only:

$$M(\omega^2)=q(1-a\ln\lambda''^2)+\text{const.} \qquad (\text{IV, 27})$$

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[7] Let us consider, for example, the case $B<1$. In the region $x>0$, Eq. (IV, 24) gives

$$aq|x|^{\epsilon-1}=\epsilon|x|^{\epsilon-1}\Big\{d|T_\beta(\infty)|^{-\epsilon}+b\int_{-1}^0 q|x'|^{\epsilon-1}|T_\beta(x')|^{-\epsilon}dx'$$
$$+a\int_0^{1-B} q|x'|^{\epsilon-1}|T_\beta(x')|^{-\epsilon}dx'\Big\}.$$

Since

$$T_\beta(x')=[(B+1)\lambda'^2x'-\lambda'^2]/[x'+(B-1)]\approx-\lambda'^2/[x'+(B-1)]$$

for $x'\approx 0$ and $B\approx 1$, and since furthermore $|T_\beta(\infty)|^\epsilon\approx 1$ and $|\lambda'^2|^\epsilon\approx 1$ for $q\ll 1$, our equation can be written as

$$a=(\ln\lambda''^2)^{-1}\Big\{d+bq\int_0^1 |x''|^{\epsilon-1}|x''+|B-1||^\epsilon dx''$$
$$+aq\int_{-|B-1|}^0 |x''|^{\epsilon-1}|x''+|B-1||^\epsilon dx''\Big\}.$$

Similarly, considering (IV, 24) for $x<0$, we obtain

$$b=(\ln\lambda''^2)^{-1}aq\int_{-1}^{-|B-1|} |x|^{\epsilon-1}|x+|B-1||^\epsilon dx.$$

Now, with (IV, 25), the constant a can be calculated. This gives us the result (IV, 26a).

This result is easily obtained from the relation

$$M(\omega^2)=\int_{-\infty}^{0}w[z]dz+\text{const}$$

$$=-\int_{\lambda'^2}^{1}w(x)dx+\text{const}\quad[\text{see Eq. (IV, 16)}].$$

With $w(x)=aq|x|^{\epsilon-1}$ in the region $\lambda'^2<x<1$, we obtain

$$M(\omega^2)=\text{const}-aq\epsilon^{-1}(1-\lambda'^{2\epsilon})$$

$$\approx\text{const}-aq\ln\lambda''^2\quad\text{for}\quad\epsilon\approx0.$$

This derivation of (IV, 27) is questionable, however. We know that $w(x)$ equals $aq|x|^{\epsilon-1}$ for small values of $x>0$ and we know that $w(x)$ is small like $aq|x|^{\epsilon-1}$ near $x=1$, but we have not proved that $aq|x|^{\epsilon-1}$ is a good approximation for $w(x)$ near $x=1$.

To prove (IV, 27) properly, we use here the same ideas which led us in Sec. II to the relation $M(\omega^2)=\int_{-\infty}^{0}w[z]dz+\text{const}$. We define ψ_n by $x_n=\tan(\frac{1}{2}\psi_n)$ and make the relation between ψ_{n+1} and ψ_n ($\psi_{n+1}=T_\alpha\{\psi_n\}$ or $\psi_{n+1}=T_\beta\{\psi_n\}$) unique by postulating that $T_\alpha\{0\}=0$; $2\pi<T_\beta\{\frac{1}{2}\pi\}<2\pi+\frac{1}{2}\pi$. Now $M(\omega^2)+\text{const}$ is equal to the prnbability that ψ_{n+1} and ψ_n include a multiple of 2π. For $\psi_{n+1}=T_\alpha\{\psi_n\}$ this is impossible. For $\psi_{n+1}=T_\beta\{\psi_n\}$ it occurs whenever x_n lies outside the interval $0<x_n<T_\beta^{-1}(0)=1/(B+1)$. Since the probability of finding x_n outside this interval is

$$1-\int_{0}^{(B+1)^{-1}}aq|x|^{\epsilon-1}dx\approx1-a\ln\lambda''^2,$$

and since furthermore the relation $\psi_{n+1}=T_\beta\{\psi_n\}$ occurs with the probability q, the relationship (IV, 27) follows.

The final result can now be stated explicitly:

$$M(\omega^2)=1-\frac{q}{(\frac{3}{2}-\frac{1}{2}|c|^{2\epsilon})^2}\quad\text{for}\quad\omega^2<\bar\omega^2\quad(\text{IV, 28})$$

$$=1-q\frac{1-|c|^{2\epsilon}}{(\frac{3}{2}-\frac{1}{2}|c|^{2\epsilon})^2}\quad\text{for}\quad\omega^2>\bar\omega^2,$$

with

$$\epsilon=\frac{q}{\ln\lambda''^2}=\frac{q}{2\ln|(2-\vartheta)/\vartheta|},\quad\vartheta=\frac{m}{M}<1,$$

$$c=B-1$$

$$=\left(\frac{\vartheta(1-\vartheta/2)}{(1-\vartheta)^2}\right)\left(\frac{\omega^2-\bar\omega^2}{\bar\omega^2}\right),\quad\bar\omega^2=\frac{2}{M}\left(\frac{1}{\vartheta(1-\vartheta/2)}\right).$$

Comparing the result (IV, 28) with Eq. (IV, 14), we note:

1. Both equations were derived under the conditions $q\ll1$ and $\omega\approx\bar\omega$.

2. Under these conditions the Eq. (IV, 14) was a rough approximation; Eq. (IV, 28), however, can be assumed to give very good results.

3. The density function $\mu[c]$ of (IV, 14) and the corresponding $m[c]\equiv(1/q)(d/dc)M(\omega^2)$ of (IV, 28) are both very sharply increasing functions near $c=0$ with weak long wings in the region of large $|c|$ values.

4. If q is very small, then the fraction of eigenvalues of the impurity band which lie in these wings [where (IV, 14) and (IV, 28) do not hold] is also very small.

5. Equation (IV, 14) differs essentially from (IV, 28). Note in particular that near $c=0$ $\mu[c]$ is proportional to $|c|^{4\epsilon-1}$ while $m[c]$ is there proportional to $|c|^{2\epsilon-1}$.

In cases where q is not quite so small that (IV, 28) can be applied, a better solution $w(x)$ of (IV, 22) might be useful. Such a solution could furthermore be improved by the iteration method (IV, 20).

The generalization of our results to electronic impurity bands presents no difficulties. Let us consider the model of Sec. III(b). Assume that the crystal consists of two types of atoms A and B, occurring with the probabilities p and q ($q\ll1$), and let the potentials of these atoms be determined by V^p and V^q. If now $V^q>V^p$, then below the lowest energy state of the pure A crystal there are energy states due to the B atoms. As shown in (III, b) the number of eigenvalues k_ν with $k_\nu<k$ is

$$NM(k)=N\int_{-\infty}^{0}w[z]dz+\text{const},$$

where $w[z]$ satisfies Eq. (IV, 15) with

$$\alpha=-\cosh(kl)+(V^p/2k)\sinh(kl),$$
$$\beta=-\cosh(kl)+(V^q/2k)\sinh(kl).\qquad(\text{IV, 29})$$

Starting from Eq. (IV, 15), we can now proceed as before with (IV, 29) and obtain the result analogous to (IV, 28):

$$M(k)=\text{const}+\begin{cases}-\dfrac{q}{(\frac{3}{2}-\frac{1}{2}|c|^{2\epsilon})^2}&\text{for}\quad B<1\\[2ex]-q\dfrac{1-|c|^{2\epsilon}}{(\frac{3}{2}-\frac{1}{2}|c|^{2\epsilon})^2}&\text{for}\quad B>1,\end{cases}$$

where now with α,β from (IV, 29),

$$c=B-1,\qquad B=(\alpha^2-1)^{\frac{1}{2}}/(\beta-\alpha),$$
$$\epsilon=q/\ln\lambda''^2,\qquad\lambda''=\alpha-(\alpha^2-1)^{\frac{1}{2}}.$$

In the special case $V^p=0$, we obtain

$$c=(k-\bar k)/\bar k,$$
$$\epsilon=q/\bar kl,$$

where $\bar k=\frac{1}{2}V^q$ is the k value at the resonance.

In conclusion I would like to thank Professor Luttinger, who suggested this problem to me, for many valuable discussions and help in completing the manuscript. Furthermore I am indebted to the American Academy of Science and to the Foreign Operations Administration for making my temporary stay in the United States possible.

APPENDIX I

We add some remarks concerning the solution $w[z]$ of Eqs. (II, 16). We write these equations as

$$w[z] = \sum_j p^j z^{-2} w[T_j^{-1}[z]],$$

$$w[z] \geq 0,$$

$$\int_{-\infty}^{\infty} w[z] dz = 1, \tag{A, 1}$$

with

$$T_j^{-1}[z] = 2\alpha^j - z^{-1}, \quad 2\alpha^j = 2 - M^j \omega^2. \tag{A, 1a}$$

It is sometimes more convenient to consider $w(\varphi)$, defined by

$$w(\varphi) d\varphi = w[z] dz, \tag{A, 2}$$

with

$$z = \tan(\tfrac{1}{2}\varphi). \tag{A, 3}$$

Then we define the operators T_j^{-1} acting on φ as

$$T_j^{-1}(\varphi) \equiv 2 \arctan\left\{ 2\alpha^j - \frac{1}{\tan(\varphi/2)} \right\}, \tag{A, 4a}$$

and make the continuous relationship $\varphi' = T_j^{-1}(\varphi)$ unique by requiring

$$T_j^{-1}(0) = \pi. \tag{A, 4b}$$

Now (A, 1) can be written in terms of $w(\varphi)$ as

$$w(\varphi) = \sum_j p^j w(T_j^{-1}(\varphi)) \, dT_j^{-1}(\varphi)/d\varphi,$$

$$w(\varphi) \geq 0,$$

$$\int_0^{2\pi} w(\varphi) d\varphi = 1, \tag{A, 5}$$

$$w(\varphi + 2\pi) = w(\varphi).$$

For $W(\varphi) = \int_0^\varphi w(\varphi') d\varphi'$, this gives

(a) $\quad W(\varphi) = \sum_j p^j W[T_j^{-1}(\varphi)] - W(-\pi),$

(b) $\quad W(\varphi)$ is monotonically non-

decreasing in φ, (A, 6)

(c) $W(\varphi + 2\pi) = W(\varphi) + 1,$

(d) $\quad W(0) = 0.$

We show first that, provided a solution $W(\varphi)$ of (A, 6) exists, this solution is continuous (α) and unique (β).

(α) Assume that $W(\varphi)$ has a jump of height d at $\varphi = \varphi_0$ and that no higher jump does occur. Then $W(\varphi)$ has a jump d also at all points $\varphi_0 + 2\pi h$. From (A, 6a) it follows that $W(\varphi)$ must also have a jump d at all points $T_j^{-1}(\varphi_0) + 2\pi h$ (note that $\sum p^j = 1$). In the same way it is seen that $W(\varphi)$ must have a jump d at all points $\varphi_0 + 2\pi h$, $T_j^{-1}(\varphi_0) + 2\pi h$, $T_k^{-1}(T_j^{-1}(\varphi_0)) + 2\pi h$, $\cdots$. Provided that we have at least two different α^j-values, there can be found an infinite number of such points in the interval $0 \leq \varphi < 2\pi$ at which $W(\varphi)$ should jump by the amount d. This is impossible since $W(\varphi)$ is monotonic and $W(2\pi) - W(0) = 1$. Hence $W(\varphi)$ must be continuous.

(β) Assume that there are two different functions satisfying (A, 6). Then the difference $U(\varphi)$ satisfies:

$$U(\varphi) = \sum_j p^j U(T_j^{-1}(\varphi)) - U(-\pi),$$

$$U(\varphi + 2\pi) = U(\varphi),$$

$$U(0) = 0; \quad |U(\varphi)| < 1, \tag{A, 7}$$

$$U(\varphi) \text{ is continuous.}$$

Let $U(\varphi)$ assume its maximum at φ_1 and its minimum at φ_2. Then, from $(A, 7)$,

$$-U(-\pi) = U(\varphi_1) - \sum p^j U(T_j^{-1}(\varphi_1)) \geq 0,$$

$$-U(-\pi) = U(\varphi_2) - \sum p^j U(T_j^{-1}(\varphi_2)) \leq 0,$$

hence $U(-\pi) = 0$. It follows further that $U(\varphi)$ must reach its maximum on a whole set S_1 of points:

$$S_1 = \{ \varphi_1 + 2\pi h, \; T_j^{-1}(\varphi_1) + 2\pi h,$$
$$T_k^{-1}(T_j^{-1}(\varphi_1)) + 2\pi h, \cdots \},$$

and its minimum value at a set S_2:

$$S_2 = \{ \varphi_2 + 2\pi h, \; T_j^{-1}(\varphi_2) + 2\pi h,$$
$$T_k^{-1}(T_j^{-1}(\varphi_2)) + 2\pi h, \cdots \}$$

We can assume that $|\alpha^1| < 1$ and $\alpha^1 \neq \alpha^2$ (the case where $|\alpha^j| > 1$ for all j has no physical interest). Then it is easily seen that for the sets S_1 and S_2 the point $\varphi = \pi$ is a common point of accumulation. [If there exists an integer n that $T_1^{-n}[z]$ is the unit transformation, then $T_1^{-(n-1)} = T_1$. From (A, 1a) we see that $T_2^{-1} T_1[z] = z + 2(\alpha^2 - \alpha^1)$. Therefore repeated application of the operator $T_2^{-1} T_1^{-(n-1)}$ transforms any z to infinity or any φ to π as near as we want. Therefore $\varphi = \pi$ is a common point of accumulation of S_1 and S_2. If $T_1^{-n}[z]$ is not the unit transformation for any integer n, then the points $T_1^{-n}[\varphi] + 2\pi h$ lie dense everywhere (for any φ_0) and the points of S_1 and S_2 lie dense everywhere.]

Since $U(\varphi)$ is continuous, it follows that

$$U(\pi) = U(\varphi_1) = U(\varphi_2), \quad \text{i.e.,} \quad U(\varphi) = U(0) = 0.$$

Now we can construct the solution $W(\varphi)$ of Eq. (A, 6). Let $W_0(\varphi)$ be any function which satisfies

$W_0(\varphi+2\pi)=W_0(\varphi)+1,$

$\qquad W_0(0)=0,$ \hfill (A, 8)

$\qquad W_0(\varphi)$ is monotonically nondecreasing in φ.

Then define, with $W_0(\varphi)$ from (A, 8), the functions $W_n(\varphi)$, $W^n(\varphi)$ by

$$W_{n+1}(\varphi)=\sum_j p^j W_n(T_j^{-1}(\varphi))-W_n(-\pi), \qquad \text{(A, 9)}$$

$$W^n(\varphi)=[W_0(\varphi)+W_1(\varphi)+\cdots+W_n(\varphi)]/$$
$$\hfill (n+1). \quad \text{(A, 10)}$$

The functions $W_n(\varphi)$ and $W^n(\varphi)$ also satisfy (A, 8). Furthermore, we see from (A, 9) and (A, 10) that

$$\left|W^n(\varphi)-\sum_j p^j W^n(T_j^{-1}(\varphi))+W^n(-\pi)\right|$$
$$=\left|\frac{W_{n+1}(\varphi)-W_0(\varphi)}{n+1}\right|\leq\frac{1}{n+1}. \quad \text{(A, 11)}$$

Since the functions $W^n(\varphi)$ are monotonic and bounded in $0\leq\varphi\leq 2\pi$, there exists a convergent subsequence $W^{c_1}(\varphi)$, $W^{c_2}(\varphi)$, $\cdots$ converging to a function $W(\varphi)$. From (A, 11), we see that $W(\varphi)$ satisfies (A, 6). Since furthermore no other solution of (A, 6) can exist, the series $W^1(\varphi)$, $W^2(\varphi)$, $\cdots$ must also converge to $W(\varphi)$. Having proved that $W[z]$ exists and is a continuous function, we shall now demonstrate as an example that $w[z]$ can be highly singular.

Assume that $|\alpha^1|<1$; $|\alpha^2|>1$. Then $z=T_2^{-1}[z]$ has two real solutions z', z'' with $|z'|<1$, $|z''|>1$. Assume now further that $p^{(2)}|z'|^{-2}>1$ and finally that T_1^{-n} is not the unit transformation for any integer n. Now $w[z]$ provided that it exists, satisfies

$$w[z]=p^{(1)}z^{-2}w[T_1^{-1}[z]]+p^{(2)}z^{-2}w[T_2^{-1}[z]]+\cdots,$$
$$w[z]\geq 0, \quad \int_{-\infty}^{\infty}w[z]dz=1. \qquad \text{(A, 12)}$$

Since all terms in (A, 12) are non-negative, this equation with $z=z'=T_2^{-1}[z']$ and $p^{(2)}|z'|^{-2}>1$ implies that

$$w[z']=0 \quad \text{or} \quad w[z']=\infty. \qquad \text{(A, 13)}$$

If $w[z']=0$, then from (A, 12) it follows that $w=0$ at $T_1^{-n}[z']$ for all integers $n>0$. These points lie dense everywhere. Hence $w[z]$ vanishes on some points of every interval. But $w[z]$ cannot vanish throughout any interval (this would imply $w[z]\equiv 0$ but $\int w[z]dz=1$). Therefore $w[z]$ cannot be continuous in any interval. The same result is obtained if $w[z']=\infty$. Here it is seen that $w[z]$ cannot be finite throughout any interval.

APPENDIX II

So far we have assumed that the atoms in our one-dimensional crystal are distributed at random. Now we consider the case where a correlation between neighboring atoms exists.

Suppose we have a two-component crystal containing A and B atoms occurring with the probabilities p and q. Comparing now many one-dimensional crystals, we call those crystals which happen to have an A atom at the nth place A crystals ($n=$any fixed number) and the crystals with a B atom at the nth place B crystals. If there is a correlation between neighboring atoms, then among the A crystals the probabilities of finding an A or B atom on the $(n-1)$th place may be different from p and q. We call these probabilities P_{AA} and P_{AB}. In the same way we define among the B crystals the probabilities of finding on the $(n-1)$th place an A or B atom as P_{BA} and P_{BB}. It is seen easily that

$$P_{AA}+P_{AB}=1,$$
$$P_{BA}+P_{BB}=1, \qquad \text{(A, 14)}$$
$$qP_{BA}=pP_{AB}.$$

We want to determine the electronic energy levels for the general crystal model discussed in (III, c). [This general formalism applies also to the vibrations of a linear chain of atoms]. The numbers φ_n [see (III, c)] for the different crystals depend only on the nature of the atoms preceding the nth atom [i.e., on the $(n-1)$th, $(n-2)$th, $\cdots$1st atom].

Since now there is an interaction between the nth atom and the $(n-1)$th atom, the distribution functions for φ_n may be different among the A crystals and among the B crystals. Let $w_A(\varphi_n)$ [$w_B(\varphi_n)$] be the distribution functions for φ_n in the A [B] crystals, where the nth place is occupied by an A [B] atom. Instead of one distribution function $w(\varphi)=w_A(\varphi)=w_B(\varphi)$, we have now two such functions. We can easily find a set of difference equations for $w_A(\varphi)$ and $w_B(\varphi)$: Let us consider the A crystals first. Here the distribution of φ_n is given by $w_A(\varphi_n)$. The distribution of φ_{n-1} is $w_A(\varphi)$ or $w_B(\varphi)$ according to whether the $(n-1)$th place is occupied by an A or B atom. These two possibilities occur with the probability P_{AA} and P_{AB}. Therefore, as in (II, 15), we obtain

$$w_A(\varphi)d\varphi=P_{AA}w_A(\varphi-\Delta^A(\varphi))d(\varphi-\Delta^A(\varphi))$$
$$+P_{AB}w_B(\varphi-\Delta^B(\varphi))d(\varphi-\Delta^B(\varphi)),$$

or with

$$W_A(\varphi)=\int_0^{\varphi}w_A(\varphi')d\varphi'; \quad W_B(\varphi)=\int_0^{\varphi}w_B(\varphi')d\varphi',$$

$$W_A(\varphi)=P_{AA}W_A(\varphi-\Delta^A(\varphi))$$
$$+P_{AB}W_B(\varphi-\Delta^B(\varphi))+C_A(k). \quad \text{(A, 15a)}$$

Considering the B crystals we obtain in the same way

$$W_B(\varphi)=P_{BA}W_A(\varphi-\Delta^A(\varphi))$$
$$+P_{BB}W_B(\varphi-\Delta^B(\varphi))+C_B(k). \quad \text{(A, 15b)}$$

Equations (A, 15), together with the relations

$$W_A(\varphi+2\pi)=W_A(\varphi)+1,$$
$$W_A(0)=0, \qquad\qquad\text{(A, 16)}$$
$$W_A(\varphi)=\text{monotonically nondecreasing in } \varphi,$$

and the same relations for W_B, determine again the functions W_A and W_B. These functions, as well as the constants $C_A(k)$ and $C_B(k)$, can be calculated from (A, 15) by iteration. Finally, for $M(k)+\text{const}=(1/2\pi)\times\langle\varphi_{n+1}-\varphi_n\rangle_{Av}$, which gives us the relative number of eigenstates below k, we obtain

$$(1/2\pi)\langle\varphi_{n+1}-\varphi_n\rangle_{Av}=p\int (\varphi_{n+1}-\varphi_n)_A w_A(\varphi_n)d\varphi_n$$

$$+q\int (\varphi_{n+1}-\varphi_n)_B w_B(\varphi_n)d\varphi_n.$$

A short calculation using (A, 15) gives the result

$$M(k)+\text{const}=pC_A(k)+qC_B(k).$$

Electron Self-Energy and Temperature-Dependent Effective Masses in Semiconductors: n-Type Ge and Si

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The electronic self-energy due to interaction with acoustic phonons is evaluated as a function of the electron propagation vector $\mathbf{k}$, and a relation is established connecting the Sommerfeld-Bethe interaction constant with the energy band separation and effective masses. For nondegenerate prolate ellipsoidal energy surfaces of revolution, the self-energy depends linearly on the temperature T at high temperatures and quadratically on T at low temperatures, this behavior being substantiated by the experimental results of Macfarlane and Roberts. The temperature dependence of the principal effective masses $m_i(T)$ at high temperatures is given by ($i=l$ or t)

$$m_i(0)/m_i(T)=1+(128\pi/9\rho h^3 s\Theta_D)m_i{}^2(0)\alpha_i(E)\langle C^2\rangle_{Av}T$$

thus indicating a decrease in effective mass with rising temperatures. The result does not explain the deviation from the $T^{-\frac{3}{2}}$ law for the lattice mobility as observed by Morin and Maita. The percentage decrease at room temperature for each of the electron effective masses amounts to less than 1%. These results do not account fully for the possible change determined by Lax and Mavroides.

1. INTRODUCTION

THE temperature variation of the electronic energy in crystals is usually attributed to radiation damping,[1] thermal expansion,[2] electron self-energy,[3] and mutual electrostatic interactions of charge carriers.[4]

In the present paper a study is made of the electron self-energy in homopolar semiconductors with specific reference to n-type Ge and Si. From the self-energy the temperature dependence of the principal effective masses is then deduced. At low temperatures the self-energy exhibits a quadratic behavior with temperature, thus substantiating the observations of Macfarlane and Roberts[5] on the temperature variation of the infrared absorption edge. In addition, the percentage change in the principal effective masses from liquid helium temperatures to room temperature is computed and found to be much less than the possible change deduced by Lax and Mavroides.[6]

2. HAMILTONIAN AND THE LATTICE FIELD

The total Hamiltonian of the system, electron plus lattice, may be written as

$$H=H_r+V(\mathbf{R},\mathbf{r})+H_R, \qquad\qquad\text{(2.1)}$$

where H_r is the Hamiltonian of a nonlocalized electron, $V(\mathbf{R},\mathbf{r})$ the electron lattice interaction and H_R the vibrational energy of the lattice. The latter two quantities are given by the relations

$$V(\mathbf{R},\mathbf{r})=-\frac{1}{2(M\mathfrak{N})^{\frac{1}{2}}}\sum_{t,\sigma} \xi_t(\sigma)\cdot\nabla V(\mathbf{r})$$

$$\times\{\alpha_t(\sigma)e^{i\sigma\cdot\mathbf{r}}+\alpha_t{}^*(\sigma)e^{-i\sigma\cdot\mathbf{r}}\}\left(\frac{2\hbar}{\omega_t(\sigma)}\right)^{\frac{1}{2}} \quad\text{(2.2)}$$

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