Lifshitz or Montroll *et al.* Anelastic potential coefficients would be used to estimate the changes in effective modulus. The dynamic problem would then be equivalent to wave propagation in a non-uniform medium.

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Effect of Imperfections on the Dynamical Correlations between the Vibrational Modes of a Lattice

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In this paper a perturbation method for evaluating the effect of defects on additive functions of the normal mode frequencies of a lattice is presented. The method is applied to the study of the effect of defects on the time correlation functions associated with the vibrational modes of a lattice.

Recent work on the theory of linear response of systems under external stimuli has revealed the connection between the correlations among the various dynamical properties of a system and its susceptibility to external stimuli[1].

The present paper is concerned with the study, by a perturbation theory method, of the dynamical correlations between the vibrational modes of a crystal lattice in which there are defects.

We will restrict ourselves to the classical mechanical approach to the problem. A calculation of such correlation functions in a perfect lattice has been done by Montroll and Mazur[2]. It can be shown that these correlation functions are additive functions of the normal mode frequencies. For instance, in a monatomic lattice of N atoms, the autocorrelation functions between the displacements and between the momenta of the s-th atom in the lattice are:

$$\langle u_s(t)u_s(0)\rangle=\frac{kT}{mN}\sum_n\frac{\cos\omega_n t}{{\omega_n}^2}, \tag{1}$$

$$\langle p_s(t)p_s(0)\rangle=\frac{mkT}{n}\sum_n\cos\omega_n t. \tag{2}$$

Here m is the mass of the atom, $u_s(t)$ and $p_s(t)$ are the displacement and the momentum of the s-th atom, and ω_n is the n-th normal mode frequency. $\langle\ \rangle$ stands for the canonical average at the absolute temperature T.

The effect of defects on such additive functions of the normal mode frequencies has been studied in detail in recent years.[3),4),5)] Here we will propose a method by which an additive function can be directly expanded in a perturbation series.

Let F be an additive function of the normal mode frequencies:

$$F=\int_{-\infty}^{\infty}G(x)A(x)dx, \tag{3}$$

where x stands for the square of the frequency and $G(x)$ is its distribution function. The limits of the integral have been chosen without loss of generality, remembering that $G(x)$ is nonvanishing only in a finite interval.

In terms of $a(y)$ defined by the equation

$$A(x)=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}a(y)\,\mathrm{e}^{-ixy}dy. \tag{4}$$

Eq. (3) can be written in the form

$$F=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}a(y)dy\int_{-\infty}^{\infty}G(x)\,\mathrm{e}^{-ixy}dx,$$

$$=\frac{1}{\sqrt{2\pi}}\,\mathrm{Trace}\int_{-\infty}^{\infty}a(y)U(y)dy, \tag{5}$$

where the operator $U(y)$ is given by

$$U(y)=\mathrm{e}^{-iyM}, \tag{6}$$

M being the dynamical matrix of the lattice whose eigenvalues are the squares of the normal mode frequencies.

In the presence of defects in the lattice, the dynamical matrix can be written in the

form

$$M=M_0+\lambda D, \tag{7}$$

where λ is a suitable parameter, M_0 is the dynamical matrix of the perfect lattice, and D is the perturbation matrix. The operator $U(y)$ can be written in the form of a contour integral

$$e^{-iyM}=\frac{1}{2\pi i}\oint e^{-iyz}R(z)dz, \tag{8}$$

where the resolvent operator $R(z)$ is

$$R(z)=(z-M)^{-1} \tag{9}$$

and the contour encloses the real axis on which the eigenvalues of M occur. The resolvent operator can be expanded in a series

$$R(z)=(z-M_0)^{-1}+\lambda(z-M_0)^{-1}D(z-M_0)^{-1}+\lambda^2(z-M_0)^{-1}D(z-M_0)^{-1}D(z-M_0)^{-1}+\cdots. \tag{10}$$

When this is substituted in Eq. (8) and the trace taken in the representation in which M_0 is diagonal, we get

$$\text{Trace } U(y)=\sum_n e^{-iy(x_n+\lambda D_{nn})}+\lambda^2(-iy)\sum_{n\neq m}\sum\frac{D_{nm}D_{mn}e^{-iyx_n}}{x_n-x_m}+O(\lambda^3). \tag{11}$$

Substituting this in Eq. (5) and using Eq. (4) we obtain the required perturbation series for F:

$$F=\sum_n A(x_n+\lambda D_{nn})+\lambda^2\sum_{n\neq m}\sum\frac{D_{nm}D_{mn}}{x_n-x_m}\frac{\partial A(x_n)}{\partial x_n}+O(\lambda^3). \tag{12}$$

The explicit form of the perturbation matrix for various types of point defects in a simple cubic lattice model has been studied elsewhere.[3),4),5)] We give below the form of the matrix elements D_{mn} for two types of point defects in a linear chain.

(i) Isotope defect of mass m' at the l-th lattice site:

$$\lambda=1-\frac{m'}{m},$$
$$D_{mn}=\frac{x_m}{N}e^{2\pi il(n-m)/N}. \tag{13}$$

(ii) Change of spring constant from γ to γ' at the l-th gap:

$$\lambda=\frac{\gamma'}{\gamma}-1,$$
$$D_{mn}=\frac{\gamma}{mN}[1+e^{2\pi i(n-m)/N}-e^{2\pi in/N}-e^{-2\pi im/N}]\,e^{2\pi il(n-m)/N}. \tag{14}$$

Using these equations and Eqs. (12), (1) and (2) one can immediately obtain a perturbation expansion for the autocorrelation functions. The momentum autocorrelation function in the isotope case, for example, becomes

$$\langle p_s(t)p_s(0)\rangle=\frac{mkT}{N}\left[\sum_n\cos\omega_n\left(1+\frac{\lambda}{N}\right)^{1/2}t-\frac{\lambda^2 t}{2N^2}\sum_{n\neq m}\sum\frac{\omega_n\omega_m{}^2}{\omega_n{}^2-\omega_m{}^2}\sin\omega_n t+O(\lambda^3)\right], \tag{15}$$

Similar expressions can be obtained in other cases.

The above method is applicable when the effect of the defect on the dynamical matrix can be taken into account by a perturbation matrix, *i.e.*, when the lattice even in the presence of defects still behaves like an assembly of coupled harmonic oscillators, though without the symmetry of the perfect lattice. Anharmonic effects are outside the purview of this formalism. However, a similar method can be developed using the Liouville operator formalism which is capable of handling the anharmoic problem. This point will be discussed in a later paper.

Montroll and Mazur[2)] show that in a coupled harmonic oscillator assembly the autocorrelation function decays asymptotically in time. One must expect that in a lattice with defects of the type we have considered the correlation function must decay. However, the manner of decay in a perfect lattice and that in a lattice with defects will be substantially different in the time range corresponding to

($\lambda^2 t$) being small. This time range can obviously be appreciable when λ itself is small.

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DISCUSSION

Dexter, D. L.: Would you please discuss the application of this formulation to the calculation of observable quantities?

Mahanty, J.: The summation of the series that occurs as the coefficient of ($\lambda^2 t$) is rather difficult for realistic lattice models. This makes it difficult to calculate observable quantities. For the linear chain with nearest neighbour interactions the series can be summed in closed form.

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Electron-Phonon Interactions Induced by Lattice Defects in Metals

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Koshino's mechanism for inelastic scattering of electrons by impurities in metals is modified, so that the perturbation Hamiltonian depends on the strain at an impurity, not on the displacement. Expressions are derived for the resulting electrical resistance and the corresponding additional phonon scattering. The effect of the local modification of the strain field of a phonon at the impurity is discussed.

S. Koshino[1] suggested that electrons are scattered inelastically by impurity ions, because of their thermal motion. This should lead to an additional electrical resistance and to substantial deviations from Matthiessen's rule. This suggestion is further explored.

While Koshino took the displacement of the impurity ion as a measure of the perturbation Hamiltonian, the displacement of the impurity ion relative to its neighbors seems a better measure of the distortion of the impurity field. Thus the perturbation Hamiltonian is taken as

$$H_p' = \int d\boldsymbol{r}\left(\frac{\partial V}{\partial \boldsymbol{r}}\cdot\boldsymbol{\varepsilon}\right)e^{i\boldsymbol{p}\cdot\boldsymbol{r}}u(\boldsymbol{q})(e^{i\boldsymbol{q}\cdot\boldsymbol{a}}-1) \qquad (1)$$

when $V(\boldsymbol{r})$ is the impurity potential, $\boldsymbol{p}$ the difference in wave-vector of the two electron states, $\boldsymbol{\varepsilon}$ the polarization and $\boldsymbol{q}$ the wave-vector of a lattice wave, the displacement of which at the impurity is $\boldsymbol{\varepsilon}u$, and $\boldsymbol{a}$ the distance between the impurity and the nearest neighbor. The integration is broken into a number of cones, each with its appropriate direction of $\boldsymbol{a}$. This expression may be compared directly to that for elastic scattering by $V(\boldsymbol{r})$ according to the Born approximation, and yields

$$\delta\rho_i = Ae^2\rho_0 \qquad (2)$$

where $\delta\rho_i$ is the increase in the temperature-dependent part of the resistivity, ρ_0 the residual resistivity, e^2 the mean square thermal strain, and A a numerical constant which, on the present model, is about 10 to 20. Thus $\delta\rho_i \propto T^4$ at low temperatures, and varies as T at high temperatures.

Since e^2 is always small, $\delta\rho_i$ is always small compared to ρ_0, but is not small compared to ideal resistivity ρ_i, particularly at low tempera-