SOLID
STATE
PHYSICS

SUPPLEMENT 3

THEORY OF
LATTICE DYNAMICS
IN THE HARMONIC
APPROXIMATION

A. A. MARADUDIN

Westinghouse Electric Corporation
Pittsburgh, Pennsylvania

E. W. MONTROLL

International Business Machines Corporation
Yorktown Heights, New York

G. H. WEISS

Institute for Fluid Dynamics and Applied
Mathematics, University of Maryland
College Park, Maryland

Preface

In these days of the explosive expansion of physics, the era of excitement in a particular branch of research sometimes spans only a few years. It is remarkable that new discoveries are still being made and papers are still being written on a topic as old as lattice vibrations, the field which started modern solid state physics. We wish to celebrate its 50th anniversary, the anniversary of the basic papers of Debye (1) (1912) and Born and von Karman (1a) (1912), by issuing this status report.

Fifty years ago, twenty years ago, and even ten years ago one investigated detailed properties of lattice vibrations for the sole purpose of understanding the basis for the macroscopic behavior of crystals. It has only been in the past few years that experimental techniques have become powerful enough so that one can essentially live among the vibrating atoms and observe their detailed motions. Refinements in X-ray techniques and the introduction of slow neutron scattering facilities have been very fruitful in this direction. It also seems likely that the Môssbauer effect will provide an important tool for the investigations of lattice vibrations.

We begin our survey of the field with a discussion of the equations of motion of a crystalline lattice and their relation to elastic properties of the crystal. Then the frequency spectrum of perfect crystals is analyzed as well as its role in the determination of thermodynamic properties of the crystal. The effect of crystal imperfections and disorder is presented. Localized vibrational modes are one consequence of imperfections. Our story will end with an investigation of correlations in the motions of pairs of atoms, both instantaneous and time relaxed. The scattering of X-rays and neutrons by lattice vibrations is directly connected to these correlations.

The aspects of phonon physics most actively investigated currently involve the interaction of phonons with other degrees of freedom of a crystal; for example, electrons in both normal metals and superconductors, spin waves in magnetic materials, etc. Although neither these interaction problems nor the interaction of phonons through anharmonicities are discussed in this book, we trust that some of our

results can be applied to these problems. With this expansion of the field one can expect the application of the old subject of lattice vibrations to remain a topic for fruitful investigation for years to come.

We would like to acknowledge the helpful discussions we have had with Drs. P. A. Flinn, R. B. Potts, H. B. Rosenstock, and R. F. Wallis in connection with various topics treated in this article.

A. A. MARADUDIN

E. W. MONTROLL

G. H. WEISS

January, 1963

Contents

I. Introduction

At every temperature, at the absolute zero as a result of zero-point motion and at finite temperatures as a result of thermal fluctuations, the atoms in a crystalline solid execute small oscillations about their equilibrium positions. If the potential energy of the crystal is expanded in powers of the amplitudes of these small oscillations and all terms past those which are quadratic in the amplitudes are neglected, we have what is known as the harmonic approximation to the potential energy. This approximation is the basis for all of the discussion of the present article.

The influence of these lattice vibrations on the thermodynamic properties of solids (especially the heat capacity), and the relation between the macroscopic elastic properties of a crystal and the atomic force constants which, together with the masses of the constituent atoms, determine the scale of lattice vibrations at a given temperature, have been the subjects of considerable study. The results of such investigations have been summarized recently in the book by Born and Huang (2) and in review articles by deLaunay (3), Blackman (3a), and Leibfried (4).

The foregoing discussions can be described collectively as being concerned with the atomic basis of the vibrational contributions to *bulk* properties of crystals. In contrast, the present article is devoted largely to a discussion of the influence of lattice vibrations on the local behavior of individual atoms in a crystal and to the types of phenomena which are influenced by local motions, although we cannot avoid some discussion of bulk properties as well. The most direct measures of the localized motions of a given atom are its position and momentum distribution functions. Neighboring lattice defects might change the vibration of a given atom while lattice vibrations give rise to an interaction between defects and between defects and boundaries.

The width of lines or levels associated with various atomic, electronic, and nuclear processes in crystals depends on the localization of motion of atoms in the crystal. One of the simplest types of processes affected is the emission or absorption of a neutron by an atomic

1

nucleus. For example, a precise determination of the properties of nuclear resonance levels by the capture of slow neutrons in a crystal is made difficult by the fact that a Doppler broadening is induced by lattice vibrations. The extent of this broadening depends on the momentum distribution of atoms in the lattice (5).

Scattering or reflection of waves by a perfectly periodic lattice gives rise to a sharp interference pattern when the wavelength of the incident radiation is of the order of the lattice spacing. Random variations in separation distance between members of atomic pairs lead to more diffuse interference patterns and to the broadening of x-ray lines (6). Impurity levels and band edges of electrons in semiconductors could be expected to be broadened by thermal lattice motions.

The theory of the local character of lattice vibrations is somewhat more difficult than that of thermodynamic quantities since the latter depends only on average properties of the vibrations while the former seeks the vibrational properties of individual atoms or individual normal modes. This means that in order to give a review of the field we must be somewhat modest in our demands for quantitative results. We will try to present our main physical ideas largely through the analysis of special models of crystals which permit otherwise intractable calculations to be carried out in a straightforward manner. The qualitative generalization of our results to real crystals should be clear.

As in the discussion of bulk thermodynamic properties of solids we will find that the vibrational frequency spectrum and the dispersion relations between frequencies and wave vectors will play a central role in our analyses. It is presumed that the reader has some familiarity with the type of material which is discussed, for example, in the articles by deLaunay and Blackman. While it is our aim to avoid duplication of material covered in these reviews, we begin (Chapter II) with a brief review of the basic theory of lattice dynamics which will be utilized in the subsequent discussions in order to make the present article reasonably self-contained. We then proceed to a discussion of the theory of vibrational frequency spectra (Chapter III), and of methods for determining the bulk thermodynamic properties of solids which do not depend upon an explicit knowledge of the frequency spectrum (Chapter IV). In Chapter V a theory of the effects of defects and disorder on the vibrational properties of crystals is presented, and in Chapter VI we discuss the consequences of imposing realistic boundary conditions on the vibrational amplitudes of the atoms in a

crystal. Finally, in Chapter VII the theory of the scattering of x-rays and cold neutrons by lattice vibrations is presented from the point of view of what experiments can tell us about the atomic force constants and frequency spectra of solids, as well as what can be predicted about the neutron differential scattering cross sections on the basis of time-relaxed position correlation functions.

In all that follows we implicitly assume the separability of the electronic and nuclear motions [the adiabatic hypothesis (7)]. Strictly speaking, this assumption restricts us to nonmetallic crystals which are in their ground states; however, in view of the successes of the conventional theory of lattice dynamics when applied to metals, for which this hypothesis certainly breaks down (8), we can be reasonably confident in the qualitative correctness of our results even when applied to metals. Consideration of the effect of the electron-phonon interaction on the dynamics of metallic lattices falls outside the scope of the present article.

crystal. Finally, in Chapter VII the theory of the scattering of x-rays and cold neutrons by lattice vibrations is presented from the point of view of what experiments can tell us about the atomic force constants and frequency spectra of solids, as well as what can be predicted about the neutron differential scattering cross sections on the basis of time-relaxed position correlation functions.

In all that follows we implicitly assume the separability of the electronic and nuclear motions [the adiabatic hypothesis (7)]. Strictly speaking, this assumption restricts us to nonmetallic crystals which are in their ground states; however, in view of the successes of the conventional theory of lattice dynamics when applied to metals, for which this hypothesis certainly breaks down (8), we can be reasonably confident in the qualitative correctness of our results even when applied to metals. Consideration of the effect of the electron-phonon interaction on the dynamics of metallic lattices falls outside the scope of the present article.

II. Elements of the Theory of Lattice Dynamics

1. EQUATIONS OF MOTION OF A VIBRATING LATTICE

It is particularly convenient to begin a discussion of the elements of lattice dynamics with the assumption of an indefinitely extended crystal since the resulting perfect lattice periodicity introduced by the absence of bounding surfaces greatly simplifies the formulation of the theory. This assumption, however, leads to infinite values for extensive properties of the crystal. Their normalization to a finite volume by a suitable choice of boundary conditions is discussed in the following section.

We thus are led to consider a crystal composed of an infinite number of unit cells, each of which is a parallelepiped bounded by three non-coplanar vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. Each unit cell contains r atoms. We denote the equilibrium position vector of the lth unit cell relative to an origin located at some atom by

$$\mathbf{x}(l) = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \tag{2.1.1}$$

where l_1, l_2, l_3 are any three integers, positive, negative, or zero, which we will refer to collectively as l. The vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are called the primitive translation vectors of the lattice. The locations of the r atoms within the unit cell are given by the vectors $\mathbf{x}(\kappa)$, where κ distinguishes the different atoms in the unit cell and takes the values 0, 1, ..., r-1. For convenience we choose the origin of coordinates in such a way that $\mathbf{x}(\kappa = 0) = 0$. Thus, in general the position vector of the κth atom in the lth unit cell is given by

$$\mathbf{x}\binom{l}{\kappa} = \mathbf{x}(l) + \mathbf{x}(\kappa). \tag{2.1.2}$$

As a result of thermal fluctuations each atom is displaced from its equilibrium position by an amount $\mathbf{u}\binom{l}{\kappa}$. The total kinetic energy of the lattice becomes

$$T = \tfrac{1}{2}\sum_{l,\kappa,\alpha} M_\kappa \dot{u}_\alpha^2\binom{l}{\kappa} \tag{2.1.3}$$

5

where M_κ is the mass of the κth kind of atom, and $u_\alpha(^l_\kappa)$ is the α-Cartesian component of $\mathbf{u}(^l_\kappa)$, $\alpha = x, y, z$.

The total potential energy Φ of the crystal is assumed to be some function of the instantaneous positions of all atoms. If Φ is expanded in a Taylor's series in powers of the atomic displacements $\mathbf{u}(^l_\kappa)$, we obtain formally that

$$\Phi = \Phi_0 + \sum_{l,\kappa,\alpha} \Phi_\alpha(^l_\kappa) \, u_\alpha(^l_\kappa) + \frac{1}{2} \sum_{\substack{l,\kappa,\alpha \\ l',\kappa',\beta}} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) \, u_\alpha(^l_\kappa) \, u_\beta(^{l'}_{\kappa'}) + \dots \quad (2.1.4)$$

where, in keeping with the harmonic approximation, we neglect all higher order terms. Φ_0 is just the static (equilibrium) potential energy of the crystal, while clearly

$$\Phi_\alpha(^l_\kappa) = \frac{\partial \Phi}{\partial u_\alpha(^l_\kappa)}\Big)_0 \quad (2.1.5a)$$

$$\Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) = \frac{\partial^2 \Phi}{\partial u_\alpha(^l_\kappa) \, \partial u_\beta(^{l'}_{\kappa'})}\Big)_0 \quad (2.1.5b)$$

where the subscript 0 means that the derivatives are evaluated in the equilibrium configuration. From its definition, Eq. (2.1.5a), we see that the physical interpretation of the coefficient $\Phi_\alpha(^l_\kappa)$ is that it is the negative of the force acting in the α-direction on the atom at $\mathbf{x}(^l_\kappa)$ in the equilibrium configuration. However, in the equilibrium configuration the force on any particle must vanish, and so we have the result that in an equilibrium configuration

$$\Phi_\alpha(^l_\kappa) = 0. \quad (2.1.6)$$

The Hamiltonian for the crystal can thus be written in the harmonic approximation as

$$H = \Phi_0 + \frac{1}{2}\sum_{l\kappa\alpha} M_\kappa \, \dot{u}_\alpha^2(^l_\kappa) + \frac{1}{2}\sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta}} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) \, u_\alpha(^l_\kappa) \, u_\beta(^{l'}_{\kappa'}), \quad (2.1.7)$$

and the equations of motion of the lattice follow immediately:

$$M_\kappa \ddot{u}_\alpha(^l_\kappa) = - \frac{\partial \Phi}{\partial u_\alpha(^l_\kappa)} = - \sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) \, u_\beta(^{l'}_{\kappa'}). \quad (2.1.8)$$

The coefficient $\Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix})$ is the force exerted in the α-direction on the atom at $\mathbf{x}(\begin{smallmatrix}l\\ \kappa\end{smallmatrix})$ when the atom at $\mathbf{x}(\begin{smallmatrix}l'\\ \kappa'\end{smallmatrix})$ is displaced a unit distance in the β-direction. From Eq. (2.1.5b) we see that $\Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix})$ satisfies the symmetry condition

$$\Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix}) = \Phi_{\beta\alpha}(\begin{smallmatrix}l'\,l\\ \kappa'\kappa\end{smallmatrix}). \tag{2.1.9}$$

The periodicity of the lattice requires that if the lattice as a whole is translated relative to itself by a lattice vector $\mathbf{x}(l)$ it coincides with itself. This fact has the consequence that the same triplet of integers (l_1, l_2, l_3) can be added to the cell index l in the coefficient $\Phi_\alpha(\begin{smallmatrix}l\\ \kappa\end{smallmatrix})$, and to both of the cell indices in the coefficient $\Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix})$ without changing its value. Thus $\Phi_\alpha(\begin{smallmatrix}l\\ \kappa\end{smallmatrix})$ must be independent of l, while $\Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix})$ can only depend on the relative cell index $l-l'$ and not on l and l' separately. These results can be expressed as

$$\Phi_\alpha(\begin{smallmatrix}l\\ \kappa\end{smallmatrix}) = \Phi_\alpha(\begin{smallmatrix}0\\ \kappa\end{smallmatrix}); \qquad \Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix}) = \Phi_{\alpha\beta}(\begin{smallmatrix}l-l'\\ \kappa\ \kappa'\end{smallmatrix}). \tag{2.1.10}$$

There exist a number of useful relations among the atomic force constants $\Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix})$ which follow from the behavior of the potential energy and the force on an atom under rigid body translations and rotations.

We first set each of the displacement vectors $\mathbf{u}(\begin{smallmatrix}l\\ \kappa\end{smallmatrix})$ equal to an arbitrary constant vector $\mathbf{v}$ which is independent of l and κ. This corresponds to a rigid body translation of the crystal as a whole by the amount $\mathbf{v}$, and its potential energy cannot be changed by this displacement. However, formally, Eq. (2.1.4) becomes

$$\Phi = \Phi_0 + \sum_{l\kappa\alpha} \Phi_\alpha(\begin{smallmatrix}l\\ \kappa\end{smallmatrix}) v_\alpha + \tfrac{1}{2}\sum_{\substack{l\kappa\alpha\\ l'\kappa'\beta}} \Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix}) v_\alpha v_\beta + \cdots. \tag{2.1.11}$$

The apparent change in Φ described by the last two terms on the right-hand side of this equation must vanish. Since $\mathbf{v}$ is an arbitrary vector, we must equate to zero the coefficient of each power of v_α. In this way, we obtain the relations

$$\sum_{l\kappa} \Phi_\alpha(\begin{smallmatrix}l\\ \kappa\end{smallmatrix}) = 0$$

$$\sum_{\substack{l\kappa\\ l'\kappa'}} \Phi_{\alpha\beta}(\begin{smallmatrix}l\,l'\\ \kappa\kappa'\end{smallmatrix}) = 0.$$

In view of Eq. (2.1.10) we can write the first of these equations as

$$\sum_{\kappa} \Phi_{\alpha}(^{0}_{\kappa}) = 0, \tag{2.1.12a}$$

which expresses the fact that even if the initial configuration is not an equilibrium one so that the net force on each atom does not vanish, it must still be one in which the net force on a unit cell vanishes.

A more restrictive condition on the $\{\Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'})\}$ follows from the behavior of the force on each atom, $F_{\alpha}(^{l}_{\kappa})$, under a rigid body translation of the crystal. We have that

$$-F_{\alpha}(^{l}_{\kappa}) = \frac{\partial \Phi}{\partial u_{\alpha}(^{l}_{\kappa})} = \Phi_{\alpha}(^{l}_{\kappa}) + \sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) u_{\beta}(^{l'}_{\kappa'}) + \cdots. \tag{2.1.13}$$

If we replace each $u_{\alpha}(^{l}_{\kappa})$ by v_{α} we have merely displaced the lattice rigidly through the vector **v**, and this operation cannot change the value of the force on an atom in the initial configuration. We are thus led to the condition

$$\sum_{l'\kappa'} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) = 0 = \sum_{l'\kappa'} \Phi_{\alpha\beta}(^{0l'}_{\kappa\kappa'}). \tag{2.1.12b}$$

We now subject the lattice to a homogeneous deformation about the point $(^{l_0}_{\kappa_0})$ which is described by

$$u_{\alpha}(^{l}_{\kappa}) = \sum_{\beta} u_{\alpha\beta} x_{\beta}(^{ll_0}_{\kappa\kappa_0}) + \epsilon_{\alpha}(^{l}_{\kappa}) \tag{2.1.14}$$

where the $u_{\alpha\beta}$ are arbitrary constant parameters, and $\epsilon_{\alpha}(^{l}_{\kappa})$ is the displacement of the atom $(^{l}_{\kappa})$ from its new mean position in the deformed crystal. We have used the notation $\mathbf{x}(^{l}_{\kappa}) - \mathbf{x}(^{l_0}_{\kappa}) = \mathbf{x}(^{ll_0}_{\kappa\kappa_0})$. If Eq. (2.1.14) is substituted into Eq. (2.1.4) and the terms are collected in powers of $\epsilon_{\alpha}(^{l}_{\kappa})$ we find that

$$\Phi = \Phi_0 + \sum_{\substack{l\kappa\alpha \\ \lambda}} \Phi_{\alpha}(^{l}_{\kappa}) u_{\alpha\lambda} x_{\lambda}(^{ll_0}_{\kappa\kappa_0}) + \frac{1}{2} \sum_{\substack{l\kappa\alpha \\ l'\kappa'\beta \\ \lambda\mu}} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) u_{\alpha\lambda} u_{\beta\mu} x_{\lambda}(^{ll_0}_{\kappa\kappa_0}) x_{\mu}(^{l'l_0}_{\kappa'\kappa_0})$$

$$+ \sum_{l\kappa\alpha} \{ \Phi_{\alpha}(^{l}_{\kappa}) + \sum_{\substack{l'\kappa'\beta \\ \lambda}} \Phi_{\alpha\beta}(^{ll'}_{\kappa\kappa'}) u_{\beta\lambda} x_{\lambda}(^{l'l_0}_{\kappa'\kappa_0}) + \cdots \} \epsilon_{\alpha}(^{l}_{\kappa}) + \cdots.$$

Now, after such a deformation the lattice still remains a lattice. The terms independent of $\epsilon_{\alpha}(^{l}_{\kappa})$ respresent the static energy of the new

deformed lattice, the terms linear in the $\epsilon_\alpha(^l_\kappa)$ give the change in the potential energy of the new lattice due to arbitrary displacements of the atoms from their new mean positions, and so on. If all of the vectors $\epsilon(^l_\kappa)$ are set equal to an arbitrary vector $\mathbf{v}$, independent of l and κ, we are merely subjecting the deformed lattice to a rigid body translation for which the potential energy remains unchanged. Equating the coefficient of v_α to zero, we thus obtain the condition that

$$\sum_\kappa \{\Phi_\alpha(^0_\kappa) + \sum_{\substack{l'\kappa'\beta \\ \lambda}} \Phi_{\alpha\beta}(^{0l'}_{\kappa\kappa'}) u_{\beta\lambda} x_\lambda(^{l'l_0}_{\kappa'\kappa_0}) + \cdots\} = 0. \qquad (2.1.15)$$

In view of Eq. (2.1.12b) we can identify the point $(^{l_0}_{\kappa_0})$ with the point $(^0_\kappa)$ in the sum over $(^{l'}_{\kappa'})$ with no loss of generality. Then since the $u_{\alpha\beta}$ are arbitrary, the satisfaction of this equation requires that we set equal to zero the coefficient of every power of $u_{\alpha\beta}$. The new condition obtained in this way is

$$\sum_{l'\kappa'\kappa} \Phi_{\alpha\beta}(^{0l'}_{\kappa\kappa'}) x_\lambda(^{l'0}_{\kappa'\kappa}) = 0. \qquad (2.1.16)$$

It should be emphasized that Eq. (2.1.15) is not the equation of equilibrium for the deformed lattice, which would be obtained by differentiating Φ with respect to $\epsilon_\alpha(^l_\kappa)$ and equating the result, evaluated at $\epsilon_\alpha(^l_\kappa) = 0$, to zero. In the general case of a lattice which contains more than one atom per unit cell the homogeneously deformed configuration described by Eq. (2.1.14) will not be an equilibrium configuration, that is, forces would have to be applied to the atoms to maintain this configuration. These forces are given by $(\partial\Phi/\partial\epsilon_\alpha(^l_\kappa))_0$. Only in the special case that each atom is located at a center of symmetry can we equate these forces to zero. The relations among the force constants which result are given by Eqs. (2.1.16) with the sum over κ suppressed.

The last conditions on the atomic force constants we consider are those which are imposed on them by the transformation properties of the potential energy and its derivatives under an infinitesimal rigid body rotation of the crystal. Consider the displacements described by

$$u_\alpha(^l_\kappa) = \sum_\beta \omega_{\alpha\beta} x_\beta(^l_\kappa) \qquad (2.1.17)$$

where the parameters $\omega_{\alpha\beta}$ are the elements of an infinitesimal antisym-

metric matrix, $\omega_{\alpha\beta} = -\omega_{\beta\alpha}$. If we substitute Eq. (2.1.17) into Eq. (2.1.4) and retain only terms linear in the $\omega_{\alpha\beta}$, we obtain

$$\Phi = \Phi_0 + \sum_{\substack{l\kappa\alpha \\ \beta}} \Phi_\alpha(\tbinom{l}{\kappa}) \, \omega_{\alpha\beta} x_\beta(\tbinom{l}{\kappa})$$

The invariance of the potential energy against rigid body rotations of the crystal requires us to equate to zero the coefficient of $\omega_{\alpha\beta} = -\omega_{\beta\alpha}$, and we find

$$\sum_{l\kappa} \Phi_\alpha(\tbinom{l}{\kappa}) \, x_\beta(\tbinom{l}{\kappa}) = \sum_{l\kappa} \Phi_\beta(\tbinom{l}{\kappa}) \, x_\alpha(\tbinom{l}{\kappa}). \tag{2.1.18}$$

If we substitute Eq. (2.1.17) into Eq. (2.1.13), we obtain

$$-F_\alpha(\tbinom{l}{\kappa}) = \Phi_\alpha(\tbinom{l}{\kappa}) + \sum_{\substack{l'\kappa'\beta \\ \gamma}} \Phi_{\alpha\beta}(\tbinom{l\,l'}{\kappa\kappa'}) \, \omega_{\beta\gamma} x_\gamma(\tbinom{l'}{\kappa'}).$$

However, $F_\alpha(\tbinom{l}{\kappa})$ must transform as the α-component of a vector when the lattice is subjected to a rigid body rotation, that is,

$$F_\alpha(\tbinom{l}{\kappa}) = \sum_\beta (\delta_{\alpha\beta} + \omega_{\alpha\beta}) \, F_\beta(\tbinom{l}{\kappa}).$$

Comparing these two equations we are led to the relation

$$\sum_{\substack{l'\kappa'\beta \\ \gamma}} \Phi_{\alpha\beta}(\tbinom{l\,l'}{\kappa\kappa'}) \, \omega_{\beta\gamma} x_\gamma(\tbinom{l'}{\kappa'}) = \sum_\beta \omega_{\alpha\beta} \Phi_\beta(\tbinom{l}{\kappa}).$$

Equating the coefficients of $\omega_{\alpha\beta}$ on both sides of this equation, we find

$$\sum_{l'\kappa'} \{\Phi_{\alpha\beta}(\tbinom{l\,l'}{\kappa\kappa'}) x_\gamma(\tbinom{l'l}{\kappa'\kappa}) - \Phi_{\alpha\gamma}(\tbinom{l\,l'}{\kappa\kappa'}) x_\beta(\tbinom{l'l}{\kappa'\kappa})\} = \delta_{\alpha\beta}\Phi_\gamma(\tbinom{l}{\kappa}) - \delta_{\alpha\gamma}\Phi_\beta(\tbinom{l}{\kappa}) \tag{2.1.19}$$

where we have used Eq. (2.1.12b) to make the left-hand side of this equation independent of the choice of origin.

The restrictions on the number of distinct atomic force constants $\Phi_{\alpha\beta}(\tbinom{l\,l'}{\kappa\kappa'})$ which are imposed by lattice symmetry and structure are discussed in detail by Leibfried (4).

In the special case that the total potential energy is the sum of pairwise interactions between all the atoms in the lattice, each pair of atoms interacting through a potential function $\phi_{\kappa\kappa'}(r)$ which depends