

- BOULESTEIX, C., PARDO, B., CARO, P. E., GASGNIER, M. & HENRY LA BLANCHETAIS, C. (1971). *Acta Cryst.* B27, 216.
 CARO, P. E. (1968). *J. Less-Common Metals*, 16, 367.
 FOËX, M. & TRAVERSE, J. P. (1966). *Rev. Int. Hautes Temp. Réfract.* 3, 429.
 GLUSHKOVA, V. B. & BOGANOV, A. G. (1965). *Bull. Acad. Sci. URSS, Chem. Ser.* 7, 1101.
 ROTH, R. S. & SCHNEIDER, S. J. (1960). *J. Res. Nat. Bur. Stand.* A64, (4), 309.
 SCHIFFMACHER, G., MALÉ, G. & TROMBE, F. (1969). *Colloque International du C.N.R.S. sur les Eléments des Terres Rares*, Paris et Grenoble, Tome I, pp. 89–99.
 SHAFER, M. W. & ROY, R. (1959). *J. Amer. Ceram. Soc.* 42 (1), 563.
 WARSHAW, J. & ROY, R. (1961). *J. Phys. Chem.* 65, 2048.
 WEIGEL, F. & SCHERER, V. (1965). *Radiochim. Acta*, 4 (4), 197.

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The Relation between Phonon Frequencies and Interatomic Force Constants*

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A method involving Fourier series is given by which interatomic force constants can be systematically derived from measured phonon frequencies and eigenvectors. The resolution in wave-vector at which the measurements must be made is related to the range of the force constants. In agreement with recent work by Leigh, Szigeti & Tewary, it is concluded that when the eigenvectors are not known there is no unique solution for the force constants. This is illustrated by a simple numerical example.

Introduction

The frequency of any normal vibration mode of a crystal can be directly determined by neutron spectroscopy. Although in principle the eigenvectors (polarization properties) of the mode can, in certain circumstances, be determined from the neutron-scattering cross section, in practice only the phonon frequencies are usually known at the conclusion of an experiment. (The recent work of Harada, Axe & Shirane, 1971, provides an exception to this rule, however.) Recently, Leigh, Szigeti & Tewary (1971) have considered whether the interatomic force constants are uniquely determined when only frequencies are known. They showed that application of a unitary transformation to the force-constant matrix of the crystal may alter individual force constants completely, while leaving them physically acceptable in the sense of satisfying symmetry conditions *etc.* and leaving the frequencies of the normal modes unchanged. Thus, an infinite number of sets of force constants give the same frequencies, although each gives the modes distinct polarization properties. This lack of uniqueness, they argued, shows itself in that the number of 'essentially independent' frequencies n_ω is in general less than the number of force constants n_f to be determined. In this paper we consider the same problem using a different approach. Specifically, we wish to show that more insight is gained by considering the

dynamical matrix (in reciprocal space) and transformations thereof. Our conclusions are in general agreement with those of Leigh *et al.*

The Fourier series method

We begin by considering a monatomic one-dimensional crystal. This is not a completely unrealistic example, since planes of atoms in a monatomic crystal such as lead behave like individual masses of the linear chain for modes propagating in certain symmetry directions. The frequency $\omega(q)$ of a mode of wave-vector q is given by

$$m\omega^2(q) = 2 \sum_{p=1}^{\infty} f_p (1 - \cos pqa), \quad (1)$$

where f_p is the force constant between atoms separated by a distance pa ; therefore the force constants can be determined by Fourier analysis (Foreman & Lomer, 1957):

$$f_p = - \frac{ma}{\pi} \int_0^{\pi/a} \omega^2(q) \cos pqa \, dq. \quad (2)$$

There is no lack of uniqueness here because the eigenvector of each mode is fixed by symmetry to be a unit vector in the transverse or longitudinal direction – for definiteness we take f_p to refer to longitudinal modes. The form of equation (2) suggests that $\omega(q)$ has to be known as a continuous function before the force constants can be determined. If, however, it is known that $f_p = 0$ for $p > n$, equation (2) can be replaced by

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$$f_p = -\frac{m}{n} \sum_{j=0}^n \omega^2(q_j) \cos pq_j a, \quad (3)$$

where $q_j = \frac{\pi j}{na}$. Since $\omega^2(q)$ and $f(r)$ are related as Fourier

transforms, sampling of $\omega^2(q)$ at an interval $\frac{\pi}{na}$ in q corresponds to repetition of $f(r)$ with spacing $2na$ in r (e.g. Lipson & Cochran, 1966). This, however, causes no overlap of the centrosymmetric function $f(r)$ if $f(r) = 0$ beyond $r = na$, and equation (3) is an exact result. Thus, in this instance only n equally spaced frequencies need to be known to determine n force constants which are confined to a range $d = na$. Conversely, if for experimental reasons the frequency cannot be measured with higher resolution than π/d in q , but force constants extend to a distance $d' > d$ in r , equation (3) will give correctly the first $(2d-d')/a$ force constants; the remainder will in general be given incorrectly.

Next, we consider a diatomic linear chain of masses alternately m_1 and m_2 , each being at a centre of symmetry. It is then readily shown that the squares of the acoustic and optic mode frequencies, $\omega_a(q)$ and $\omega_b(q)$ respectively, are the eigenvalues of the dynamical matrix $\mathbf{D}(q)$ with corresponding eigenvectors $[e_a(1|q), e_a(2|q)]$ and $[e_b(1|q), e_b(2|q)]$. In terms of force constants,

$$\mathbf{D}(q) = \begin{pmatrix} D(11|q) & D(12|q) \\ D(12|q) & D(22|q) \end{pmatrix}, \quad (4)$$

where

$$D(11|q) = \frac{2}{m_1} \left\{ \sum_{p=1}^{\infty} f_p(11)(1 - \cos pqa) + \sum_{p=0}^{\infty} f_p(12) \right\}$$

$$D(22|q) = \frac{2}{m_2} \left\{ \sum_{p=1}^{\infty} f_p(22)(1 - \cos pqa) + \sum_{p=0}^{\infty} f_p(12) \right\}$$

and

$$D(12|q) = -\frac{2}{(m_1 m_2)^{\frac{1}{2}}} \sum_{p=0}^{\infty} f_p(12) \cos (p + \frac{1}{2})qa. \quad (5)$$

For example, $f_p(12)$ is the force constant between unlike atoms that are in unit cells separated by pa . Clearly, if $D(11|q)$, $D(22|q)$ and $D(12|q)$ are known at an interval π/d in q , the force constants can be uniquely determined by the Fourier series method already outlined, assuming they are confined to a range d . If only the eigenvalues $\omega_a^2(q)$ and $\omega_b^2(q)$ are known, however closely, there is no unique solution. We define the eigenvalue matrix $\omega^2(q)$ and the eigenvector matrix $\mathbf{e}(q)$ as follows:

$$\omega^2(q) = \begin{pmatrix} \omega_a^2(q) & 0 \\ 0 & \omega_b^2(q) \end{pmatrix} \quad (6)$$

$$\mathbf{e}(q) = \begin{pmatrix} e_a(1|q) & e_b(1|q) \\ e_a(2|q) & e_b(2|q) \end{pmatrix} = \begin{pmatrix} e(q) & -[1 - e^2(q)]^{\frac{1}{2}} \\ [1 - e^2(q)]^{\frac{1}{2}} & e(q) \end{pmatrix}. \quad (7)$$

Note that because of the orthogonality and orthonormality of the eigenvectors only one quantity $e(q)$ is required to specify them for each value of q . From the relation

$$\mathbf{e}(q)\omega^2(q) = \mathbf{D}(q)\mathbf{e}(q),$$

we then have

$$\mathbf{D}(q) = \mathbf{e}(q)\omega^2(q)\tilde{\mathbf{e}}(q). \quad (8)$$

This equation could be used to determine the elements of the dynamical matrix and hence the force constants when all three of $\omega_a^2(q)$, $\omega_b^2(q)$ and $e(q)$ had been determined experimentally for the appropriate values of q .

Symmetry considerations fix the values of $e(q)$ at $q = 0$ and π/a , namely

$$e^2(0) = \frac{m_1}{m_1 + m_2} \text{ and } e(\pi/a) = 1. \quad (9)$$

Let $e'(q)$ be any continuous function having $|e'(q)| \leq 1$ and which takes the values given by equation (9) at $q = 0$ and π/a . The corresponding matrix $\mathbf{e}'(q)$ [see equation (7)] gives a possible set of eigenvectors and the relation

$$\mathbf{D}'(q) = \mathbf{e}'(q)\omega^2(q)\tilde{\mathbf{e}}'(q) \quad (10)$$

defines a new dynamical matrix which for all values of q has precisely the same eigenvalues as has $\mathbf{D}(q)$. Fourier analysis of the elements of $\mathbf{D}'(q)$ gives the corresponding force constants which will generally have a different range from those corresponding to $\mathbf{D}(q)$. Note that if the range of force constants is $d = na$ there are $3n$ independent force constants (n each of type 11, 22, and 12) with $n_\omega = 2n$ frequencies and $n_e = n$ values of $e(q)$ required, so that

$$n_f = n_\omega + n_e. \quad (11)$$

Leigh *et al.* do not consider n_e but emphasize the fact that $n_f - n_\omega$ is of the same order of magnitude as n_f . Equation (11) also holds for the monatomic linear crystal considered earlier since then $n_e = 0$.

It is instructive to consider a numerical example, constructed so that Fourier analysis is required to give the force constants between unlike atoms only. Suppose the correct result is that there is only one nonzero force constant $f_0(12)$ (abbreviated f_0) so that only nearest neighbours interact. Then:

$$D(11|q) = \frac{2}{m_1} f_0, \quad D(22|q) = \frac{2}{m_2} f_0, \quad D(12|q) = -\frac{2}{(m_1 m_2)^{\frac{1}{2}}} f_0 \cos \frac{1}{2}qa. \quad (12)$$

Frequencies $\omega_a(q)$ and $\omega_b(q)$ were evaluated for $m_1 = 2$, $m_2 = 1$, $f_0 = 1$. A new set of force constants was now constructed by taking

$$D'(11|q) = \frac{2}{m_1} f_0 + \frac{2}{m_1} f'(1 - \cos 2qa)$$

$$D'(22|q) = \frac{2}{m_2} f_0 - \frac{2}{m_1} f'(1 - \cos 2qa). \quad (13)$$

This leaves $D'(11|q) + D'(22|q)$ equal to $D(11|q) + D(22|q)$ which is a necessary condition, and with $f' = \frac{1}{2}$ corresponds to the introduction of force constants $f'_2(11) = \frac{1}{2}$ and $f'_2(22) = -\frac{1}{4}$, comparable in magnitude with $f_0 = 1$. $D'(12|q)$ is then determined by the condition that the determinants of $\mathbf{D}'(q)$ and $\mathbf{D}(q)$ must be equal. It follows that

$$D'(12|q) = -\sqrt{2} \cos \frac{1}{2}qa (1 + 2\cos^2 qa \sin^2 \frac{1}{2}qa)^{\frac{1}{2}}. \quad (14)$$

This function was put in the form of equation (5) by numerical Fourier analysis; values of $f'_p(12)$ are shown in Table 1 and were not evaluated beyond $p=7$. The functions $e(q)$ and $e'(q)$ are compared in Fig. 1. The two sets of force constants given in Table 1 corresponded to the same frequencies. This was checked by recalculating the frequencies; they were unchanged within 0.01% except near $q=0$ in the acoustic branch where the difference was $\sim 1\%$, reflecting the sensitivity of the 'elastic region' to the very small force constants $f'_p(12)$ for $p > 7$. In fact, setting $f'_p(12)$ equal to zero for $p > 3$ gives frequencies which in practice would be regarded as agreeing with the original frequencies well within experimental error, except in the elastic region. It is interesting that although the force constants between like atoms have been drastically altered, the compensating change in force constants between unlike atoms is not greater than 6% of the original single force constant, but the range is considerably increased.

Table 1. Two sets of force constants which give the same frequencies for a diatomic one-dimensional crystal

p	$f_p(11)$	$f_p(22)$	$f_p(12)$	$f'_p(11)$	$f'_p(22)$	$f'_p(12)$
0	---	---	1	---	---	1.0571
1						-0.0511
2				$\frac{1}{2}$	$-\frac{1}{4}$	0.0490
3						-0.0507
4						-0.0060
5						0.0024
6						-0.0004
7						-0.0004

Practical implications

Essentially, the same considerations apply to a three-dimensional crystal. Leigh *et al.* (1971) have considered the example of germanium, using their method to generate alternative sets of force constants which are equivalent in the sense discussed above. Most recent work on the interpretation of the phonon dispersion curves of covalent and ionic crystals has attempted to take account of the polarizability of the atoms or ions, usually by means of the shell model. (For a review, see the article by Dick, 1965.) This raises additional problems of nonuniqueness of interpretation which are not considered here. In several studies of the lattice dynamics of metals, however, the dispersion curves have been fitted using force-constant models (see, for example, the investigation of nickel by Birgeneau, Cordes, Dolling & Woods, 1965). Therefore, we briefly

consider the problem of deriving force constants for a face-centered cubic structure such as nickel. First, we note that the eigenvectors could be determined experimentally by neutron spectroscopy without difficulty of principle in this instance. (Derivation of the eigenvectors from the measured cross section is by no means straightforward when the atoms are not on centers of symmetry; Cochran, 1968.) For a general value of \mathbf{q} , the eigenvectors are specified by three mutually perpendicular unit vectors $\mathbf{e}_a(\mathbf{q})$, $\mathbf{e}_b(\mathbf{q})$, $\mathbf{e}_c(\mathbf{q})$. The Cartesian components $e_a(x|\mathbf{q})$ *etc.* of $\mathbf{e}_a(\mathbf{q})$ are the elements of the first row of a unitary 3×3 matrix $\mathbf{e}(\mathbf{w})$. Thus, in general three numbers must be known to specify the eigenvector matrix. This number is reduced by symmetry when \mathbf{q} lies in various special directions. For example, when \mathbf{q} is in the [100] direction $\mathbf{e}(\mathbf{q})$ reduces to an identity matrix. A qualitative measurement of the neutron-scattering cross section is, however, still necessary in that one must be able to say which frequency corresponds to the longitudinal mode and which corresponds to the (doubly-degenerate) transverse mode. Equation (8) now applies (with q replaced by \mathbf{q}) and the force constant $f_{xy}(0l)$ (between an atom at the origin and that in the l th unit cell) can be determined as a coefficient of the three-dimensional Fourier series for $D(xy|\mathbf{q})$. The interval in \mathbf{q} at which $\omega_a(\mathbf{q})$, $e_a(x|\mathbf{q})$ *etc.* must be determined depends on the range of the force constants. Suppose all nonzero force constants $f_{xy}(0l)$ *etc.* can be inscribed in a regular solid (such as a cube, parallelepiped, truncated octahedron, *etc.*) drawn about the origin and containing N crystallographic unit cells. Repetition of this regular solid produces no overlapping of the force constants. Its repetition to fill all space defines a superlattice whose unit cell is the regular solid. The lattice reciprocal to this superlattice defines the reciprocal sublattice of points \mathbf{q}_j for which the frequencies and eigenvectors are to be determined. N points of the reciprocal sublattice are in the unit cell of the crystallographic reciprocal lattice, that is in the Brillouin zone. Therefore, we have

$$f_{xy}(0l) = -\frac{m}{N} \sum_{j=1}^N D(xy|\mathbf{q}) \cos \mathbf{q}_j \cdot \mathbf{l} \quad (15)$$

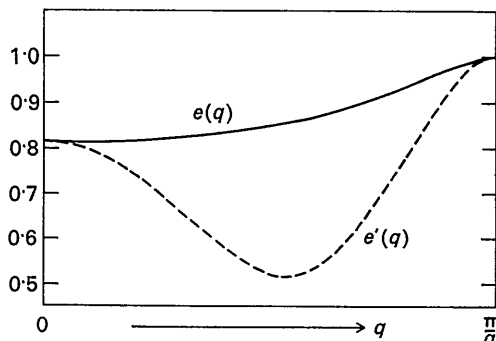


Fig. 1. The functions $e(q)$ and $e'(q)$ for the two different sets of force constants given in Table 1.

where \mathbf{l} is the lattice translation between atoms labelled 0 and l . In this instance, there are in general six force constants between an atom pair. For each general value of \mathbf{q}_j there are three frequencies and three quantities required to specify the eigenvectors. Thus, the relation $n_f = n_\omega + n_e$ is again satisfied, in the sense implied by this discussion. Of course, not all $6N$ force constants are independent; the number of independent force constants is reduced by symmetry to $\frac{1}{48}$ of the total, at least when the range is large, which was noted by Leigh *et al.* (1971). However, approximately the same factor applies to n_ω and to n_e .

By analogy with the one-dimensional example which we considered in more detail above, it is clear that when the eigenvectors have not been determined, no solution can be unique. In the absence of other physical information, any unitary matrix $\mathbf{e}'(\mathbf{q})$ which satisfies the symmetry conditions (and there are no conditions for a general value of \mathbf{q}) is acceptable, subject to considerations of continuity. While it seems improbable in practice that there will ever be an equivalent set of force constants having a shorter range than the

correct set, there must always be an infinite number of equivalent sets of greater range.

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References

- BIRGENEAU, R. J., CORDES, J., DOLLING, & WOODS, A. D. B. (1965). *Phys. Rev.* **136A**, 1359.
 COCHRAN, W. (1968). *Neutron Inelastic Scattering*. Vol. I, p. 275. Vienna: International Atomic Energy Agency.
 DICK, B. G. (1965). *Lattice Dynamics*, p. 159. Oxford: Pergamon Press.
 FOREMAN, A. J. E. & LOMER, W. M. (1957). *Proc. Phys. Soc. London*, **B70**, 1143.
 HARADA, J., AXE, J. D. & SHIRANE, G. (1971). *Acta Cryst.* **A26**, 608.
 LEIGH, R. S., SZIGETI, B. & TEWARY, V. K. (1971). *Proc. Roy. Soc.* **A320**, 505.
 LIPSON, H. S. & COCHRAN, W. (1966). *The Determination of Crystal Structures*. London: Bell.

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The Streaking of X-ray Diffraction Spots in Platelet-Shaped Polytypic Crystals

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The c -axis oscillation X-ray diffraction photographs of platelet-shaped polytypic crystals exhibit 10. l , 20. l , etc. rows which are sharply divided into two zones, one having streaked diffraction spots and the other having sharp spots. Evidence and arguments have been advanced to show that this behaviour is due to shape-effect on the diffraction, and the observed streaking is not representative of any real disorder in the stacking of the layers in the crystal.

Introduction

The streaking of X-ray diffraction spots in the case of polytypic crystals has special significance since it directly indicates the disorder, in the stacking of close-packed layers, in the polytype. The polytypic crystals have trigonal lattices, the close-packed layers being stacked along the c axis; often, the stacking is not ordered and thus a streaking along c^* reciprocal-lattice rows, characteristic of stacking disorder, is observed in the disordered crystals. All the spots in the 10. l , 20. l , etc. rows of the disordered crystals are connected through streaks, and the amount of streaking is directly related to the amount of disorder, *i.e.* the greater the disorder the more pronounced the streaking. Many polytypic crystals, however, exhibit a curious type of disorder in which 10. l and other similar rows consist of two parts; one part comprises reflexions that show

streaking indicative of disorder; the other part is perfectly sharp, as observed in crystals exhibiting no disorder. It is the purpose of this paper to point out that the existence of partly streaked and partly unstreaked reciprocal-lattice rows is due to shape-effect and does not represent any lattice disorder that results from random arrangement of stacked layers in the polytype.

c -axis oscillation photographs of cadmium iodide polytype

The polytypic crystals, like SiC, CdI₂, ZnS, PbI₂ etc. grow in the shape of platelets with flat faces parallel to the (0001) plane and often have hexagonal shapes. The lateral extent of the platelets is a few millimetres while the thickness of the crystals ranges from 10 to 100 μ . Since the various polytypic modifications of a polytypic substance differ in the number and arrange-