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Inelastic Scattering in Neutron Diffraction and Structure Studies by Neutron Diffraction

Interatomic Forces in Crystals from Neutron Scattering*

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The problem is discussed of determining the interatomic force constants in crystals from measurements of lattice vibrations by means of neutron inelastic scattering. For all except the simplest crystals it is necessary to determine the polarization vectors of the vibrations as well as their frequencies. In principle this can be done by measurement of the intensities as well as the energies of the one-phonon neutron groups. Such measurements seem to be feasible with the new "constant momentum transfer" method. A brief review (without figures) is given of the Chalk River work on the crystal dynamics of metals, alkali halides and semiconductors.

The paper discusses the problem of determining the forces between atoms in crystals from measurements of neutron inelastic scattering, through use of the Born-von Kármán theory of crystal dynamics[1]. In this theory the atomic motions are described in terms of normal modes characterized by a wave vector $\boldsymbol{q}$, a frequency $\nu_j(\boldsymbol{q})$ and a set of polarization vectors $\xi(K,j;\boldsymbol{q})$. If there are n atoms (denoted by the index K) per primitive unit cell then to each wave vector $\boldsymbol{q}$ there correspond $3n$ different frequencies and polarization vectors, indicated by the label j which runs from 1 to $3n$. If there are N unit cells in the crystal (denoted by an index L) the wave vector $\boldsymbol{q}$ takes on the N values within the first Brillouin zone. However $\boldsymbol{q}$ can be defined in any zone: the lattice vibrations for wave vector $\boldsymbol{q}$ are identical with those for $(\boldsymbol{q}-2\pi\boldsymbol{\tau})$ where $\boldsymbol{\tau}$ is any reciprocal lattice vector.

The frequencies and polarization vectors are related to the interatomic force constants through a set of equations:

$$4\pi^2\nu_j^2(\boldsymbol{q})\xi_\alpha(K,j;\boldsymbol{q}) = \sum_{\beta=1}^{3}\sum_{K'=1}^{n}\xi_\beta(K',j;\boldsymbol{q})D_{\alpha\beta}(K,K';\boldsymbol{q}) \qquad (1)$$

$$D_{\alpha\beta}(K,K';\boldsymbol{q}) = (M_K M_{K'})^{-\frac{1}{2}}\sum_{L-L'=0}^{N} \times\Phi_{\alpha\beta}(K,K';\boldsymbol{R}_{LL'})\exp(-i\boldsymbol{q}\cdot\boldsymbol{R}_{LL'}) \qquad (1a)$$

The ξ_α, ξ_β are spatial components of the polarization vector for atom K and mode j. In general they are complex and obey certain orthonormality relations (ref. 1 p. 298). The indices α, β denote any of three selected mutually perpendicular coordinate directions. $\Phi_{\alpha\beta}(K,K';\boldsymbol{R}_{LL'})$ gives the force exerted in the direction α on atom K in the Lth unit cell when atom K' in the L'th unit cell is moved a unit distance away from its equilibrium position in the direction β. It is these force constants in which we are interested.

The condition for solubility of the set of $3n$ linear equations [Eqs. (1)] in the ξ's is that the secular determinant of the coefficients of the ξ's should vanish. The frequencies are found by solving the algebraic equation (of order $3n$ in $M\nu^2$ and in the force constants) which is obtained by expanding the determinant. Since the set of non-linear equations for different frequencies has many solutions it is not possible in general to solve for the force constants, if only values of the frequencies are known[2),3)]

If the point in reciprocal space has sufficiently high symmetry, however, the ξ's may be fixed by symmetry and then Eqs. (1) reduce to *linear* equations involving only $M\nu^2$ and the Φ's. It is necessary that the measured frequency involved be completely identified, i.e. as to $(j, \boldsymbol{q})$, in order to be sure that it is assigned the correct equation.

This method is limited to crystals of simple structure and high symmetry. Even in such crystals the number of independent frequencies which can be treated is small, and hence

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the method is also limited to crystals in which the force system is simple and can be described by a small number of parameters.

As often discussed before[3)-6)] the frequencies can be determined simply from measurements of the *positions* of neutron groups in the energy distributions of the neutrons scattered by a single crystal in the one-phonon process. Intensity measurements are not required except for identification purposes[3)]. The frequency and wave vector of a lattice vibration are related to the incoming and outgoing neutron energies (E_0 and E') and wave vectors ($\boldsymbol{k}_0$ and $\boldsymbol{k}'$) corresponding to the group, through the conservation equations

$$|E_0-E'|=h\nu$$
$$\boldsymbol{Q}\equiv\boldsymbol{k}_0-\boldsymbol{k}'=2\pi\boldsymbol{\tau}-\boldsymbol{q}. \qquad (2)$$

In the conventional methods the crystal is set at some angle ψ with respect to $\boldsymbol{k}_0$ and the scattered neutrons observed at some angle of scattering ϕ. Then the frequency and wave vector corresponding to an observed group are found from Eqs. (2). The values of ν and $\boldsymbol{q}$ so found may not be of interest in a particular problem; in the conventional methods there is no way of preselecting $\boldsymbol{q}$, except where considerable knowledge of the dispersion relation already exists, i.e. in the 'method of successive approximations'[3)].

In the conventional method the intensities of the neutron groups depend not only on the frequency at the particular $\boldsymbol{q}$ involved but also on the behaviour of the dispersion relation in the vicinity of that $\boldsymbol{q}$, to first order on grad $\boldsymbol{q}(\nu)$[7)]. Thus it is difficult to obtain accurate intensities with the conventional methods.

With crystal spectrometers it is possible to use a method of constant momentum transfer or 'constant $\boldsymbol{Q}$ method'[6)]. Here the angles ϕ and ψ are varied simultaneously and non-linearly in step with the analyzing spectrometer setting, that is with E' and $|\boldsymbol{k}'|$, in such a way that $\boldsymbol{Q}$ is kept constant. Thus measurements are made at the desired position in reciprocal space.

In the constant $\boldsymbol{Q}$ method the integrated intensity of a group depends to first order only on the value of the frequency at the particular $\boldsymbol{Q}$, and not on the gradient of the frequency, as in the conventional method, so intensities are easily measurable. In practice we usually keep the analyzer setting (E' and $|\boldsymbol{k}'|$) fixed and change the spectrometer setting for the incoming neutrons (E_0 and $|\boldsymbol{k}_0|$). Thus no corrections for analyzer sensitivity are required and exceptionally accurate values for the intensities should be obtained.

It was remarked earlier that force constants can be obtained from measurements of the frequencies alone only for highly symmetric crystals with simple structure and simple force systems, since only for such crystals will sufficient 'linear' information be available. Thus an extensive series of measurements on lead[8)] demonstrated the existence of long range forces in the metal, but did not provide enough independent pieces of information to permit solution for the Born-von Kármán force constants. More recent experiments on lead[9)] have indicated the existence of an effect predicted by Kohn[10)], which implies that the forces have a substantially infinite range. [For sodium metal[11)] on the other hand there is hope that the forces are sufficiently simple that the force constant analysis can be carried out.]

Studies of both germanium[3)] and the alkali halides (NaI and KBr)[12)] have encountered similar difficulties. In both systems it has been found necessary to compare the experimental results with calculations based on models in order to attempt to draw quantitative conclusions. For germanium the force constant analysis[3,13)] gave only the result that the forces were of long range. Calculations by Cochran[14)] on a specific model (the shell model) made plausible the suggestion of Lax[15)] that the long range forces arise from the mutual polarizabilities of the ions, which are known to be important from the far-infra-red absorption[3)]. For the alkali halides the shell model gave good initial results[12)], but discrepancies still exist which are proving difficult to eliminate by including additional forces in the model.

To apply the force constant analysis to any except the simplest crystals, it appears to be necessary to carry out a kind of generalized crystallography. From measurements of the intensities of the neutron groups produced at different points $\boldsymbol{Q}$ in reciprocal space by interaction with a particular phonon $(j\,;\boldsymbol{q})$, it should be possible to deduce the polarization vectors $\boldsymbol{\xi}(K, j\,;\, q)$. (It is possible for certain simple cases we have looked at.) The measured components of $\boldsymbol{\xi}$ and the corresponding measured frequencies are then inserted into Eqs. (1). Each component (and frequency) gives an equation which is linear in the force constants.

The differential cross section for production of a neutron group at $\boldsymbol{Q}$ with creation or annihilation of one phonon, in the constant $\boldsymbol{Q}$ method, is given by the equation

$$\sigma_j(\boldsymbol{k}_0\rightarrow\boldsymbol{k}')=\frac{k'}{k_0}\frac{\hbar}{4\pi}\left\{\begin{matrix} N_j(\boldsymbol{q}) \\ N_j(\boldsymbol{q})+1\end{matrix}\right\}|g_j(\boldsymbol{q}, \tau)|^2 \quad (3)$$

$$g_j(\boldsymbol{q}, \tau)=\sum_K\frac{b_K\boldsymbol{Q}\cdot\xi\exp\left[-W_K(\boldsymbol{Q})\right]}{(M_K\nu)^{\frac{1}{2}}}\exp\left(i\boldsymbol{Q}\right)\cdot\boldsymbol{R}_K) \quad (3a)$$

where $\boldsymbol{R}_K$ is the position, M_K is the mass, and b_K is the scattering length of the Kth atom in the unit cell, $\exp(-W_K)$ is the Debye-Waller factor, and $N_j=[\exp h\nu/k_BT)-1]^{-1}$ is the population factor in an energy gain experiment. In an energy loss experiment the factor N_j+1 is used.

If the atoms are at *special positions* in the unit cell and $\boldsymbol{q}$ is in a symmetry direction, then except for the factor $\exp(-W_K)$ and the easily removed factor $\boldsymbol{Q}$, the inelastic structure factor g repeats over a certain unit in reciprocal space[3]. This unit resembles the 'large zone' sometimes employed[16] in discussing electronic bands in crystals, but may not be identical with it.

The procedure to determine the polarization vectors is as follows: For a given $\boldsymbol{q}$ the energy distributions are studied at as many values of $\boldsymbol{Q}$ as are available. Note, however, that independent information will often be obtained principally for $\boldsymbol{Q}$-points within the unit discussed above, except for information about the Debye-Waller factor. Since orthonormality relations exist for the different branches j at a particular $\boldsymbol{q}$ it is probably advisable to study them together. For a particular $(j\,;\,\boldsymbol{q})$ the polarization vectors are determined from the intensities by procedures similar to those used in determination of an antiferromagnetic structure in neutron diffraction, except that the polarization vectors may be complex. A phase problem is often involved.

A group at Chalk River consisting of L. N. Becka, K. R. Rao and the author are attempting to carry out this procedure on germanium, using the constant $\boldsymbol{Q}$ method with fixed analyzer. In this method the factor k'/k_0 in Eq. (3) is automatically eliminated by use of a $(1/v)$ detector as monitor of the incoming neutrons. Preliminary intensity measurements show internal inconsistencies of $\sim 10\%$, whereas an accuracy of better than 5% is probably necessary for the program to be carried out. We have hopes of obtaining this accuracy in the near future.

Finally, a brief discussion should be given of the use of neutron scattering to study the anharmonic forces in crystals. These forces cause a shift and broadening of the lines, particularly at high temperatures. The effects have been observed previously for the optical mode by infra-red measurements, and within the last few years have been studied by neutron inelastic scattering in alumium[17], lead[8], potassium bromide[12], and sodium[11].

The shift with temperature in the mean position of the lines is usually small, of the order of a few percent, and varies considerably from mode to mode. Indeed, a few frequencies (in lead) have been observed actually to increase with increasing temperature.

The broadening of the lines is very marked. Indeed, near the melting point it appears that the lifetimes of some of the phonons, as indicated by the energy widths of the neutron groups through the uncertainty principle, are shorter than the vibrational periods of the phonons.

It is not easy to get accurate energy widths from the measured neutron groups, because a large temperature-dependent background must be subtracted. Since the broadened lines themselves have large 'wings,' this is difficult to do with any accuracy. In the Chalk River work[8),11),12] the assumption has been made that the intensity of the broadened groups are given by the conventional expression for unbroadened groups, and thus that the integrated intensity can be computed from low temperature measurements on the same mode. This assumption permits a background to be assigned.

The theoretical basis for interpretation of the measurements is not well developed. Discussions of line widths have been given by Elliott and Stern[18] and, more formally, by Van Hove[19], and by Baym[20]. However, no adequate frame in which experimental results can be discussed yet exists for anharmonic crystal dynamics (cf. the Born theory of harmonic crystal dynamics). A useful approach can be made by including in the equations of motion of the atoms for the Born theory, dissipative forces between atoms proportional to the differences in their velocities[8]. For symmetry directions the observed widths can then be discussed in terms of dissipative force constants similar to the restoring force constants of the Born theory.

The conference paper was illustrated with slides drawn from the references. Due to circumstances beyond my control the paper was actually delivered by Dr. A.D.B. Woods. This was fitting since in much of the work discussed Dr. Woods was a leading spirit. Many other people contributed to the work; to all of them my thanks are due.

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DISCUSSION

H. PALEVSKY: How do you separate the effects of multiphonon interactions from the broadening due to damping of single phonons?

A. D. B. WOODS: We do not calculate multiple phonon scattering directly but draw in the background on the assumption (which may not be a good one) that, when known temperature dependent factors are removed, the integrated intensities must be the same at all temperatures.

H. PALEVSKY: What I am really after is what is the shape of the background you finally subtract; is it monotonic or does it have a shape?

A. D. B. WOODS: We do not know if the multiphonon scattering has any structure under the peak but if it does have a hump under the peak then the measured widths must be even larger than reported here.

P. P. EWALD: Can the broadening of the phonon with increasing temperature shown in the last slide be correlated to the temperature dependence of the thermal conductivity?

A. D. B. WOODS: There is undoubtedly a connection but we have not attempted to make any correlation between these widths and mean free paths from thermal conductivity.

R. D. LOWDE: I think it would be interesting to bring out the particular features of the "constant Q" method in the matter of intensity calculations, where it offers a special advantage.

A. D. B. WOODS: In the standard method of taking energy distributions the expression for the integrated intensity of the neutron group corresponding to a phonon contains a factor $1/|J|$ which takes into account the fact that q is changing. (see references 3, 5 and 7). This factor $1/|J|$ depends on the gradient of the dispersion curve at each q—a term which we just do not know much about, particularly in off symmetry directions. When the experiment is done at constant Q the factor $1/|J|=1$, and thus a very serious complication in the intensity analysis is removed.

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Lattice Dynamics of the Ammonium Halides

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The cold neutron scattering technique has been applied to the study of the ammonium halides. The hindered rotation and "optical" vibrations are observed as single quantum transitions in contrast to the conbination lines observed in optical measurements. In the high temperature phase (I) of NH_4I the motion of the ammonium ion may be described as a super position of a large amplitude hindered rotation and optical vibration.

The understanding of the nature of the phase transitions in the ammonium halides is a very old problem in chemical physics. As long ago as 1930, Pauling[1] suggested that the transition in NH_4Cl at −30°C could be explained by the motion of the NH_4^+ ions (in the field of the Cl^- ions) changing from a hindered to a free rotation. Frenkel[2] was the first to put forth the alternative scheme of an order-disorder transition of the equilibrium positions of the NH_4^+ ion relative to the chlorine lattice. Specific heat[3] and infra-red[4] measurements established that the transition from phase III to phase II in the NH_4 halides are of the order-disorder nature. Recent infra-red[5] and neutron diffraction[6] studies of the transition from phase II to phase I have again raised the possibility that in the high temperature phase I the ammonium ion can freely rotate in the halogen lattice.

The study of the motion of atoms in condensed matter by the scattering of cold neutrons has been utilized in the past to determine the phonon dispersion relations in solids[7),8)] and correlated motions of liquid molecules[9),10)]. When a cold neutron is scattered by a typical solid, the energy of single "phonon" or quantum of lattice vibration energy is usually gained by the neutron and the resulting change in energy and momentum of the neutron allows determination of the same quantities for the absorbed phonon[9)]. Since the interaction of the neutron and the atom (nucleus) is a point interaction the selection rules governing the types of motions which may be observed are much less restrictive than the selection rules governing the optical (infra-red and Raman) experiments. In principle, the neutron measurements can sample all the motions whereas the optical measurements are restricted to those associated with some dipolar distribtion