Crystal Dynamics and Inelastic Scattering of Neutrons

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A general discussion is given for the angular and energy distribution of neutrons inelastically scattered by a crystal, with special emphasis on those features of the distribution in which the dynamical properties of the crystal manifest themselves most immediately. The direct relationship between the energy changes in scattering and the dispersion law of the crystal vibrations is analyzed. While for x-rays, due to the extremely small relative size of these energy changes, the dispersion law has to be inferred indirectly from intensity measurements, it is shown that the very much larger relative magnitude of energy transfers in the case of slow neutrons opens the possibility of direct determination of the frequency-wave vector relationship and the frequency-distribution function of the crystal vibrations by energy measurements on scattered neutrons. The general properties of the outgoing neutron distribution in momentum space which are relevant for this purpose are derived by first considering the particularly instructive limiting case of neutrons initially at rest and subsequently generalizing the results to incident neutrons of arbitrary energy.

I. INTRODUCTION

THE diffraction of neutrons by crystals has been in recent years the object of an increasing number of investigations and has been recognized as a promising tool for crystallographic research.[1] Considerable work has been done on elastic scattering, the coherent part of which exhibits Bragg reflections in full analogy with x-rays, and on transmission measurements, dealing with total cross sections. The influence of crystal dynamics on neutron scattering was discussed by various authors[2–14a] and quantitative calculations of total cross sections were carried out on the basis of a greatly simplified model for the crystal elastic vibrations, the familiar Debye model, in which the velocity of sound waves (phonons) is assumed independent of wavelength, direction, and polarization.

From its success in describing specific heats, the Debye model is known to be a fair approximation for effects which involve the average of a smooth function over all crystal vibrations. It gives, therefore, at least for cubic crystals, a reliable estimate of the Debye-Waller factor affecting Bragg reflections of neutrons and x-rays and can be expected to provide a good orientation as to the magnitude and energy dependence of total inelastic neutron cross sections for the incoherent[15] part of the scattering. For other effects, however, in particular for the angular and energy distribution of inelastically scattered neutrons, the details of the vibration spectrum play a much more important role and the theoretical discussion has to take them into account. It is the aim of the present investigation to show how they manifest themselves in this distribution.

The analogous problem for the inelastic scattering of x-rays has been the object of detailed theoretical and experimental study[16–23] with the purpose of determining from scattering data the actual vibrational spectrum of the crystal, i.e., the exact relation $\omega=\omega_j(\mathbf{q})$ between frequency ω, wave vector $\mathbf{q}$, and polarization j of a plane wave vibration (phonon). This function manifests itself directly in the wavelength shift of x-rays scattered by one-phonon processes. Because of its extremely small relative size, however, this shift is not readily accessible to measurement, and hence the function $\omega_j(\mathbf{q})$ has to be inferred from measurements of the scattered intensity.

Because of the different relation between energy and momentum the energy balance is entirely altered in the case of slow neutrons. While this is generally true, it may be exemplified more concretely by considering the important particular case of coherent one-phonon processes. For an incident wavelength of the order of the lattice constant the absolute energy changes in a

[1] For surveys see: J. M. Cassels, Progr. Nuclear Phys. **1**, 185 (1950); D. J. Hughes, *Pile Neutron Research* (Addison-Wesley Publishing Company, Cambridge, 1953); G. E. Bacon and K. Lonsdale, Repts. Progr. in Phys. **16**, 1 (1953).
[2] G. C. Wick, Physik. Z. **38**, 403, 689 (1937).
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[12] P. O. Fröman, Arkiv. Fysik **4**, 191 (1951); **5**, 53 (1952).
[13] G. Placzek, Phys. Rev. **86**, 377 (1952).
[14] G. L. Squires, Proc. Roy. Soc. (London) **A212**, 192 (1952).
[14a] G. Placzek, Phys. Rev. **93**, 897 (1954).

[15] Using the same terminology as Hughes, reference 1, we call coherent the interferent part of the slow neutron scattering, and incoherent the noninterferent part due to spin and isotope disorder. The existence of these two types of scattering has been discussed first by Wick (reference 2). Both types comprise elastic as well as inelastic processes.
[16] J. Laval, Bull. soc. franç. minéral. **64**, 1 (1941).
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[20] P. Olmer, Acta Cryst. **1**, 57 (1948); Bull. soc. franç. minéral. **71**, 144 (1948).
[21] H. Curien, thèse, Paris, 1952; Acta Cryst. **5**, 393 (1952).
[22] H. Cole and B. E. Warren, J. Appl. Phys. **23**, 335 (1952).
[23] H. Cole, J. Appl. Phys. **24**, 482 (1953).

general direction are, for neutrons, not radically different from those for x-rays, being in both cases of the order of average phonon energies. For neutrons, however, the energy corresponding to such an incident wavelength is of the same order of magnitude and the relative change in energy or wavelength is therefore of order one, which considerably reduces the difficulty of its direct measurement.

As the incident wavelength increases, the contrast between the x-ray and neutron cases becomes even more pronounced. For x-rays, in the case of a Bravais lattice, the absolute energy change in a given scattering direction becomes proportional to the incident energy, with a relative change of the order of the ratio of sound velocity to light velocity. For neutrons, on the other hand, the absolute energy changes in a given scattering direction do not systematically decrease with increasing incident wavelength; in fact, they ultimately become independent of it, tending to finite values. Thus, a limiting case is approached for which the incident energy and momentum can be put equal to zero both in the conservation laws which determine the energy shift, and in the transition probabilities. Physically, this is the case of a neutron initially at rest which takes up energy and momentum by absorbing a phonon. For finite incident wavelength this description will be adequate if the outgoing wavelength is small compared to the incoming one. Under this condition the transition probability is approximately constant, and hence the scattering cross section becomes proportional to the wavelength. The actual wavelength beyond which the condition is satisfied depends on the scattering direction and on crystal structure, but it often lies in the accessible region of the subthermal neutron spectrum in which transmission experiments are already quite common. Scattering experiments in this region[24] still present a certain intensity problem and may be easier at somewhat shorter wavelengths, which, as we shall see, have to be used anyhow if one wishes to determine the function $\omega_j(\mathbf{q})$ for all $\mathbf{q}$.

In the above remarks we have been concerned with coherent one-phonon scattering only. The energy distribution of neutrons incoherently scattered by one-phonon processes is also of considerable interest in connection with crystal dynamics, especially for cubic crystals, for which, as will be shown later, it is directly connected with the frequency-distribution function of the crystal. For multiphonon processes, coherent as well as incoherent, the relation between neutron scattering and dynamical properties of the crystal is much more complicated, except for the limiting of high incident energies.[13] For the purpose of the determination of the frequency spectrum of the crystal from scattering data these processes are therefore of less interest, and for this reason we shall concentrate on one-phonon processes.

One has, however, to inquire under what conditions one-phonon scattering can be experimentally separated from multiphonon processes. For a single crystal, one-phonon coherent scattering is distinguishable from all other processes by its energy distribution in each outgoing direction, which will be seen to comprise a finite number of discrete energy values, appearing as sharp peaks above the continuous background of one-phonon incoherent and multiphonon scattering. No such direct distinction is possible between neutrons scattered in one-phonon incoherent and multiphonon processes. While the contribution of the latter to the cross section is always decisive at high incident energies and often appreciable even in the limiting case of zero incident energy,[25] it would, however, seem quite feasible to carry out scattering experiments under conditions (moderately low temperature and incident energy and high nuclear mass) which make multiphonon effects either entirely negligible or reduce them to the size of a manageable correction, thus allowing the isolation of the incoherent one-phonon processes.

In the following sections, we discuss the angular and energy distribution of neutrons scattered by one-phonon processes, both coherent and incoherent. Sections II and III deal with the limiting case of infinite incident wavelength. Apart from its direct interest, this case illustrates with particular clarity the essential aspects of the problem. The complications arising for finite incident wavelength are of a purely formal nature and are taken care of in Sec. IV.

Regarding the crystal structure, we consider for convenience a Bravais lattice, with one nucleus per cell. For a lattice with more particles per cell, our discussion has to be supplemented by consideration of a structure factor and of optical branches in the frequency spectrum. With minor modifications, our treatment can also be extended to neutron scattering by spin waves in ferromagnetic crystals, a problem already studied by Moorhouse[26] from a slightly different point of view.

II. ANGULAR AND ENERGY DISTRIBUTION FOR INFINITE INCIDENT WAVELENGTH

In the limiting case of infinite incident wavelength, energy can only be transferred from the crystal to the neutron, and inelastic scattering is therefore possible only if the crystal is at a nonvanishing temperature. In one-phonon scattering, a phonon initially excited in the crystal is absorbed by the neutron initially at rest which picks up its energy. Energy conservation is expressed by

$$k^2=(2m/\hbar)\omega_j(\mathbf{q}), \tag{1}$$

where m and $\mathbf{k}$ are the mass and final wave vector of the neutron; $\mathbf{q}$, j, and $\hbar\omega_j(\mathbf{q})$ are the wave vector, polarization index ($j=1, 2, 3$ for a Bravais lattice), and energy of the absorbed phonon.

Equation (1) holds for both coherent and incoherent

[24] P. Egelstaff, Nature **168**, 290 (1951).

[25] For estimates see Squires, reference 14.

[26] R. G. Moorhouse, Proc. Phys. Soc. (London) **64**, 1097 (1951).

scattering. For the latter it is the only condition relating the phonon variables to the momentum $\hbar\mathbf{k}$ transferred to the neutron; Eq. (1) has then only to be supplemented by an intensity formula given in Sec. III. For coherent scattering, the interference between waves scattered by the various nuclei imposes a further relation

$$\mathbf{k}=\mathbf{q}+2\pi\boldsymbol{\tau}, \tag{2}$$

where $\boldsymbol{\tau}$ is an arbitrary vector of the reciprocal lattice.[7] It is well known that the wave vector $\mathbf{q}$ of a lattice vibration is only defined apart from 2π times an arbitrary reciprocal lattice vector $\boldsymbol{\tau}$; the frequency $\omega_j(\mathbf{q})$ is accordingly a periodic function of $\mathbf{q}$,

$$\omega_j(\mathbf{q}+2\pi\boldsymbol{\tau})=\omega_j(\mathbf{q}). \tag{3}$$

To a phonon of wave vector $\mathbf{q}+2\pi\boldsymbol{\tau}$ can be attributed a momentum $\hbar(\mathbf{q}+2\pi\boldsymbol{\tau})$, and in this sense Eq. (2) is conventionally regarded as expressing momentum conservation.[27]

The conservation laws determine the main features of the angular and energy distribution of scattered neutrons. To show this, we shall use the following properties of the $\omega_j(\mathbf{q})$ function, valid for any Bravais lattice: for each $j=1, 2, 3$, $\omega_j(\mathbf{q})$ is a continuous function with the periodicity (3) of the reciprocal lattice; for $\mathbf{q}$ approaching $2\pi\boldsymbol{\tau}$, it has the form

$$\omega_j(\mathbf{q})=c_j(\boldsymbol{\xi}/\xi)\xi; \quad \boldsymbol{\xi}=\mathbf{q}-2\pi\boldsymbol{\tau}, \tag{4}$$

where $c_j(\boldsymbol{\xi}/\xi)$, the sound velocity for long wavelengths in the direction $\boldsymbol{\xi}/\xi$, can be calculated from the elastic constants.[28]

For incoherent scattering, the energy equation (1) shows that the length of $\mathbf{k}$ is restricted to the interval

$$0\leqslant k\leqslant k_{\max}=(2m\omega_{\max}/\hbar)^{\frac{1}{2}}, \tag{5}$$

where $\omega_{\max}$ is the maximum of $\omega_j(\mathbf{q})$ for all $\mathbf{q}$ and j; the direction of $\mathbf{k}$ is unrestricted. Equation (5) defines in $\mathbf{k}$ space a sphere Σ of radius $k_{\max}$ and center $\mathbf{k}=0$. Any vector with endpoint inside or on Σ is a possible value for the outgoing neutron wave vector. Hence, neutrons are scattered in all directions, with energies ranging continuously from 0 to $\hbar\omega_{\max}$. This conclusion holds for single crystals as well as for powders.

The restrictions affecting $\mathbf{k}$ are more severe for coherent scattering. Combining Eqs. (1), (2), (3) one obtains them in the simple form

$$k^2=(2m/\hbar)\omega_j(\mathbf{k}). \tag{6}$$

For each j, (6) defines in $\mathbf{k}$ space a surface S_j, which may be composed of several disconnected parts. The surfaces S_1, S_2, S_3 in general cross each other, and the set of all three will be called S. We suppose the origin $\mathbf{k}=0$ not to be counted as a point of S. For neutrons scattered coherently with absorption of one phonon, the outgoing wave vector is thus restricted to have its endpoint on S.

In order to discuss the general properties of the surface S, let us call lattice vectors in $\mathbf{k}$ space the reciprocal lattice vectors $\boldsymbol{\tau}$ multiplied by 2π, and let us speak accordingly of lattice points and cells in $\mathbf{k}$ space. We state

(i) The surface S is entirely contained in the sphere Σ.
(ii) Each radius of the sphere Σ crosses S at least once and in general a finite number of times not smaller than 3.
(iii) Each connected region of $\mathbf{k}$ space inside Σ which contains a lattice point $2\pi\boldsymbol{\tau}\neq 0$ and a point $\mathbf{k}_1$, where $\omega_j(\mathbf{k}_1)=\omega_{\max}$ for some j, is crossed by S; in particular, S crosses any cell of $\mathbf{k}$ space, centered at a lattice point $2\pi\boldsymbol{\tau}\neq 0$ and fully contained in Σ.

Property (i) is obvious. To establish (ii), we notice first that, S being a two-dimensional surface, if a radius of Σ crosses it at all, it will in general do so a finite number of times. To show that every radius crosses S, consider

$$\varphi_j(\mathbf{k})=k^2-(2m/\hbar)\omega_j(\mathbf{k})$$

as a function of k for fixed direction of $\mathbf{k}$ and fixed j: for small k, Eq. (4) gives

$$\varphi_j(\mathbf{k})=k^2-(2m/\hbar)c_j(\mathbf{k}/k)\cdot k<0,$$

whereas, for $k=k_{\max}$,

$$\varphi_j(\mathbf{k})=k_{\max}{}^2-(2m/\hbar)\omega_j(\mathbf{k})=(2m/\hbar)[\omega_{\max}-\omega_j(\mathbf{k})]\geqslant 0.$$

Since the function is continuous, it must vanish for at least one value k_j of k, giving a point on S. For general directions of $\mathbf{k}$, the three k_j's will be different. Property (iii) is established by a similar continuity argument, considering $\varphi_j(\mathbf{k})$ for the polarization j which gives $\omega_j(\mathbf{k}_1)=\omega_{\max}$, along a path in $\mathbf{k}$ space from $2\pi\boldsymbol{\tau}$ to $\mathbf{k}_1$.

The physical meaning of property (i) is quite trivial: it states that the outgoing neutron energy never exceeds the maximum phonon energy $\hbar\omega_{\max}$. Property (ii) determines the main features of the angular and energy distribution for coherent one-phonon scattering by a single crystal: neutrons are scattered in every direction and for each direction the outgoing energy has a finite number of discrete values, in general three or more. Measurement of outgoing energy as function of direction determines the surface S and thus yields $\omega_j(\mathbf{k})$.[29] This type of scattering is, therefore, particularly well fitted to give information on the crystal vibrations.

As mentioned in the introduction, the discrete nature of their energy spectrum allows an experimental separation of neutrons scattered in one-phonon coherent processes. It is, indeed, easily established that in

[27] The momentum $\hbar\mathbf{q}$ thus attributed to a vibration is not to be confused with the momentum of the crystal considered as a system of particles, and Eq. (2) has nothing in common with momentum conservation in the sense of particle dynamics.

[28] H. A. Jahn, Proc. Roy. Soc. (London) **A179**, 320 (1941).

[29] In order to measure in this way $\omega_j(\mathbf{q})$ for every $\mathbf{q}$ and j, one has to use neutrons with nonvanishing initial momentum. See Eqs. (17) and (18) below.

multiphonon coherent processes, as well as in incoherent inelastic scattering, the final wave vector $\mathbf{k}$ depends on three or more parameters, giving in each direction an outgoing energy which ranges continuously over one or more finite intervals. The latter type of energy distribution is also obtained for coherent one-phonon scattering by a powder, as is shown by averaging over orientations the energy distribution for a single crystal. In this respect, powders are less convenient than single crystals for study of the elastic vibrations by means of neutron scattering.

Returning to one-phonon coherent scattering by a single crystal, we have still to consider the implications of property (iii) above. (iii) is of interest particularly when the sphere Σ contains a rather large number of lattice points of $\mathbf{k}$ space. It then shows that the surface S is distributed in Σ with a certain uniformity, since it passes through every cell inside Σ, except possibly the cell centered at the origin. In every direction, the discrete values of the outgoing wave vector $\mathbf{k}$ will be distributed over the interval $0\leqslant k\leqslant k_{\max}$ with a corresponding amount of uniformity.

While such conclusions are bound to be rather vague, it is instructive to compare the size of the sphere Σ with the size of the lattice cell in $\mathbf{k}$ space. The ratio of their volumes is

$$\frac{(4\pi/3)k_{\max}{}^3}{(2\pi)^3/v_0}=\frac{v_0}{6\pi^2}\left(\frac{2m\omega_{\max}}{\hbar}\right)^{\frac{3}{2}}=F, \tag{7}$$

where v_0 is the volume per particle in the crystal.

The parameter F plays an important role in determining the general shape of the surface S. When F is very small compared to 1, the sphere Σ is entirely in the region where the approximation (4) applies with $\tau=0$. Equation (6) reduces to

$$k=(2m/\hbar)c_j(\mathbf{k}/k), \quad (j=1, 2, 3). \tag{8a}$$

Hence, S is formed of three closed surfaces around the origin of $\mathbf{k}$ space, intersecting each other and fully contained in the lattice cell of center $\mathbf{k}=0$. For slightly larger F, S can be expected to have the same general shape, but Eq. (8a) will have to be completed with correction terms of relative order $F^{\frac{1}{2}}$, $F^{\frac{2}{3}}$, $\cdots$. For $F\gg 1$ on the other hand, the shape of S is again simple in the region of $\mathbf{k}$ space where k is small compared to $k_{\max}$. S is there composed of three closed surfaces around each lattice point $2\pi\tau\neq 0$, of approximate equation

$$\xi=4\pi^2\hbar\tau^2[2mc_j(\xi/\xi)]^{-1}+\cdots, \quad (j=1, 2, 3),$$
$$\xi=\mathbf{k}-2\pi\tau, \tag{8b}$$

with correction terms of relative order $F^{-\frac{1}{2}}$, $F^{-\frac{2}{3}}$, $\cdots$. In the region where k is comparable to $k_{\max}$, S behaves quite differently: it runs continuously from cell to cell in $\mathbf{k}$ space.

For actual crystals F seems to be larger than one, but in general not large enough for (8b) to apply. This is thus the case intermediate between those considered above. Here even the general shape of S cannot be predicted without a fairly accurate knowledge of the $\omega_j(\mathbf{q})$ function. Conversely this case would appear to be all the more favorable for the determination of the $\omega_j(\mathbf{q})$ function from the measured shape of the surface S.

The calculation of F for an actual substance requires the knowledge of $\omega_{\max}$, which is accurately available only for a very few crystals. It is, however, only the order of magnitude of F which is of interest, and this is easily obtained by remarking that the order of magnitude of $\omega_{\max}$ is given by the Debye temperature θ

$$\omega_{\max}\simeq k_B\theta/\hbar,$$

(k_B=Boltzmann constant).[30] The approximate value of F thus obtained, defined by

$$F_D=\frac{v_0}{6\pi^2}\frac{(2mk_B\theta)^{\frac{3}{2}}}{\hbar^3}, \tag{9}$$

is given in Table I for a few substances.

III. INTENSITY FORMULAS FOR LONG INCIDENT WAVELENGTH

The discussion of Sec. II has to be supplemented by the consideration of the scattered intensity per unit angular and energy range. This intensity is simply expressed in terms of the differential cross section $d\sigma/d\mathbf{k}$ per unit volume in $\mathbf{k}$ space.

We consider a single crystal and measure the coherent cross section per nucleus in units of $\langle a\rangle_{\text{Av}}{}^2$ and the incoherent cross section per nucleus in units of $\langle a^2\rangle_{\text{Av}}-\langle a\rangle_{\text{Av}}{}^2$. a is the spin- and isotope-dependent scattering length. The units are, respectively, the coherent and incoherent scattering cross sections of the bound nucleus per unit solid angle. With the aid of standard methods[7] it is then found that

$$\frac{d\sigma_1{}^{\text{inc}}}{d\mathbf{k}}=\frac{2}{Mk_0}\exp[-\langle(\mathbf{k}\cdot\mathbf{u})^2\rangle_{\text{Av}}]\frac{v_0}{(2\pi)^3}\sum_j\int d\mathbf{q}$$
$$\times\frac{[\mathbf{k}\cdot\mathbf{e}_j(\mathbf{q})]^2}{k^2}\frac{\delta[k^2-2m\hbar^{-1}\omega_j(\mathbf{q})]}{\exp[\beta\omega_j(\mathbf{q})]-1}, \tag{10}$$

$$\frac{d\sigma_1{}^{\text{coh}}}{d\mathbf{k}}=\frac{2}{Mk_0}\exp[-\langle(\mathbf{k}\cdot\mathbf{u})^2\rangle_{\text{Av}}]\sum_j\frac{[\mathbf{k}\cdot\mathbf{e}_j(\mathbf{k})]^2}{k^2}$$
$$\cdot\frac{\delta[k^2-2m\hbar^{-1}\omega_j(\mathbf{k})]}{\exp[\beta\omega_j(\mathbf{k})]-1}. \tag{11}$$

The suffix 1 in $\sigma_1{}^{\text{inc}}$ and $\sigma_1{}^{\text{coh}}$ refers to one-phonon scattering. M is the ratio of nuclear to neutron mass. In the Debye-Waller factor $\exp[-\langle(\mathbf{k}\cdot\mathbf{u})^2\rangle_{\text{Av}}]$, $\mathbf{u}$ is the displacement vector of any nucleus in the crystal from its equilibrium position, and the average is taken over

[30] For tungsten, calculations by P. C. Fine [Phys. Rev. **56**, 355 (1939)] give $\hbar\omega_{\max}/k_B=336°$, as compared to $\theta=373°$ from the elastic constants and $\theta=310°$ from specific heats.

the thermal equilibrium distribution. $\mathbf{e}_j(\mathbf{q})$ is the polarization vector of the phonon defined by j and $\mathbf{q}$, β is the reciprocal temperature multiplied by $\hbar k_B^{-1}$. The integration over $\mathbf{q}$ in (10) extends over one cell in $\mathbf{k}$ space. The argument of the δ function in (11) gives directly the Eq. (6) of the surface S discussed in the previous section and the functions $\mathbf{e}_j(\mathbf{k})$ as well as $\omega_j(\mathbf{k})$ are defined for all $\mathbf{k}$ through the periodicity condition corresponding to (3).

The cross sections (10) and (11) correspond to transition probabilities for a neutron initially at rest, in conformity with the limiting case discussed in the previous section. The incident momentum $\hbar k_0$ thus appears only in the factor relating transition probability to cross section. This limiting case applies if $k \gg k_0$. For coherent scattering, as follows from our discussion of the surface S, k has a nonvanishing minimum, and hence (11) holds for all outgoing energies as soon as $k_0 \ll k_{\min}$. For incoherent scattering, on the other hand, there is no such minimum. However small k_0 may be, therefore, the limiting case will not apply in the small region of the outgoing energy spectrum where k is not large compared to k_0. Here (10) must be replaced by the general expression (15).

Equation (10) can be considerably simplified for cubic crystals. As is well known, a quadratic form $\Sigma_{xy} A_{xy} k_x k_y$ invariant under the operations of any of the cubic point groups is a multiple of $\Sigma_x k_x^2$, i.e., $A_{xy} = A\delta_{xy}$ (δ_{xy} = Kronecker symbol). For cubic crystals, this fact implies, firstly,[19]

$$\langle (\mathbf{k}\cdot\mathbf{u})^2 \rangle_{\text{Av}} = k^2 \langle u_0^2 \rangle_{\text{Av}},$$

where u_0 is the component of $\mathbf{u}$ in an arbitrary direction. The Debye-Waller factor is thus independent of the direction of $\mathbf{k}$. Secondly,

$$\sum_j \int d\mathbf{q} e_j^x(\mathbf{q}) e_j^y(\mathbf{q}) \frac{\delta[k^2 - 2m\hbar^{-1}\omega_j(\mathbf{q})]}{\exp[\beta\omega_j(\mathbf{q})] - 1} = A\delta_{xy},$$

with

$$A = \frac{1}{3}\sum_j \int d\mathbf{q} \frac{\delta[k^2 - 2m\hbar^{-1}\omega_j(\mathbf{q})]}{\exp[\beta\omega_j(\mathbf{q})] - 1}.$$

Introducing the frequency distribution function $g(\omega)$, defined as the number of normal vibrations per unit frequency interval, divided by the total number of vibrations,

$$g(\omega)d\omega = \frac{1}{3}\frac{v_0}{(2\pi)^3}\sum_j \int_{\omega \leqq \omega_j(\mathbf{q}) \leqq \omega + d\omega} d\mathbf{q},$$

$$g(\omega) = 0 \quad \text{for} \quad \omega > \omega_{\max},$$

we find:

$$\frac{d\sigma_1^{\text{inc}}}{d\mathbf{k}} = \frac{2}{Mk_0} \exp[-k^2\langle u_0^2\rangle_{\text{Av}}] \times \int_0^{\omega_{\max}} \frac{\delta(k^2 - 2m\hbar^{-1}\omega)}{\exp(\beta\omega) - 1} g(\omega) d\omega,$$

TABLE I. The parameter F_D.

Substance	Lattice type	$10^{24}\, v_0$ in cm^3	θ in °K	F_D
Pb	cu face-cent.	30.0	88	3.6
W	cu body-cent.	15.7	310	12
Fe	cu body-cent.	11.7	462	17
Al	cu face-cent.	16.5	398	19

or

$$\frac{d\sigma_1^{\text{inc}}}{d\mathbf{k}} = \frac{\hbar}{Mmk_0} \exp[-k^2\langle u_0^2\rangle_{\text{Av}}] \frac{g(\hbar k^2/2m)}{\exp(\beta\hbar k^2/2m) - 1}. \quad (12)$$

For cubic crystals the one-phonon incoherent scattering has thus, for small k_0, an energy distribution independent of direction and simply expressed in terms of the frequency distribution $g(\omega)$ of the crystal.

It has been shown elsewhere[31] that the $g(\omega)$ function of a general crystal contains a finite number of singularities resulting from the periodic structure; they are singular points ω_c in the neighborhood of which $g(\omega)$ has one of the two forms

$$g(\omega) = g(\omega_c) + \begin{cases} A|\omega - \omega_c|^{\frac{1}{2}} + O(\omega - \omega_c) & \text{for } \omega < \omega_c \\ O(\omega - \omega_c) & \text{for } \omega > \omega_c \end{cases}, \quad (13)$$

or the same with $\omega < \omega_c$ and $\omega > \omega_c$ interchanged. The constant A can have either sign; it is usually negative for $\omega_c < \omega_{\max}$ and positive for $\omega_c = \omega_{\max}$ [$\omega_{\max}$ is in general a singular point of $g(\omega)$]. The symbol $O(\omega - \omega_c)$ denotes a rest term of order $|\omega - \omega_c|$ for $\omega \to \omega_c$. The singular frequencies ω_c are simply related to the $\omega_j(\mathbf{q})$ function of the crystal: apart from exceptional cases, they are the values of $\omega_j(\mathbf{q})$ at the points where grad $\omega_j(\mathbf{q}) = 0$, ($j = 1, 2, 3$).[31] We shall call them the singular frequencies of the crystal. The general shape of the energy distribution $(2mk/\hbar^2)(d\sigma_1^{\text{inc}}/d\mathbf{k})$ (for fixed direction of $\mathbf{k}$) can be predicted from the behavior of $g(\omega)$ and a typical distribution is given in Fig. 1. Its singularities are of the same analytical type as (13), ω being replaced by k or the energy $E = \hbar^2 k^2/2m$.[32]

Apart from (10), the inelastic incoherent cross section contains terms due to multiphonon processes. In general they depend on the direction of $\mathbf{k}$, but the energy distribution in each direction can be shown to be continuously differentiable. The energy distribution in each direction for inelastic incoherent scattering by a cubic

[31] L. Van Hove, Phys. Rev. **89**, 1189 (1953); in the formulas on p. 1191 of this paper $(\nu - \nu_c)^{\frac{1}{2}}$ must be replaced by $|\nu - \nu_c|^{\frac{1}{2}}$. The vector $\mathbf{q}$ there used is our present vector $\mathbf{q}$ divided by 2π. The frequency distribution of a simple cubic crystal has been calculated with its correct singularities by G. F. Newell, J. Chem. Phys. **21**, 1877. See also H. B. Rosenstock and G. F. Newell, J. Chem. Phys. **21**, 1607 (1953); H. B. Rosenstock and H. M. Rosenstock, J. Chem. Phys. **21**, 1608 (1953).

[32] All our statements concerning singularities in the $g(\omega)$ function and in energy distributions of scattered neutrons hold for general values of the force constants of the crystal. The origin and nature of possible exceptions have been discussed by Van Hove (reference 31).

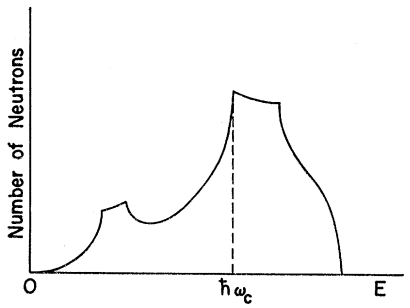

FIG. 1. Schematic shape of the energy distribution of scattered neutrons for long incident wavelength in the case of one-phonon incoherent scattering. E is the outgoing neutron energy, and ω_c a singular frequency of the crystal.

crystal has, therefore, still the shape illustrated in Fig. 1; its singularities in the first derivative are all due to one-phonon processes and are the same in all directions.

For noncubic crystals, the one-phonon incoherent cross section cannot be expressed in terms of the frequency distribution $g(\omega)$ of the crystal. The polarization terms of Eq. (10) cannot be eliminated, and the energy distribution of scattered neutrons varies with direction. In each direction, however, it has the shape illustrated in Fig. 1 and its singularities, unaffected by multiphonon processes occur, as for cubic crystals, at neutron energies E_c independent of direction and related by $E_c=\hbar\omega_c$ to the singular frequencies of the crystal.[33] As mentioned later, the singular frequencies of the crystal do not show up in coherent cross sections. Incoherent scattering of neutrons, for crystals where it is appreciable, seems to be the simplest phenomenon singling out these frequencies, which are important in determining the analytical singularities of the frequency distribution of the crystal.

The foregoing discussion was concerned with single crystals. For inelastic scattering by a powder, according to (12) nothing is changed for a cubic crystal, whereas Eq. (10) must be averaged over orientations in the noncubic cases. As we have seen, however, the singularities in the energy distribution occur at energies independent of direction and are thus retained in the averaging; consequently, the qualitative behavior shown in Fig. 1 remains unchanged.

Turning now to coherent scattering, we note that in one-phonon processes, the neutrons scattered in a given direction have a discrete energy spectrum, corresponding to outgoing wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, $\cdots$. From (11) the cross section per unit solid angle for the outgoing beam of energy $\hbar^2k_i^2/2m$ is

$$\left(\frac{d\sigma_1^{\text{coh}}}{d\Omega}\right)_{k_i}=\frac{2}{Mk_0}\exp[-\langle(\mathbf{k}_i\cdot\mathbf{u})^2\rangle_{\text{Av}}]\cdot\frac{[\mathbf{k}_i\cdot\mathbf{e}_j(\mathbf{k}_i)]^2}{\{\exp[\beta\omega_j(\mathbf{k}_i)]-1\}\cdot|2k_i-2m\hbar^{-1}d\omega_j/dk|}, \quad (14)$$

[33] L. Van Hove (to be published).

where j is the polarization index for which $k_i^2=2m\hbar^{-1}\omega_j(\mathbf{k}_i)$, and the derivative of $\omega_j(\mathbf{k})$ is taken at $\mathbf{k}=\mathbf{k}_i$, for fixed orientation of $\mathbf{k}$. For a powder, Eq. (14) must be averaged over all crystal orientations, producing in each direction an outgoing energy distribution continuous over finite intervals.

As mentioned before, multiphonon coherent scattering by a single crystal gives in each direction a continuous energy distribution of outgoing neutrons. Without entering into its detailed discussion, we shall mention that the energy distribution contains again, in general, singularities of type (13), produced by two-phonon processes. In this case the singularities occur at energies unrelated to the singular frequencies of the crystal and varying with the outgoing direction considered. They are thereby distinguishable from the singularities resulting from one-phonon incoherent scattering (which occur at the same energies in all directions), and for a powder they disappear by directional averaging.

To summarize the results obtained in the previous sections, we shall now briefly recall the main properties derived for the angular and energy distribution of inelastically scattered neutrons by single crystals in the limit of long incident wavelengths. In each outgoing direction the energy distribution of scattered neutrons contains a discrete part, resulting from one-phonon coherent scattering, and a continuous part produced by incoherent and multiphonon coherent scattering. The discrete part gives direct information on the crystal vibrations: the outgoing momentum $\mathbf{k}$ verifies Eq. (6) for some j. The continuous part has singularities of the analytical type (13) (with ω replaced by outgoing energy), the shape of which is illustrated in Fig. 1. Some of these singularities occur at energies E_c independent of direction: they are produced by incoherent one-phonon scattering and $\hbar^{-1}E_c$ are the singular frequencies of the crystal. The other singularities, which occur at energies varying with direction, originate from two-phonon coherent scattering.

IV. EXTENSION TO ARBITRARY INCIDENT WAVELENGTHS

The previous considerations are easily extended to the inelastic scattering of neutrons of arbitrary initial momentum $\hbar\mathbf{k}_0$. The only important change is the occurrence of scattering with energy transfer from the neutron to the crystal. Apart from this fact, we shall see that all essential features of the angular and energy distribution are retained. As the discussion runs entirely parallel to that presented in Secs. II and III, we shall make it very brief and restrict ourselves to scattering by a single crystal.

Considering first one-phonon incoherent scattering, we find for the case of energy gain by the neutron that the final wave vector $\mathbf{k}$ has in every direction a length ranging from k_0 to $(k_0^2+2m\hbar^{-1}\omega_{\max})^{\frac{1}{2}}$, whereas for energy loss by the neutron, k ranges from k_0 down

to 0 if $k_0^2 \leqslant 2m\hbar^{-1}\omega_{\max}$, or to $(k_0^2-2m\hbar^{-1}\omega_{\max})^{\frac{1}{2}}$, if $k_0^2 > 2m\hbar^{-1}\omega_{\max}$. The differential cross sections are

$$\frac{d\sigma_1^{\text{inc}}}{d\mathbf{k}} = \frac{2}{Mk_0}\exp[-\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle_{\text{Av}}]\frac{v_0}{(2\pi)^3}\sum_j \int d\mathbf{q} \times \frac{[\boldsymbol{\kappa}\cdot\mathbf{e}_j(\mathbf{q})]^2}{|k^2-k_0^2|}\times\left[\frac{1}{\exp[\beta\omega_j(\mathbf{q})]-1}+\tfrac{1}{2}(1\mp 1)\right] \cdot\delta[k^2-k_0^2\mp 2m\hbar^{-1}\omega_j(\mathbf{q})]. \quad (15)$$

The upper (lower) signs correspond to scattering with energy gain (loss) by the neutron, i.e., to $k > k_0$ ($k < k_0$). The integration is extended over one cell in $\mathbf{k}$ space. $\hbar\boldsymbol{\kappa}$, with $\boldsymbol{\kappa}=\mathbf{k}-\mathbf{k}_0$, is the momentum transfer.

For cubic crystals, Eq. (15) can be simplified with the help of the frequency distribution function $g(\omega)$:

$$\frac{d\sigma_1^{\text{inc}}}{d\mathbf{k}} = \frac{\hbar}{Mmk_0}\exp[-\kappa^2\langle u_0^2\rangle_{\text{Av}}]\times\frac{\kappa^2}{|k^2-k_0^2|} \times\left(\frac{1}{\exp(\beta\hbar|k^2-k_0^2|/2m)-1}+\tfrac{1}{2}(1\mp 1)\right) \times g(\hbar|k^2-k_0^2|/2m). \quad (16)$$

For cubic as well as noncubic crystals, the energy distribution in each outgoing direction has singularities of the type shown in Fig. 1 and Eq. (13) (ω being replaced by the neutron energy), occurring at energies

$$\hbar^2k^2/2m = (\hbar^2k_0^2/2m) \pm \hbar\omega_c,$$

where the ω_c are the singular frequencies of the crystal. Multiphonon incoherent scattering produces no such singularities.

For coherent scattering the situation is again similar to that prevailing in the limiting case of $k_0=0$. For one-phonon processes with energy gain by the neutron, momentum and energy conservation are expressed by the single equation

$$k^2-k_0^2 = (2m/\hbar)\omega_j(\mathbf{k}-\mathbf{k}_0), \quad j=1, 2, 3, \quad (17)$$

the obvious generalization of Eq. (6). Equation (17) defines in $\mathbf{k}$ space a surface located between the spheres of radii k_0 and $(k_0^2+2m\hbar^{-1}\omega_{\max})^{\frac{1}{2}}$, centered at the origin. Each radius of the large sphere intersects the surface at least once, in general a finite number of times, and each cell of $\mathbf{k}$ space contained between the two spheres is crossed by the surface [compare properties (i), (ii), (iii) in Sec. II]. Some points of the surface may, however, correspond to a vanishing energy transfer: they give rise to elastic coherent scattering. If we include them, the main feature of the angular and energy distribution is, therefore, retained: neutrons are scattered in each direction with a discrete energy spectrum.

The situation is slightly more complicated for one-phonon coherent scattering with energy loss by the neutron, which is governed by the equation

$$k_0^2-k^2 = (2m/\hbar)\omega_j(\mathbf{k}-\mathbf{k}_0). \quad (18)$$

This equation has no solution, and the type of scattering considered is thus impossible when k_0 is smaller than a minimum value $k_0^{(1)}$; it is only for k_0 larger than a value $k_0^{(2)} > k_0^{(1)}$ that neutrons are scattered in *every* direction. Both for $k_0 > k_0^{(2)}$ and $k_0 < k_0^{(2)}$ the scattered neutrons have a discrete energy spectrum in each outgoing direction. The actual values of $k_0^{(1)}$ and $k_0^{(2)}$ depend on the details of the $\omega_j(\mathbf{q})$ function. It is, however, generally true that

$$k_0^{(1)} \leqslant \pi\tau_0, \quad (19)$$

$$k_0^{(2)} \leqslant (2m\hbar^{-1}\omega_{\max})^{\frac{1}{2}}, \quad (20)$$

where τ_0 is a reciprocal lattice vector of minimum length.[34]

The differential cross section for one-phonon coherent scattering is

$$\frac{d\sigma_1^{\text{coh}}}{d\mathbf{k}} = \frac{2}{Mk_0}\exp[-\langle(\boldsymbol{\kappa}\cdot\mathbf{u})^2\rangle_{\text{Av}}]\sum_j \frac{[\boldsymbol{\kappa}\cdot\mathbf{e}_j(\boldsymbol{\kappa})]^2}{|k^2-k_0^2|} \times\left[\frac{1}{\exp[\beta\omega_j(\boldsymbol{\kappa})]-1}+\tfrac{1}{2}(1\mp 1)\right] \times\delta[k^2-k_0^2\mp 2m\hbar^{-1}\omega_j(\boldsymbol{\kappa})], \quad (21)$$

with the same use of double signs as in Eq. (15). An expression similar to (14) is easily deduced from Eq. (21).

There exists for one-phonon coherent scattering a special case deserving a discussion of its own: it is the case when $\mathbf{k}_0$ approximately verifies the Bragg condition

$$|\mathbf{k}_0+2\pi\boldsymbol{\tau}|^2 \simeq k_0^2.$$

Inelastic scattering with $\boldsymbol{\kappa}$ nearly equal to $2\pi\boldsymbol{\tau}$ and with small energy transfer is then taking place, with a large differential cross section increasing proportionally to $(k^2-k_0^2)^{-2} \sim |\boldsymbol{\kappa}-2\pi\boldsymbol{\tau}|^{-2}$ when the Bragg condition is approached. This is seen from Eq. (21) by using

$$\exp[\beta\omega_j(\boldsymbol{\kappa})-1] \simeq \beta\omega_j(\boldsymbol{\kappa}) = \frac{\beta\hbar}{2m}|k^2-k_0^2| \simeq \beta c_j\left(\frac{\boldsymbol{\kappa}-2\pi\boldsymbol{\tau}}{|\boldsymbol{\kappa}-2\pi\boldsymbol{\tau}|}\right)|\boldsymbol{\kappa}-2\pi\boldsymbol{\tau}|.$$

The nature of the conservation laws for this special case was discussed by Seeger and Teller;[5] Waller and Fröman[11] gave a detailed treatment of the differential cross section.[34a]

[34] The condition $k_0 \geqslant \pi\tau_0$ insures the possibility of the type of scattering under discussion for some but not all orientations of the crystal. It can be written $\lambda_0 \leqslant \lambda_B$ where λ_0 is the incident wavelength and $\lambda_B = (2\tau_0)^{-1}$ the Bragg cut-off wavelength. It was first given by Wick (reference 2). The inequality (20) applies to an arbitrary orientation of the crystal.

[34a] *Note added in proof.*—See also the recent paper by R. D. Lowde, Proc. Roy. Soc. (London) **A221**, 206 (1954).

Regarding multiphonon coherent scattering, the general situation is again the same as in the case of long incident wavelength: in each outgoing direction the scattered neutrons have a continuous energy spectrum, with singularities resulting from two-phonon processes and occurring at energies which vary with direction.

It has been the main purpose of this paper to put in evidence the direct relationship between the energy changes of neutrons scattered by a crystal and the dispersion law of the crystal vibrations as expressed by the $\omega_j(\mathbf{q})$ and $g(\omega)$ functions. We hope to have shown that energy measurements on scattered neutrons provide a new approach to the problem of determining these functions from scattering data. While the few experimental data so far available[24,35,36] do not as yet permit an analysis along these lines, the foregoing discussion indicates that further experimental work in this field would be of considerable interest.

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Calculation of the Energy Band Structures of the Diamond and Germanium Crystals by the Method of Orthogonalized Plane Waves*

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The mathematical procedure employed in recent exploratory calculations of the energy band structures of the diamond and germanium crystals is described. Some of the symmetry properties of the eigensolutions of diamond-type lattices and the construction of an approximate potential for the diamond crystal are reviewed.

The relative order of the crystal eigenvalues $E_\gamma(\mathbf{k})$ for a particular $\mathbf{k}$ was found to depend more upon the symmetry of the crystal potential than upon the detailed nature of this potential. On the other hand, the curvatures of the energy surfaces calculated by perturbation theory were found to depend in a rather critical manner upon the exact form of the crystal potential.

It would appear that more reliable estimates of the energy band structures of actual crystals can be obtained with the aid of Herring's method of orthogonalized plane waves than by means of other approximational methods requiring comparable effort provided (1) reliable crystal potentials are employed, (2) calculations are carried to the point where the eigensolutions are satisfactorily "convergent," and (3) eigensolutions for more than just the points of high symmetry in the reduced zone are investigated.

A more elaborate calculation of the energy band structure of the germanium crystal has been undertaken; the work is now in progress.

1. INTRODUCTION

RECENT developments in the field of semiconductor physics[1,2] have stimulated widespread interest in the diamond-type valence crystals. Although the general behavior of these crystals can be readily understood in terms of simple phenomenological models, a detailed knowledge of their energy band structures should prove useful in many problems.

This paper describes the mathematical procedure employed in recent exploratory calculations of the electronic structures of the diamond[3,4] and germanium[5] crystals. The method of orthogonalized plane waves (OPW), first proposed by Herring[6] and already successfully applied to metallic lithium[7,8] and beryllium,[9] is used here for the first time to study valence crystals.

The exploratory studies of diamond and germanium have revealed some hitherto unexpected features in the energy band structures of these crystals.

In particular, the lowest conduction band states at the central point of the reduced zone in each case were found to be triply degenerate, rather than nondegenerate, as earlier work on diamond,[10,11] and silicon[12,13] had suggested. Moreover, by means of perturbation-type calculations, it was found that the states normally

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