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Interaction of Waves in Crystals*

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1. GENERAL NATURE OF WAVES IN CRYSTALS AND THEIR INTERACTIONS

MANY phenomena concerned with waves in crystals follow very similar theoretical patterns, and it helps greatly in understanding them if we realize these resemblances. It is the purpose of this paper to point out some of these features. Some of the phenomena, such as Bragg scattering, are familiar to every crystallographer, and others, such as the theory of energy bands, are known to every solid-state physicist. The general theory of elastic or thermal vibrations in a crystal is somewhat less well known; and relatively few physicists are well enough acquainted with the theory of temperature diffuse scattering to realize its very close resemblance to the scattering of electrons by thermal waves, which is responsible for most of the resistivity of a metal, or to the scattering of light waves by ultrasonic waves. We shall consider all these cases, and others besides.

In this introductory section we shall outline the general argument which we shall follow, and then we pass on to a somewhat more mathematical treatment, though without going very deeply into the mathematical aspects of any of the effects. Fundamental to all of them is Bragg scattering. The earlier treatments of Bragg scattering of x-rays were based on the scattering by individual atoms, combining them into linear arrays, planes, and then three-dimensional crystals. This is perfectly correct; but we gain a greater insight into the problem if we analyze the charge distributions of the atoms by Fourier series, into sinusoidal functions of position, or essentially plane waves. Then a single Bragg reflection proves to be produced by a single plane wave or Fourier component. Pointed out first by W. H. Bragg in 1915 (references to all the points we are taking up in this paper will be found in the Bibliography at the end), the method of Fourier analysis was brought into practical use by Duane, Compton, and their co-workers about 1925, and now underlies a great deal of the practical work in crystal analysis. The strength of the method is shown particularly when we have to deal with problems other than the scattering by a perfect crystal, for instance, scattering by the temperature vibrations of the crystal. The essential features of Bragg's law come merely from the geometrical character of waves; they arise whenever we have the interaction of one wave of one type with another wave of another type, so that one scatters the other.

In all such cases, we start with a wave which is to be scattered, which we can write as the real part of $\exp i(\omega_0 t-\mathbf{k}_0\cdot\mathbf{r})$, where ω_0 is its angular frequency, $\mathbf{k}_0$ the propagation vector, and $\mathbf{r}$ the vector whose components are x, y, z. In the classical Bragg case, this is the wave of x-rays. Next, we have a wave which is to do the scattering, which we can write as the real part of $\exp i(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r})$. In the Bragg case, where we are scattering by a sinusoidal component of the stationary electron density, ω_1 would be zero, and $\mathbf{k}_1$ would be the vector representing the particular Fourier component we were considering. However, by including ω_1 in the formulation, we can consider scattering by progressive waves, such as sound waves. Then, if the interaction between the two waves is small, we find that the scattered wave will be represented by the real part of $\exp i[(\omega_0\pm\omega_1)t-(\mathbf{k}_0\pm\mathbf{k}_1)\cdot\mathbf{r}]$, and its amplitude will be proportional to the interaction between the wave which is being scattered, and the wave which is doing the scattering. In the x-ray case, this scattered wave has the angular frequency ω_0, since $\omega_1=0$, and it is one of the ordinary coherently scattered waves encountered in x-ray diffraction. In order that the scattered wave may have the same angular frequency ω_0 as the incident wave, it is necessary that the propagation vector $(\mathbf{k}_0\pm\mathbf{k}_1)$ of the scattered wave have the same magnitude as the propagation vector $\mathbf{k}_0$ of the incident wave. In the more general case where ω_1 is different from zero, it is still necessary that $(\mathbf{k}_0\pm\mathbf{k}_1)$ should be so chosen that the wave with this propagation vector may have the appropriate angular frequency $\omega_0\pm\omega_1$.

It is well known that the condition that the vector $(\mathbf{k}_0+\mathbf{k}_1)$ have the same length as the vector $\mathbf{k}_0$ is equivalent to the Bragg condition. Thus, in Fig. 1, the horizontal plane is the plane of a wave front of the scattering wave, and the vector $\mathbf{k}_1$, which is perpendicular to it, has a magnitude $2\pi/d$, where d is the spacing between wave fronts. The magnitude of $\mathbf{k}_0$, and of $(\mathbf{k}_0+\mathbf{k}_1)$, is $2\pi/\lambda$, where λ is the wavelength of the scattered wave, in this case of the x-rays. Then from Fig. 1 it is obvious that $\sin\theta=|k_1|/2|k_0|$, or

$$\lambda=2d\sin\theta, \tag{1}$$

which is Bragg's law. We do not have the additional factor n, met in the form $n\lambda=2d\sin\theta$, because only first-order scattering results from a sinusoidal disturbance (provided the interaction is not too great, as we shall see in the next section).

In case ω_1 is not zero, so that the sinusoidal disturbance which is doing the scattering is a progressive

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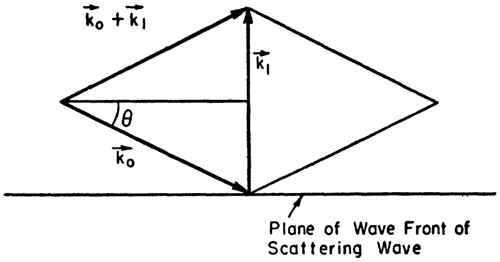

FIG. 1. Diagram to illustrate Bragg's law.

wave rather than a fixed disturbance, the frequency of the scattered wave is different from that of the incident wave. This fact is interpreted as a Doppler effect, since the reflection is from a moving rather than a stationary set of waves. Thus, if the scattering waves are traveling upward, in Fig. 1, the scattered wave may be considered to be emitted from a moving image which is traveling upward twice as fast as the scatterer, so that its emitted frequency will appear greater than the true frequency. We remember that in the theory of the Doppler effect it is shown that a source moving with a velocity v, emitting radiation whose frequency in a system of reference in which the source is stationary would be ω_0, will have an apparent frequency if observed in a direction making an angle ϕ with the velocity v equal to

$$\omega=\omega_0[1+(v/c)\cos\phi], \tag{2}$$

where c is the velocity of light. In our present case we are observing in the direction shown as $(\mathbf{k}_0+\mathbf{k}_1)$ in Fig. 1, so that $\cos\phi=\sin\theta$. The velocity of the scattering wave is $\omega_1/|k_1|$, and the velocity v of the image emitting the scattered wave is twice this velocity. The velocity of light c is $\omega_0/|k_0|$. When we substitute these values in Eq. (2), and use Eq. (1), we find that the observed frequency of the scattered wave should be $\omega_0+\omega_1$, in accordance with our general statement of the scattering condition. In other words, we have verified the interpretation of the frequency shift in terms of the Doppler effect.

There is another interpretation which we can give to the scattering process. Let us suppose that we are considering the scattering of electromagnetic waves, either x-rays or light waves, by a wave of sound. We remember the quantum interpretation of a light wave: The radiation consists of photons, of energy $h\nu_0=\hbar\omega_0$, where $\hbar=h/2\pi$, and of momentum $h/\lambda=\hbar k_0$, where λ is the wavelength. In a scattering process in which a wave of angular frequency ω_0 changes to $\omega_0+\omega_1$, and in which $\mathbf{k}_0$ changes to $\mathbf{k}_0+\mathbf{k}_1$, we must assume that the energy increases by $\hbar\omega_1$, and the momentum by $\hbar\mathbf{k}_1$. But at the same time, we remember that vibrational waves of sound are quantized. One of the quanta, referred to as a phonon, has energy $\hbar\omega_1$, and momentum $\hbar\mathbf{k}_1$. The interpretation of the scattering process which we have just described, then, is that a photon of energy $\hbar\omega_0$ and momentum $\hbar\mathbf{k}_0$ is destroyed, a new photon of energy $\hbar(\omega_0+\omega_1)$ and momentum $\hbar(\mathbf{k}_0+\mathbf{k}_1)$ is created, and conservation of energy and momentum are achieved by the destruction of a phonon of energy $\hbar\omega_1$ and momentum $\hbar\mathbf{k}_1$. In an analogous way, the scattering process in which the final frequency is $\omega_0-\omega_1$, the final propagation vector $\mathbf{k}_0-\mathbf{k}_1$, is one in which a phonon of energy $\hbar\omega_1$, momentum $\hbar\mathbf{k}_1$, is created.

We now see the general properties of the scattering of one wave, such as a wave of light or x-rays, by another, such as a wave of sound. In the cases we are most interested in, there are many scattering waves; in ordinary x-ray scattering, we have all the Fourier components of charge density, and in scattering by temperature agitation, or thermal diffuse scattering, we have a very large number of waves of mechanical oscillation. In case the interactions are small, the processes of scattering by the various waves can be handled independently. This is ordinarily the case, to a fair approximation, with x-rays. On the other hand, if the interactions are large, multiple scattering becomes very important. This is the case in the corresponding situation of scattering of electrons by the periodic potential met in a crystal. In any case, a study of the scattering by an individual sinusoidal wave forms a very good preliminary to the more complicated general case. In the next sections we shall take up this case of scattering by a single sinusoidal disturbance, leading to the Bragg law; we shall find that there is much more complication inherent in the problem than one might have believed from the very elementary description we have given so far. For comparison, we shall take up two cases, and show that they both lead to similar results: the scattering of an electronic wave by a sine wave of potential energy, handled by Schrödinger's equation, and the scattering of an electromagnetic wave by a sound wave, handled by Maxwell's equations. The electronic case is slightly simpler, since we are dealing with scalar rather than vector quantities, and we take it up first.

2. SCATTERING OF AN ELECTRONIC WAVE BY A SINUSOIDAL PERTURBATION

Let us have a particle of mass m, moving in a region in which the potential energy V is given by $V_1\cos(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r})$, a plane wave traveling along the direction of the vector. Schrödinger's equation for this particle is

$$\frac{-\hbar^2}{2m}\nabla^2\psi+V_1\cos(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r})\psi=i\hbar\frac{\partial\psi}{\partial t}. \tag{3}$$

We shall try to solve this equation, to show precisely the way in which the wave function representing the particle is scattered by the perturbing potential. We can easily visualize a physical problem to which this formulation is applicable. Consider a crystal, in particular a metal, in which a plane wave of sound proportional to $\cos(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r})$ is traveling along the z axis. The alternate condensations and rarefactions connected with this sound wave will be equivalent to periodic changes of density in the crystal. If we regard the particle as an electron, moving in a potential representing the average electrostatic potential of the nuclei and electrons of the crystal (Hartree's self-consistent field for a crystal), the sinusoidal changes of density will introduce a sinusoidal component $V_1\cos(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r})$ into the potential energy acting on the electron. We shall see later how this change in potential energy is to be computed; it is what is usually called a deformation potential. We are interested in the scattering of the electron's wave by this particular Fourier component in the Fourier analysis of the potential acting on it. If the electron has a small energy, such as it would have if it were a conduction electron, this scattering would lead to electrical resistivity, as we shall mention later. If it were a fast electron, concerned in electron diffraction, the scattering would lead to thermal diffuse scattering of electrons. As an alternative example of Eq. (3) we may take ω_1 to be zero, and assume that the sinusoidal potential is one of the Fourier components of the periodic potential in an undistorted crystal.

Now we must solve Eq. (3). In the one-dimensional case (ψ depends only on z, not on x and y), and in the case where $\omega_1=0$, the equation has a form known in mathematics as Mathieu's equation, which has been discussed a great deal. Even in the general case, however, we can use the same method of solution used for Mathieu's equation, which we shall proceed to do. The first step is to assume that ψ can be expressed as a linear combination of an infinite number of plane waves: not only the incident wave $\exp i(\omega_0 t-\mathbf{k}_0\cdot\mathbf{r})$ and the scattered waves $\exp i[(\omega_0\pm\omega_1)t-(\mathbf{k}_0\pm\mathbf{k}_1)\cdot\mathbf{r}]$ mentioned in Sec. 1, but more generally the waves $\exp i[(\omega_0+n\omega_1)t-(\mathbf{k}_0+n\mathbf{k}_1)\cdot\mathbf{r}]$, where n is an arbitrary integer, positive or negative, representing an nth-order scattering process, in which n phonons are concerned. We find that all orders of scattering are required to get a rigorous solution of Eq. (3). Furthermore, we must use the exponential in the form $\exp-i[(\omega_0+n\omega_1)t-(\mathbf{k}_0+n\mathbf{k}_1)\cdot\mathbf{r}]$, in order that the time exponential may occur with a negative sign in the exponent, as is required for a solution of Schrödinger's equation with positive energy. We then assume

$$\psi=\sum(n)A_n\exp-i[(\omega_0+n\omega_1)t-(\mathbf{k}_0+n\mathbf{k}_1)\cdot\mathbf{r}],\quad(4)$$

and inquire whether we can get a solution of Eq. (3) in this form, by appropriate choice of the amplitudes A_n.

When we substitute Eq. (4) into Eq. (3), we find

$$\sum(n)A_n\exp-i[(\omega_0+\omega_1)t-(\mathbf{k}_0+n\mathbf{k}_1)\cdot\mathbf{r}]$$
$$\times\left[\frac{\hbar^2}{2m}(\mathbf{k}_0+n\mathbf{k}_1)^2+V_1\cos(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r})\right.$$
$$\left.-\hbar(\omega_0+n\omega_1)=0\right].\quad(5)$$

We can expand the cosine in exponentials, combine with the other exponential factor, and change the numbering of the terms arising from this cosine, so as to transform Eq. (5) into the form

$$\sum(n)\exp-i[(\omega_0+\omega_1)t-(\mathbf{k}_0+n\mathbf{k}_1)\cdot\mathbf{r}]$$
$$\left\{\left[\frac{\hbar^2}{2m}(\mathbf{k}_0+n\mathbf{k}_1)^2-\hbar(\omega_0+n\omega_1)\right]A_n\right.$$
$$\left.+\frac{V_1}{2}[A_{n-1}+A_{n+1}]\right\}=0.\quad(6)$$

Equation (6) states that the sum of an infinite number of plane waves is equal to zero. This cannot happen unless the coefficient multiplying each of the plane waves is zero. Hence the equations satisfied by the A's are

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}_0+n\mathbf{k}_1)^2-\hbar(\omega_0+n\omega_1)\right]A_n$$
$$+\frac{V_1}{2}(A_{n-1}+A_{n+1})=0.\quad(7)$$

In Eq. (7) we have something very much like the familiar perturbation theory treatment of a problem in wave mechanics. We remember that if we write the wave function of a problem as a sum, $\sum(n)A_n u_n$, where the u_n's form a complete set of orthogonal functions, and if the matrix components of the Hamiltonian between these unperturbed functions are H_{nm}, then the sum will satisfy Schrödinger's equation, provided the A_n's satisfy the equations

$$(H_{nn}-E)A_n+\sum(m\neq n)H_{nm}A_m=0.\quad(8)$$

Here E is the energy. Our situation of Eq. (7) is equivalent to this: $(\hbar^2/2m)(\mathbf{k}_0+n\mathbf{k}_1)^2-\hbar n\omega_1$ takes the place of H_{nn}, $\hbar\omega_0$ takes the place of the energy E, $V_1/2$ takes the place of $H_{n,n\pm1}$, and the other nondiagonal matrix components of H are zero.

We remember from quantum mechanics that a set of equations like Eq. (8) does not have solutions in general; in order that there be nonvanishing solutions for the A_n's, the determinant of coefficients, det $(H_{nm}-E\delta_{nm})$, must equal zero, where $\delta_{nm}=1$ if $n=m$, 0 if $n\neq m$. This determinantal or secular equation is satisfied for certain energies, the eigenvalues of the problem, and for each eigenvalue there is a set of A_n's, determining the wave function or eigenfunction by Eq. (8). In this way Eq. (7) will not in general have solutions, but the quantity ω_0 must be determined from the secular equation in order to get an eigenfunction. This determines ω_0 as a function of $\mathbf{k}_0$; that is, for each propagation constant k_0 we can find the frequency, and hence the energy, of the electron wave.

Since we have an infinite set of A_n's, the determinantal equation would have an infinite number of rows and columns, and could not in practice be solved. However, on account of the specially simple form of Eq. (7) a solution is entirely practical. We can solve Eq. (7) for A_{n+1} in terms of A_n and A_{n-1}, provided we know ω_0 and $\mathbf{k}_0$. In practice, we can assume values for two successive A's, say A_0 and A_1, and of ω_0 and $\mathbf{k}_0$. Then we can find A_2, from the recursion relation. We then use A_1 and A_2 to find A_3, A_2 and A_3 to find A_4, and so on. Hence we can extend the procedure to finding all A_n's for positive n's. Similarly we can find from Eq. (7) an equation for A_{n-1} in terms of A_n and A_{n+1}, and this recursion relation can be used, again starting with A_0 and A_1, to find A_{-1}, A_{-2}, and so on for all negative n's. This calculation is very simple to carry out.

When we do this, we find in general that the A_n's will increase in magnitude without limit as n becomes positively or negatively infinite. This is much like our experience in solving Schrödinger's equation directly: a difference equation like Eq. (7) is similar to a differential equation, A_n standing in a sense for the wave function as a function of a variable n, while $(A_{n+1}-A_n)$ is similar to a first derivative of A with respect to n, and $(A_{n+1}-2A_n+A_{n-1})$ is similar to a second derivative, so that Eq. (7) has an analogy to a second-order differential equation, just as Schrödinger's equation is. The choice of A_0 and A_1 corresponds to the choice of the initial value of the function and its slope in solving a second-order differential equation. We know that in solving Schrödinger's equation with arbitrary initial value and slope, we generally find that the function goes infinite at infinite values of the coordinate. By choosing the ratio of initial slope to function properly we can make the value of the function go to zero when the variable goes to plus infinity, or minus infinity, but not in general at both limits. Only by choosing the energy properly can the function be made to go to zero at both limits. In a similar way, we can choose the ratio A_1/A_0 to make A_n go to zero when n becomes positively infinite, or negatively infinite, but not both; only by choosing the energy, or ω_0, properly, can we make A_n go to zero at both limits, or secure a convergent series for Eq. (4). This is not hard to carry out in practice.

The net result, then, is that we can find ω_0 as a function of $\mathbf{k}_0$, and can find the A_n's for any one of the eigenvalues. If the amplitude V_1 of the sinusoidal oscillation is small, we can use approximations equivalent to the perturbation theory. These are the approximations usually made in the dynamical theory of x-ray diffraction, which as we shall see in the next section has a very close analogy to the problem we are discussing. They throw a good deal of light on this problem, and we shall now describe them.

If V_1 is zero, then the solution of Eq. (7) is trivial. We set $A_0=1$, all other A_n's equal to zero, and $\hbar^2\mathbf{k}_0^2/2m=\hbar\omega_0$ and see that all equations of the set given by Eq. (7) are satisfied. If V_1 is small, we may then assume that the A_n's will be small for $n\neq 0$, and the relation between ω_0 and k_0 will depart only slightly from the relation $\hbar^2\mathbf{k}_0^2/2m=\hbar\omega_0$, characteristic of the free particle. This equation states that the energy $\hbar\omega_0$ equals $1/2m$ times the square of the momentum $\hbar k_0$, or equals the ordinary kinetic energy. In this case we can use ordinary second-order perturbation theory, which leads to

$$\hbar\omega_0=\frac{\hbar^2\mathbf{k}_0^2}{2m}-\frac{V_1^2}{4}\left\{\frac{1}{(\hbar^2/2m)(\mathbf{k}_0+\mathbf{k}_1)^2-\hbar(\omega_0+\omega_1)}+\frac{1}{(\hbar^2/2m)(\mathbf{k}_0-\mathbf{k}_1)^2-\hbar(\omega_0-\omega_1)}\right\},\qquad (9)$$

$$A_{\pm1}=\frac{-V_1}{2}A_0\frac{1}{(\hbar^2/2m)(\mathbf{k}_0\pm\mathbf{k}_1)^2-\hbar(\omega_0\pm\omega_1)}.$$

This is correct up to terms in V_1^2 in the energy, and to terms in V_1 in the A's. We can show that A_n starts off with terms in $V_1^{|n|}$, so that to the first order of small quantities, the sinusoidal perturbation produces only first-order scattering, $n=\pm1$, but as we consider higher powers of V_1, we see that it produces nth-order scattering proportional to $V_1^{|n|}$.

Let us inquire, however, what happens when we approach the condition for Bragg scattering. In Sec. 1 we saw that this was the condition that $(\mathbf{k}_0+\mathbf{k}_1)^2$ should equal $\mathbf{k}_0^2$, or more precisely, in the case where ω_1 is not zero, it is the condition that $(\hbar^2/2m)\times(\mathbf{k}_0+\mathbf{k}_1)^2-\hbar\omega_1$ should equal $(\hbar^2/2m)\mathbf{k}_0^2$, which according to our earlier interpretation means that both waves, for $n=0$ and $n=1$, have the same diagonal matrix components of the Hamiltonian, so that we have a degenerate system. In this case, Eq. (9) would be inapplicable, for we should have

$$(\hbar^2/2m)(\mathbf{k}_0+\mathbf{k}_1)^2-\hbar(\omega_0+\omega_1)=0.\qquad (10)$$

One of the denominators would be zero, which shows that an expansion in powers of V_1 would diverge. We must then use the form of perturbation theory adapted for degenerate problems. We must assume that two of the A_n's, namely A_0 and A_1, are simultaneously large, and solve Eq. (7) under this assumption, treating all other A_n's as being negligibly small. That is, we have the equations

$$\begin{aligned}\left(\frac{\hbar^2}{2m}\mathbf{k}_0^2-\hbar\omega_0\right)A_0+\frac{V_1}{2}A_1&=0,\\ \left[\frac{\hbar^2}{2m}(\mathbf{k}_0+\mathbf{k}_1)^2-\hbar(\omega_0+\omega_1)\right]A_1+\frac{V_1}{2}A_0&=0.\end{aligned}\qquad (11)$$

It is a simple matter to solve these simultaneously; $\hbar\omega_0$ is given as the solution of a quadratic. In the special case where

$$\frac{\hbar^2}{2m}(\mathbf{k}_0+\mathbf{k}_1)^2-\hbar\omega_1=\frac{\hbar^2}{2m}\mathbf{k}_0^2, \tag{12}$$

or where the Bragg condition is met precisely, we find that the equations are satisfied if

$$\hbar\omega_0=\frac{\hbar^2}{2m}\mathbf{k}_0^2\pm\frac{V_1}{2},\quad A_1/A_0=\pm1, \tag{13}$$

so that in this case there are two values, not one, for ω_0 as a function of $\mathbf{k}_0$, and the scattered wave has the same amplitude as the incident wave.

To show the nature of the solution of the quadratic, we plot in Fig. 2 the value of $\hbar\omega_0$ as a function of the component of k_0 parallel to k_1, which we may take to be in the z direction, keeping the other components, k_{x0} and k_{y0}, constant. The figure is computed for the classical Bragg case where $\omega_1=0$. The Bragg condition of Eq. (12) is met when $k_{0z}=-k_1/2$. Similarly we have a Bragg reflection corresponding to $n=-1$ when $k_{0z}=k_1/2$. We see from Fig. 2 that at these points the curve of $\hbar\omega_0$ *vs* k_{0z} has a discontinuity. There is a range of energies, equal in magnitude to V_1, centered about the energy for which Bragg reflection occurs, for which the curve indicates no values of $\hbar\omega_0$. This is called an energy gap: it is a range of energies for which no solutions of Schrödinger's equation of the type given in Eq. (4) exist. Closer examination shows that within these energy gaps there are solutions of formally the same nature, but in which the propagation vector is complex, corresponding to a wave damped along the z direction.

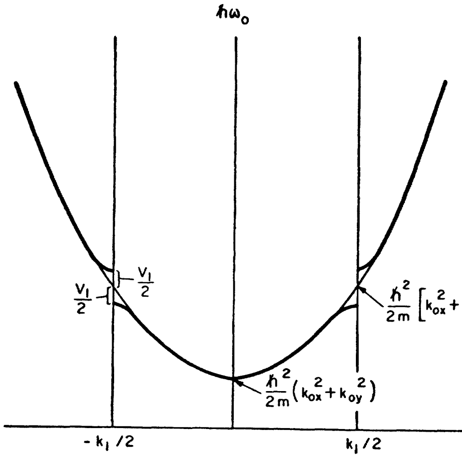

FIG. 2. Energy $\hbar\omega_0$ as function of z component of propagation vector, for electron wave scattered by sinusoidal potential.

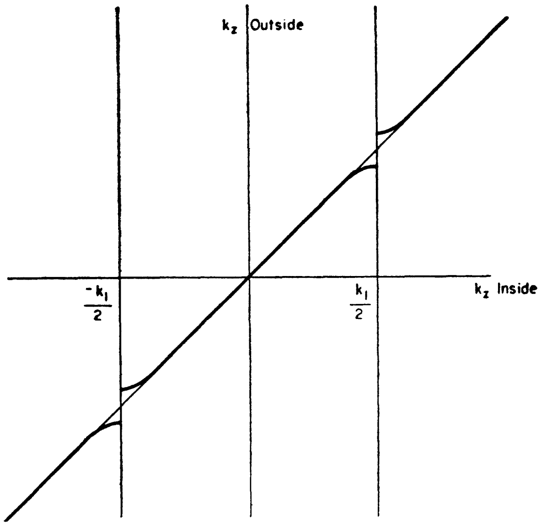

FIG. 3. Plot of k_z, z component of propagation vector outside crystal, as a function of k_z inside crystal.

Let us consider the physical meaning of this energy gap, and of the phenomena which occur in its immediate neighborhood. We can interpret the situation better if we consider a simple diffraction experiment. Let us assume a semi-infinite crystal, bounded by a plane parallel to the sound waves which are doing the scattering; that is, it is as if the plane shown in Fig. 1 as the plane of the wave front were also the surface of the crystal. Then in the empty space above this surface, we have an incident wave of electrons, indicated by the vector $\mathbf{k}_0$ in Fig. 1, and a scattered wave, indicated by the vector $\mathbf{k}_0+\mathbf{k}_1$. Schrödinger's equation in empty space is like Eq. (3) with omission of the term involving V_1; its solutions are plane waves, satisfying the relation $\hbar^2\mathbf{k}^2/2m=\hbar\omega$, characteristic of free electrons. The solution in the empty space must fit smoothly onto the solution within the crystal, satisfying the boundary conditions that the wave function, and its first derivative, must be continuous at the surface. This cannot be done, unless the components of propagation vector parallel to the surface, k_x and k_y, are continuous at the surface, or equal in the empty space and in the crystal. But there is no requirement that k_z be continuous, and in fact it is not. Instead, in the classical Bragg case where $\omega_1=0$, the condition is that each wave, both within and without the crystal, must have the same energy $\hbar\omega_0$, or the same frequency.

Now the relation between ω_0 and k_z is slightly different in the crystal from what it is in empty space. In the crystal, the relation is shown graphically in Fig. 2. In free space, the relation is $\hbar\omega=(\hbar^2/2m)(k_x^2+k_y^2+k_z^2)$, a parabola, shown by a light line in Fig. 2. We see, then, that in the immediate neighborhood of Bragg reflection, there is a difference between the relations inside and outside the crystal. We may convert Fig. 2 into a figure giving k_z outside the crystal, which equals $[(2m\omega/\hbar)-k_x^2-k_y^2]^{\frac{1}{2}}$, as a function of k_z inside, which is the k_{0z} of Fig. 2. When we do so, the parabola is converted into a straight line, as in Fig. 3, but the characteristic gap remains.

We see from Fig. 3 that there is a range of k_z outside the crystal over which we cannot join the incident and scattered waves outside onto progressive waves inside the crystal; we must instead use damped waves, as we have already indicated. Over this range, there is total reflection, the amplitude of the scattered wave equaling that of the incident wave. If we compute the amplitude of the scattered wave as a function of angle of incidence, in the neighborhood of the gap, we find that it is very small some distance from the gap, rapidly rises to equal the amplitude of the incident wave within the gap, and falls again on the other side.

We can easily compute the range of angle of incidence corresponding to this forbidden gap, under the conditions we have described. If θ is the angle of incidence, θ_B is the Bragg angle, then we find that the forbidden gap is encountered for angles within the range given by

$$\sin\theta=\left[\sin^2\theta_B\pm\frac{V_1}{2\hbar\omega_0}\right]^{\frac{1}{2}}. \tag{14}$$

If V_1 is of the order of magnitude of the Fourier components in the expansion of the potential arising from the regular crystalline arrangement of the solid, we find that these gaps are of very considerable breadth in angle; but if we are considering a thermal wave, they are very narrow.

The only gaps proportional to V_1 come at $\pm k_1/2$. However, if we carry out the solution of Eq. (7) to a higher approximation, we find that gaps appear at $nk_1/2$, where n is any integer. The width of the gap corresponding to n, or to an nth-order Bragg reflection, is represented by a power series in V_1, starting with the term in $V_1^{|n|}$. Thus, if V_1 is small, we need consider only the gap at $k_1/2$, and hence only first-order Bragg reflection. For larger V_1's, however, we must realize that a perfectly sinusoidal disturbance will produce higher order reflections. If we are considering thermal waves, these higher order reflections are ordinarily negligible; but this is by no means the case if we are dealing with scattering by the regular crystalline arrangement of the solid.

We have now investigated the general nature of Bragg scattering, showing that it arises over a range of angles about the Bragg angle, and is connected with a forbidden gap in the energy or frequency of the electron wave within the crystal, which results in total reflection of incident waves approaching the crystal within the forbidden range of angles. We shall next take up the corresponding problem in electromagnetic theory, the scattering of an electromagnetic wave by a sinusoidally varying refractive index, and shall show that though the details are different, the final result is substantially the same.

3. SCATTERING OF AN ELECTROMAGNETIC WAVE BY A SINUSOIDAL PERTURBATION

The electromagnetic problem is more complicated than the Schrödinger one on account of the polarization of the incident wave. Let the propagation vector of the scattering wave, $\mathbf{k}_1$, be in the z direction, and let the incident propagation vector $\mathbf{k}_0$ be in the yz plane. Then the electric vector $\mathbf{E}$ may be either in the yz plane, or may be along the x direction. We shall work through only the case where it is along x, in which case it can be handled like a scalar. The other case is somewhat more complicated, but leads to similar results.

We wish to solve Maxwell's equations, which we shall write in the mks system of units. These are

$$\nabla\times\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t},\quad \nabla\cdot\mathbf{B}+0,\quad \nabla\times\mathbf{H}=\frac{\partial\mathbf{D}}{\partial t},\quad \nabla\cdot D=0, \tag{15}$$

where we assume that the current density and charge density are zero. These equations must be supplemented by the relations $\mathbf{B}=\mu\mathbf{H}$, $\mathbf{D}=\epsilon\mathbf{E}$, where μ, ϵ, are the magnetic and dielectric constants. We shall assume that μ equals μ_0, the value characteristic of empty space, but that

$$\epsilon=\epsilon_0+\epsilon_1\cos(\omega_1 t-\mathbf{k}_1\cdot\mathbf{r}), \tag{16}$$

where ϵ_0 may be the value characteristic of empty space, or may be another constant value, while the sinusoidal term represents the traveling wave which is going to scatter the electromagnetic wave. As before, we could have $\omega_1=0$, in which case this represents a Fourier component of the dielectric effect arising from the periodic distribution of charge density in the crystal; or we could have a progressive sound wave, and in this case the sinusoidal term of Eq. (16) represents the perturbing effect of this sound wave on the dielectric constant, an effect which will be felt both in the visible and in the x-ray part of the spectrum.

We now derive a wave equation for $\mathbf{E}$, eliminating the magnetic vectors $\mathbf{B}$ and $\mathbf{H}$, by taking the curl of the first of Maxwell's equations in the usual way. We have

$$\nabla\times\nabla\times\mathbf{E}=-\mu_0\frac{\partial^2\mathbf{D}}{\partial t^2}=\nabla(\nabla\cdot\mathbf{E})-\nabla^2\mathbf{E}. \tag{17}$$

Since we are assuming that E is in the x direction, and since the dielectric constant does not depend on x, the equation $\nabla\cdot\mathbf{D}=0$ leads to $\nabla\cdot\mathbf{E}=0$, and Eq. (17) becomes

$$\nabla^2\mathbf{E}=\mu_0\frac{\partial^2\mathbf{D}}{\partial t^2}\cdot=\mu_0\frac{\partial^2}{\partial t^2}[\epsilon_0+\epsilon_1\cos(\omega_1 t-k_1 z)]\mathbf{E}. \tag{18}$$

To solve this equation, let us make an assumption for E equivalent to our assumption of Eq. (4). That is, we assume

$$E_x=\sum(n)A_n\exp-i[(\omega_0+n\omega_1)t-(\mathbf{k}_0+n\mathbf{k}_1)\cdot\mathbf{r}], \tag{19}$$

where as stated above $\mathbf{k}_1$ is along the z direction, $\mathbf{k}_0$ has only y and z components. We substitute the function (19) into Eq. (18), proceed as in the derivation of Eq. (7), and find that we have a solution of Maxwell's equations provided

$$\left[\epsilon_0-\frac{(\mathbf{k}_0+n\mathbf{k}_1)^2}{\mu_0(\omega_0+n\omega_1)^2}\right]A_n+\frac{\epsilon_1}{2}(A_{n-1}+A_{n+1})=0. \quad (20)$$

The general structure of this equation, and its method of solution, are like the earlier problem resulting in Eq. (7). If $\epsilon_1=0$, we have only a single wave, A_0, all the other A_n's being zero, and the relation between ω_0 and $\mathbf{k}_0$ is given by

$$\omega_0=\frac{1}{(\epsilon_0\mu_0)^{\frac{1}{2}}}|\mathbf{k}_0|, \quad (21)$$

which is in accordance with ordinary electromagnetic theory, in which $1/(\epsilon_0\mu_0)^{\frac{1}{2}}$ is the velocity of propagation of an electromagnetic wave. The condition for Bragg reflection, as before, is that two waves, say for $n=0$ and $n=1$, have identical diagonal matrix components. That is, we must have

$$\epsilon_0-\frac{\mathbf{k}_0^2}{\mu_0\omega_0^2}=\epsilon_0-\frac{(\mathbf{k}_0+\mathbf{k}_1)^2}{\mu_0(\omega_0+\omega_1)^2}. \quad (22)$$

In case $\omega_1=0$, this leads to $k_{0z}=-\frac{1}{2}k_{1z}$, as before. The curve of ω_0 as a function of k_{0z} resembles the linear curve of Fig. 3 rather than the parabola of Fig. 2. The energy or frequency gaps are interpreted in the same way as in the case of electron scattering. The gap comes between angles θ given by

$$\sin\theta=\left[\sin^2\theta_B\pm\frac{\epsilon_1}{2\epsilon_0}\right]^{\frac{1}{2}} \quad (23)$$

similar to Eq. (14).

The treatment which we have given is equivalent to the standard treatment of the dynamical theory of x-ray diffraction. If we have reflection of a wave from the surface of a crystal, as we discussed in detail for the electron case in Sec. 2, the reflection will be total in the narrow range of angles given by Eq. (23). The wave inside the crystal in this case has a complex propagation constant, and is damped as we go into the crystal. This is the phenomenon of primary extinction. We shall not go further into these details, which are familiar to the crystallographer, and which are described thoroughly, for instance, by James.[1] Our only purpose in bringing up these matters has been to show the general nature of Bragg reflection, and the similarity of the problems of electron scattering and the scattering of electromagnetic waves.

At least three phenomena form examples of the treatment which we have just given. First is ordinary x-ray diffraction. In this case $\omega_1=0$, and the sinusoidal wave of dielectric constant arises from the scattering of x-rays by the periodic distribution of charge in the atoms. The way in which this comes about is well known to crystallographers. If we are far from a region of anomalous dispersion, it is a familiar fact of wave mechanics, which can also be proved from the classical treatment of Thomson scattering, that the current density J produced in a sample of matter by an electromagnetic field whose vector potential is A equals $-(e^2/m)AN$, where e and m are the charge and mass of the electron, and N is the number of electrons per unit volume, a quantity varying from point to point within the atom. Now by the ordinary equations $\mathbf{E}=-\partial\mathbf{A}/\partial t$, and $\mathbf{J}=\partial\mathbf{P}/\partial t$, where $\mathbf{P}$ is the polarization vector, these relations are equivalent to

$$\frac{\partial^2\mathbf{P}}{\partial t^2}=-\frac{e^2}{m}\frac{\partial\mathbf{A}}{\partial t}N=\frac{e^2N}{m}\mathbf{E}, \quad (24)$$

from which, if we have a disturbance of angular frequency ω_0, we have $\partial^2\mathbf{P}/\partial t^2=-\omega_0^2\mathbf{P}$, and

$$\mathbf{P}=\frac{-e^2N}{\omega_0^2m}\mathbf{E}, \quad (25)$$

giving a polarization proportional to the electric field. In the mks units, $\mathbf{P}$ contributes directly to $\mathbf{D}$, without any additional factor, so that we have

$$\mathbf{D}=\left(\epsilon_0-\frac{e^2N}{\omega_0^2m}\right)\mathbf{E}. \quad (26)$$

If we make a Fourier analysis of the electron density function N, one term out of the Fourier analysis of $-e^2N/\omega_0^2m$ will give the term $\epsilon_1\cos(\mathbf{k}_1\cdot\mathbf{r})$ which we have encountered in Eq. (16). In this way we can evaluate the numerical values of the coefficients ϵ_1 in terms of the electronic form factor and structure factor. We then find the well-known relations for connecting the intensities of x-ray diffracted beams with the Fourier components of the charge density. The case where we are in a region of anomalous dispersion is more complicated, and we shall omit it in this discussion.

The second phenomenon which forms an example of this treatment is the scattering of a light wave by a sound wave. Since the index of refraction of a solid or liquid is a function of its density, a longitudinal wave of sound will produce a sinusoidal disturbance of the dielectric constant, and refractive index. As a result of this, light is scattered according to Bragg's law by a sound wave. This phenomenon, first discovered experimentally by Debye and Sears, is a striking and easily observed ultrasonic effect. It is often used to

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[1] R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, London, 1948).

measure the velocity of sound in the ultrasonic region. The sound is generated by an oscillator of known frequency, and the wavelength is determined from Bragg's law, so that the velocity can be found. The amplitude is ordinarily so great that a number of orders of diffraction are observed. Though the scattered radiation has a frequency $\omega_0+n\omega_1$, where we are considering nth-order scattering, the frequency ω_1 of the ultrasonic wave is so small compared to the optical frequency ω_0 that the frequency displacement is not observed.

The third phenomenon of the same sort is the scattering of x-rays by sound waves of very high frequency, which constitute the thermal energy of the crystal. This is the thermal diffuse scattering. As we shall see later, sound waves or elastic vibrations produce sinusoidal waves of polarization, and of effective dielectric constant, which can scatter waves of x-rays. We shall postpone further discussion of this case until we have considered the thermal vibrations of a crystal, so that we can go into the nature of the waves of polarization in detail.

4. ENERGY BANDS IN CRYSTALS

In most of the cases we are interested in, we have scattering not only by a single wave, but by a great number of them, with different amplitudes, propagation vectors, and frequencies. If the scattering by each one is small, so that it can be handled by first-order approximations, we can superpose the scattering arising from the various waves, and do not need to trouble with multiple scattering. This is the ordinary case with x-ray scattering. However, if the scattering by individual waves is greater, multiple scattering becomes important, and we must consider the whole problem of scattering by all the sinusoidal waves as a single problem. This is the case which we meet with electrons scattered by the sinusoidal potential present in a perfect crystal. It is the problem which leads to the theory of energy bands, the wave functions and energy levels of an electron in a periodic potential, and we shall now give a short sketch of that theory, to show how closely analogous it is to the questions which we have already been taking up.

Let us assume that we are dealing with a crystal in which the primitive translation vectors are $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$, and the corresponding reciprocal vectors are $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$, so that $\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij}$. Then if we set up a plane wave by the expression $\exp i\mathbf{K}_j\cdot\mathbf{r}$, where

$$\mathbf{K}_j=2\pi(h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3), \tag{27}$$

where h_1, h_2, h_3 are integers (equal to the ordinary Miller indices h, k, l), this plane wave will have the same value at corresponding points in each unit cell, or will be a periodic function which repeats in each unit cell. To see this, we note that if $\mathbf{r}$ is increased by $\mathbf{R}_i=m_1\mathbf{a}_1+m_2\mathbf{a}_2+m_3\mathbf{a}_3$, where m_1, m_2, m_3 are integers, we go from a point $\mathbf{r}$ to the corresponding point in another unit cell. In this case the exponential is multiplied by a factor $\exp i\mathbf{K}_j\cdot\mathbf{R}_i=\exp 2\pi i(m_1h_1+m_2h_2+m_3h_3)=1$, since the m's and h's are integers. The most general function which repeats in corresponding points of each unit cell is an arbitrary linear combination of all plane waves of this sort, with all sets of h's. The self-consistent potential energy of an electron in a crystal will have this property of periodicity. Hence we can write it in the form

$$V=\sum (\mathbf{K}_j)W(\mathbf{K}_j)\exp i(\mathbf{K}_j\cdot\mathbf{r}), \tag{28}$$

where K_j is given in Eq. (27), and where the summation over $\mathbf{K}_j$ is a summation over all sets of integers h_1, h_2, h_3. The amplitudes $W(\mathbf{K}_j)$ must satisfy the condition that $W(-\mathbf{K}_j)$ is the complex conjugate of $W(\mathbf{K}_j)$ in order that the potential energy may be real.

We now set up the Schrödinger equation of the problem, analogous to Eq. (3), and try to get a solution of the form

$$\psi=\exp -iEt/\hbar\sum (\mathbf{K}_j)A(\mathbf{K}_j)\exp i(\mathbf{k}_0+\mathbf{K}_j)\cdot\mathbf{r}. \tag{29}$$

This is analogous to Eq. (4). In place of the time exponential $\exp -i(\omega_0+n\omega_1)t$ of Eq. (4), we have taken the single exponential $\exp -iEt/\hbar$, where E is the energy, since ω_1 is zero in this case. The plane waves whose space dependence is given by $\exp i(\mathbf{k}_0+\mathbf{K}_j)\cdot\mathbf{r}$ represent all scattered waves, of all orders, scattered by all Fourier components of the potential. We substitute this expression in the Schrödinger equation arising from the potential energy of Eq. (28), proceed as in the derivation of Eq. (7), and find

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}_0+\mathbf{K}_1)^2-E\right]A(\mathbf{K}_1)+\sum (\mathbf{K}_j)W(\mathbf{K}_j)A(\mathbf{K}_i-\mathbf{K}_j)=0. \tag{30}$$

If Eq. (30) is satisfied, then the function of Eq. (29) forms an exact solution of Schrödinger's equation for the periodic potential problem.

As in the preceding cases, we can start a discussion of Eq. (30) by using perturbation methods. If all the coefficients $W(\mathbf{K}_j)$ are negligible [aside from $W(0)$, which represents the average potential energy through the crystal], we can use a single plane wave, $A(0)$, whose energy will be given by $E=(\hbar^2/2m)(\mathbf{k}_0^2)+W(0)$. If we are in the neighborhood of a Bragg reflection, and the $W(\mathbf{K}_j)$'s are small enough to disregard multiple

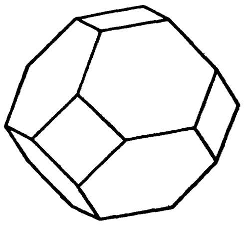

FIG. 4. Central Brillouin zone for the face-centered cubic lattice.

scattering, we may consider only the incident and the scattered wave. Thus, if there is a vector $\mathbf{K}_1$ such that $(\mathbf{k}_0+\mathbf{K}_1)^2$ is approximately equal to $\mathbf{k}_0^2$, just two waves, corresponding to $\mathbf{K}_i=0$ and $\mathbf{K}_i=\mathbf{K}_1$, will have appreciable amplitudes, and we have the equations

$$\left(\frac{\hbar^2}{2m}\mathbf{k}_0^2+W(0)-E\right)A(0)+W(-\mathbf{K}_1)A(\mathbf{K}_1)=0$$

$$\left(\frac{\hbar^2}{2m}(\mathbf{k}_0+\mathbf{K}_1)^2+W(0)-E\right)A(\mathbf{K}_1)+W(\mathbf{K}_1)A(0)=0, \quad (31)$$

analogous to Eq. (11), and leading in an exactly similar way to Bragg reflection. We see, then, that we shall find Bragg reflection if the propagation vector of the incident wave, drawn out from the origin in k space, terminates on a plane which is the perpendicular bisector of the vector $-\mathbf{K}_1$. This is the origin of the famous construction of Brillouin, leading to the concept of the Brillouin zones.

It occurred to Brillouin to take a reciprocal lattice, draw all the vectors $\mathbf{K}_i$ leading from the origin to all lattice points, set up the planes forming the perpendicular bisectors of these vectors, and examine the resulting construction. Diagrams indicating the results, for the two-dimensional case, are very familiar. If we find the energy E as a function of $\mathbf{k}_0$, where $\mathbf{k}_0$ can take on any value, we expect to find that there is a discontinuity like that shown in Fig. 2 when we cross any one of these planes. First we shall fix our attention on that part of reciprocal space enclosed by those planes closest to the origin. This is called the central Brillouin zone. In simple cases it has the form of a regular polyhedron. Thus, in Fig. 4, we show the central Brillouin zone for the face-centered cubic lattice. This central Brillouin zone for any type of lattice contains all those parts of reciprocal space which are closer to the origin than to any other lattice point, since it extends out to those planes which are equally far from the origin and from another lattice point. Hence if we locate a similar polyhedron centered on each lattice point of the reciprocal lattice, they will just touch and fill all space. This shows us immediately that such a zone must have the same volume as a unit cell in reciprocal space, and for many purposes it is convenient to use the central Brillouin zone in place of such a unit cell.

If we assume that all matrix components $W(\mathbf{K}_i)$ of the periodic potential are very small, the energy will be given approximately by $E=\hbar^2\mathbf{k}_0^2/2m+W(0)$, constant on spheres in k space or reciprocal space, but with perturbations like that shown in Fig. 2 on each of the planes given by Brillouin's construction, and in particular at the surface of the first Brillouin zone. Brillouin considered not only this first zone, but also further zones, which he made up by combining segments enclosed by planes further from the origin. Before considering these, however, there is a feature of Eq. (30) which we should consider.

This equation, as we have already pointed out, is an eigenvalue problem: if we fix $\mathbf{k}_0$, it allows us to determine the energy E, in order to have coefficients $A(\mathbf{K}_j)$ which will result in the series of Eq. (29) being convergent. But now let us point out a feature which we have not emphasized previously. We can add any lattice vector $\mathbf{K}_s$ of the reciprocal lattice to $\mathbf{k}_0$, without changing the results of the solution of Eq. (30), except in a purely formal way. Thus, the wave function for a propagation vector $\mathbf{k}_0+\mathbf{K}_s$, according to Eq. (29), may be written as

$$\psi=\exp-iEt/\hbar\sum(\mathbf{K}_j)A(\mathbf{K}_j)\exp i(\mathbf{k}_0+\mathbf{K}_s+\mathbf{K}_j)\cdot\mathbf{r}. \quad (32)$$

Let us however define $\mathbf{K}_s+\mathbf{K}_j$ as $\mathbf{K}_j'$, and let $A(\mathbf{K}_j)$ be rewritten in the form $A'(\mathbf{K}_j')$. Then Eq. (32) becomes

$$\psi=\exp-iEt/\hbar\sum(\mathbf{K}_j')A'(\mathbf{K}_j')\exp i(\mathbf{k}_0+\mathbf{K}_j')\cdot\mathbf{r}. \quad (33)$$

This has the same form as Eq. (29), except for the primes. When we substitute in Schrödinger's equation, we find

$$\left[\frac{\hbar^2}{2m}(\mathbf{k}_0+\mathbf{K}_i')^2-E\right]A'(\mathbf{K}_i')+\sum(\mathbf{K}_j)A'(\mathbf{K}_i'-\mathbf{K}_j)=0, \quad (34)$$

which has the same form as Eq. (30), except for the primes. Hence the secular equation arising from Eq. (34) must have the same eigenvalues as Eq. (30), showing that the energies associated with the propagation vector $\mathbf{k}_0+\mathbf{K}_s$ are identical with those associated with $\mathbf{k}_0$, and furthermore the $A'(\mathbf{K}_i')$ values found from Eq. (34) must be identical with the $A(\mathbf{K}_i)$'s found from Eq. (30), so that the wave function derived from Eq. (33) must be identical with that found from Eq. (29). In other words, the eigenvalues and eigenfunctions of the problem are periodic functions of $\mathbf{k}_0$, repeating at equivalent points in each unit cell of the reciprocal lattice.

We can understand this periodic behavior from the one-dimensional case. If the potential energy is a periodic function of x, the energy as a function of k_0 will have a form similar to that of Fig. 2, with a break at each of the points $nk_1/2$, corresponding to the nth-order Bragg reflections. The central Brillouin zone in this case reduces to the interval along the k axis between $-k_1/2$ and $k_1/2$, extending out from the origin to the first break in each direction. This interval, of k_1, is the fundamental translation in the reciprocal of k space, corresponding to a unit cell in the reciprocal lattice. The energy must then repeat in each such region; and to secure this, we show in Fig. 5 the figure similar to Fig. 2, but repeated periodically in each equivalent region. We see that the curve of E *vs* k_0 consists of an infinite number of branches, each a periodic function of k_0 with period k_1 (and also each an

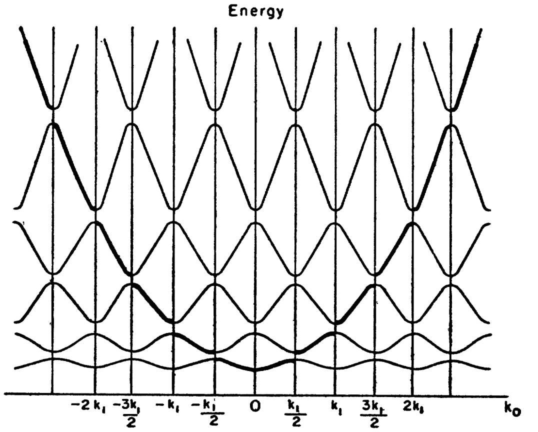

FIG. 5. Energy as function of propagation constant k_0, in a one-dimensional periodic lattice, showing periodicity of energy curves.

even function of k_0, having identical values for equal positive and negative values of k_0). These are the so-called energy bands.

For any value of k_0, we now see that we have an infinite number of eigenvalues. This is natural, for the secular equation arising from Eq. (30) comes from a determinant with an infinite number of rows and columns, and hence having an infinite number of roots. Furthermore, we may limit k_0 to the central Brillouin zone, or to the range between $-k_1/2$ and $k_1/2$ in Fig. 5, and get all possible eigenvalues, and hence all possible eigenfunctions. This is not the procedure which Brillouin used. In Fig. 5, he would have considered only that single eigenvalue for each value of k_0, indicated by the heavily drawn portion of the curve, which departs only slightly from the parabolic curve $E=\hbar^2k_0/2m+W(0)$, which represents the energy in the absence of perturbations. In the central Brillouin zone, for k_0 between $-k_1/2$ and $k_1/2$, he would have used the lowest curve in Fig. 5; the second Brillouin zone in this case consists of the two ranges, from $-k_1$ to $-k_1/2$ and from $k_1/2$ to k_1, and here he would have used the second lowest curve; and so on. Such a construction, using many Brillouin zones built up from segments of reciprocal space, becomes very complicated in the three-dimensional case, but it is convenient when the perturbations are small, and the energy does not deviate far from the parabolic value. However, we can equally well use only the central Brillouin zone, and consider all the infinitely many values of energy within this region.

When the potential energy components $W(\mathbf{K}_j)$ have the magnitudes actually found in a crystal, this latter scheme, in which only the central Brillouin zone is used, becomes much more natural to use, because the departure from the parabolic energy becomes so great that there is no longer any point in trying to show a parallelism between the true energy and the parabolic value. For a given k_0 within the central Brillouin zone, we have, as we have mentioned earlier, an infinite number of eigenvalues. The lowest eigenvalue for each k_0 will form a smoothly varying function of $\mathbf{k}_0$, and these energies form the lowest energy band. Similarly the second lowest eigenvalues for each $\mathbf{k}_0$ form the second energy band, and so on. We may denote the energies as $E_\beta(\mathbf{k}_0)$, where $\beta=1$ for the lowest band, 2 for the next, etc; and we may denote the corresponding eigenfunctions as $\psi_\beta(\mathbf{k}_0,\mathbf{r})$.

There is one point of importance, in understanding these energy bands. If we have a finite crystal, rather than an infinite one, all values of $\mathbf{k}_0$ are not allowed. Rather, there are boundary conditions at the surface of the crystal, which limit k_0 to discrete values, subject to the restriction that the electronic wave functions must go to zero at the boundary of the crystal, so that the dimensions of the crystal must be integral numbers of half wavelengths, or equivalent conditions. The allowed values of $\mathbf{k}_0$ are nevertheless very close together, and the number of allowed values of $\mathbf{k}_0$ equals the number of unit cells in the crystal, an enormous value. These allowed $\mathbf{k}_0$'s are spaced with uniform density in the Brillouin zone. This existence of a discrete set of $\mathbf{k}_0$'s is of great importance in understanding the role of Pauli's exclusion principle in energy-band theory. The wave function associated with a given k_0, and a given energy band, forms a distinct wave function in the sense of Pauli's principle. Hence each such wave function can hold only one electron of each spin, which means that each energy band can hold one electron of each spin per unit cell of the crystal.

From Eq. (29), we can deduce one very important property of the wave functions. We can rewrite Eq. (29) in the form

$$\psi=\exp-i(\omega_0t-\mathbf{k}_0\cdot\mathbf{r})\sum(\mathbf{K}_j)A(\mathbf{K}_j)\exp i\mathbf{K}_j\cdot\mathbf{r}, \quad (35)$$

where $\hbar\omega_0=E$. That is, the wave function can be rewritten as the plane wave $\exp-i(\omega_0t-\mathbf{k}_0\cdot\mathbf{r})$, multiplied by the summation, which from its form must be a periodic function of $\mathbf{r}$, repeating its value at corresponding points of each unit cell in the crystal. This result was pointed out by Bloch very early in the development of wave mechanics. There is another way in which the same result can be stated: if $\mathbf{r}$ increases by one of the vectors $\mathbf{R}_i$, pointing from one point in the crystal to the corresponding point in another unit cell, the wave function is multiplied by a factor $\exp\times i\mathbf{k}_0\cdot\mathbf{R}_i$, as we can see from Eq. (29) (since each of the products $\mathbf{K}_j\cdot\mathbf{R}_i$ equals 2π times an integer). This means that apart from this factor, which is a complex number of unit magnitude, the wave function will have an identical form in each unit cell, and the product $\psi^*\psi$, for one of the wave functions, will have identical values in each unit cell. That means that the charge density arising from any wave function of the type of Eq. (29), often called a crystal wave function, will be identical at corresponding points in each unit cell.

We can now understand the way in which the energy band theory is used in applying Hartree's self-consistent field method to a crystal. We start with a periodic potential energy of the form given in Eq. (28), representing an approximation to the potential energy arising from the nuclei and all other electrons of the crystal aside from the one being considered. We solve Schrödinger's equation for this potential, and find the resulting crystal wave functions and energy bands. We assume that enough of the energy levels are filled, starting from the bottom, to accommodate all electrons of the crystal, allowing one of each spin in each crystal wave function, or one of each spin per unit cell in each energy band. When we have accounted for all the electrons, we take the corresponding crystal wave functions $\psi_\beta(\mathbf{k},\mathbf{r})$, find the resulting charge densities $\psi^*\psi$, add these for all occupied energy bands, getting a corresponding charge density for all electrons of the crystal, determine the electrostatic potential arising from this charge density plus that of the nuclei, and apply a condition of self-consistency, namely that the final potential must equal the initial potential. In doing this properly, we should correct for exchange, obtaining the Hartree-Fock equations rather than the simpler Hartree equations, and automatically correcting for the fact that an electron does not act electrostatically on itself. This whole program has never been carried through completely for any crystal, but fairly good approximations to it are used in many energy-band calculations.

Now we consider the energy bands more in detail, and can understand why the deviation from the free electron case is so great that the assumption of small $W(\mathbf{K}_j)$'s is not valid. The lowest energy band in any crystal will arise from the K level in the heaviest atom in the crystal, next bands will arise from the L levels, and so on. The energies of these inner electrons will not depend on the fact that the atoms are bound in a crystal; in other words, the energies will not depend appreciably on $\mathbf{k}$. It is not until we come to the outermost electrons of the atom that we find energy bands in which the dependence of the energy on $\mathbf{k}$ is appreciable. Above the occupied bands we have an infinite number of higher bands, which could be occupied by excited electrons, but are empty in the ground state of the system. If the electrons are just sufficient to fill certain bands, leaving an unoccupied gap above them, and empty bands above that, we have an insulator or semiconductor, in which case the highest occupied band is called the valence band, and the lowest unoccupied band is the conduction band. If on the contrary the topmost occupied band is only partially filled, we have a metal. Most of our interest in the study of energy bands is centered around these highest occupied bands, for they are the ones taking part in electrical conductivity, optical absorption, and other important solid-state phenomena.

The wave functions ψ for the lowest bands, arising from the K and L shells of the atoms, look almost exactly like the corresponding atomic wave functions, except that they must repeat in each unit cell, and be multiplied by the factor $\exp i\mathbf{k}\cdot\mathbf{R}_i$ in going from one unit cell to another distant by the vector $\mathbf{R}_i$. A very good approximation to such a wave function is provided by a so-called Bloch sum, a linear combination of the corresponding atomic orbitals which has the proper symmetry. If $a(\mathbf{r})$ is an atomic wave function of the suitable type, located in the unit cell at the origin, then the Bloch sum formed from this atomic orbital is $\sum(\mathbf{R}_i)\exp i\mathbf{k}\cdot\mathbf{R}_i a(\mathbf{r}-\mathbf{R}_i)$, where $a(\mathbf{r}-\mathbf{R}_i)$ is a corresponding atomic function located in the unit cell at vector position $\mathbf{R}_i$. Once we realize that the functions ψ can have forms like this, we see why a free-electron approximation is not valid. The expansion of Eq. (29) is a Fourier expansion of such a wave function, and it must have Fourier components of appreciable magnitudes of wavelengths as short as the smallest features present in the wave function; that is, as short as the dimensions of the K wave functions. Such a slowly convergent Fourier expansion means that in Eq. (30), the interaction of very large numbers of Fourier coefficients is essential if we are going to get a good solution. As a rule of thumb, Fourier components consisting of plane waves which, if taken by themselves, would correspond to free electrons of kinetic energy as large as the ionization potential of the heaviest atom in the crystal will occur in the expansion of Eq. (29) with appreciable amplitudes. This holds, not only for the crystal wave functions arising from the K and L electrons, but for all crystal wave functions up to very high energies. In other words, a simple expansion of the wave function in which we treat the perturbations from the free-electron case as small is not appropriate even if we are dealing with energies as large as the ionization potential of the heaviest atom in the crystal.

We must realize that the energy band theory, with essentially identical mathematical features, enters in two quite different ways into solid-state theory. First, we have the applications which we have just been sketching, in which we are dealing with the occupied or slightly excited energy bands, and hence the normal constitution of a crystal, or those electrons which are excited by thermal action, optical absorption, electrical conductivity, and so on. Secondly, we may have fast electrons traversing a crystal, as in the case where we are dealing with the problem of electron diffraction. From what we have said in the preceding paragraph, we can see that the standard approximations made in treating electron diffraction, namely, that we can handle each Bragg reflection independently of the others, and treat it as a small perturbation, will not be valid even if the kinetic energy of the electron is as great as the ionization energy of the heaviest atom in the crystal; one must go considerably above this energy to have it approximately valid. Consequently electron diffraction by slow electrons is a much more complicated process than x-ray diffraction or electron diffraction by fast electrons, and it should properly be handled as a branch of energy band theory. Unfortunately such treatments of the problem have not been given. Again, the fine structure of x-ray absorption edges deals with the transitions of electrons from the bound levels to the energy bands some hundreds of electron volts above the top of the occupied bands. This can only be handled theoretically by means of a thorough study of these excited energy bands, and such a thorough study has never been made. The existing theoretical treatments of the fine structure of absorption edges are based on very inadequate theories of the excited energy bands.

There is one feature of energy bands which is of great importance in their detailed treatment. This is the question of their symmetry properties. We can illustrate these properties by a simple example. Let us consider a cubic crystal, and the energy band arising from an atomic p state of an atom located at a symmetry point of the crystal, so that this atom is in an environment of cubic symmetry. We remember that the p state is threefold degenerate (if we disregard the electron spin), and that the three atomic orbitals can be expressed as $xf(r)$, $yf(r)$, $zf(r)$, where $f(r)$ is a function of the radial distance from the nucleus. These may be denoted as p_x, p_y, p_z. We can form Bloch sums from each of these types of atomic function; in general, a linear combination of these three Bloch sums must be used to approximate a solution of Schrödinger's equation. However, for the case where the propagation vector $\mathbf{k}$ is along the x direction, each Bloch sum by itself is a good approximation, and there are no interactions between them. The sum formed from p_x is in a sense a longitudinal wave, and the two formed from p_y and p_z are in a sense transverse waves. By symmetry one can show that the two sums formed from p_y and p_z functions will be degenerate with each other, whereas that formed from p_x will have a different energy. At $k=0$, where there is no wave propagation at all, all three states will be degenerate with each other. Thus, we shall find energy bands which are threefold degenerate at $k=0$, and which split into a single and a doubly degenerate state as we go out along the x axis, or the 100 direction. Similarly in the 111 direction such a state will split into a single and a doubly degenerate state. On the other hand, in an arbitrary direction, the degeneracy will be removed. Here we have three separate bands, capable of holding three electrons of each spin per unit cell, which nevertheless must touch on account of symmetry at $k=0$. They are referred to as degenerate bands.

The problem of indicating graphically the energy in an energy band as a function of k is obviously difficult, since we are dealing with a three-dimensional problem. To show the results fairly adequately, the common procedure is to show the energy along one or more lines in k space. Thus, for example, one shows the energy first along the x axis in k space, the 100 direction (in a cubic crystal), from the origin of the Brillouin zone out to its boundary, corresponding to the point $k_1/2$ in our one-dimensional case. One also shows the energy along a line in the 111 direction in k space, again from the origin to the boundary of the zone. Finally one can join up these two points on the boundary by a path crossing the various faces of the Brillouin zone and can give the energy as a function of position along this path. In this way a fairly adequate picture of the energy as a function of k is given.

We have tried in this section to give something of an introduction to the theory of energy bands, enough to serve as a preliminary to the reading of more detailed papers, and at the same time enough to show the close connection between this theory and the theories of Bragg scattering which we have outlined in Secs. 2 and 3 of the present paper. Now we shall go on to quite a different problem, namely, the elastic vibrations of crystals, and shall show that in spite of the differences still there are important resemblances. Here again we meet the Brillouin zones, and the frequency of vibration (which for harmonic oscillators is proportional to the energy of the phonon) is given as a function of k throughout the zone. We shall consider this problem in the next section; and then we shall be prepared to go on to the interactions between thermal waves and electronic or electromagnetic waves, which we have already mentioned in a descriptive way.

5. THERMAL VIBRATIONS OF A CRYSTAL

The fundamental theory of the vibrations of a crystal was set up by Born and von Karman many years ago. Its main features can be presented in very simple form. We proceed by classical mechanics to set up Newton's equations of motion for the elastic vibrations of the atoms of a crystal, acting on each other by linear restoring forces. Let us assume that each unit cell of the crystal contains g atoms, and that the undisplaced position of the sth atom in the ith unit cell is $\boldsymbol{\rho}_s+\mathbf{R}_i$, where $\boldsymbol{\rho}_s$ is the vector displacement of the atom from the corner of the unit cell, $\mathbf{R}_i$ is the vector from the origin of the coordinates to the corresponding point in the ith unit cell. When the atoms are at these undisplaced positions, it is assumed that they are all in equilibrium. However, we consider the case where the sth atom in the ith cell is displaced from its equilibrium position by a small amount $\mathbf{u}(s,i)$. Then we assume that there will be a force acting on each atom, which is a linear combination of the displacements of all atoms. The ordinary linear theory of vibrations disregards the terms in the force involving higher powers than the first of the displacements.

We must, then, express the fact that each of the three vector components $\mathbf{u}(s,i)$ is a linear combination of the three vector components of the $\mathbf{u}(t,j)$'s of all other atoms in the crystal. That is, we have

$$F_p(s,i)=\sum\ (q,t,j)C_{pq}(s,t,\mathbf{R}_j-\mathbf{R}_i)u_q(t,j). \qquad (36)$$

Here the subscripts p, q take on three values, corresponding to x, y, and z components. $F_p(s,i)$ is the p component of force acting on the sth atom in the unit cell at $\mathbf{R}_i$, and $u_q(t,j)$ is the q component of displacement of the tth atom in the unit cell at $\mathbf{R}_j$. The coefficient $C_{pq}(s,t,\ \mathbf{R}_j-\mathbf{R}_i)$ in the linear relation depends on the components p and q, on the question of which atoms in the two unit cells are being considered (the indices s, t), and on the vector displacement $\mathbf{R}_j-\mathbf{R}_i$ between the two unit cells, but not on the absolute position in the crystal of each of the unit cells, on account of the periodicity of the crystal. There is no implication in Eq. (36) that the forces are derived from central forces between atoms, or any such restriction.

We can now set up Newton's second law for the motion of the atoms. If m_s represents the mass of the sth atom in the unit cell, we have

$$m_s\frac{d^2u_p}{dt^2}(s,i)=F_p(s,i)$$
$$=\sum(q,t,j)C_{pq}(s,t,\ \mathbf{R}_j-\mathbf{R}_i)u_q(t,j). \quad (37)$$

We shall try to satisfy these equations by assuming that the solution consists of an elastic wave, in which the displacements are given by

$$u_p(s,i)=w_p(s)\ \exp i(\omega t-\mathbf{k}\cdot\mathbf{R}_i), \quad (38)$$

where $w_p(s)$, ω are to be found as functions of the propagation constant $\mathbf{k}$. If we insert this assumption in Eq. (37), that equation reduces to

$$-m_s\omega^2w_p(s)=\sum(q,t,v)C_{pq}(s,t,\mathbf{R}_v)\exp-i\mathbf{k}\cdot\mathbf{R}_vw_q(t), \quad (39)$$

where we have replaced $\mathbf{R}_j-\mathbf{R}_i$ by $\mathbf{R}_v$. In Eq. (39) we have $3g$ simultaneous equations for the $3g$ displacements of the g atoms in a unit cell. These are linear homogeneous equations for the constant quantities $w_p(s)$, where p goes through the three indices x, y, z and s goes from 1 to g, running over the atoms in the unit cell. We know that such simultaneous equations will not have a nonvanishing solution unless the determinant of the coefficients vanishes. This is an equation of the $3g$th degree determining ω^2, in terms of $\mathbf{k}$. It is a secular equation similar to those of quantum mechanics, but on account of the finite number of atoms in the unit cell, it is of finite order, and with digital computers it can be solved exactly, if we know the C's. Once we have found the frequency, we can find the w's. We shall then find the frequencies, and atomic displacements, for $3g$ normal modes of vibration of the crystal, for each value of $\mathbf{k}$.

We note that the displacements defined by Eq. (38) are unchanged if the propagation vector $\mathbf{k}$ is increased by one of the translation vectors $\mathbf{K}_i$ in the reciprocal lattice defined by Eq. (27); for $\mathbf{K}_j\cdot\mathbf{R}_i$ equals 2π times an integer. Hence all distinct solutions will be found if $\mathbf{k}$ is allowed to run through a unit cell of reciprocal space. We may equally well let $\mathbf{k}$ run through the central Brillouin zone, since this is equivalent to a unit cell, and if we choose, we may interpret ω^2 as being a periodic function of position in K space, just as the energy is in the problem of energy bands. We can plot ω as a function of $\mathbf{k}$, by using the same sort of device that we use in plotting energy bands, giving ω along certain lines in $\mathbf{k}$ space, such as the 100 or 111 directions, passing from the center to the edge of the Brillouin zone. We shall have $3g$ separate curves, which in some cases can show degeneracy at certain points in $\mathbf{k}$ space, in a way entirely analogous to the energy bands. In particular, we find that for three of the curves, called the acoustical branch, ω goes to zero as $\mathbf{k}$ goes to zero, which is the reason why this is called the acoustical branch, since it leads to vibrations of acoustical frequency in the limit of long wavelengths (small $\mathbf{k}$). These three modes are degenerate at $\mathbf{k}=0$, each having zero frequency. In a cubic crystal, and for propagation along the 100 direction, the degeneracy will split for $\mathbf{k}\neq0$, in such a way that we have one longitudinal wave, and a doubly degenerate transverse wave, for which the oscillation could be either along y or z. In general directions of propagation, the degeneracy is entirely removed, and the oscillations cannot be described as either longitudinal or transverse. In addition to the acoustical modes, the other $3g-3$ modes have frequencies which never go to zero, but lie in the infrared region of the spectrum, and consequently are called optical modes.

If we have a finite crystal, then just as in the energy band case the waves of Eq. (38) must satisfy certain boundary conditions, as a result of which only discrete values of $\mathbf{k}$ lead to allowed vibrations, the normal modes of vibration. As before, these $\mathbf{k}$'s are uniformly distributed through the Brillouin zone, and are N in number, if there are N unit cells in the crystal. Thus the total number of modes is $3Ng$. In the theory of specific heat, each of these normal modes is treated as an ideal linear oscillator, so that at high temperatures it has an average energy of kT, where k is Boltzmann's constant, T the absolute temperature, leading to a heat capacity of $3Ngk$, which is the familiar law of Dulong and Petit. At lower temperatures, we must treat the vibrational energy of each oscillator by the quantum theory, and are led to the sort of treatment of specific heat given by Blackman; the Debye theory forms a very crude first approximation to this treatment.

There has been a good deal of treatment of the vibrations of crystals in the literature; but most of it is based on very arbitrary assumptions regarding the coefficients $C_{pq}(s,t,\mathbf{R}_v)$, which are really independent microscopic elastic constants, subject only to certain interrelations on account of crystal symmetry. There are an infinite number of such constants, though there is every reason to think that they decrease rapidly to zero as the two atoms concerned get further and further apart, so that in practice one need use only a small number of such constants. The principal ways of determining these constants experimentally are by the use of thermal diffuse scattering of x-rays, or by the inelastic scattering of neutrons, as we shall describe later. The macroscopic elastic constants can be determined as linear combinations of the C's, since in the limit of low frequencies the vibrations approach ordinary acoustic oscillations, which can be described in terms of classical elasticity theory. Many workers have tried to work backward, from the macroscopic elastic constants, to deduce the C's, and hence set up Eq. (39) and determine the vibrational frequencies. This in principle is impossible, however, for the number of macroscopic elastic constants is very small, and we have theoretically an infinite number of C's. The only proper procedure seems to be to find the C's, as we have mentioned, by thermal diffuse scattering of x-rays or by neutron scattering, and then to test these C's by computing the macroscopic elastic constants from them. In cases where such tests have been carried out, they have given a satisfactory check with experiment.

The theory of elastic vibrations as we have presented it assumes only linear restoring forces between the atoms. Of course, this forms merely the first term in a power series expansion of the forces in terms of the displacements. Once the higher order terms are included, different elastic modes can no longer propagate independently of each other; there is rather an interaction between different waves. In other words, one elastic wave can scatter another. When it does so, we come back to the sort of problem which has been our main concern in this paper: either wave can be considered to undergo Bragg reflection by the other. Such scattering of one thermal wave by another is operating in the problem of thermal conductivity. Heat flows through a body in the form of elastic vibrations. These waves are scattered by other thermal waves, so that there is the equivalent of a thermal resistance. The well-known theory of thermal conductivity of Peierls is based on an analysis of this scattering. The reader will see from this that the departures from linearity in the elastic vibrations, which become particularly important at high temperatures, involve the same sort of problem which we have been considering. But such problems have not been by any means completely treated in actual crystals.

We have now presented the theory of the thermal vibrations of crystals in sufficient detail so that the reader will be able to understand the next problem which we shall take up, namely thermal scattering of x-rays or of electrons. This involves examining the way in which the thermal oscillations of a crystal introduce waves of dielectric constant (in the case of x-rays) or of electrostatic potential (in the case of electrons), capable of scattering x-rays or electron waves according to the principles taken up in Secs. 2 and 3.

6. SCATTERING OF X-RAYS BY THERMAL OSCILLATIONS

The treatment of the coherent scattering of x-rays by crystals is based on making a Fourier analysis of the electron density function, analyzing it into plane waves. By means of Eq. (26), we can convert this into an analysis of the dielectric constant into plane waves, and by the methods of Sec. 3 we can study the scattering of an electromagnetic wave by such plane waves. The scattering is weak enough so that each plane wave can be handled separately, so that we can associate the scattering of an incident wave of x-rays of monochromatic wavelength, through a given scattering angle, uniquely with a single Fourier component of the electron density. By the methods of Sec. 3 we can find the amount of scattering produced by a wave of given amplitude, in an infinite perfect crystal. The amplitude of the scattered wave is proportional to the amplitude of the wave of dielectric constant, or of electron density, doing the scattering. Of course, the problem of scattering by real crystals of finite extent is much more complicated than this; when proper account is taken of the size of the crystal, and its mosaic structure, it is well known that the final scattered intensity is proportional to the square of the corresponding amplitude of the wave of electron density. We shall not go through any of this elaborate theory, but shall merely use the fact that the coherent scattering from a crystal in a given direction is uniquely related to the amplitude of the Fourier component of electron density, arising from the propagation constant $\mathbf{k}_1$ which must be added to the propagation constant $\mathbf{k}_0$ of the incident x-rays to yield the propagation constant $\mathbf{k}_0+\mathbf{k}_1$ of the scattered x-rays, according to Fig. 2. The magnitude of this vector $\mathbf{k}_1$, as we see from the derivation of Eq. (1), is

$$|k_1| = 4\pi \sin\theta/\lambda, \tag{40}$$

where θ is the glancing angle of incidence, or 2θ is the scattering angle.

We now wish to consider the scattering by a crystal in which the atoms are undergoing thermal oscillation; and we see from the preceding paragraph that our problem is simply to carry through a Fourier analysis of the electronic charge density of the crystal, or its analysis into plane waves. Each such plane wave will scatter radiation according to the principles we have already considered. First we remind the reader of the well-known results of this Fourier analysis in the case of the undistorted crystal. To find the amplitude of the Fourier component of propagation constant $\mathbf{k}_1$ we multiply the charge density by $\exp-i\mathbf{k}_1\cdot\mathbf{r}$, and integrate over the crystal, multiplying by a suitable constant depending on the type of normalization we use. If we can approximate the charge distribution as the superposition of spherical distributions for each atom, as we can do to a good though not perfect approximation, the resulting integral can be written as a sum of terms, one for each atom. For the atom located at the vector position $\boldsymbol{\rho}_s+\mathbf{R}_i$ (as in Sec. 5), it is convenient to rewrite the exponential as $\exp-i\mathbf{k}_1\cdot(\boldsymbol{\rho}_s+\mathbf{R}_i)\exp-i\mathbf{k}_1\cdot(\mathbf{r}-\boldsymbol{\rho}_s-\mathbf{R}_i)$, in which the second factor now involves the vector distance from the nucleus of the atom considered. We multiply this latter factor by the charge density of the atom, and integrate, obtaining a result which is the atomic scattering factor f_s of the atom of the sth type, a function of the magnitude of k_1 only, or of $4\pi\sin\theta/\lambda$, according to Eq. (40). Since the nature of these atomic scattering factors is so well known, we shall not go further into their nature here.

Next we must sum over all atoms, and in doing this, we may sum separately over the index i involved in $\mathbf{R}_i$, and the index s involved in $\boldsymbol{\rho}_s$. As for the sum of the factor $\exp-i\mathbf{k}_1\cdot\mathbf{R}_i$, we are summing over the whole crystal, and we find as the crystal becomes larger and larger that the sum becomes smaller and smaller, unless $\mathbf{k}_1$ is very close to one of the vectors $\mathbf{K}_j$ defined in Eq. (27). If $\mathbf{k}_1$ exactly equals one of the $\mathbf{K}_j$'s, the sum is equal to the number of unit cells in the crystal. Since we are not concerning ourselves here with the problem of the finite crystal and its influence on the breadth of scattered beams, we shall merely assume that the sum is zero unless $\mathbf{k}_1$ precisely equals one of the $\mathbf{K}_j$'s, so that it can be characterized by the integers h_1, h_2, h_3. Then the summation over s becomes a summation of the factor $f_s\exp-i\mathbf{K}_j\cdot\boldsymbol{\rho}_s$ over the atoms of the unit cell, which is the structure factor

$$F(h_1,h_2,h_3)=\sum(s)f_s\exp-2\pi i(h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3)\cdot\boldsymbol{\rho}_s. \quad (41)$$

This quantity, then, is proportional to the amplitude of the plane wave of electronic charge density with propagation constant $\mathbf{K}_j$, and hence its square is proportional to the intensity of scattering from this plane wave in a real finite crystal. For the undistorted crystal we then have Fourier components of the charge density only for those propagation constants $\mathbf{k}_1$ which equal vectors $\mathbf{K}_j$ of the reciprocal lattice (the $\mathbf{K}$'s are actually 2π times the vectors in the reciprocal lattice).

Now our problem is to inquire how this situation is modified by thermal agitation. We may assume that the atom which would be located at $\boldsymbol{\rho}_s+\mathbf{R}_i$ in the undistorted crystal is displaced by an amount $\mathbf{u}(s,i)$, as in Sec. 5. If it is legitimate to write the charge density of each atom as a spherical distribution, it is equally legitimate to assume that when the atoms are displaced, their spherical distributions are rigidly displaced along with the nuclei. Neither of these assumptions is of course rigorously correct, but the errors of the assumptions are so small that extreme care is required even to detect them experimentally, so that the usual assumption of rigid displacement of the atoms is justified to a very good approximation, though it is not perfect. If we make this assumption, we can then again integrate first over the charge density of the atom s, i, obtaining the same atomic scattering factor f_s as before; and our problem is resolved into calculating the sum $\sum(s,i)f_s\exp-i\mathbf{k}_1\cdot[\boldsymbol{\rho}_s+\mathbf{R}_r+\mathbf{u}(s,i)]$. We must now investigate the nature of $\mathbf{u}(s,i)$, according to the methods of Sec. 5, so as to be able to evaluate this sum.

In Eq. (38) we have an expression for the displacements of the various atoms, provided we have one plane wave of thermal oscillation traversing the crystal. The general thermal oscillation is a superposition of all possible plane waves, with amplitudes which on the average are determined from statistical mechanics. To describe this mathematically, we need somewhat more notation than we have used. We have mentioned that for each value of $\mathbf{k}$, we have $3g$ normal modes of oscillation, where g is the number of atoms in the unit cell. Let these modes be denoted by an index f, which runs from 1 to $3g$, and by the value of $\mathbf{k}$, so that we may write the frequency of the mode as $\omega(f,\mathbf{k})$. In writing the displacement of an atom, analogously to Eq. (38), we should use a real function of time rather than the complex exponential of Eq. (38), since otherwise we shall get into trouble when we take the square of the displacement, as we must do. When we do this, we note that the quantity $w_p(s)$, the amplitude function for the pth component of the sth atom, will in general be a complex quantity, for different atoms in the unit cell will vibrate not only with different amplitude, but with different phase as well. If we write $w_p(s)$ as $W_p(s)\exp-i\alpha(s)$, where $W_p(s)$ is real, and α is a phase factor, the real part of Eq. (38) can be written in the form $W_p(s)\cos[\omega t-\mathbf{k}\cdot\mathbf{R}_i-\alpha(s)]$. We must really have indices f, $\mathbf{k}$ attached to the quantities $W_p(s)$ and $\alpha(s)$, as well as to ω. Furthermore, it is convenient to normalize the W_p's, and to have a separate amplitude for each plane wave. Thus, we shall write

$$\mathbf{u}(s,i)=\sum(f,\mathbf{k})A(f,\mathbf{k})\mathbf{W}(s,f,\mathbf{k}) \times\cos[\omega(f,\mathbf{k})t-\mathbf{k}\cdot\mathbf{R}_i-\alpha(s,f,\mathbf{k})]. \quad (42)$$

This equation gives the vector displacement $\mathbf{u}(s,i)$ of the sth atom in the ith unit cell. The summation over f and k is over the normal modes of vibration. The amplitude $A(f,k)$ is arbitrary. The quantity $\mathbf{W}(s,f,k)$ will be assumed to be normalized according to the rule

$$\sum(s,i)m_s[\mathbf{W}(s,f,k)]^2=1, \quad (43)$$

where the summation is over all atoms of the crystal, m_s is the mass of the sth atom in the unit cell and $[\mathbf{W}(s,f,k)]^2$ is the square of the magnitude of the vector. The phase $\alpha(s,f,\mathbf{k})$ is not determined by the normalization; the relative phases of vibration of the various atoms are uniquely fixed by the solution of Eq. (39), but we may assume an arbitrary additional phase associated with each normal mode.

Our problem now is to calculate the summation $\sum(s,i)f_s\exp-i\mathbf{k}_1\cdot[\boldsymbol{\rho}_s+\mathbf{R}_i+\mathbf{u}(s,i)]$, where f_s is the atomic scattering factor, and where $\mathbf{u}(s,i)$ is given by

Eq. (42). This can be rewritten in the form

$$\begin{aligned}&\sum(s,i)f_s \exp -i\mathbf{k}_1\cdot[\boldsymbol{\rho}_s+\mathbf{R}_i+\mathbf{u}(s,i)]\\&\quad=\sum(s,i)f_s \exp -i\mathbf{k}_1\cdot(\boldsymbol{\rho}_s+\mathbf{R}_i)\Pi(f,\mathbf{k}) \exp -i\mathbf{k}_1\\&\qquad\cdot\{A(f,\mathbf{k})\mathbf{W}(s,f,\mathbf{k})\\&\qquad\qquad\times\cos[\omega(f,\mathbf{k})t-\mathbf{k}\cdot\mathbf{R}_i-\alpha(s,f,\mathbf{k})]\}. \quad (44)\end{aligned}$$

Let us consider one of the terms from the product. It can be written as $\exp iz\cos\phi$, where

$$\begin{aligned}z&=-A(f,\mathbf{k})\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k}),\\\phi&=\omega(f,\mathbf{k})t-\mathbf{k}\cdot\mathbf{R}_i-\alpha(s,f,\mathbf{k}).\end{aligned}\quad (45)$$

Now we note that

$$\exp[iz\cos\phi]=J_0(z)+\sum_{n=1}^{\infty}2i^nJ_n(z)\cos n\phi, \quad (46)$$

which follows from the well-known integral relation

$$J_n(z)=\frac{(-i)^n}{2\pi}\int_0^{2\pi}\exp i(z\cos\phi+n\phi)dz, \quad (47)$$

$J_n(z)$ being the Bessel function of the nth order, and where by definition

$$J_{-n}(z)=(-1)^nJ_n(z). \quad (48)$$

The expression of Eq. (46) can be rewritten in the form

$$\begin{aligned}\exp[iz\cos\phi]=J_0(z)+\sum_{n=1}^{\infty}i^nJ_n(z)&\\\times(\exp in\phi+\exp -in\phi).&\quad (49)\end{aligned}$$

We now substitute the expression of Eq. (46) or (49) in Eq. (44), and remember the definitions (45) of z and ϕ. We see that we can combine the exponentials $\exp\pm in\phi$ with the exponential $\exp -i\mathbf{k}_1\cdot(\boldsymbol{\rho}_s+\mathbf{R}_i)$, to give exponentials whose dependence on $\mathbf{R}_i$ is given by

$$\exp -i(\mathbf{k}_1+\sum\pm n\mathbf{k})\cdot\mathbf{R}_i, \quad (50)$$

where the summation is over all normal modes, each having its appropriate value of n, and $\mathbf{k}$. When we carry out the summation over $\mathbf{R}_i$, then as before we find that we get nothing, unless the propagation vector $\mathbf{k}_1+\sum\pm n\mathbf{k}$ equals one of the vectors $\mathbf{K}_j$ of the reciprocal lattice. Hence we find Fourier components, or plane waves, with propagation constants $\mathbf{k}_1$ given by

$$\mathbf{k}_1=\mathbf{K}_j+\sum(\pm n\mathbf{k}), \quad (51)$$

or one of the $\mathbf{K}_j$'s plus or minus an arbitrary number of propagation vectors of the various thermal waves. In practice, as Laval has shown, the only important terms in this summation are that where all n's are zero, giving the propagation constant equal to $\mathbf{K}_j$, and leading to an undisplaced Laue spot in the x-ray scattering, and the terms for which one of the n's equals ±1, the others all being zero, leading to single scattering of the x-rays by a single elastic wave. We shall therefore consider only these two types of terms.

First we take the case where all n's are zero. For this term, we have from Eq. (44)

$$\begin{aligned}\sum(s,i)f_s \exp -i\mathbf{k}_1\cdot(\boldsymbol{\rho}_s+\mathbf{R}_i)\Pi(f,\mathbf{k})&\\\times J_0[\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})A(f,\mathbf{k})].&\quad (52)\end{aligned}$$

The product of Bessel functions is known as the Debye-Waller factor. Let us evaluate it. In doing so, we must average over the thermal distribution. We shall carry out this average in the case of classical statistics, where we have equipartition, in which case it can be carried out very easily, and shall quote the result of the same calculation for the quantum-theoretical case which must be used at low temperatures. In classical statistics, the amplitude $A(f,\mathbf{k})$ acts like the amplitude of a classical oscillator of frequency $\omega(f,\mathbf{k})$ and we know that the probability of finding this amplitude in a range dA is given by the Boltzmann factor exp−Energy/kT, where k is Boltzmann's constant, T the absolute temperature, and the energy concerned is the energy of the oscillator. The first step in carrying out the calculation is to find the energy of the oscillator, in terms of A.

We can find the energy by finding the mean kinetic energy, and doubling it, for we remember that for a linear oscillator the mean kinetic energy equals the mean potential energy. Let us then start with Eq. (42) for the displacement, differentiate with respect to time, find the kinetic energy from this velocity, and average over time. Since the single summation of Eq. (42) must be squared, we have a double summation, in which we have products of cosine factors to be averaged. The time average of a square of a cosine is ½, that of the product of two cosines is zero, on account of the different frequencies (or the arbitrary phases), and we are left with the result that

$$\begin{aligned}&\text{Mean energy of whole crystal}\\&\quad=\sum(s,i,f,\mathbf{k})\tfrac{1}{2}m_sA^2(j,\mathbf{k})[\mathbf{W}(s,f,\mathbf{k})]^2\omega^2(f,\mathbf{k})\\&\quad=\sum(f,\mathbf{k})\tfrac{1}{2}A^2(f,\mathbf{k})\omega^2(f,\mathbf{k}),\end{aligned}\quad (53)$$

in which we have used Eq. (43). Hence we may interpret $(1/2)\omega^2(f,\mathbf{k})A^2(f,\mathbf{k})$ as the energy of the mode $f,\mathbf{k}$.

Next we must set up an expression for the probability of finding A in the range dA, in thermal equilibrium. We must remember that in classical statistics, equal areas in a phase space in which the coordinate and momentum of a particle are plotted as variables have equal a priori probabilities. The area of phase space enclosed by a curve of constant energy for a linear oscillator is an ellipse, whose area is proportional to A^2, so that the increment of area between two curves of constant energy corresponding to A and $A+dA$ is proportional to $d(A^2)$, or proportional to AdA. The probability of finding the system in unit area of phase space is, according to the Boltzmann factor and the expression of Eq. (53) for the energy, proportional to $\exp -A^2\omega^2/2kT$. Thus the probability of finding the system between A and $A+dA$ is

$$\text{probability} = \frac{A\exp(-A^2\omega^2/2kT)dA}{\int_0^\infty A\exp(-A^2\omega^2/2kT)dA}. \tag{54}$$

We now must find the average over A of the quantity $J_0[\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})A(f,\mathbf{k})]$, of Eq. (52). To get this, we multiply the Bessel function by the probability of Eq. (54), and integrate over dA from 0 to ∞. In doing this, we use the theorem

$$\frac{\int_0^\infty A\exp(-aA^2)J_0(bA)dA}{\int_0^\infty A\exp(-aA^2)dA} = \exp -b^2/4a, \tag{55}$$

which can be proved by expanding the Bessel function in series and integrating term by term. Thus we find that the average value of the Bessel function $J_0[\mathbf{k}_1\cdot(\mathbf{W}(s,f,\mathbf{k}))A(f,\mathbf{k})]$ is $\exp-[\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})]^2kT/2\omega^2(f,\mathbf{k})$. The whole factor from Eq. (52) is the product of such terms over all values of f and $\mathbf{k}$ so that we may write the average value of Eq. (52), as

$$\sum(s,i)f_s\exp-M_s\exp-i\mathbf{k}_1\cdot(\boldsymbol{\rho}_s+\mathbf{R}_i),$$

where

$$M_s=\sum(f,\mathbf{k})[\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})]^2kT/2\omega^2(f,\mathbf{k}). \tag{56}$$

We can rewrite this expression in terms of the average square displacement of the sth atom in the direction of the vector $\mathbf{k}_1$. To do this, we remember that the average energy of the mode $f,\mathbf{k}$ is $\frac{1}{2}\omega^2(f,\mathbf{k})[A^2(f,\mathbf{k})]_{Av}$, and also equals kT, by equipartition, where k, Boltzmann's constant, is not to be confused with $\mathbf{k}$, the propagation constant. Thus we may rewrite Eq. (56) in the form

$$M_s=\sum(f,\mathbf{k})[\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})]^2[A^2(f,\mathbf{k})]_{Av}/4. \tag{57}$$

But from Eq. (42), we can find the mean square of any component of the displacement of the sth atom, by squaring and averaging over time, and we find

$$[u_p^2(s,i)]_{Av}=\sum(f,\mathbf{k})[\mathbf{W}_p(s,f,\mathbf{k})]^2[A^2(f,\mathbf{k})]_{Av}/2. \tag{58}$$

Thus finally we may rewrite Eq. (57) in the form

$$M_s=\tfrac{1}{2}[u_{k1}^2(s,i)]_{Av}|\mathbf{k}_1|^2=8\pi^2[u_{k1}^2(s,i)]_{Av}\frac{\sin^2\theta}{\lambda^2}, \tag{59}$$

where we have used Eq. (40). This furnishes a simple and rigorous derivation of the Debye-Waller formula for the temperature factor, in the region of classical statistics; substantially this form of proof was used by Waller in his thesis. It shows us that in calculating the structure factor of the crystal, we are to use the product of the atomic scattering factor f_s and the Debye-Waller factor $\exp-M_s$, in place of the factor f_s alone, which would be used in the absence of thermal oscillation. In the scattered intensity from a real crystal, in which we are concerned with the square of the structure factor, the factor $\exp-2M_s$ enters.

The proof we have given holds only at high temperatures; but Ott, and Born and Sarginson, have given the means of carrying out the same calculation at low temperatures, where the quantum theory must be used. To understand the wave-mechanical problem, we must first recapitulate what we have done. We have started with the sum $\sum(s,i)f_s\exp-i\mathbf{k}_1\cdot[\boldsymbol{\rho}_s+\mathbf{R}_i+\mathbf{u}(s,i)]$ and have then taken the time average, which is essentially what we have done by using Eq. (49) and keeping only the term independent of time, as in Eq. (52). Then we have averaged over different amplitudes A, according to the Boltzmann distribution. We must proceed otherwise in wave mechanics, for we are not allowed to localize the displacement $u(s,i)$ of the atom s,i, or to write it as a sinusoidal function of time, on account of the uncertainty principle. Rather, we must assume that the oscillator is in the nth stationary state, and find the average of the quantity we desire, which in this case is $\exp-i\mathbf{k}_1\cdot\mathbf{u}(s,i)$, over this stationary state. This can be done, if we know the wave function of the stationary state, which we do, since we are dealing with linear oscillators. Then, having found this average, we must assume that the probability of finding the system in the nth stationary state is proportional to $\exp-E_n/kT$, where E_n is the energy of the state, and must average over this distribution. Ott has carried out this process, showing by an ingenious method that the twofold procedure of averaging over the wave function, and over the statistical distribution, can be combined into a single mathematical process, and has been able to evaluate the quantity which we desire in the general case (though he does not actually carry the steps through as we have sketched them). Born and Sarginson have carried through an equivalent proof by another method. The net result of this derivation is that Eq. (59) is rigorously true at all temperatures, where it is understood that $[u_{k1}^2(\mathbf{r},i)]_{Av}$ is to be computed properly according to the quantum theory, including the zero-point oscillation. Of course, the form of Eq. (56) holds only at high temperatures.

We have now considered the Debye-Waller temperature factor, by which the scattering of an individual atom is modified, thus reducing the amplitude of scattering of the Fourier components of charge density which would be present even without temperature agitation. But in addition, we are interested in the temperature diffuse scattering, the result of scattering of the x-rays by a plane wave of charge density which is made up from a single acoustical wave. From Eq. (44) and Eq. (46) we can see that if only the f,k mode is concerned, and if we use only the term $n=1$ for it, corresponding to first-order scattering, the corresponding structure factor is to be found from the summation

$$i\sum (s,i) f_s \exp - M_s \frac{J_1[-A(f,\mathbf{k})\mathbf{k}_1\cdot \mathbf{W}(s,f,\mathbf{k})]}{J_0[-A(f,\mathbf{k})\mathbf{k}_1\cdot \mathbf{W}(s,f,\mathbf{k})]} \times \exp - i\mathbf{k}_1\cdot(\boldsymbol{\rho}_s+\mathbf{R}_i) \times \{\exp i[\omega(f,\mathbf{k})t-\mathbf{k}\cdot\mathbf{R}_i-\alpha(s,f,\mathbf{k})] + \exp - i[\omega(f,\mathbf{k})t-\mathbf{k}\cdot\mathbf{R}_i-\alpha(s,f,\mathbf{k})]\}. \quad (60)$$

Here the factor i in front of the expression is $(-1)^{\frac{1}{2}}$, not to be confused with the index of summation i. As before, the sum will be zero when we sum over i unless $\mathbf{k}_1$ equals $\mathbf{K}_j \pm \mathbf{k}$, where $\mathbf{k}$ is the propagation constant of the particular acoustical wave considered, and $\mathbf{K}_j$ is one of the vectors of the reciprocal lattice. Since these vectors $\mathbf{k}$ can fill up the complete Brillouin zone, we see that the propagation constants of the waves of charge concerned in this single scattering can have any possible value, so that we are led to a diffuse scattering, the so-called thermal diffuse scattering. Though it is distributed throughout reciprocal space, however, nevertheless the scattering becomes much stronger near the lattice points of the reciprocal lattice, as we can show simply.

The essential point is that the amplitude of such a wave of charge distribution is proportional to the ratio of J_1 to J_0 in the expression of Eq. (60). These Bessel functions are to be computed for small values of the argument, for the quantities $A(f,\mathbf{k})\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})$ will always be small under the circumstances of experiment. In this limit, J_0 is approximately unity, and J_1 is proportional to its argument. Hence the amplitude of this wave of charge distribution, and consequently the amplitude of the scattered x-rays, will be proportional to $A(f,\mathbf{k})\mathbf{k}_1\cdot\mathbf{W}(s,f,\mathbf{k})$. The intensity will be proportional to the square of this quantity. But by Eq. (53), the average value of the quantity $A^2(f,\mathbf{k})$ will be equal to $2kT/\omega^2(f,\mathbf{k})$, becoming infinite as the frequency goes to zero. If we are considering the acoustical branches of the vibration spectrum, their frequency will go to zero as the propagation vector $\mathbf{k}$ goes to zero, or as the propagation vector of the scattering wave of charge density approaches $\mathbf{K}_j$, one of the vectors of the reciprocal lattice. Hence we have a scattering which becomes infinitely large as we approach these values $\mathbf{K}_j$, and which can give us information about the acoustical modes of the vibration spectrum. The optical branches, which have much higher frequencies, will contribute to a diffuse scattering which is not peaked in the same way about the lattice points of the reciprocal lattice, but is distributed more uniformly between these lattice points.

We see, then, the general nature of the temperature diffuse scattering. It helps our understanding of the problem if we state very simply the way in which the information about the vibration spectrum can be found from the measurements of the temperature diffuse scattering. Using a monochromatic beam of x-rays, one observes scattering in a given direction, in which we should not have Bragg scattering from the undistorted crystal. This scattering must come from the plane wave of charge density whose normal is the bisector of the angle between incident and scattered waves, and whose wave length is related to the scattering angle by Bragg's law. The intensity of this scattered wave then gives information about a particular thermal wave. But we have just seen that this intensity is proportional to $2kT/\omega^2(f,\mathbf{k})$. Thus measurement of the scattered intensity gives the frequency of the wave, whose propagation vector is already known from the scattering angle. It is clear that the method is not as simple as it seems at first sight, for we can actually have scattering not only by the three acoustical modes but also by the optical modes; for this reason, in a crystal having more than one atom in the unit cell, special means have to be used to separate out the scattering by the various branches of the spectrum.

In the cases which have been carried through, it has been possible to work through to find experimental values of a number of the elastic constants $C_{pq}(s,t,\mathbf{R}_v)$ which we have considered in Sec. 5. Then by use of Eq. (39) the frequencies of modes with arbitrary propagation constants have been found. From this information one can in a well-known way find the vibrational specific heat of the solid, and in cases where this has been calculated, it is in good agreement with experiment. It is worthwhile pointing out, however, that in addition the Debye-Waller factor could be calculated once the vibrational frequencies are known, and it would be a valuable addition to present experimental procedures to find the Debye-Waller factors theoretically in this way, and compare with direct observation.

7. SCATTERING OF ELECTRONS AND NEUTRONS BY THERMAL OSCILLATIONS

The principles of the scattering of electrons by thermal oscillations are essentially the same as those of the scattering of x-rays, as will be obvious from our general mode of treatment. The scattering will be produced by the sinusoidal waves of effective potential energy set up by the thermal oscillation, rather than by waves of density. To a fairly good approximation, the potential energy within a crystal can be regarded as the sum of potential energies arising from the separate atoms, and to the approximation to which this can be done, we can proceed with the theory along lines exactly parallel to those which we have used in the preceding section, merely substituting for the atomic scattering factor f_s the Fourier transform of the potential energy inside the atom, rather than the charge density. A good deal of discussion has been given of the adequacy of this approximation, and the net result of this is that the approximation is not quantitatively very good, though qualitatively it is correct.

The importance of the scattering of electrons by thermal oscillations comes not principally from the problem of electron diffraction, but much more because it is the main cause of electrical resistivity. In the study of electrical conductivity, we are dealing with very slow electrons. Their wave functions must be set up by use of energy-band theory, as described in Sec. 4; they can be described as a superposition of plane waves, as a Bloch sum, or in various other ways. In any case, however, we use the wave functions characteristic of a perfect crystal as a starting point in the discussion of the scattering of the waves by thermal oscillations. Each electron wave is characterized by a propagation vector $\mathbf{k}_0$, though it is far from a sinusoidal wave, and such a wave undergoes scattering by the thermal oscillations of the crystal, just like the thermal diffuse scattering of x-rays which we have just been discussing. The intensity of scattering is proportional to the temperature, provided we are at high enough temperature to use classical statistics, and this is the origin of the term in the resistivity of a metallic conductor which is proportional to the absolute temperature. There has been a good deal of theoretical study of resistivity from this point of view; but this study has not been correlated to any extent with our knowledge of the thermal diffuse scattering of x-rays, and our knowledge of the microscopic elastic constants of crystals derived from that method. It would seem that a correlation of these two types of problems would be very fruitful.

Neutron scattering by thermal oscillations differs from the scattering of x-rays or electrons in one rather striking way, as a result of the large mass of neutrons. We have pointed out that in all cases the frequency of a scattered wave is changed when it is scattered by a wave which oscillates sinusoidally in time, as a thermal wave does. However, with x-rays, the frequency of the acoustic vibration is so small that this change of frequency is negligible. With electrons, it is not quite negligible, but still small compared to the total energy of the electron. It has its importance: it is the mechanism by which the electron scattered by a lattice vibration transfers energy, which it has picked up from the external electric field, to vibrational energy of the lattice, in the case where we have scattering with the production of a phonon. This, in other words, is the mechanism of the production of Joulean heat in a conductor. With neutrons, on the contrary, the energy of a neutron whose wavelength is of the order of magnitude of interatomic spacings is comparable with thermal energies, so that the $\hbar\omega$ of the vibrational wave of thermal oscillation is comparable with, or in some cases much larger than, the neutron's energy. Hence the final energy of the scattered neutron can be very different from its incident energy.

This fact is used in the method of investigation of lattice vibrations by inelastic neutron scattering. Very slow incident neutrons are used, corresponding to a very small value of ω_0. When they are scattered by a thermal wave, they cannot lose energy equal to that of a thermal phonon, for they do not have enough energy to start with. Rather, they must gain an energy equal to that of a phonon, and this gives them a recoil energy far larger than their incident energy. The measurement is then of these recoil neutrons, which have gained the energy of a phonon from the lattice. This is a very different sort of experiment, in its practical arrangements, from the thermal diffuse scattering of x-rays; but as we see, the principles are not essentially different.

8. COMPTON EFFECT

There are many other examples which we could give to illustrate the interaction of waves in crystals, but we shall omit them, except for a brief mention of the Compton effect. In Sec. 1 we have seen that scattering of x-rays by a thermal wave can be regarded as a problem in which a photon with one energy and momentum is converted into a photon with another energy and momentum, and simultaneously one of the lattice vibrations emits or absorbs a photon; that is, the vibrating system has a change of energy and momentum which compensates the changes produced in the photon, so that we have conservation.

In the ordinary coherent scattering of x-rays by a crystal, the role of conservation of energy and momentum is not so obvious. The photon changes its momentum on scattering, but not its energy; what takes up the resulting change in momentum? The answer is that if we have a crystal freely suspended, as by a very fine fiber, the crystal as a whole will take up this momentum, and the resulting change of energy is so small as to be negligible, on account of the large mass. If the crystal is fastened, the change of momentum transmits itself as an impulse to the support. In this way we see that the coherent scattering still fits in with the general picture of the conservation of energy and momentum, but in this case the momentum transferred to the crystal does not change its internal state, but merely the motion of the crystal as a whole.

On the other hand, in the Compton effect, the momentum transferred to the crystal goes into producing an internal change. With the Compton effect of a free electron, the situation is very familiar: an electron at rest before the scattering process has a recoil momentum, and correspondingly a recoil energy, after the scattering. If we are dealing with the Compton effect in a crystal, an electron which before the scattering is bound to an atom becomes free after the scattering process to travel through the crystal with a momentum which compensates the change of momentum of the photon. This shows us that to investigate the Compton effect in a crystal, we must understand the structure of the wave functions and energy levels of both bound and free electrons.

The way to do this is through the energy-band theory. The electrons ejected in the Compton effect will ordinarily be the most loosely bound electrons in the atom. Their wave functions will be energy-band wave functions, from the valence or conduction bands, characterized by a propagation constant $\mathbf{k}$, and an energy $E_\beta(\mathbf{k})$. After the scattering process, the electron will have gained energy enough to lie in a higher, excited energy band, but still its wave function will be of the same general sort, and it will have a propagation constant $\mathbf{k}'$, and an energy $E_{\beta'}(\mathbf{k}')$, having been transferred to a different band β' from the initial band β. The change of energy and momentum will compensate the change of energy and momentum of the photon. This is entirely analogous to the case of scattering by phonons, in which the change of energy and momentum of the vibrational wave compensates the change of energy and momentum of the scattered photon. Most of the existing theories of the Compton effect use a very crude approximation, either a plane wave or a hydrogenic wave function, for the excited electronic state. The Fourier resolution of the bound state, which takes the place of the initial electronic state, gives the momentum distribution of the electron, as has been emphasized particularly by DuMond and his collaborators, thereby leading to an experimental determination of this momentum; but the theory cannot be regarded as satisfactory until we do a more careful job than has so far been attempted on the excited wave functions of the electrons in the crystal, a problem which is met also in the treatment of the fine structure of the x-ray absorption edge, as we have mentioned earlier, and which has received only very inadequate theoretical treatment.

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Rather than giving references through the body of this paper, I have preferred to collect here at the end a rather complete bibliography of a number of the topics which have been treated in the text. By giving the titles as well as the references, it will be obvious to the reader which topic each paper deals with. In the first place, I have included most of the old and standard papers in which the first and fundamental treatments of x-ray scattering were given. The reader will be surprised, if he is not already familiar with the field, how rapidly the main theoretical features of x-ray scattering, and of the Debye temperature factor, were worked out, by von Laue, the Braggs, Darwin, Debye, Ewald, and Born, in the years immediately following the first announcement of x-ray diffraction by Friedrich, Knipping, and Laue in 1912 (the first paper, in the Proceedings of the Bavarian Academy of Sciences, is not included in our bibliography, since that journal is not generally available, but the paper which we have listed, in the Annalen, followed shortly afterward). In W. H. Bragg's paper in the Philosophical Transactions in 1915 we find the first use of Fourier analysis, and we find that Duane's paper of 1925, based on Epstein and Ehrenfest's of 1924, led to the first practical use of Fourier methods by Havighurst in 1925. We meet the reciprocal lattice for the first time explicitly in Ewald's paper of 1921. Other steps in the development of standard x-ray theory will be clear from the papers we have listed.

Then we can follow the development of the theory of temperature vibrations, and their effect on the scattering of x-rays. We start with Einstein's 1907 paper on the theory of specific heat, followed by Debye's theory in 1912 and that of Born and von Karman almost immediately after. These latter theories came just before the discovery of x-ray diffraction, so that it was very natural that the theory of the temperature factor was worked out almost immediately. As far as the theory of lattice vibrations was concerned, Debye's specific heat theory worked so well that it tended to delay the progress of Born's more exact treatment, and it was not until Blackman in 1935 started applying the ideas of Born to the vibrations of real crystals that Born's methods began to come into their own. In the years since then, there have been many treatments of the vibrational spectra of various crystals, which are included in the bibliography.

As for the effect of lattice vibrations on x-ray scattering, though the Debye effect was interpreted immediately, it is surprising how long it took to understand completely the nature of temperature diffuse scattering, and its value in the investigation of lattice vibrations. Faxen's papers are generally regarded as the first ones which showed an understanding of the situation, and the complete treatment is essentially contained in Waller's thesis in 1925, but there has really been only a small amount of general understanding of the situation, until about 1940. Laval's experiments, and his theoretical paper in 1941, laid the ground for the development which has occurred since then, and his work was taken up in England by Lonsdale, Wooster, and their colleagues, and in America by Warren's students, so that now it has developed into a tool of great power in the investigation of the elastic vibrations and elastic constants of solids; but even now it is known to only few physicists, and has not been exploited nearly as much as it might be. The inelastic scattering of neutrons, which is just now coming into use, at Chalk River and at Brookhaven, and which has so far hardly formed a body of literature, is likely to prove as valuable as the temperature diffuse scattering of x-rays for investigating these same phenomena.

Most of the x-ray scattering experiments and theory deal with frequencies far from the absorption frequencies of the various atoms in the crystal; but when one is near an absorption frequency, one runs into anomalous dispersion, and into absorption. These topics are hardly mentioned at all in the text, but it seemed worth while including the references to them in this bibliography. The fundamental paper in this field is probably that of Hönl, and work of Prins and others supplements it. As far as absorption is concerned, Kronig and Penney, and Beeman and Friedman, have made the principal contributions. But when we are dealing with anomalous dispersion, we have a problem which leads over into the Compton effect of bound electrons, as Waller has pointed out particularly clearly. We have included a number of papers on the Compton effect in the bibliography, among them the fundamental paper by Gordon, a number of other theoretical ones by Klein, Wentzel, and others, but also the semi-experimental papers by DuMond and his collaborators, who pointed out the relation between the Compton effect and the momentum distribution in the atom, and a number of theoretical papers, by Burkhardt, Duncanson and Coulson, and others, working along the general lines suggested by DuMond.

We have included a very few of the earliest experimental papers which were directed toward verifying the general correctness of the theories, such as those of James and his collaborators, investigating heat motion, atomic scattering factors, and other features. We also include several of the papers concerned with the calculation of atomic scattering factors; though we have not given the many theoretical papers dealing with atomic structure, Hartree's self-consistent field, or the Thomas-Fermi method, which underlie these calculations. In these features, and in fact in all aspects of x-ray diffraction theory, the great source of convenient information is James's book on the *Optical Principles of the Diffraction of X-Rays*, which should be familiar to every physicist interested in these problems.

Then we have taken up some of the papers on the dynamics of electrons in crystals. The fundamental papers of Bethe, Bloch, Brillouin, Morse, and Wilson laid the foundation of the theories both of electron diffraction and of the energy-band structure of solids. We have given the references to these papers; but the further literature of the subject is so extensive that it seemed impractical to give it here. I have included references to several of my own papers and review articles which seemed to be particularly applicable to the present subject; in particular, my article in Vol. 19 of the third edition of the *Handbuch der Physik* contains a bibliography of papers on the electronic structure of solids, approximately as long as the present bibliography, and similarly arranged. The reader who is interested may well use that article as a companion to the present one, in the field of energy bands. As for the theory of electrical conductivity, as it is affected by the scattering of electron waves by the elastic waves of the crystal, I have included some of the main references in this bibliography.

As a final comment, I might mention that Brillouin's book, *Wave Propagation in Periodic Structures*, has much the same aim as the present review article: to show the similarity of the scattering of one wave by another, in many fields of physics. He takes up a number of applications, to such problems as the propagation of waves in loaded electrical networks, and in loaded wave guides such as one meets in linear accelerators and magnetrons, which I have naturally not included in the present treatment, but which have interested me as they have interested him. The theory of the linear accelerator, for instance, is practically identical with our theory of Sec. 3. The student who will become familiar with all these various branches of physics will find that many facts can be carried over from one to another. He will cease to find it remarkable that one book which we have not even included in this bibliography—Rayleigh's *Theory of Sound*—can contain practically everything that has been found out since in the matter of the theory of waves and their interactions.

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X-Ray Scattering by Thermal Agitation of Atoms in a Crystal

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THERMAL agitation of atoms in a crystal produces plane wave trains in the electronic density of a crystal. These wave trains, which exist in great number and are propagated in all directions with different wavelengths, selectively reflect incident x-rays in all directions. The intensity of scattering produced in this way is determined by the frequency, the amplitude, and the shape of the atomic oscillations which form the reflecting waves, and by the electronic density. Conversely, when the intensity of the scattering is known, it is possible to determine the electronic density.

We use the following notation: **m**, a translation of the crystal lattice; **j**, the vector which defines the average position of an atom in the unit cell; and **M**, a translation of the reciprocal lattice. The **M** and **m** vectors are related by

$$\mathbf{M}\cdot\mathbf{m}=\cdots,\,-2,\,-1,\,0,\,1,\,2,\,\cdots.$$

Also, g is the number of atoms in a unit cell; N, the number of unit cells in the crystal; μ_j, the mass of an atom in the position j, where here j is an index that runs over the values 1 to g; μ, mass and v, volume of the unit cell; m, mass of the crystal; and E, the number of electrons in a unit cell; so that

$$\mu=\sum_j \mu_j \quad\text{and}\quad m=\mu N.$$

Also **S**, **T**, $\cdots$ are the fundamental wave vectors of the plane-wave trains of the atomic oscillations. They are vectors inscribed in the first Brillouin zone with their origin at the center and their extremities distributed with uniform density, their number being equal to N. An harmonic oscillation of the atoms that is related to **S**, forms an infinity of plane wave trains[1] piloted by the vectors, **S**+**M**.

We denote by $\nu_{S\gamma}$, $\nu_{T\delta}\cdots$ the frequencies of atomic oscillations associated with the fundamental wave vectors **S**, **T**, $\cdots$ and the $3g$ modes of oscillation of the g atoms of a unit cell, where γ and δ are indexes that

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[1] (a) J. Laval, Bull. soc. franç. minéral. **64**, 1 (1941). (b) J. phys. radium **15**, 545, 657 (1954).