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IV—On the Absorption of Polar Crystals in the Infra-Red

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A cubical crystal of the NaCl type should, according to the lattice theory,[†] possess only one frequency which would respond to infra-red light, this vibration being caused by the motion of the rigid lattice of positive ions against the rigid lattice of negative ions. We should, therefore, expect a single maximum in the absorption and in the reflexion; this presupposes an harmonic motion of the particles of the lattice.

This main maximum is a well-known feature of the properties of ionic crystals in the infra-red, but the work of Czerny and his collaborators[‡] has shown that, besides this, there are subsidiary maxima both in absorption and in reflexion; furthermore, the representation of the optical constants, in particular of the absorption coefficient (K) by means of a dispersion formula with a damping constant as suggested by Drude, broke down completely on the short wave-length side of the maximum.

The theoretical explanation of the above results was given by Born and Blackman[§] in an investigation of the damping of the main vibration. It was possible to show, following the work of Pauli[||] and Peierls,[¶] that the damping was due to the anharmonic character of the vibrations, which resulted in the main vibration being coupled to certain combinations between other normal vibrations. The main results can easily be seen if we refer to the one-dimensional case. Taking a linear chain consisting alternatively of N particles of mass m (charge $+ e$) and N of mass M (charge $- e$), we find the frequency of the normal vibrations to be given by the expression

$$\nu_k = \nu_0\,(2)^{-\frac{1}{2}}\left\{1 \pm \left(1 - \frac{4\mathrm{M}m}{(\mathrm{M}-m)^2}\sin^2\frac{\pi k}{\mathrm{N}}\right)^{\frac{1}{2}}\right\}^{\frac{1}{2}}, \qquad \text{(fig. 1.)}$$

where k varies from O to N. ν_0 is the maximum frequency and is given by

$$\nu_0{}^2 = 2\alpha\left(\frac{1}{m} + \frac{1}{\mathrm{M}}\right),$$

where α is the constant of the restoring force between neighbouring particles.

[†] Born, 'Atom Theorie des festen Zustandes,' Berlin (1923).

[‡] Czerny, 'Z. Physik,' vol. 65, p. 600 (1930). Czerny and Barnes, 'Z. Physik,' vol. 75, p. 732 (1932). R. Bowling Barnes 'Z. Physik,' vol. 75, p. 732 (1932).

[§] Born and Blackman, 'Z. Physik,' vol. 82, p. 551 (1933). Blackman, 'Z. Physik,' vol. 86, p. 421 (1933), quoted hereafter as I.

[||] Pauli, 'Verh. deuts. phys. Ges.' vol. 6, p. 10 (1925).

[¶] 'Ann. Physik,' vol. 3, p. 1055 (1929).

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Now the rule that governs the coupling is that ν_0 is coupled only to combinations between vibrations having the same value of k but belonging to different branches. It is then easy to see that the summation tones extend from $\nu = \nu_0$ to $\nu = \nu_1 + \nu_2$ (where ν_1 is the maximum frequency in the acoustical branch and ν_2 the lowest in the optical branch), and the difference tones from $\nu = \nu_0$ to $\nu = \nu_1 - \nu_2$. Furthermore, the density of the normal vibrations is large in the neighbourhood of ν_1 and ν_2, hence the combination vibrations $\nu_1 + \nu_2$, $\nu_1 - \nu_2$ are associated with a large number of frequencies.

Now if we send in light of frequency ν then the main vibration responds, and since this is coupled to the combination vibrations, those for which the frequency is ν will be able to take up energy. Since the spectrum of the combination tones extends only up to $\nu = \nu_1 + \nu_2$ any frequency higher than this cannot be absorbed (if we confine ourselves to the first anharmonic term in the displacement); hence for these frequencies the crystal behaves as if it were undamped. The same happens for any frequency smaller than $\nu = \nu_1 - \nu_2$. Furthermore, since the points $\nu_1 + \nu_2$ and $\nu_1 - \nu_2$ in the frequency scale are associated with a relatively large number of normal vibrations, we should expect maxima of the absorption (and reflexion) at these frequencies.

This is, roughly speaking, what one does find from the calculation of the one-dimensional case; in the two- and three-dimensional case the effects are more complicated but the same general principles apply. It is perhaps as well to state which of the general results quoted apply to all crystals and which are of special nature.

The first point concerns the fall of the absorption on the short wave-length side of the maximum. This effect depends only on the fact that the vibrational spectrum of a crystal has a finite upper limit, and that the spectrum of the combination tones has a similar upper limit. Hence the effect should appear in all polar crystals.

The existence of an absorption continuum is a result of the existence of a more or less continuous vibrational spectrum, and is, as such, a general effect. The maxima in this continuum due to the splitting up of the frequency branches can be taken to be practically as general an effect, though in particular cases they might not be noticeable. The size of the continuum may vary greatly from crystal to crystal. As an example, we may note the fine structure of the 6·8μ reflexion maximum found by PLYLER† for $CaCO_3$. Besides the two maxima usually attributed to the vibrations of the carbonate ion, there are two other maxima at present unexplained. These lie on each side of one vibration, and their distances from the vibrations correspond to wave-lengths varying from about 200μ to 500μ. Now it can hardly be doubted that these maxima come from the combination of the CO_3 lattice vibrations with lattice vibrations. Since there is a large number of frequency branches it is quite possible that we have here a superposition of several maxima of varying intensity.

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† 'Phys. Rev.', vol. 33, p. 948 (1929).

In all such cases† where we have an inner vibration in a crystal, there will be a narrow band attached to it in the absorption and reflexion spectrum with possibly additional maxima.

1—If we consider a linear chain containing alternately two types of particles of mass m, M and charge $+e$, $-e$, and take only the effect of neighbours on each other, then the total energy of the lattice may be written as

$$\mathrm{H} = \sum_{-\frac{\mathrm{N}}{2}}^{+\frac{\mathrm{N}}{2}} \Big\{ \frac{m}{2}\,\dot{u}_{2n}{}^{2} + \frac{\mathrm{M}}{2}\,\dot{u}_{2n+1}{}^{2} + \frac{\alpha}{2}\,(u_{2n+1}-u_{2n})^{2} + \frac{\alpha}{2}\,(u_{2n-1}-u_{2n})^{2}$$

$$+ \frac{\beta}{6}\,(u_{2n+1}-u_{2n})^{3} - \frac{\beta}{6}\,(u_{2n-1}-u_{2n})^{3} - e\mathrm{E}\,(u_{2n}-u_{2n+1})\Big\}. \quad . \quad (1.1)$$

The last two terms are the anharmonic terms, and the electrical term due to an electro-magnetic wave of amplitude E falling on the lattice; u_{2n} represents the displacement of the $2n^{\text{th}}$ particle.

If we transform the energy‡ to normal coordinates by means of transformation

$$\left.\begin{aligned} u_{2n} &= \frac{1}{\sqrt{\mathrm{N}}}\,\Sigma\, e^{\frac{\pi i k}{\mathrm{N}}\,2n}\left(\frac{\xi_k}{\sqrt{m}}\cos\alpha_k + \frac{\eta_k}{\sqrt{m}}\sin\alpha_k\right) \\ u_{2n+1} &= \frac{1}{\sqrt{\mathrm{N}}}\,\Sigma\, e^{\frac{\pi i k}{\mathrm{N}}\,(2n+1)}\left(-\frac{\xi_k}{\sqrt{\mathrm{M}}}\sin\alpha_k + \frac{\eta_k}{\sqrt{\mathrm{M}}}\cos\alpha_k\right) \end{aligned}\right\}, \quad . \quad . \quad (1.2)$$

where

$$\xi_k = \xi^*{}_{-k}, \qquad \eta_k = \eta^*{}_{-k}, \qquad \text{and} \qquad \tan 2\alpha_k = \frac{2\sqrt{m\mathrm{M}}}{\mathrm{M}-m}\cos\frac{2\pi k}{\mathrm{N}},$$

the harmonic part of the energy has now the usual form with frequencies given by the formula in the introduction. The anharmonic part of the energy becomes

$$\mathrm{H_A} = \frac{\beta}{6\sqrt{\mathrm{N}}} \sum_{k+l+m=0,\ \pm 2\pi} \{\mathrm{D}^{(1)}_{klm}\,\xi_k\xi_l\xi_m + \mathrm{D}^{(2)}_{klm}\,\xi_k\xi_l\eta_m + \mathrm{D}^{(3)}_{klm}\,\xi_k\eta_l\eta_m + \mathrm{D}^{(4)}_{klm}\,\eta_k\eta_l\eta_m\}, \qquad (1.3)$$

and the electrical part

$$\mathrm{H_E} = \sqrt{\mathrm{N}}e\mathrm{E}\,(\xi_0\mathrm{A}_0 + \eta_0\mathrm{B}_0),$$

where

$$\left.\begin{aligned} &\mathrm{A}_k = \left(\frac{\cos\alpha_k}{\sqrt{m}} + \frac{\sin\alpha_k}{\sqrt{\mathrm{M}}}\,e^{\frac{\pi i k}{\mathrm{N}}}\right), \qquad \mathrm{B}_k = \left(\frac{\sin\alpha_k}{\sqrt{m}} - \frac{\cos\alpha_k}{\sqrt{\mathrm{M}}}\,e^{\frac{\pi i k}{\mathrm{N}}}\right) \\ &\mathrm{D}^{(1)}_{klm} = (\mathrm{A}_k\mathrm{A}_l\mathrm{A}_m - \mathrm{A}^*{}_k\mathrm{A}^*{}_l\mathrm{A}^*{}_m), \qquad \mathrm{D}^{(2)}_{klm} = 3\,(\mathrm{B}_m\mathrm{A}_k\mathrm{A}_l - \mathrm{B}^*{}_m\mathrm{A}^*{}_k\mathrm{A}^*{}_l) \\ &\mathrm{D}^{(3)}_{klm} = 3\,(\mathrm{A}_k\mathrm{B}_l\mathrm{B}_m - \mathrm{A}^*{}_k\mathrm{B}^*{}_l\mathrm{B}^*{}_m), \qquad \mathrm{D}^{(4)}_{klm} = (\mathrm{B}_k\mathrm{B}_l\mathrm{B}_m - \mathrm{B}^*{}_k\mathrm{B}^*{}_l\mathrm{B}^*{}_m) \end{aligned}\right\}. \qquad (1.4)$$

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† *Cf.* also E. Teller " Handbuch der Chemischen Physik," vol. 9, part II, Leipzig (1934).

‡ Only an outline of the one-dimensional theory is given here, for details see I.

As can be seen from (1·4), the electric field affects only the vibration of higher frequency ; (η_0 is the translation).

A rather special type of perturbation theory is necessary to solve the problem. This consists in transforming the normal coordinates by means of the transformation†

$$\left.\begin{aligned} \xi_k &= c_{k1}\, e^{iw^{(1)}_{k1}t} + c_{k-1}\, e^{iw^{(1)}_{k-1}t} = \sum_{j=\pm 1} c_{kj}\, e^{iw_{kj}t} \\ \eta_k &= \sum_j d_{kj} e^{iw_{kj}t} \end{aligned}\right\} . \qquad (1.5)$$

The c_{kj}, d_{kj} are now taken as new canonical variables, and the corresponding impulses are defined by the relation

$$p_{kj} = iw_{kj}\, c_{-k-j}, \text{ etc.}$$

It will be noted that the c_{kj} d_{kj} are constant in zero approximation (when we have only harmonic vibrations).

In the first approximation they become variable and can be calculated from the equations

$$\left.\begin{aligned} \dot{c}_{fj} &= \frac{1}{iw^{(1)}_{fj}} \frac{\partial H}{\partial c_{-f-j}} = \frac{1}{iw^{(1)}_{fj}} \frac{\partial V}{\partial c_{-f-j}}, \qquad (f \neq 0) \\ \dot{c}_{0j} &= \frac{1}{iw^{(1)}_{0j}} \frac{\partial V}{\partial c_{0-j}} + \frac{aE_0}{iw^{(1)}_{0j}}\, e^{-iw^{(1)}_{0j}t}, \qquad \text{etc.} \end{aligned}\right\}, \qquad (1.6)$$

where in the new coordinates

$$\begin{aligned} V\,(c_{kj}\, d_{kj}) = \frac{\beta}{6\sqrt{N}} \sum_{k+l+m=0,\ \pm 2\pi} \{ & D^{(1)}_{klm}\, c_{kj}\, c_{lj'}\, c_{mj''}\, e^{i\,(w^{(1)}_{kj}+w^{(1)}_{lj'}+w^{(1)}_{mj''})\,t} \\ & + D^{(2)}_{klm}\, c_{kj}\, c_{lj'}\, d_{mj''}\, e^{i\,(w^{(1)}_{kj}+w^{(1)}_{lj'}+w^{(2)}_{mj''})\,t} \\ & + D^{(3)}_{klm}\, c_{kj}\, d_{lj'}\, d_{mj''}\, e^{i\,(w^{(1)}_{kj}+w^{(2)}_{lj'}+w^{(2)}_{mj''})\,t} \\ & + D^{(4)}_{klm}\, d_{kj}\, d_{lj'}\, d_{mj''}\, e^{i\,(w^{(2)}_{kj}+w^{(2)}_{lj'}+w^{(3)}_{mj''})\,t} \}. \end{aligned}$$

We now write down the expressions for $\dot{c}_{fj}$, $\dot{d}_{fj}$, $\dot{c}_{0j}$, noting that $D^{(\tau)}_{l0} \neq 0$ only if $\tau = 2$. We furthermore separate in the expression for $\dot{c}_{fj'}$ those terms containing $c_{0j'}$; we then put

$$\left.\begin{aligned} c_{fj} &= c^{(0)}_{fj} + c^{(1)}_{fj} \\ d_{fj} &= d^{(0)}_{fj} + d^{(1)}_{fj} \\ c_{0j} &= \eta_j\, e^{i\,(w+w^{(1)}_{0j})\,t} \end{aligned}\right\}, \qquad (1.7)$$

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† Peierls, 'Ann. Physik,' vol. 3, p. 1055 (1929).

where the $c_{kj}^{(1)}$ are of course small. These expressions are substituted in $\dot{c}_{fj}$ and then the integration is performed. This leads to

$$\left(\beta' = \frac{\beta}{\sqrt{N}}\right) \qquad \left.\begin{aligned} c_{fj}^{(1)} = \frac{\beta'}{\omega_{fj}^{(1)}} \Bigg\{ & \sum_{lj'j''} D^{(1)}_{-fl}\, c^{(0)}_{lj'}\, c^{(0)}_{f-lj''} \frac{e^{i\,(w^{(1)}_{f-lj''}+w^{(1)}_{lj'}-w^{(1)}_{fj})\,t}-1}{(w^{(1)}_{f-lj''}+w^{(1)}_{lj'}+w^{(1)}_{fj})} \\ & + \sum_{lj'j'} D^{(3)}_{-fl}\, d^{(0)}_{lj'}\, d^{(0)}_{f-lj''} \frac{e^{i\,(w^{(2)}_{f-lj''}+w^{(2)}_{lj'}-w^{(1)}_{fj})\,t}-1}{(w^{(2)}_{f-lj''}+w^{(2)}_{lj'}-w^{(1)}_{fj})} \\ & + \Sigma'\, 2D^{(2)}_{-fl}\, c^{(0)}_{lj'}\, d^{(0)}_{f-lj''} \frac{e^{i\,(w^{(1)}_{lj'}+w^{(2)}_{f-lj''}-w^{(1)}_{fj})\,t}-1}{(w^{(1)}_{lj'}+w^{(2)}_{f-lj''}-w^{(1)}_{fj})} \\ & + \sum_{j'j''} 2D^{(2)}_{-f0}\, d^{(0)}_{fj''}\, \eta_{j'} \frac{e^{i\,(w+w^{(2)}_{fj''}-w^{(1)}_{fj})\,t}-1}{(w+w^{(2)}_{fj''}-w^{(1)}_{fj})} \Bigg\} \end{aligned}\right\} . \quad . \quad . \quad (1.8)$$

It will be noted that in the last line j' occurs only in $\eta_{j'}$.

The expression for $\dot{c}_{0j}$ is given by

$$\dot{c}_{0j} = \frac{\beta'}{iw_{0j}^{(1)}} \Sigma\, 2D^{(2)}_{0f}\, c_{fj'}\, d_{-fj''}\, e^{i\,(w^{(1)}_{fj'}+w^{(2)}_{-fj''}-w^{(1)}_{0j})\,t} + \frac{aE_0}{iw_{0j}^{(1)}}\, e^{i\,(w-w^{(1)}_{0j})\,t}. \quad . \quad . \quad . \quad (1.9)$$

Substituting (1.8), etc. and (1.5) we obtain the expression for η_j,

$$\eta_j\,(w-w_{0j}^{(1)}-\gamma'_j)-\eta_{-j}\gamma'_j = \frac{aE_0}{w_{0j}^{(1)}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.10)$$

There are, of course, two such equations, and in order to find the electric moment we must add the η values.

The damping factor can be written in the form $i\Gamma_j$ where

$$\Gamma_j = \frac{\beta'^{2}_{j}A_0^2}{w_{0j}^{(0)}} \sum_{lj'j''} \left\{ \frac{\sin^2\dfrac{\pi l}{N}}{\omega^{(1)}_{lj'}} |d^{(0)}_{lj''}|^2 \frac{\sin\,(w+w^{(2)}_{lj''}+w^{(1)}_{lj'})\,t}{(w+w^{(1)}_{lj'}+w^{(2)}_{lj''})} + \frac{\sin^2\dfrac{\pi l}{N}}{w^{(2)}_{lj''}} |c^{(0)}_{lj'}|^2 \frac{\sin\,(w+w^{(2)}_{lj''}+w^{(1)}_{lj'})\,t}{(w+w^{(2)}_{lj''}+w^{(1)}_{lj'})} \right\}. \quad . \quad . \quad (1.11)$$

In (1·9) we have to average† over all values of the independent phases of the $c_{kj}\, d_{kj}$.

The method of finding the average value of the complex normal coordinates is discussed in Appendix I. The final value of Γ is given by‡

$$\Gamma = \frac{16\beta^2 kT}{Mmw_0^5} \frac{(M+m)}{2mM\sqrt{mM}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1.12)$$

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† Peierls, *loc. cit.*

‡ Detailed calculations are given in I. The three possibilities given by $k+k'+k''=0, \pm 2\pi$ have also been taken into account here; in I only the first condition was used.

When we work out the value for the electric moment we find this to be

$$p = \frac{c\mathrm{E}}{w_0^2 - w^2 - 2i\Gamma w_0}. \qquad (1.13)$$

There are several points to be noted here. Firstly, this differs from the result given in the previous paper, where w replaced w_0 in the damping factor.

Secondly, it differs from the usual form given by DRUDE's theory of dispersion, as can be seen from the fact that

$$2nk = \frac{c'\,\Gamma w_0}{(w_0^2 - w^2)^2 + 4\Gamma^2 w_0^2}. \qquad (1.14)$$

Here ω_0 replaces ω in the numerator and denominator. It is perhaps instructive to note that one can deduce this difference from the general principles underlying the theory. The fact that Γ is not zero means that we have combination vibrations which are capable of absorbing energy; hence we must conclude that the absorption coefficient cannot tend to zero as long as Γ remains finite. On the old dispersion theory k tends to zero as ω tends to zero, which does not fit in with the conclusions we have just reached. The above formula shows that k tends to a constant value as ω tends to zero, which is in agreement with the general conclusions. It may, however, be noted that in general Γ will become zero before we come to very long waves.

2—TWO-DIMENSIONAL THEORY

a—We shall start here with a consideration of a simple two-dimensional case, namely, a lattice having a square cell and containing one particle per cell. The general features of the vibrational spectrum have already been worked out.[†]

We consider that particles at a distance a and $a\sqrt{2}$ can act on one another (a being the lattice constant). The binding constants in the two cases are α and γ respectively, and the mass of each particle is denoted by M. The displacements of the particle (l, m) in the two directions is given by u_{lm}, v_{lm}.

The total energy for harmonic vibrations is given by

$$\mathrm{H} = \sum_{lm=0}^{2\mathrm{N}} \left\{\frac{\mathrm{M}}{2}\dot{u}_{lm}^2 + \frac{\mathrm{M}}{2}\dot{v}_{lm}^2\right\} + \frac{\alpha}{2}\left\{(u_{lm} - u_{l+1\,m})^2 + (v_{lm} - v_{l\,m+1})^2\right\}$$
$$+ \frac{\gamma}{2}\left\{(u_{lm} + v_{lm} - u_{l+1\,m+1} - v_{l+1\,m+1})^2 + (u_{lm} + v_{lm} - u_{l+1\,m-1} - v_{l+1\,m-1})^2\right\}. \qquad (2.1)$$

The transformation to normal coordinates can be made by using the expressions

$$\left.\begin{aligned} u_{lm} &= a' \sum_{rs=-\mathrm{N}}^{+\mathrm{N}} e^{\frac{\pi i}{\mathrm{N}}(lr+ms)} \left(\xi_{rs}\cos\alpha_{rs} - \eta_{rs}\sin\alpha_{rs}\right) \\ v_{lm} &= a' \sum_{rs=-\mathrm{N}}^{+\mathrm{N}} e^{\frac{\pi i}{\mathrm{N}}(lr+ms)} \left(\xi_{rs}\sin\alpha_{rs} + \eta_{rs}\cos\alpha_{rs}\right) \end{aligned}\right\}, \qquad (2.2)$$

[†] BLACKMAN, 'Proc. Roy. Soc.,' A, vol. 148, p. 365 (1935); quoted hereafter as II.

where a' is a normalization constant. Also $\xi_{rs} = \xi^*_{-r-s}$ and $\eta_{rs} = \eta^*_{-r-s}$; and the usual condition of periodicity replaces the boundary conditions. The angles α_{rs} are defined by the relation

$$\tan 2\alpha_{rs} = \frac{4\gamma}{\alpha} \frac{\sin \frac{\pi r}{N} \sin \frac{\pi s}{N}}{\cos \frac{\pi r}{N} - \cos \frac{\pi s}{N}}. \qquad \qquad (2.3)$$

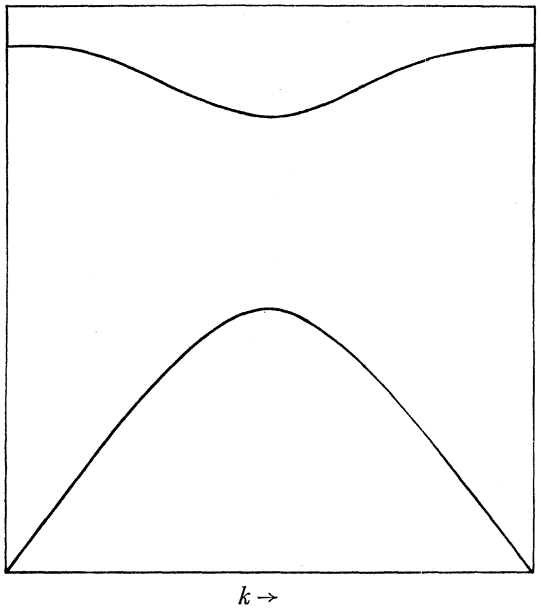

FIG. 1—Frequency diagram for a one-dimensional lattice $\left(\frac{m}{M} = \frac{1}{3}\right)$.

Substituting in (2.1) we obtain the energy expression in the usual form with frequencies given by the relations

$$w^2_{rs} = 4\pi^2\nu^2_{rs} = \alpha\,(1 - \cos\phi_1 + 1 - \cos\phi_2) + 4\gamma\,(1 - \cos\phi_1 \cos\phi_2)$$
$$\pm (\alpha^2 (\cos\phi_1 - \cos\phi_2)^2 + 16\gamma^2 \sin^2\phi_1 \sin^2\phi_2)^{\frac{1}{2}}, \quad . \qquad (2.4)$$

where

$$\phi_1 = \frac{\pi r}{N}, \qquad \phi_2 = \frac{\pi s}{N}.$$

These equations are exactly the same as have already been derived in a previous paper from the equation of motion of the particles.

The knowledge of the form of the transformation to normal coordinates is essential if we wish to find out whether a particular combination of normal vibrations is allowed or forbidden in infra-red absorption, as will be shown below. The transformation is also of use if we wish to discuss the form of the normal vibrations of our lattice in special cases (*cf.* Appendix II).

As can be seen from (2.4), we have two frequency surfaces; actually the ϕ's are not continuous variables, but we may consider them to be so, and we are then dealing with the frequency surface carrying the points corresponding to the normal vibrations. As regards the spectrum, we may repeat that the main features are the maxima of the density of the normal vibrations which occur when the frequency is in the region $\nu_{0\pi}$, $\nu_{\pi\pi}$.

b—If we now assume that the particles in a lattice contain alternately positive and negative charges, we are strictly speaking incorrect in saying that we have one particle per cell. If, however, we assume that the binding forces are exactly the same for each particle, the frequency surfaces will be the same as in the case of §2(*a*).

There are two questions which are of interest in this case. The first is whether the maxima of the density of the vibrations mentioned above affect the absorption; the second question concerns the possibility of combination between vibrations belonging to different frequency branches.

It we examine the electric moment we find that there are two normal vibrations ξ_{NN} and η_{NN} which alone are associated with a change of the electric moment. These have the same frequency and are exactly similar vibrations.

The form of the calculation is exactly similar to the one-dimensional case, and in view of the complicated nature of the damping constant and the number of constants occurring in it, it has been thought better to discuss its properties rather that its actual form.

If we consider anharmonic terms in the energy of the form

$$\mathrm{H_A} = \Sigma\,(u_{lm} - u_{l+1m})^3, \text{ etc.,}$$

then expressed in the normal coordinates we have again the form

$$\mathrm{H_A} = \sum_{\substack{r+r'+r''=0\pm 2\mathrm{N}\\ s+s'+s''=0\pm 2\mathrm{N}}} \{\mathrm{D}^{(1)}_{rsr's'r''s''}\,\xi_{rs}\,\xi'_{r's'}\,\xi''_{r''s''} + \mathrm{D}^{(2)}_{rsr's'r''s''}\,\xi_{rs}\,\xi'_{r's'}\,\eta''_{r''s''}$$
$$+ \mathrm{D}^{(3)}_{rsr's'r''s''}\,\xi_{rs}\,\eta'_{r's'}\,\eta''_{r''s''} + \mathrm{D}^{(4)}_{rsr's'r''s''}\,\eta_{rs}\,\eta'_{r's'}\,\eta''_{r''s''}\}.$$

where

$$\left.\begin{aligned} \mathrm{D}^{(1)} &= \mathrm{A}_{rs}\,\mathrm{A}_{r's'}\,\mathrm{A}_{r''s''}\,\mathrm{C}_{rr'r''}\\ \mathrm{D}^{(2)} &= \mathrm{A}_{rs}\,\mathrm{A}_{r's'}\,\mathrm{B}_{r''s''}\,\mathrm{C}_{rr'r''}\\ \mathrm{D}^{(3)} &= \mathrm{A}_{rs}\,\mathrm{B}_{r's'}\,\mathrm{B}_{r''s''}\,\mathrm{C}_{rr'r''}\\ \mathrm{D}^{(4)} &= \mathrm{B}_{rs}\,\mathrm{B}_{r's'}\,\mathrm{B}_{r''s''}\,\mathrm{C}_{rr'r''} \end{aligned}\right\}, \quad \ldots\ldots\ldots \quad (2.5)$$

and

$$\mathrm{A}_{rs} = \cos\alpha_{rs}, \qquad \mathrm{B}_{rs} = \sin\alpha_{rs},$$

$$\mathrm{C}_{rr'r''} = 2i\left\{\sin\frac{\pi r}{\mathrm{N}} + \sin\frac{\pi r'}{\mathrm{N}} + \sin\frac{\pi r''}{\mathrm{N}}\right\}.$$

It will be noted that $\mathrm{D}^{(\tau)}_{\mathrm{NN}r's'} \neq 0$ only if $\tau = 1$. This would mean that in the expression for $\dot{a}_{\mathrm{NN}j}$† only $\mathrm{D}^{(1)}_{\mathrm{NN}r's'}$ would appear; a consideration of the calculation

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† In carrying through the calculation we use again the transformation $\xi_{rs} = \sum_{j=\pm 1} a_{rsj}e^{iw^{(1)}_{rsj}t}$, etc.

of §1 will then show that in this case the combination between the two frequency branches is forbidden.

As regards the combination between the (0π) $(\pi 0)$ frequencies in the same frequency branch, a little consideration shows that the controlling factor is $D^{(1)}_{\mathrm{NO,\,ON}}$, and as $C_{rr'r''}$ is zero for $r = 0$ or $r = \mathrm{N}$, it is clear that these combination tones are forbidden.

The combination between the neighbouring frequencies is, of course, not forbidden though weak; if the density of the vibrations is sufficient there is a possibility that the maximum due to combinations will appear as a maximum of the damping factor and of the absorption.

The considerations can now be extended by taking the next type of anharmonic term

$$\Sigma\ (u_{lm} + v_{lm} - u_{l+1m+1} - v_{l+1m+1})^3.$$

These give again terms of the form (2.4) where

$$\left.\begin{aligned} D'^{(1)} &= A'^{+}_{rs}\, A'^{+}_{r's'}\, A'^{+}_{r''s''}\, C'_{rsr's'r''s''} \\ D'^{(2)} &= A'^{+}_{rs}\, A'^{+}_{r's'}\, A'^{-}_{r''s''}\, C'_{rsr's'r''s''} \\ D'^{(3)} &= A'^{+}_{rs}\, A'^{-}_{r's'}\, A'^{-}_{r''s''}\, C'_{rsr's'r''s''} \\ D'^{(4)} &= A'^{-}_{rs}\, A'^{-}_{r's'}\, A'^{-}_{r''s''}\, C'_{rsr's'r''s''} \end{aligned}\right\}, \quad \ldots\ldots\ldots \quad (2.6)$$

with

$$A'^{\pm}_{rs} = (\cos\alpha_{rs} \pm \sin\alpha_{rs})$$

$$C'_{rsr's'r''s''} = 2i\left\{\sin\frac{\pi}{\mathrm{N}}(r+s) + \sin\frac{\pi}{\mathrm{N}}(r'+s') + \sin\frac{\pi}{\mathrm{N}}(r''+s'')\right\}.$$

From these coefficients we can see that $D^{(\tau)}_{\mathrm{ON\,NO}}$ is zero; on the other hand, $D^{(\tau)}_{\mathrm{NN}rs}$ is not zero, because although $\sin\phi_{\mathrm{NN}} = 0$ $\cos\phi_{\mathrm{NN}} \neq 0$.

This means that combinations between branches will contribute to the optical absorption, as can be seen by forming the expression for $\dot{a}_{\mathrm{NN}j}$ with the new term in the expression for the energy. In this case the combination between the (0π) $(\pi 0)$ frequencies is again forbidden because $D^{(0)}_{\mathrm{ONNO}}$ is zero.

Such being the case one might not expect any prominent features in the absorption of the two-dimensional lattice under discussion (except the fall on the short wave side of the maximum). It is, however, quite probable that the (0π) $(\pi 0)$ combinations might, in spite of the above restriction, be sufficiently intense to give maxima of absorption.

The general condition for combinations is given by the relations

$$r + r' + r'' = 0 \pm 2\mathrm{N}$$
$$s + s' + s'' = 0 \pm 2\mathrm{N}.$$

In this case one of the frequencies is $(\phi_1\phi_2) = (\pi\pi)$; hence the vibration $(\phi_1\ \phi_2)$ can combine only with the vibrations defined by $((\pi - \phi_1), (\pi - \phi_2))$.

The above condition shows that vibrations in the lower part of any branch $\left(\phi_1 < \frac{\pi}{2},\ \phi_2 < \frac{\pi}{2}\right)$ can combine only with vibrations in the upper part of the branch. This might be taken to mean that in the more general case of different masses combination is allowed only between optical and acoustical branches and not between branches of the same type. This is not so, except in the limit, because the translational symmetry is different in the general case.

3—Two-Dimensional Lattice with Two Particles per Cell

The treatment of the next case where we have two types of particles calls for some consideration. In the case where we have only one type of particle we can use either a square cell, as has been done in the previous section (fig. 2*a*), or a parallelogram (fig. 2*b*), one particle being located in the corner of the cell in each case. The square cell is much more convenient to use because of its symmetry.

It is natural to try to use a similar cell in the more complicated cases, especially where the spectrum is under consideration, as this has been worked out in the case of one particle for such a square cell. A little consideration of the lattice for two types of particles (fig. 2*c*) shows, however, that if a square cell is to be used, four particles have to be allowed in the unit, which has obvious disadvantages. If we wish to use the simple cell containing two particles we must use a parallelogram as shown in the diagram fig. 2*d*. From this we can in the usual way express the displacement of any particle in terms of the components along the two independent directions defined by the axes. We call these $u_{2lm}\, v_{2lm}$, $u_{2l+1m}\, v_{2l+1m}$ where m runs from 1 to N and l from 1 to N, the odd values of l referring to particles of mass m, the even values to particles of mass M. We can then write down the equation of motion in terms of the binding forces and expressing the solution in the form

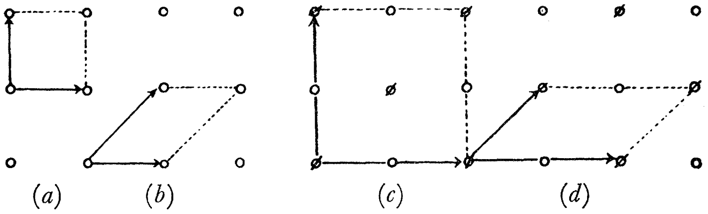

Fig. 2—Different types of lattice cells.

$$\left.\begin{aligned} u_{2lm} &= u_o\, e^{i(wt+2l\phi_1+m\phi_2)} \\ v_{2lm} &= v_o\, e^{i(wt+2l\phi_1+m\phi_2)} \end{aligned}\right\}, \quad \ldots \ldots \ldots \quad (3.1)$$

where $\phi_1 = \frac{\pi a_1}{\mathrm{N}}$, $\phi_2 = \frac{\pi a_2}{\mathrm{N}}$ and a_1 and a_2 are integers running from 1 to N.

$$\begin{vmatrix} -mw^2 + \mathrm{A}(\phi_1\phi_2) & \mathrm{C}(\phi_1\phi_2) & \mathrm{D}(\phi_1) & 0 \\ 0 & -mw^2 + \mathrm{B}(\phi_1\phi_2) & \mathrm{E}(\phi_1\phi_2) & \mathrm{D}(\phi_1 - \phi_2) \\ \mathrm{D}(\phi_1) & 0 & -\mathrm{M}w^2 + \mathrm{A}(\phi_1\phi_2) & \mathrm{C}(\phi_1\phi_2) \\ \mathrm{E}(\phi_1\phi_2) & \mathrm{D}(\phi_1 - \phi_2) & 0 & -\mathrm{M}w^2 + \mathrm{B}(\phi_1\phi_2) \end{vmatrix} = 0 \quad (3.2)$$

$$\begin{aligned} &\mathrm{A}(\phi_1\,\phi_2) = 2\alpha + 2\gamma'(1 - \cos(2\phi_1 - \phi_2))\,; && \mathrm{C}(\phi_1\,\phi_2) = \gamma'\sqrt{2}\,(\cos(\phi_1 - \phi_2) - \cos\phi_2) \\ &\mathrm{B}(\phi_1\,\phi_2) = 2\alpha + 2\gamma'(1 - \cos\phi_2)\,; && \mathrm{E}(\phi_1\,\phi_2) = \alpha\sqrt{2}\,(\cos(\phi_1 - \phi_2) - \cos\phi_1) \\ &\mathrm{D}(\phi_1) = -2\alpha\cos\phi_1\,; && \end{aligned}$$

The force constants here are defined in a similar way to those in the case of §2*a*. α is identical in the two cases, and $\gamma' = 2\gamma$.

One can, however, choose an equation which is rather more suitable for our purpose than the one above. This consists in principle in substituting for the phases ϕ_1, ϕ_2 the phases ψ_1, ψ_2, which can be defined with respect to the orthogonal axes. It is easy to see that if ψ_1, ψ_2 are the phase differences between neighbouring particles in the two directions for a particular normal vibration, then we have the relations

$$\left.\begin{aligned} \psi_1 + \psi_2 &= \phi_2 \\ \psi_1 &= \phi_1 \end{aligned}\right\} \quad \text{where} \quad 0 \leqq \begin{Bmatrix} \phi_1 \\ \phi_2 \end{Bmatrix} < 2\pi. \quad . \; . \; . \; . \; . \; . \quad (3.3)$$

Substituting for ψ in equation (3.2) and multiplying out, we obtain the relation

$$\begin{aligned} &\mathrm{X}_1^2\,\mathrm{Y}_1^2 - 4\gamma'^2 \sin^2\psi_1 \sin^2\psi_2\,(\mathrm{X}_1^2 + \mathrm{Y}_1^2) - \mathrm{X}_1\,\mathrm{Y}_1\,(4\alpha^2\cos^2\psi_1 + 4\alpha^2\cos^2\psi_2) \\ &\quad + 16\alpha^4\cos^2\psi_1\cos^2\psi_2 + 16\gamma'^4\sin^4\psi_1\sin^4\psi_2 - 32\gamma'^2\alpha^2\sin^2\psi_1\sin^2\psi_2\cos\psi_1\cos\psi_2 \\ &\qquad = 0, \quad (3.4) \end{aligned}$$

where

$$\begin{aligned} \mathrm{X}_1 &= -mw^2 + 2\alpha + 2\gamma'(1 - \cos\psi_1\cos\psi_2)\,; \\ \mathrm{Y}_1 &= -\mathrm{M}w^2 + 2\alpha + 2\gamma'(1 - \cos\psi_1\cos\psi_2). \end{aligned}$$

This can also be expressed in the form of a determinant :

$$\begin{vmatrix} \begin{matrix}-\mathrm{M}w^2+2\alpha \\ +2\gamma'(1-\cos\psi_1\cos\psi_2)\end{matrix} & 2\gamma'\sin\psi_1\sin\psi_2 & -2\alpha\cos\psi_1 & 0 \\ 2\gamma'\sin\psi_1\sin\psi_2 & \begin{matrix}-\mathrm{M}w^2+2\alpha \\ +2\gamma'(1-\cos\psi_1\cos\psi_2)\end{matrix} & 0 & -2\alpha\cos\psi_2 \\ -2\alpha\cos\psi_1 & 0 & \begin{matrix}-\mathrm{M}w^2+2\alpha \\ +2\gamma'(1-\cos\psi_1\cos\psi_2)\end{matrix} & 2\alpha'\sin\psi_1\sin\psi_2 \\ 0 & -2\alpha\cos\psi_2 & 2\gamma'\sin\psi_1\sin\psi_2 & \begin{matrix}-\mathrm{M}w^2+2\alpha \\ +2\gamma(1-\cos\psi_1\cos\psi_2)\end{matrix} \end{vmatrix} = 0. \quad (3.5)$$

This determinant can also be obtained, as was done in the first instance by Dehlinger,† by writing the equation of motion for the two particles of the unit cell in terms of their components along the orthogonal axes and substituting a periodic solution involving the ψ_1 ψ_2 defined above. It will be noted that the limits of ψ_2 are -2π and $+2\pi$ instead of 0 and 2π (*cf.* 3.3).

We shall use equation (3.4) and (3.5) in the further discussion.

There is another point to be noted here. Firstly, the γ' forces act between like particles only. Hence we might just as well have chosen two kinds of forces γ'_1, γ'_2, and the only difference in the determinant (3.5) would be that we should have γ'_1 in the rows containing mw^2 and γ'_2 in those containing $\mathrm{M}w^2$. The distinction between the two types of particles lies, therefore, not only in the masses but also in the forces.

Taking (3.4) and putting $m = \mathrm{M}$, *i.e.*, $\mathrm{X} = \mathrm{Y}$, we note that the equation may be written in the form

$$\mathrm{X}^4 - \mathrm{X}^2\,(4\alpha^2\cos^2\psi_1 + 4\alpha^2\cos^2\psi_2 + 8\gamma^2\sin^2\psi_1\sin^2\psi_2) \\ + (4\alpha^2\cos\psi_1\cos\psi_2 - 4\gamma'^2\sin^2\psi_1\sin^2\psi_2)^2 = 0, \quad . \qquad (3.6)$$

which may be put into the form

$$\{\mathrm{X}^2 - 2\alpha(\cos\psi_1 + \cos\psi_2) + 4\gamma'^2\sin^2\psi_1\sin^2\psi_2 + 4\alpha^2\cos\psi_1\cos\psi_2\} \\ .\,\{\mathrm{X}^2 + 2\alpha\,(\cos\psi_1 + \cos\psi_2) + 4\gamma'^2\sin^2\psi_1\sin^2\psi_2 + 4\alpha^2\cos\psi_1\cos\psi_2\} = 0. \qquad (3.7)$$

Each of these two solutions represents the two wave surfaces in the case of equal masses, and the variables in the one case are related to those in the other case by the transformation

$$\psi_1 \rightarrow \pi - \psi_1$$

$$\psi_2 \rightarrow \pi - \psi_2.$$

This is shown in fig. 4*a* and *b*.‡ Only the outlines are given. For the form of the contour lines we refer to a previous paper.§

We deal here only with the range $0 \leqq \psi_1, \psi_2 \leqq \pi$. Actually ψ_2 extends from -2π to $+2\pi$ and ψ_1 from 0 to 2π, but since we can put $\psi'_1 = 2\pi - \psi_1$, $\psi'_2 = \psi_2$ or $\psi'_2 = 2\pi - \psi_2$, $\psi'_1 = \psi_1$ in equation (3.5) without changing this in any way, we can confine ourselves to the range $0 \leqq \psi \leqq 2\pi$; the frequency surfaces for the range $0 \leqq \psi \leqq 2\pi$ can be obtained by reflexion in the planes $\psi_1 = \pi$, $\psi_2 = \pi$.

We shall now proceed to discuss qualitatively how the frequency surfaces split up. Since the roots of (3.4) cannot be expressed in a simple form we fall back on a discussion of certain cross-sections, from which we can obtain the desired information. Certain general results are of use in this connexion. For $\gamma'_1 = \gamma'_2$ and

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† 'Phys. Z.,' vol. 15, p. 275 (1914).

‡ In all these diagrams the frequency is plotted as a function of ψ_1 and ψ_2.

§ Blackman, *loc. cit.*

$m = \mathrm{M}$ we must go over into the case shown in figs. 4*a* and *b* and for $\gamma \simeq 0$ and $m \neq \mathrm{M}$ we have the quasi one-dimensional form (*cf.* II), which is known for all values of m/M. In the case of $m \ll \mathrm{M}$ we know, for instance, that the surfaces are widely separated (optical from acoustical) and that the optical branches are nearly monochromatic. Furthermore, it is clear that the splitting of the frequency branches takes place along certain curves in the two-dimensional case instead of at points.

We consider first the cross-sections $\psi_1 = 0$, $\psi_2 = x$. Since the determinant is symmetrical in ψ_1, ψ_2, we have identical results for $\psi_1 = x$, $\psi_2 = 0$; similar results hold also for $\psi_1 = \pi$, $\psi_2 = x$, etc.

We have in the above case,

$$\mathrm{X}_1^2\,\mathrm{Y}_1^2 - \mathrm{X}_1\,\mathrm{Y}_1\,(4\alpha^2 + 4\alpha^2\cos^2 x) + 16\alpha^4 \cos{}^2 x = 0,$$

where

$$\left.\begin{aligned} \mathrm{X}_1 &= -\,mw^2 + 2\alpha + 2\gamma'\,(1 - \cos x) \\ \mathrm{Y}_1 &= -\,\mathrm{M}w^2 = 2\alpha + 2\gamma'\,(1 - \cos x) \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (3.8)$$

Here we can, of course, find the explicit solutions. The figs. 3 show the cross-sections for the cases $m/\mathrm{M} = 1$, $1/1{\cdot}1$ and $1/3$.

The values of the two middle frequencies $\left(0\,\frac{\pi}{2}\right)$ which will be used later, are given by

$$\left.\begin{aligned} w_1 &= (2\alpha + 2\gamma'/m)^{\frac{1}{2}} \\ w_2 &= (2\alpha + 2\gamma'/\mathrm{M})^{\frac{1}{2}} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (3.9)$$

A very interesting fact is the asymmetry which is apparent in fig. 3*c*, i. The extreme points of the middle curves are not given by (3.9) as we might have expected, but lie on opposite sides of the $\left(0\,\frac{\pi}{2}\right)$ frequencies. For all practical applications this shift is, however, so small that (3.9) may be used.

The second set of cross-sections, which we shall use, is given by $(\psi_1\,\psi_2) = \left(\frac{\pi}{2}\,x\right)$. These are defined by the equations

$$\mathrm{X}_1^2\,\mathrm{Y}_1^2 - 4\alpha^2\cos^2 x\,\mathrm{X}_1\,\mathrm{Y}_1 - 4\gamma'^2\,(\mathrm{X}_1^2 + \mathrm{Y}_1^2)\sin^2 x + 16\gamma'^4\sin^4 x = 0$$

where

$$\left.\begin{aligned} \mathrm{X}_1 &= -\,mw^2 + 2\alpha + 2\gamma', \\ \mathrm{Y}_1 &= -\,\mathrm{M}w^2 + 2\alpha + 2\gamma' \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (3.10)$$

It will be noted that (3.10) is symmetrical about $x = \frac{\pi}{2}$. Starting with $m = \mathrm{M}$ we have the form shown in fig. 3*a*, ii. The $\left(0\frac{\pi}{2}\right)$ frequencies are w_1 and w_2 (3.9) with $w_1 = w_2$ and $w_3 = (2\gamma'/m)^{\frac{1}{2}}$, $w_4 = (4\alpha + 4\gamma'/m)^{\frac{1}{2}}$ for the lowest and highest frequencies respectively. The four $\left(\frac{\pi}{2}\frac{\pi}{2}\right)$ frequencies are given by $w'_1 = w'_2 = (2\alpha/m)^{\frac{1}{2}}$ and $w'_3 = w'_4 = (2\alpha + 4\gamma'/m)^{\frac{1}{2}}$.

When we have different masses we have the values

$$\left.\begin{array}{ll} w'_1 = (2\alpha/\mathrm{M})^{\frac{1}{2}}, & w'_2 = (2\alpha/m)^{\frac{1}{2}} \\ w'_3 = (2\alpha + 4\gamma'/\mathrm{M})^{\frac{1}{2}}, & w'_4 = (2\alpha + 4\gamma'/m)^{\frac{1}{2}} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad (3.11)$$

The frequencies w_3 and w_4 have a more complicated form, and will be omitted as we do not need them here.

Considering (3.11) we see that of the $\left(\frac{\pi}{2}, \frac{\pi}{2}\right)$ frequencies w'_1 has always the lowest, w'_4 always the highest value, whatever values we choose for m, M, α, and γ (α and γ

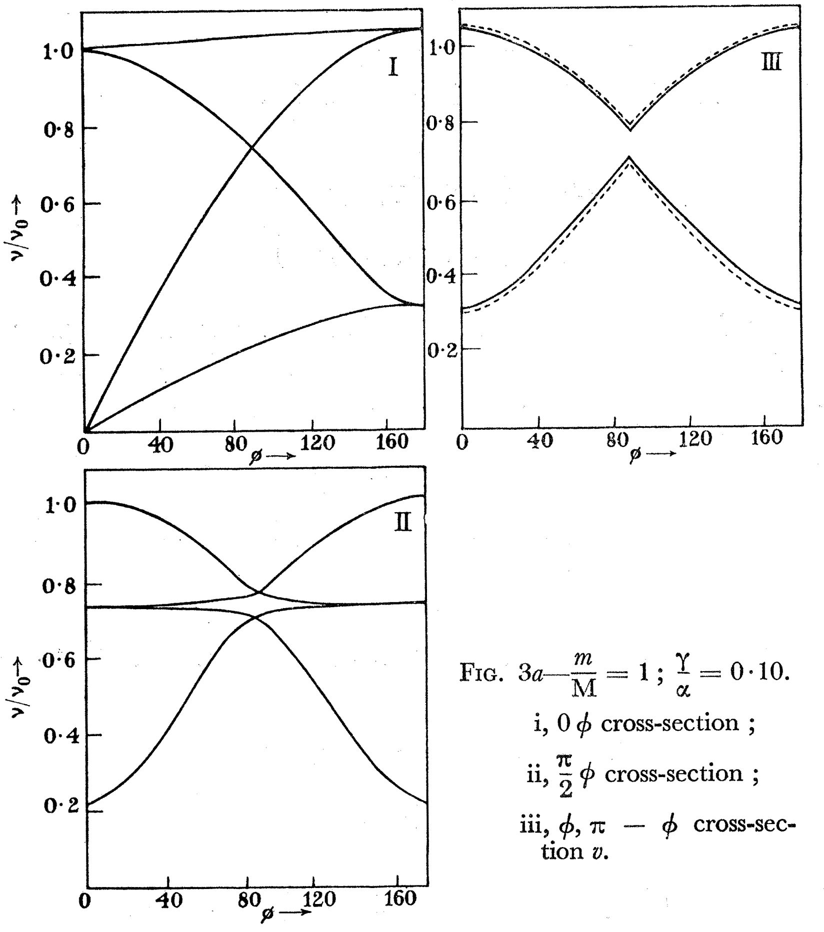

FIG. 3*a*—$\frac{m}{\mathrm{M}} = 1$; $\frac{\gamma}{\alpha} = 0\cdot 10$.
i, 0 ϕ cross-section;
ii, $\frac{\pi}{2}$ ϕ cross-section;
iii, ϕ, $\pi - \phi$ cross-section *v*.

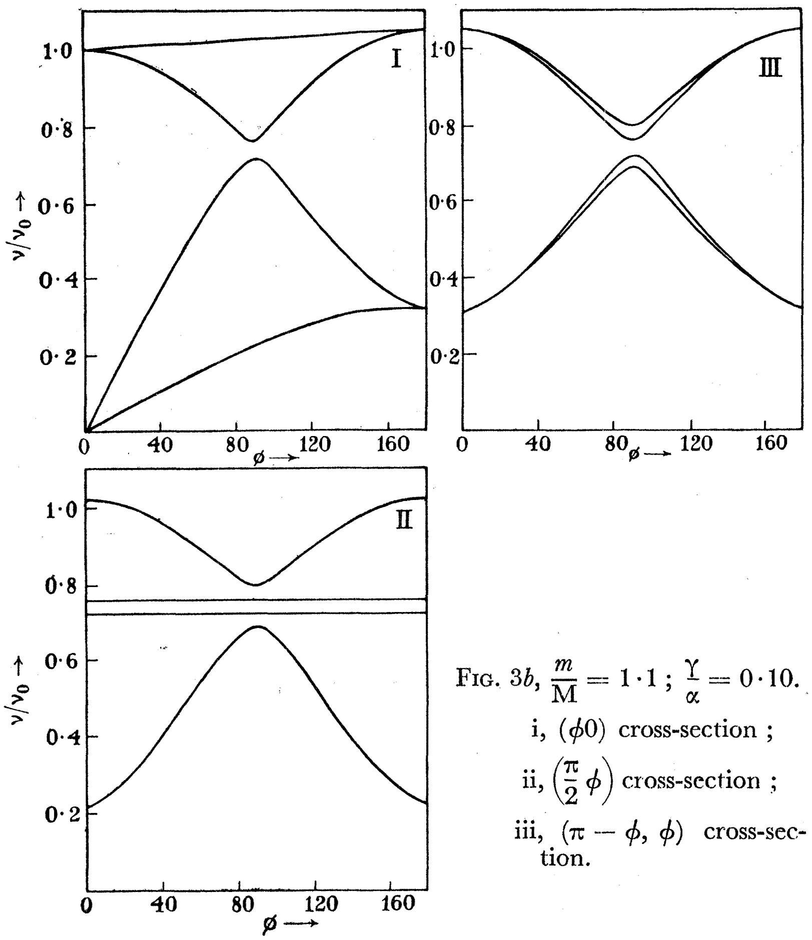

FIG. 3b, $\frac{m}{M} = 1\cdot1$; $\frac{\Upsilon}{\alpha} = 0\cdot10$.
i, $(\phi 0)$ cross-section ;
ii, $\left(\frac{\pi}{2}\,\phi\right)$ cross-section ;
iii, $(\pi - \phi,\ \phi)$ cross-section.

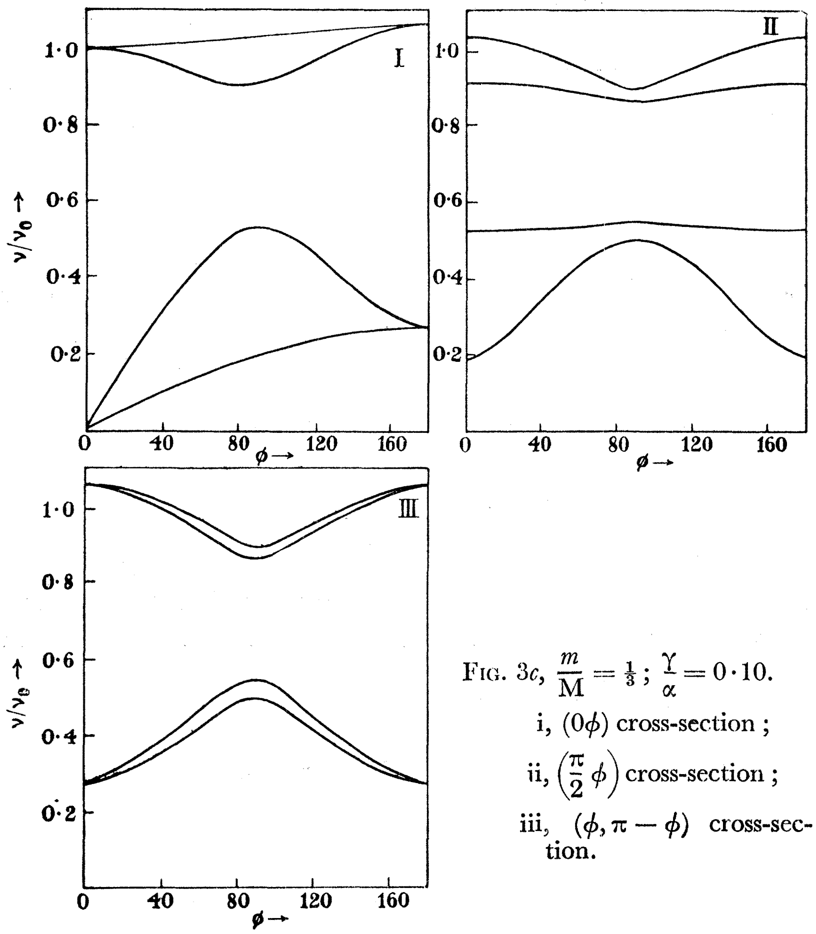

FIG. 3c, $\frac{m}{M} = \frac{1}{3}$; $\frac{\Upsilon}{\alpha} = 0\cdot10$.
i, (0ϕ) cross-section ;
ii, $\left(\frac{\pi}{2}\,\phi\right)$ cross-section ;
iii, $(\phi, \pi - \phi)$ cross-section.

must, of course, be positive). On the other hand, $w'_2 < w'_3$ if m/M is sufficiently near to unity. As soon as we allow m/M to vary, we see that $w'_2 > w'_3$ if

$$1+\frac{2\gamma'}{\alpha}<\frac{\mathrm{M}}{m}. \qquad (3.12)$$

An idea of what this means can be obtained from the diagrams (figs. 3). (All these figures are drawn to scale.)

It will be noticed that the frequency w'_3 belongs in fig. 3*b* (where $m/\mathrm{M} \approx 1$) to an optical branch, but in the case of $m/\mathrm{M} \ll 1$ (fig. 3*c*), it belongs to an acoustical branch. The reverse is the case for the frequency w'_2.

The third set of cross-sections are defined by the relations $\psi_1 = \pi - x$, $\psi_2 = x$† which is a diagonal section. The equation for the curves becomes

$$\mathrm{X}_1^2\,\mathrm{Y}_1^2 - \mathrm{X}_1\,\mathrm{Y}_1\,8\alpha^2\cos^2 x - 4\gamma'^2(\mathrm{X}_1^2+\mathrm{Y}_1^2)\sin^2 x \\ - 32\gamma'^2\,\alpha^2\sin^4 x\cos^2 x + 16\alpha^4\cos^4 x + 16\gamma'^4\sin^8 x = 0, \qquad (3.13)$$

where
$$\mathrm{X}_1 = -mw^2 + 2\alpha + 2\gamma'(1+\cos^2 x)$$
$$\mathrm{Y}_1 = -\mathrm{M}w^2 + 2\alpha + 2\gamma'(1+\cos^2 x).$$

In the case of $m = \mathrm{M}$, *i.e.*, $\mathrm{X} = \mathrm{Y}$ (3.13) reduces to

$$[\mathrm{X}_1^2 - (4\alpha^2\cos^2 x + 4\gamma'^2\sin^4 x)]^2 = 0,$$

i.e., a complete square. This is indicated in fig. 3*a*, iii. The separation of the curves in the general case is now similar to the previous case in that we again have an interchange of vibrations between two frequency branches. This takes place at the $\left(\frac{\pi}{2}\frac{\pi}{2}\right)$ point as before.

With the help of the above cross-sections, the form of the wave surfaces as indicated in fig. 4*c*, *d*, *e*, *f*, will be understood. Only the outlines have been drawn and the contours omitted. The case has been taken where the surfaces are well separated. Other cases can be visualized with the help of the cross-sections.

As indicated above, the wave surfaces touch again at the $\left(\frac{\pi}{2}\frac{\pi}{2}\right)$ points when

$$1+\frac{2\gamma'}{\alpha}=\frac{\mathrm{M}}{m}.$$

The interchange which occurs here is a rather curious feature. Since this interchange of vibrations between the optical and acoustical branches is confined to the $\left(\frac{\pi}{2}\frac{\pi}{2}\right)$ point, it is unlikely to have special significance or practical applications.

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† These are not the same as the (x, x) cross-sections.

4—The first question of importance with regard to the vibrational spectrum is the number and the position of the maxima of the density of the vibrations. It has been shown (*cf.* II) that even for one particle per cell we have maxima of the density near some of the points characterized by the values (0π), $(\pi\ \pi)$, for $(\psi_1\ \psi_2)$. For all such values as is shown by (3.4) the frequency surfaces touch; there are always four solutions falling into two parts. It can be shown that $\frac{\partial\nu}{\partial\psi_1}$ and $\frac{\partial\nu}{\partial\psi_2}$ are always zero at these points, and hence we have zero gradient at all points where $(\psi_1\ \psi_2) = (0\ \pi), (\pi\ 0), (\pi\ \pi)$ in this case also.

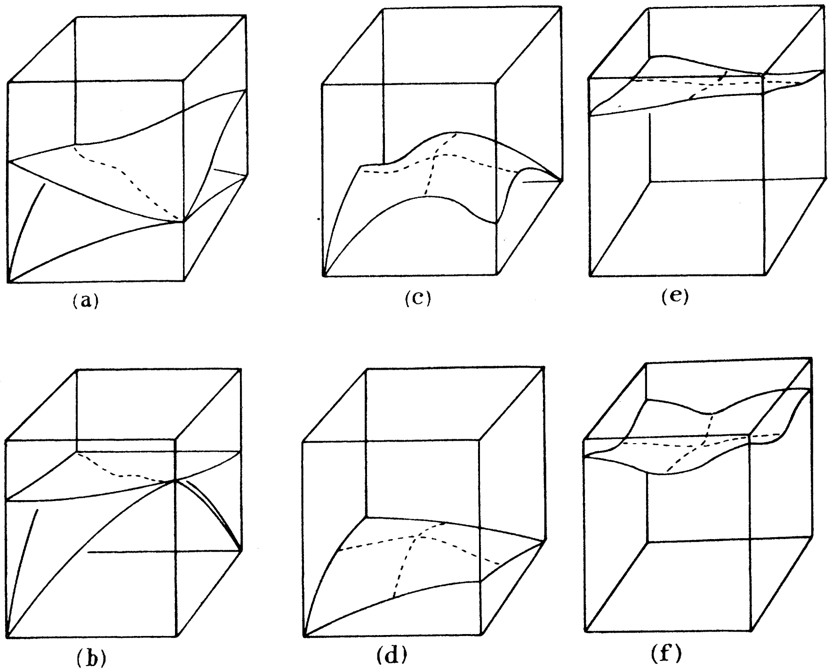

Fig. 4—*a*, *b*, frequency branches $\frac{m}{\mathrm{M}} = 1$.

c, *d*, acoustical branches
e, *f*, optical branches $\Big\}\ \frac{m}{\mathrm{M}} \neq 1$. Frequency is plotted along the vertical lines. The variables $\psi_1\ \psi_2$ along the other two axes.

It is necessary to emphasize here that the fact that $\frac{\partial\nu}{\partial\psi_1} = 0\ \frac{\partial\nu}{\partial\psi_2} = 0$, means merely that the surface runs " flat " at a certain point, and not necessarily that the density of the normal vibrations is a maximum at that point.† It may as often indicate a minimum. Nevertheless, these points form a very useful starting point for the consideration of where the maxima are likely to be, and are certainly associated with maxima in some cases, *e.g.*, the maximum in the lower frequency branch in the case of one particle per cell discussed in § 2.

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† I am greatly indebted to Dr. R. Peierls for some helpful discussions on this point.

For the two-dimensional lattice with two particles per cell (§ 3), there are new points of zero gradient as compared with the simpler case (§ 2). One set is certainly the $\left(\frac{\pi}{2}\,\frac{\pi}{2}\right)$ points, as is clear from a study of the cross-sections. The splitting of the frequency branches produces, however, another set of such points. These lie near two of the $\left(0,\,\frac{\pi}{2}\right)$ frequencies $w_1 = \sqrt{\frac{2\alpha + 2\gamma'}{m}}$ $w_2 = \sqrt{\frac{2\alpha + 2\gamma'}{M}}$ which fall together when $m = M$. To show this we note that the tangent to the surface in the $(0,\ \psi_2)$ plane is certainly parallel to the $(\psi_1\ \psi_2)$ plane at the points where the frequencies have their extreme values. These are not the $\left(0\,\frac{\pi}{2}\right)$ points (*cf.* fig. 3*b*, i), but lie near these in all practical cases. Furthermore, the tangent to the surface at right angles to the $(0\ \psi_2)$ plane is always zero. Hence at these points both $\frac{\partial\nu}{\partial\psi_1}$ and $\frac{\partial\nu}{\partial\psi_2}$ are zero.

We have in this case four sets of points where the gradient is zero as compared with two when the particles are identical.

The number and approximate position of the actual maxima of the density of the normal vibrations may be determined by a study of the frequency surfaces. From figs. 3 and 4 it will be seen that in the acoustical branches we have one maximum in each case, near $(0\ \pi)$ in the lower branch and near $\left(0\,\frac{\pi}{2}\right)$ in the upper branch; and no maximum at $\left(\frac{\pi}{2}\,\frac{\pi}{2}\right)$. Similar results are obtained for the optical branches. In the lower branch the maximum will lie near $\left(0\,\frac{\pi}{2}\right)$, in the upper branch near $(\pi\ \pi)$. The $\left(\frac{\pi}{2}\,\frac{\pi}{2}\right)$ points are hence of no great importance.

We have, therefore, four maxima in all, two being due to the splitting of the frequency branches.

5—The general selection rules governing the infra-red absorption are again given by the relations

$$\psi_1 + \psi'_1 + \psi''_1 = 0, \pm 2\pi. \qquad \left(\psi_1 = \frac{\pi r}{N},\ \psi_2 = \frac{\pi s}{N}\right)$$
$$\psi_2 + \psi'_2 + \psi''_2 = 0, \pm 2\pi.,$$

where one of these vibrations is the optical vibration $(\pi\ \pi)$. Hence combination of vibrations belonging to different optical and acoustical branches is allowed. Maxima in the spectrum of the combination tones will be produced by combination of the two middle maxima. The $(0\ \pi)$ maxima will probably yield only weak maxima if at all. We should therefore expect two summation tones and two difference tones to appear in the absorption, the former lying on the short-wave, the latter on the long-wave side of the main line.

6—THREE-DIMENSIONAL THEORY

In the three-dimensional problem we consider a cubical lattice of the NaCl type, *i.e.*, containing two different types of particles. For reasons given above, the cell containing the smallest number of particles is preferable, and this is not a cubical cell. One can however deduce, as was indicated in § 2, a six-rowed determinant containing the frequency as a function of certain phases $(\psi_1\ \psi_2\ \psi_3)$ which are referred to the normal axes. The equation, which is the same as was found by Dehlinger (*loc. cit.*) except that it has included the forces between particles at a distance $a\sqrt{3}$ (where a is the lattice constant).

$$\begin{vmatrix}
-\mathrm{M}w^2+\mathrm{A}(\psi_1;\psi_2\psi_3) & \mathrm{B}(\psi_1;\psi_2\psi_3) & \mathrm{C}(\psi_1\psi_2) & \mathrm{D}(\psi_1\psi_2;\psi_3) & \mathrm{C}(\psi_1\psi_3) & \mathrm{D}(\psi_1\psi_3;\psi_2) \\
\mathrm{B}(\psi_1;\psi_2\psi_3) & -mw^2+\mathrm{A}(\psi_1;\psi_2\psi_3) & \mathrm{D}(\psi_1\psi_2;\psi_3) & \mathrm{C}(\psi_1\psi_2) & \mathrm{D}(\psi_1\psi_3;\psi_2) & \mathrm{C}(\psi_1\psi_3) \\
\mathrm{C}(\psi_2\psi_1) & \mathrm{D}(\psi_2\psi_1;\psi_3) & -\mathrm{M}w^2+\mathrm{A}(\psi_2;\psi_3\psi_1) & \mathrm{B}(\psi_2;\psi_3\psi_1) & \mathrm{C}(\psi_2\psi_3) & \mathrm{D}(\psi_2\psi_3;\psi_1) \\
\mathrm{D}(\psi_2\psi_1;\psi_3) & \mathrm{C}(\psi_2\,\psi_1) & \mathrm{B}(\psi_2;\psi_3\psi_1) & -mw^2+\mathrm{A}(\psi_2;\psi_3\psi_1) & \mathrm{D}(\psi_2\psi_3;\psi_1) & \mathrm{C}(\psi_2\psi_3) \\
\mathrm{C}(\psi_3\psi_1) & \mathrm{D}(\psi_3\psi_1;\psi_2) & \mathrm{C}(\psi_3\psi_2) & \mathrm{D}(\psi_3\psi_2;\psi_1) & -\mathrm{M}w^2+\mathrm{A}(\psi_3;\psi_2\psi_1) & \mathrm{B}(\psi_3;\psi_2\psi_1) \\
\mathrm{D}(\psi_3\psi_1;\psi_2) & \mathrm{C}(\psi_3\psi_1) & \mathrm{D}(\psi_3\psi_2;\psi_1) & \mathrm{C}(\psi_3\psi_2) & \mathrm{B}(\psi_3;\psi_2\psi_1) & -mw^2+\mathrm{A}(\psi_3;\psi_2\psi_1)
\end{vmatrix} = 0$$

where

$$\mathrm{A}(\psi_1;\psi_2\psi_3) = 2\alpha + 8\delta + 4\gamma\,(2 - \cos\psi_1\cos\psi_2 - \cos\psi_1\cos\psi_3); \qquad \mathrm{C}(\psi_1\,\psi_2) = 4\gamma\sin\psi_1\sin\psi_2$$

$$\mathrm{B}(\psi_1;\psi_2\psi_3) = -2\alpha\cos\psi_1 - 8\delta\cos\psi_1\cos\psi_2\cos\psi_3 \qquad \mathrm{D}(\psi_1\psi_2;\psi_3) = 8\delta\sin\psi_1\sin\psi_2\cos\psi_3. \quad . \quad . \quad (6.1)$$

The definitions of α and γ are as before (§ 2 (a)).

The frequencies which are of interest for our purpose are, firstly, the $\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$ group, given by

$$\left.\begin{aligned} w_1 &= (2\alpha + 8\delta + 4\gamma/m)^{\frac{1}{2}} \\ w_2 &= (2\alpha + 8\delta + 4\gamma/\mathrm{M})^{\frac{1}{2}} \end{aligned}\right\}\ \text{twice}$$

$$w_3 = (2\alpha + 8\delta + 16\gamma/m)^{\frac{1}{2}}$$

$$w_4 = (2\alpha + 8\delta + 16\gamma/\mathrm{M})^{\frac{1}{2}}.$$

Of the $\left(0\,\frac{\pi}{2}\,\frac{\pi}{2}\right)$ group four are of interest,

$$w_5 = (2\alpha + 8\delta + 12\gamma/m)^{\frac{1}{2}} \qquad w_6 = (2\alpha + 8\delta + 12\gamma/\mathrm{M})^{\frac{1}{2}}$$

$$w_7 = (2\alpha + 8\delta + 4\gamma/m)^{\frac{1}{2}} \qquad w_8 = (2\alpha + 8\delta + 4\gamma/\mathrm{M})^{\frac{1}{2}}. \quad . \quad . \quad . \quad (6\cdot2)$$

and of the $\left(0\,0\,\frac{\pi}{2}\right)$ group, two :

$$w_9 = (2\alpha + 8\delta + 8\gamma/m)^{\frac{1}{2}}$$

$$w_{10} = (2\alpha + 8\delta + 8\gamma/\mathrm{M})^{\frac{1}{2}}.$$

Furthermore,

$$w_{\pi\pi\pi} = \sqrt{(2\alpha + 8\delta)\left(\frac{1}{m} + \frac{1}{\mathrm{M}}\right)}.$$

It will be noticed that of the six $\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$ frequencies two fall together when the masses are different. An examination of the normal vibrations in this case shows that the two vibrations are identical as long as we have cubical symmetry (Appendix III).

If we take different values of γ for the two ions, the frequencies (6.1) are changed only so far as $\gamma_1(\gamma_2)$ replaces γ in the expressions containing m (M). It will be seen that even if the masses are made equal, we still have a splitting in the frequency branches in this case.

A full discussion of the features of the spectrum would necessitate a careful examination of the cross-sections in $\psi_1\ \psi_2\ \psi_3$ space. This is, however, not essential for the purposes of this paper, as we can obtain sufficient information as to main features of the spectrum without a detailed study.

We have three optical and three acoustical branches, which will in general not cut one another, though they touch at certain points (*e.g.*, the $(00\ \pi)$ points). The "interchange" mentioned in a previous section (§4) occurs again, the vibrations concerned being ω_1, ω_4 and ω_6, ω_7, belonging to the $\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$ and $\left(0\frac{\pi}{2}\frac{\pi}{2}\right)$ group respectively.

The gradient will be zero at all points where $(\psi_1\ \psi_2\ \psi_3) = (0\ \pi\ \pi)\ (0\ 0\ \pi)\ (\pi\ \pi\ \pi)$ and $\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$. There will also be other points lying near the $\left(0\,0\frac{\pi}{2}\right)\left(0\frac{\pi}{2}\frac{\pi}{2}\right)$ frequencies given in (6.2), as has been shown in the analogous two-dimensional case.

The maxima of the density may be divided into three types, as can be seen by a consideration of the quasi one-dimensional case ($\gamma = 0$, $\delta = 0$). There are, firstly, those maxima which depend on γ and δ only, and which disappear when $\gamma = 0$, $\delta = 0$; these should lie in the neighbourhood of the $(0\ 0\ \pi)\ (\pi\ \pi\ 0)$ points in the acoustical branches; there should be at least one prominent maximum of this type. The second kind of maxima is due to the splitting of the frequency branches into acoustical and optical, and forms the maxima at the $\nu_0\sqrt{\frac{m}{M+m}}\ \nu_0\sqrt{\frac{M}{M+m}}$ points in the limit $\gamma = 0$, $\delta = 0$. Since the spectrum is split into three parts in the general case, it seems reasonable to suppose that each maximum is split at the most into three smaller maxima; it is highly probable that there will be less than this number. These maxima will lie in the region bounded by the extreme values of the $\left(0\,0\frac{\pi}{2}\right)\left(0\frac{\pi}{2}\frac{\pi}{2}\right)\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$ frequencies. It will be seen that the $\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$ frequencies form the extreme points of the region in the case of a BORN-v. KÁRMÁN lattice (*cf.* (6.2)). The third type of maxima forms the maximum at the point ν_0 (the optical frequency) in the limit. These lie in a region bounded by the extreme values of the $(0\,0\,\pi)$ $(0\,\pi\,\pi)$ $(\pi\,\pi\,\pi)$ points; they all lie in the optical branches.

The above classification is a very rough one, but it will be noticed that we can fix a region in which the maxima belonging to the various types will lie, and this does give useful results when applied to the optical absorption.

The selection rules are

$$\begin{aligned} \psi'_1 + \psi'_2 + \psi'_3 &= 0, \quad \pm 2\pi \\ \psi'_2 + \psi''_2 + \psi''_2 &= 0, \quad \pm 2\pi \\ \psi'_3 + \psi''_3 + \psi'''_3 &= 0, \quad \pm 2\pi \end{aligned} \qquad \left(\psi_1 = \frac{\pi r}{N}, \qquad \psi_2 = \frac{\pi s}{N}, \qquad \psi_3 = \frac{\pi t}{N}\right)$$

where one of the vibrations is the optical frequency $(\pi\,\pi\,\pi)$. This means that combination is allowed between all the frequency branches. Combination between the $(0\ 0\ \pi)$ $(\pi\ \pi\ 0)$ frequencies is, however, again forbidden by symmetry, as in the two-dimensional case ; it is probable, though not certain, that the maxima which lie near these points will be of less importance for our work than the maxima due to the splitting of the frequency branches, because in the latter case there is no restriction whatsoever.

7—Discussion

a—Prominent Maxima—The one-dimensional theory gave one secondary maximum on the short-wave side of the main line λ_0 at a distance $\lambda_0/\sqrt{2}$, and one on the long-wave side. The first three-dimensional theory developed for small values of γ and δ gave again one maximum on the short-wave side, but modified the $\sqrt{2}$ law by a factor containing the binding constants. As will be shown below, this is a good approximation in the case of KCl. The general theory, as was shown in §6, yields a large number of such maxima.

In order to show that these do fit at least some of the maxima found experimentally, we can tabulate the values deduced from theoretical considerations. We have three constants α, γ, δ, which we can determine from the two elastic constants c_{11}, c_{12} and from the known value of the optical frequency ν_0 measured experimentally by Czerny and Barnes.

The relations which we use are the following :

$$c_{11}a = \alpha + 4\delta + 4\gamma$$

$$c_{12}a = 2\gamma + 4\delta$$

$$\nu_0 = \frac{1}{2\pi}\sqrt{(2\alpha + 8\delta)\left(\frac{1}{m} + \frac{1}{M}\right)}.$$

From these we obtain the data given in Tables I and II. The experimental results are also given.

Tables I

	NaCl	KCl
Elastic constants Kg/mm²	$c_{11} = 4770 \quad c_{12} = 1294$ $c_{44} = 1320.$	$c_{11} = 3750 \quad c_{12} = 685$ $c_{44} = 650$
Absorption maxima λ_0 in μ	$61\cdot1\mu$	$70\cdot6\mu$
Minding constants abs. units	$\alpha = 8465 \quad \delta = 616$ $\gamma = 558$	$\alpha = 9340 \quad \delta = 343$ $\gamma = 313$

From these values we can now write down the different frequencies we want, and also the combination frequencies.

TABLE II

	Frequencies $\left(\frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}\right)$	Summation tones	Difference tones	Observed
NaCl	$\nu_1 = 0{\cdot}924\nu_0$	$\lambda_1^+ = 35{\cdot}0\mu$; $\lambda_2^+ = 36{\cdot}6\mu$;	$\lambda_1^- = 222\mu$; $\lambda_2^- = 333\mu$	40μ
	$\nu_2 = 0{\cdot}818\nu_0$	$\lambda_3^+ = 38{\cdot}6\mu$; $\lambda_4^+ = 39{\cdot}1\mu$;	$\lambda_3^- = 382\mu$; $\lambda_4^- = 562\mu$	50μ
	$\nu_3 = 0{\cdot}1744\nu_0$			$\sim 200\mu$
	$\nu_4 = 0{\cdot}658\nu_0$	$\lambda_5^+ = 41{\cdot}4\mu$; $\lambda_6^+ = 46{\cdot}7\mu$;	$\lambda_5^- = 698\mu$; $\lambda_6^- = 825\mu$	$>200\mu$
KCl	$\nu_1 = 0{\cdot}803\nu_0$	$\lambda_1^+ = 45{\cdot}5\mu$; $\lambda_2^+ = 45{\cdot}6\mu$;	$\lambda_1^- = 763\mu$; $\lambda_2^- = 1122\mu$	47μ
	$\nu_2 = 0{\cdot}763\nu_0$	$\lambda_3^+ = 46{\cdot}3\mu$; $\lambda_4^+ = 46{\cdot}9\mu$;	$\lambda_3^- = 1350\mu$; $\lambda_4^- = 1760\mu$	60μ
	$\nu_3 = 0{\cdot}741\nu_0$	$\lambda_5^+ = 47{\cdot}6\mu$; $\lambda_6^+ = 49{\cdot}5\mu$;	$\lambda_5^- = 2200\mu$; $\lambda_6^- = 3300\mu$	200μ
	$\nu_4 = 0{\cdot}710\nu_0$			$>200\mu$

We have chosen the $\left(\frac{\pi}{2}\frac{\pi}{2}\frac{\pi}{2}\right)$ frequencies, as the actual frequencies should lie within the limits given in the table. It should be noted that the first short-wave maximum is represented very well by the theoretical values, especially when we note that the actual absorption band is several μ in width. The second maximum is, however, not represented very well, the agreement being better for NaCl than for KCl, where there is actually little sign of there being two bands.

All these frequencies lie very close to one another and to the $\sqrt{2}$ value, thus confirming the method adopted in the previous paper (*cf.* I). The calculated results for KCl can be deduced without any calculation if one notes that for small values of γ and δ the whole spectrum bends to a quasi one-dimensional case. Hence for moderately small mass differences the summation tones must all tend to the $\sqrt{2}$ value. On applying the same idea to the difference tones we arrive at the conclusion that they must lie very far in the infra-red, in accordance with the one-dimensional formula; this is also what we find in the table.

Experimentally, however, we find something quite different for KCl. The investigations show a pronounced anomaly in the absorption on the long-wave side of the main line at about 200μ, which is at first sight rather unexpected. One might think of taking into account a factor omitted in the original form of the theory, namely the possibility of different values of γ discussed in §6, as this would give an additional splitting of the frequency branches. This argument could be expected to hold in a case where γ or δ were fairly large, but not where they were already small. In order to go into the numerical side of the question we need some new assumption since there is now a new constant; we put $\gamma_1 = 0\ \gamma_2 = \gamma$, *i.e.*, we take the extreme case to see whether we can obtain any kind of agreement. The calculations show that for NaCl we can shift the whole band so as to run from 40μ to 50μ on the short-wave side, and from 100μ upwards on the long-wave side. In the case of KCl we still obtain a narrow band at 48μ, and the long-wave band starts at about 500μ.

Hence, although for NaCl we can, with the help of the two values of γ, obtain better agreement with the experimental results, we are left in the case of KCl with the same unexplained maxima lying close to the main line.

One possibility of explaining these results is that the combination between the $(0\ 0\ \pi)$ $(\pi\ \pi\ 0)$ vibrations is sufficiently intense to cause a large maximum. These frequencies are of two types, those which contain α and those which do not. The former tend to the optical frequency and the latter to zero, as γ and δ tend to zero. It is hence clear that in the limiting case we have, from combination between such frequencies, two maxima lying on each side of the main maximum, and tending towards this frequency as α and δ tend to zero. One might therefore think that this is the explanation of the behaviour of KCl and NaCl in the region near the main maximum.

To test the conclusion we may calculate the various frequencies involved from (6.1), assuming if necessary different values of γ. The results are, however, rather inconclusive. The four combination frequencies obtained for KCl are $1{\cdot}73\ \nu_0$, $1{\cdot}97\nu_0$, $1{\cdot}07\nu_0$, $0{\cdot}92\nu_0$.

We must, however, point out that a quantitative calculation of these frequencies can be made with the help of the investigations of BORN and THOMPSON,[†] where the actual forces between ions are introduced. It is possible that the connexion between the frequencies and the elastic constants is not quite as rigid as is required by the theory of the model, and hence that the splitting of the $\sqrt{2}$ levels in the case of KCl may be comparable with that of NaCl. In this case, the KCl maxima would be explained in the same way as those of NaCl.

b—Smaller Maxima—Several other maxima have been reported by MENTZL.[‡] He finds, for instance, that the 40μ maximum of NaCl is double. In view of the large number of maxima which may form this band, it will be obvious that theoretically a number of fluctuations in the band is extremely likely. The theory is, however, not sufficiently advanced to make an attempt at a detailed analysis worth while at present. Other maxima given by MENTZL are at about 30μ for NaCl and for KI ; now both these maxima lie above the harmonic of the main vibration ; it is possible to explain these maxima only if the higher order terms in the energy are taken into account. A quantitative discussion is hardly feasible at present in view of the small number of these maxima recorded.

c—Absorption in the Far Infra-Red—We shall confine ourselves mainly to the question of the difference tones. As outlined above, it seems that as long as the frequency branches are separate, we have a lower limit to the difference vibrations and hence after a certain point the absorption should go to zero. Of course, the terms of higher order will again modify this conclusion, as will the fact that combination between similar branches is allowed ; but it seems justifiable to expect an appreciable drop

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[†] ‘Proc. Roy. Soc.,’ A, vol. 147, p. 594 (1935).

[‡] ‘Z. Physik,’ vol. 88, p. 178 (1934).

on the absorption after a certain value of the frequency. At present the systematic measurements of CZERNY and his school have reached 300μ but no further, and the other measurements at isolated points are too few to allow definite conclusions to be drawn.

APPENDIX I

Note on the Use of Complex Normal Coordinates in the One-Dimensional Lattice Theory

(*a*) We consider the case dealt with in §2 where we have a linear chain of particles of mass *m* and M.

The transformation to normal coordinates is given by :

$$u_{2n} = \frac{1}{\sqrt{\mathrm{N}m}} \sum_{k=-\frac{\mathrm{N}}{2}}^{+\frac{\mathrm{N}}{2}} e^{\frac{\pi i k}{\mathrm{N}}2n} (\xi_k \cos \alpha_k + \eta_k \sin \alpha_k)$$

$$u_{2n+1} = \frac{1}{\sqrt{\mathrm{NM}}} \Sigma\, e^{\frac{\pi i \kappa}{\mathrm{N}}(2n+1)} (- \xi_k \sin \alpha_k + \eta_k \cos \alpha_k),$$

where α_k is given by the relation $\tan 2\alpha_k = \frac{2\sqrt{m\mathrm{M}}}{\mathrm{M}-m} \cos \frac{2\pi k}{\mathrm{N}}$ and $\xi_k = \xi^*_{-k}$, $\eta_k = \eta^*_{-k}$.

Putting $\xi_k = a_k + i\, b_k$; $\xi_{-k} = a_k - i\, b_k$; $\eta_k = c_k + i\, d_k$; $\eta_{-k} = c_k - i\, d_k$;

we have

$$u_{2n} = \frac{1}{\sqrt{\mathrm{N}m}} \sum_{k=0}^{\frac{\mathrm{N}}{2}} ({}^{\frac{\pi i k}{\mathrm{N}}2n} \xi_k + e^{\frac{-\pi i k}{\mathrm{N}}2n} \xi_{-k}) \cos \alpha_k + \sin \alpha_k\, (e^{\frac{\pi i k}{\mathrm{N}}2n} \eta_\kappa + e^{\frac{-\pi i \kappa}{\mathrm{N}}2n} \eta_{-k})$$

$$= \frac{1}{\sqrt{\mathrm{N}m}} \sum_{k=0}^{\frac{\mathrm{N}}{2}} \left\{ \left(a_k \cos \frac{\pi k 2n}{\mathrm{N}} - b_k \sin \frac{\pi k}{\mathrm{N}} . \, 2n \right) 2 \cos \alpha_k \right.$$

$$\left. + \left(c_k \cos \frac{\pi k}{\mathrm{N}}\, 2n - d_k \sin \frac{\pi k}{\mathrm{N}}\, 2n \right) 2 \sin \alpha_k \right\}$$

and a similar expression for u_{2n+1}.

Now if we can express the energy as a sum of terms containing $\xi_{-k}\xi_k$ and $\dot{\xi}_{-k}\dot{\xi}_k$, we can obviously express this equally well as the sum of terms containing a_k^2, $\dot{a}_k^2$, b_k^2, $\dot{b}_k^2$, etc. We notice that k runs from 0 to N/2. Actually, we have for every value of the frequency two normal vibrations of phase k and $2\mathrm{N} - k$; the exceptions are the translation and the maximum frequency respectively.

It will be seen that we have obtained in this way exactly the right number of normal vibrations, viz., 2N.

This is interesting because in the two- and three-dimensional cases this resolution leads usually to double the number of normal vibrations.

(*b*) We can further extend the use of these real normal coordinates. In the transformation which is used in § 1

$$\xi_k = c_{k1}\, e^{i\omega_{k1}t} + c_{k-1}\, e^{i\omega_{k-1}t},$$

we can put $\xi_k = a_k + ib_k$, etc., where

$$a_k = \mathrm{A}_k \cos(\omega_k t + \varepsilon_k) \qquad b_k = \mathrm{B}_k \cos(\omega_k t + \beta_k).$$

Hence we can express c_{kj} in terms of the above constants and find

$$c_{k1} = \tfrac{1}{2}\{\mathrm{A}_k \cos\varepsilon_k - \mathrm{B}_k \sin\beta_k + i(\mathrm{A}_k \sin\varepsilon_k + \mathrm{B}_k \cos\beta_k)\}$$

$$c_{k-1} = \tfrac{1}{2}\{\mathrm{A}_k \cos\varepsilon_k + \mathrm{B}_k \sin\beta_k - i(\mathrm{A}_k \sin\varepsilon_k - \mathrm{B}_k \cos\beta_k)\}$$

and

$$c_{k1}\, c^*_{k-1} = \tfrac{1}{4}(\mathrm{A}_k^2 + \mathrm{B}_k^2).$$

These vibrations are necessary for a discussion of the mean energy of the normal coordinates.

The kinetic energy of a normal vibration in the notation used will be $\dot{a}^2$, hence we have

$$\overline{\dot{a}_k^2} = \tfrac{1}{2}\mathrm{A}_k^2 w_k^2 = \frac{k\mathrm{T}}{2} \text{ and } \mathrm{A}_k^2 = \frac{k\mathrm{T}}{w_k^2}\ .$$

Hence $|c_{k1}|^2 = \tfrac{1}{4}(\mathrm{A}_k^2 + \mathrm{B}_k^2) = \dfrac{k\mathrm{T}}{2w_k^2}$.

APPENDIX II

A Note on the Form of the Normal Vibrations of a Two-Dimensional Lattice

The form of the normal vibrations is of special interest in certain cases, viz., those characterized by the values (0π) $(\pi\pi)$ $\left(\dfrac{\pi}{2}\,\dfrac{\pi}{2}\right)$ for the phases (ψ_1, ψ_2).

The transformation to normal coordinates has been found to be

$$u_{lm} = a \sum_{rs} e^{\frac{\pi i}{\mathrm{N}}(lr+ms)} (\xi_{rs} \cos\alpha_{rs} - \eta_{rs} \sin\alpha_{rs})$$

$$v_{lm} = a \sum_{rs} e^{\frac{\pi i}{\mathrm{N}}(lr+ms)} (\xi_{rs} \sin\alpha_{rs} + \eta_{rs} \cos\alpha_{rs}),$$

where a is a normalization constant and $\xi_{rs} = \xi^*_{-r-s}$, etc.
Also

$$\tan 2\alpha_{rs} = -\frac{4\gamma}{\alpha}\, \frac{\sin\frac{\pi r}{\mathrm{N}} \sin\frac{\pi s}{\mathrm{N}}}{\cos\frac{\pi r}{\mathrm{N}} - \cos\frac{\pi s}{\mathrm{N}}} \qquad \left(\psi_1 = \frac{\pi r}{\mathrm{N}}\ \psi_2 = \frac{\pi s}{\mathrm{N}}\right).$$

When $(\psi_1, \psi_2) = (0\,\pi)$, $\alpha_{rs} = 0$ and

$$u^{0\pi}_{lm} = \xi'_{0\mathrm{N}}\, e^{i\pi m} \qquad u^{\pi 0}_{lm} = \xi'_{\mathrm{N}0}\, e^{i\pi l}$$

$$v^{0\pi}_{lm} = \eta'_{0\mathrm{N}}\, e^{i\pi m}, \qquad v^{\pi 0}_{lm} = \eta'_{\mathrm{N}0}\, e^{i\pi l}.$$

Hence these two normal vibrations take the form shown in figs. 5*a* and 5*b*. It will be clear from the figures that in 5*a* only the γ force comes into play, not the α force; whereas in 5*b* both forces take part in the motion. Hence we should expect the frequency of the vibration to depend on γ only in case (*a*) and on α and γ in case (*b*). This is found to be so, *cf.* §2.

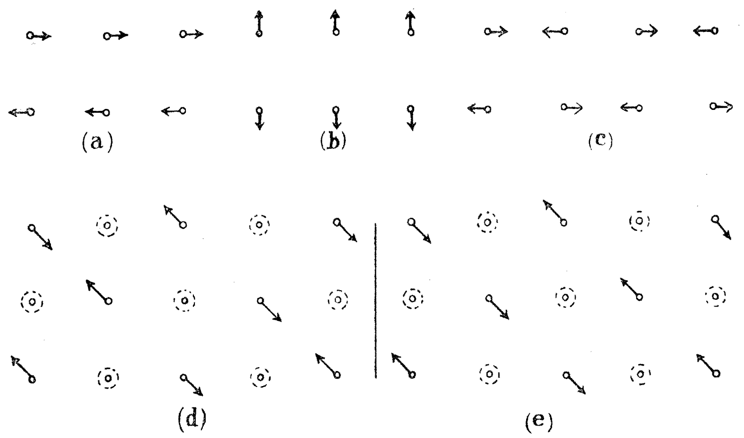

FIG. 5—Normal vibrations, *a* and *b* $(\psi_1\psi_2) = (0\pi)$; *c* $(\psi_1\psi_2) = (\pi\pi)$; *d* and *e* $(\psi_1\psi_2) = \left(\frac{\pi}{2}\,\frac{\pi}{2}\right)$.

An examination of the frequency equation shows that $\alpha_{rs} = 0$ also for the $(\pi\pi)$. The amplitudes of the normal vibrations are

$$u^{\pi\pi}_{lm} = \xi'_{\mathrm{NN}}\, e^{i\pi(l+m)}, \qquad v^{\pi\pi}_{lm} = \eta'_{\mathrm{NN}}\, e^{i\pi(l+m)}.$$

The form of the vibration shown in fig. 5*c* indicates that the γ force is not influenced, and that the frequency should depend on α only. The two normal vibrations are of course identical in the case under consideration.

For the $\left(\frac{\pi}{2}\,\frac{\pi}{2}\right)$ vibrations we find $\tan 2\alpha_{rs} = \infty$ and $\alpha_{rs} = \frac{\pi}{4}$.

We may then write

$$\xi'_{\frac{\mathrm{N}}{2}\frac{\mathrm{N}}{2}} = \frac{1}{\sqrt{2}}\left(u^{\frac{\pi}{2}\frac{\pi}{2}}_{lm} + v^{\frac{\pi}{2}\frac{\pi}{2}}_{lm}\right) e^{i\frac{\pi}{2}(l+m)}$$

$$\eta'_{\frac{\mathrm{N}}{2}\frac{\mathrm{N}}{2}} = \frac{1}{\sqrt{2}}\left(u^{\frac{\pi}{2}\frac{\pi}{2}}_{lm} - v^{\frac{\pi}{2}\frac{\pi}{2}}_{lm}\right) e^{i\frac{\pi}{2}(l+m)}$$

The relation of the amplitudes u_{lm}, v_{lm} can be given quite generally as

$$\frac{u_{lm}}{v_{lm}} = \frac{u'}{v'}\, e^{i((l-l')\psi_1+(m-m')\psi_2)}$$

where

$$\frac{u'}{v'} = -\frac{4\gamma \sin\psi_1 \sin\psi_2}{\alpha\,(\cos\psi_2 - \cos\psi_1) \pm \sqrt{(\cos\psi_2 - \cos\psi_1)^2 + 16\gamma^2 \sin^2\psi_1 \sin^2\psi_2}}\,.$$

Hence $u_{lm}^{\frac{\pi}{2}\frac{\pi}{2}} = \pm\, v_{lm}^{\frac{\pi}{2}\frac{\pi}{2}}$.

The two normal vibrations are shown in figs. 5*d* and *e*.

APPENDIX III

On the $\left(\frac{\pi}{2}\,\frac{\pi}{2}\,\frac{\pi}{2}\right)$ *Vibrations of a Simple Cubical Crystal.*

We confine ourselves for simplicity to the case where we have only one type of particle. In that case the equation of motion (when the phases are as above) can be written down in terms of the amplitudes in the form

$$\begin{array}{llll}
(-mw^2 + 2\alpha + 8\delta + 8\gamma)\, u' + & 4\gamma\, v' + & 4\gamma & w = 0 \\
4\gamma' \quad u' + & (-mw^2 + 2\alpha + 8\delta + 8\gamma)\, v' + & 4\gamma & w' = 0 \\
4\gamma' \quad u' + & 4\gamma\, v' + & (-mw^2 + 2\alpha + 8\delta + 8\gamma) & w' = 0.
\end{array}$$

If we now put

$$u' = \frac{1}{\sqrt{2}}(\xi + \eta + \zeta)$$

$$v' = \frac{1}{\sqrt{2}}(\xi - \eta)$$

$$w' = \frac{1}{\sqrt{2}}(\xi - \zeta)$$

we obtain the equations

$$\begin{aligned}
A\xi + B\eta + B\zeta &= 0, \\
A\xi - B\eta + B\zeta &= 0, \\
A\xi + B\eta - B\zeta &= 0,
\end{aligned}$$

where

$$A = -mw^2 + 2\alpha + 8\delta + 16\gamma \qquad B = -mw^2 + 2\alpha + 8\delta + 4\gamma.$$

For the existence of a solution it is necessary that A or B is zero ; it is obvious that both A and B are zero since the one condition follows from the other. Hence we have the three normal frequencies (two of which are equal) from the conditions A = 0, B = 0.

It is also clear that $\xi\eta\zeta$ are the amplitudes of the normal vibrations. These can be put in the form

$$\xi = \frac{\sqrt{2}}{3}(u' + v' + w')$$

$$\eta = \frac{\sqrt{2}}{3}(u' + v' - 2w')$$

$$\zeta = \frac{\sqrt{2}}{3}(u' + w' - 2v').$$

Since η, ζ are obtained from each other by interchanging v' and w', it is clear that they are exactly similar vibrations.

APPENDIX IV

A Note on the Relation of the Reflexion and Absorption Maxima

(*a*) The reflexion and absorption maxima can be correlated under certain circumstances. The secondary maxima on the short-wave side of the main maximum, fall usually in a region where the refractive index is very small. Assuming for the moment that we have no absorption, we have the well-known relation

$$n^2 = n_0^2 + \frac{\rho}{\nu^2 - \nu_0^2}.$$

For

$$n = 0, \qquad \frac{\rho}{\nu_k^2 - \nu_0^2} = -n_0^2$$

or

$$\nu_k^2 = \nu_0^2 - \frac{\rho}{n_0^2}.$$

In general the secondary maxima have a frequency smaller than ν_k, so that when there is absorption they lie in the region in which n is small. The reflexion coefficient may be written in the form

$$R = 1 - \frac{4n}{(1+n)^2 + k^2} = 1 - \frac{4n}{1 + k^2}$$

for small values of n.

If no subsidiary effects were present the refractive index would fall steadily in this region to minimum value and then increase. The damping factor will cause a small maximum to appear and hence there will be two minima. Since n_{min} corresponds to R_{max} here, we have two maxima of the reflexion with a minimum value corresponding to n_{max}.

We cannot measure n directly so we turn to a consideration of the transmission. We should expect a minimum of transmission (maximum of absorption) to lie near n_{max}. Hence the minimum value of the transmission and the reflexion should lie at practically the same point in the frequency scale. The above considerations hold only in the $\sqrt{2}$ region.

TABLE I

	Reflexion minimum	Transmission minimum
NaCl	40·5μ	~ 41μ
KCl	45·5μ	~ 47μ
LiF	~18μ	18–20μ

(*b*) The variation of the reflexion of a crystal with the thickness of the material has already been investigated theoretically.[†] The data of CZERNY for NaCl was used in conjunction with the theoretical formula, and it was found that as the thickness of the material became small compared with the wave-length, the maximum of reflexion moved to longer wave-lengths and the secondary maxima disappeared entirely. Hence no information as to the character of these secondary maxima could be obtained from an investigation of the reflexion of thin films, in contrast to the importance of the experiments on transmission.

Note added 14 *January*, 1936—After the completion of the above work, an interesting and important paper on the same topic by SEITZ, BARNES, and BRITTAIN appeared in the 'Physical Review,' 15 October. The points where the energy (or frequency) surface has extreme values are found with the help of group theory. It is assumed that all these will be maxima in the energy spectrum, and that the combinations will be corresponding maxima (subject to certain selection rules) in the infra-red spectrum. As has been discussed above, it is extremely unlikely that the maxima of the density of the normal vibrations will always coincide with the extreme points of the energy or frequency spectrum, and hence a much closer analysis is needed. Furthermore, the maxima of the frequency spectrum are usually fairly broad, and it is difficult to see how these could be used to explain the extremely sharp maxima found in the infra-red absorption spectrum of MgO.

SUMMARY

The features of the spectrum of a two-dimensional square lattice containing two particles per cell—especially the splitting of the frequency branches into acoustical and optical branches—are studied; the corresponding features of the three-dimensional case are also obtained. This information is applied to a consideration of the properties of the infra-red spectrum of polar crystals. Good agreement with experiment is obtained for NaCl, but the results for KCl are not so satisfactory. Various possibilities of explaining the discrepancy are discussed.

[†] BLACKMAN, 'Phil. Mag.,' vol. 18, p. 262 (1934).