

# On the Vibrational Spectrum of a Three-Dimensional Lattice

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1—All those properties of a crystal which depend on the heat motion of the constituent particles, require for their detailed explanation a knowledge of the actual form of the vibrational spectrum; about this very little is known, even qualitative features being difficult to obtain. It was supposed at first (Born and v. Kármán 1913) that the  $\nu^2$  law proposed by Debye formed a good approximation to the truth, but the experimental evidence, which gradually accumulated, tended to show that the specific heat did not vary exactly as  $T^3$  at temperatures where this law was expected to hold. Theoretical investigations (Blackman 1935) of the properties of a two-dimensional lattice showed that the spectrum could have markedly different features from those of a continuum distribution. It was furthermore found that large variations of  $\theta_D$  with temperature could occur and that spurious  $T^2$  regions were possible. On account of the similarity of the two- and three-dimensional cases as regards the frequency equation and in certain particular features, it was assumed that the spectrum would not be very different in the three-dimensional case; with this assumption it was possible to explain the rise in the  $\theta_D$  value of substances like KCl at low temperatures, and the discrepancies between elastic and thermal data.

The theoretical predictions have been confirmed to some extent by the recent experimental work of Keesom and Clark (1935). They find that the rise of the  $\theta_D$  curve stops at helium temperatures, as had been expected, but that the values decrease at still lower temperatures. Whether this last effect is real or not does not appear to be definitely settled. A possible theoretical explanation will be considered below.

The main object of this paper is to discuss the spectrum of a three-dimensional Born-v. Kármán lattice. This has been calculated numerically, and the results are completely analogous to those of the two-dimensional case.

2—We consider a simple cubic lattice containing one type of particle of mass  $m$ . Forces between neighbours along the axes and along the face diagonals only, are taken into account; these are of the quasi-elastic kind and are labelled  $\alpha$  and  $\gamma$  respectively. Any normal vibration of the lattice is

of a periodic nature and is described, *inter alia*, by three quantities  $(\phi_1, \phi_2, \phi_3)$  which are the phase differences of neighbouring particles along the three axes.

The frequency equation is given by:

$$\begin{vmatrix} A(\phi_1) + B(\phi_1; \phi_2, \phi_3) - m\omega^2 & C(\phi_1, \phi_2) & C(\phi_1, \phi_3) \\ C(\phi_2, \phi_1) & A(\phi_2) + B(\phi_2; \phi_3, \phi_1) - m\omega^2 & C(\phi_2, \phi_3) \\ C(\phi_3, \phi_1) & C(\phi_3, \phi_2) & A(\phi_3) + B(\phi_3; \phi_1, \phi_2) - m\omega^2 \end{vmatrix} = 0, \quad (1)$$

where

$$A(x) = 2\alpha(1 - \cos x),$$

$$B(x; y, z) = 4\gamma(2 - \cos x \cos y - \cos x \cos z),$$

$$C(x, y) = 4\gamma \sin x \sin y.$$

For every  $(\phi_1, \phi_2, \phi_3)$  we have three solutions, corresponding to the three modes of vibration obtained by interchanging the phases. In general we have three frequency hypersurfaces. Any value of the frequency  $\nu = \text{const.}$  gives three surfaces in  $\phi$  space. It will be sufficient for our purpose to consider the range  $0 \leq \phi_1, \phi_2, \phi_3 \leq \pi$  only, because

$$\nu(\phi_1, \phi_2, \phi_3) = \nu(-\phi_1, -\phi_2, -\phi_3), \text{ etc.}$$

It is clear that the spectrum of the lattice can be obtained only by some sort of numerical calculation. The study of the cross-sections in  $\phi$  space as in the two-dimensional case is, however, not practicable, but a somewhat similar method can be used. The  $\phi$  space was divided evenly into a three-dimensional array of points; the frequency was calculated for each of these points and the number between two values of the frequency was determined. It is obvious that a good approximation can be obtained by taking a very large number of points. It was found that about 30,000 points were needed to give a smooth curve for the density of the normal vibrations. Of course even this will give no more than a qualitative representation, but that is all we desire for the present.

In order to shorten the work as much as possible it was decided to avoid the laborious solution of the third order equations. This can be done when the  $\gamma/\alpha$  ratio is sufficiently small. Treating this as a perturbation it will be seen that the diagonal terms give the first order approximation. The square of the frequency is now linear in  $\cos \phi$ . This approximation amounts to crossing over the frequency surfaces in  $\phi$  space in a certain way; in the region of small frequencies it is equivalent to replacing the frequency surfaces by ellipsoids as discussed in a previous paper (Blackman 1935). This was shown to be perfectly justified. The correctness of the assumption over the whole frequency range can be tested in the two-dimensional case where the spectrum has been worked out using the correct expression for frequency

(Blackman 1935). It is found that the spectrum is qualitatively correct, the only difference being in the intensity at certain points, e.g. the maxima will tend to be less sharp. Since we are interested here in qualitative results only, not in an absolutely correct representation of the density, this is no essential disadvantage. It should be emphasized that the position of the maxima will be given with fair accuracy and that there will be no very great relative errors in intensity.

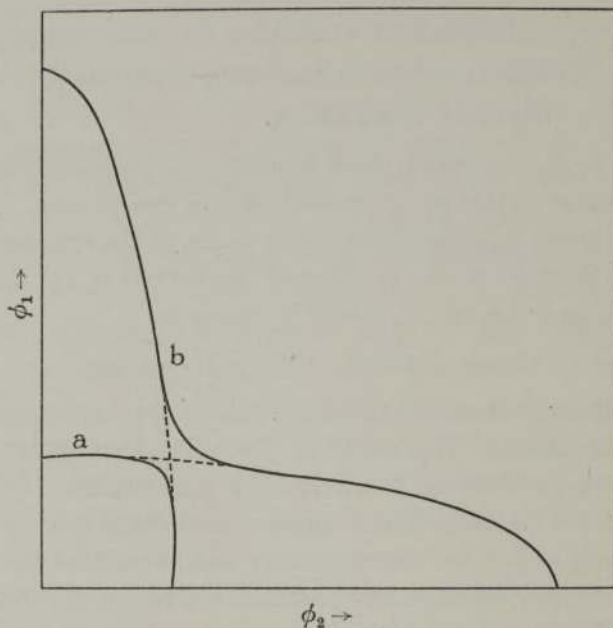


FIG. 1—Cross-sections of the frequency surfaces of a two-dimensional lattice ( $\gamma/\alpha = 0.05$ ).

The solutions of the frequency equation in this case becomes

$$\left. \begin{aligned} (a) \quad m\omega^2 &= 2\alpha(1 - \cos \phi_1) + 4\gamma(2 - \cos \phi_1 \cos \phi_2 - \cos \phi_1 \cos \phi_3), \\ (b) \quad m\omega^2 &= 2\alpha(1 - \cos \phi_2) + 4\gamma(2 - \cos \phi_2 \cos \phi_1 - \cos \phi_2 \cos \phi_3), \\ (c) \quad m\omega^2 &= 2\alpha(1 - \cos \phi_3) + 4\gamma(2 - \cos \phi_3 \cos \phi_1 - \cos \phi_3 \cos \phi_2). \end{aligned} \right\} \quad (2)$$

It will be noted that each equation can be obtained from the other by interchanging  $\phi_1, \phi_2, \phi_3$  suitably, and that hence each of these solutions will give the same frequency distribution, i.e. the same spectrum. The problem now arises as to whether we can calculate the spectrum for each of the frequency branches separately. This can be done. The method will be discussed first in the two-dimensional case, as this is very much simpler.

We consider the cross-sections in the two-dimensional  $\phi$  space; these yield two curves *a* and *b* (fig. 1) for a definite value of the frequency  $\nu$

which we are taking to be very small for the present. The curves enclose all points corresponding to a frequency smaller than  $\nu$ . Our approximation consists in replacing the two curves by parts of an ellipse indicated by the dotted lines. These new curves are now identical. It will be noticed that the area enclosed by the curve  $a$  is very nearly that which is covered by both the ellipses. Hence, if we cover the  $\phi$  space evenly with a number of points and if we know which points are enclosed by each ellipse, then the number of points which are common to both ellipses is a measure for the area enclosed by the lower curve. Knowing the points enclosed by one ellipse we can immediately write down those enclosed by the other. Having found the number in the overlapping region, we can obtain the number enclosed by the upper curve by subtracting it from the total number of points. Where the frequency is not small the curves are no longer ellipses but the same principle holds.

The three-dimensional treatment is very much the same. Here the three frequency surfaces in  $\phi$  space are replaced by three others which for small values of the frequency are three intersecting ellipsoids. For a definite value of the frequency  $\nu$  we can work out all points having frequency values from 0 to  $\nu$  belonging to each of these ellipsoids. The number of triple "coincidences" will give a measure for the volume enclosed by the lowest surface. The number of "pairs" and of "singles" then give, when suitably combined with the number of "triples", the corresponding volumes enclosed by the other two surfaces.

In this way the curve  $a^*$  (fig. 2) was found for the density of the normal vibrations, and from the detailed results the curves  $b, c, d$ , the contributions of the individual branches, were obtained. The value  $\gamma/\alpha = 0.05$  was chosen; each axis in  $\phi$  space was divided into 30 parts, so that the total number of points was  $31^3 = 29,791$ ; the frequency scale had 16 divisions, so that on the average about 2000 points fell into each region considered.

The main feature of the spectrum as a whole is the large heaping up of frequencies in the middle. For small values of the frequency the  $\nu^2$  law holds, but then there is an immediate rise to a maximum after which the density remains more or less constant until the optical frequency is reached, when a sudden increase occurs. The general form is very much the same as in the two-dimensional case, the resemblance being much closer than had been expected. It will be noted that the density curve tends to approach that of the one-dimensional case, the flattening out of the curve being one

\* A detailed account of the data used in constructing the curves has been given in an appendix at the end of the paper, in order not to disturb the argument at this stage.

of its main features; for small frequencies the three-dimensional character will of course predominate.

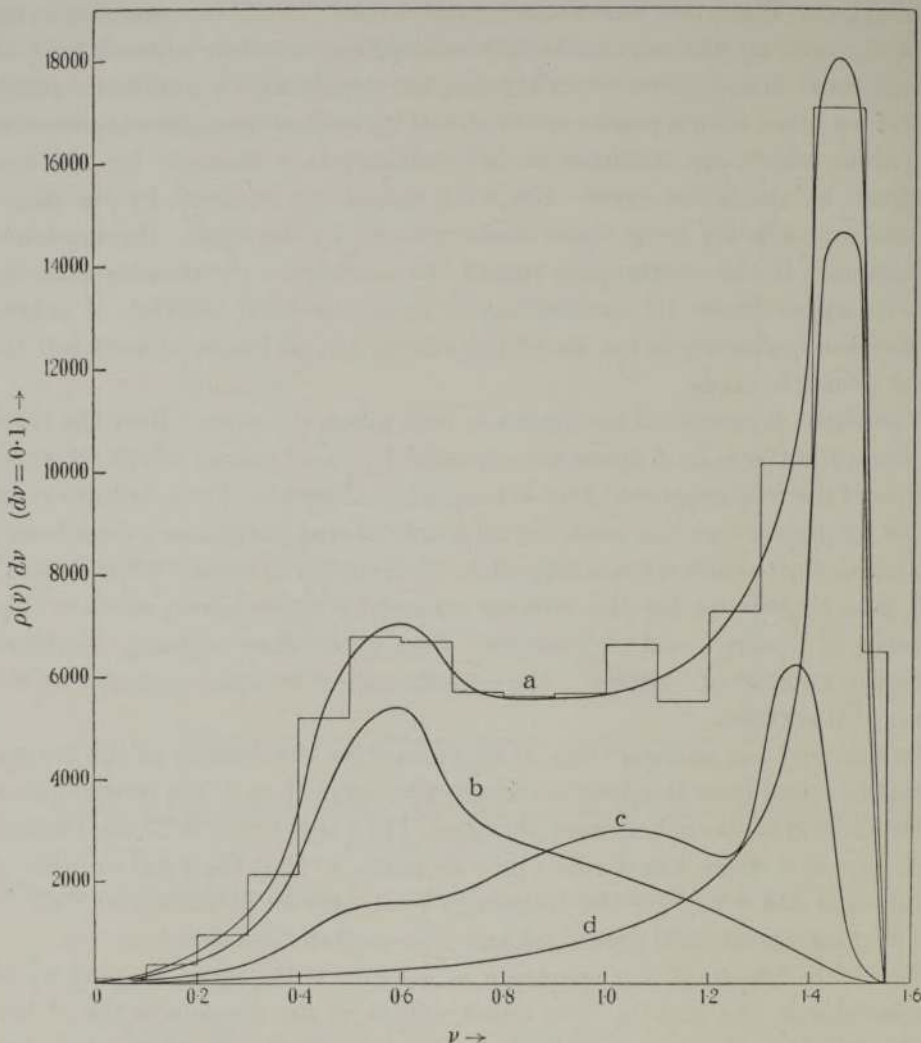


FIG. 2—The density of normal vibrations as a function of the frequency for a simple cubic lattice ( $\gamma/\alpha = 0.05$ ,  $\nu_D = 1.32$ ,  $\nu_{\max.} = 1.55$  in arbitrary units; the unit of the density is such that the total number of points is 89,373). The upper curve *a* represents the total spectrum, the lower curves *b*, *c*, *d* the spectrum for each of the three frequency branches. The “step” curve through which curve *a* is drawn is given to illustrate the method used in constructing the curves. The “steps” are obtained by calculation (Appendix I), and represent the total number of vibrations (i.e. total area) for a frequency range of 0.1; the curves are drawn through these “steps” in such a way as to keep the area under the curve equal to the area of the “step” for any particular frequency range.

The various frequency branches contain some rather interesting features. The branches  $b$ ,  $d$  are very similar to those of the two-dimensional case in that they have only one maximum, in the middle and at the end of the spectrum respectively (for small values of  $\gamma/\alpha$ ). The branch  $c$  is rather like a mixture of the other two; it possesses a rather small maximum at the end of the spectrum, and a very slight though broad one in the middle. It should be noted that, although there certainly seems to be a "hump" of some kind, the existence of this slight maximum is difficult to guarantee, as its height is probably of the same order as the error of the calculation. It was thought important to have some check on the small but distinct maximum at the end, and this can fortunately be obtained without difficulty. The case  $\gamma = 0$  was used, as explicit formulae for the density curves can be obtained. All cross-sections are planes in this limiting case.

The frequency equations become

$$\left. \begin{aligned} (a) \quad m\omega^2 &= 2\alpha(1 - \cos \phi_1), \\ (b) \quad m\omega^2 &= 2\alpha(1 - \cos \phi_2), \\ (c) \quad m\omega^2 &= 2\alpha(1 - \cos \phi_3). \end{aligned} \right\} \quad (3)$$

Putting  $a = \text{arc cos}(1 - m\omega^2/2\alpha)$  the volumes included by the three surfaces corresponding to a frequency  $\nu$  are respectively

$$\begin{aligned} (i) \quad V_1 &= a^3, \\ (ii) \quad V_2 &= 3a^2\pi - 2a^3, \\ (iii) \quad V_3 &= 3\pi^2a - 3a^2\pi + a^3. \end{aligned}$$

The density of the normal vibrations can be obtained by differentiating the volumes with respect to the frequency. The formulae for the three curves are

$$\left. \begin{aligned} \rho_1(\nu) &= 3a^2 \frac{\partial a}{\partial \nu}, \\ \rho_2(\nu) &= 6a(\pi - a) \frac{\partial a}{\partial \nu}, \\ \rho_3(\nu) &= 3(\pi - a)^2 \frac{\partial a}{\partial \nu}, \end{aligned} \right\} \quad (4)$$

where on putting  $\omega = 2\pi\nu$

$$\frac{\partial a}{\partial \nu} = \frac{4\pi^2 m \nu}{\alpha} [1 - (1 - 2\pi^2 m \nu^2 / \alpha)^2]^{-\frac{1}{2}}.$$

The sum of the three curves gives the density for the one-dimensional case (fig. 3, curve  $a$ ) as is to be expected.

It will be noted that curve  $d$  changes hardly at all as  $\gamma \rightarrow 0$ . The vibrations concerned are essentially longitudinal and these are little affected by the

value of  $\gamma$  as long as  $\gamma/\alpha$  remains small (the  $\theta_D$  value for this curve is proportional to  $\sqrt{(\alpha + 4\gamma)}$ ). Such a curve is probably the nearest approach to a Debye curve that can be obtained from considerations of lattice theory.\*

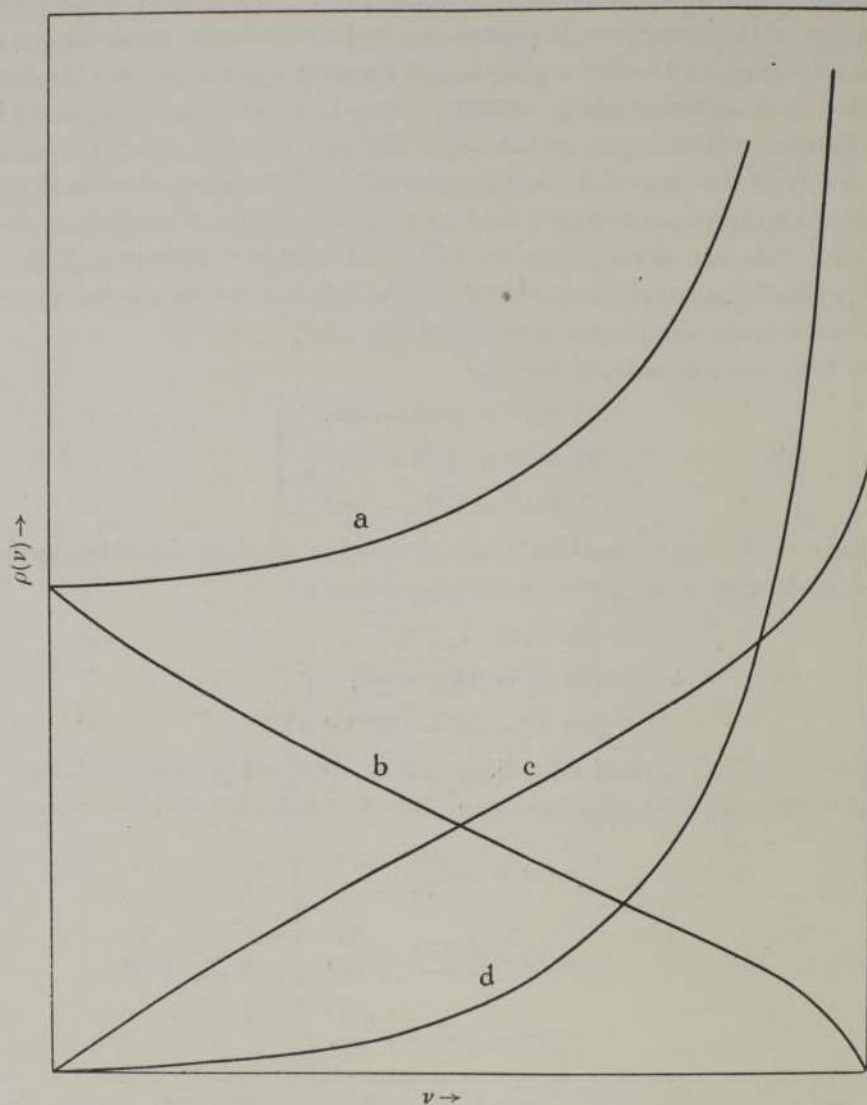


FIG. 3—The vibrational spectrum of a simple cubic lattice in the particular case where  $\gamma = 0$ ,  $\alpha \neq 0$ . The total spectrum is given by curve *a*; *b*, *c* and *d* are the contributions of the three frequency branches.

The second curve *c* rises to a constant value at the end of the spectrum. This is of course rounded off when  $\gamma \neq 0$  (as then the spectrum extends to

\* This does not mean that it is a better representation with which to work.

a higher frequency than the optical frequency), and hence the small maximum of fig. 2, curve *c* is certainly real. It may also be noted that the height of maxima is nearly the same when the curves are adjusted to the same scale; this is an additional confirmation of the correctness of the numerical calculation. At the lower end of the spectrum the linear rise in density changes into a  $\nu^2$  law and a certain number of vibrations will be transferred to a higher part of the spectrum. Hence some kind of irregularity is to be expected here though the reason for a maximum is not quite clear.

The curve *b* will drop from a constant value to zero at  $\nu = 0$  when  $\gamma \neq 0$ , and since the main part of the curve at comparatively high frequencies will be little affected by the change in  $\gamma$ , we shall expect the additional vibrations, which originate around  $\nu = 0$ , to be accommodated in a maximum not very far from this point (it being clear that the total number of vibrations in a branch is constant for all values of the forces).

3—It will be noted that there are very few maxima (one of importance per branch), and that the whole character of the density curves is rather smooth (fig. 2). It might be argued that the method of calculation would show only an averaged curve, but there is good reason to believe that these curves are really smooth. Even the theoretical density is in itself an average over an enormous number of vibrations. Taking, for instance, a crystal of ordinary dimensions, one can easily estimate that a range of  $\frac{1}{10}\%$  of the frequency (taken anywhere except at the extreme lower end of the spectrum) will contain something of the order of  $10^{18}$  vibrations travelling in all directions through the crystal. Hence violent fluctuations of the density over an appreciable frequency range would be extremely puzzling. Furthermore, one can see from a careful examination of the two-dimensional case that there are no such fluctuations, and the similarity of the two- and three-dimensional cases suggests that this is also true for the latter.

The next point to be decided is whether it is possible to indicate where the maxima in the various branches lie. We consider the cube  $0 \leq \phi_1, \phi_2, \phi_3 \leq \pi$  in  $\phi$  space and the cross-sections  $\nu = \text{const.}$ , taking each branch separately. For the lowest branch (fig. 2, curve *c*) the end-points of the cube have the following values:

$(\phi_1, \phi_2, \phi_3)$			Frequency
$(0\ 0\ 0)$			$\nu = 0$
$(0\ 0\ \pi)$	$(0\ \pi\ 0)$	$(\pi\ 0\ 0)$	$\nu = \frac{1}{2\pi} (8\gamma/m)^{\frac{1}{2}}$
$(0\ \pi\ \pi)$	$(\pi\ 0\ \pi)$	$(\pi\ \pi\ 0)$	$\nu = \frac{1}{2\pi} (16\gamma/m)^{\frac{1}{2}}$
$(\pi\ \pi\ \pi)$			$\nu = \frac{1}{2\pi} (4\alpha/m)^{\frac{1}{2}}$



As we increase  $\nu$  from zero, the surfaces expand outwards, at first uniformly (continuum region), and reach the end-points of the cube in the order given above. It is clear that, on passing the  $(0\ 0\ \pi)$  points, the surfaces have plenty of space in which to expand, and it is only after the  $(0\ \pi\ \pi)$  points are passed that the surfaces will contract inwards towards the point  $(\pi\ \pi\ \pi)$ . One can therefore conclude that a considerable increase in the density will occur when the frequency passes the value  $\nu_{(0\ 0\ \pi)}$ , and that a maximum will be reached before the  $(0\ \pi\ \pi)$  points are passed; after this there will be a steady decrease to zero. These conclusions fit in with the curve found, e.g. it will be noticed that the maximum is at 0.55, whereas  $\nu_{(0\ \pi\ \pi)} = 0.65$  in the same units ( $\nu_{(0\ 0\ \pi)} = 0.4$ ).

The end-points of the cube have the following values for the second branch (fig. 3, curve *c*):

$(\phi_1, \phi_2, \phi_3)$			Frequency
	$(0\ 0\ 0)$		$\nu = 0$
$(0\ 0\ \pi)$	$(\pi\ 0\ 0)$	$(0\ \pi\ 0)$	$\nu = \frac{1}{2\pi} (8\gamma/m)^{\frac{1}{2}}$
$(0\ \pi\ \pi)$	$(\pi\ 0\ \pi)$	$(\pi\ \pi\ 0)$	$\nu = \frac{1}{2\pi} (4\alpha + 8\gamma/m)^{\frac{1}{2}}$
	$(\pi\ \pi\ \pi)$		$\nu = \frac{1}{2\pi} (4\alpha/m)^{\frac{1}{2}}$

The  $(0\ 0\ \pi)$  points correspond to a comparatively small value of the frequency, the  $(0\ \pi\ \pi)$  points, on the other hand, to a higher frequency than  $(\pi\ \pi\ \pi)$ . Hence the surfaces, after expanding across the  $(0\ 0\ \pi)$  points, will extend towards the centre of the cube and will avoid the  $(0\ \pi\ \pi)$  corners. This continues until  $(\pi\ \pi\ \pi)$  is reached when the surfaces shrink in towards  $(0\ \pi\ \pi)$ , etc. One should expect a steady increase in the density at first, and a maximum just before the  $(\pi\ \pi\ \pi)$  point is reached because here the surfaces break through the centre portion; what happens in between is rather difficult to see because of the peculiar form of the surfaces. We have not considered the distances between surfaces, assuming tacitly that these will not vary in such a way as to disturb the general conclusions; one can in general see in which way the variation will affect the result as long as the surfaces are not very complicated, e.g. when the surfaces pass a corner of the cube the distances between surfaces tend to increase, and hence the maxima which arise near these points are all the more pronounced. In the case we are considering a closer examination of the cross-sections is necessary. This shows that after the  $(0\ 0\ \pi)$  points are passed the surfaces are crowded together especially near the  $(0\ \phi_2\ \phi_3)$ ,  $(\phi_1\ 0\ \phi_3)$ ,  $(\phi_1\ \phi_2\ 0)$  faces; this suggests

that there will be little variation in the density over quite a wide frequency range, though the slight maximum does not follow; a more detailed numerical calculation of the cross-sections is needed to establish the existence of the maximum if it is real, and this is not of sufficient importance at present.

In the case of the third branch (fig. 3, curve *a*) the relation between the end-points of the cube and the frequency is given in the following scheme:

$(\phi_1, \phi_2, \phi_3)$			Frequency
(0 0 0)			$\nu = 0$
(0 $\pi$ 0)	(0 0 $\pi$ )	( $\pi$ 0 0)	$\nu = \frac{1}{2\pi} (4\alpha + 16\gamma/m)^{\frac{1}{2}}$
(0 $\pi$ $\pi$ )	( $\pi$ 0 $\pi$ )	( $\pi$ $\pi$ 0)	$\nu = \frac{1}{2\pi} (4\alpha + 8\gamma/m)^{\frac{1}{2}}$
( $\pi$ $\pi$ $\pi$ )			$\nu = \frac{1}{2\pi} (4\alpha/m)^{\frac{1}{2}}$

Here both the (0 0  $\pi$ ) and the (0  $\pi$   $\pi$ ) points have higher frequency values than that corresponding to ( $\pi$   $\pi$   $\pi$ ). Hence the frequency surfaces extend in towards the middle of the cube avoiding all corners; they increase more or less steadily towards the ( $\pi$   $\pi$   $\pi$ ) point. It would seem likely that the maximum should lie a little on the high frequency side of this point, but the calculations can hardly decide this. The density falls off rapidly after the maximum is reached and even more so after the (0  $\pi$   $\pi$ ) points are passed, but that again cannot be detected on the curve as the effect is too small.

It should be noted that the end-points of the cube do not play an important part\* in fixing the maxima although they are useful in the discussion of the qualitative features; they do not in general coincide with the maxima as had at first been thought likely (cf. Blackman 1935), e.g. the very important maximum of curve *b* cannot be linked to any such point.

All the above remarks apply only if the  $\gamma/\alpha$  ratio is sufficiently small. It will, however, be seen that the same results hold as long as the end-points of the cube retain their relative positions, i.e.  $\gamma/\alpha < 0.25$ . After that, the curve *c* will probably change a little in appearance but the general form of the total spectrum will not be changed very much; the small maximum will be replaced by a "hump" and the spectrum will extend appreciably above the main maximum. It is only when  $\gamma/\alpha \div 0.5^\dagger$  that the main maxi-

\* This is of interest in view of the theory of Seitz, Brittain and Barnes (1935) in which such points are assumed to be associated with maxima of the density.

† The effect will occur before  $\gamma/\alpha = 0.5$  because the maximum of curve *c* lies between  $\nu_{(00\pi)}$  and  $\nu_{(0\pi\pi)}$ .

imum will overlap with the "hump" and over a range of values of  $\gamma/\alpha$  the spectrum will consist of a single maximum in the middle.

The  $\theta_D$ - $T$  curves obtained from crystals having the above type of spectrum will depend to a large extent on what values of  $\gamma/\alpha$  we choose. For  $\gamma/\alpha = 0.05$  (cf. Appendix II and fig. 4) the initial  $\theta_D$  value (i.e.  $T=0$ ) is lower than the value for high temperatures. There is first the drop in  $\theta_D$  which is a feature of all these lattices, and then a sharp rise to a constant value. For much smaller values of  $\gamma/\alpha$  there will be a slight drop followed by an appreciable rise. For  $\gamma/\alpha$  values near 0.05 we should also expect to find a maximum of  $\theta_D$  after the minimum. When the  $\gamma/\alpha$  value reaches the neighbourhood of 0.5, the  $\theta_D$  value will probably fall steadily with increasing temperature to a constant value, though it is possible that there is a minimum followed by a slight rise.

4—The above considerations apply, strictly speaking, only to a simple cubic lattice consisting of particles of the same kind, where the forces are of the central force type and fall off very rapidly with distance. There are no crystals fitting this description exactly. From the point of view of the forces the nearest are probably the rare gases in the solidified form,\* but these have the wrong lattice structure. If, as seems likely, the effect of symmetry is not such as to alter a general qualitative result, the conclusions reached above suggest that the  $\theta_D$  value should fall initially. Since in no case does the true continuum region appear to have been reached, this cannot be tested by considering the experimental results at present available.

The Born-v. Kármán model is, however, often used as an approximate representation of polar crystals of the KCl type. Here of course the forces between particles extend over comparatively large distances, and we have to consider what effect this would have on the qualitative results. It seems reasonable to suppose that good agreement can be obtained by introducing a number of parameters of the type  $\alpha$ ,  $\gamma$ , where some of these parameters can be negative as well as positive. Two are sufficient to give the elastic constants (if the Cauchy relation holds) and fair values for the points  $(0\ 0\ \pi)$ , etc. The  $(\pi\ \pi\ \pi)$  point is usually within a range of 10–20% about the experimental value, though the others may be considerably different (Blackman 1933). Since the end-points of the cube in  $\phi$  space are represented sufficiently well for qualitative purposes, one might think that the model should give a good qualitative representation of the spectrum. There is, however, one restriction on the application of the above results to KCl,

\* Helium must be excluded because of its unusual properties.

and this concerns the behaviour of the spectrum for small values of the frequency. An independent investigation (to be published shortly) has shown that a lattice of the kind discussed here has a density which always increases faster than  $\nu^2$  immediately outside the continuum region; but that it is possible, by introducing additional negative parameters, to change this so that the density does not increase as fast as  $\nu^2$  over a small region though this variation soon changes into the usual steep rise. Now the parameters  $\alpha$ ,  $\gamma$  correspond to second derivatives of the potential, and these are usually negative when the particles concerned are not neighbours. Since the forces in polar crystals extend over large ranges, the possibility of such an effect cannot be excluded at present. This point is of special interest, because although the qualitative features of the  $\theta_D$  curve of KCl do agree with the predictions of the theory (the effective value of  $\gamma/\alpha$  being larger than 0.05 as shown by the ratio  $\theta_0/\theta_D$  (initial)),\* there is a discrepancy at the lowest temperatures where the  $\theta_D$  value instead of remaining constant appears to fall slightly. This † fall could be explained by the hypothesis made above; there remains, however, one further point, that the effect still exists for a  $\theta_D/T$  value of about 100. According to previous work the continuum region for a Born-v. Kármán lattice (and  $\gamma/\alpha = 0.05$ ) is reached when  $\theta_D/T$  is about 50. Here only nearest neighbours were considered. When the forces from particles which are farther away are important, this limit for  $\theta_D/T$  is of course removed to a larger value, and it would not be surprising to find the continuum region at 100 or even more. At present too little is known about the variation to make a definite pronouncement; in particular it would be important to find out when the continuum region does appear. There does not seem to be any case where one can be certain that it has been reached.

In the case where the Cauchy relation does not hold, an additional parameter is sufficient to describe this new feature. No qualitative changes need to be made in the description of the spectrum. This is true also for two or more particles per cell as long as the mass differences are not large.‡

The model is not directly applicable where one cannot speak of the forces between particles as such, e.g. in metals. Here one would need either an

\*  $\theta_0 = h\nu_{(\pi\pi\pi)}/k$  and  $\nu_{(\pi\pi\pi)}$  is known from the constants of the lattice.

† The explanation offered does not exclude the possibility of the effect being due to another cause; it disagrees with the  $\theta_D$  values deduced from recent measures of the elastic constants of KCl at low temperatures (Durand 1936).

‡ The splitting of the frequency branches leads to more complicated frequency surfaces, a phenomenon termed "zone structure" by Seitz, Brittain and Barnes (1935). This, however, does not lead to great complications in the spectrum, as these authors maintain, indeed for small mass differences there will hardly be any fluctuations.

independent investigation of the frequency equation or a careful examination of the specific heat curves from which it might be possible to deduce a fair representation of the spectrum.

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#### SUMMARY

The vibrational spectrum of a simple cubic lattice of the Born-v. Kármán type is calculated in a particular case ( $\gamma/\alpha = 0.05$ ) by a numerical method. The features of this spectrum are checked by considering an extreme case ( $\gamma = 0, \alpha \neq 0$ ) in which formulae for the spectrum of each of the frequency branches are derived. General considerations on the form of the frequency surfaces in "phase" space are used to determine qualitatively the form of the spectrum for simple cubical lattices characterized by other values of the parameter  $\gamma/\alpha$ . The results obtained are used in a discussion of the type of specific heat curves to be expected for these lattices. The applicability of the conclusions to actual crystals is considered.

#### APPENDIX I

In order to give an indication of the scattering from the smooth density curve (fig. 2) the data used is given in Table I.

The calculations yield the total spectrum directly, given in the second column. Actually only a third of these points were counted because the contributions could be divided into three similar parts. The total density is hence three times the density found for one of the parts (cf. equation (2)). The density varies regularly over the spectrum except for the two regions from 1.0 to 1.2. The reason for the irregularity can be seen from equation (2) (a), where on putting  $\phi_1 = \frac{1}{2}\pi$  all frequency values become equal to  $(2\alpha + 8\gamma/m)^{\frac{1}{2}}$ , whatever the value of  $\phi_2$  or  $\phi_3$ . These points are among those calculated, and hence  $31^2 = 961$  points have the same frequency value instead of having a range of frequency values. This has the effect of forcing up the density of the region 1.0-1.1, and of depressing the density for the next region. The irregularity would be smoothed out if one were to take a much larger number of points, and is of no theoretical significance.

The method of obtaining the density for the individual branches has been

discussed in § 2. It should be noted that we should expect the fluctuations here to be much larger than in the original spectrum. The method adopted leads necessarily to additional errors in counting the number of "triples", "doubles" and "singles", and the errors are multiplied by factors of three, two, and one respectively when the density of the branches are determined from these numbers. Since the total number of points should be the same for all the three branches, the fluctuations should average out. The totals are shown in the last line and it will be seen that they are within 260 of the correct value 29,791. This is satisfactory because one has no method of checking except by repeating the same work.

TABLE I

Density (number of points per frequency range)

Frequency range	Density (number of points per frequency range)				Total $d+b+c$
	Total spectrum	Branch $d$	Branch $c$	Branch $b$	
0.0-0.1	81	8	26	47	81
0.1-0.2	366	19	109	238	366
0.2-0.3	966	34	247	667	948
0.3-0.4	2136	47	524	1566	2137
0.4-0.5	5217	228	1209	3776	5213
0.5-0.6	6801	176	1570	5285	7031
0.6-0.7	6714	195	1809	4700	6704
0.7-0.8	5727	607	1870	3154	5631
0.8-0.9	5642	413	2527	2779	5719
0.9-1.0	5708	992	2913	1952	5857
1.0-1.1	6645	1303	2986	2341	6630
1.1-1.2	5529	1643	2973	1191	5807
1.2-1.3	7293	2558	2142	1212	5912
1.3-1.4	10161	4380	5829	810	11019
1.4-1.5	17031	14492	3206	164	17864
1.5-1.55	3253	2853	111	0	2964
Total number of points	89270	29948	30051	29882	89883

The fluctuations in the neighbourhood of  $\nu = 1.2$  are produced by the fluctuation in the original spectrum already discussed, and have thus a different cause. This fluctuation does not affect the tendency of the curves for the density to any appreciable extent; the maximum of branch  $b$  at  $\nu = 1.2$  is made uncertain by this factor, but there is no doubt about the flattening out of the curve in this region.

## APPENDIX II

(a) From the calculated curve for the density of the normal vibrations of a simple cubical lattice, it is possible to find the numerical constants

involved in the density function for small values of the frequency. We express the function in the form\*

$$\rho(\nu) = 3a\nu_D^{-3}\nu^2 + 5b\nu_D^{-5}\nu^4,$$

where  $\nu_D$  is the Debye maximum frequency defined in the usual way.

The total number of vibrations between  $\nu = 0$  and  $\nu = \nu'$  is

$$n = \int_0^{\nu'} \rho(\nu) d\nu = a\nu_D^{-3}\nu'^3 + b\nu_D^{-5}\nu'^5.$$

Taking the actual curve (fig. 3) one can draw the corresponding Debye curve and can estimate the area ( $a\nu_D^{-3}\nu'^3$ ) under the Debye curve, and the area ( $b\nu_D^{-5}\nu'^5$ ) between the Debye curve and the actual curve. For  $\nu' = 0.3$ ,  $\nu_D = 1.32$ , the ratio of the two areas is  $b\nu'^2/a\nu_D^2 = 0.22$  and  $b/a = 4.26$ . We can calculate the mean energy of the lattice, making the assumption that the temperature is sufficiently small as this is the range we are interested in.

$$\begin{aligned} E &= \frac{3a}{\nu_D^3} \int_0^\infty \frac{h\nu}{e^{h\nu/kT} - 1} \nu^2 d\nu + \frac{5b}{\nu_D^5} \int_0^\infty \frac{h\nu}{e^{h\nu/kT} - 1} \nu^4 d\nu \\ &= \frac{3ah}{\nu_D^3} \left(\frac{kT}{h}\right)^4 \sum_n \frac{6}{n^4} + \frac{5bh}{\nu_D^5} \left(\frac{kT}{h}\right)^6 \sum_n \frac{120}{n^6}. \end{aligned}$$

Putting  $a = 3N$  and  $Nk = R$  so as to obtain the usual formulae, and using the relations

$$\sum_n \frac{1}{n^4} = \frac{\pi^4}{90}, \quad \sum_n \frac{1}{n^6} = \frac{\pi^6}{945}, \quad \theta_D = \frac{h\nu_D}{k},$$

we obtain for the specific heat

$$\begin{aligned} C_\nu &= \frac{12\pi^4}{5} \frac{R}{\theta_D^3} T^3 \left( 1 + 47.05 \frac{b}{a} \frac{T^2}{\theta_D^2} \right) \\ &= \frac{12\pi^4}{5} \frac{R}{\theta_D^3} T^3 \left( 1 + 201 \frac{T^2}{\theta_D^2} \right). \end{aligned}$$

This shows that for  $\theta_D/T = 100$  the change in the specific heat is 2%, which means a 0.7% change in the  $\theta_D$  value.

(b) One can also calculate the  $\theta_D$  value as a function of the temperature numerically throughout the temperature range. The calculated curve is shown in fig. 4. The  $\theta_D$  value drops from 132 at  $T = 0^\circ$  to 114 at  $T = 8^\circ$  and then rises sharply to its final value 144. It should be noted that the value is remarkably constant from  $40^\circ$  K. onwards, this remaining so for values

\* This form follows from an investigation of the low frequency end of the spectrum of a lattice of the above type (to be published shortly). It is probable that it holds generally for a three-dimensional lattice.

of  $\theta_D$  higher than those shown in the figure. The high temperature value is not far from the low temperature value of 132, but there is a wide variation between these values, showing that one can draw no conclusions from the knowledge of the  $\theta_D$  values for very low and for high temperatures as to the probable  $\theta_D$  curve; a qualitative knowledge of the spectrum is necessary before the  $\theta_D$  curve can be predicted.

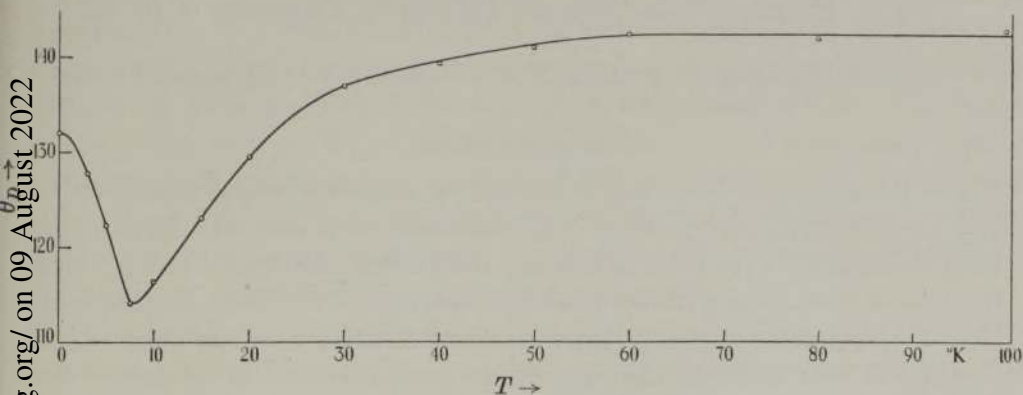


FIG. 4—The Debye  $\theta_D$  value as a function of the temperature for a simple cubic lattice ( $\gamma/\alpha = 0.05$ ).

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