

On the Distribution of Lattice Vibrations of the KCl Crystal

MARIO IONA, JR.*

Institution för Mekanik och Matematisk Fysik, Universitetet, Uppsala, Sweden

(Received September 5, 1941)

The distribution of characteristic vibrations of the KCl crystal has been calculated following Born, v. Kármán and Blackman under the assumption of both electrostatic and repulsive forces between the ions, the latter calculated for the 18 nearest neighbors from the elastic constants and the residual ray frequency. Application of this distribution has been made to the evaluation of the specific heat at low temperatures.

INTRODUCTION

TO give detailed explanation of many properties of crystals, e.g., temperature dependence of the specific heat and the diffuse scattering of x-rays, it is desirable to know the equation of motion and the distribution of characteristic vibrations. These can be calculated from the lattice configuration and the forces between the atoms. The latter have often been calculated by means of the elastic constants, but this method allows the determination of only a few force constants and is therefore only useful as long as short range forces are considered. This method is hence applicable to atomic crystals, such as the tungsten crystal, which has been treated in detail by Fine.¹ In the case of ion crystals it is necessary to notice that the electrostatic forces act also between ions of greater separation and have to be considered in a different way. The method of considering the electrostatic forces separately has been used by Lyddane and Herzfeld² for calculation on NaCl, more recently by Kellermann³ for the same crystal. Ljungquist⁴ and Foldy⁵ use this method on the KCl crystal. Lyddane, Herzfeld and Foldy use theoretical statements for the short range forces. Kellermann calculated the force constants between 6, Ljungquist between 18 nearest neighbors using the experimental values of the elastic constants.

THE FREQUENCY SPECTRUM†

To calculate the distribution function for the simplest cubic crystal, the KCl crystal, the masses of the ions may be assumed to be equal and, under the assumption of equal forces (except for the difference in sign of the charge) between the ions, the crystal may be considered as a simple cubic lattice. In order to find the number of characteristic vibrations in given frequency intervals it is necessary to consider the equation of motion of the ions, which may be taken to be oscillating as a whole. One obtains these equations from the general equation of motion in the following way: the gradient of the potential energy of the ions, expanded in a power series of the displacement of the particles, is substituted for the force and the motion is taken to be oscillatory. If one assumes a plane wave solution, the displacement of the ions, whose rest position is characterized by the vector l with integral components, may be described as follows:

$$\mathbf{u}_l = U e^{-i\omega t} \exp[i(\phi l)]. \quad (1)$$

U indicates the amplitude of the oscillations with frequency $\omega = 2\pi\nu$, ϕ is a vector in the direction of wave propagation of the magnitude $2\pi a/\lambda$, a is the distance between nearest lattice points and λ the wave-length. The vector ϕ , whose components ϕ_i are usually called phase components, characterizes thus both wave-length and direction of the waves. To be free from the boundary conditions of the crystal it is convenient, following Born, to consider a "cyclic lattice;" that is an infinite lattice which repeats the finite lattice inclusive of its motion periodically in each direc-

* Now at the University of Chicago.

¹ P. C. Fine, Phys. Rev. **56**, 355 (1939).

² R. H. Lyddane and K. F. Herzfeld, Phys. Rev. **54**, 846 (1938).

³ E. W. Kellermann, Phil. Trans. Roy. Soc. **238**, 513 (1940).

⁴ S. Ljungquist, Uppsala. To be published.

⁵ L. L. Foldy, Phys. Rev. **60**, 64 (1941).

† For the formulae used see reference 11.

tion. If the considered finite lattice has n elementary cells in each direction, each cell containing one particle, the condition of periodicity of motion makes $n\varphi_i$ an integral multiple of 2π . Since the wave function has physical significance only at the lattice points the φ_i may be restricted to $-\pi \leq \varphi_i \leq \pi$. The values φ_i ($\varphi_i = 2\pi p_i/n$) build a cubic lattice with the lattice constant $2\pi/n$ and the edge length 2π ; this is the so-called phase cube. The number of lattice points in a volume element ($d\varphi$), or the number of characteristic vibrations which is proportional to this number is given by

$$dn = 3(n/2\pi)^3(d\varphi) \quad (2)$$

since to each point of the phase cube three characteristic vibrations correspond. The integration of expression (2) gives $3n^3$, the number of degrees of freedom. In order to find from the number of vibrations in the volume element of the phase cube the distribution of lattice vibrations along the frequency scale the relation between frequency and phase components must be found. One obtains this relation from the

condition that the equations of motion give the ratios between the amplitude components, so that the determinant of the equations of motion vanishes.

With the assumed oscillation (1) the equations of motion turn out to be:

$$\begin{aligned} (A_{11} + m\omega^2)U_1 + A_{12}U_2 + A_{13}U_3 &= 0, \\ A_{21}U_1 + (A_{22} + m\omega^2)U_2 + A_{23}U_3 &= 0, \\ A_{31}U_1 + A_{32}U_2 + (A_{33} + m\omega^2)U_3 &= 0. \end{aligned} \quad (3)$$

The coefficients $A_{ik}(\phi)$ are given from the derivatives of the potential energy of the ions in direction of the i and k coordinates by

$$A_{ik}(\phi) = \sum'_l \psi_{ik}^l [\exp(-i(l\phi)) - 1] = A_{ik}^e + A_{ik}^r. \quad (4)$$

These coefficients can be divided into two parts, one due to the electrostatic forces (A_{ik}^e) and the other to the repulsive forces (A_{ik}^r).

The method given by Ewald⁶ allows the calculation of the electrostatic parts. Following Waller^{7*} one obtains:

$$\begin{aligned} A_{ik}^e(\phi) = -\frac{4\pi e^2}{a^3} \sum_N \left\{ \frac{(N_i + \mu_i)(N_k + \mu_k)}{\sum_{m=1}^3 (N_m + \mu_m)^2} \exp\left[-\frac{\pi^2}{4\eta^2} \sum_{m=1}^3 (N_m + \mu_m)^2\right] - \frac{N_i N_k}{\sum_{m=1}^3 N_m^2} \exp\left[-\frac{\pi^2}{4\eta^2} \sum_{m=1}^3 N_m^2\right] \right\} \\ + \frac{e^2}{a^3} \sum'_l (-1)^{l_1+l_2+l_3} [\exp(i(\phi\mathbf{l})) - 1] \frac{1}{l^3} \left\{ \left(\frac{3l_i l_k}{l^2} - \delta_{ik} \right) \left(1 - G(\eta l) - \frac{G''(\eta l)}{2} \right) - \eta^2 l_i l_k G''(\eta l) \right\}. \quad (5) \end{aligned}$$

In these equations \sum_N is a sum over all triplets of odd numbers, and \sum'_l a sum over all triplets of integral numbers except (0, 0, 0), $G(x)$ is the error function

$$G(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\alpha^2) d\alpha$$

and $G''(x)$ its second derivative. The length of the vector \mathbf{l} is l and $\mu_i = \varphi_i/\pi$. By assuming a proper value for the constant η it is possible to find sufficiently convergent series of both types. The calculations have been carried out with $\eta = 1$ which give the higher number of terms in the more convenient second sum. The coefficients have been checked by means of the Laplace equation or by using different values for η . To

check the method the electrostatic parts of the elastic constants have been calculated and compared with the sums given by Born.

The coefficients A_{ik}^r have been calculated by following the method of Born, v. Kármán,⁸ and Blackman.⁹ For this purpose the force constants P and Q have been used which Ljungquist⁴ obtained from the experimental values of the

⁶ P. Ewald, Ann. d. Physik **64**, 253 (1921).

⁷ I am much indebted to Professor I. Waller for giving me these unpublished formulae.

* At the same time Kellermann calculated in England the coefficients for the NaCl crystal. The coefficients given above may be obtained from his formulae as the special case for equal ion masses.

⁸ M. Born, Th. v. Kármán, Physik. Zeits. **13**, 297 (1912); **14**, 15, 65 (1913).

⁹ M. Blackman, Proc. Roy. Soc. **A148**, 365, 384 (1935); **A159**, 416 (1937).

elastic constants (c_{11} and c_{12}) given by Försterling¹⁰ from the residual ray frequency ($\lambda_0=70.7\times 10^{-4}$ cm) and from the equilibrium condition after splitting these values in electrostatic parts¹¹ and the parts due to the repulsive forces.

$$A_{ii}^r(\phi) = -2(Q_{12}a^2 + P_{12})(1 - \cos\phi_i) - 2P_{12}(2 - \cos\phi_k - \cos\phi_l) - 4(Q_{11}a^2 + P_{11})(2 - \cos\phi_i \cos\phi_k - \cos\phi_i \cos\phi_l) - 4P_{11}(1 - \cos\phi_k \cos\phi_l), \quad (6)$$

$$A_{ik}^r(\phi) = -4Q_{11}a^2 \sin\phi_i \sin\phi_k, \quad i \neq k \neq l \neq i.$$

The numerical values of the constants are:

$$P_{11} = -0.0469 \times 10^3; \quad P_{12} = -1.992 \times 10^3; \\ Q_{11} = -0.0315 \times 10^{19}; \quad Q_{12} = 2.5218 \times 10^{19}.$$

TABLE I. Values of electrostatic parts of coefficients A_{ik} .

μ_1	μ_2	μ_3	$A_{11}^e \times 10^{-3}$	$A_{22}^e \times 10^{-3}$	$A_{33}^e \times 10^{-3}$	$A_{12}^e \times 10^{-3}$	$A_{13}^e \times 10^{-3}$	$A_{23}^e \times 10^{-3}$
0	0	$\frac{1}{2}$	-2.82	-2.82	+5.63	0	0	0
0	0	$\frac{1}{3}$	-9.78	-9.78	+19.55	0	0	0
0	0	$\frac{2}{3}$	-16.97	-16.97	+33.93	0	0	0
0	0	1	-20.01	-20.01	+40.03	0	0	0
0	$\frac{1}{2}$	$\frac{1}{2}$	-6.12	+3.06	+3.06	0	0	-2.69
0	$\frac{1}{2}$	$\frac{1}{3}$	-14.34	-3.35	+17.68	0	0	-4.02
0	$\frac{1}{2}$	$\frac{2}{3}$	-22.97	-9.98	+32.95	0	0	-2.99
0	$\frac{1}{2}$	1	-26.66	-12.83	+39.48	0	0	0
0	$\frac{1}{3}$	$\frac{1}{3}$	-25.95	+12.98	+12.98	0	0	-6.00
0	$\frac{1}{3}$	$\frac{2}{3}$	-38.51	+8.03	+30.49	0	0	-4.52
0	$\frac{1}{3}$	1	-44.03	+5.88	+33.14	0	0	0
0	$\frac{2}{3}$	$\frac{1}{3}$	-55.83	+27.92	+27.92	0	0	-3.43
0	$\frac{2}{3}$	$\frac{2}{3}$	-63.59	+26.81	+36.79	0	0	0
0	$\frac{2}{3}$	1	-72.44	+36.22	+36.22	0	0	0
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	-3.35	-3.35	-3.35
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{3}$	-7.70	-7.70	+15.40	-5.10	-5.08	-5.08
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	-15.89	-15.89	+31.78	-7.17	-3.87	-3.87
$\frac{1}{2}$	$\frac{1}{2}$	1	-19.45	-19.45	+38.90	-8.14	0	0
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{3}$	-19.07	+9.54	+9.54	-8.11	-8.11	-7.88
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{2}{3}$	-31.86	+3.06	+28.80	-11.90	-6.49	-6.14
$\frac{1}{2}$	$\frac{1}{3}$	1	-37.66	+0.16	+37.50	-13.76	0	0
$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{3}$	-50.95	+25.48	+25.48	-9.73	-9.73	-4.94
$\frac{1}{2}$	$\frac{2}{3}$	$\frac{2}{3}$	-60.07	+23.98	+36.09	-11.84	0	0
$\frac{1}{2}$	$\frac{2}{3}$	1	-71.03	+35.52	+35.52	0	0	0
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{1}{3}$	0	0	0	-13.52	-13.52	-13.52
$\frac{1}{2}$	$\frac{1}{3}$	$\frac{2}{3}$	-11.97	-11.97	+23.96	-21.54	-11.53	-11.53
$\frac{1}{2}$	$\frac{1}{3}$	1	-17.98	-17.98	+35.96	-25.88	0	0
$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{3}$	-34.49	+17.25	+17.25	-20.64	-20.64	-10.89
$\frac{1}{2}$	$\frac{2}{3}$	$\frac{2}{3}$	-47.87	+13.46	+34.42	-26.42	0	0
$\frac{1}{2}$	$\frac{2}{3}$	1	-67.58	+33.79	+33.79	0	0	0
$\frac{2}{3}$	$\frac{2}{3}$	$\frac{1}{3}$	0	0	0	-25.82	-25.82	-25.82
$\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$	-16.36	-16.36	+32.74	-41.23	0	0
$\frac{2}{3}$	$\frac{2}{3}$	1	-64.09	+32.05	+32.05	0	0	0
$\frac{2}{3}$	1	1	-62.66	+31.33	+31.33	0	0	0 (x,1,1)*
1	1	1	-15.67	-15.67	+31.33	-46.99	0	0 (x,x,1)
			0	0	0	-31.33	-31.33	-31.33(x,x,x)

* Indicates the direction in which this point is approached.

¹⁰ K. Försterling, *Zeits. f. Physik* 2, 172 (1920).

¹¹ M. Born and M. Göppert-Mayer, *Handbuch der Physik* Vol. 24-2 (1934); M. Born, *Enzyklopädie d. Math. Wiss.* Vol. 5-3 (1923).

The coefficients A_{ik} are uniquely determined at all points of the phase cube except at the point (π, π, π) . Terms of the magnitude of the reciprocal vacuum wave-length have been neglected in comparison to terms of at least the magnitude of the reciprocal lattice constant, which means we have neglected the retardation. At the point (π, π, π) these latter terms vanish and the coefficients A_{ik}^e depend on the direction from which this point is approached. At this point only the retardation cannot be disregarded but the distribution of vibrations is not changed by the value at this cornerpoint. Even at this point the solution of the secular equation gives a distinct set of frequencies.‡

Because the coefficients depend only on the magnitude of the phase components it is sufficient to carry out the calculations for the positive octant of the phase cube. As a permutation of the ϕ_i gives the same frequency triplets it is sufficient to calculate the frequencies at 35 points in order to know them at all points differing by $\frac{1}{4}\pi$ in the phase coordinates. Because of the symmetry of the coefficients all but one of the secular equations split up into equations of lower degree.

The numerical values of the coefficients and the frequencies are collected in Tables I-III. Table I gives the electrostatic parts of the coefficients calculated with the factor $e^2/a^3=7.479 \times 10^3$. Table II contains the coefficients A_{ik}^r and Table III gives the frequencies.

Born, v. Kármán, and Blackman obtain with coefficients analogous to (6) at the point (π, π, π) of the phase cube three equal frequencies corresponding to the residual ray frequency. Considering the long range Coulomb forces one obtains two vibrations with residual ray frequency and one of almost double this frequency ($\lambda_0=39.9 \times 10^{-4}$ cm).

The three frequencies at each point of the phase cube have been arranged in three branches of vibrations, one containing the highest, one the medium and one the lowest frequencies at each point. It was possible in this way to combine all frequencies by three smooth surfaces of the

‡ For more detailed discussion of the effect of retardation see reference 3, and J. H. Thompson, *Proc. Roy. Soc. A149*, 487 (1935).

TABLE II. Values of repulsive parts of coefficients A_{ik} .

μ_1	μ_2	μ_3	$A_{11}^r \times 10^{-3}$	$A_{22}^r \times 10^{-3}$	$A_{33}^r \times 10^{-3}$	$A_{12}^r \times 10^{-3}$	$A_{13}^r \times 10^{-3}$	$A_{23}^r \times 10^{-3}$
0	0	$\frac{1}{4}$	+ 1.64	+ 1.64	-12.53	0	0	0
0	0	$\frac{1}{2}$	+ 5.60	+ 5.60	-42.76	0	0	0
0	0	$\frac{3}{4}$	+ 9.56	+ 9.56	-73.00	0	0	0
0	0	1	+11.20	+11.20	-85.53	0	0	0
0	$\frac{1}{4}$	$\frac{1}{4}$	+ 3.26	-11.01	-11.01	0	0	+0.62
0	$\frac{1}{4}$	$\frac{1}{2}$	+ 7.18	- 7.34	-41.54	0	0	+0.88
0	$\frac{1}{4}$	$\frac{3}{4}$	+11.10	- 3.68	-72.08	0	0	+0.62
0	$\frac{1}{4}$	1	+12.73	- 2.16	-84.72	0	0	0
0	$\frac{1}{2}$	$\frac{1}{2}$	+11.01	-38.59	-38.59	0	0	+1.24
0	$\frac{1}{2}$	$\frac{3}{4}$	+14.84	-35.64	-69.84	0	0	+0.88
0	$\frac{1}{2}$	1	+16.42	-34.42	-82.78	0	0	0
0	$\frac{3}{4}$	$\frac{3}{4}$	+18.57	-67.60	-67.60	0	0	+0.62
0	$\frac{3}{4}$	1	+20.11	-66.68	-80.84	0	0	0
0	1	1	+21.64	-80.04	-80.04	0	0	0
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	- 9.51	- 9.51	- 9.51	+0.62	+0.62	+0.62
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	- 5.88	- 5.88	-40.34	+0.62	+0.88	+0.88
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	- 2.26	- 2.26	-71.16	+0.62	+0.62	+0.62
$\frac{1}{4}$	$\frac{1}{4}$	1	- 0.76	- 0.76	-83.94	+0.62	0	0
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	- 2.35	-37.43	-37.43	+0.88	+0.88	+1.24
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	+ 1.18	-34.52	-68.97	+0.88	+0.62	+0.88
$\frac{1}{4}$	$\frac{1}{2}$	1	+ 2.64	-33.31	-82.03	+0.88	0	0
$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	+ 4.62	-66.77	-66.77	+0.62	+0.62	+0.62
$\frac{1}{4}$	$\frac{3}{4}$	1	+ 6.03	-65.86	-80.13	+0.62	0	0
$\frac{1}{4}$	1	1	+ 7.45	-79.35	-79.35	0	0	0
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	-34.61	-34.61	-34.61	+1.24	+1.24	+1.24
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	-31.79	-31.79	-66.86	+1.24	+0.88	+0.88
$\frac{1}{2}$	$\frac{1}{2}$	1	-30.62	-30.62	-80.23	+1.24	0	0
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	-29.07	-64.76	-64.76	+0.88	+0.88	+0.62
$\frac{1}{2}$	$\frac{3}{4}$	1	-27.94	-63.89	-78.42	+0.88	0	0
$\frac{1}{2}$	1	1	-26.83	-77.67	-77.67	0	0	0
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	-62.75	-62.75	-62.75	+0.62	+0.62	+0.62
$\frac{3}{4}$	$\frac{3}{4}$	1	-61.92	-61.92	-76.70	+0.62	0	0
$\frac{3}{4}$	1	1	-61.10	-75.99	-75.99	0	0	0
1	1	1	-75.30	-75.30	-75.30	0	0	0

TABLE III. Values of the frequencies.

μ_1	μ_2	μ_3	$\omega_1 \times 10^{-13}$	$\omega_2 \times 10^{-13}$	$\omega_3 \times 10^{-13}$
0	0	$\frac{1}{4}$	1.06	0.44	0.44
0	0	$\frac{1}{2}$	1.94	0.82	0.82
0	0	$\frac{3}{4}$	2.51	1.09	1.09
0	0	1	2.71	1.19	1.19
0	$\frac{1}{4}$	$\frac{1}{4}$	1.27	0.97	0.68
0	$\frac{1}{4}$	$\frac{1}{2}$	1.99	1.27	1.08
0	$\frac{1}{4}$	$\frac{3}{4}$	2.52	1.47	1.39
0	$\frac{1}{4}$	1	2.70	1.56	1.50
0	$\frac{1}{2}$	$\frac{1}{2}$	2.21	1.84	1.55
0	$\frac{1}{2}$	$\frac{3}{4}$	2.55	2.07	1.96
0	$\frac{1}{2}$	1	2.69	2.15	2.11
0	$\frac{3}{4}$	$\frac{3}{4}$	2.62	2.45	2.44
0	$\frac{3}{4}$	1	2.67	2.65	2.54
0	1	1	2.86	2.66	2.66
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1.55	1.05	1.05
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2.14	1.54	1.21
$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	2.56	1.94	1.36
$\frac{1}{4}$	$\frac{1}{4}$	1	2.70	2.12	1.43
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{2}$	2.55	1.85	1.60
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	2.82	2.32	1.80
$\frac{1}{4}$	$\frac{1}{2}$	1	2.76	2.68	1.85
$\frac{1}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	3.08	2.44	2.31
$\frac{1}{4}$	$\frac{3}{4}$	1	3.13	2.67	2.38
$\frac{1}{4}$	1	1	3.20	2.66	2.66
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	3.10	1.90	1.90
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{4}$	3.41	2.38	1.95
$\frac{1}{2}$	$\frac{1}{2}$	1	3.44	2.67	1.97
$\frac{1}{2}$	$\frac{3}{4}$	$\frac{3}{4}$	3.79	2.45	2.29
$\frac{1}{2}$	$\frac{3}{4}$	1	3.85	2.67	2.36
$\frac{1}{2}$	1	1	3.90	2.66	2.66
$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	4.27	2.46	2.46
$\frac{3}{4}$	$\frac{3}{4}$	1	4.38	2.66	2.47
$\frac{3}{4}$	1	1	4.50	2.66	2.66
1	1	1	4.72	2.67	2.67

$\varphi_1\varphi_2\varphi_3$ space. At points where two frequencies are equal the frequency branches change from one smooth surface to the other. The branch of highest frequency contains mainly longitudinal, the two other mainly transverse vibrations.

This combination of vibrations enables one to interpolate frequency values at other points of the phase cube. The frequencies have been interpolated at points in the center between each pair of points of distance $\frac{1}{4}\pi$. To find, following Blackman, the number of vibrations in frequency intervals the whole frequency range has been divided into 24 intervals and three sets of curves of constant frequency, corresponding to the three frequency branches, have been determined in the 9 planes $\varphi_3=0, \frac{1}{8}\pi, \frac{1}{4}\pi, \dots, \pi$. By means of graphical integration the areas between curves of constant frequency have been evaluated and from these the volumes between surfaces of constant frequency for all three branches have been determined by repeated graphical integration. These volumes are proportional to the

number of characteristic vibrations. The smooth curve in each frequency interval containing the number of vibrations which has been calculated in this way was assumed to be the distribution function.

The two branches of lower frequency show maxima of vibration density near the residual ray frequency. The lowest branch has this frequency as maximum frequency, the medium branch has a small number of vibrations with frequencies higher than the residual ray frequency. Both have second density maxima at lower frequencies, thus causing a second maximum of the distribution of all three branches together. The branch of highest frequency has its maximum also near the residual ray frequency but has a high number of vibrations between this

and almost the double frequency. Figure 1 gives the sum of the distribution functions of all three branches.

SPECIFIC HEAT

The specific heat of a system of N oscillators of frequency ν is given by

$$C_v = kN \int_0^{\nu_{\max}} \frac{(h\nu/kT)^2 \exp(h\nu/kT) dn}{(\exp[h\nu/kT] - 1)^2} \frac{dn}{d\nu} d\nu.$$

In the case of a quadratic distribution function $dn/d\nu = \text{const.} \times \nu^2$, with a maximum frequency, which is determined by the total number of degrees of freedom, a characteristic temperature θ can be defined, which is related to the maximum frequency by $\theta = h\nu_{\max}/k$.

For the lower frequencies the distribution function of the KCl crystal is in agreement with the Debye quadratic distribution of the continuum with the characteristic temperature $\theta = 230^\circ$. This θ value is in agreement with the value obtained from specific heat measurements because this parabola is a good approximation for the distribution function even at higher frequencies because it continues to frequencies higher than the residual ray frequency. However, in temperature intervals where the first maximum of the distribution function gives the main contribution one may expect a minimum of the corresponding θ values of the continuum which would give the same specific heat at this temperature. Blackman's qualitative considerations

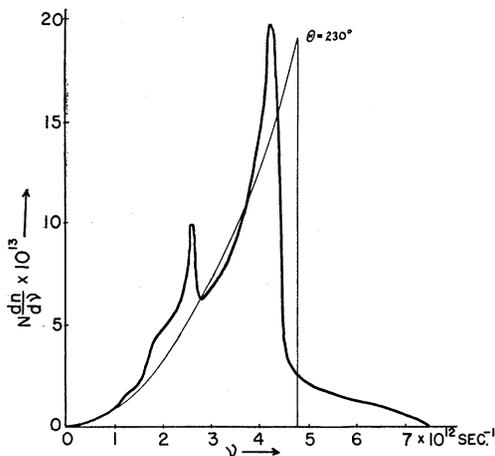


FIG. 1. Density distribution of the lattice vibrations of the KCl crystal.

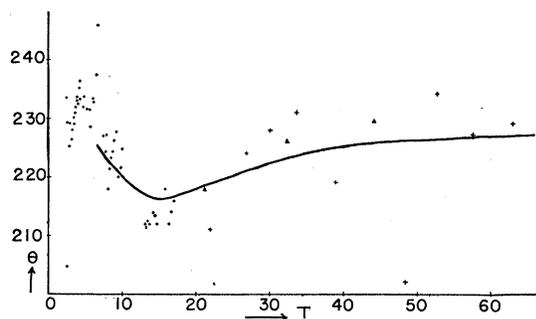


FIG. 2. Specific heat. ●—Keesom and Clark. +—Nernst and Lindemann. ▲—Southard and Nelson. ————calculated.

and Kellermann's¹² calculation of the NaCl crystal show the same feature. It is hardly possible to give a quantitative discussion of this feature without calculating the distribution with elastic constants at lower temperatures. But under the assumption that the distribution function does not change with temperature, although the elastic constants do,¹³ the dependence of the characteristic temperature on the absolute temperature can be calculated. This leads to the function given in Fig. 2. In this diagram the experimental values given by different authors are also plotted. Keesom and Clark¹⁴ find a probable increase of θ in a range between 2°K and 4°K but it is not possible to make any decision about the reality of such an increase from the present calculations because the frequency intervals used are too large and the number of calculated frequencies too small. Above these temperatures they find a decrease to about 17°K , but the given values may be interpreted as a slight increase for θ at the end of this interval. The measurements are extended to higher temperatures by Nernst and Lindemann,¹⁵ and Southard and Nelson.¹⁶ The combined values seem to indicate a minimum near 15°K .

I am much indebted to Professor I. Waller for suggesting this subject and for much advice during the work and to Internationella Studenthjälpnen (I.S.S.) Uppsala for making it possible for me to do this work.

¹² E. W. Kellermann, Proc. Roy. Soc. **A178**, 17 (1941).

¹³ M. A. Durand, Phys. Rev. **50**, 449 (1936).

¹⁴ W. H. Keesom and W. Clark, Physica **2**, 698 (1935).

¹⁵ W. Nernst and T. Lindemann, Zeits. f. elec. Chemie **17**, 817 (1911).

¹⁶ J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. **55**, 4865 (1933).