

THE THERMAL EXPANSION OF SOLIDS

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[Manuscript received February 18, 1959]

Summary

From the theory of normal vibrations of a lattice, a practical means of obtaining the equation of state of an ionic solid is developed from which the thermal expansion can be derived. Using previous work by Kellermann, application is made to the case of sodium chloride and the results compared with experiment. Possible reasons for the discrepancy between theory and experiment, which is very large at high temperatures, are discussed. The variation with temperature of the specific heat at constant volume and the isothermal compressibility are also investigated.

I. INTRODUCTION

In a previous paper by the author (Fletcher 1957) it was pointed out that a number of workers have attempted to draw qualitative and quantitative conclusions regarding the presence of defects in solids from their behaviour as regards thermal expansion, particularly at high temperatures. It was pointed out that this procedure was a dubious one since almost nothing was known of the thermal expansion of ideal solids, i.e. not containing defects. In that paper an equation of state, based on the theories of Debye and Grüneisen and from which the thermal expansion could be obtained, was developed and applied to an ionic solid, potassium chloride. In the present work an attempt has been made in Section II to develop a more accurate equation of state, based on the theory of normal modes of vibration of a lattice. In Section III this has again been applied to an ionic solid, sodium chloride, since one is most justified in ignoring the electrons explicitly for such a case. A wide discrepancy between theory and experiment, not explicable by the presence of defects, is found and possible reasons for this are discussed in Section V. In attempting to explain the discrepancy it was considered useful to calculate the specific heat C_V and compressibility κ_T also, as described in Section IV. Here agreement with experiment is considerably better.

II. EQUATION OF STATE

A brief resumé of part of a paper by Kellermann (1940) will be given first in order to define certain quantities $\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix}$ used later. Consider a crystal, in which unit cell of volume v_a is determined by lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and contains s particles, whose positions in the cell are given by the basis vectors

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\mathbf{r}_κ ($\kappa=1, 2, \dots, s$). Let the κ th particle in cell $\mathbf{l}=(l_1, l_2, l_3)$ (l_i integral or zero), whose equilibrium position is

$$\mathbf{r}_\kappa^{\mathbf{l}} = \mathbf{a}^{\mathbf{l}} + \mathbf{r}_\kappa = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3 + \mathbf{r}_\kappa, \quad \dots \dots \dots (1)$$

suffer a displacement $\mathbf{u}_\kappa^{\mathbf{l}}$ to the position $\mathbf{r}_\kappa^{\mathbf{l}}$. Assuming central forces between pairs of particles and neglecting external forces on the particles, the total potential energy of the crystal may be written

$$\Phi = \frac{1}{2} \sum_{\kappa, \kappa'} \sum'_{\mathbf{l}, \mathbf{l}'} \varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'}(|\mathbf{r}_\kappa^{\mathbf{l}} - \mathbf{r}_{\kappa'}^{\mathbf{l}'}|), \quad \dots \dots \dots (2)$$

where

$$\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'} = \varphi_{\kappa \kappa'}(|\mathbf{r}_\kappa^{\mathbf{l}} - \mathbf{r}_{\kappa'}^{\mathbf{l}'}|) \quad \dots \dots \dots (3)$$

is the mutual potential energy of the (\mathbf{l}, κ) and (\mathbf{l}', κ') particles, assumed to be a function only of their distance apart, and terms with $\kappa=\kappa', \mathbf{l}=\mathbf{l}'$ are omitted from the summation in (2). Expansion of this in powers of the Cartesian components $u_{\kappa x}^{\mathbf{l}}, u_{\kappa y}^{\mathbf{l}}, u_{\kappa z}^{\mathbf{l}}$ of the displacements $\mathbf{u}_\kappa^{\mathbf{l}}$ up to the second order gives $\Phi \simeq \Phi_0 + \Phi_2$, where

$$\Phi_0 = \frac{1}{2} \sum_{\kappa, \kappa'} \sum'_{\mathbf{l}, \mathbf{l}'} \varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'}(|\mathbf{r}_\kappa^{\mathbf{l}} - \mathbf{r}_{\kappa'}^{\mathbf{l}'}|), \quad \dots \dots \dots (4)$$

$$\Phi_2 = -\frac{1}{2} \sum_{\kappa, \kappa'} \sum'_{\mathbf{l}, \mathbf{l}'} \sum_{x, y} (\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'})_{xy} u_{\kappa x}^{\mathbf{l}} u_{\kappa' y}^{\mathbf{l}'}, \quad \dots \dots \dots (5)$$

where

$$(\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'})_{xy} = \left[\frac{\partial^2 \varphi_{\kappa \kappa'}(r)}{\partial x \partial y} \right]_{\mathbf{r}} \quad (\mathbf{r} = \mathbf{r}_\kappa^{\mathbf{l}} - \mathbf{r}_{\kappa'}^{\mathbf{l}'}), \quad (\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'})_{xy} = -\sum_{\kappa'} \sum'_{\mathbf{l}'} (\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'})_{xy},$$

and Σ refers to summation over the three Cartesian directions. The Lagrangian equations of motion for the system are then

$$m_\kappa \ddot{u}_{\kappa x}^{\mathbf{l}} - \sum_{\kappa'} \sum'_{\mathbf{l}'} \sum_y (\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}'})_{xy} u_{\kappa' y}^{\mathbf{l}'} = 0. \quad \dots \dots \dots (6)$$

where m_κ is the mass of the (\mathbf{l}, κ) particle. Assumption of a normal mode of vibration of the form

$$\mathbf{u}_\kappa^{\mathbf{l}} = \mathbf{U}_\kappa \exp [i(2\pi \mathbf{k} \cdot \mathbf{r}_\kappa^{\mathbf{l}} - \omega t)], \quad \dots \dots \dots (7)$$

where t denotes the time variable, leads to a $3s$ -dimensional secular equation

$$\left| \begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} + m_\kappa \omega^2 \delta_{\kappa \kappa'} \delta_{xy} \right| = 0, \quad \dots \dots \dots (8)$$

where

$$\begin{bmatrix} \kappa & \kappa' \\ x & y \end{bmatrix} = \sum_{\mathbf{l}} (\varphi_{\kappa \kappa'}^{\mathbf{l}, \mathbf{l}})_{xy} \exp 2\pi i \mathbf{k} \cdot (\mathbf{r}_\kappa^{\mathbf{l}} - \mathbf{r}_{\kappa'}^{\mathbf{l}}), \quad \dots \dots \dots (9)$$

for each vector \mathbf{k} . Here $\mathbf{0}$ denotes the triumvirate of numbers $\mathbf{l}'=(0, 0, 0)$. Application of the usual cyclic boundary condition restricts \mathbf{k} to the values $\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3$, where $\mathbf{a}_i \cdot \mathbf{b}_j = \delta_{ij}$, $k_i = h_i/n$ ($h_i=0, 1, \dots, n-1$), and $n^3=N$ is the number of cells in the lattice.

If it is assumed further that the interparticle potential energy may be expressed as the sum of two terms

$$\varphi = \varphi_C + \varphi_R = -c\rho^{-m} + b\rho^{-n}, \quad \dots\dots\dots (10)$$

ρ being the interparticle distance, then $\begin{bmatrix} x & x' \\ x & y \end{bmatrix}$ may correspondingly be rewritten

$$\begin{bmatrix} x & x' \\ x & y \end{bmatrix} = {}^C \begin{bmatrix} x & x' \\ x & y \end{bmatrix} + {}^R \begin{bmatrix} x & x' \\ x & y \end{bmatrix}. \quad \dots\dots\dots (11)$$

A lattice parameter a may be chosen so that $\mathbf{a}_i \propto a$, $\mathbf{b}_i \propto a^{-1}$, and $v_a \propto a^3$. Then obviously $\mathbf{k} \cdot (\mathbf{r}_{x'}^1 - \mathbf{r}_x^1)$ is independent of a so that

$$\left. \begin{aligned} {}^C \begin{bmatrix} x & x' \\ x & y \end{bmatrix} &\propto a^{-m-2} \propto v_a^{-\frac{1}{3}(m+2)}, \\ {}^R \begin{bmatrix} x & x' \\ x & y \end{bmatrix} &\propto v_a^{-\frac{1}{3}(n+2)}. \end{aligned} \right\} \dots\dots\dots (12)$$

Defining

$$\begin{pmatrix} x & x' \\ x & y \end{pmatrix} = v_a^{\frac{1}{3}(m+2)} e^{-2} (m_x m_{x'})^{-\frac{1}{2}} \begin{bmatrix} x & x' \\ x & y \end{bmatrix}, \quad \dots\dots\dots (13)$$

where, for future convenience, e is the magnitude of the charge on the electron, then ${}^C \begin{pmatrix} x & x' \\ x & y \end{pmatrix}$ is independent of v_a while ${}^R \begin{pmatrix} x & x' \\ x & y \end{pmatrix} \propto v_a^{\frac{1}{3}(m-n)}$ and (8) may be rewritten

$$\left| {}^C \begin{pmatrix} x & x' \\ x & y \end{pmatrix} + {}^R \begin{pmatrix} x & x' \\ x & y \end{pmatrix} + \Omega^2 \delta_{xx'} \delta_{xy} \right| = 0, \quad \dots\dots\dots (14)$$

where

$$\Omega^2 = v_a^{\frac{1}{3}(m+2)} e^{-2} \omega^2. \quad \dots\dots\dots (15)$$

If now ${}^C \begin{pmatrix} x & x' \\ x & y \end{pmatrix}$ and ${}^R \begin{pmatrix} x & x' \\ x & y \end{pmatrix}$ are calculated for one value a_0 of a (the suffix zero will be used hereafter to refer to this value) and equation (14) solved for all \mathbf{k} , it is comparatively simple to repeat this process for any other value of a . Putting $g = v_a/v_0 = a^3/a_0^3$,

$$\left. \begin{aligned} {}^C \begin{pmatrix} x & x' \\ x & y \end{pmatrix} &= {}^C \begin{pmatrix} x & x' \\ x & y \end{pmatrix}_0, \\ {}^R \begin{pmatrix} x & x' \\ x & y \end{pmatrix} &= {}^R \begin{pmatrix} x & x' \\ x & y \end{pmatrix}_0 g^{\frac{1}{3}(m-n)}, \end{aligned} \right\} \dots\dots\dots (16)$$

so that it is only necessary to multiply the ${}^R \begin{pmatrix} x & x' \\ x & y \end{pmatrix}_0$ by a factor independent of \mathbf{k} to obtain the equations determining the normal frequencies of vibration of the crystal for any value of the lattice parameter.

Denoting these frequencies by $\omega(\mathbf{k},i)$, where $i=1, 2, \dots, 3s$, the energy of a given state of the crystal is

$$E_m = \Phi_0 + \sum_{\mathbf{k},i} [m(\mathbf{k},i) + \frac{1}{2}] \hbar \omega(\mathbf{k},i), \dots \dots \dots (17)$$

where the $m(\mathbf{k},i)$ are positive integers or zero (not to be confused with the index m in (10)). The relevant partition function at temperature T is

$$Z = \sum_m \exp(-E_m/kT) = \exp(-\Phi_0/kT) \prod_{\mathbf{k},i} [2 \sinh(\hbar\omega/2kT)]. \dots (18)$$

The free energy of the crystal is therefore

$$F = -kT \ln Z = \Phi_0 + kT \sum_{\mathbf{k},i} [\ln 2 + \ln \sinh(\hbar\omega/2kT)] \} \dots (19)$$

$$= \Phi_0 + \mathcal{F}.$$

The equation of state for the crystal may be obtained from the equilibrium condition

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial \Phi_0}{\partial V}\right)_T - \left(\frac{\partial \mathcal{F}}{\partial V}\right)_T, \dots \dots \dots (20)$$

which is sufficient to give the variation of volume with temperature at constant pressure.

III. APPLICATION TO SODIUM CHLORIDE

It was decided to apply this method to determine the theoretical thermal expansion of sodium chloride, for which Kellermann (1940) had determined the normal frequencies of vibration at room temperature. It was possible, therefore, to use this work as a starting point, apart from the relative simplicity of investigating an ionic crystal, for which the assumption that the interparticle potential energy depends only on the interparticle distance is most likely to be valid (see Fletcher (1957) for a discussion of this point). Kellermann did not consider the electrons explicitly but treated the Na^+ and Cl^- ions as basic particles so that $s=2$ and, taking a as the nearest-neighbour distance, $v_a=2a^3$. Then in (10), with $c=\pm e^2$ and $m=1$, the first term corresponds to the Coulomb force between two ions and the second to all other forces, e.g. van der Waals. In the case of the latter he ignored all but nearest-neighbour interactions (see Section V), thereby obtaining

$$-\alpha_M e^2/a + 6v(a) = -\alpha_M e^2/a + 6b/a^n, \dots \dots \dots (21)$$

where α_M is the Madelung number for the lattice, as the contribution per cell to Φ_0 . To determine values of b and n for use in calculating $\begin{pmatrix} x & x' \\ x & y \end{pmatrix}$ he used the relations

$$(d\Phi_0/dr)_{r=a} = 0 \text{ and } 9V\kappa_T^{-1} = (r^2 d^2\Phi_0/dr^2)_{r=a}, \dots \dots (22)$$

where κ_T is the compressibility. Neither of these is correct; this point and correction for the error introduced are discussed in Section IV. Kellermann

tabulated $(v_a/e^2)^C \begin{bmatrix} x & x' \\ x & y \end{bmatrix} = (m_x m_{x'})^{\frac{1}{2}} \begin{bmatrix} x & x' \\ x & y \end{bmatrix}^C$ and $(m_x m_{x'})^{\frac{1}{2}} \begin{bmatrix} x & x' \\ x & y \end{bmatrix}^R$ for about 50 wave vectors \mathbf{k} covering the relevant region of \mathbf{k} -space. Using these as $\begin{bmatrix} x & x' \\ x & y \end{bmatrix}_0^C$ and $\begin{bmatrix} x & x' \\ x & y \end{bmatrix}_0^R$, the six normal frequencies of vibration were calculated in the present work by means of a digital computer for these vectors \mathbf{k} and for $g=1(0.01)1.14$, a range designed to cover the possible change of volume from room temperature to the melting point. For each \mathbf{k} and i $\omega(\mathbf{k},i)$ was tabulated against g and $\partial\omega/\partial g$, $\partial^2\omega/\partial g^2$ evaluated by numerical methods.

Considering now one mole of the crystal, for which $V=2Na^3$,

$$\Phi_0 = N(-\alpha_M e^2 a_0^{-1} g^{-\frac{1}{2}} + 6ba_0^{-n} g^{-\frac{1}{2}n}), \dots\dots\dots (23)$$

and

$$(\partial\Phi_0/\partial V)_T = (2Na_0^3)^{-1} (d\Phi_0/dg) = a_0^{-4} (\frac{1}{6}\alpha_M e^2 g^{-4/3} - nba_0^{-n+1} g^{-\frac{1}{2}(n+3)}), \dots\dots\dots (24)$$

while

$$\left(\frac{\partial\mathcal{F}}{\partial V}\right)_T = \frac{\hbar}{4Na_0^3} \sum_{\mathbf{k},i} \coth\left(\frac{\hbar\omega(\mathbf{k},i)}{2kT}\right) \left(\frac{\partial\omega(\mathbf{k},i)}{\partial g}\right)_T \dots\dots\dots (25)$$

Since the normal frequencies had been calculated only for certain points in \mathbf{k} -space, the relevant region of \mathbf{k} -space was divided into cells, volume ΔK , each containing one of these points. If the total volume of \mathbf{k} -space for each i , and therefore corresponding to N states of the crystal, is K , (25) may be rewritten

$$\left(\frac{\partial\mathcal{F}}{\partial V}\right)_T = \frac{\hbar}{4Ka_0^3} \sum_{\mathbf{k},i} \coth\left(\frac{\hbar\omega(\mathbf{k},i)}{2kT}\right) \left(\frac{\partial\omega(\mathbf{k},i)}{\partial g}\right)_T \Delta K, \dots (26)$$

summation now being carried out only over the values of \mathbf{k} for which $\omega(\mathbf{k},i)$ had been calculated.

The actual procedure used was for a given value of g , to evaluate (24) and also (26) for two or more suitable values of T . By interpolation it was then possible to find the temperature for which (20) was satisfied, i.e. corresponding to the value of g chosen (p was in fact neglected since at normal pressure its magnitude was less than 0.01 per cent of either of the other terms).

IV. DETERMINATION OF PARAMETERS

The form of interparticle potential energy assumed by Kellermann and the present author involves two parameters, b and n . Although these could be calculated in principle from atomic theory, Kellermann's determination of them from experimental data appears more realistic for the purpose of the present approximate theory. As will be seen, this amounts to fitting the theoretical (V,T) and (α_T,T) curves to experiment at one point. It is convenient to introduce here two parameters defined by Kellermann

$$A = 4a_0^3 e^{-2} (d^2v/dr^2)_{r=a_0} = 4n(n+1)be^{-2}a_0^{-n+1}, \dots\dots (27)$$

and

$$B = 4a_0^2 e^{-2} (dv/dr)_{r=a_0} = -4nbe^{-2}a_0^{-n+1}, \dots\dots\dots (28)$$

whence

$$n = -A/B - 1 \text{ and } b = -\frac{1}{4}e^2 n^{-1} a_0^{n-1} B. \dots\dots\dots (29)$$

In terms of these the condition (20) becomes, using (26),

$$\left(\frac{\alpha_M + B}{6} + \frac{B}{4}\right) \frac{e^2}{a_0^4} g^{-4/3} + \frac{\hbar}{4Ka_0^3} \sum_{\mathbf{k},i} \coth\left(\frac{\hbar\omega}{2kT}\right) \left(\frac{\partial\omega}{\partial g}\right)_T \Delta K = -p. \dots\dots (30)$$

Further, the isothermal compressibility is given by

$$\begin{aligned} \kappa_T^{-1} &= -V(\partial p/\partial V)_T = V[(\partial^2\Phi_0/\partial V^2)_{T,T} + (\partial^2\mathcal{F}/\partial V^2)_{T,T}] \\ &= (-8\alpha_M + 3A - 6B)e^2/36a_0^4 g^{4/3} \\ &\quad + \frac{\hbar g}{4Ka_0^3} \sum_{\mathbf{k},i} \left[\coth\left(\frac{\hbar\omega}{2kT}\right) \left(\frac{\partial^2\omega}{\partial g^2}\right)_{T,T} - \frac{\hbar}{2kT} \operatorname{cosech}^2\left(\frac{\hbar\omega}{2kT}\right) \left\{ \left(\frac{\partial\omega}{\partial g}\right)_T \right\}^2 \right] \Delta K. \end{aligned} \dots\dots\dots (31)$$

The aim of choosing A and B so that (30) and (31) are satisfied by experimental values of T , a_0 , and κ_T cannot be attained before calculating the normal frequencies, however, since the frequencies are required for evaluating certain terms in these relations. Thus it is necessary to obtain approximate values at first by some such means as that used by Kellermann, namely, the use of (22), which is equivalent to ignoring the frequency-dependent terms. Having calculated the normal frequencies ω_1 , using these incorrect values, A_1, B_1, n_1, b_1 , of the parameters, the present author obtained approximate corrections to them as follows. These ω_1 and their derivatives were substituted into (30) and (31)

to obtain new values of the parameters, A_2, B_2, n_2 , and b_2 . Now $\begin{matrix} C \\ \left[\begin{matrix} x & x' \\ x & y \end{matrix} \right] \end{matrix}$ is independent of the parameters and it can be shown that

$$\left. \begin{aligned} \begin{matrix} R \\ \left[\begin{matrix} x & x \\ x & x \end{matrix} \right] \end{matrix} v_0/e^2 &= -(A+2B); & \begin{matrix} R \\ \left[\begin{matrix} x & x' \\ x & y \end{matrix} \right] \end{matrix} &= 0 & (x \neq y), \\ \begin{matrix} R \\ \left[\begin{matrix} x & x' \\ x & x \end{matrix} \right] \end{matrix} v_0/e^2 &= A \cos 2\pi k_x a_0 + B(\cos 2\pi k_y a_0 + \cos 2\pi k_z a_0) & (x \neq x'). \end{aligned} \right\} \dots\dots (32)$$

The approximation was made of assuming all $\begin{matrix} R \\ \left[\begin{matrix} x & x' \\ x & y \end{matrix} \right] \end{matrix} \propto (A+2B)$; then consideration of (16) shows that a recalculation with the new values, A_2, B_2 , would produce the same values of Ω for different values, g_2 , of g instead of those, g_1 , used before, where

$$(A_2 + 2B_2)g_2^{\frac{1}{2}(1-n_2)} = (A_1 + 2B_1)g_1^{\frac{1}{2}(1-n_1)}. \dots\dots\dots (33)$$

From (15) the frequencies ω_2 corresponding to g_2 are

$$\omega_2 = (g_1/g_2)^{\frac{1}{2}} \omega_1. \dots\dots\dots (34)$$

By this means a new tabulation of ω against g was prepared, interpolation made for $g_2=1$, and further values of the parameters found by substitution in (30)

and (31). This procedure was repeated until self-consistency was obtained. The final results were

$$A=10.68; B=-1.048; n=9.188; b=9.902 \times 10^{-83},$$

as compared with Kellermann's values

$$A=10.18; B=-1.165; n=7.738; b=1.148 \times 10^{-71},$$

both being based on the values $\alpha_M=1.7476$; $e=4.8 \times 10^{-10}$ e.s.u.; $a_0=2.814 \times 10^{-8}$ cm; and $\chi_T=4.16 \times 10^{-12}$ cm²/dyne, corresponding to $g=1$; $T=288$ °K.

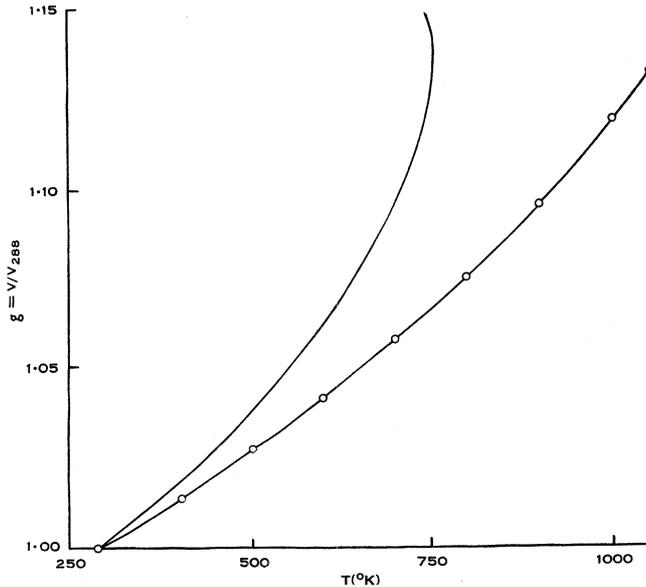


Fig. 1.—Expansion of sodium chloride.

—o—o— Experimental (Eucken and Dannöhl 1934).
 ——— Theoretical.

With these corrected values of the parameters, the procedure described in Section III was carried out to obtain V as a function of T at constant (zero) pressure. The results are shown in Figure 1; the experimental curve was obtained from the values of Eucken and Dannöhl (1934) for the thermal expansion of sodium chloride. Owing to the wide discrepancy between theory and experiment, it was decided to try to check the tables of normal frequencies by calculating the specific heat at constant volume and the isothermal compressibility. To do this it was necessary to obtain temperatures T corresponding to the values of g , under which the frequencies were tabulated, and for this Eucken and Dannöhl's figures were used. The expression (31) was used to evaluate χ_T , while for the specific heat

$$E = \Phi_0 + \frac{N\hbar}{2K} \sum_{\mathbf{k}, i} \omega(\mathbf{k}, i) \coth \left(\frac{\hbar\omega(\mathbf{k}, i)}{2kT} \right) \Delta K, \dots \dots (35)$$

and

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{N\hbar^2}{4KkT^2} \sum_{k,i} \omega^2 \operatorname{cosech}^2 \left(\frac{\hbar\omega}{2kT} \right) \Delta K. \dots\dots (36)$$

The results are shown in Figures 2 and 3. The experimental values for C_V were taken from Hunter and Siegel (1942) while those for κ_T were obtained from their values of κ_s by use of the relation

$$\kappa_T = \kappa_s + \alpha^2 VT / C_p, \dots\dots\dots (37)$$

together with the figures quoted by Hunter and Siegel for C_p and the results of Eucken and Dannöhl (1934) for V and for the coefficient of thermal expansion α .

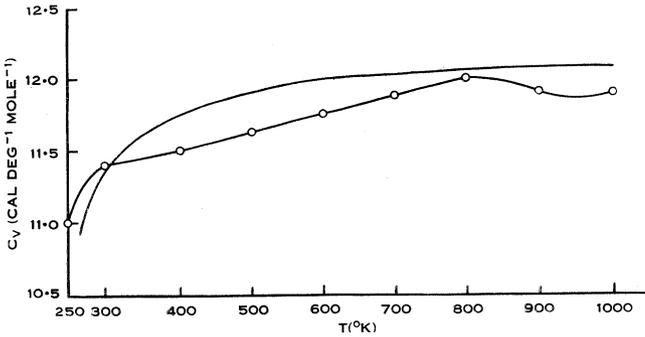


Fig. 2.—Specific heat of sodium chloride.
 —○—○— Experimental (Hunter and Siegel 1942).
 ————— Theoretical.

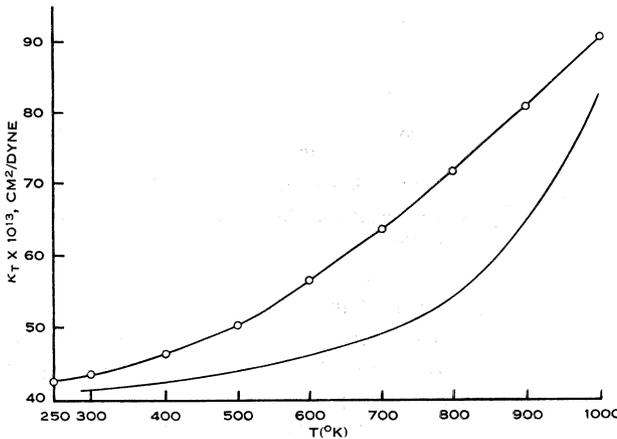


Fig. 3.—Compressibility of sodium chloride.
 —○—○— Experimental (Hunter and Siegel 1942).
 ————— Theoretical.

V. COMPARISON WITH EXPERIMENT AND DISCUSSION

Figure 1 shows that the theory used here predicts a much more rapid increase of volume with temperature than is found experimentally. Analysis of this discrepancy is complicated by the fact that the form of potential energy assumed and the values used for the parameters A , B , n , and b affect both $(\partial\Phi_0/\partial V)_T$

and $(\partial\mathcal{F}/\partial V)_T$, although the total effect on the (V, T) curve of quite large changes in these parameters was found to be surprisingly small. Essentially the method used has involved the finding of a temperature T to which a given set of ω 's, and hence a given value of V , corresponds. The good agreement with experiment in the case of C_V might seem to indicate that the ω 's are tabulated against the correct values of V (and hence of T). However, $\operatorname{cosech} x$ is so insensitive a function of x when x is small, as $x = \hbar\omega/2kT$ is here, especially for high temperatures, that one could vary T considerably (and hence alter the tabulation of the ω 's against V) without affecting this agreement appreciably. It does indicate that the ω 's obtained are of the right order of magnitude. In the case of κ_T , however, the frequency-dependent terms are both very sensitive to the choice of T , are relatively independent of one another, and their magnitudes are ~ 25 and 40 – 50 per cent. of the other terms in (31). The reasonable agreement with experiment does, therefore, suggest that the ω 's are correctly tabulated against V and that the fault lies elsewhere in the development of the theory of thermal expansion used here.

Assuming for the moment that the form assumed for the potential energy and the values used for the parameters are essentially correct, $(\partial\Phi_0/\partial V)_T$ is determined, but inclusion of anharmonic terms in the expansion of Φ would affect $(\partial\mathcal{F}/\partial V)_T$. With cubic symmetry quartic terms in the \mathbf{u}_x^4 are the first to be considered; their coefficients will be of the same sign as those of the quadratic terms and by perturbation theory they will contribute to E_m terms proportional to $(m^2 + m + \frac{1}{2})/\omega^2$. Thus E_m would be increased, which can be interpreted in terms of a larger effective ω . Since the important factors in $(\partial\mathcal{F}/\partial V)_T$ are the $\coth(\hbar\omega/2kT)$, this would mean a larger value of T would be necessary to keep $-(\partial\mathcal{F}/\partial V)_T = (\partial\Phi_0/\partial V)_T$. Thus inclusion of anharmonic terms would improve agreement with experiment. An attempt to assess this was made but it seemed obvious that a fairly exact calculation would be necessary before any worthwhile conclusions could be drawn.

As far as the form assumed for the potential energy Φ is concerned, Kellermann makes the point that only nearest-neighbour interactions are considered for the repulsive part. This does not seem so, however, since, provided one assumes a repulsive interparticle potential energy proportional to ρ^{-n} , the contribution to Φ_0 from all particles will be of the form C/a^n , where C is just the coefficient of a^{-n} determined here (from experiment), and similarly for Φ_2 . Regarding the constancy of the form of Φ , e.g. of the parameters, assumed here, one expects an increase in temperature to spread out the electron clouds about the ions. Provided these clouds stay spherically symmetrical, the Coulomb terms $\pm e^2/\rho$ will be unchanged, but the others will be increased owing to greater repulsion between the electrons. This would increase the restoring force on a displaced ion, increase the ω 's, and decrease $-(\partial\mathcal{F}/\partial V)_T$ ($\partial\mathcal{F}/\partial V$ is negative) if T is kept fixed. On the other hand, $-B$, which is essentially the repulsive force between two ions, would be increased; this increase would result in a decrease in $(\partial\Phi_0/\partial V)_T$ also. Thus, one cannot say without further investigation whether one would have to increase or decrease T , thereby improving or worsening agreement with experiment, to maintain $-(\partial\mathcal{F}/\partial V)_T = (\partial\Phi/\partial V)_T$.

One further point is that, if some or all of the electrons were considered as separate particles, they would be expected to perform high frequency oscillations, thereby increasing the average normal frequency and decreasing $-(\partial\mathcal{F}/\partial V)_T$. The effect on $(\partial\Phi/\partial V)_T$ is difficult to estimate, since it would involve Coulomb, correlation, and exchange effects between the electrons.

Reference to Figure 1 shows that the theoretical coefficient of thermal expansion eventually becomes infinite and then negative. Obviously this has no connexion with observations where α becomes zero and then negative. With regard to the theoretical work of Blackman (1958) on this point, practically all $\gamma_\nu = -(\partial \ln \nu / \partial \ln V)_T$ are positive, but for a few wave vectors \mathbf{k}_ν , is negative and the number of these increases as V , i.e. T , decreases.

One further point is that the approximate summation procedure introduced over the wave vectors \mathbf{k} , for which the normal frequencies had been calculated, may have affected the results obtained. Error is most likely to enter through the factors $\partial\omega/\partial g$ since these do vary quite rapidly with \mathbf{k} in some regions of \mathbf{k} -space. Since, however, the summation was carried out over 384 wave vectors, the overall effect on the calculations was not considered serious.

VI. CONCLUSIONS

An attempt, based on lattice theory, has been made to calculate the theoretical thermal expansion of sodium chloride. The agreement with experiment is very poor, the theoretical value of α increasing far too rapidly with temperature, eventually becoming infinite and then negative. Investigation of the variation with temperature of C_V and κ_T using the tables of normal frequencies of vibration of the crystal obtained in the work, indicates that these frequencies are essentially correct in absolute magnitude and as functions of the volume of the crystal. The discrepancy between theoretical and experimental values of α seems most likely to be due to the neglect of anharmonic terms in the expansion of the potential energy Φ but may partly be caused by the assumptions as to the form of Φ and the constancy of this form.

With regard to future work along the lines indicated here, it would be relatively simple to obtain correct values of the parameters A , B , n , and b exactly by an iterative process, since at each stage it would only be necessary to recalculate the ω 's for three or four values of g covering the value at which (30) and (31) are to be satisfied, using a digital computer. It would be simplest and most satisfactory to do this at 0 °K, since then the frequency-dependent terms are greatly simplified; however, experimental values of a_0 and κ_T at 0 °K would be difficult to obtain accurately. If some other temperature is chosen, the method is easily extended to lower temperatures by considering values $g < 1$; this was not done here owing to an oversight in carrying out the calculations.

VII. ACKNOWLEDGMENTS

The author wishes to thank the Adolph Basser Computing Laboratory, University of Sydney, for the use of SILLIAC; their staff for advice and assistance in programming the problem; and Dr. P. G. Klemens of C.S.I.R.O. for useful discussions in connexion with the work.

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