

ANHARMONICITY AND THE THERMAL EXPANSION OF SOLIDS

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Summary

Using many-particle perturbation theory an attempt has been made to improve the author's previous calculation of the thermal expansion of sodium chloride and to assess the effect of including anharmonic terms in the crystal potential. The results are disappointing; agreement with experiment is poor except at low and moderate temperatures. One reason for this is the poor convergence of a method based on the series expansion of the crystal potential in terms of particle displacements, a point further illustrated by calculations of specific heat and compressibility.

I. INTRODUCTION

A previous calculation of the thermal expansion of sodium chloride by the author (Fletcher 1959; hereafter referred to as I) exhibited a large discrepancy between theory and experiment. The most likely reason for this appeared to be neglect of the anharmonicity of the interionic forces and in the present work a calculation has been made in which the lowest order anharmonic terms in the potential energy of the crystal have been included. In developing an expression for their contribution to the free energy of the crystal a development of many-particle perturbation theory by van Hove (1959; hereafter referred to as vH), designed to avoid spurious divergencies, has been used. In Section II a brief review is given of the notation used in I with certain changes made, bringing it more into conformity with that of vH. In Section III parts of vH which are essential for the present work are briefly summarized and in Section IV the specific formula used for the quartic contribution to the free energy in this work is derived. Practical details of the calculation of the thermal expansion, specific heat at constant volume, and isothermal compressibility of sodium chloride are given in Section V and a discussion of the results in Section VI.

II. REVIEW OF THE HARMONIC PROBLEM

As in I, 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 \mathbf{r}_x ($x=1, 2, \dots, s$). Let the x th particle of mass m_x in cell $\mathbf{l}=(l_1, l_2, l_3)$ (l_i integral or zero), whose equilibrium position is

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

suffer a displacement $\mathbf{u}_x^{\mathbf{l}}$ to the position $\mathbf{r}_x^{\mathbf{l}}$. Assuming central forces between pairs of particles, depending only on their distances apart, the total potential

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energy Φ of the crystal may be expanded in powers of the Cartesian components $u_{\alpha\alpha}^1$ ($\alpha=x, y, z$) of the \mathbf{u}_α^1 , i.e. $\Phi=\Phi^{(0)}+\Phi^{(2)}+\Phi'$, where $\Phi^{(0)}$, $\Phi^{(2)}$ are as given by Φ_0 , Φ_2 in I and $\Phi'=\sum_{v=3}^{\infty}\Phi^{(v)}$, where

$$\Phi^{(v)}=\sum_{1_1, \dots, 1_v} \sum_{x_1, \dots, x_v} \sum_{\alpha_1, \dots, \alpha_v} C_{1_1 x_1 \alpha_1, \dots, 1_v x_v \alpha_v}^{(v)} u_{x_1 \alpha_1}^{1_1} \dots u_{x_v \alpha_v}^{1_v}. \quad (2)$$

The Hamiltonian of the system is then $H=H^{(2)}+\Phi'$, where

$$H^{(2)}=\Phi^{(0)}+\frac{1}{2}\sum_{\alpha, 1} m_\alpha |\dot{\mathbf{u}}_\alpha^1|^2+\Phi^{(2)} \quad (3)$$

will be termed the harmonic Hamiltonian. In general the expectation value of $\Phi^{(v)}$ can be shown to be of order $\omega(u/d)^{v-2}$ per unit volume, where ω is a typical particle vibration frequency, u an average particle displacement for a given temperature T , and d the separation of the mean positions of two neighbouring particles. Thus this series expansion of Φ and the subsequent treatment of Φ' as a perturbation to the harmonic problem will only be valid when $u \ll d$, i.e. for T reasonably small compared with the melting point T_M of the crystal.

If Φ' is neglected, normal solutions

$$\mathbf{u}_\alpha^1=(\alpha_{\mathbf{q}j}-i\alpha'_{\mathbf{q}j})\mathbf{V}_{\alpha\mathbf{q}j}\exp i\mathbf{q}\cdot\mathbf{r}_\alpha^1 \quad (4)$$

of the Lagrangian equations of motion may be found as in I. As compared with I, \mathbf{k} has been replaced by $\mathbf{q}/2\pi$ and $\mathbf{U}_\alpha(\mathbf{k}, i)\exp[-i\omega(\mathbf{k}, i)t]$ by $(\alpha_{\mathbf{q}j}-i\alpha'_{\mathbf{q}j})\mathbf{V}_{\alpha\mathbf{q}j}$, $\alpha_{\mathbf{q}j}$ and $\alpha'_{\mathbf{q}j}$ being real; the notation $\omega(\mathbf{k}, i)$ will be changed to $\omega_{\mathbf{q}j}$. $\mathbf{V}_{\alpha\mathbf{q}j}$ corresponds to $\mathbf{e}_{\mathbf{q}j}^{(n)}-i\mathbf{f}_{\mathbf{q}j}^{(n)}$ of vH so that $\mathbf{V}_{\alpha, -\mathbf{q}j}=\mathbf{V}_{\alpha\mathbf{q}j}^*$ while

$$\alpha_{-\mathbf{q}j}=\alpha_{\mathbf{q}j}; \quad \alpha'_{-\mathbf{q}j}=-\alpha'_{\mathbf{q}j}; \quad \dot{\alpha}_{-\mathbf{q}j}=\dot{\alpha}_{\mathbf{q}j}; \quad \dot{\alpha}'_{-\mathbf{q}j}=\dot{\alpha}'_{\mathbf{q}j}, \quad (5)$$

a dot denoting differentiation with respect to time t . It is assumed that

$$\ddot{\alpha}_{\mathbf{q}j}=-\omega_{\mathbf{q}j}^2\alpha_{\mathbf{q}j}; \quad \ddot{\alpha}'_{\mathbf{q}j}=-\omega_{\mathbf{q}j}^2\alpha'_{\mathbf{q}j}. \quad (6)$$

The usual cyclic boundary conditions restrict \mathbf{q} to the vectors $\mathbf{q}=q_1\mathbf{b}_1+q_2\mathbf{b}_2+q_3\mathbf{b}_3$, where $\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij}$, $q_i=2\pi h_i/L$, ($h_i=0, 1, \dots, L-1$), and $L^3=N$ is the number of cells in the lattice. A translation vector of the reciprocal lattice will be denoted by $\boldsymbol{\tau}=\tau_1\mathbf{b}_1+\tau_2\mathbf{b}_2+\tau_3\mathbf{b}_3$ (τ_i integral or zero) and α , α' , $\dot{\alpha}$, and $\dot{\alpha}'$ are unaltered in changing \mathbf{q} to $\mathbf{q}+2\pi\boldsymbol{\tau}$.

There are $3s$ solutions of the form (4) for each vector \mathbf{q} , denoted by the suffix j ($j=1, 2, \dots, 3s$). The $\mathbf{V}_{\alpha\mathbf{q}j}$ with weighting factors $m_\alpha^{\frac{1}{2}}$ are orthogonal to one another for the same \mathbf{q} and different j and may be assumed normalized to unity in the sense that

$$\sum_\alpha m_\alpha \mathbf{V}_{\alpha\mathbf{q}j} \cdot \mathbf{V}_{\alpha\mathbf{q}j'} = \delta_{jj'}. \quad (7)$$

A general solution of the harmonic problem may then be taken as a linear combination of solutions (4). For the quantum mechanical treatment of the problem the normal coordinates α , α' and their conjugate momenta $\dot{\alpha}$, $\dot{\alpha}'$ must be replaced by operators. The most convenient ones are combinations of the form

$$A_{\mathbf{q}j}=\frac{1}{2}(V/8\pi^3\hbar)^{\frac{1}{2}}[\omega_{\mathbf{q}j}^{\frac{1}{2}}(\alpha_{\mathbf{q}j}-i\alpha'_{\mathbf{q}j})+i\omega_{\mathbf{q}j}^{-\frac{1}{2}}(\dot{\alpha}_{\mathbf{q}j}-i\dot{\alpha}'_{\mathbf{q}j})], \quad (8)$$

and $A_{\mathbf{q}j}^*$, where $V = Nv_a$ ($=\Omega$ of vH). These obey the commutation relations

$$[A_{\mathbf{q}j}, A_{\mathbf{q}'j'}^*] = \delta_{jj'} \Delta(\mathbf{q} - \mathbf{q}'); \quad [A_{\mathbf{q}j}, A_{\mathbf{q}'j'}] = [A_{\mathbf{q}j}^*, A_{\mathbf{q}'j'}^*] = 0, \quad (9)$$

where $\Delta(\mathbf{q}) = (V/8\pi^3) \delta_{\mathbf{q}, 2\pi\tau}$. The general solution of the harmonic problem then takes the form

$$\mathbf{u}_x^1 = (4\pi^3 \hbar / NV)^{\frac{1}{2}} \sum_{\mathbf{q}j} \omega_{\mathbf{q}j}^{-\frac{1}{2}} (A_{\mathbf{q}j} + A_{-\mathbf{q}j}^*) \mathbf{V}_{x\mathbf{q}j} \exp i\mathbf{q} \cdot \mathbf{r}_x^1, \quad (10)$$

and the harmonic Hamiltonian the form

$$H^{(2)} = \Phi^{(0)} + \sum_{\mathbf{q}j} [(8\pi^3/V) A_{\mathbf{q}j}^* A_{\mathbf{q}j} + \frac{1}{2}] \hbar \omega_{\mathbf{q}j}. \quad (11)$$

Now the eigenfunctions of this must be products of simple harmonic wave functions with eigenvalues

$$E_m^{(2)} = \Phi^{(0)} + \sum_{\mathbf{q}j} (m_{\mathbf{q}j} + \frac{1}{2}) \hbar \omega_{\mathbf{q}j} \quad (12)$$

($m_{\mathbf{q}j}$ positive integers or zero); they will be described by the numbers $m_{\mathbf{q}j}$ of quanta of energy $\hbar \omega_{\mathbf{q}j}$ (or simply phonons (\mathbf{q}, j)) that their eigenvalues contain and denoted by $|\Psi_m^{(2)}\rangle$ or more specifically by $|\mathbf{q}_1 j_1, \mathbf{q}_2 j_2, \dots\rangle$. This is consistent with $A_{\mathbf{q}j}$, $A_{\mathbf{q}j}^*$ being annihilation and creation operators, i.e. with

$$A_{\mathbf{q}j} |\Psi_a^{(2)}\rangle = m_{\mathbf{q}j} (V/8\pi^3) |\Psi_c^{(2)}\rangle, \quad (13)$$

where the state $|\Psi_a^{(2)}\rangle$ contains $m_{\mathbf{q}j}$ phonons (\mathbf{q}, j) and $|\Psi_c^{(2)}\rangle$ contains $m_{\mathbf{q}j} - 1$, while $A_{\mathbf{q}j}^* |\Psi_c^{(2)}\rangle = (V/8\pi^3) |\Psi_a^{(2)}\rangle$. The ground (or vacuum) state eigenfunction $|0\rangle$ of $H^{(2)}$ involves no phonons (all $m_{\mathbf{q}j}$ zero) and will be assumed normalized to unity, i.e. $\langle 0 | 0 \rangle = 1$. Any other eigenfunction can be regarded as generated from this by creation operators, its normalization being so chosen that, in fact,

$$|\mathbf{q}_1 j_1, \mathbf{q}_2 j_2, \dots, \mathbf{q}_m j_m\rangle = A_{\mathbf{q}_1 j_1}^* A_{\mathbf{q}_2 j_2}^* \dots A_{\mathbf{q}_m j_m}^* |0\rangle. \quad (14)$$

It is convenient to put $H^{(2)} = \Phi^{(0)} + \varepsilon_{zp} + H_0$, where $\varepsilon_{zp} = \frac{1}{2} \hbar \sum_{\mathbf{q}j} \omega_{\mathbf{q}j}$ and $H_0 = (8\pi^3 \hbar / V) \sum_{\mathbf{q}j} \omega_{\mathbf{q}j} A_{\mathbf{q}j}^* A_{\mathbf{q}j}$, and to note that

$$\exp(-\beta H_0) |\mathbf{q}_1 j_1, \dots, \mathbf{q}_m j_m\rangle = \exp[-\beta \hbar (\omega_{\mathbf{q}_1 j_1} + \dots + \omega_{\mathbf{q}_m j_m})] |\mathbf{q}_1 j_1, \dots, \mathbf{q}_m j_m\rangle. \quad (15)$$

III. FREE ENERGY OF THE CRYSTAL

The free energy F of the crystal, which forms the basis for the calculations made, is derived as usual from the partition function $Z = \sum_{\mu} \exp(-\beta E_{\mu})$, where $\beta = 1/kT$ and E_{μ} is the energy of the crystal in state $|\Psi_{\mu}\rangle$, summation being over all possible states. This may be written

$$Z = \sum_{\mu} \langle \Psi_{\mu} | e^{-\beta H} | \Psi_{\mu} \rangle = \text{Sp} \{e^{-\beta H}\}, \quad (16)$$

i.e. as the spur of the operator $e^{-\beta H}$ in the representation of the eigenfunctions $|\Psi_{\mu}\rangle$ of H . Since, however, the spur of a matrix is unaltered by a unitary transformation, Z is also equal to the spur of $e^{-\beta H}$ in the representation of the eigenfunctions $|\Psi_m^{(2)}\rangle$ of $H^{(2)}$. Putting

$$Z = Z' \exp[-\beta(\Phi^{(0)} + \varepsilon_{zp})], \quad (17)$$

one therefore has

$$\begin{aligned} Z' &= \text{Sp} \{ \exp [-\beta(H_0 + \Phi')] \} \\ &= \sum_{m=0}^{\infty} (1/m!)(8\pi^3/V)^m \times \\ &\quad \sum_{\mathbf{q}_1 j_1 \dots \mathbf{q}_m j_m} \langle \mathbf{q}_m j_m \dots \mathbf{q}_1 j_1 | \exp [-\beta(H_0 + \Phi')] | \mathbf{q}_1 j_1 \dots \mathbf{q}_m j_m \rangle. \end{aligned} \quad (18)$$

The first step in evaluating this is to expand the operator in powers of Φ'

$$\begin{aligned} &\exp [-\beta(H_0 + \Phi')] \\ &= e^{-\beta H_0} + \sum_{r=1}^{\infty} (-1)^r \int_0^{\beta} \int_0^{\beta_1} \dots \int_0^{\beta_{r-1}} \exp [-(\beta - \beta_1)H_0] \Phi' \exp [-(\beta_1 - \beta_2)H_0] \Phi' \\ &\quad \dots \Phi' \exp (-\beta_r H_0) d\beta_r \dots d\beta_2 d\beta_1. \end{aligned} \quad (19)$$

Considering next the operator $\Phi' = \sum_{\nu=3}^{\infty} \Phi^{(\nu)}$, substitution of (10) in (2) gives

$$\Phi^{(\nu)} = \sum_{\mathbf{q}_1 j_1 \dots \mathbf{q}_{\nu} j_{\nu}} B_{1,2,\dots,\nu}^{(\nu)} (A_1 + A_{-1}^*) \dots (A_{\nu} + A_{-\nu}^*) \Delta_{\mathbf{q}_1 + \mathbf{q}_2 + \dots + \mathbf{q}_{\nu}}, \quad (20)$$

where $\Delta_{\mathbf{q}} = 1$ if $\mathbf{q} = 2\pi\tau$ and is zero otherwise and the abbreviations i for $\mathbf{q}_i j_i$ and $-i$ for $-\mathbf{q}_i j_i$ have been used in the suffices of $A_{\mathbf{q}j}$ and $A_{\mathbf{q}j}^*$. The coefficients $B_{1,2,\dots,\nu}^{(\nu)}$ differ slightly from those of van Hove but are still essentially the Fourier transforms of the $C_{1,\kappa_1\alpha_1,\dots,\nu,\kappa_{\nu}\alpha_{\nu}}^{(\nu)}$ of (2). They involve factors $(\omega_1 \omega_2 \dots \omega_{\nu})^{-\frac{1}{2}}$ but the normal modes of zero frequency, which occur for $\mathbf{q} = 0$, do not cause any problem since they are excluded from the calculations as being pure translations of the crystals as a whole. For small \mathbf{q} some frequencies are small but it can be verified that other factors in the $B^{(\nu)}$ prevent them becoming unduly large.

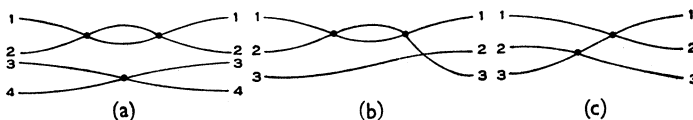


Fig. 1.—Perturbation diagrams (read from right to left). (a) Dis-connected, (b) connected, (c) connected reduced.

After substitution of (19) and (20) in (18) it is obvious that the first quantities of interest have the form

$$\begin{aligned} \langle m, \dots, 1 | \exp [-(\beta - \beta_1)H_0] A_i A_j^* \dots \exp [-(\beta_1 - \beta_2)H_0] \dots \\ \dots A_k^* A_l \dots \exp (-\beta_r H_0) | 1, \dots, m \rangle. \end{aligned} \quad (21)$$

Each of these may be represented by a diagram with a vertex for each operator $A_i A_j^* \dots$, at which phonons i, \dots are annihilated and j, \dots created. Diagrams of the types shown in Figures 1 (a) and 1 (b) are termed disconnected and connected respectively by van Hove, who has shown that calculations may be made in terms of the latter only. There are still two essentially different types of connected diagrams, as illustrated in Figures 1 (b) and 1 (c). Van Hove terms

the latter reduced diagrams and shows that only these need be considered if the operators A_i, A_i^* are replaced by

$$A_i[1 - \exp(-\beta\hbar\omega_i)]^{-\frac{1}{2}}, A_i^*[1 - \exp(-\beta\hbar\omega_i)]^{-\frac{1}{2}}.$$

Denoting the complete operator so modified by $\exp[-\beta(H_0 + \Phi')]$, and summation over reduced diagrams by $\sum_{\text{red.}}$, the final expression for the free energy is

$$F = \Phi^{(0)} + \frac{1}{2}\hbar \sum_{\mathbf{q}j} \omega_{\mathbf{q}j} + F', \quad (22)$$

where

$$\begin{aligned} F' &= -(1/\beta) \ln Z' \\ &= F'^{(2)} - \frac{1}{\beta} \sum_{\text{red.}} \left(\frac{V}{8\pi^3} \right)^{n_r} \frac{1}{n_r!} \sum_{1, \dots, n_r} \langle n_r \dots 1 | \exp[-\beta(H_0 + \Phi')]_r | 1 \dots n_r \rangle \end{aligned} \quad (23)$$

where n_r is the number of initial (or final) phonons in a reduced diagram and $F'^{(2)} (= \mathcal{F} \text{ of I})$ is the (harmonic) contribution from diagrams with no vertices, that is,

$$F'^{(2)} = \beta \sum_{\mathbf{q}j} \ln [1 - \exp(-\beta\hbar\omega_{\mathbf{q}j})]. \quad (24)$$

IV. QUARTIC CONTRIBUTION TO F

The present calculation was made for a cubic crystal ($\Phi^{(3)}=0$) and only the lowest order (quartic) anharmonic terms in the $\mathbf{u}_{\alpha\alpha}^1$ were included so that $\Phi' = \Phi^{(4)}$. In this case each annihilation-creation factor in (21) consists of a product of four operators A_i or A_j^* corresponding to a fourfold vertex. Diagrams involving any number of such vertices should be considered but each additional vertex reduces the contribution of a diagram considerably. (This arises from the fact that $\Phi^{(4)}/\Phi^{(2)}$ is of the order of u^2/d^2 .) For this reason diagrams with more than one vertex were ignored and this left only the three reduced diagrams shown in Figures 2 (a), 2 (b), and 2 (c) to be considered. Furthermore, the only annihilation-creation operators of interest must contain two operators A_i, A_j and two corresponding ones A_i^*, A_j^* since $\langle \Psi_a^{(2)} | A_i A_j^* \dots | \Psi_a^{(2)} \rangle = \langle \Psi_a^{(2)} | \Psi_b^{(2)} \rangle$ is zero unless $|\Psi_a^{(2)}\rangle$ and $|\Psi_b^{(2)}\rangle$ are the same state, owing to the orthogonality of the $|\Psi_m^{(2)}\rangle$. With this point in mind $\Phi' = \Phi^{(4)}$ may be replaced by

$$\sum_{\mathbf{q}_1 j_1 \dots \mathbf{q}_4 j_4} B_{1,2,3,4}^{(4)} (A_1 + A_{-1}^*) \dots (A_4 + A_{-4}^*), \quad (25)$$

where either (i) $3 \equiv -1, 4 \equiv -2$, (ii) $2 \equiv -1, 4 \equiv -3$, or (iii) $3 \equiv -2, 4 \equiv -1$ (it is convenient to replace suffix 3 by 2 in (ii) so that in all cases there are just two different suffices 1 and 2). In each case one has a sum of 16 fourfold annihilation-creation factors, of which one corresponds to each of Figures 2 (a) and 2 (c) and two to Figure 2 (b) while the other 12 are of no interest.

In the practical calculation of the quartic contribution $F'^{(4)}$ to the free energy the coefficients $B_{1,2,3,4}^{(4)}$ remain to be evaluated. This was not done explicitly as it proved simpler to substitute (10) into the classical expression

$$\Phi^{(4)} = \frac{1}{2} \frac{1}{4!} \sum_{\alpha\alpha'} \sum_{\mathbf{r}} \sum_{\alpha_1 \dots \alpha_4} \left(\frac{\partial^4 \Phi_{\alpha\alpha'}^{\text{II}}(\mathbf{r})}{\partial \alpha_1 \partial \alpha_2 \partial \alpha_3 \partial \alpha_4} \right)_0 (u_{\alpha\alpha_1}^1 - u_{\alpha'\alpha_1}^1) \dots (u_{\alpha\alpha_4}^1 - u_{\alpha'\alpha_4}^1) \quad (26)$$

(where $r^2 = x^2 + y^2 + z^2$, each α_i may be x , y , or z , the differential coefficients are to be evaluated with $\mathbf{r} = \mathbf{r}_x^1 - \mathbf{r}_{x'}^1$, and the primed summation sign indicates that the case $x = x'$, $1 = 1'$ is omitted) and consider sets of terms with the same α_1 , α_2 , α_3 , and α_4 . Ignoring for the moment the factors $(4\pi^3\hbar/NV)^{\frac{1}{2}}\omega_{\mathbf{q}j}^{-\frac{1}{2}}(A_{\mathbf{q}j} + A_{-\mathbf{q}j}^*)$ and the summations over \mathbf{q} and j , consider the following cases.

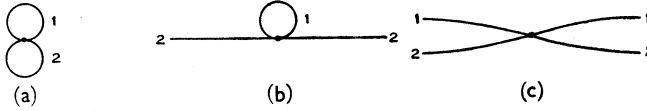


Fig. 2.—Perturbation diagrams (read from right to left).

(a) If $\alpha_1 = \alpha_2 = \alpha_3 = \alpha_4 = x$, the remaining factor in the contribution of such terms to $\Phi^{(4)}$ may be reduced to

$$\frac{N}{2} \sum_{xx'} \sum_1 \left(\frac{\partial^4 \Phi_{xx'}^{10}}{\partial x^4} \right)_0 f_x(1; xx'; 1) f_x(1; xx'; 2), \quad (27)$$

where

$$f_x(1; xx'; i) = V_{xix}^2 - 2V_{xix}V_{x'ix} \cos \mathbf{q}_i \cdot (\mathbf{r}_x^1 - \mathbf{r}_{x'}^1) + V_{x'ix}^2. \quad (28)$$

(b) If $\alpha_1 = \alpha_2 = \alpha_3 = x$ and $\alpha_4 = y$, say, the corresponding factor is a complicated one. In the case of a crystal of cubic symmetry, every part of it contains factors of the form $\cos \mathbf{q} \cdot (\mathbf{r}_x^1 - \mathbf{r}_{x'}^1)$, which may be replaced by

$$\sin q_x (\hat{r}_{xx}^1 - \hat{r}_{x'x}^1) \sin q_y (\hat{r}_{xy}^1 - \hat{r}_{x'y}^1) \cos q_z (\hat{r}_{xz}^1 - \hat{r}_{x'z}^1).$$

(c) If $\alpha_1 = \alpha_2 = x$ and $\alpha_3 = \alpha_4 = y$, say, the corresponding factor is

$$\begin{aligned} \frac{N}{2} \sum_{xx'} \sum_1 \left(\frac{\partial^4 \Phi_{xx'}^{10}}{\partial x^2 \partial y^2} \right)_0 \{ f_x(1; xx'; 1) f_y(1; xx'; 2) + f_y(1; xx'; 1) f_x(1; xx'; 2) \\ + 4g_{xy}(1; xx'; 1) g_{xy}(1; xx'; 2) \}, \end{aligned} \quad (29)$$

where

$$g_{xy}(1; xx'; i) = V_{xix}V_{xiy} - (V_{xix}V_{x'iy} + V_{x'ix}V_{xiy}) \cos \mathbf{q}_i \cdot (\mathbf{r}_x^1 - \mathbf{r}_{x'}^1) + V_{x'ix}V_{x'iy}. \quad (30)$$

(d) If $\alpha_1 = \alpha_2 = x$, $\alpha_3 = y$, $\alpha_4 = z$, say, the factor is again a complicated one but again for cubic symmetry every part of it contains factors of the form $\cos \mathbf{q} \cdot (\mathbf{r}_x^1 - \mathbf{r}_{x'}^1)$, which may be replaced by

$$\cos q_x (\hat{r}_{xx}^1 - \hat{r}_{x'x}^1) \sin q_y (\hat{r}_{xy}^1 - \hat{r}_{x'y}^1) \sin q_z (\hat{r}_{xz}^1 - \hat{r}_{x'z}^1).$$

In each of the cases (a)-(d) there are contributions from pairs of particles of the same type ($x = x'$) and from pairs of different types. For the former the notation

$$\begin{aligned} \sum_1' \left(\frac{\partial^4 \Phi_{xx}^{10}}{\partial \alpha_1 \partial \alpha_2 \partial \alpha_3 \partial \alpha_4} \right)_0 = (\alpha_1 \alpha_2 \alpha_3 \alpha_4; 1); \quad \sum_1' \left(\frac{\partial^4 \Phi_{xx}^{10}}{\partial \alpha_1 \partial \alpha_2 \partial \alpha_3 \partial \alpha_4} \right)_0 \cos \mathbf{q} \cdot \mathbf{r}_x^1 = (\alpha_1 \alpha_2 \alpha_3 \alpha_4; \mathbf{q}; 1); \\ \sum_1' \left(\frac{\partial^4 \Phi_{xx}^{10}}{\partial \alpha_1 \partial \alpha_2 \partial \alpha_3 \partial \alpha_4} \right)_0 \cos (\mathbf{q}_1 + \mathbf{q}_2) \cdot \mathbf{r}_x^1 = (\alpha_1 \alpha_2 \alpha_3 \alpha_4; \mathbf{q}_1, \mathbf{q}_2; 1) \end{aligned} \quad (31)$$

will be introduced, while for the latter, for which there is no prime on the summation signs, 1 is replaced by λ .

It was appreciated at this stage of the work that, despite the approximations made so far, the necessary calculation of $F'^{(4)}$ for several temperatures and volumes of the crystal would prove far too lengthy for the value of the results obtained without further approximation. It seemed necessary to simplify the dependence of expressions (a)-(d) on \mathbf{q}_1 and \mathbf{q}_2 and this was investigated for $\mathbf{q}_1 = (q_{1x}, 0, 0)$, $\mathbf{q}_2 = (q_{2x}, 0, 0)$ in the case of sodium chloride, for which $\mathbf{V}_{\kappa\mathbf{q}j}$, $\mathbf{V}_{\kappa'\mathbf{q}j}$ were known from the calculations of I. The following conclusions were reached.

(i) Expressions for $\kappa \neq \kappa'$ were larger than corresponding ones for $\kappa = \kappa'$ by factors ~ 100 except for a few values of q_x where both were small.

$$(ii) \quad \left. \begin{aligned} (x^4; q_x; \lambda) &\simeq (x^4; \lambda) \cos \pi q_x; & (y^4; q_x; \lambda) &\simeq (x^4; \lambda), \\ (x^2 y^2; q_x; \lambda) &\simeq (x^2 y^2; \lambda) \cos \frac{\pi q_x}{2}; & (y^2 z^2; q_x; \lambda) &\simeq (y^2 z^2; \lambda), \end{aligned} \right\} \quad (32)$$

where $(x^4; \lambda)$ is $(x^4; q_x; \lambda)$ with $q_x = 0$ etc.

(iii) All expressions involved in (b) and (d) were identically zero.

It was therefore decided, for all values of \mathbf{q}_1 , \mathbf{q}_2 , to neglect (b), (d) and the contributions to (a) and (c), for which $\kappa = \kappa'$. Further reduction of the remaining parts of (a) and (c) is then possible by use of crystal symmetry. Thus preliminary summation of these over the 48^2 wave-vector pairs obtained by applying cubic symmetry operations to \mathbf{q}_1 and \mathbf{q}_2 was carried out. Thereafter summation over a \mathbf{q} could be restricted to a basic region of \mathbf{q} -space,

$$\pi/a \geq q_x \geq q_y \geq q_z \geq 0; \quad q_x + q_y + q_z \leq 3\pi/2a,$$

where a is the lattice constant of the crystal, i.e. $v_a = 2a^3$. In carrying out this preliminary summation (denoted by \sum_e) the symmetry permits the factor $\cos \mathbf{q}_1 \cdot (\hat{\mathbf{r}}_x^1 - \hat{\mathbf{r}}_{x'}^1) \cos \mathbf{q}_2 \cdot (\hat{\mathbf{r}}_x^1 - \hat{\mathbf{r}}_{x'}^1)$ to be replaced by $\cos (\mathbf{q}_1 + \mathbf{q}_2) \cdot (\hat{\mathbf{r}}_x^1 - \hat{\mathbf{r}}_{x'}^1)$. Then from terms of type (a) one obtains

$$\begin{aligned} & \frac{N}{2} \sum_e \sum_{\kappa\kappa'} \sum_{\lambda} \sum_{\alpha} \left(\frac{\partial^4 \Phi_{\kappa\kappa'}^{\lambda 0}}{\partial \alpha^4} \right)_0 f_{\alpha}(\lambda; \kappa\kappa'; 1) f_{\alpha}(\lambda; \kappa\kappa'; 2) \\ & = 12N \operatorname{Re} \{ (x^4; \lambda) P(\mathbf{q}_1 j_1) P(\mathbf{q}_2 j_2) \}, \end{aligned} \quad (33)$$

where

$$P(\mathbf{q}_j) = \mathbf{V}_{\kappa\mathbf{q}j} \cdot \mathbf{V}_{\kappa\mathbf{q}j} + \mathbf{V}_{\kappa'\mathbf{q}j} \cdot \mathbf{V}_{\kappa'\mathbf{q}j} - 2 \sum_{\alpha} V_{\kappa\mathbf{q}j\alpha} V_{\kappa'\mathbf{q}j\alpha} e^{i\pi q_{\alpha}}. \quad (34)$$

Similarly from terms of type (c) one obtains

$$\begin{aligned} & \frac{N}{2} \sum_e \sum_{\kappa\kappa'} \sum_{\lambda} \sum_{\alpha_1 \alpha_2} \left(\frac{\partial^4 \Phi_{\kappa\kappa'}^{\lambda 0}}{\partial \alpha_1^2 \partial \alpha_2^2} \right)_0 \{ f_{\alpha_1}(\lambda; \kappa\kappa'; 1) f_{\alpha_2}(\lambda; \kappa\kappa'; 2) + f_{\alpha_2}(\lambda; \kappa\kappa'; 1) f_{\alpha_1}(\lambda; \kappa\kappa'; 2) \\ & \quad + 4g_{\alpha_1 \alpha_2}(\lambda; \kappa\kappa'; 1) g_{\alpha_1 \alpha_2}(\lambda; \kappa\kappa'; 2) \} \\ & = 24N \operatorname{Re} \{ (x^2 y^2; \lambda) Q(\mathbf{q}_1 j_1) Q(\mathbf{q}_2 j_2) \} + 48N \operatorname{Re} \{ (x^2 y^2; \lambda) R(\mathbf{q}_1 j_1) R(\mathbf{q}_2 j_2) \}, \end{aligned} \quad (35)$$

where

$$Q(\mathbf{q}j) = \mathbf{V}_{\kappa\mathbf{q}j} \cdot \mathbf{V}_{\kappa\mathbf{q}j} + \mathbf{V}_{\kappa'\mathbf{q}j} \cdot \mathbf{V}_{\kappa'\mathbf{q}j} - \sum_{\text{cyc.}} (V_{\kappa\mathbf{q}jx} V_{\kappa'\mathbf{q}jx} + V_{\kappa\mathbf{q}jy} V_{\kappa'\mathbf{q}jy}) e^{i\pi(q_x + q_y)/2}, \quad (36)$$

and

$$R(\mathbf{q}j) = \sum_{\text{cyc.}} [V_{\kappa\mathbf{q}jx} V_{\kappa\mathbf{q}jy} + V_{\kappa'\mathbf{q}jx} V_{\kappa'\mathbf{q}jy} - (V_{\kappa\mathbf{q}jx} V_{\kappa'\mathbf{q}jy} + V_{\kappa'\mathbf{q}jx} V_{\kappa\mathbf{q}jy}) e^{i\pi(q_x + q_y)/2}], \quad (37)$$

Σ denoting cyclic permutation of x, y , and z . Thus the approximate expression for $\Phi^{(4)}$ proves to be

$$\Phi^{(4)} \simeq \frac{64N}{4!} \left(\frac{\hbar}{2N} \right)^2 \left(\frac{8\pi^3}{V} \right)^2 \sum_{\mathbf{q}_1 \mathbf{q}_2}^{\text{basic}} \sum_{j_1 j_2} \frac{12B_{1,2}^{(4)'}}{\omega_1 \omega_2} (A_1 A_2 A_1^* A_2^* + \dots), \quad (38)$$

where

$$B_{1,2}^{(4)'} = \text{Re} \{ (x^4; \lambda) P(1)P(2) + 2(x^2 y^2; \lambda) Q(1)Q(2) + 4(x^2 y^2; \lambda) R(1)R(2) \}, \quad (39)$$

and the final bracket of (38) contains 12 different fourfold operators, of which 3 correspond to Figure 2 (a), 6 to Figure 2 (b), and 3 to Figure 2 (c). This expression has to be substituted in the approximate quartic contribution to the free energy

$$F'^{(4)} \simeq \frac{1}{\beta} \sum_{\text{red.}} \left(\frac{V}{8\pi^3} \right)^{n_r} \frac{1}{n_r!} \sum_{\mathbf{q}_1 j_1 \dots \mathbf{q}_{n_r} j_{n_r}} \frac{\langle n_r \dots 1 | \int_0^\beta e^{-(\beta-\beta_1)H_0} \Phi^{(4)} e^{-\beta_1 H_0} d\beta_1 | 1 \dots n_r \rangle}{[1 - \exp(-\beta \hbar \omega_1)][1 - \exp(-\beta \hbar \omega_2)]}. \quad (40)$$

For the operators in $\Phi^{(4)}$ corresponding to Figure 2 (a) $n_r=0$ and each one, e.g. $A_1 A_2 A_1^* A_2^*$, produces a term

$$\langle 0 | \int_0^\beta e^{-(\beta-\beta_1)H_0} A_1 A_2 A_1^* A_2^* e^{-\beta_1 H_0} d\beta_1 | 0 \rangle = \beta (V/8\pi^3)^2. \quad (41)$$

For an operator such as $A_1^* A_2 A_1 A_2^*$ corresponding to Figure 2 (b) $n_r=1$ and one similarly obtains

$$\left(\frac{V}{8\pi^3} \right) \langle 1 | \int_0^\beta e^{-(\beta-\beta_1)H_0} A_1^* A_2 A_1 A_2^* e^{-\beta_1 H_0} d\beta_1 | 1 \rangle = \beta \exp(-\beta \hbar \omega_1) (V/8\pi^3)^2. \quad (42)$$

For an operator such as $A_1^* A_2^* A_1 A_2$ corresponding to Figure 2 (c) $n_r=2$ and one obtains

$$\left(\frac{V}{8\pi^3} \right)^2 \frac{1}{2!} \langle 2, 1 | \int_0^\beta e^{-(\beta-\beta_1)H_0} A_1^* A_2^* A_1 A_2 e^{-\beta_1 H_0} d\beta_1 | 1, 2 \rangle = \frac{\beta}{2} \exp[-\beta \hbar (\omega_1 + \omega_2)] \left(\frac{V}{8\pi^3} \right)^2. \quad (43)$$

It may be noted that in obtaining these results various positive and negative powers of $(V/8\pi^3)$ arise from (13), from the normalization of the harmonic eigenfunctions, and from the fact that, when a summation over \mathbf{q} and j becomes redundant (e.g. for Figure 2 (b) one of the Σ in $\Phi^{(4)}$ is redundant since it is duplicated by another Σ in $F'^{(4)}$), a factor $V/8\pi^3$ must be introduced (see vH). Substituting these results in (40), one obtains

$$F'^{(4)} = \frac{24\hbar^2}{N} \sum_{\mathbf{q}_1 \mathbf{q}_2}^{\text{basic}} \sum_{j_1 j_2} B_{1,2}^{(4)'} \frac{[1 + \exp(-\beta \hbar \omega_1)][1 + \exp(-\beta \hbar \omega_2)]}{\omega_1 \omega_2 [1 - \exp(-\beta \hbar \omega_1)][1 - \exp(-\beta \hbar \omega_2)]}. \quad (44)$$

Now $B_{1,2}^{(4)'}$ consists of three parts, each of which is separable in $\mathbf{q}_1, \mathbf{q}_2$ and the corresponding contribution to $F'^{(4)}$ can therefore be expressed as the square of a

single sum over \mathbf{q}, j . Finally, if the real and imaginary parts of P, Q , and R are denoted by $R_P, R_Q, R_R, I_P, I_Q, I_R$ respectively, one obtains

$$F^{(4)} = \frac{24\hbar^2}{N} \sum_{k=P,Q,R} \left\{ \left[\sum_{\mathbf{q}}^{\text{basic}} \sum_j \frac{R_k \coth(\beta\hbar\omega_{\mathbf{q}j}/2)}{\omega_{\mathbf{q}j}} \right]^2 - \left[\sum_{\mathbf{q}}^{\text{basic}} \sum_j \frac{I_k \coth(\beta\hbar\omega_{\mathbf{q}j}/2)}{\omega_{\mathbf{q}j}} \right]^2 \right\}. \quad (45)$$

V. APPLICATION TO SODIUM CHLORIDE

The purpose of this work was to examine the effect of inclusion of the quartic terms in the expansion of Φ on the theoretical thermal expansion of sodium chloride. Thus, as in I, solutions of the equation of state

$$p = -(\partial F / \partial V)_T \quad (46)$$

for various values of the lattice parameter a were sought, with the quartic contribution to the free energy included at all stages. Thus, one mole of the crystal was considered, for which $V = 2Na^3$, N being Avogadro's number; let $V/V_0 = g$, where the suffix zero will always denote values for a standard value a_0 of a (the experimental value at $T = 288^\circ\text{K}$). It was assumed that

$$\Phi^{(0)} = N(-\alpha_M e^2 a_0^{-1} g^{-1/3} + 6ba_0^{-n} g^{-n/3}), \quad (47)$$

where α_M is the Madelung number for the lattice, e is the charge on an electron, and b, n are parameters; as before the latter were replaced by

$$A = 4n(n+1)be^{-2}a_0^{-n+1} \text{ and } B = -4nbe^{-2}a_0^{-n+1}.$$

A and B were determined as in I, i.e. by satisfying (46) and $\kappa_T^{-1} = V(\partial^2 F / \partial V^2)_{T,T}$ at $T = 288^\circ\text{K}$, $p = 0$ with the experimental values for a_0 (2.814×10^{-8} cm) and the isothermal compressibility κ_T (4.16×10^{-12} cm²/dyne). At each stage of the iterative procedure (see I for details) $F^{(2)}$ and $F^{(4)}$ were calculated for $T = 288^\circ\text{K}$ and six values of g by digital computer, as this proved simpler than a direct computation of their derivatives. A further approximation was made in

TABLE 1
COMPARISON OF VALUES OF PARAMETERS

	A	B	n	b
Kellermann ..	10.18	-1.165	7.738	1.148×10^{-71}
I	10.68	-1.048	9.188	9.902×10^{-83}
Present work..	10.40	-1.063	8.779	1.587×10^{-78}

the case of $F^{(4)}$; it was decided that the dependence of R_k, I_k ($k = P, Q, R$) on g would be relatively small so that, in order to reduce the amount of computation, their values calculated for one value of g (and the 300 values of (\mathbf{q}, j) used in the further summations) were used for all g . The normal frequencies $\omega_{\mathbf{q}j}$ having only been calculated for about 50 points in the basic region of \mathbf{q} -space, summations were restricted to these values of \mathbf{q} with suitable weighting factors (ΔK of I). The derivatives, e.g. $(\partial F^{(2)} / \partial V)_T$, $(\partial^2 F^{(2)} / \partial V^2)_{T,T}$, were found numerically from

difference tables prepared from the computations. The values obtained for A , B , n , and b are compared in Table 1 with those of Kellermann (who essentially ignored the dependence of the vibrational energy on g) and of the calculation I (where $F''^{(4)}$ was not included).

With these values of the parameters $F''^{(2)}$ and $F''^{(4)}$ were computed and $(\partial F''^{(2)}/\partial V)_T$ and $(\partial F''^{(4)}/\partial V)_T$ determined numerically for various values of g and T , and thereby pairs of values (g, T) determined for which (46) was satisfied (with $p=0$). In order that comparison with experiment could be made for temperatures below $T=288^\circ\text{K}$, normal frequencies for the crystal were computed for $g=0.975(0.005)1.000$. The theoretical curve so obtained is shown in comparison with the experimental results of Eucken and Dannöhl (1934) and of Srinivasan (1955) in Figure 3; also shown is the theoretical curve obtained in I.

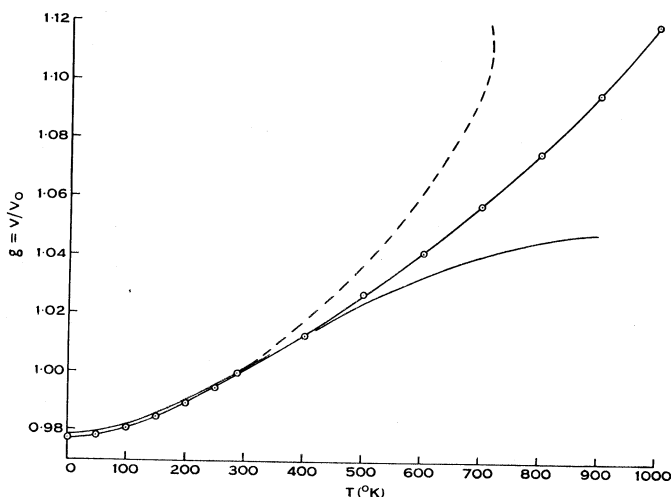


Fig. 3.—Expansion of sodium chloride. — \odot — \odot — Experimental (Eucken and Dannöhl 1934; Srinivasan 1955); — theoretical (present work); ---- theoretical (I).

As in I there is wide discrepancy between theory and experiment at the higher temperatures and again it seemed of interest to calculate the specific heat C_v at constant volume and κ_T , using the experimental figures for the thermal expansion to relate the values of g , for which the normal frequencies to be used had been calculated, to temperature T . They were both calculated numerically from suitable difference tables for $F''^{(2)}$ and $F''^{(4)}$ and the relations

$$C_v = -T(\partial^2 F / \partial T^2)_{v,v} \text{ and } \kappa_T^{-1} = V(\partial^2 F / \partial V^2)_{T,T}.$$

(Note that the first group of terms in expression (31) for κ_T^{-1} in I is incorrect except when $g=1$.) The results are again compared with experiment in Figures 4 and 5. As an indication of the magnitude of the quartic contributions, curves, for which these have been omitted, have also been inserted. (They are, however, calculated with the values of A and B obtained by inclusion of quartic effects. If quartic effects are completely ignored, the curves of I are obtained.)

VI. DISCUSSION OF RESULTS

As can be seen from Figure 3 agreement between theory and experiment has not been improved greatly by the inclusion of the lowest order anharmonic terms in this calculation of thermal expansion. Although a number of approximations were made in obtaining the expression (45) for $F''^{(4)}$, ultimately aimed

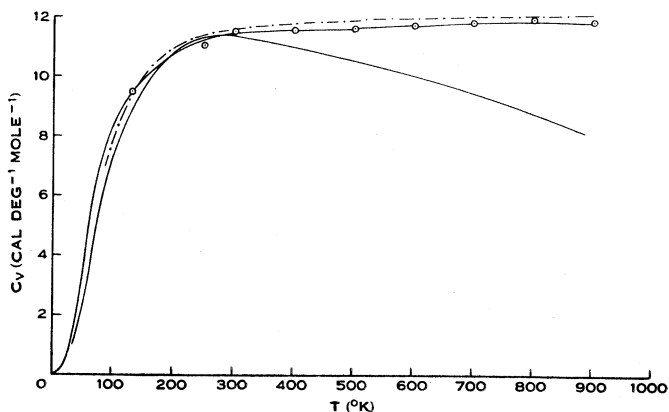


Fig. 4.—Specific heat of sodium chloride. — \odot — \odot — Experimental (Hunter and Siegel 1942; Clusius, Goldmann, and Perlick 1949); — theory; - - - - anharmonic contribution omitted.

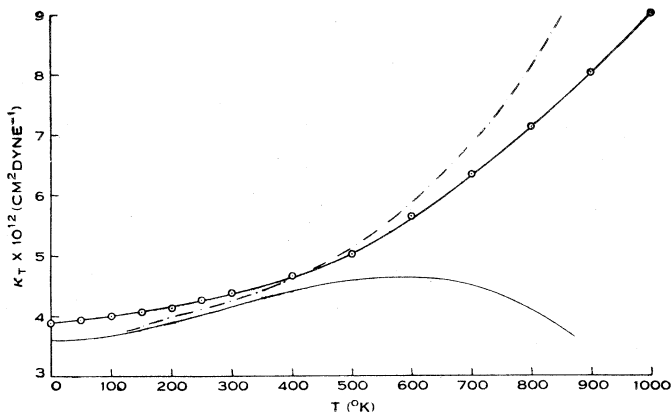


Fig. 5.—Compressibility of sodium chloride. — \odot — \odot — Experimental (Hunter and Siegel 1942; Overton and Swim 1951); — theory; - - - - anharmonic contribution omitted.

at making its computation a reasonable proposition, these are not thought to have affected the result essentially. The factors

$$(\omega_1\omega_2)^{-1} \coth(\beta\hbar\omega_1/2) \coth(\beta\hbar\omega_2/2)$$

will obviously increase with T and the great majority with V also (since most $\partial\omega/\partial V < 0$). At high temperatures the arguments $\beta\hbar\omega/2$ are so small that the rate of increase of these factors with V causes $(\partial F''^{(4)}/\partial V)_T$ to outstrip

$-(\partial F^{(2)}/\partial V)_T - \partial \Phi^{(0)}/\partial V$ at all volumes, i.e. no equilibrium volume can be found. This stems originally from the use of a Taylor expansion for Φ up to quartic terms only in the $u_{\alpha\alpha}$. Inclusion of higher order terms, which would increase the computation enormously, might improve agreement with experiment but, as stated in Section II, the use of such an expansion for Φ can never be satisfactory at high temperatures. At the lower temperatures (below $T=288^\circ\text{K}$) agreement with experiment is reasonable but little better than is obtained by ignoring the quartic terms, as would also be expected. The unrealistic influence of the quartic terms at higher temperatures is also well illustrated by Figures 4 and 5.

It appears to the author that it would be unprofitable to proceed any further with the investigation of thermal expansion, even for ionic solids, on the basis of the expansion in powers of particle displacements of the form used here for the potential energy Φ of a crystal. Replacement of the repulsive term b/r^n in the interparticle potential by an exponential term might be worth while but it would probably be even more profitable to examine the effect of deviations from central symmetry in the interparticle forces (Born and Huang 1954, especially Chapter V).

VII. ACKNOWLEDGMENT

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VIII. REFERENCES

- BORN, M., and HUANG, K. (1954).—"Dynamical Theory of Crystal Lattices." (Oxford Univ. Press.)
- CLUSIUS, K., GOLDMANN, J., and PERLICK, A. (1949).—*Z. Naturf.* **4a**: 424.
- EUCKEN, A., and DANNÖHL, W. (1934).—*Z. Electrochem.* **40**: 814.
- FLETCHER, G. C. (1959).—*Aust. J. Phys.* **12**: 237.
- VAN HOVE, L. (1959).—Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Tech. Rep. No. 11.
- HUNTER, L., and SIEGEL, S. (1942).—*Phys. Rev.* **61**: 84.
- OVERTON, W. C., and SWIM, R. T. (1951).—*Phys. Rev.* **84**: 758.
- SRINIVASAN, R. (1955).—*J. Indian Inst. Sci.* A **37**: 232.