THERMAL EXPANSION AND OTHER PROPERTIES OF SODIUM CHLORIDE

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Summary

A previous calculation by one of the authors of the equation of state of an anharmonic rigid-ion model of sodium chloride has been corrected. The results are valid above room temperature and reasonable agreement with experiment is obtained to within about 200° of the melting point. Comparison with experiment is also made for specific heats C_V , C_P and compressibilities κ_T , κ_S .

I. INTRODUCTION

Previous attempts have been made by one of the authors (Fletcher 1959, 1961, hereafter referred to as FI and FII) to reproduce the observed thermal expansion of an ionic solid (sodium chloride) on a rigid-ion model. The solid was in fact treated as a collection of point ions with a mutual potential energy $\phi = \phi_{\rm C} + \phi_{\rm R} = \pm e^2/\rho + b/\rho^n$ for any pair of them, distance ρ apart, and the repulsive term $\phi_{\rm R}$ was ignored except between nearest neighbours. Neither attempt was very successful but in the second one, which was intended to include anharmonic effects of lowest order, a mistake was made. In the expansion of the crystal potential energy in powers of the displacements of the ions from their mean positions it was assumed that cubic terms would be absent. This is not so and in the present work this is corrected. Inclusion of the cubic terms, however, has meant restriction of the calculations so far to high temperatures as in the treatment of Maradudin, Flinn, and Coldwell-Horsfall (1961*a*, 1961*b*).

Thus formal expressions for the free energy of an anharmonic crystal are obtained in Section II, their approximation at high temperature is deduced in Section III, and application of them is made in Sections IV and V to the evaluation of the coefficient of thermal expansion α , compressibilities κ_T , κ_S , and specific heats C_V , C_P of sodium chloride. The results are discussed and compared with experiment in Section VI.

II. FREE ENERGY OF ANHARMONIC CRYSTAL

The basic treatment of the problem is the same as in FI and FII and the relevant nomenclature is recalled here. m_{κ} , $\mathring{\mathbf{r}}^{\mathbf{l}}_{\kappa}$, $\mathbf{u}^{\mathbf{l}}_{\kappa}$ are respectively the mass, mean position, and displacement from its mean position of the κ th particle in the 1th unit cell of the crystal ($\kappa = 1, 2, \ldots, s$). $\phi^{\mathbf{l}\mathbf{l}'}_{\kappa\kappa'} = \phi_{\kappa\kappa'}(|\mathbf{r}^{\mathbf{l}}_{\kappa} - \mathbf{r}^{\mathbf{l}'}_{\kappa'}|)$ is the mutual potential energy of the (κ , 1) and (κ' , 1') particles. $\Phi^{(\nu)}$ is the term in the Taylor expansion

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of the potential energy of the crystal which is of ν th order in the Cartesian components $u_{\kappa a}^{\mathbf{l}} (a = x, y, z)$. $\omega_{\mathbf{q}j}$ is the frequency of the *j*th normal mode of vibration with wave vector \mathbf{q} for the crystal in the harmonic approximation. $A_{\mathbf{q}j}$, $A_{\mathbf{q}j}^*$ are respectively annihilation and creation operators for the phonon $\hbar \omega_{\mathbf{q}j}$.

The Hamiltonian for a volume V of the crystal in the harmonic approximation is then

$$H^{(2)} = \Phi^{(0)} + H_0 + \epsilon_{zp} = \Phi^{(0)} + (8\pi^3/V) \sum_{\mathbf{q}j} A^*_{\mathbf{q}j} A_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j} + \frac{1}{2} \sum_{\mathbf{q}j} \hbar \omega_{\mathbf{q}j}$$
(1)

and the anharmonic perturbing term is

$$\Phi' = \sum_{\nu=3}^{\infty} \Phi^{(\nu)},$$

where

$$\Phi^{(\nu)} = \sum_{1,2,\ldots,\nu} B^{(\nu)}_{1,2,\ldots,\nu} (A_1 + A_1^*) \dots (A_{\nu} + A_{-\nu}^*) \Delta_{\mathbf{q}_1 + \mathbf{q}_2 + \ldots + \mathbf{q}_{\nu}},$$
(2)

the abbreviations k for $\mathbf{q}_k j_k$ and -k for $-\mathbf{q}_k j_k$ have been used in the suffices, and $\Delta_{\mathbf{q}} = 1$ if $\mathbf{q}/2\pi$ is a reciprocal lattice vector and is zero otherwise. The coefficients, which were not given explicitly in F II but are required here, are

$$B_{1,2,\ldots,\nu}^{(\nu)} = \frac{N}{2\nu!} \left(\frac{4\pi^{3\hbar}}{NV} \right)^{\frac{1}{2}\nu} \sum_{\substack{\alpha_{1},\ldots,\alpha_{\nu} \\ \boldsymbol{\lambda}}} \left[\frac{\partial^{\nu}\phi_{\kappa\kappa'}(r)}{\partial \alpha_{1}\ldots\partial \alpha_{\nu}} \right]_{\mathbf{r}=\boldsymbol{\lambda}} \times \prod_{k=1}^{\nu} \left\{ V_{\kappa\alpha_{k}}(\mathbf{q}_{k}j_{k})\exp(\mathrm{i}\mathbf{q}_{k}\cdot\boldsymbol{\lambda}) - V_{\kappa'\alpha_{k}}(\mathbf{q}_{k}j_{k}) \right\} \omega_{k}^{-\frac{1}{2}}\exp(\mathrm{i}\mathbf{q}_{k}\cdot\overset{\circ}{\mathbf{r}}_{\kappa}^{\mathbf{0}}), \qquad (3)$$

where N is the number of unit cells in the crystal, the $\mathbf{V}_{\kappa}(\mathbf{q}_{k}j_{k})$ are the amplitudes of the normal modes, $\lambda \equiv \mathring{\mathbf{r}}_{\kappa}^{\mathbf{l}} - \mathring{\mathbf{r}}_{\kappa'}^{\mathbf{0}}$ and \sum_{λ} denotes summation over \mathbf{l} , κ , and κ' , a notation used wherever possible for brevity.

The free energy of the crystal is given by

$$F = F^{(2)} - \frac{1}{\beta} \sum_{\text{red.}} \left(\frac{V}{8\pi^3} \right)^{n_r} \frac{1}{n_r!} \sum_{1,\ldots,n_r} \langle n_r,\ldots,1 | \exp[-\beta(H_0 + \Phi')]_r | 1,\ldots,n_r \rangle, \quad (4)$$

where $F^{(2)}$ is the harmonic contribution, $\beta = 1/kT$, and $|1,2,\ldots,n_r\rangle = A_1^*A_2^*$ $\ldots A_{n_r}^*|0\rangle$ is an eigenstate of the crystal in the harmonic approximation; $\exp[-\beta(H_0+\Phi')]_r$ denotes the operator $\exp[-\beta(H_0+\Phi')]$ expanded in powers of Φ' , Φ' expressed in terms of A_k , A_k^* , and these replaced by $A_k[1-\exp(-\beta\hbar\omega_k)]^{-\frac{1}{2}}$, $A_k^*[1-\exp(-\beta\hbar\omega_k)]^{-\frac{1}{2}}$ respectively. F then consists of a number of terms, each of which is represented by a diagram and $\sum_{\text{red.}}$ refers to the fact that only reduced diagrams with at least one vertex are to be considered. The ones with no vertices correspond to part of the harmonic contribution, which is, of course,

$$F^{(2)} = \Phi^{(0)} + \epsilon_{zp} + \frac{1}{\beta} \sum_{\mathbf{q}j} \ln[1 - \exp(-\beta \hbar \omega_{\mathbf{q}j})].$$
⁽⁵⁾

The lowest order anharmonic contributions correspond to diagrams with two threefold vertices or one fourfold vertex. The latter give the contribution obtained previously in F II,

$$F^{(4)} = \frac{3V^2}{64\pi^6} \sum_{\substack{\mathbf{q}_1 j_1 \\ \mathbf{q}_2 j_2}} B^{(4)}_{\mathbf{1},\mathbf{2},-\mathbf{1},-\mathbf{2}} \coth(\frac{1}{2}\beta\hbar\omega_1) \coth(\frac{1}{2}\beta\hbar\omega_2).$$
(6)

The diagrams to be considered for the former are

For those of type (b) the occurrence of the factor $\Delta_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3}$ at each vertex means that the line joining the vertices must correspond to zero wave vector. Then the *B*-factors involved are $B^{(3)}_{\mathbf{0}j,\mathbf{q}j',\mathbf{r}',\mathbf{q}j'}$ and these are zero, provided that for every lattice vector $\mathbf{r}^1_{\kappa\kappa'}$ there is another $\mathbf{r}^1_{\kappa\kappa'} = -\mathbf{r}^1_{\kappa\kappa'}$. This is true for the sodium chloride type lattice and so diagrams (b) will be ignored. The contribution to *F* from diagrams (a) then proves to be

$$F^{(3)} = \frac{-6}{\hbar} \sum_{\substack{\mathbf{q}_{1}j_{1} \\ \mathbf{q}_{2}j_{2} \\ \mathbf{q}_{3}j_{3}}} \left[\frac{1 - \exp\{-\beta\hbar(\omega_{1} + \omega_{2} + \omega_{3})\}}{\omega_{1} + \omega_{2} + \omega_{3}} + \frac{\exp(-\beta\hbar\omega_{1}) - \exp\{-\beta\hbar(\omega_{2} + \omega_{3})\}}{\omega_{2} + \omega_{3} - \omega_{1}} + \frac{\exp(-\beta\hbar\omega_{2}) - \exp\{-\beta\hbar(\omega_{1} + \omega_{2})\}}{\omega_{3} + \omega_{1} - \omega_{2}} + \frac{\exp(-\beta\hbar\omega_{3}) - \exp\{-\beta\hbar(\omega_{1} + \omega_{2})\}}{\omega_{1} + \omega_{2} - \omega_{3}} \right] \\ \times \frac{(V/8\pi^{3})^{3} |B_{1,2,3}^{(3)}|^{2} \Delta_{\mathbf{q}_{1} + \mathbf{q}_{2} + \mathbf{q}_{3}}}{\{1 - \exp(-\beta\hbar\omega_{1})\}\{1 - \exp(-\beta\hbar\omega_{2})\}\{1 - \exp(-\beta\hbar\omega_{3})\}}.$$
(7)

The carrying out of the double summation involved in $F^{(4)}$ and the triple one in $F^{(3)}$ is not feasible in practice. For the former Fletcher in F II approximated to $B^{(4)}_{1,2,-1,-2}$ so that only a single summation was involved. Without any approximation, however, it may be written in the form

$$F^{(4)} = \frac{N\hbar^2}{64} \sum_{\substack{a_1 a_2 a_3 a_4 \\ \boldsymbol{\lambda}}} \left[\frac{\partial^4 \phi_{\kappa\kappa'}(r)}{\partial a_1 \partial a_2 \partial a_3 \partial a_4} \right]_{\mathbf{r} = \boldsymbol{\lambda}} F_{a_1 a_3}(\boldsymbol{\lambda}) F_{a_2 \boldsymbol{a_4}}(\boldsymbol{\lambda}), \tag{8}$$

where

$$F_{\alpha\alpha'}(\lambda) = \frac{1}{N} \sum_{\mathbf{q}j} \frac{\coth(\frac{1}{2}\beta\hbar\omega_{\mathbf{q}j})}{\omega_{\mathbf{q}j}} \bigg[V_{\kappa\alpha} \exp(\mathrm{i}\mathbf{q}\cdot\lambda) - V_{\kappa'a} \bigg] \bigg[V_{\kappa\alpha'} \exp(-\mathrm{i}\mathbf{q}\lambda) - V_{\kappa'\alpha'} \bigg]. \tag{9}$$

However, no such simplification seems possible in the case of $F^{(3)}$ and it was therefore decided to restrict calculations at present to high temperatures ($\beta\hbar\omega \ll 1$), where approximations could be made aimed at overcoming this problem.

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III. HIGH TEMPERATURE APPROXIMATION

For $\beta \hbar \omega \ll 1$ the series expansion of $\exp(-\beta \hbar \omega)$ may be terminated after a few terms and a high temperature approximation to $F^{(3)}$ obtained. For consistency the same approximation is made to $F^{(2)}$ and $F^{(4)}$. This was first carried out by Maradudin, Flinn, and Coldwell-Horsfall (1961*a*), and in the case of $F^{(2)}$ the result is

$$F^{(2)} = \Phi^{(0)} + \frac{1}{2\beta} \sum_{\mathbf{q}j} \ln(\beta^2 \hbar^2 \omega_{\mathbf{q}j}^2) + \frac{\beta \hbar^2}{24} \sum_{\mathbf{q}j} \omega_{\mathbf{q}j}^2 - \frac{\beta^3 \hbar^4}{2880} \sum_{\mathbf{q}j} \omega_{\mathbf{q}j}^4 + \dots$$
(10)

Now $\omega_{\mathbf{q}i}^2$ are the eigenvalues of the matrices $\mathbf{D}(\mathbf{q})$ with elements

$$D_{aa'}(\mathbf{q}) = \frac{-1}{(m_{\kappa}m_{\kappa'})^{\frac{1}{2}}} \sum_{\mathbf{l}} \left[\frac{\partial^2 \phi_{\kappa\kappa'}(\mathbf{r})}{\partial a \partial a'} \right]_{\mathbf{r}=\boldsymbol{\lambda}} \exp(\mathbf{i}\mathbf{q}\cdot\boldsymbol{\lambda}), \tag{11}$$

and therefore

$$F^{(2)} = \Phi^{(0)} + \frac{3sN}{\beta} \ln(\beta\hbar) + \frac{1}{2\beta} \sum_{\mathbf{q}} \ln|\mathbf{D}(\mathbf{q})| + \frac{\beta\hbar^2}{24} \sum_{\mathbf{q}} \mathrm{Tr}\mathbf{D} - \frac{\beta^3\hbar^4}{2880} \sum_{\mathbf{q}} \mathrm{Tr}(\mathbf{D}^2) + \dots \quad (12)$$

With regard to the quartic contribution, expression (9) becomes at high temperatures

$$F_{\alpha\alpha'}(\boldsymbol{\lambda}) = \frac{2}{\beta\hbar N} \sum_{\mathbf{q}j} \left\{ \frac{1}{\omega_{\mathbf{q}j}^2} + \frac{\beta^2\hbar^2}{12} + \ldots \right\} \left\{ V_{\kappa\alpha} \exp(i\mathbf{q}\cdot\boldsymbol{\lambda}) - V_{\kappa'\alpha} \right\} \left\{ V_{\kappa\alpha'} \exp(-i\mathbf{q}\cdot\boldsymbol{\lambda}) - V_{\kappa'\alpha'} \right\} \dots,$$
(13)

and hence $F^{(4)} = F_1^{(4)} + F_2^{(4)} + \dots$, where

$$F_{1}^{(4)} = \frac{Nk^{2}T^{2}}{4} \frac{v_{a}^{2}}{e^{4}} \sum_{\substack{a_{1},\ldots,a_{4} \\ \lambda}} \left[\frac{\partial^{4}\phi_{\kappa\kappa'}(r)}{\partial a_{1}\ldots\partial a_{4}} \right]_{\mathbf{r}=\lambda} \{f_{a_{1}a_{2}}(\mathbf{0}) - f_{a_{1}a_{2}}(\lambda)\}\{f_{a_{3}a_{4}}(\mathbf{0}) - f_{a_{3}a_{4}}(\lambda)\}$$
(14)

and

$$f_{aa'}(\lambda) = N^{-1} \sum_{\mathbf{q}} \exp(\mathrm{i}\mathbf{q}\cdot\lambda) (\mathbf{C}^{-1})_{aa',\kappa\kappa'}$$

C being the matrix with elements

$$C_{_{\substack{aa'\\\kappa\kappa'}}}=-(m_{\kappa}m_{\kappa'})^{\frac{1}{2}}(v_a/e^2)D_{_{\substack{aa'\\\kappa\kappa'}}}.$$

The volume v_a of the unit cell and charge -e on the electron have been introduced for convenience in the application to sodium chloride later. In obtaining (14) and later results the theorem proved in the appendix has been used. The next term

$$F_{2}^{(4)} = \frac{-N\hbar^{2}}{48} \frac{v_{a}}{e^{2}} \sum_{\substack{\alpha_{1}\alpha_{2}\alpha_{3}\\\lambda}} \left[\frac{\partial^{4}\phi_{\kappa\kappa'}(r)}{\partial\alpha_{1}\partial\alpha_{2}\partial\alpha_{3}^{2}} \right]_{\mathbf{r}=\lambda} \left\{ f_{a_{1}a_{2}}(\mathbf{0}) - f_{a_{1}a_{2}}(\lambda) \right\} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}} \right).$$
(15)

When the cubic contribution $F^{(3)}$ is similarly expanded in powers of β , the leading term is again proportional to β^{-2} . Every term involves the awkward factor $\Delta_{\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3}$ but if the device of Maradudin, Flinn, and Coldwell-Horsfall (1961*a*) of expressing

this as $N^{-1}\sum_{\mathbf{l}} \exp[i(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\cdot \mathbf{\dot{r}_{\kappa\kappa}^{l}}]$, is used, this leading term can be expressed as

$$F_{1}^{(3)} = \frac{Nk^{2}T^{2}}{192} \frac{v_{a}^{3}}{e^{6}} \sum_{\substack{a_{1}a_{2}a_{3}\\a_{1}'a_{2}'a_{3}'}} \sum_{\lambda\lambda'\lambda''} \left[\frac{\partial^{3}\phi_{\kappa\kappa'}(r)}{\partial a_{1}\partial a_{2}\partial a_{3}} \right]_{\mathbf{r}=\lambda} \left[\frac{\partial^{3}\phi_{\kappa'\kappa''}(r)}{\partial a_{1}'\partial a_{2}'\partial a_{3}'} \right]_{\mathbf{r}=\lambda'} \times \prod_{i=1}^{3} \left\{ f_{a_{i}a_{i}'}(\lambda-\lambda'+\lambda'') + f_{a_{i}a_{i}'}(\lambda'') - f_{a_{i}a_{i}'}(\lambda+\lambda'') - f_{a_{i}a_{i}'}(-\lambda'+\lambda'') \right\}.$$
(16)

The next term $F_2^{(3)}$, independent of temperature, vanishes identically.

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IV. Application to Sodium Chloride

As in F I and F II numerical calculations of certain thermodynamic functions by means of the above theory were made for sodium chloride for comparison with experiment, but, of course, many of the expressions below are applicable to other diatomic substances with the sodium chloride structure. For these, if a is the nearest-neighbour separation, $v_a = 2a^3$, s = 2, and the Madelung number $a_{\rm M} = 1.7476$. With the same form of interionic potential as used in F I and F II (see Section I of this paper), the quantities

$$A = 4n(n+1)be^{-2}a^{-n+1};$$
 $B = -4nbe^{-2}a^{-n+1};$ $g = v_a/v_0 = a^3/a_0^3,$

where the suffix zero refers to values at room temperature $T = T_0 = 288^{\circ}$ K, will be defined (note that A and B are functions of a, not a_0 as in F I and F II). The 4th and 5th terms in the expression (12) for $F^{(2)}$ can then be reduced to

$$\frac{\beta\hbar^{2}}{24} \sum_{\mathbf{q}} \operatorname{Tr} \mathbf{D} = \frac{\beta\hbar^{2}N}{16} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}}\right) \frac{e^{2}}{a^{3}} (A + 2B), \qquad (17)$$

$$\frac{-\beta^{3}\hbar^{4}}{2880} \sum_{\mathbf{q}} \operatorname{Tr}(\mathbf{D}^{2}) = \frac{-\beta^{3}\hbar^{4}N}{2880} \sum_{\substack{aa'\\ \boldsymbol{\lambda}}} \frac{1}{m_{\kappa}m_{\kappa'}} \left[\frac{\partial^{2}\phi_{\kappa\kappa'}(r)}{\partial a \,\partial a'}\right]_{\mathbf{r}=\boldsymbol{\lambda}}^{\mathbf{r}}$$

$$= \frac{-\beta^{3}\hbar^{4}Ne^{4}}{3840a^{6}} \left\{ \left[14 \cdot 24\left(\frac{1}{m_{1}^{2}} + \frac{1}{m_{2}^{2}}\right) + \frac{101 \cdot 3}{m_{1}m_{2}}\right] - \frac{16(A - B)}{m_{1}m_{2}} + \left[(A + 2B)^{2}\left(\frac{1}{m_{1}^{2}} + \frac{1}{m_{2}^{2}}\right) + \frac{A^{2} + 2B^{2}}{m_{1}m_{2}}\right] \right\}, \qquad (18)$$

the three parts coming respectively from products of second derivatives of two Coulomb terms, a Coulomb and a repulsive term, and two repulsive terms. In the case of sodium chloride investigated here (18) proves negligible. Putting $a_0 = 2 \cdot 814 \times 10^{-8}$ cm and values of the right order for A and B, namely, $10 \cdot 6$ and $-1 \cdot 05$ respectively, its contribution to the specific heat $C_V/N = -(T/N)(\partial^2 F/\partial T^2)_V$ is $15 \cdot 7 \times 10^{-9}T^{-4}$, while that of the leading term $6NkT \ln(k/kT)$ in $F^{(2)}$ is $6k = 8 \cdot 28 \times 10^{-16}$, i.e. the ratio of the two is about 1:300 at room temperature and decreasing with increasing temperature. Similarly, as regards thermal expansion, its contribution to $N^{-1}(\partial F/\partial V)_T$ is $-1 \cdot 09 \times 10^{14}T^{-3}$, while that of the leading term $\Phi^{(0)}$ in

 $F^{(2)}$ is $1 \cdot 1 \times 10^{10}$. As regards compressibility, its contribution to $(N\kappa_T)^{-1} = (V/N)(\partial^2 F/\partial V^2)_T$ is $-3 \cdot 27 \times 10^{14} T^{-3}$, while that of $\Phi^{(0)}$ is $-2 \cdot 48 \times 10^{11}$. Thus with sufficient accuracy for all purposes the harmonic contribution to the free energy was taken as

$$\frac{F^{(2)}}{N} = -a_{\rm M} \frac{e^2}{a} + 6\phi_{\rm R}(a) - 6kT \ln T + \frac{kT}{2N} \sum_{\bf q} \ln|{\bf D}({\bf q})| + \frac{\hbar^2 e^2}{16ka^3} \left(\frac{1}{m_1} + \frac{1}{m_2}\right) \frac{A + 2B}{T}.$$
 (19)

In $F_1^{(4)}$ for $\lambda = a(1, 0, 0)$ there are four essentially different types of term given by $(a_1a_2a_3a_4) = (xxxx)$, (yyyy), (yyzz), and (xxyy); their contributions in suitable units were found to be 510, -3, -1, and -170 so that terms of the second and third types could be neglected. For $\lambda = a(0, 1, 1)$ there are the same four types of term and their contributions in the same units were found to be 12, -21, 30, and -21, i.e. approximately zero together as well as being individually quite small, so these were all neglected also. Contributions from other λ were smaller still so that it was taken with good accuracy that

$$\frac{F_{1}^{(4)}}{NT^{2}} = \frac{12k^{2}a}{e^{2}} \left[\left\{ \frac{(n+2)(n+3)}{4}A - 24 \right\} \left\{ f_{xx}(\mathbf{0}) - f_{xx}(1,0,0) \right\}^{2} - \left\{ 2(A-B) + (n+2)A - 48 \right\} \left\{ f_{xx}(\mathbf{0}) - f_{xx}(1,0,0) \right\} \left\{ f_{xx}(\mathbf{0}) - f_{xx}(0,1,0) \right\} \right].$$
(20)

The other quartic contribution $F_2^{(4)}$ was evaluated approximately, summing over the six smallest vectors λ , and found to be about one-tenth of $F_1^{(4)}$ at room temperature, the ratio of the two being proportional to $1/T^2$, and it was decided to neglect $F_2^{(4)}$ entirely. A similar analysis of the cubic term $F_1^{(3)}$ showed that only contributions from $\lambda = a(\pm 1, 0, 0), a(0, \pm 1, 0), a(0, 0, \pm 1); \lambda' = \pm \lambda; a_1 = a_2 = a_3 = a'_1 = a'_2 = a'_3$ need be considered and that then λ'' could be restricted to the zero vector and the six given above with sufficient accuracy so that

$$\frac{F_{1}^{(3)}}{NT^{2}} = \frac{4k^{2}a}{e^{2}} \left[\frac{n+2}{4}A - 6 \right]^{2} \left[8 \left\{ f_{xx}(\mathbf{0}) - f_{xx}(1, 0, 0) \right\}^{3} + \left\{ 2f_{xx}(1, 0, 0) - f_{xx}(\mathbf{0}) - f_{xx}(2, 0, 0) \right\}^{3} \right].$$
(21)

It is of interest at this stage to summarize the approximations made.

(i) $\Phi^{(\nu)}$ for $\nu > 4$ have been ignored, as would appear necessary if use of the adiabatic approximation is to remain valid (Born and Huang 1954, pp. 166 ff.) and for consistency with (ii).

(ii) Diagrams with more than two triple or one fourfold vertex have been ignored. This is justified as they should correspond to contributions to F smaller than those retained by a factor $\leq (u/a)^2$, where u is an average ionic displacement.

(iii) Expanding F in inverse powers of the temperature T, this has been assumed high enough to neglect terms of order T^{-3} in $F^{(2)}$ and temperature-independent

terms in $F^{(3)}$, $F^{(4)}$. For $T > 288^{\circ}$ K it is estimated that errors so caused will be < 0.3% for $F^{(2)}$, < 10% for $F^{(4)}$, and less than this for $F^{(3)}$ since $F_2^{(3)}$ vanishes identically. To complete the picture the anharmonic contributions to $(\partial F/\partial V)_T$ varied from 5% of the leading harmonic term at room temperature to 46% at 1000°K, the figures for κ_T were 1.5% and 62%, and those for C_V were 1.5% and 15%.

(iv) In evaluating $F^{(3)}$ and $F^{(4)}$ only a few (smallest) vectors in the summations over λ , λ' , and λ'' were retained, the error caused by this being < 2%.

V. NUMERICAL CALCULATIONS

As in F I and F II it was first necessary to fix the parameters A_0 , B_0 and these were chosen to fit the experimental values $a_0 = 2 \cdot 814 \times 10^{-8}$ cm and $\kappa_T = 4 \cdot 16 \times 10^{-12} \text{ cm}^2/\text{dyne}$ of the lattice constant and isothermal compressibility at $T = T_0 = 288^{\circ}\text{K}$. Thus the equations $(\partial F/\partial V)_T = 0$ and $\kappa_T^{-1} = V(\partial^2 F/\partial V^2)_T$ lead to

$$B_{0} = \frac{-2a_{M}}{3} - \frac{a_{0}kT_{0}}{Ne^{2}} \left(\frac{\mathrm{d}}{\mathrm{d}g} \sum_{\mathbf{q}} \ln|\mathbf{D}(\mathbf{q})|\right)_{0} + \frac{(n+2)\hbar^{2}}{24ka_{0}^{2}} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}}\right) \frac{A_{0} + 2B_{0}}{T_{0}} - \frac{2a_{0}}{Ne^{2}} \left(\frac{\mathrm{d}}{\mathrm{d}g}(F^{(3)} + F^{(4)})\right)_{0},$$
(22)

$$A_{0}-2B_{0} = \frac{12a_{0}^{4}}{e^{2}\kappa_{T}} + \frac{8a_{M}}{3} - \frac{3a_{0}kT_{0}}{Ne^{2}} \left(\frac{\mathrm{d}^{2}}{\mathrm{d}g^{2}}\sum_{\mathbf{q}}\ln|\mathbf{D}(\mathbf{q})|\right)_{0} - \frac{(n+2)(n+5)\hbar^{2}}{24ka_{0}^{2}} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}}\right) \frac{A_{0}+2B_{0}}{T_{0}} - \frac{6a_{0}}{Ne^{2}} \left(\frac{\mathrm{d}^{2}}{\mathrm{d}g^{2}}(F^{(3)} + F^{(4)})\right)_{0}.$$
(23)

TABLE 1 COMPARISON OF CALCULATED VALUES OF A_0 , B_0 , and n

Author	A_{0}	B_0	n
Kellermann (1940)	10.18	-1.165	7.738
Fletcher (1959)	10.68	-1.048	9.188
Fletcher (1961)	$10 \cdot 40$	-1.063	8.779
Present work	10.45	$-1 \cdot 052$	$8 \cdot 933$

Using Kellermann's (1940) values of A_0 and B_0 first to evaluate the right-hand sides of (22) and (23), an iterative process sufficed to solve these equations after two iterations. ($\sum_{\mathbf{q}} \ln |\mathbf{D}(\mathbf{q})|$, $F^{(3)}$, $F^{(4)}$ and their derivatives with respect to g were evaluated by computer, summations over \mathbf{q} being carried out over the 48 wave vectors used by Kellermann, associated with suitable weighting factors as in F I and F II.) The values obtained for A_0 , B_0 , and the repulsive index n are shown in Table 1 in comparison with those of Kellermann (1940) and of Fletcher using the harmonic approximation (F I) and including $F^{(4)}$ (F II) (to show the influence of the cubic term $F^{(3)}$). With these values of A_0 and B_0 , the free energy of the



Fig. 1.—Variation of anharmonic free energy $F_a = F^{(3)} + F^{(4)}$ and its derivatives dF_a/dg , d^2F_a/dg^2 with relative volume $g = V/V_0$ for sodium chloride (CGS units).



Fig. 2.—Expansion of sodium chloride. ——Present work; ---harmonic model (F I); .—. with quartic anharmonicity (F II). Experimental values: \bigcirc Eucken and Dannöhl (1934); \triangle Walther, Haschkowsky, and Strelkow (1937); \bigcirc Fischmeister (1956).

crystal and its first and second derivatives with respect to g were evaluated for g = 0.98(0.01)1.13. The dependence of the anharmonic contribution and its derivatives on volume is shown in Figure 1.

To determine the thermal expansion coefficient the equation $(\partial F/\partial g)_T = 0$ was solved for T as a function of g. The equation may be written

$$\frac{T}{N}\frac{\mathrm{d}}{\mathrm{d}g}\sum_{\mathbf{q}}\ln|\mathbf{D}(\mathbf{q})| = -\frac{(2\alpha_{\mathrm{M}}+3B)e^2}{3a_0\,kg^{4/3}} + \frac{(n+2)\hbar^2e^2}{24a_0^3\,k^2g^2} \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{A+2B}{T} - \frac{2}{Nk}\frac{\mathrm{d}}{\mathrm{d}g}(F^{(3)} + F^{(4)}),$$
(24)

and it was solved iteratively for each value of g. The results are compared with experiment in Figure 2.



 \odot Hunter and Siegel (1942); \triangle Durand (1936).

As in F I and F II the isothermal compressibility and specific heat at constant volume were also calculated and compared with experiment. However, in F I and F II the theoretical variation of volume with temperature was so at variance with experiment that it was felt necessary to use experimental thermal expansion results to relate the calculated free energy to T before evaluating κ_T and C_V . Their agreement with experiment could then be regarded only as partial support of the theory. In the present work this seemed unnecessary and F(V) was converted to F(T)where necessary by means of the (V,T) curve given by the theory itself. The expressions evaluated were

$$\begin{aligned} \frac{1}{\kappa_{T}} &= \frac{(3A - 6B - 8a_{M})e^{2}}{36a_{0}^{4}g^{4/3}} + \frac{gkT}{4Na_{0}^{3}}\frac{\mathrm{d}^{2}}{\mathrm{d}g^{2}}\sum_{\mathbf{q}}\ln|\mathbf{D}(\mathbf{q})| \\ &+ \frac{(n+2)(n+5)\hbar^{2}e^{2}}{288ka_{0}^{6}g^{(n+5)/3}} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}}\right) \frac{A + 2B}{T} + \frac{g}{2Na_{0}^{3}}\frac{\mathrm{d}^{2}}{\mathrm{d}g^{2}} \left(F^{(3)} + F^{(4)}\right), \end{aligned}$$
(25)

$$C_{V} = 6Nk - \frac{N\hbar^{2}e^{2}}{8 \cdot a_{0}^{3} \gamma} \left(\frac{1}{m_{1}} + \frac{1}{m_{2}}\right) \frac{A + 2B}{I^{2}} - \frac{2}{T} (F^{(3)} + F^{(4)}).$$
⁽²⁶⁾

The results are compared with experiment and with the results of previous calculations in Figures 3 and 5. For reasons explained later it was also decided to calculate the adiabatic compressibility and specific heat at constant pressure and these are



Fig. 4.—Adiabatic compressibility of sodium chloride. Experimental values: ○ Hunter and Siegel (1942); △ Stepanov and Eidus (1956); ⊡ Durand (1936).



compared with experiment in Figures 4 and 6. The expressions evaluated were

$$\begin{aligned} \kappa_{s} &= \kappa_{T} C_{V} / C_{P}, \end{aligned} \tag{27} \\ C_{P} &= -T [\partial^{2} F / \partial T^{2} + (\partial^{2} F / \partial T \partial V) (\partial V / \partial T)_{P}] \\ &= 6Nk - \frac{N \hbar^{2} e^{2}}{8k a_{0}^{3} g} \Big(\frac{1}{m_{1}} + \frac{1}{m_{2}} \Big) \frac{A + 2B}{T^{2}} - \frac{2}{T} (F^{(3)} + F^{(4)}) \\ &+ \Big[\frac{N a_{M} e^{2}}{3 a_{0} g^{1/3}} + \frac{N B e^{2}}{2 a_{0} g^{1/3}} - \frac{N(n + 2) \hbar^{2} e^{2}}{24 k a_{0}^{3} g} \Big(\frac{1}{m_{1}} + \frac{1}{m_{2}} \Big) \frac{A + 2B}{T} + g \frac{d}{dg} (F^{(3)} + F^{(4)}) \Big] \frac{1}{g} \frac{dg}{dT}. \end{aligned}$$
(28)

VI. DISCUSSION OF RESULTS

Figure 2 shows that quite good agreement with experiment has been obtained in the case of thermal expansion. In the harmonic approximation (F I) the model expanded far too rapidly and became unstable for $T \gtrsim 750^{\circ}$ K, well below the actual melting point $T_{\rm M}$. Inclusion of cubic and quartic anharmonic terms has removed both of these discrepancies, but now the theoretical curve, which is very nearly linear, falls below the experimental results above 800° K $\sim 0.8T_{\rm M}$. According to Fischmeister (1956), this cannot be due to the presence of Schottky defects, since there is no difference between macroscopic (dilatometer) and microscopic (X-ray) measurements, nor to Frenkel defects, which do not have any effect on volume. Two recent calculations of the thermal expansion of sodium chloride may be mentioned here. Mitskevich (1962), who allowed for the deformation of the ions



Fig. 6.—Specific heat at constant pressure for sodium chloride.
 — Present work; - - - with omission of T² terms in F.
 Experimental values: ○ Magnus (1913); △ Roth and Bertram (1929); □ Kelley (1934).

in a very detailed way, obtained very good agreement with experiment but did not carry his calculations above 300°K. Verma and Dayal (1963) have carried out a harmonic calculation very similar to FI but with an exponential repulsive term in the interparticle potential. Again the harmonic model expands too rapidly, more and more so as $T \to T_{\rm M}$, but it does not become unstable until $T \sim T_{\rm M}$. (Their criticism of FI and FII, that in summations over the reciprocal lattice all points were equally weighted, is unjustified; both there and in the present work all points have been suitably weighted, e.g. by the factor $\Delta K(\mathbf{k})$ in (26) of FI.) It would appear that, at least at high temperatures, a rigid-ion model of an ionic solid is unlikely to be satisfactory as far as the equation of state is concerned, whether anharmonicity is taken into account or not. So far the equation of state of a non rigid-ion model does not seem to have been considered, except by Mitskevich (1962).

In the case of compressibility, Figure 3 shows that agreement with experiment for κ_T is also considerably better than with the harmonic model although still not satisfactory for $T \gtrsim 0.8T_{\rm M}$. Verma and Dayal's (1963) results with the harmonic, exponential law model are similar to those in F I and the use of a rigid-ion model may again be questioned. The derivation of "experimental" results for κ_T from measurements of κ_S is unfortunately subject to considerable possibility of error since the correction term a^2VT/C_P involves the square of a. Although different experimental (V,T) curves for sodium chloride agree quite well, the corresponding values for α differ considerably, especially at high temperatures, giving very different values for κ_T . For this reason it would seem preferable to calculate κ_S ; this has been done and compared with experiment in Figure 4. Agreement is not good but it may be pointed out that even the "experimental" values of κ_S are deduced from actual measurements of elastic constants, of which c_{12} is very uncertain, there being large differences between the values reported by different workers. From the mathematical point of view it may be pointed out that the sudden increase in the calculated values of κ_T , and κ_S above 950°K, which seems unlikely physically, can be attributed to the sudden decrease in d² F_a/dg^2 , as shown in Figure 1.

In the case of the specific heat at constant volume, Figure 5 shows that inclusion of the cubic anharmonic terms has gone some way to restoring the good agreement with experiment obtained with the harmonic model and lost on inclusion of the quartic terms only. Once again, however, it seems unsatisfactory to compare theory with "experimental" results for C_V that have been obtained from measurements of C_P by applying a correction $\alpha^2 V T / \kappa_T$ depending on the square of the thermal expansion coefficient (and an uncertain κ_T). Direct comparison with C_P is possible since a theoretical expression can be obtained, which depends explicitly on a only linearly. The result is shown in Figure 6 and shows good agreement with experiment to a considerably higher temperature than for C_{ν} . From a mathematical point of view a major cause of the discrepancies between theory and experiment at high temperatures seems to be the T^2 terms $F_1^{(4)}$ and $F_1^{(3)}$. Their effect can be studied most easily in the case of C_V and C_P , which are not affected by the other anharmonic, temperature-independent term $F_{2}^{(4)}$. Their omission thus leaves a harmonic model for the specific heats, and the dashed curve in Figure 6 shows that excellent agreement is then obtained for C_P with the experimental results of Roth and Bertram (1929), while the curve for C_{ν} of the harmonic model F I also agrees with Hunter and Siegel's (1942) results. Now the coefficients of $F_1^{(4)}$, $F_1^{(3)}$ have opposite signs and so, unless they are known with considerably accuracy, it would seem preferable to omit these terms, leaving a harmonic model for C_{ν} , C_{P} but an anharmonic one for a, κ_{τ} , and κ_{s} .

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Appendix

Theorem. If λ_i, \mathbf{u}_i are the eigenvalues and normalized eigenvectors of a non-singular matrix **A**, then, for any positive or negative integer n (or zero)

$$\sum_{i} \lambda_i^n \mathbf{u}_i \mathbf{u}_i^T = \mathbf{A}^n.$$

Thus consider the matrix $\mathbf{B} = \sum_{i} \mathbf{u}_{i} \mathbf{u}_{i}^{T}$. Then

$$\mathbf{B}\mathbf{u}_{j} = \sum_{i} \mathbf{u}_{i} \mathbf{u}_{i}^{T} \mathbf{u}_{j} = \sum_{i} \mathbf{u}_{i} \delta_{ij} = \mathbf{u}_{j}$$

for all \mathbf{u}_i so that $\mathbf{B} = \mathbf{I}$.

Also $\mathbf{A}\mathbf{u}_i = \lambda_i \mathbf{u}_i$ and, by multiplying this equation by $(1/\lambda_i)\mathbf{A}^{-1}$, $\mathbf{A}^{-1}\mathbf{u}_i = \lambda_i^{-1}\mathbf{u}_i$ and hence, for any positive or negative integer n

$$\mathbf{A}^n \mathbf{u}_i = \lambda_i^n \mathbf{u}_i.$$

But then

$$\mathbf{A}^n = \mathbf{A}^n \mathbf{B} = \sum_i \mathbf{A}^n \mathbf{u}_i \mathbf{u}_i^T = \sum_i \lambda_i^n \mathbf{u}_i \mathbf{u}_i^T,$$

which proves the theorem.

