are used. The Zil'berman result for oscillation in the conductivity $\tilde{\sigma}_{11}$ matches the experimental values for conditions somewhat intermediate between the two and three band models, but the Zil'berman result for oscillation in the thermoelectric coefficient $\tilde{\epsilon}_{11}''$ favors the two-band model. The right order of magnitude for oscillation in the Nernst-Ettinghausen effect ϵ_{12}'' is obtained from the oscillations in the density of states.

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Equation of State of Alkali Halides (NaCl)*

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The equation of state of NaCl is given using the Kellermann model of NaCl as well as a modified model making use of a repulsive potential energy of the Born-Mayer form Ae^{-Br}. The Grüneisen parameter $\gamma_i=-d\ln\nu_i/d\ln V$, where ν_i is the normal mode frequency and V is the volume, is derived by the development of a perturbation method in the volume. This is then used where needed to calculate all thermodynamic quantities of interest using an IBM 7090. A spectrum of 11 454 frequencies and γ_i's are used in finding these quantities rather than the approximations made previously of utilizing the elastic constants and the moment expansion $\gamma(S)=\sum_i\gamma_i\nu_i^s/\sum_i\nu_i^s=-(1/S)d\ln\langle\nu_i^s\rangle/d\ln V$, where $\langle\nu_i^s\rangle$ is the Sth moment of the frequency distribution. To check previous work by Barron and Blackman $\gamma(0)$, $\gamma(2)$, $\gamma(1)$, and $\gamma(-3)$ were calculated where $\gamma(0)=\gamma_\infty$, the high-temperature γ, and $\gamma(-3)=\gamma_0$, the low temperature γ. Fair agreement is found for $\gamma(-3)$, whereas the deviation in $\gamma(2)$ is high.

I. INTRODUCTION

THE equation of state of a real crystal such as NaCl has been considered by several investigators. Barron[1,2] and Blackman[3] using a Kellermann model[4] of NaCl and assuming equal masses for simplicity have recently obtained values for the low-temperature ($T\rightarrow 0$) Grüneisen[5] parameter γ_0. Barron was able to find a high-temperature ($T\gtrsim\Theta$, where Θ is the Debye temperature) Grüneisen parameter γ_∞ by defining a weighted γ in terms of the moments of the frequency spectrum with $\langle\nu_j^s\rangle$ the Sth moment

$$\gamma(S)=\sum_i\gamma_i\nu_i^s/\sum_i\nu_i^s=-\left(\frac{1}{S}\right)d\ln\langle\nu_j^s\rangle/d\ln V\,, \quad (1)$$

where

$$\gamma_i=-d\ln\nu_i/d\ln V \quad (2)$$

and ν_i is a normal vibration frequency, V is the volume, and the sum over i here and in all such expressions is to be taken over all normal modes of vibration. He found expressions for $\gamma(2)$ which he maintained should be approximately equal to $\gamma(0)\equiv\gamma_\infty$ and by making use of the elastic constants found a $\gamma_0=\gamma(-3)$. It was found that deviations from Grüneisen's relation should occur at 0.3Θ. Barron then compared his work to Born's[6] and Slater's.[7] Slater's formula, which is derived from a consideration of the elastic constants, is

$$\gamma_s=\tfrac{1}{2}d\ln(\chi V^{-1/3})/d\ln V\,, \quad (3)$$

where χ is the compressibility and V is the volume. This formula was derived under two assumptions, one being that Poisson's ratio is constant and the other that there is a characteristic temperature given by Debye's expression for an isotropic continuum,

$$\Theta=\frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{1}{C_l^3}+\frac{2}{C_t^3}\right)^{-1/3}, \quad (4)$$

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† Much of the material included in this paper was used in a Ph.D. dissertation at New York University (1963).

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[5] E. Grüneisen, in *Handbuch der Physik*, edited by A. Geiger and Karl Scheel (Julius Springer–Verlag, Berlin, 1926), Vol. 10, p. 22.

[6] M. Born, *Atomtheorie des Festen Zustandes* (B.G. Teubner, Leipzig, 1923).

[7] J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), Chap. XIV.

TABLE I. Grüneisen γ's for NaCl found by various investigators. n is the exponent in the repulsive potential energy.

	Barron			Blackman		Born	Arenstein *et al.*		Yates and Panter
n	7.6	8	8.3	7	8.55	8	7.6	8.3	Experimental
γ_0		1		1.15	1.46	1.47	1.002	1.071	
$\gamma(2)$	1.60	1.67	1.72	1.50	1.76		1.379	1.498	
γ_∞						2.2	1.480	1.595	1.59

where N is the total number of particles and C_l and C_t are the longitudinal and transverse elastic wave velocities, respectively. Slater's formula gives us directly $\gamma_s=\frac{1}{6}(n+6)$, where n is the exponent in the repulsive potential energy. The γ's found by these various investigators are given in Table I.

In our study of NaCl we use both the Kellermann model of NaCl and a modified Kellermann model. The Kellermann model is modified by assuming that the repulsive term is the Born-Mayer potential Ae^{-Br}, where A and B are constants. It is summed over nearest neighbors and put into the form used by Kellermann. This potential was picked because of its use in various problems using interatomic potentials. However, since we do not have as yet good values for A and B we consider them independent of r and vary them so as to give comparisons with experimental results. Using perturbation theory[8] we are able to derive a formula for the γ_i's. Thus, we calculated with an IBM 7090 all physical quantities of interest using the following formulas, substituting the derived γ_i where needed. For pressure as a function of volume and temperature [from $p=-(\partial F/\partial V)T$, where F is the free energy]

$$P=-\frac{dU_0}{dV}+\frac{1}{V}\sum_i \gamma_i E_i, \tag{5}$$

or

$$P=-\frac{dU_0'}{dV}+\frac{1}{V}\sum_i \gamma_i E_i', \tag{6}$$

where U_0 is the static lattice energy $-\alpha e^2/r+6Ae^{-Br}$; α is Madelung's constant; U_0' is the static lattice energy plus the zero-point energy $\sum_i(\frac{1}{2}h\nu_i)$;

$$E_i=\{h\nu_i/2+h\nu_i/[\exp(h\nu_i/kT)-1]\}$$

and

$$E_i'=h\nu_i/[\exp(h\nu_i/kT)-1].$$

We can express Eqs. (5) and (6) in the Mie-Grüneisen form if we define two temperature- and volume-dependent γ's, $\gamma(V,T)=\sum_i\gamma_iE_i/\sum_iE_i$ and $\gamma'(V,T)=\sum_i\gamma_iE_i'/\sum_iE_i'$. For compressibility we have

$$\frac{1}{\chi}=V\frac{d^2U_0}{dV^2}-\frac{1}{V}\sum_i\gamma_iE_i+\frac{1}{V}\sum_i\frac{\partial}{\partial V}(\gamma_iE_i). \tag{7}$$

For thermal expansion we have

$$\beta=\frac{\chi}{V}\sum_i\gamma_i\partial E_i/\partial T \tag{8}$$

and we compare this to the Grüneisen relation

$$\beta=\frac{\chi\gamma''}{V}\sum_i\partial E_i/\partial T. \tag{9}$$

Since the specific heat at constant volume C_V was needed for the thermal expansion it has been evaluated at different temperatures and volumes. We have

$$C_V=8.6368\times10^{16}\sum_i\partial E_i/\partial T \tag{10}$$

(where the factor before the summation sign gives us the units cal/g-mole-°C).

Comparisons with experimental results are made where possible. Since many of the thermodynamic quantities are derived from indirect measurements (for example, the relationships used to relate the actual measurements to compressibility or to specific heat at constant volume make use of the thermal expansion and Grüneisen's relation), they cannot be exactly correct for low temperature ($T\leq0.3\Theta$).

II. KELLERMANN AND MODIFIED KELLERMANN MODEL OF NaCl

Kellermann assumed in his model that the energy per cell ϕ could be written in the form

$$\phi=-\alpha e^2/r+c/r^n, \tag{11}$$

where r is the interionic separation and c and n are some constants which are eliminated in the coupling coefficients by applying the equilibrium and compressibility conditions. The coupling coefficients are split into Coulomb and repulsive terms. For the Coulomb terms we have

$$\begin{bmatrix} kk' \\ xy \end{bmatrix}^c=\frac{e^2}{V_a}G\begin{pmatrix}\boldsymbol{\sigma} \\ xy\end{pmatrix}, \tag{12}$$

where $\boldsymbol{\sigma}$ is the wave vector; x and $y=(x,y,z)$; k is the basis index and is 1 and 2 for the NaCl crystal; G is a dimensionless quantity; e is the charge of the electron; $V_a=2r_0^3$, is the volume of a unit cell, where r_0 is the nearest neighbor equilibrium distance. For the repulsive

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[8] E. M. Arase and R. D. Hatcher, J. Chem. Phys. 33, 1704 (1960).

terms we have

$$\begin{bmatrix} kk \\ xy \end{bmatrix}^R = -\frac{e^2}{V_a}(R+2S)\delta_{xy},$$

$$\begin{bmatrix} kk' \\ xy \end{bmatrix}^R = \frac{e^2}{V_a}[R\cos 2\pi\sigma_x r_0 + S(\cos 2\pi\sigma_y r_0 + \cos 2\pi\sigma_z r_0)]\delta_{xy}, \tag{13}$$

where R and S are given by

$$R = 12r_0^4/\chi_0 e^2 + \tfrac{4}{3}\alpha,$$
$$S = -\tfrac{2}{3}\alpha, \tag{14}$$

and χ_0 is the isothermal compressibility.

It can be seen from Eq. (14) that the only quantities in the coupling coefficients varying with a change in volume are r_0 and the isothermal compressibility χ_0.

For our purposes in investigating the equation of state and then finding the compressibility from it we do not eliminate the parameters in the repulsive term. For the Born-Mayer potential energy form we have

$$\phi = -\alpha e^2/r + Ae^{-Br}, \tag{15}$$

where A and B are adjustable parameters. Putting the repulsive term in the Kellermann bracket form, we have

$$\begin{bmatrix} kk' \\ xy \end{bmatrix}^R = \sum_l (\phi_{kk'}{}^l)_{xy} \exp(2\pi i \boldsymbol{\sigma}\mathbf{r}_{kk'}{}^l). \tag{16}$$

When $k' \neq k$ the sum extends over 6 nearest neighbors given by vectors $r_0(\pm 1, 0, 0)$, $r_0(0, \pm 1, 0)$ and $r_0(0, 0, \pm 1)$. Thus, we find

$$\begin{bmatrix} 1 & 2 \\ x & x \end{bmatrix}^R \frac{V_a}{e^2} = \frac{4BAr_0^2 e^{-Br_0}}{e^2} \times [Br_0 \cos\pi q_x - (\cos\pi q_y + \cos\pi q_z)], \tag{17}$$

$$\begin{bmatrix} 1 & 1 \\ x & x \end{bmatrix}^R \frac{V_a}{e^2} = \frac{4BAr_0^2 e^{-Br_0}}{e^2}[2 - Br_0].$$

It may be seen from Eq. (17) that the only quantity varying with volume is r_0.

III. PERTURBED FREQUENCIES

Letting[9]

$$a_{ij}{}^0 = -\frac{1}{(m_k m_{k'})^{1/2}} \begin{bmatrix} k & k' \\ x & y \end{bmatrix},$$

we write the equation for the ionic displacements for NaCl as

$$(\omega_m{}^0)^2 U_{im}{}^0 - \sum_j a_{ij}{}^0 U_{jm}{}^0 = 0, \tag{18}$$

where the eigenfrequency ω^0, the eigenvector U^0, and the coupling coefficients $a_{ij}{}^0$ are the unperturbed quantities.

To eliminate the volume from the Coulomb terms and thus to have only the repulsive terms depending on the volume, we write (where V_0 is the volume of a basic cell)

$$b_{ij}{}^0 = (V_0/e^2) a_{ij}{}^0, \tag{19a}$$

and

$$\lambda_m{}^0 = (V_0/e^2)(\omega_m{}^0)^2. \tag{19b}$$

Rewriting Eq. (18), we have

$$\lambda_m{}^0 U_{im}{}^0 - \sum_j b_{ij}{}^0 U_{jm}{}^0 = 0. \tag{20}$$

To find the eigenfrequencies at a new volume we must express the new eigenfrequencies in terms of the unperturbed frequencies and eigenvectors at the initial volume. This is possible since the eigenfrequencies belonging to the same wave vector change but little with small changes in volume. In addition, this method may be extended to include second neighbor repulsive forces as a perturbation. Thus, we have

$$\lambda_m' U_{im}' - \sum_j b_{ij}' U_{jm}' = 0, \tag{21}$$

where $\lambda_m' = V'(\omega_m')^2/e^2$; V' is the new volume and ω_m' is the new frequency.

Since the perturbed quantities vary but little from the unperturbed ones, we may expand the perturbed eigenvalues, eigenvectors, and coupling coefficients in a series

$$U_m' = U_m{}^0 + \epsilon U_m{}^1 + \epsilon^2 U_m{}^2 + \cdots,$$
$$\lambda_m' = \lambda_m{}^0 + \epsilon\lambda_m{}^1 + \epsilon^2\lambda_m{}^2 + \cdots, \tag{22}$$
$$b_{ij}' = b_{ij}{}^0 + \epsilon b_{ij}{}^1 + \cdots.$$

The zero-order terms result in Eq. (20) while the first-order equation is

$$\lambda_m{}^0 U_{im}{}^1 + \lambda_m{}^1 U_{im}{}^0 - \sum_j (b_{ij}{}^0 U_{jm}{}^1 + b_{ij}{}^1 U_{jm}{}^0) = 0. \tag{23}$$

In the case where $\lambda_m{}^0$ is nondegenerate, even though some other eigenvalues belonging to the complete set of eigenvectors may be degenerate, we may expand the perturbed eigenvectors in terms of the unperturbed set such that

$$U_{im}{}^1 = \sum_k g_k{}^m U_{ik}{}^0, \tag{24}$$

where $g_k{}^m$ is a constant, and substituting Eq. (24) into Eq. (23) we obtain

$$\sum_k \lambda_m{}^0 g_k{}^m U_{ik}{}^0 + \lambda_m{}^1 U_{im}{}^0 = \sum_j b_{ij}{}^0 \sum_k g_k{}^m U_{jk}{}^0 + \sum_j b_{ij}{}^1 U_{jm}{}^0. \tag{25}$$

In the term $\sum_j b_{ij}{}^0 \sum_k g_k{}^m U_{jk}{}^0$ the summations may be interchanged and since from Eq. (20) $\sum_i b_{ij}{}^0 U_{jm}{}^0 = \lambda_m{}^0 U_{im}{}^0$ we obtain after substituting in Eq. (25)

$$\sum_k \lambda_m{}^0 g_k{}^m U_{ik}{}^0 + \lambda_m{}^1 U_{im}{}^0 = \sum_k g_k{}^m \lambda_k{}^0 U_{ik}{}^0 + \sum_j b_{ij}{}^1 U_{jm}{}^0. \tag{26}$$

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[9] We introduce for convenience new notation $i=1, 2, \cdots, 6$ standing for $(Kx) = 1x, 2x, 1y, 2y, 1z, 2z$.

Multiplying Eq. (26) by $U_{ni}{}^0$, since the vectors $U_{ni}{}^0$ are real, and summing over i, making use of the orthonormality of the unperturbed eigenvectors $U_{ni}{}^0$ we obtain

$$\lambda_m{}^1\delta_{mn}+(\lambda_m{}^0-\lambda_n{}^0)g_n{}^m=\sum_{i,j}U_{ni}{}^0b_{ij}{}^1U_{jm}{}^0=B_{nm}'. \quad (27)$$

If $m=n$ we obtain

$$\lambda_m{}^1=\sum_{i,j}U_{mi}{}^0b_{ij}{}^1U_{jm}{}^0=B_{mm}'. \quad (28)$$

Thus, we may write for the perturbed circular frequencies,

$$\omega'^2=\frac{V_0}{V}\omega_0{}^2+\frac{e^2}{V}B_{mm}'. \quad (29)$$

Equations (28) and (29) are valid for degenerate eigenvalues only if $B_{nm}'=0$. In this event the perturbed eigenvalues are again degenerate. For the NaCl crystal the degeneracy is due to the symmetry of the crystal itself. The degeneracy would not be removed by going to higher order terms in the perturbation series. Hence, the above equations may also be used to find the perturbed frequencies for the degenerate case.

For the Kellermann model of NaCl we have

$$B_{mm}'=\Delta R\left\{\frac{1}{m_1}[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]\right.$$
$$+\frac{1}{m_2}[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]$$
$$+\frac{2}{(m_1m_2)^{1/2}}(U_{1m}{}^0U_{2m}{}^0\cos\pi q_x+U_{3m}{}^0U_{4m}{}^0\cos\pi q_y$$
$$\left.+U_{6m}{}^0U_{5m}{}^0\cos\pi q_z)\right\}, \quad (30)$$

where ΔR is the change in R as defined in Eq. (14):

$$\Delta R=12r^4/e^2\chi-12r_0{}^4/e^2\chi_0, \quad (31)$$

where r and χ are the new lattice constant and compressibility, respectively.

For the modified Kellermann model of NaCl we have

$$B_{mm}'=b_{11}{}^1\left\{(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2\right.$$
$$\left.+\frac{m_1}{m_2}[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]\right\}$$
$$+2[b_{12}{}^1U_{1m}{}^0U_{2m}{}^0+b_{34}{}^1U_{3m}{}^0U_{4m}{}^0$$
$$+b_{56}{}^1U_{5m}{}^0U_{6m}{}^0], \quad (32)$$

where

$$b_{11}{}^1=\frac{1}{m_1}[R(r)+2S(r)-R(r_0)-2S(r_0)], \quad (33)$$

$$R(r_0)=4B^2Ar_0{}^3e^{-Br_0}/e^2,$$
$$S(r_0)=-4BAr_0{}^2e^{-Br_0}/e^2, \quad (34)$$

and

$$b_{12}{}^1=-\frac{1}{(m_1m_2)^{1/2}}[(R(r)-R(r_0))\cos\pi q_x$$
$$+(S(r)-S(r_0))(\cos\pi q_y+\cos\pi q_z)], \quad (35)$$

with similar terms for $b_{34}{}^1$ and $b_{56}{}^1$.

IV. THE Υ_i'S

For the Kellermann model we obtain

$$\omega^2=\frac{r_0{}^3\omega_0{}^2}{r^3}+\frac{e^2}{2r^3}\left[\frac{12r^4}{e^2\chi}-\frac{12r_0{}^4}{e^3\chi_0}\right]\Gamma, \quad (36)$$

where

$$\Gamma=\frac{1}{m_1}[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]$$
$$+\frac{1}{m_2}[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]$$
$$+\frac{1}{(m_1m_2)^{1/2}}(U_{1m}{}^0U_{2m}{}^0\cos\pi q_x+U_{3m}{}^0U_{4m}{}^0\cos\pi q_y$$
$$+U_{5m}{}^0U_{6m}{}^0\cos\pi q_z). \quad (37)$$

We have then from Eq. (2)

$$\gamma_i=\frac{-V}{2\omega_i{}^2}\frac{dr}{dV}\frac{d\omega_i{}^2}{dr}. \quad (38)$$

and

$$\frac{d\omega_i{}^2}{dr}=\frac{-3r_0\omega_0{}^2}{r^4}-\frac{3e^2}{2r^4}\left[\frac{12r^4}{e^2\chi}-\frac{12r_0{}^4}{e^2\chi_0}\right]\Gamma$$
$$+\frac{e^2}{2r^3}\left[\frac{48r^3}{e^2\chi}-\frac{12r^4}{e^2\chi^2}\left(\frac{\partial\chi}{\partial r}\right)_T\right]\Gamma. \quad (39)$$

Thus, we write for γ_{ik} at $r=r_0$

$$\gamma_{ik}=\frac{1}{2}\left\{1-\frac{2}{\omega_0{}^2}\left[\frac{4r_0}{\chi_0}-\frac{r_0{}^2}{\chi_0{}^2}\left(\frac{\partial\chi}{\partial r}\right)_T\right]\Gamma\right\}. \quad (40)$$

This formula for γ_{ik} can be used in an equation of state and a self-consistent technique developed to get the compressibility, the thermal expansion, and the other quantities of physical interest at different temperatures.

It is of interest to compare this γ_{ik} to Slater's γ_s. Thus, γ_s can be written as

$$\gamma_s=\frac{1}{2}\frac{d\ln\chi V^{-1/3}}{d\ln V}=\frac{1}{2}\left\{1-\frac{\chi_0}{3r_0}\left[\frac{4r_0}{\chi_0}-\frac{r_0{}^2}{\chi_0{}^2}\left(\frac{\partial\chi}{\partial r}\right)_T\right]\right\}. \quad (41)$$

If we assume that γ_s equals γ_i at some particular frequencies, the condition for equality is

$$2\Gamma/\omega_0{}^2=\chi_0/3r_0. \quad (42)$$

To see that this assumption is approximately correct we pick a particular direction in the crystal such that $q_x=q_y=q_z=0$ and for simplicity we assume equal masses taking the average mass in the equation for Γ. This gives $\Gamma=1/\bar{m}$ and $\omega_0^2=6r_0/\langle m\chi_0\rangle$. Using $r_0=2.8\times10^{-8}$ cm, $\chi_0=4.0\times10^{-12}$ cm²/dyn, and $\bar{m}=4.8\times10^{-24}$ g, we have $\omega_0=3.0\times10^{13}$ cycles/sec which is close to the resonance frequency. Thus, γ_{ik} at the same resonance frequency 3.0×10^{13} cycles/sec should be equal to γ_s.

The γ_i's for the modified Kellermann model (γ_{im}) have been found for a total of 11 454 frequencies obtained for the first-Brillouin zone and it is to be expected that the γ_{im} should be approximately equal to the γ_{ik} for the Kellermann model so that the γ_{im} for 3×10^{13} cycles/sec should be approximately equal to γ_s. We find for $A=1.474\times10^{-9}$ erg, $B=3.048\times10^8$ cm^{-1}, and $R=2.814\times10^{-8}$ cm that γ_i equals 2.44 and this is sufficiently close to γ_s which equals 2.33 for $n=8$ to justify our assumption that $\gamma_{ik}=\gamma_s$ at the resonance frequency.

For the modified Kellermann model we obtain

$$\omega^2=\frac{r_0^3\omega_0^2}{r^3}+\frac{e^2}{2r^3}B_{mm'} \tag{43}$$

(where $B_{mm'}$ is defined in Sec. C). We find for γ_{im}

$$\gamma_{im}=\frac{1}{2}\left[1-\frac{e^2}{6r_0^2\omega_0^2}\frac{dB_{mm'}}{dr}\right], \tag{44}$$

where

$$\begin{aligned}\frac{dB_{mm'}}{dr}=R'\Bigg\{&\frac{1}{m_1}[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]\\&+\frac{1}{m_2}[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]\\&-\frac{2}{(m_1m_2)^{1/2}}(\cos\pi q_xU_{1m}{}^0U_{2m}{}^0+\cos\pi q_yU_{3m}{}^0U_{4m}{}^0\\&\qquad+\cos\pi q_zU_{5m}{}^0U_{6m}{}^0)\Bigg\}\\+2S'\Bigg\{&\frac{1}{m_1}[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]\\&+\frac{1}{m_2}[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]\\&-\frac{1}{(m_1m_2)^{1/2}}[(\cos\pi q_y+\cos\pi q_z)U_{1m}{}^0U_{2m}{}^0\\&+(\cos\pi q_x+\cos\pi q_z)U_{3m}{}^0U_{4m}{}^0\\&\qquad+(\cos\pi q_x+\cos\pi q_y)U_{5m}{}^0U_{6m}{}^0]\Bigg\},\end{aligned} \tag{45}$$

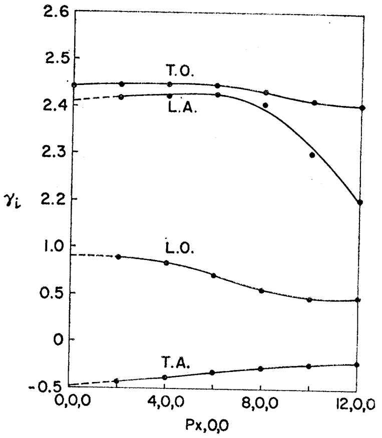

FIG. 1. Grüneisen parameter γ_i versus $P_{x,0,0}$ for a lattice separation of 2.814 $\times10^{-8}$ cm and with $A=1.474\times10^{-9}$ erg; $B=3.048\times10^8$ cm^{-1}. Four curves corresponding to the six branches of the crystal with the transverse modes being double. Dashed lines indicate extrapolation to the (0,0,0) values.

with

$$R'=(4B^2A/e^2)(3r_0^2-Br_0^3)e^{-Br_0},$$
$$S'=-(4BA/e^2)(2r_0-Br_0^2)e^{-Br_0}. \tag{46}$$

V. CHOICE OF PARAMETERS

The calculations depend on the choice for parameters A and B in the repulsive term, and it is found that many different sets of A and B will give good results for compressibility, for example, but poor results for the resonance frequency. We chose, therefore, several sets of A and B and compared results. For one set we took the values found in Born and Huang[10] with a nearest neighbor distance of 2.814×10^{-8} cm and $A=1.474\times10^{-9}$ erg, $B=3.048\times10^8$ cm^{-1} which give good results for the cohesive energy and compressibility. For another set we took $A=2.550\times10^{-9}$ erg and $B=3.291\times10^8$ cm^{-1} which were chosen to give a better value of the resonance frequency as well as the compressibility. Other sets of A and B are chosen, for example, $B=3.198\times10$ cm^{-1} while $A=2.247\times10^{-9}$, 2.147×10^{-9}, and 2.100×10^{-9} to see how much the γ's vary when B is held fixed and A changes. If we assume the equilibrium condition holds, then we can relate our choices of B in the Born-Mayer potential with the exponent n in the r^{-n} repulsive potential energy used by Kellermann. For example, $B=3.048\times10^{-8}$ cm^{-1} gives $n=7.6$ and $B=3.291\times10^8$ cm^{-1} gives $n=8.3$, where, in general, $n=Br_0-1$.

VI. VALUES OF THE Γ'S

In our calculations we use the frequencies and the γ's for 73 choices of the wave vector $\boldsymbol{\sigma}$ totalling 11 454 frequencies and γ_i's when weighted by their multiplicities. This was done for different lattice separations and parameters A and B. Since the program used did not give the correct values for the (0,0,0) position we have found them by extrapolation as in Fig. 1 where we plotted γ_i against a particular direction in the

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[10] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), Chap. I.

crystal; namely, the [$Px00$] direction, where Px varies from 12 to 0. We see that the γ_i's vary over a wide range and, as Blackman[11] and Barron[12] have found, from about $-\frac{1}{2}$ to about 3. Thus, Grüneisen's[13] contention that they are constant is far from true.

Using the variation of the resonance frequency with nearest neighbor distance (see Table II) we have calculated $\gamma_i = -(r/3\omega)(\Delta\omega/\Delta r)$, where $\Delta\omega$ is the change of frequency for two different nearest neighbor distances and Δr is the change in the nearest neighbor distance.

This was done for the values $r_0 = 2.8100$, 2.8140, and 2.8200 giving two values for $\Delta\omega/\Delta r$ which we averaged to find $\langle\Delta\omega\rangle_{\text{av}}/\Delta r = -7.21$ and thus $\gamma_i = 2.44$ which agrees exactly with the value found using the equation for γ_i at the peak frequency. Since we also calculated $\partial\gamma/\partial r$ for each frequency this value was checked the same way. The average value of $\Delta\gamma/\Delta r$ was 0.560×10^9 cm^{-1} while the equation gives 0.5581×10^9 cm^{-1}, a deviation of less than 0.4%.

TABLE II. Resonance frequency and γ_i.

r_0 (10^{-8} cm)	$A = 1.474\times10^{-9}$ erg; $B = 3.048\times10^8$ cm^{-1} ω (10^{13} cps)	γ_i	$A = 2.550\times10^{-9}$ erg; $B = 3.291\times10^8$ cm^{-1} ω (10^{13} cps)	γ_i
2.7886	2.9656	2.3112	3.1094	2.4606
2.7893	2.9604	2.3146	3.1036	2.4643
2.7944	2.9229	2.3395	3.0617	2.4917
2.8000	2.8819	2.368	3.0160	2.5228
2.8036	2.856	2.386	2.9867	2.5433
2.8088	2.8177	2.414	2.9445	2.5738
2.8100	2.8090	2.4206	2.9348	2.5810
2.8140	2.780	2.4427	2.9025	2.6054
2.8200	2.7367	2.4768	2.8542	2.6432

TABLE III. $\gamma(S)$ for different lattice separations r_0; γ' for different lattice separations r_0 and for different temperatures T. $A = 2.550\times10^{-9}$ erg, $B = 3.291\times10^8$ cm^{-1}.

r_0 (10^{-8} cm)	2.7886	2.7893	2.8036	2.8088	2.8140	2.8200
$\gamma(0)\equiv\gamma_\infty$	1.5188	1.5207	1.5628	1.5789	1.5954	1.6151
$\gamma(2)$	1.4831	1.4838	1.4916	1.4949	1.4976	1.5010
$\gamma(1)$	1.5305	1.5319	1.5566	1.5664	1.5759	1.5874
$\gamma(-3)$	1.0712		1.1776		1.2534	1.2981
T (°K)						
320	1.5106	1.5129	1.5615	1.5800	1.5990	1.6215
280	1.5086	1.5110	1.5606	1.5795	1.5990	1.6218
200	1.5006	1.5031	1.5562	1.5763	1.5970	1.6214
120	1.4714	1.4738	1.5359	1.5587	1.5830	1.6111
80	1.4131	1.4156	1.4892	1.5154	1.5442	1.5770
60	1.3376	1.3400	1.4242	1.4534	1.4866	1.5237
40	1.1737	1.1748	1.2749	1.3072	1.3480	1.3914
30	1.0382		1.1454		1.2232	1.2696
20	0.89283		1.0025		1.0819	1.1293
15	0.84503		0.95803		1.0396	1.0870
11	0.83122		0.95342		1.0394	1.0898
10			0.95881		1.0472	

The values for the various temperature dependent γ's can be found in Table I and in Tables III–VI. It is of interest to compare these values with those obtained theoretically by Barron[14] and Blackman[15] and with the experimental γ'' values found by Yates and Panter.[16] We notice a difference of up to 7% between $\gamma(2)$ and $\gamma(0)\equiv\gamma_\infty$ for the various sets of A and B in the above tables. Using Eq. (1) given the second moment for NaCl, (assuming equal mass M for the ions)

$$\langle\nu_i^2\rangle = 1.74\left(\frac{e^2}{12\pi^2a^3M}\right)(n-1)\left(\frac{a}{r_1}\right)^{n+2},$$

where e is the charge of the electron, a is the nearest neighbor distance at equilibrium, r_1 is the new distance, and n is the exponent of the repulsive potential energy, Barron[17] found that $\gamma(2) = \frac{1}{6}(n+2)$. A high-temperature experimental value quoted by Born[18] and Yates and Panter[19] which is 1.59 is in extremely good agreement with our γ_∞ for the $n = 8.3$ case. Apparently the correction for the volume dependence of γ_i and ω_i was not taken into account in the calculations of γ_0 by Barron and Blackman. In Table I we listed our values of γ_0 taking the lattice separation to be 2.7886×10^{-8} cm at 0°K. At a room temperature lattice separation of 2.8140×10^{-8} cm we have for $A = 2.550\times10^{-9}$ erg, $B = 3.291\times10^8$ cm^{-1} that $\gamma_0 = 1.253$; and for $A = 1.474\times10^{-9}$ erg, $B = 3.048\times10^8$ cm^{-1} that $\gamma_0 = 1.166$, giving better agreement with Blackman's results. The experimental values of Yates and Panter[19] are given from 30 to 270°K. Their results are uncertain below 60° and at 60°K they differ from our values by about 19%. In computing their values from other thermal data such as specific heat and compressibility no correction was made considering the new expansion data and they expect an accuracy for their data at low temperatures to within 15%. The deviations in the low-temperature values may be partially due to the above lack of corrections as well as the experimental uncertainties near and below 60°K. Slightly better comparisons can be expected by varying our A and B values. Yates and Panter's contention that the predicted numerical values of low-temperature γ be revised does not seem to be justified since their accuracy below 60°K is not high. As seen in Tables III and IV γ' and γ'' approach a minimum at about 11°K and then rise to the $\gamma_0\equiv\gamma(-3)$ value. This was not predicted from previous

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[11] M. Blackman, Ref. 3.

[12] T. H. K. Barron, Refs. 1 and 2.

[13] E. Grüneisen, Ref. 5.

[14] T. H. K. Barron, Refs. 1 and 2.

[15] M. Blackman, Ref. 3.

[16] B. Yates and C. H. Panter, Proc. Phys. Soc. (London) **80**, 373 (1962).

[17] T. H. K. Barron, Refs. 1 and 2.

[18] M. Born, Ref. 6.

[19] B. Yates and C. H. Panter, Ref. 16.

TABLE IV. γ'' for different lattice separations r_0 and for different temperatures T; γ'' calculated from thermal data by Yates and Panter at 293°K volume. $A=2.550\times10^{-9}$ erg, $B=3.291\times10^{8}$ cm^{-1}.

r_0 (10^{-8} cm) T (°K)	2.7886	2.7893	2.8036	2.8088	2.8140	2.8200	V_{293}
750					1.5962		
500					1.5971		
400					1.5979		
280	1.5203	1.5224	1.5663	1.5830	1.6002	1.6206	
270							1.59
240	1.5206	1.5227	1.5673	1.5842	1.6017	1.6223	1.57
200	1.5209	1.5230	1.5686	1.5860	1.6038	1.6249	1.54
160	1.5206	1.5228	1.5703	1.5883	1.6069	1.6287	1.53
120	1.5171	1.5194	1.5709	1.5902	1.6102	1.6338	1.51
100	1.5106	1.5130	1.5681	1.5887	1.6101	1.6352	1.49
80	1.4934	1.4960	1.5572	1.5799	1.6036	1.6312	1.42
60	1.4451	1.4481	1.5200	1.5462	1.5740	1.6060	1.22
50	1.3923		1.4755		1.5354	1.5709	1.06
40	1.3005	1.3037	1.3942	1.4264	1.4616	1.5016	0.82
30	1.1485		1.2526		1.3280	1.3729	
20	0.94846		1.0566		1.1353	1.1824	
15	0.86683		0.97559		1.0544	1.1014	
11	0.83150		0.94446		1.0252	1.0731	
10					1.0258		

analyses[20] although their experimental values of γ'' for LiF seem to indicate a minimum at 120°K. That it occurs at a high temperature for this crystal is probably due to the high value of the Debye temperature in this case. From our data we see verification of Barron's result that $\gamma'(V,T)$ and $\gamma''(V,T)$ should decrease significantly below $0.3\Theta\approx80$°K. In table V we have $\gamma(V,T)$ data tabulated and we find that a minimum occurs at about 50°K. It is about here that the zero-point energy contribution to the thermal expansion becomes significant and the values smoothly tend to the limit $\gamma(1)$ at 0°K. In Fig. 2 we have γ'' versus r_0 at a constant temperature of 280°K where we see that γ'' varies fairly linearly with r_0. Several γ's were calculated for very high temperatures and we find that γ reaches a maximum at about 300°K and then decreases slightly tending to its $\gamma_\infty\equiv\gamma(0)$ value. It must be remembered, however, that the change in volume and anharmonic terms at higher temperatures may make a considerable difference here.

TABLE V. γ for different lattice separations r_0 and for different temperatures T. $A=2.550\times10^{-9}$ ergs; $B=3.291\times10^{8}$ cm^{-1}.

r_0 (10^{-8} cm) T (°K)	2.7886	2.8036	2.8100	2.8140	2.8200
280			1.5793	1.5906	
200			1.5759	1.5868	
120	1.5139	1.5506	1.5682	1.5780	1.5946
80	1.5148	1.5471	1.5627	1.5712	1.5859
60	1.5180	1.5474	1.5617	1.5694	1.5826
50	1.5208	1.5489		1.5698	1.5824
40	1.5242	1.5513	1.5644	1.5713	1.5833
30	1.5276	1.5540		1.5735	1.5852
20	1.5298	1.5560		1.5753	1.5869
15	1.5303	1.5564		1.5757	1.5873
11	1.5304	1.5566		1.5758	1.5874
10		1.5566			1.5874
0	1.5305	1.5566	1.5684	1.5759	1.5874

TABLE VI. $\gamma(S)$ for different A's and B's ($r_0=2.814\times10^{-8}$ cm).

B (10^8 cm^{-1})	3.048	3.198	3.198	3.198
A (10^{-9} erg)	1.474	2.100	2.147	2.247
$\gamma(1)$	1.457	1.5214	1.5096	1.4876
$\gamma(2)$	1.379	1.4522	1.4523	1.4522
$\gamma(0)$	1.480	1.5327	1.5090	1.4642
$\gamma(-3)$	1.166	1.1699	1.1050	0.97425

VII. COMPRESSIBILITY AND THERMAL EXPANSION

In Table VII the compressibility for various volumes and temperatures is compared to experimental values,[21] the maximum deviation being about 4% at low temperatures. As noted before, approximate calculations were used in relating the experimental information to

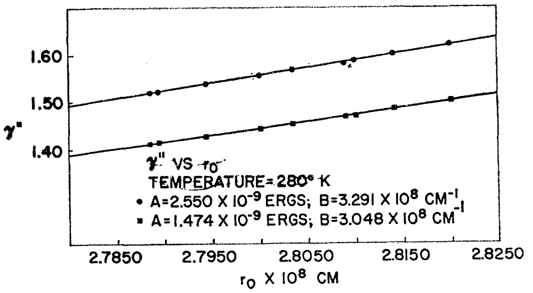

FIG. 2. Grüneisen parameter γ'' versus r_0 at a constant temperature of 280°K for two sets of parameters A and B.

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[20] Recent experimental and theoretical work on MnO at low temperatures by S. Ganesan, Phil. Mag. **7**, 197 (1962), indicates a rise in the values of the Grüneisen parameter. He shows that $\gamma(2)<\gamma(-3)$ and it is certainly possible as our work indicates that $\gamma(0)>\gamma(-3)>\gamma(2)$.

[21] W. C. Overton and R. T. Swim, Phys. Rev. **84**, 758 (1951).

TABLE VII. Compressibility (in units of 10^{-12} cm^2/dyn) for different temperatures keeping lattice separation r_0 constant and compressibility for different lattice separations keeping temperature constant at 280°K.

$r_0=2.800\times10^{-8}$ cm $A=2.550\times10^{-9}$ erg $B=3.291\times10^{8}$ cm^{-1}			$A=2.550\times10^{-9}$ erg $B=3.291\times10^{8}$ cm^{-1}	$A=1.474\times10^{-9}$ erg $B=3.048\times10^{8}$ cm^{-1}	Experimental compressibility Constant entropy	 Constant temperature
T (°K)	χ	r_0 (10^{-8} cm)	χ_T	χ_T	χ_S	χ_T
320	3.9630	2.7886	3.74	3.80	3.89	3.89
280	3.9625	2.7893	3.76	3.81	3.90	3.91
240	3.9619	2.7944	3.85	3.90	3.95	4.01
200	3.9613	2.8000	3.96	4.00	3.97	4.06
160	3.9606	2.8036	4.04	4.07	4.01	4.13
120	3.9601	2.8088	4.15	4.18	4.05	4.20
100	3.9598	2.8100	4.17	4.20		
80	3.9595	2.8140	4.26	4.28	4.07	4.27
60	3.9593	2.8200	4.39	4.40		
40	3.9591					

the compressibility values so that little more error would be introduced in using our theoretical values of the compressibility to find the thermal expansion. In Table VIII the thermal expansion at various temperatures and lattice separations is given using Eq. (8). Since experimental values of β are found at atmospheric pressure the values of the thermal expansion in our table must be read at the correct lattice separation for a particular temperature in order to compare results.

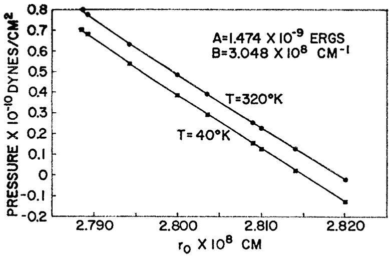

FIG. 3. Pressure versus lattice separation r_0 at two constant temperatures.

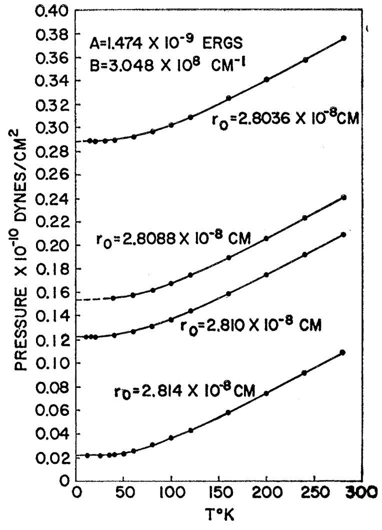

FIG. 4. Pressure versus temperature at various constant lattice separations.

Approximate calculations of the lattice separation for a particular temperature using an empirical formula

TABLE VIII. Thermal coefficient of expansion β (10^{-5} deg^{-1}). $A=2.550\times10^{-9}$ erg, $B=3.291\times10^{8}$ cm^{-1}.

r_0 (10^{-8} cm) T (°K)	2.7886	2.7893	2.8036	2.8088	2.8140	2.8200	$\left(\frac{1}{V_{293}}\right)\frac{dv}{dT}$
320		10.430	11.377	11.749	12.138	12.607	
280		10.291	11.235	11.606	11.993	12.460	
270							11.75
240		10.084	11.023	11.391	11.776	12.241	11.39
200		9.7553	10.685	11.051	11.432	11.893	10.77
160		9.1925	10.106	10.465	10.840	11.293	9.96
120	8.0928	8.1331	9.0086	9.3535	9.7137	10.1498	8.69
100	7.2022	7.2406	8.0757	8.4056	8.7504	9.1686	7.64
80	5.8973	5.9323	6.6922	6.9940	7.3100	7.6946	6.03
60	4.0238	4.0518	4.6627	4.9081	5.1664	5.4828	3.73
50	2.8816		3.3933		3.8021	4.0610	2.40
40	1.71209	1.7274	2.0590	2.1961	2.3415	2.5226	1.17
30	0.72889		0.89817		1.0393	1.1313	0.32
20	0.17116		0.21482		0.25176	0.27613	
15	0.059067		0.074419		0.08734	0.095848	
11	0.019796		0.025058		0.02944	0.032310	
10					0.021285		

TABLE IX. Specific heat at constant volume $C_v = 8.6368 \times 10^{16} \Sigma_i \partial E_i / \partial T$. $A = 2.550 \times 10^{-9}$ erg, $B = 3.291 \times 10^{8}$ cm^{-1}.

r_0 (10^{-8} cm) T (°K)	2.7886	2.8036	2.8140	2.8200	Experimental values
280		11.2768	11.2970		
200		10.7127	10.7494		
120	8.9045	9.0218	9.1016	9.1469	
100	7.9593	8.1024	8.2004	8.2565	8.180
80	6.5926	6.7618	6.8792	6.9469	6.820
60	4.6486	4.8270	4.9537	5.0279	4.848
50	3.4553	3.6188	3.7372	3.8073	3.609
40	2.1980	2.3240	2.4177	2.4742	2.297
30	1.0596	1.1283	1.1811	1.2137	1.109
20	0.30130	0.31992	0.33467	0.34395	0.3124
15	0.11377	0.12004	0.12503	0.12818	
11	0.039750	0.04175	0.043342	0.044345	
10		0.03017	0.031318		0.03024
5					0.003561

such as $\rho = \rho_0[1 - (1.12 \times 10^{-4} T) - 5 \times 10^{-8} T^2]$ g/cm^3, where ρ_0 is the density, gives at zero deg $r_0 = 2.7886 \times 10^{-8}$ cm while at room temperatures the lattice separation is 2.8140×10^{-8} cm. Thus, using the approximate values of 2.7893×10^{-8} cm for the lattice separation at 60°K our results for β compared to Yates and Panter differ by less than 9% while at 240°K and a lattice separation of 2.8088×10^{-8} cm they differ by about 0%. In Table IX the values of C_v are given for various lattice separations along with some experimental values.[22]

IX. EQUATION OF STATE CURVES

In Figs. 3 and 4 we have plotted pressure against lattice separation and temperature. In the pressure, lattice separation curve we note that the pressure goes to zero at certain lattice separations indicating the equilibrium position. In the pressure, temperature curve we note that the slope of the curves approach zero and this is as it should be since $(\partial P/\partial T)_v = \beta/\chi$ where β, the thermal expansion, goes to zero at 0°K.

X. CONCLUSIONS

It is seen that perturbation theory leads to a formula for γ_i which is found to be very accurate and of wide applicability. Fairly good results for the physical properties of NaCl are found with $A = 2.550 \times 10^{-9}$ erg and $B = 3.291 \times 10^{8}$ cm^{-1} corresponding to an $n = 8.3$ for the Kellermann model. Better results could have been achieved with a better model, one in which next-nearest neighbor interactions were used in calculating the repulsive terms and polarization effects were taken into account. Experimental information below 60°K may indicate the predicted minimum and subsequent increase of values to the $\gamma(-3)$ value as calculated. The connection found between γ_i and Slater's γ also seems to indicate the validity and usefulness of the perturbation method. It is not clear what effects will occur by introducing anharmonic terms in the potential energy. However, for low temperatures ($T < \Theta$) we should not expect these terms to be very significant.

The contention that $\gamma(2) \approx \gamma(0)$ is not a good approximation makes it necessary to calculate $\gamma(0)$ directly from the spectrum of the γ_i's unless a good interpolation method using $\gamma(s)$ presents itself. In fact, for NaCl $\gamma(0) > \gamma(2) > \gamma(4)$ while $\gamma(2) > \gamma(-3)$ so that in this case we do not have a good interpolation method if $\gamma(0)$ is unknown.

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[22] Private communication to E. Arase from J. A. Morrison, National Research Council, Canada.