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Equation of State of Certain Ideal Lattices[*]

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The equation of state of a face-centered cubic lattice and a two-dimensional diatomic square lattice considering nearest and next nearest neighbors is given as well as a preliminary investigation of a simple cubic lattice. 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 and used to determine the thermal expansion coefficient for these crystals assuming different forms of the interatomic potential energy. Negative thermal expansion at low temperatures is found for the two-dimensional model when the ratio of the next nearest neighbor interaction is negative and for the simple cubic lattice with positive ratio of next nearest to nearest neighbor interaction.

I. THE EQUATION OF STATE OF CERTAIN IDEAL CRYSTALS

A. Introduction

RECENT experimental work on the thermal expansion of metals at low temperatures[1] has indicated that these materials do not follow very closely the predictions of the Mie-Grüneisen[2] relationship (Mie-Grüneisen to be abbreviated M-G) which is $\beta=X\gamma C_v/V$, where β is the thermal expansion, X is the compressibility, γ is a constant called the Grüneisen parameter, C_v is the specific heat at constant volume, and V is the volume. Indications are that since deviations from the M-G relation occur in the range 20° to 90° that the lattice vibrations rather than the electron gas causes the effect. Barron[3] using lattice dynamics analyzed the face-centered cubic lattice since many metals and nonmetallic solids have this structure. He specifically considered this lattice to be a model of a solid such as argon. Several temperature-dependent M-G parameters were introduced which had been previously assumed to be constant and in fact equal. Barron found the variation in the γ's became most pronounced below about 0.3Θ ($\Theta=h\nu_D/k$, where h is Planck's constant, k is Boltzmann's constant, and ν_D is the Debye frequency) and, in fact, found a spread from the very high temperature value of γ to the low temperature value to be about 0.3. Blackman[4] has recently investigated certain two-dimensional crystals with equal masses and a three-dimensional crystal showing the possibility of negative thermal expansion.

Grüneisen,[5] by considering the vibration of one atom while all others remained fixed, derived temperature-independent expressions for γ assuming the following potential energy for an ion in a crystal: $U=-\lambda r^{-m}+\zeta r^{-n}$ (where λ, ζ, m, and n are constants characteristic of the crystal). He found $\gamma=\frac{1}{2}V(dr/dv)r^{-1}\,(m+n+3)$, so that for an l-dimensional crystal we have $(m+n+3)/2l$. When using a repulsive potential energy of the Born-Mayer form Ae^{-Br}, where A and B are constants characteristic of the crystal, we find

$$\gamma=\frac{1}{2l}\left[\frac{Br^2-(m+1)(m+2)}{Br-(m+1)}\right].$$

In the present study we obtained the various γ's and their temperature dependence for a two-dimensional diatomic lattice and the face-centered cubic lattice considering nearest and next nearest neighbors. We also give the thermal expansion for these lattices comparing our results to the thermal expansion found using the M-G relation. The specific heat at constant volume is also computed. Computations were performed on an IBM 7090 digital computer.

In a following paper the equation of state of a real crystal such as NaCl will be given and compared to work on NaCl done by Barron[6] and Blackman[7] and others.

B. The Equation of State

From statistical mechanics the complete Helmholtz free energy of a crystal is given by Born and Huang.[8]

$$F=U_0+\tfrac{1}{2}\textstyle\sum_i h\nu_i+kT\sum_i\ln[1-\exp(-h\nu_i/kT)]\,,\qquad(1)$$

where h is Planck's constant, k is Boltzmann's constant, T is the absolute temperature, and where U_0 is the static lattice energy and ν_i is a normal mode frequency, U_0 and ν_i being dependent only on the volume. Using the ex-

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[1] D. Bijl and H. Pullan, Phil. Mag. **45**, 290 (1954); Physica **21** 285, (1955).

[2] E. Grüneisen, in *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer, Berlin, 1926), Vol. 43, p. 1083.

[3] T. H. K. Barron, Phil. Mag. **46**, 720 (1955); Ann. Phys. (N. Y.) **1**, 77 (1957).

[4] M. Blackman, Phil. Mag. **3**, 831 (1958); Proc. Phys. Soc. (London) **B74**, 17 (1959).

[5] E. Grüneisen, Ref. 2.

[6] T. H. K. Barron, Ref. 3.

[7] M. Blackman, Proc. Phys. Soc. (London) **B70**, 827 (1957).

[8] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. 2.

pression for the pressure P from thermodynamics, $P=-(\partial F/\partial V)T$, where V is the volume, we have

$$P=-\frac{dU_0}{dV}-\tfrac{1}{2}\sum_i\frac{hd\nu_i}{dV}-\sum_i\left(\frac{1}{\exp[h\nu_i/kT]-1}\right)\frac{hd\nu_i}{dV}. \tag{2}$$

M-G introduced the dimensionless quantities

$$\gamma_i=-d\ln\nu_i/d\ln V=-(V/\nu_i)d\nu_i/dV,$$

and so we can write

$$P=-\frac{dU_0}{dV}+\frac{1}{V}\sum_i\frac{\gamma_i h\nu_i}{2}+\frac{1}{V}\sum_i\left(\frac{\gamma_i h\nu_i}{\exp[h\nu_i/kT]-1}\right). \tag{3}$$

The zero-point energy term $\frac{1}{2}\sum_i h\nu_i$ is combined either with the static energy term or with the thermal energy. We let

$$E_i=\frac{h\nu_i}{2}+\left(\frac{h\nu_i}{\exp(h\nu_i/kT)-1}\right)$$

$$\text{and}\quad E_i'=\left(\frac{h\nu_i}{\exp[h\nu_i/kT]-1}\right),$$

so Eq. (3) can be written as

$$\text{(a)}\quad P=\frac{-dU_0}{dV}+\frac{1}{V}\sum_i\gamma_iE_i,$$
$$\text{(b)}\quad P=\frac{-dU_0'}{dV}+\frac{1}{V}\sum_i\gamma_iE_i', \tag{4}$$

where $U_0'=U_0+\sum_i h\nu_{i/2}$.

If γ_i is considered to be constant, we have the M-G equation of state,

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

$$P=\frac{-dU_0'}{dV}+\frac{\gamma'}{V}\sum_i E_i'. \tag{5b}$$

For the moment we assume $\gamma'=\gamma$ which will be true if the γ_i are all equal.

From either Eq. (5a) or (5b) the M-G relation is derived:

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{\beta}{\chi}=\frac{\sum_i\gamma_i\partial E_i/\partial T}{V}$$
$$=\frac{\gamma''\sum_i\partial E_i/\partial T}{V}=\frac{\gamma''C_v}{V}, \tag{6}$$

which introduces a new parameter γ'' which should be the same as the γ' and the γ if we again assume that the γ_i are all equal.

If we are to use the equation of state in the form given by M-G then we see that if the γ_i's, which depend only on the volume as seen by their definition, are not all equal, the γ's must be temperature- and volume-dependent and defined by

$$\gamma(T,V)=\sum_i\gamma_iE_i/\sum_iE_i,$$
$$\gamma'(T,V)=\sum_i\gamma_iE_i'/\sum_iE_i', \tag{7}$$
$$\gamma''(T,V)=\sum_i\gamma_i\partial E_i/\partial T/\sum_i\partial E_i/\partial T.$$

The γ's are no longer equal except at special temperatures. Thus at very high and at very low temperatures γ' and γ'' should be equal. At very high temperatures we have $\gamma_\infty=\gamma'=\gamma''=\sum_i\gamma_{i/3N}$. At very low temperatures γ' and γ'' both go to the same indeterminate form but γ can be seen to approach $\sum_i\gamma_i\nu_i/\sum_i\nu_i$.

Barron,[9] introduced a set of weighted averages of the γ_i:

$$\gamma(S)=\sum_{i=1}^{3N}\gamma_i\nu_i^s/\sum_{i=1}^{3N}\nu_i^s=-\frac{1}{S}\frac{d\ln\mu_s}{d\ln V}, \tag{8}$$

where the μ_s are moments of the frequency distribution and have often been used in the theory of specific heats. Thus, $\gamma(0)=\sum_i\gamma_i/3N=\gamma_\infty$, where N is the total number of atoms for a monatomic crystal ,and $\gamma(1)=\sum_i\gamma_i\nu_i/\sum_i\nu_i$, where $\gamma(1)$ is just the value of γ at zero degrees. For very low temperatures γ_0 was defined by Barron[9] as $-d\ln\theta_0/d\ln V$, where θ_0 is the Debye characteristic temperature in the limit as $T\rightarrow 0$:

$$\theta_0=\frac{h}{k}\left(\frac{9N}{4\pi}\right)^{1/3}V^{-1/3}(C_l^{-3}+2C_t^{-3})^{-1/3}, \tag{9}$$

where N is the total number of particles; V is the volume; C_l is the longitudinal velocity and C_t the transverse velocity of the elastic waves. We can write for γ_i the expression $\gamma_i=-d\ln(V^{-1/3}C_i(\theta,\phi))/d\ln V$ (where C_i is the velocity of an elastic wave in a particular direction determined by the angles θ and ϕ in spherical coordinates), since λ the wavelength is directly proportional to $V^{1/3}$ and, thus, $\nu_i\sim V^{-1/3}C_i(\theta,\phi)$. For a crystal of volume V, the number of frequencies within the range $\nu,\nu+d\nu$ is equal to V times the element of wave vector space K, or

$$VK^2dKd\omega=V\nu^2d\nu d\omega/C_i^3(\theta,\phi), \tag{10}$$

and $d\omega=\sin\theta d\theta d\phi$, so that we have

$$\gamma_0=\int\int(\sum_i\gamma_iC_i^{-3})d\omega\bigg/\int\int(\sum_i C_i^{-3})d\omega. \tag{11}$$

Comparing Eq. (8) with Eq. (11), we have

$$\gamma_0=\sum_i\gamma_i\nu_i^{-3}/\sum_i\nu_i^{-3} \tag{12}$$

which is $\gamma(-3)$. By similar reasoning we have for a two-dimensional crystal

$$\theta_0=\frac{h}{k}\left(\frac{4N}{\pi}\right)^{1/2}V^{-1/2}[C_l^{-2}+C_t^{-2}]^{-1/2}, \tag{13}$$

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[9] T. H. K. Barron, Ref. 3.

where V is now the area of the crystal, and

$$\gamma_i = -d\ln(V^{-1/2}C_i(\theta))/d\ln V, \tag{14}$$

since now $\lambda \sim V^{1/2}$ and $\nu_i \sim V^{-1/2}C_i(\theta)$, where $C_i(\theta)$ is the velocity of the elastic waves in two dimensions, its direction dependent on only one angle.

$$\gamma_0 = \int \Big(\sum_{i=1}^{2} \gamma_i C_i(\theta)^{-2}\Big)d\omega \Big/ \int \Big(\sum_{i=1}^{2} C_i(\theta)^{-2}\Big)d\omega, \tag{15}$$

where $d\omega = d\theta$. Thus, comparing Eq. (8) with Eq. (15), we have

$$\gamma_0 = \gamma(-2). \tag{16}$$

Since measurements of the thermal expansion have usually been made at high temperature, the usual experimental Grüneisen γ may be identified with γ_∞.

C. Derivation of γ_i

Expanding the potential energy $f(r^2)$ between ions, we have

$$f(r^2) = f(r_0^2) + (2\boldsymbol{\varepsilon}_n\cdot\mathbf{s}_n + \mathbf{s}_n\cdot\mathbf{s}_n/r_0)r_0 f' + 2(\boldsymbol{\varepsilon}_n\cdot\mathbf{s}_n)^2 r_0^2 f'' + \cdots, \tag{17}$$

where $\boldsymbol{\varepsilon}_n = \mathbf{i}\lambda_n + \mathbf{j}\mathbf{u}_n + \mathbf{k}\mathbf{v}_n$ is the unit vector along the position vector of the nth particle relative to the 0th, λ, μ, ν being direction cosines $\mathbf{s}_n = \mathbf{i}h_n + \mathbf{j}l_n + \mathbf{k}m_n$, where $h_n = u_0 - u_n$; $l_n = v_0 - v_n$; $m_n = w_0 - w_n$, the u's, v's and w's being the displacements of the ions from their equilibrium position. The prime indicates the derivative with respect to r^2. The force in the x direction $X_n(r^2)$ is

$$X_n(r^2) = -\frac{\partial f(r^2)}{\partial h_n} = -\left(2\lambda_n + \frac{2h_n}{r_0}\right)r_0 f' - 4(\boldsymbol{\varepsilon}_n\cdot\mathbf{s}_n)\lambda_n r_0^2 f'', \tag{18}$$

where we do not drop f' terms because the lattice is not necessarily in equilibrium. When summing over the particles of the lattice, the terms $-2\lambda_n r_0 f'$, $-2\mu_n r_0 f'$, and $-2\nu_n r_0 f'$ will vanish if the lattice is symmetrical with respect to inversion through the zeroth particle. Considering such monatomic symmetrical lattices, we have

$$\mu\ddot{u}_0 = \textstyle\sum_n X_n(r^2), \tag{19}$$

with similar equations for v and w, where μ is the mass of the ions. Letting $2f' = \alpha_2$ and $4r_0^2 f'' = \alpha_1$, Eq. (19) gives us

$$\mu\ddot{u}_0 = \textstyle\sum_n [\alpha_2(u_n - u_0) + \alpha_1\lambda_n \times[\lambda_n(u_n - u_0) + \mu_n(v_n - v_0) + \nu_n(w_n - w_0)]], \tag{20}$$

with similar equations for v and w.[10]

By substituting a plane-wave solution in the equations of motion of various lattices, for example, the two-dimensional diatomic square lattice or the face-centered cubic lattice, the squares of the frequencies of the normal vibrations are obtained as eigenvalues of the matrix.

$$(\alpha_1 A/2\pi^2\mu) + (\alpha_2 yI/2\pi^2\mu), \tag{21}$$

where I is the unit matrix, μ the mass of the particles, A the matrix for the lattices as given in the Appendix, and y, also given in the Appendix, is the additional term which results because of the inclusion of f' terms.

We have for the frequencies

$$\nu_i^2(=\alpha_1 g_i^2/2\pi^2\mu) + (\alpha_2 y/2\pi^2\mu), \tag{22}$$

where g_i^2 are the eigenvalues of the A matrix. Thus, we have for γ_i

$$\gamma_i = \frac{-V}{\nu_i}\frac{d\nu_i}{dV} = \frac{-V}{2\nu_i^2}\frac{d\nu_i^2}{dV} = \frac{-V}{2\nu_i^2}\frac{dr^2}{dV}\frac{d\nu_i^2}{dr^2}. \tag{23}$$

From Eq. (22),

$$\frac{d\nu_i^2}{dr^2} = \frac{\alpha_1' g_i^2}{2\pi^2\mu} + \frac{\alpha_2' y}{2\pi^2\mu},$$

where the primes indicate derivatives with respect to r^2. Thus, we have

$$\gamma_i = \frac{-V}{2\nu_i^2}\frac{dr^2}{dV}\left[\frac{\alpha_1' g_i^2}{2\pi^2\mu} + \frac{\alpha_2' y}{2\pi^2\mu}\right] = \frac{-V dr^2}{2dV}\left[\frac{\alpha_1'}{\alpha_1} + \frac{\alpha_2' y}{\alpha_1 g_i^2}\right]. \tag{24}$$

In Eq. (24) $\alpha_2 = 0$ since we are letting our lattice expand from one equilibrium position to another. In particular, we have for the face-centered cubic lattice and the two-dimensional diatomic square lattice the following:

$$\text{fcc}\quad \gamma_i = -\tfrac{1}{3}\left[\frac{r^2\alpha_1'}{\alpha_1} + \frac{3 - [\cos\phi_1\cos\phi_2 + \cos\phi_1\cos\phi_3 + \cos\phi_2\cos\phi_3]}{g_i^2}\right] \tag{25}$$

and

$$\text{2-d.d.}\quad \gamma_i = -\tfrac{1}{2}\left[\frac{r^2\alpha_1'}{\alpha_1} + \frac{[2 - \cos\phi_1 - \cos\phi_2]}{4g_i^2}\right], \tag{26}$$

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[10] The form of Eq. (20) is of the same form our equations would have taken had we dropped f' but had included angular forces; the equivalent equation being $\mu\ddot{u}_0 = \Sigma\{\alpha'(u_n - u_0) + (\alpha - \alpha')\lambda_n \times [\lambda_n(u_n - u_0) + \cdots]\}$ so that the angular Hookes' law constant $\alpha' \rightarrow \alpha_2$ and $\alpha - \alpha' \rightarrow \alpha - \alpha_2 \rightarrow \alpha_1$.

TABLE I. Face-centered cubic Lattice ($\delta=0.0$; $R_0=3.72\times10^{-8}$ cm; $X=9.15\times10^{-11}$ cm^2/dyn).

					Thermal expansion coefficient (1/°C)	
$\gamma(S)$	°K	γ	γ'	γ''	$\left(\beta=\frac{X}{V}\sum_i \gamma_i \frac{E_i}{T}\right)\times10^4$	$\left(\beta=\frac{X(3.0)}{V}\sum_i \frac{\partial E_i}{\partial T}\right)\times10^4$
$\gamma(4)=3.217$	85	3.1023	2.837	2.864	2.05	2.14
$\gamma(2)=3.149$	80	3.1027	2.831	2.855	1.71	1.80
$\gamma(1)=3.104$	75	3.1030	2.824	2.846	1.40	1.48
$\gamma(0)=3.051$	70	3.1033	2.819	2.837	1.13	1.19
$\gamma(-3)=2.855$	65	3.1035	2.813	2.828	0.887	0.941
$\gamma_\infty-\gamma_0=0.196$	60	3.1037	2.809	2.820	0.681	0.724
	55	3.1038	2.806	2.813	0.509	0.543
	50	3.1039	2.803	2.807	0.370	0.395
	45	3.1040	2.802	2.804	0.261	0.279
	40	3.1040	2.802	2.801	0.178	0.190

TABLE II. Face-centered cubic lattice ($\delta=0.1$; $R_0=3.72\times10^{-8}$ cm; $X=9.15\times10^{-11}$ cm^2/dyn).

					Thermal expansion coefficient 1/°C	
$\gamma(S)$	°K	γ	γ'	γ''	$\left(\beta=\frac{X}{V}\sum_i \gamma_i \frac{\partial E_i}{\partial T}\right)\times10^4$	$\left(\beta=\frac{X(3.0)}{V}\sum_i \frac{\partial E_i}{\partial T}\right)\times10^4$
$\gamma(4)=3.232$	85	3.1359	2.946	2.960	1.85	1.88
$\gamma(2)=3.173$	80	3.1362	2.943	2.954	1.54	1.56
$\gamma(1)=3.137$	75	3.1364	2.940	2.949	1.25	1.27
$\gamma(0)=3.096$	70	3.1365	2.938	2.945	0.995	1.01
$\gamma(-3)=2.968$	65	3.1366	2.936	2.940	0.775	0.791
$\gamma_\infty-\gamma_0=0.129$	60	3.1368	2.934	2.937	0.590	0.603
	55	3.1368	2.934	2.934	0.438	0.448
	50	3.1369	2.934	2.933	0.317	0.325
	45	3.1369	2.935	2.933	0.223	0.229
	40	3.1370	2.936	2.934	0.152	0.156

where ϕ_i ($i=1, 2, 3$, for three dimensions and $i=1, 2$, for two dimensions) is related to the wave vector K, $\phi_{i\,\text{fcc}}=2\pi k_i/N$, N being the total number of particles; $\phi_{1\ \text{2-d.d.}}=\pi k_1/N$; $\phi_{2\ \text{2-d.d.}}=2\pi k_2/N$; where ϕ_1 and ϕ_2 differ because of the Born–Von Kármán boundary conditions which are applied to these lattices. Since the first term in both expressions is independent of the frequency and, thus, will not change, we have explicitly

$$\frac{-1}{l}\frac{r^2\alpha_1'}{\alpha_1}=\frac{-r^2f'''}{lf''}-\frac{1}{l}=\frac{m+n+4}{2l} \tag{27}$$

for a potential of the form $\lambda r^{-m}+\zeta r^{-n}$, where l is the dimension of the crystal. For a potential of the form $\lambda r^{-m}+Ae^{-Br}$, we have

$$\frac{1}{l}\frac{r^2\alpha_1'}{\alpha_1}=\frac{1}{2l}\left[\frac{B^2r^2+3Br+1-(m+2)(m+4)}{(Br+1)-(m+2)}\right]. \tag{28}$$

TABLE III. Calculated values of the γ(S).

γ(S)	IBM 7090 results	Barron's results	Absolute difference	Percent difference
$\gamma(4)$	3.2166	3.2334	0.017	0.52
$\gamma(2)$	3.1493	3.1667	0.017	0.55
$\gamma(1)$	3.1041	3.121	0.017	0.55
$\gamma(0)$	3.0508	(interpolated value) 3.062	0.011	0.36
$\gamma(-3)$	2.8548	(interpolated value) 2.760	0.095	3.3
$\gamma(0)-\gamma(-3)$	0.1960	(by numerical integration) 0.302	0.106	54.1

D. Results

For the face-centered cubic lattice we have taken $m=6$ and $n=12$ since these values have been found to give good results when considering some rare gases such as argon. Since the two-dimensional diatomic square lattice can represent NaCl we have taken the values $A=1.474\times10^{-9}$ erg, $B=3.048\times10^8$ cm^{-1}, $R_0=2.814\times10^{-8}$ cm, and $m=1$. With this information we can write for the face-centered cubic lattice that $\frac{1}{6}(m+n+4)=3.667$ and for the two-dimensional diatomic lattice that $\frac{1}{4}[B^2r^2+3Br+1-(m+2)(m+4)]/[(Br+1)-(m+2)]=3.242$, although by evaluating $-\frac{1}{2}r^2f'''/f''-\frac{1}{2}$ without assuming the equilibrium condition we get a value of about 3.5.

The masses of the ions of the diatomic lattice are chosen to be 60×10^{-24} and 30×10^{-24} g, giving us when assuming a nearest neighbor distance of 2.8×10^{-8} cm a maximum frequency of 1.2×10^{13} cycles/sec. For the face-centered cubic lattice, assuming a nearest neighbor

TABLE IV. Two dimensional diatomic square lattice (central forces $\delta=0.1$; $R_0=2.814\times10^{-8}$ cm; $X=2.46\times10^{-4}$ cm²/dyn).

					Thermal expansion coefficient 1/°C	
$\gamma(S)$	°K	γ	γ'	γ''	$\left(\beta=\frac{X}{V}\sum_i \gamma_i\frac{\partial E_i}{\partial T}\right)\times10^4$	$\left(\beta=\frac{X(3.0)}{V}\sum_i \frac{\partial E_i}{\partial T}\right)\times10^4$
$\gamma(2)=3.137$	200	2.8285	2.347	2.559	1.03	1.28
$\gamma(1)=2.998$	160	2.8610	2.243	2.478	0.849	1.10
$\gamma(0)=2.720$	120	2.9034	2.087	2.328	0.608	0.836
$\gamma(-1)=2.240$	100	2.9277	1.984	2.210	0.468	0.678
$\gamma(-2)=1.487$	80	2.9522	1.866	2.053	0.326	0.509
$\gamma(-3)=0.950$	60	2.9744	1.748	1.866	0.195	0.335
$\gamma_\infty-\gamma_0=1.232$	50	2.9835	1.698	1.770	0.138	0.249
	40	2.9905	1.668	1.688	0.0879	0.167
	30	2.9952	1.672	1.652	0.0486	0.0941
	20	2.9976	1.685	1.699	0.0215	0.0404

distance of 3.72×10^{-8} cm and a mass of 66.4×10^{-24} g, the maximum frequency is 0.668×10^{13} cycles/sec.

In Tables I and II the γ's, and the thermal expansion are given for the case when nearest neighbors only were considered and for the case of nearest and next nearest neighbors.

For $\delta=0$, where δ is the ratio of the Hooke's law constant for next nearest neighbors to nearest neighbors, we have the lattice investigated by Barron[11] and we compare our results to his in Table III. Very good results are obtained for all but the $\gamma(-3)$ value which was evaluated by Barron by numerical integration after he expanded the matrix as an even power series in the wave number and went to the limit of long waves. Our values are derived by calculating a large number of frequencies and γ_i's by dividing each axis into 10 parts giving us a total of 3000 frequencies and γ_i's.

In Table II we have the values for the face-centered cubic lattice when $\delta=0.1$ and we find that, in general, all values found are larger than the values found when $\delta=0$. We notice that $\gamma_\infty-\gamma_0=0.129$ and this is smaller than the 0.196 value obtained when $\delta=0$. This corresponds to the work by Barron where he found $\gamma_\infty-\gamma_0=0.14$ when considering all neighbors.

Using the formula $1/x=Vd^2U/dV^2$ where $U=-\lambda r^{-6}+\zeta r^{-12}$ and picking a value for $\zeta=6.1\times1.62\times10^{-103}$ erg-cm [12] from Born and Huang,[12] we have (assuming equilibrium) a reasonable value for the compressibility: $x=9.15\times10^{-11}$ cm²/dyn so that values of the thermal expansion of the lattice could be given assuming Grüneisen's relation,

$$\beta=\frac{x(3.0)}{V}\sum_i \frac{\partial E_i}{\partial T}.$$

The value 3.0 was picked since this is close to the value of γ at high temperatures and such high-temperature γ's have been used by various investigators when utilizing the Grüneisen relation. As seen in Table I the values of β differ by 4.9% at 85°K to 7.1% at 40°K. In Table II less variation in β is noted.

TABLE V. Two dimensional diatomic square lattice (noncentral forces $\delta=0.1$; $\delta'=.1$; $R_0=2.814\times10^{-8}$ cm; $X=2.46\times10^{-4}$ cm²/dyn).

					Thermal expansion coefficient 1/°C	
$\gamma(S)$	°K	γ	γ'	γ''	$\left(\beta=\frac{X}{V}\sum_i \gamma_i\frac{\partial E_i}{\partial T}\right)\times10^4$	$\left(\beta=\frac{X(1.6)}{V}\sum_i \frac{\partial E_i}{\partial T}\right)\times10^4$
$\gamma(2)=3.170$	200	3.0214	2.787	2.878	1.11	1.23
$\gamma(1)=3.091$	160	3.0371	2.741	2.837	0.913	1.03
$\gamma(0)=2.964$	120	3.0565	2.675	2.764	0.653	0.756
$\gamma(-1)=2.780$	100	3.0668	2.636	2.710	0.502	0.593
$\gamma(-2)=2.493$	80	3.0764	2.597	2.647	0.349	0.421
$\gamma(-3)=2.232$	60	3.0842	2.568	2.588	0.205	0.254
$\gamma_\infty-\gamma_0=0.471$	50	3.0869	2.561	2.568	0.142	0.177
	40	3.0888	2.559	2.560	0.0889	0.111
	30	3.0899	2.556	2.563	0.0483	0.0603
	20	3.0905	2.540	2.561	0.0212	0.0265

Similar work was done for the two-dimensional diatomic square lattice for central and noncentral forces. (See Tables IV, V, and VI.) A negative thermal expan-

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[11] T. H. K. Barron, Ref. 3.

[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chap. 1, Table IX.

TABLE VI. Two dimensional diatomic square lattice (central forces $\delta=-0.1$; $R_0=2.814\times10^{-8}$ cm; $X=2.462\times10^{-4}$ cm^2/dyn)

					Thermal expansion coefficient 1/°C	
$\gamma(S)$	°K	γ	γ'	γ''	$\left(\beta=\frac{X}{V}\sum_i \gamma_i\frac{\partial E_i}{\partial T}\right)\times10^4$	$\left(\beta=\frac{X(1.6)}{V}\sum_i \frac{\partial E_i}{\partial T}\right)\times10^4$
$\gamma(2)=3.130$	200	2.202	0.1956	1.385	1.12	1.29
$\gamma(1)=2.932$	160	2.305	−0.4271	1.104	0.763	1.11
$\gamma(0)=1.880$	120	2.445	−1.585	0.5095	0.267	0.839
$\gamma(-1=-7.821$	100	2.530	−2.572	−0.05359	−0.0227	0.677
$\gamma(-2)=-68.32$	80	2.624	−4.082	−0.9810	−0.310	0.505
$\gamma(-3)=-134.1$	60	2.721	−6.593	−2.605	−0.552	0.339
$\gamma_\infty-\gamma_0=70.21$	50	2.770	−8.571	−3.934	−0.641	0.261
	40	2.817	−11.46	−5.972	−0.699	0.187
	30	2.860	−15.98	−9.399	−0.706	0.120
	20	2.897	−23.87	−15.86	−0.627	0.063

sion is found[13] at low temperatures when considering central forces and $\delta=-0.1$. A negative thermal expansion was found by Barron[14] for a lattice having harmonic forces and by Blackman[15] for a lattice having the zincblende structure at low temperature and under special conditions (in the repulsive term $1/r^n$ n was taken as 21) for a lattice having the rocksalt structure. In fact, when considering a real model of NaCl it was found that the γ_i could be negative for some values of the acoustic mode frequencies and, thus, one may imagine that a crystal with many negative γ_i's could have a resulting negative expansion. Water about the 4°C temperature as well as several crystals such as AgI, zincblende, and silicon at low temperature have been found which do have negative thermal expansions. Since our values of γ go from positive to negative values we should have zero thermal expansion a little above 100°K. It should be noted that the two-dimensional diatomic lattice is unstable when $\delta=-0.1$. It is suggested that for a real crystal, as an instability is approached, negative thermal expansion or an anomalous positive thermal expansion will result.

The potential used for the two-dimensional diatomic square lattices was similar to that for NaCl, where $U=-\alpha e^2/r+Ae^{-Br}$, and the values of A, B, and r are chosen to be 1.474×10^{-9} erg, 3.048×10^{8} cm^{-1}, and 2.814×10^{-8} cm, respectively. The spectrum of frequencies and γ_i's is given by dividing up the space into 25 steps in one direction and 50 steps in the other.

The specific heat is calculated from $\sum_i \partial E_i/\partial T$ for the three-dimensional and two-dimensional crystals and their variation is consistent with previous theory and experiment.

E. Conclusions

It is seen that γ varies with temperature, although not as much for the face-centered cubic lattice as was found by Barron. In fact, we see that the various γ's approach a minimum and then rise to the limiting value $\gamma_0=\gamma(-3)$. We also see the possibility of negative thermal expansion explained by lattice dynamics. Extrapolation using the Grüneisen relation is not reliable below about 0.3θ, and, in fact, additional information concerning the interatomic forces in the crystal should be obtainable from thermal expansion measurements in the low-temperature range. The frequencies are vibrations found under the assumption of small amplitude and the anharmonicity of the lattice can be found by looking at the change in the frequencies as the lattice expands through introduction of various expressions for the potential energies. The consideration of explicit anharmonic terms in the potential energy expansion will be considered in future work.

APPENDIX I

The matrices resulting from the equations of motion of the ions in the lattices considered, namely, the two-dimensional diatomic square lattice with central and noncentral forces and the face-centered cubic lattice are given along with γ_i and y. We also include the matrices, γ_i and y for the simple cubic and body-centered cubic lattices. We introduce the notation $S_i=\sin\phi_i$; $C_i=\cos\phi_i$; $i=1,2$ for two-dimensional lattices and $i=1, 2, 3$, for three-dimensional ones; $\phi_i=2\pi k_i/N$ (k_i being the wave vectors and N the total number of particles) for the three-dimensional lattices; $\phi_1=\pi k_1/N$, $\phi_2=2\pi k_2/N$ for the two-dimensional diatomic square lattice. We also have δ as the ratio of next-nearest neighbor Hooke's law constant to nearest neighbor Hooke's law constant, where g_i^2 is the eigenvalue of the matrix.

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[13] Some preliminary calculations on the equation of state of simple cubic lattices having nearest and next nearest neighbors (see Appendix), using 2997 frequencies and γ_i's, with the potential energy and constants the same as for the two-dimensional diatomic square lattice, were done on an IBM 7090. The values of γ are $\gamma(4)=2.0135$, $\gamma(2)=1.9729$, $\gamma(1)=1.9282$, $\gamma(0)=1.7470$, and $\gamma(-3)=-105.46$, with negative values of the thermal expansion starting below 80°K.

[14] T. H. K. Barron, Ref. 3.

[15] M. Blackman, Ref. 7.

A. Two-dimensional Diatomic Square Lattice (One Mass Double the Other)

$$A=\begin{bmatrix} \frac{2}{3}[1+\delta(1-C_1C_2)] & \frac{2}{3}\delta S_1S_2 & -\frac{1}{3}\sqrt{2}C_1 & 0 \\ \frac{2}{3}\delta S_1S_2 & \frac{2}{3}[1+\delta(1-C_1C_2)] & 0 & -\frac{1}{3}\sqrt{2}C_2 \\ -\frac{1}{3}\sqrt{2}C_1 & 0 & \frac{1}{3}[1+\delta(1-C_1C_2)] & \frac{1}{3}\delta S_1S_2 \\ 0 & -\frac{1}{3}\sqrt{2}C_2 & \frac{1}{3}\delta S_1S_2 & \frac{1}{3}[1+\delta(1-C_1C_2)] \end{bmatrix},$$

$$y=[2-C_1-C_2],$$

$$\gamma_i=-\tfrac{1}{2}\left[\frac{r^2\alpha_1'}{\alpha_1}+\frac{y}{4g_i^2}\right],$$

where r is the equilibrium distance. [With noncentral forces (see Ref. 10) add to A_{11},A_{44} the quantity $(0.2/3)(2-C_1-C_2)$ and to A_{33},A_{44} the quantity $(0.1/3)(2-C_1-C_2)$, where $\delta'=\alpha_2/\alpha_1=0.1$.]

B. Face-Centered Cubic

$$A=\begin{bmatrix} 2-C_1(C_3+C_2)+2\delta S_1^2 & S_1S_2 & S_1S_3 \\ S_1S_2 & 2-C_2(C_1+C_3)+2\delta S_2^2 & S_2S_3 \\ S_1S_3 & S_2S_3 & 2-C_3(C_1+C_2)+2\delta S_3^2 \end{bmatrix},$$

$$y=12-4[C_1C_2+C_2C_3+C_1C_3],$$

$$\gamma_i=-\tfrac{1}{3}\left[\frac{r^2\alpha_1'}{\alpha_1}+\frac{3-[C_1C_2+C_2C_3+C_1C_3]}{g_i^2}\right].$$

C. Simple Cubic

$$A=\begin{bmatrix} 2(1-C_1)+4\delta(2-C_1C_2-C_1C_3) & 4\delta S_1S_2 & 4\delta S_1S_3 \\ 4\delta S_1S_2 & 2(1-C_2)+4\delta(2-C_2C_3-C_1C_2) & 4\delta S_2S_3 \\ 4\delta S_1S_3 & 4\delta S_2S_3 & 2(1-C_3)+4\delta(2-C_1C_3-C_2C_3) \end{bmatrix},$$

$$y=2[3-C_1-C_2-C_3],$$

$$\gamma_i=-\tfrac{1}{3}\left[\frac{r^2\alpha_1'}{\alpha_1}+\frac{(3-C_1-C_2-C_3)}{g_i^2}\right].$$

D. Body-Centered Cubic

$$A=\begin{bmatrix} 1-C_1C_2C_3+\frac{3}{2}\delta S_1^2 & S_1S_2C_3 & S_1C_2S_3 \\ S_1S_2C_3 & 1-C_1C_2C_3+\frac{3}{2}\delta S_2^2 & C_1S_2S_3 \\ S_1C_2S_3 & C_1S_2S_3 & 1-C_1C_2C_3+\frac{3}{2}\delta S_3^2 \end{bmatrix},$$

$$y=8-2[\cos(\phi_1+\phi_2+\phi_3)+\cos(-\phi_1+\phi_2+\phi_3)+\cos(\phi_1-\phi_2+\phi_3)+\cos(\phi_1+\phi_2-\phi_3)],$$

$$\gamma_i=-\tfrac{1}{3}\left[\frac{r^2\alpha_1'}{\alpha_1}+\frac{4-[\cos(\phi_1+\phi_2+\phi_3)+\cos(-\phi_1+\phi_2+\phi_3)+\cos(\phi_1-\phi_2+\phi_3)+\cos(\phi_1+\phi_2-\phi_3)]}{g_i^2}\right].$$