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Theory of Melting Based on Lattice Instability

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A lattice instability which may be related to melting is proposed as follows: The energy of thermal vibration cannot exceed a critical value, because of anharmonicity, and the lattice may be unstable above the temperature corresponding to this critical energy. The effect of anharmonicity arises from the effective increase in interatomic distances due to the lattice vibrations. This increase is called "vibrational elongation." The critical temperature of instability is written in terms of atomic volume, elastic constants, and the Grüneisen parameter under the assumption of a linear dispersion relation, and is shown to be in fairly good agreement with the observed melting point. The Lindemann formula and the empirical law that the product of thermal expansivity and melting point is approximately constant are examined on the basis of the present theory. The thermal expansion and the elastic properties predicted by the theory up to the melting point are qualitatively consistent with the observed values.

1. INTRODUCTION

ALTHOUGH melting is a very common phenomenon in nature, its physical mechanism is poorly understood. Lindemann[1] gave a formula assuming that the amplitude of thermal vibration approaches lattice dimensions at melting. Since Lindemann's treatment lacks sufficient physical basis, many attempts have been made to find a more reasonable formulation of the limit of stability of lattices.[2–7] Unfortunately, most attempts have been unsuccessful. On the other hand, Lennard-Jones and Devonshire[8] developed a theory which interprets melting as an order-disorder transition, and suggested that this treatment, based on statistical mechanics, is consistent with the Lindemann law. More recently, Cartz[9] and Gilvarry[10] reformulated the Lindemann criterion utilizing the Debye[11] and Waller[12] theory of the temperature dependence of the mean-square amplitude of vibration, and showed that the amplitude attains a value of less than 10% of interatomic distances at melting. A detailed examination also showed that the Lindemann "constant" is not strictly constant from one lattice type to another.[10] These situations suggest that, in spite of its partial success, there are many problems with the Lindemann law, and the physical relation between lattice instability and melting has not yet been clarified.

The Lindemann formula, which contains a parameter to be determined empirically, cannot predict an absolute value of the melting point, but it gives a fusion curve at high pressure if this parameter is assumed to be constant with pressure and if a suitable equation of state is used for the solid. For instance, the derivation of the Simon equation,[13] an empirical relation describing the fusion curve, was investigated in this manner.[10,14] Since the investigation of Bridgman[15] many experiments have been made to determine the fusion curve at high pressure, and it has been indicated that the Lindemann law did not adequately estimate the pressure dependence of melting temperature.[16–19] This inadequacy was confirmed by the experiment during which much higher pressures were obtained with shock-wave compression.[20] Quite recently, some attempts have been made to establish an empirical law of fusion curves,[21,22] or to analyze them on phenomenological ground.[23] A basic consideration of melting may be required to examine these investigations in the light of theory.

The present paper describes a theoretical approach which shows the relation between the instability of a solid and melting. A new idea is proposed to describe the instability of a lattice. The anharmonicity of the lattice plays an important role in the concept of vibrational elongation introduced in this theory. Quantum-mechanical effects will not be taken into account, since it may not be essential for this phenomenon. We shall sacrifice some unessential accuracies to make the

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mathematical structure of the theory as simple and as clear as possible.

2. VIBRATIONAL ELONGATION

We shall show that the interatomic distances are effectively increased as the result of lattice vibrations. To help intuitive understanding, we begin by considering a lattice wave with one definite frequency (i.e., a single normal vibration). A longitudinal wave will cause interatomic distances to be longer than equilibrium distances at one instant and shorter at another, and the time average of the interatomic distances is equal to the equilibrium length in the direction of wave propagation. For transverse waves, however, interatomic distances may be equal to or longer, but never shorter than the equilibrium distance along the propagation direction at any time, and thus the time average will be longer than the equilibrium distance. An actual crystal at an elevated temperature contains a large number of normal vibrations, each of which will be feeling, on the average, the interatomic forces corresponding to the interatomic separation greater than equilibrium one, as a result of the other normal vibrations. We shall refer to this effective elongation of the lattice dimension as vibrational elongation, and we shall treat it analogously to thermal expansion. It is important to distinguish vibrational elongation from thermal expansion; the latter is the change of the equilibrium dimension itself.

For simplicity, let us consider a lattice composed of one kind of atom. The displacement $\mathbf{u}_n$ of the atom at a lattice point $\mathbf{a}_n$ may be written as a function of time t:

$$\mathbf{u}_n=\sum_{\mathbf{f}s} A_{\mathbf{f}s}\cos(\mathbf{f}\cdot\mathbf{a}_n-\omega_{\mathbf{f}s}t+\phi_{\mathbf{f}s})\mathbf{v}_{\mathbf{f}s}, \tag{1}$$

where $\mathbf{f}$ is the wave vector and A, ω, ϕ, and $\mathbf{v}$ are the amplitude, the angular frequency, the phase factor, and the unit vector along the direction of vibration, respectively, all of which correspond to a normal vibration $(\mathbf{f},s)$. We denote the mode of vibration by s; we shall express one longitudinal mode by $s=1$, and two transverse modes by $s=2$ and $s=3$. Most of the notations used here corresponds to those used by Peierls.[24] If the crystal in question contains N atoms, the number of normal vibrations, i.e., the number of the sets $(\mathbf{f},s)$ is $3N$. The total energy of the crystal is

$$E=U(a)+\sum_{\mathbf{f}s}\epsilon_{\mathbf{f}s}, \tag{2}$$

where $U(a)$ is the potential energy when all the atoms are at rest at their equilibrium positions corresponding to the lattice dimension a. The energy $\epsilon_{\mathbf{f}s}$ of each normal vibration is written in the well-known form,

$$\epsilon_{\mathbf{f}s}=\tfrac{1}{2}mN\omega_{\mathbf{f}s}^2A_{\mathbf{f}s}^2, \tag{3}$$

where m is the mass of the atom. At thermal equilibrium at a temperature T, we have a statistical expression

$$\epsilon_{\mathbf{f}s}=\tfrac{1}{2}\hbar\omega_{\mathbf{f}s}+\hbar\omega_{\mathbf{f}s}(e^{\hbar\omega_{\mathbf{f}s}/kT}-1)^{-1}, \tag{4a}$$

where $\hbar$ is the Planck constant divided by 2π and k is the Boltzmann constant. Since the melting point is usually much higher than the Debye temperature, we can use, for a first approximation, a high-temperature form of (4a),

$$\epsilon_{\mathbf{f}s}=kT, \tag{4b}$$

which is known as the Dulong-Petit law.

Now we shall derive a mathematical expression Q for the vibrational elongation. Let Q be defined as a time average of the fractional increase of the interatomic distance, i.e.,

$$Q=\lim_{t_1\to\infty}\frac{1}{t_1}\int_0^{t_1}\frac{|\mathbf{r}_{n'}-\mathbf{r}_n|-|\mathbf{a}_{n'}-\mathbf{a}_n|}{|\mathbf{a}_{n'}-\mathbf{a}_n|}dt, \tag{5}$$

where $\mathbf{r}_n=\mathbf{a}_n+\mathbf{u}_n$. Q depends on the relative position of the two points n and n'. We can expand $|\mathbf{r}_{n'}-\mathbf{r}_n|$ with respect to $\mathbf{u}=\mathbf{u}_{n'}-\mathbf{u}_n$ up to the quadratic terms, as follows:

$$|\mathbf{r}_{n'}-\mathbf{r}_n|=|\mathbf{a}|\{1+\mathbf{a}\cdot\mathbf{u}/\mathbf{a}^2+\tfrac{1}{2}[\mathbf{u}^2/\mathbf{a}^2-(\mathbf{a}\cdot\mathbf{u})^2/|\mathbf{a}|^4]\}, \tag{6}$$

where

$$\mathbf{a}=\mathbf{a}_{n'}-\mathbf{a}_n. \tag{7}$$

Substituting (6) and (1) into (5), we find that the linear term $\mathbf{a}\cdot\mathbf{u}/\mathbf{a}^2$ in (6) does not contribute to (5). When we estimate the contribution of the quadratic terms, we encounter the following expression in the summation with respect to $\mathbf{f}$, s, $\mathbf{f}'$, s':

$$\lim_{t_1\to\infty}\frac{1}{t_1}\int_0^{t_1}\sin[\tfrac{1}{2}\mathbf{f}(\mathbf{a}_n+\mathbf{a}_{n'})-\omega_{\mathbf{f}s}t+\phi_{\mathbf{f}s}]\times\sin[\tfrac{1}{2}\mathbf{f}'(\mathbf{a}_n+\mathbf{a}_{n'})-\omega_{\mathbf{f}'s'}t+\phi_{\mathbf{f}'s'}]dt. \tag{8a}$$

We can show that (8a) vanishes except when $\omega_{\mathbf{f}'s'}=\omega_{\mathbf{f}s}$, and in that case yields

$$\tfrac{1}{2}\cos[\tfrac{1}{2}(\mathbf{f}-\mathbf{f}')(\mathbf{a}_n+\mathbf{a}_{n'})+(\phi_{\mathbf{f}s}-\phi_{\mathbf{f}'s'})]. \tag{8b}$$

If the phase factor $\phi_{\mathbf{f}s}$ is distributed completely at random (this assumption may be satisfied during thermal equilibrium), the terms in the form of (8b) cancel out one another in the summation with respect to f', s', unless $(\mathbf{f}', s')$ is identical with $(\mathbf{f}, s)$. Thus some simple calculation gives

$$Q=\sum_{\mathbf{f}s}A_{\mathbf{f}s}^2|\mathbf{a}|^{-2}\sin^2(\tfrac{1}{2}\mathbf{f}\cdot\mathbf{a})[1-|\mathbf{a}|^{-2}(\mathbf{a}\cdot\mathbf{v}_{\mathbf{f}s})^2]. \tag{9}$$

Physically, Q is important for small values of $|\mathbf{a}|$, since the interactions between atoms are dominant for the pairs situated relatively close to each other. In this case, we can replace $\sin\frac{1}{2}\mathbf{f}\cdot\mathbf{a}$ by $\frac{1}{2}\mathbf{f}\cdot\mathbf{a}$ for most wave vectors

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[24] R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York 1955), Chaps. I and II.

$\mathbf{f}$ and obtain

$$Q=\tfrac{1}{4}\sum_{\mathbf{f}s} A_{\mathbf{f}s}^2(\mathbf{f}\cdot\mathbf{e})^2[1-(\mathbf{v}_{\mathbf{f}s}\cdot\mathbf{e})^2], \tag{10}$$

where Q depends only upon the direction $\mathbf{e}=\mathbf{a}/|\mathbf{a}|$ of $\mathbf{a}$.

In the present paper we assume that the distribution of $\mathbf{f}$ is continuous and isotropic, and that the dispersion relation is given in a simple linear form

$$\omega_{\mathbf{f}s}=c_s f, \tag{11}$$

where $f=|\mathbf{f}|$. The quantity c_s corresponds to the velocity of elastic waves for the mode s. The above assumption, which is similar to the treatment used by Debye[25] in the discussion of heat capacity of solids, is not a good approximation for actual crystals.[26] It may be useful and interesting, however, to develop our theory on the basis of this assumption, because of its mathematical simplicity and the great success of the Debye theory. This assumption may be plausible because it will be used to evaluate the summation (10) over the whole frequency spectrum, as in the case treated by Debye. Using (3) and (11) to eliminate $A_{\mathbf{f}s}$ in (10), and substituting (4b) into the resulting equation, we have

$$Q=\frac{kT}{2mN}\sum_{\mathbf{f}s} c_s^{-2}\left(\frac{\mathbf{f}}{f}\cdot\mathbf{e}\right)^2[1-(\mathbf{v}_{\mathbf{f}s}\cdot\mathbf{e})^2]. \tag{12}$$

According to usual methods, the summation in (12) over the whole range of $\mathbf{f}$ can be replaced by an integral over the continuous space of $\mathbf{f}$. In this integration we should notice that $\mathbf{v}_{\mathbf{f}1}$ is parallel to $\mathbf{f}$ and $\mathbf{v}_{\mathbf{f}2}$ and $\mathbf{v}_{\mathbf{f}3}$ are perpendicular to $\mathbf{f}$, and that the total number of wave vectors $\mathbf{f}$ is N. Finally, we have

$$Q=\frac{kT}{15m}\left(\frac{1}{c_1^2}+\frac{4}{c_2^2}\right). \tag{13}$$

Here the relation $c_2=c_3$ is used.

3. ANHARMONICITY AND LATTICE INSTABILITY

Thermal expansion results from the anharmonic effect in which the force constants of the lattice vary with the volume. In other words, the frequency $\omega_{\mathbf{f}s}$ is a function of the lattice dimension a (to specify a without ambiguity, let a^3 be the volume per atom) and decreases with increasing value of a. It is natural to suppose that the vibrational elongation should have a similar anharmonic effect on $\omega_{\mathbf{f}s}$. Under the assumption in (11), the dependence of a on $\omega_{\mathbf{f}s}$ is changed to a dependence on c_s.[27] Remembering the definition (5) of Q, we assume intuitively that c_s depends on Q in the same manner as it depends on the lattice dimension. If the Taylor's series for $\ln c_s$ up to the linear term is used, the dependence of c_s is expressed, according to the above assumption as

$$\ln c_s=\ln c_{s0}-b[(a-a_0)/a_0+Q], \tag{14}$$

or

$$c_s=c_{s0}\exp\{-b[(a-a_0)/a_0+Q]\}, \tag{15}$$

where c_{s0} and a_0 are the values at $T=0$. For simplicity, we further assume that the coefficient b in (15) is the same for different modes s. Grüneisen made a similar assumption.[28] It is only for mathematical convenience that we employ the Taylor series for $\ln c_s$ instead of that for c_s itself. The difference can be shown to be unimportant.

We shall consider how the lattice becomes unstable as a result of anharmonicity. Since finite amplitudes produce a vibrational elongation Q after (9), $\omega_{\mathbf{f}s}$ is reduced by the anharmonicity through (11) and (15) with increasing amplitudes $A_{\mathbf{f}s}$. This correlation between $A_{\mathbf{f}s}$ and $\omega_{\mathbf{f}s}$ suggests that the energy $\epsilon_{\mathbf{f}s}$, which is proportional to the squares of both $A_{\mathbf{f}s}$ and $\omega_{\mathbf{f}s}$ [see (3)], may have an upper limit. We can start from (13) to examine this suggestion. Substituting (15) into (13), we have

$$Q\exp\left[-2b\left(\frac{a-a_0}{a_0}+Q\right)\right]=\frac{kT}{15m}\left(\frac{1}{c_{10}^2}+\frac{4}{c_{20}^2}\right). \tag{16}$$

First, for easy understanding, we consider the lattice instability by neglecting the term $(a-a_0)/a_0$, i.e.,

$$Qe^{-2bQ}=\frac{kT}{15m}\left(\frac{1}{c_{10}^2}+\frac{4}{c_{20}^2}\right). \tag{17}$$

The function of Q in the left-hand side of (17) increases from zero with increasing Q, but decreases after it arrives at the maximum value $1/2eb$ at $Q=1/2b$. Hence, the temperatures for which a value of Q satisfies (17) are limited to values below a critical temperature T_m. At temperatures above T_m, no state of lattice vibration exists and hence the lattice must be unstable. T_m is obtained from the maximum point $Q=1/2b$, as

$$T_m=\frac{15m}{2ekb}\left(\frac{1}{c_{10}^2}+\frac{4}{c_{20}^2}\right)^{-1}, \tag{18}$$

which is expected to be related to the melting point.

Practically, (18) is not a good approximation to the critical temperature of instability, since the effect of thermal expansion is not really negligible. We shall formulate the theory in which this effect is also taken into consideration. The Helmholtz free energy of the

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[25] P. Debye, Ann. Physik **39**, 789 (1912).

[26] J. M. Zimann, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), Chap. I.

[27] We shall ignore the dependence of f on a, to prevent the following expressions from being complicated by this unessential dependence. Alternatively, we may suppose that all the dependence of $\omega_{\mathbf{f}s}$ is included in the exponential term in (14).

[28] E. Grüneisen, *Handbuch der Physik* (Julius Springer, Berlin, 1926), Vol. 10, pp. 1–59.

solid can be written as

$$F=U(a)+\sum_{fs}\tfrac{1}{2}\hbar\omega_{fs}+kT\sum_{fs}\ln(1-e^{-\hbar\omega_{fs}/kT}), \quad (19)$$

from which the so-called Mie-Grüneisen equation of state[28] can be obtained:

$$P=-\frac{dU(a)}{dV}+\frac{1}{V}\sum_{fs}\left(-\frac{\partial\ln\omega_{fs}}{\partial\ln V}\right)\epsilon_{fs}, \quad (20)$$

where P is the pressure, and V is the volume. Because of (11) and (15), the quantity $-\partial\ln\omega_{fs}/\partial\ln V$ turns out to be independent of $(\mathbf{f},s)$, as in the treatment of Grüneisen in which this quantity is denoted by γ. Grüneisen's treatment is related to ours by the equation[27]

$$\gamma=\tfrac{1}{3}b\cdot\frac{a}{a_0}\left(1+a_0\frac{\partial Q}{\partial a}\right). \quad (21)$$

Here the partial derivative $\partial Q/\partial a$ should be taken for the dependence of Q on a through the relation (16) under the condition that T is fixed.[29] Thus,

$$\frac{\partial Q}{\partial a}=\frac{2bQ}{a_0(1-2bQ)}. \quad (22)$$

Utilizing (22) and taking a/a_0 to be nearly unity, we have

$$\gamma=\tfrac{1}{3}b(1-2bQ)^{-1}. \quad (23)$$

Here we shall discuss the case of zero pressure. In estimating the first term of (20), we may take $U'(a)$, to a first approximation, to be

$$U'(a)=9Na_0K(a-a_0), \quad (24)$$

where K is the bulk modulus. Substituting (23) and (24) into (20), with $P=0$, we have

$$\frac{a-a_0}{a_0}=\frac{b}{9Na_0^3K}\frac{1}{1-2bQ}\sum_{fs}\epsilon_{fs}. \quad (25)$$

Using (4b), we have

$$\frac{a-a_0}{a_0}=\frac{b}{3a_0^3K}\frac{kT}{1-2bQ}. \quad (26)$$

Coupling (16) and (26), we obtain

$$Q\exp\left[-2b\left(\frac{b}{3a_0^3K}\frac{kT}{1-2bQ}+Q\right)\right]=\frac{kT}{15m}\left(\frac{1}{c_{10}^2}+\frac{4}{c_{20}^2}\right). \quad (27)$$

For convenience in treating (27), we introduce the new variables

$$\tau=(2kb^2/3a_0^3K)T \quad (28)$$

and

$$q=2bQ. \quad (29)$$

We can say that τ and q are a *reduced* temperature and a *reduced* vibrational elongation, respectively. Then (27) yields

$$q\exp[-\tau/(1-q)-q]=z\tau, \quad (30)$$

where z is a nondimensional constant defined as

$$z=\frac{a_0^3K}{5mb}\left(\frac{1}{c_{10}^2}+\frac{4}{c_{20}^2}\right). \quad (31)$$

The relation between q and τ was calculated numerically with the aid of the FACOM 202 computer in our Institute, and the results are given in Fig. 1 for some values of z. It should be noted that the curves τ versus q have maxima analogous to the curve discussed in (17). The thermal expansion and the velocity of sound calculated as a function of temperature from (26) and (15) are also given in a reduced form in Fig. 2 ($z=0.4$) and Fig. 3 ($z=0.8$).

In order to evaluate the critical temperature T_m, we have to couple Eq. (30) and the condition that τ is maximum i.e., $d\tau/dq=0$. From (30) we have

$$\frac{d\tau}{dq}=\frac{(1-q)^3-q\tau}{(1-q)\{z(1-q)\exp[\tau/(1-q)+q]+q\}}, \quad (32)$$

and the latter condition therefore yields

$$\tau=(1-q)^3/q. \quad (33)$$

Thus, we have the critical reduced temperature τ_m as

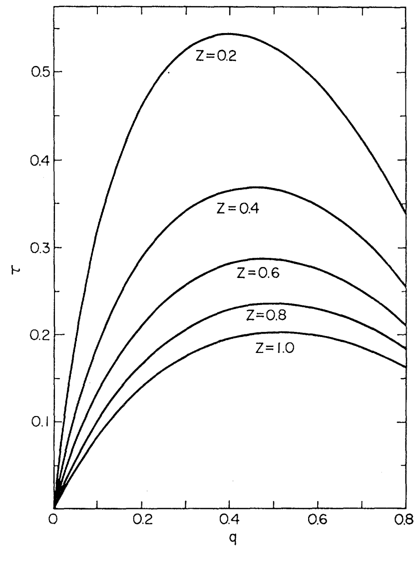

FIG. 1. Relations between q and τ given by (30) for various parameters z.

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[29] This means that the expressions of γ which were derived by Slater (Ref. 32) and by Dugdale and MacDonald [Phys. Rev. **89**, 832 (1953)] should be slightly modified to include the effect of vibrational elongation.

a function of z, i.e.,

$$\tau_m = Mi(z). \tag{34}$$

$Mi(z)$ is defined with the aid of the function

$$f(q) = [q^2/(1-q)^3] \exp[-(1-q)^2/q - q] \tag{35}$$

as

$$Mi(z) = [1 - f^{-1}(z)]^3 / f^{-1}(z), \tag{36}$$

where $f^{-1}(z)$ denotes the inverse function of $f(q)$. Numerical values of $Mi(z)$ are given in Table I. From (28), T_m is obtained as

$$T_m = (3a_0^3 K/2kb^2)\, Mi(z), \tag{37}$$

which is the desired equation.

4. LINDEMANN LAW AND OTHER RELATIONS

Here we shall study the relations connecting the quantities which have appeared in this theory. Noting a_0^3 is the volume per atom, we can rewrite (37) and (31) as

$$T_m = (3MK/2R\rho b^2)\, Mi(z) \tag{38}$$

and

$$z = \frac{K}{5\rho b}\left(\frac{1}{c_{10}^2} + \frac{4}{c_{20}^2}\right), \tag{39}$$

where R is the universal gas constant, ρ is the density, and M the atomic weight. Let us consider the quantity z. Coupling Eqs. (32) and (26) in the case of $q=0$, we have the following equations which hold at $T=0$: Noting that

$$\left(\frac{\partial Q}{\partial[(a-a_0)/a_0]}\right)_P = \frac{(\partial Q/\partial T)_P}{(\partial[(a-a_0)/a_0]/\partial T)_P},$$

we obtain

$$z = \left(\frac{\partial Q}{\partial[(a-a_0)/a_0]}\right)_P = \lim_{T\to 0} \frac{Q}{(a-a_0)/a_0}. \tag{40}$$

Equation (40) shows that z gives the ratio of vibrational elongation to thermal expansion. Strictly speaking, (40) does not hold at zero temperature, since (4b) is not satisfied there, but the above description of the physical meaning of z may be still approximately right. Sound velocities can be written in terms of Poisson's ratio σ as

TABLE I. Numerical values of $Mi(z)$ and q_m.

z	$Mi(z)$	q_m
0	∞	0
0.1	0.7628	0.3538
0.2	0.5427	0.3994
0.3	0.4348	0.4288
0.4	0.3676	0.4508
0.5	0.3208	0.4684
0.6	0.2858	0.4832
0.7	0.2584	0.4958
0.8	0.2363	0.5070
0.9	0.2181	0.5170
1.0	0.2027	0.5258
1.1	0.1895	0.5340
1.2	0.1781	0.5414
1.5	0.1512	0.5606
2.0	0.1216	0.5856

$$c_{10}^2 = \frac{3K}{\rho}\,\frac{1-\sigma}{1+\sigma}, \quad c_{20}^2 = \frac{3K}{2\rho}\,\frac{1-2\sigma}{1+\sigma}, \tag{41}$$

giving another expression for z, i.e.,

$$z = \frac{1}{15b}\,\frac{(1+\sigma)(9-10\sigma)}{(1-\sigma)(1-2\sigma)}. \tag{42}$$

At a moderate temperature which is sufficiently higher than the Debye temperature but not close to the melting point, (25) may be nearly equivalent to

$$(a-a_0)/a_0 = (b/3a_0^3K)kT;$$

hence we have a (volumetric) thermal expansion coefficient α as

$$\alpha = kb/a_0^3K. \tag{43}$$

Combining (43) with (37), we have

$$\alpha T_m = \tfrac{3}{2}(1/b)\, Mi(z). \tag{44}$$

It is empirically known that αT_m is approximately constant for certain groups of materials.[30,31] This rule can be understood with use of (44). The right-hand side of (44) does not vary over a wide range and tends to be nearly the same for certain types of material (see Tables II and III, whose interpretation will be prepared in Sec. 5).

Finally, we look back at the Lindemann Law,[1] which is written

$$T_m = C_L M v^{2/3} \omega_E^2, \tag{45}$$

where v is the molar volume, ω_E is the Einstein characteristic frequency, and C_L is a constant to be determined

TABLE II. Calculated and observed melting temperature of cubic metals.

	γ[a]	K Mb[b]	z	$\frac{3}{2\text{b}}Mi(z)$	T_m°K (calc)	T_m°K (obs)
Li	1.17	0.120	0.960	0.089	475	453
Na	1.25	0.046	0.620	0.112	393	371
K	1.34	0.402	0.830	0.086	464	337
Cu	1.96	1.38	0.464	0.086	1730	1356
Ag	2.47	1.04	0.437	0.071	1220	1234
Au	3.05	1.73	0.619	0.046	1070	1336
Al	2.17	0.764	0.384	0.087	1220	933
Pb	2.73	0.447	0.614	0.052	618	600
Mo	1.57	2.68	0.396	0.118	7570	2893
Ta	1.68	1.96	0.489	0.097	4940	3300

[a] From Refs. 32–34.

[b] Elastic constants C_{11}, C_{12}, and C_{44} are after Refs. 38 and 39; K was computed with use of Eq. (51).

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[30] C. Zwikker, *Physical Properties of Solid Materials* (Pergamon Press, Inc., London, 1954), p. 157.

[31] A. R. Ubbelohde, *Melting and Crystal Structure* (Clarendon Press, Oxford, England, 1965), p. 51.

Table III. Calculated and observed melting temperature of cubic compounds.

	γ^{a}	K Mb[b]	z	$\frac{3}{2b}Mi(z)$	T_m°K (calc)	T_m°K (obs)
LiF	1.34	0.76	0.384	0.141	1560	1121
LiCl	1.52	0.318	0.326	0.136	1173	886
NaCl	1.63	0.246	0.296	0.134	1097	1073
NaBr	1.56	0.199	0.314	0.136	1095	1028
KF	1.45	0.318	0.388	0.129	1329	1153
KCI	1.60	0.184	0.361	0.122	1053	1043
KBr	1.68	0.154	0.353	0.118	927	1003
KI	1.63	0.118	0.342	0.124	946	1046
RbBr	1.37	0.138	0.491	0.118	1180	955
RbI	1.41	0.107	0.486	0.116	678	915
MgO	1.53	1.57	0.228	0.165	3820	3073
TlBr	2.29	9.223	0.307	0.094	696	733
CaF	1.68	0.825	0.334	0.122	1961	1633

[a] From Refs. 32–37.
[b] Elastic constants C_{11}, C_{12}, and C_{44} are after Refs. 35–40; K was computed with use of Eq. (51).

empirically. According to a more recent modification[9,10] of this formula, ω_E in (45) is replaced by the Debye frequency ω_D given by

$$\omega_D=\left[\frac{1}{3}\left(\frac{1}{c_{10}{}^3}+\frac{2}{c_{20}{}^3}\right)\right]^{-1/3}\left(\frac{6\pi^2 N_A}{v}\right)^{1/3}, \tag{46}$$

where N_A is Avogadro's number. From the viewpoint of the present theory, the basic equation (38), combined with (41) and (46), leads to the equation

$$T_m=C_L'Mv^{2/3}\omega_D{}^2, \tag{47}$$

which is similar to (45). Here C_L' corresponds to the Lindemann constant C_L and is given by

$$C_L'=\frac{1}{2R}(18\pi^2 N_A)^{-2/3}\left[\left(\frac{1+\sigma}{1-\sigma}\right)^{3/2}+2\left(\frac{2+2\sigma}{1-2\sigma}\right)^{3/2}\right]^{2/3} b^{-2}\,Mi(z). \tag{48}$$

Although C_L' is not strictly a constant, it should be noted that (48) contains only the parameters σ, b (or γ), and $b^{-1}\,Mi(z)$, which do not vary much.

5. APPLICATIONS TO ACTUAL CRYSTALS

Now we shall examine the agreement of the theory with observations. We have assumed in the present treatment that sound velocities c_s are isotropic, while they are more or less anisotropic for actual crystals; hence in applying the theory we need a certain average for elastic properties. Since c_s appears in the form of $1/c_s{}^2$ [see (13)], a suitable average $\bar{c}_s$ may be given by

$$\frac{1}{\bar{c}_s{}^2}=\frac{1}{4\pi}\int\frac{d\Omega_{\mathrm{f}}}{c_s{}^2}, \tag{49}$$

where the integration should be extended over the whole solid angle. We employ, however, an easier way to estimate the average, since the direct computation with the use of (49) is too elaborate for the present purposes. For the cubic crystals, to which we will restrict the present consideration, we used a convenient average, the average for the velocities along [100], [110], and [111] directions, the weighting factor being the number of equivalent directions. Averaging the velocity for each mode in this way, we have the following expression needed to calculate z (and therefore T_m):

$$\frac{1}{5}\left(\frac{1}{\bar{c}_1{}^2}+\frac{4}{\bar{c}_2{}^2}\right)=\frac{3\rho}{65}\left(\frac{1}{C_{11}}+\frac{4}{C_{11}+C_{12}+2C_{44}}+\frac{4}{C_{11}+2C_{12}+4C_{44}}+\frac{8}{C_{44}}+\frac{8}{C_{11}-C_{12}}+\frac{16}{C_{11}-C_{12}+C_{44}}\right), \tag{50}$$

where C_{11}, C_{12}, and C_{44} are the elastic stiffness constants. Ignoring the difference between adiabatic and isothermal bulk modulus, we determined K with use of the relation

$$K=\tfrac{1}{3}(C_{11}+C_{12}). \tag{51}$$

There are some possibilities to evaluate the parameter describing the anharmonicity.[32] Here we determined b from the Grüneisen parameter γ by using the relation

$$b=3\gamma, \tag{52}$$

which (23) yields at low temperature. For γ we used the value obtained from the Grüneisen relation[32–37]

$$\gamma=\alpha K/\rho C_p, \tag{53}$$

where C_p is the specific heat per unit mass.

In applying the present formula to the crystals composed of more than two kinds of atoms, we simply assumed that all the relations in this treatment hold except that the mass m is replaced by the average

$$\frac{1}{n}\sum_{j=1}^{n} m_j$$

of the composing atoms. This assumption may be valid for the relation (3) for the energy, but the expression (9) for vibrational elongation can not be extended so simply. We may expect, however, that Eq. (9) with the above replacement of m is also valid in the limit for

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long wavelengths of the acoustical modes, in which every kind of atom has the same amplitude.

The values of T_m calculated from (38) with (39) and (50)–(53) are listed with the melting temperatures observed in Table II (metals)[32–39] and in Table III (compounds).[32–40] In this calculation we used the data obtained at room temperature without any correction. The agreement between theory and observation is fairly good and may be satisfactory in view of some of the approximations involved in (11), (14), etc.

6. TEMPERATURE DEPENDENCE OF ELASTIC CONSTANTS

As has already been suggested in Sec. 3, the present theory predicts thermal expansion and elastic property at high temperature. There is not much reliable data on thermal expansion close to the melting point, but it was reported that the thermal expansion coefficient of some materials increases quite rapidly close to the melting point.[41,42] This anomalous behavior was partly explained by the generation of defects in the crystal at high temperature.[43,44] Since the detailed discussion of this problem deviates too far from the present purposes, suffice it to say that the rapid increase of thermal expansion can also be interpreted using our theory (see Figs. 2 and 3).

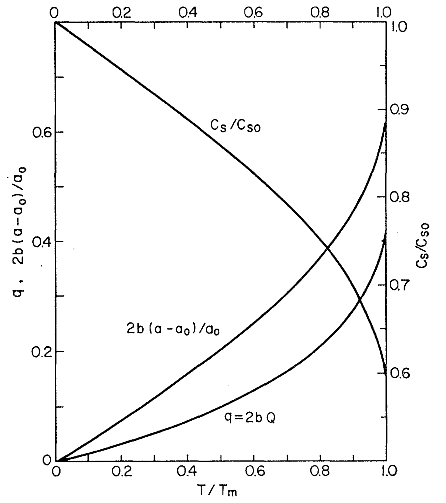

FIG. 2. Calculated curves of the vibrational elongation Q, the thermal expansion $(a-a_0)/a_0$, and the sound velocity c_s as a function of the temperature T for $z=0.4$. All the quantities are given in the *reduced* form up to the melting point T_m.

We have a basic interest in the problem of whether the sound velocities of shearing modes disappear at melting continuously or abruptly. Born believed that melting is a mechanical instability of the lattice in which a certain elastic constant, such as C_{44}, $\frac{1}{2}(C_{11}-C_{12})$, or $\frac{1}{3}(C_{11}+C_{12})$, vanishes.[5] But it was proved experimentally that Born's idea is not the case.[45] The present theory, in which the instability of the lattice is specified in different manner, does not require that any elastic constant vanish close to the melting point. Now, we designate the elastic constant corresponding to the sound velocity c_s by C_s, i.e., $c_s=(C_s/\rho)^{1/2}$. Neglecting the change of ρ with temperature, we have from (15),

$$C_s=C_{s0}\exp\{-2b[(a-a_0)/a_0+Q]\}, \qquad (54)$$

where C_{s0} is the value at 0°K. Figure 4 shows the theoretical curve thus calculated for NaCl ($z=0.296$) with the observation[45–47] in the case of $C_s=C_{44}$ and $C_s=\frac{1}{2}(C_{11}-C_{12})$. We find that the theory gives the correct temperature dependence qualitatively, even though we cannot make a quantitative comparison because of the assumption in the theory that every velocity has the same dependence (15) expressed by a unique parameter b.

Next we shall take up the fact which suggests the presence of vibrational elongation directly. Remembering the cause of vibrational elongation Q, we may expect that Q is much more strongly dependent on temperature than on pressure. This leads to the conclusion that the decrease of the elastic constants with increasing temperature should be greater than the increase with pressure by the contribution due to

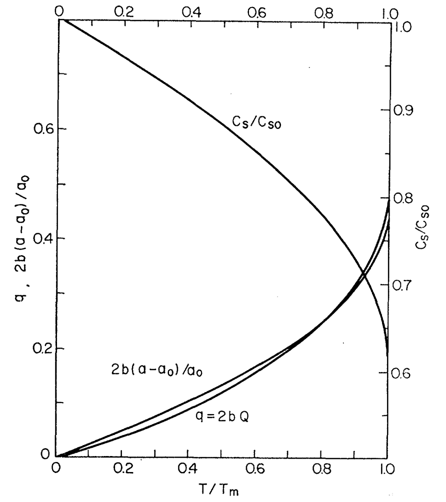

FIG. 3. Calculated curves of the vibrational elongation Q, the thermal expansion $(a-a_0)/a_0$, and the sound velocity c_s as a function of the temperature T for $z=0.8$. All the quantities are given in the *reduced* form up to the melting point T_m.

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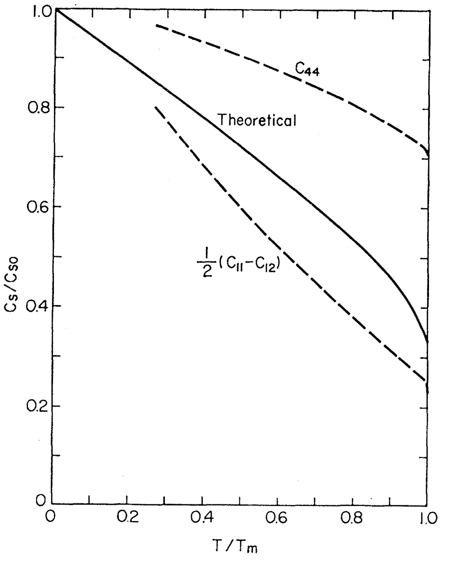

FIG. 4. Temperature dependence of elastic constants of NaCl. The theoretical curve is obtained for $z=0.296$ with use of (54). Experimental curves (the dashed lines) are according to the data from Refs. 45–47 for high temperature, where the data from Ref. 40 for 4.2°K are used for the values at 0°K.

vibrational elongation [see (54)], i.e.,

$$\left|\left(\frac{\partial C_s}{\partial V}\right)_P\right| > \left|\left(\frac{\partial C_s}{\partial V}\right)_T\right|,$$

which is consistent with observations. More quantitatively, we obtain an approximate expression for the intrinsic temperature dependence of elastic constants with the aid of (54),

$$\left(\frac{\partial \ln C_s}{\partial \ln V}\right)_P - \left(\frac{\partial \ln C_s}{\partial \ln V}\right)_T = -\tfrac{2}{3}bz. \qquad (55)$$

Here the variation of Q with pressure is completely neglected, and $(\partial \ln Q/\partial \ln V)_P$ is replaced by $\frac{1}{3}z$ according to (40). In Table IV, we examine (55) using the value of the left-hand side [which is reduced to $(1/\alpha)(\partial \ln C_s/\partial T)_V$ from the thermodynamical relation] obtained from experiments.[36,48–51] It is remarkable that the effect of vibrational elongation gives an almost correct magnitude for the intrinsic temperature dependence.

TABLE IV. Intrinsic temperature dependence of elastic constants.

	α $(10^{-4}\ \mathrm{deg}^{-1})$	$\frac{1}{\alpha}\left(\frac{\partial \ln C_{44}}{\partial T}\right)_v$[a]	$\frac{1}{\alpha}\left(\frac{\partial \ln(C_{11}-C_{44})}{\partial T}\right)_v$[a]	$\frac{2}{3}bz$
Cu	0.70	2.34	3.98	1.80
Ag	0.81	1.42	2.78	2.16
Au	0.58	0.02	2.26	3.76
LiF	1.14	1.23	3.76	1.03
NaCl	1.20	1.59	3.88	0.97
KCl	1.11	3.60	5.26	1.15
TlBr	1.48	1.51	2.46	1.41

[a] From Refs. 36 and 48–51.

7. CONCLUDING REMARKS

We have seen that the anharmonicity makes the lattice unstable above a critical energy, and have shown the close correlation between the temperature corresponding to the critical energy and the observed melting point. From the viewpoint of statistical mechanics, however, it is not sufficient to introduce temperature as treated in the present theory, because the energy per normal mode is not strictly kT because of another effect of anharmonicity. Taking this effect into account, we can construct a self-consistent theory and evaluate the relation between energy and temperature.[52] This treatment, which contains rather complicated calculations, also shows that there is a maximum temperature for a solid, which is somewhat lower than the value of T_m predicted in the present treatment. The estimation in this paper, however, is more simple and sufficient to demonstrate that the anharmonicity of the lattice is connected with melting.

One may be sure that the real melting temperature is determined by the comparison between the free energies of solid and liquid, and that the consideration of the stability of the solid gives *only* an upper limit to the melting point.[53] This concept, however, cannot explain the above-mentioned connection between the critical temperature of the solid and the melting point. This correlation would be ensured by the empirical fact that superheating of solids, i.e., the heating without fusion above the melting point, is scarcely known, while supercooling of liquid is not at all rare in nature.[54] To make the situation clearer, more elaborate investigations will be necessary on the basis of statistical mechanics. There is a possiblity that the vibrational elongation is related to the degree of *disorder* by which melting is governed.

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