MgO has relatively high (cubic) symmetry. In any case the vibrational spectra in $\alpha-Al_2O_3$ are considerably more complicated than the $MgO:V^{2+}$ spectrum indicated in Fig. 6. It is in fact difficult (especially for $\alpha-Al_2O_3:Mn^{4+}$) to separate the effective "one-phonon" density of states from the multiphonon contributions to the vibrational structure.

If and when the lattice spectrum of MgO is determined, the $MgO:V^{2+}$ and $MgO:Cr^{3+}$ cases seem to be promising ones for an attempt to calculate the impurity-phonon interaction from first principles. Not only is the lattice an exceptionally simple one, but the point-charge model has been shown to give quantitatively correct results for the effect on the ^2E state of static strain.[9,16] It remains to be seen if equally good agreement can be obtained for interaction with the phonons.

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Instability in Crystals and Thermal Expansion Coefficients

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An analysis is made of the Grüneisen parameter $\gamma_i=-d\ln\nu_i/d\ln V$, where ν_i is a normal mode frequency and V is the volume for certain ideal and real crystals. It is shown that negative thermal expansion or anomalous positive expansion in a solid is a possible result of an approach to instability of the modes of vibration.

A. INTRODUCTION

THIS paper is an extension of two previous papers,[1] hereafter referred to as I and II. An analysis of the expressions for the Grüneisen parameter derived in these papers indicates the conditions under which a crystal can have negative thermal expansion coefficients or anomalous positive thermal expansion coefficients. Recent experimental evidence[2] shows that certain crystals, such as silicon, ZnS, InSb, SiO_2, and AgI, undergo negative thermal expansion. Blackman[3] has considered an ionic zincblende structure and found from an analysis of the elastic constants that it would have a negative expansion at low temperatures. It was concluded that open structures, those with a coordination number of four and having a very low shear elastic constant (C_{44}), should have a negative thermal expansion.

In I, we considered some ideal cubic crystals having short-range interactions, such as a two-dimensional diatomic square lattice and a simple cubic lattice. It was found that they exhibited negative expansion when they were unstable or approached instability.[4] The following analysis suggests that the instability or approach to instability may be the cause for negative expansion or anomalous positive expansion in a real crystal. Such a possibility is interesting since the explanations for the melting of solids[5] and the ferroelectric transition[6] have been sought in the approach to instability of the acoustic modes in the former situation and the transverse optical modes in the latter.

The volume coefficient of thermal expansion β of a crystal can be written as

$$\beta=(X\Sigma_i\gamma_i\partial E_i/\partial T)/V, \tag{1}$$

with γ_i the Grüneisen parameter given as

$$\gamma_i=-d\ln\nu_i/d\ln V. \tag{2}$$

Here X is the isothermal compressibility, V is the volume, E_i is the thermal energy $\{h\nu_i/[\exp(h\nu_i/kT)-1]\}$, and ν_i is a normal mode frequency. T, h, and k have their usual meaning and the sum over i is to be taken over all normal modes. Since X, V, and $\partial E_i/\partial T$ are always positive, it can be seen that if γ_i is negative for a large number of frequencies or if γ_i is very large and negative ($\gamma_i\to-\infty$) for just a few frequencies, then β will be negative. Expressions for γ_i have been found for several ideal lattices and for a real crystal such as NaCl.[1] It is expected that γ_i will take the same form for many molecular and ionic solids. It can be shown that the conditions under which the lattice approaches nega-

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[1] By paper I, we refer to "Equation of State of Certain Ideal Lattices," Phys. Rev. **131**, 2087 (1963), and by paper II to "Equation of State of Alkali Halides (NaCl)," Phys. Rev. **132**, 73 (1963) both by M. Arenstein, R. D. Hatcher, and J. Neuberger.

[2] R. D. McCammon and G. K. White, Phys. Rev. Letters **10**, 234 (1963).

[3] M. Blackman, Phil Mag. **3**, 831 (1958).

[4] For a discussion of stability of simple lattices, see M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England 1954), Chap. 3.

[5] M. Born, J. Chem. Phys. **7**, 591 (1939); J. H. C. Thompson, Phil. Mag. **44**, 131 (1952).

[6] W. Cochran, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1960), Vol. 9, p. 387.

tive thermal expansion or anomalous positive expansion ($\gamma_i \to \infty$) are the same as the conditions for the lattice to approach instability.

B. IDEAL CRYSTALS

By an ideal crystal, we mean one having short-range forces; that is, we consider nearest and next-nearest-neighbor interactions. Thus, considering a two-dimensional square lattice, the simple cubic, face-centered cubic, and body-centered cubic lattices, an expression for γ_i can be derived[1] from lattice dynamics and put into the form

$$\gamma_i = -(1/L)[r^2\alpha_1'/\alpha_1 + r^2\alpha_2' y/2\pi^2\mu\nu_i^2], \tag{3}$$

where L is the dimension of the lattice, r is the lattice separation, $\alpha_1 = 4r^2 f''(r^2)$, $\alpha_2 = 2f'(r^2)$; $f(r^2)$ is the interatomic potential energy, y is a function of the wave vectors and the lattice separation and depends on the structure of the crystal (for convenience, the values of y for the various lattices are given in the Appendix), μ is the reduced mass of the ions, and the prime indicates derivatives with respect to r^2.

The first term in Eq. (3), $-r^2\alpha_1'/L\alpha_1$, is positive if we consider a Mie-Lennard-Jones interatomic potential energy having the form $-\lambda r^{-m} + \zeta r^{-n}$. where m, n, λ, and ζ are positive parameters characteristic of the lattice. This potential energy has been used often before in the study of crystals. If we assume the equilibrium condition, we have

$$-r^2\alpha_1'/L\alpha_1 = (m+n+4)/2L. \tag{4}$$

The second term $-r^2\alpha_2' y/2\pi^2 L\mu\nu_i^2$ can be shown to be negative. The only quantity in this term which needs examination is $\alpha_2' = 2f''(r^2)$ since all other quantities are obviously positive. We show that this is positive using the equilibrium condition and assuming that the repulsive force is short range so that $n > m$. We have

$$f''(r^2) = n(n-m)\zeta r^{-n-2}/4 > 0. \tag{5}$$

Thus, γ_i will be negative when

$$|r^2\alpha_2' y/2\pi^2 L\mu\nu_i^2| > |r^2\alpha_1'/L\alpha_1| \tag{6}$$

and since the quantity on the right side of Eq. (6) is fixed this condition should be met when $\nu_i^2 \to 0$. Since ν_i varies with y, it is important to look at this term in the long-wave limit. It can be seen from the values of y in the Appendix that $y \to 4\pi^2 K^2 a^2$ for all lattices considered, where a is a lattice constant and K is the wave vector. Thus

$$r^2\alpha_2' y/2\pi^2 L\mu\nu_i^2 \to 2r^2\alpha_2' a^2/L\mu U^2, \tag{7}$$

where U is the elastic wave velocity. U can be expressed in terms of the elastic constants C_{11}, C_{12}, and C_{44}. For certain directions in the crystals (for example, the [100] direction) we have for longitudinal (U_l) and transverse (U_t) elastic waves, the relations $\rho U_l^2 = C_{11}$ and $\rho U_t^2 = C_{44}$, where ρ is the density.

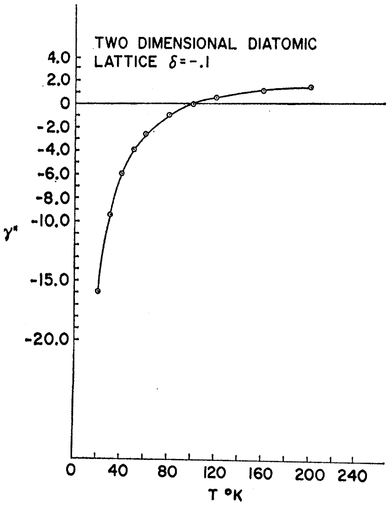

FIG. 1. Grüneisen parameter γ'' vs temperature for a two-dimensional diatomic lattice with one mass double the other and with central forces $\sigma_2/\sigma_1 = \delta = -0.1$.

For cubic lattices with central forces, $C_{12} = C_{44}$ and the stability conditions can be written as $C_{12} > 0$ and $C_{11} - C_{12} > 0$. More generally a crystal will be stable for all small deformations if the normal modes have real frequencies. Thus as $\nu \to 0$ or as $C_{44} = C_{12} \to 0$ we see that $2r^2\alpha_2' a^2/L\mu U^2 \to \infty$ giving us a large negative value for γ_i and at the same time the lattice approaches instability. That this occurs for the two-dimensional square lattice and the simple cubic lattice can easily be seen. We have for the two-dimensional lattice that

$$\rho U_l^2 = \sigma_1 + \sigma_2, \quad \rho U_t^2 = \sigma_2, \tag{8}$$

where σ_1 and σ_2 are, respectively, the nearest-neighbor and next-nearest-neighbor Hooke's law constants. Thus $\sigma_2 = C_{44}$ and for σ_2 negative the lattice is unstable. In finding the thermal expansion coefficient for this lattice in I, negative eigenvalues of the dynamical matrix were excluded. However, the reduction of ρU_t^2, as well as the over-all smaller values for the frequencies, cause the thermal expansion coefficient to become negative. If we define a weighted temperature-dependent Grüneisen parameter as

$$\gamma''(V,T) = \Sigma_i\gamma_i\partial E_i/\partial T/\Sigma_i\partial E_i/\partial T \tag{9}$$

such that Eq. (1) can be written as

$$\beta = X\gamma''(V,T)\Sigma_i\partial E_i/\partial T/V_a, \tag{10}$$

then we can characterize the thermal expansion by the value of γ'' at a particular temperature. Examining Fig. (1) we note that $\gamma''(V,T)$ is zero at 100°K and negative below that temperature.

The simple cubic lattice is known to be unstable under homogeneous deformations as all neighbors are considered and the interatomic potential energy is of the Mie-Lennard-Jones form.[4] For the simple cubic lattice we have

$$(\sigma_1 + 2\sigma_2)/a = C_{11} - C_{44} \tag{11}$$
$$2\sigma_2/a = C_{44} = C_{12}.$$

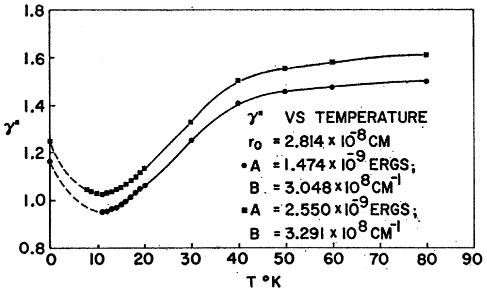

FIG. 2. Grüneisen parameter γ'' vs temperature for a modified Kellermann model of NaCl utilizing a frequency spectrum of 11 454 frequencies and γ_i's.

Thus choosing σ_2 to be very small, we have C_{44} small. σ_2/σ_1 was chosen in I to be 0.1 with the result that the lattice underwent negative thermal expansion at low temperatures.

C. REAL CRYSTALS

By a real crystal we refer to a model of a solid which considers long range forces. Thus a Kellermann model of NaCl,[7] as well as a modified Kellermann model, is considered. In these models the Coulomb interaction between all ions was taken into account along with short range repulsive forces. The models differ in that repulsive term for the modified model is taken to be a Born-Mayer repulsive potential energy Ae^{-Br}, where A and B are variable parameters which are adjusted to give good results compared to experiment, whereas the Kellermann model considers a repulsive potential energy of the form cr^{-n}, where c and n are constants which are eliminated in the final equations by applying the equilibrium and compressibility conditions.

An expression for γ_i was obtained in II for these models of NaCl by perturbation theory and we expect the same general form for many other ionic crystals. For the modified Kellermann model we have

$$\gamma_i=\tfrac{1}{2}[1-(e^2/6r_0^2\omega^2)(dB_{mm}/dr)], \tag{12}$$

where ω is the circular frequency, e is the charge of the electron, r_0 is the lattice separation;

$$\begin{aligned} dB_{mm}/dr=R'\{&(1/\mu_1)[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]\\ &+(1/\mu_2)[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]\\ &-2/(\mu_1\mu_2)^{1/2}(U_{1m}{}^0U_{2m}{}^0\cos\pi q_x\\ &+U_{3m}{}^0U_{4m}{}^0\cos\pi q_y+U_{5m}{}^0U_{6m}{}^0\cos\pi q_z)\}\\ &+2S'\{(1/\mu_1)[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]\\ &+(1/\mu_2)[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m}{}^0)^2]\\ &-1/(\mu_1\mu_2)^{1/2}[(\cos\pi q_y+\cos q_z)U_{1m}{}^0U_{2m}{}^0\\ &+(\cos\pi q_x+\cos\pi q_z)U_{3m}{}^0U_{4m}{}^0\\ &\qquad+(\cos\pi q_x+\cos\pi q_y)U_{5m}{}^0U_{6m}{}^0]\} \end{aligned} \tag{13}$$

with

$$\begin{aligned} R'&=(4B^2A/e^2)(3r_0^2-Br_0^3)e^{-Br_0},\\ S'&=-(4BA/e^2)(2r_0-B_0r^2)e^{-Br_0}; \end{aligned} \tag{14}$$

where μ_1 and μ_2 are the masses of the ions, U^0 is an unperturbed orthonormalized eigenvector which comes from the equation of motion of the ions and is therefore the amplitude of the displacement, and $\mathbf{q}=2r_0\boldsymbol{\sigma}$, where $\boldsymbol{\sigma}$ is the wave vector. If it can be shown that we can have $dBmm/dr>0$, then as $\omega\rightarrow 0$, we will have $\gamma_i\rightarrow-\infty$. Consider Eq. (13) and let $\mu_1=\mu_2=\mu$, which should not affect our results, but will make our expression easier to handle. We then have

$$\begin{aligned} dBmm/dr=(R'+2S'/\mu)-2R'/\mu(&U_{1m}{}^0U_{2m}{}^0\cos\pi q_x\\ &+U_{3m}{}^0U_{4m}{}^0\cos\pi q_y+U_{5m}{}^0U_{6m}{}^0\cos\pi q_z)\\ &-2S'/\mu[(\cos\pi q_y+\cos\pi q_z)U_{1m}{}^0U_{2m}{}^0\\ &+(\cos\pi q_x+\cos\pi q_z)U_{3m}{}^0U_{4m}{}^0+(\cos\pi q_x\\ &\qquad+\cos\pi q_y)U_{5m}{}^0U_{6m}{}^0]. \end{aligned} \tag{15}$$

The first term $(R'+2S'/\mu)=4BAr_0e^{-Br_0}/e^2\mu(Br_0-4)\times(-Br_0+1)$ is negative except when $1\leqq Br_0\leqq 4$. Thus, for some particular directions in the crystal where the second and third terms vanish or do not overweight the first term,[8] we have $dBmm/dr>0$. A small value for Br_0 corresponds to a rather long range repulsive force, whereas it is found for a crystal such as NaCl that $Br_0\sim 9$ and, therefore, one finds mostly positive γ_is. Negative values for γ_i were found for NaCl for the transverse acoustic branch indicating that even for $Br_0\sim 9$ that the second term on the right of Eq. (15) can dominate and with $R'<0$ cause $dBmm/dr>0$. Since these negative γ_i's were very small in number compared with the total spectrum and were small in magnitude, negative expansion could not occur. In fact, since $dBmm/dr<0$, then as $\omega\rightarrow 0$ we should expect rather large values for γ_i. Examining Fig. (2), we note that $\gamma''(V,T)$ approaches a minimum at 11°K and then rises to its value at 0°K. Low frequencies or acoustic modes dominate at low temperature and this accounts for the behavior of $\gamma''(V,T)$. Recently, S. Ganesan and R. Srinivasan,[9] have investigated an equivalent temperature-dependent Grüneisen parameter for the CsCl structure. This lattice is known to become unstable for $n\leqq 7.3$. As they reduced the value of n from 30 to 8, it was found that γ'' grew very large at low temperatures, indicating that as instability is approached the lattice undergoes an anomalous positive thermal expansion.

An interesting aspect of negative thermal expansion with regard to the compressibility X can be seen by examining the Grüneisen parameter γ_i derived in II from the Kellermann model.

We have

$$\gamma_i=\tfrac{1}{2}\left\{1-\frac{2\Gamma}{\omega^2}\left[\frac{4r}{X}-\frac{r^2}{X^2}\frac{\partial X}{\partial r}\right]_T\right\}, \tag{16}$$

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[7] E. W. Kellermann, Trans. Roy. Soc. (London) **238**, 513 (1940).

[8] It should be noted that due to the orthonormality of the eigenvectors some of the terms $U_{im}{}^0\cdot U_{jm}{}^0$ $i\neq j$ are negative and therefore the terms in parentheses and brackets can be either positive or negative depending on direction in the crystal and the frequency.

[9] S. Ganesan and R. Srinivasan, Proc. Roy. Soc. (London) **271**, 154 (1963).

where

$$\Gamma=(1/\mu_1)[(U_{1m}{}^0)^2+(U_{3m}{}^0)^2+(U_{5m}{}^0)^2]$$
$$+(1/\mu_2)[(U_{2m}{}^0)^2+(U_{4m}{}^0)^2+(U_{6m})^2]$$
$$+[2/(\mu_1\mu_2)^{1/2}](U_{1m}{}^0U_{2m}{}^0\cos\pi q_x+U_{3m}{}^0U_{4m}{}^0\cos\pi q_y$$
$$+U_{5m}{}^0U_{6m}{}^0\cos\pi q_z)\,. \quad (17)$$

For positive Γ the condition for negative thermal expansion is

$$\left[\frac{4r}{X}-\frac{r^2}{X^2}\left(\frac{\partial X}{\partial r}\right)_T\right]>0 \quad \text{as} \quad \omega\rightarrow 0.$$

This will occur when $\partial X/\partial r$ is very small, zero, or negative. We may expect then that the isothermal compressibility approaches a minimum as the lattice contracts and then increases as the lattice expands.

Since, as was indicated in the introduction, instability in the optical or acoustical modes may be present at a phase transition, the thermal expansion at these transitions may give valuable information concerning the mechanism causing the transition. For example, the anomalous thermal expansion in antiferromagnetic materials[10] indicates that either phonon modes or magnon modes or both approach instability.

The ferroelectric transition from the cubic to the tetragonal phase in $BaTiO_3$ is thought to occur when the transverse optic mode frequencies ω_T approach zero.[6] One may expect large positive or negative γ_i's associated with these low transverse optical modes. We can write for ω_T that

$$\mu\omega_T{}^2=R_0'-[4\pi(\epsilon+2)(Z'e)^2/9V_a], \quad (18)$$

where μ is the reduced mass of the ions, R_0' is the short range force constant, $Z'e$ is the effective ionic charge, ϵ is the high-frequency dielectric constant, and V_a is the volume of the unit cell. We have for γ_i

$$\gamma_i=-\frac{V_a}{2\mu\omega_T{}^2}\left[\frac{dR_0'}{dV}+\frac{4\pi(\epsilon+2)(Z'e)^2}{9V_a{}^2}\right]. \quad (19)$$

The term $4\pi(\epsilon+2)(Z'e)^2/9V_a{}^2$ is positive, and even if dR'/dV is negative, as the lattice contracts, the former term can become larger than the latter. Therefore, if

$$|4\pi(\epsilon+2)(Z'e)^2/9V_a{}^2|>|dR_0'/dV|, \quad (20)$$

γ_i will be negative and becomes quite large as $\omega_T\rightarrow 0$. Experimental evidence[11] shows that as the transition point is approached from the cubic phase a single crystal of $BaTiO_3$ contracts. At the transition point a spontaneous expansion occurs apparently due to electrostrictive effects. It is suggested that the lattice vibrations also contribute to this effect although it is difficult to estimate the magnitude of their contribution. One must remember that no large negative expansion should be expected since it is only the transverse optical mode which is assumed to become unstable while the other modes remain uneffected. However, one may find fairly large effects, i.e., negative thermal expansion or anomalous positive expansion, if experiments which properly account for the electrostrictive effect are performed on single crystal ferro-electrics having low-temperature transition points.

D. CONCLUSIONS

We conclude that those crystals which approach an instability in some of their normal mode frequencies will either undergo negative thermal expansion or anomalous positive thermal expansion. If we follow the rule of thumb that the stability of a crystal varies with the coordination number (being most stable for the highest coordination number and less stable for low coordination number), we see why Blackman found that those crystals with a coordination number of four undergo negative thermal expansion. It is suggested that the nature of a phase transition in a crystal as well as the nature of the ionic and covalent forces in the low coordination number crystals may be determined through careful thermal expansion experiments.

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APPENDIX

The values of y for the various ideal lattices which were derived in I are given here for convenience. K_i $i=1$, 2, 3 is the wavevector and a is the distance between nearest neighbors in the two-dimensional square lattice and simple cubic lattice, whereas it is the distance between next-nearest neighbors in the face-centered cubic and body-centered cubic lattices.

(a) Two-dimensional square lattice;
$y=4-2[\cos 2\pi K_1a+\cos 2\pi K_2a]$.

(b) Simple cubic lattice;
$y=6-2[\cos 2\pi K_1a+\cos 2\pi K_2a+\cos\pi K_3a]$.

(c) Face-centered cubic lattice;
$y=12-4[\cos\pi K_1a\,\cos\pi K_2a+\cos\pi K_3a\,\cos\pi K_2a+\cos\pi K_1a\,\cos\pi K_3a]$.

(d) Body-centered cubic lattice;
$y=8-2[\cos\pi a(K_1+K_2+K_3)+\cos\pi a(-K_1+K_2+K_3)+\cos\pi a(K_1-K_2+K_3)+\cos\pi a\times(K_1+K_2-K_3)]$.

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[10] C. G. Skull and E. O. Wollan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 137.

[11] F. Jona and G. Shirane, in *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962), Chap. 4.