

## Fourth-order elastic constants and the temperature dependence of second-order elastic constants in cubic materials\*

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A theory analyzing the temperature dependence of second-order elastic constants on the basis of a quasiharmonic-anisotropic-continuum model is applied to LiBr, KCl, RbF,  $\beta$ -brass, Cu, Ag, and Au. The number of fourth-order elastic constants is reduced from 11 to 2 by assuming that nearest-neighbor (nn) and next-nearest-neighbor (nnn) central-force interactions predominate in fourth order. The fourth-order elastic constants found from the experimental results show that nn interactions are dominant for the NaCl structure and that nnn interactions are dominant for the CsCl structure, as would be expected for a potential containing a term describing a rapidly varying central-core repulsion. Using recent measurements for Cu in the low-temperature  $T^4$  regime where the anisotropic-continuum theory should be exact, a potential is derived which is in close agreement with one used extensively in point-defect calculations.

### I. INTRODUCTION

Information about higher-order elastic constants is extremely useful for understanding the nature of short-range repulsive forces in solids.<sup>1,2</sup> This information is most readily obtainable through study of the anharmonic properties of particular materials. For example, the thermal expansion<sup>3</sup> and the pressure dependence of second-order elastic constants<sup>1,2</sup> are both expressible in terms of second- and third-order elastic constants, while the temperature dependence of second-order elastic constants<sup>2,4,5</sup> is expressible in terms of second-, third-, and fourth-order elastic constants. This latter relation, which was derived in the preceding article<sup>5</sup> (hereafter referred to as I) on the basis of a quasiharmonic-anisotropic-continuum model, will be used here.

Explicit expressions for the high-temperature (linear), low-temperature ( $T^4$ ), and zero-point ( $T=0$ ) elastic constant changes are given in I. The low-temperature  $T^4$  regime corresponds to the  $T^3$  regime of the Debye theory of specific heat, and the elastic theory given in I should agree with the thermal data in the same sense that the Debye temperature can be calculated from elastic data. More explicitly, the theory takes account of polarization and orientation dependence of phonon frequencies and their strain derivatives, but assumes the derivatives are wavelength independent. At low temperatures, where the phonons have long wavelengths, these quantities should be describable in terms of the static second-, third- and fourth-order elastic constants.

In particular the fourth-order elastic constants of LiBr, KCl, RbF,  $\beta$ -brass, Cu, Ag, and Au will be estimated using known values of second-order elastic constants near 0 K and at 300 K in con-

junction with experimental and theoretical estimates of the second- and third-order elastic constants. This is an extension of the approach of Hiki *et al.*<sup>4</sup> (noble metals), Swartz<sup>2</sup> (NaCl), and Swartz *et al.*<sup>6</sup> ( $\beta$ -brass), who worked solely in the high-temperature region. Another difference in the present work is that theoretical expressions rather than experimental results will be used for the isothermal to adiabatic and constant-volume to constant-pressure corrections to the temperature dependence of the second-order elastic constants. It will be seen that the fourth-order elastic constants found here are quite reasonable, although there are not yet sufficient low-temperature data available for crucial tests of the theory.

A great deal of experimental work has been done on the alkali halides,<sup>7-11</sup>  $\beta$ -brass,<sup>6,12,13</sup> and the noble metals.<sup>14-16</sup> The data, where available at the highest temperatures, show that the elastic constants are linear functions of temperature up to the melting point.<sup>16</sup> This justifies the quasiharmonic approximation used in I, as anharmonic effects would lead to nonlinear temperature dependences at high temperatures. However, most of these results are of such a form that they cannot be readily compared with theory. For example, measurements on the same material by different workers often show variations which are greater than the effects under examination here. Also there is only one material (Cu) for which data in the low-temperature  $T^4$  regime are available. In this work only a small sample of experimental results will be dealt with. This will be materials for which suitable information exists for both third-order elastic constants and the temperature dependence of the second-order elastic constants. Agreement between theory and experiment will be seen to be dependent on the particular material and

second-order elastic constant under consideration.

## II. TREATMENT OF FOURTH-ORDER ELASTIC CONSTANTS

The expressions for the temperature dependence of the second-order elastic constants derived in I show a linear relationship to the fourth-order elastic constants, which will be treated as parameters of the model. As listed in Table I of I there are eleven fourth-order elastic constants in cubic materials. However, there are only three second-order elastic constants to work with. In order to reduce the number of parameters to be determined, a number of assumptions will be made. First, it will be assumed that the following Cauchy relations<sup>17,18</sup> hold for the fourth-order elastic constants:

$$C_{1112} = C_{1155}, \quad (2.1)$$

$$C_{1122} = C_{1266} = C_{4444}, \quad (2.2)$$

$$C_{1123} = C_{1144} = C_{1255} = C_{1456} = C_{4455}. \quad (2.3)$$

Then only four of the constants need to be considered, e.g.,  $C_{1111}$ ,  $C_{1112}$ ,  $C_{1122}$ , and  $C_{1123}$ . Basically we are assuming that the short-range repulsive forces, which contribute the most to the higher-order elastic constants, may be reasonably represented by central forces. Secondly, it will be assumed that only nearest-neighbor and (in the case of the alkali halides and  $\beta$ -brass) next-nearest-neighbor interactions contribute to the fourth-order elastic constants.<sup>2,4,6</sup> This assumption follows from the predominant contribution of the short-range forces to these higher-order elastic constants. The following relations hold under the above assumptions<sup>18</sup>:

for the NaCl structure:

$$C_{1112} = C_{1122} \text{ and } C_{1123} = 0;$$

for the CsCl structure:

$$C_{1112} = C_{1122} = C_{1123};$$

for the fcc structure:

$$C_{1112} = C_{1122} = \frac{1}{2} C_{1111}$$

and

$$C_{1123} = 0.$$

For the NaCl structure only next-nearest-neighbor interactions contribute to  $C_{1112}$  and  $C_{1122}$ . For the CsCl structure only nearest-neighbor interactions contribute to  $C_{1112}$ ,  $C_{1122}$ , and  $C_{1123}$ . For the fcc structure next-nearest-neighbor interactions contribute nothing to  $C_{1112}$ ,  $C_{1122}$ , and  $C_{1123}$  and contribute relatively little to  $C_{1111}$  in comparison with nearest-neighbor interactions; hence only the latter are being taken into account for the fcc struc-

ture.

The number of parameters has now been reduced from eleven to two, say  $C_{1111}$  and  $C_{1112}$ , in the case of the NaCl and CsCl structures, and to one, say  $C_{1111}$ , in the case of the fcc structure. Thus, an analysis of the temperature dependence of three second-order elastic constants should overdetermine their coefficients and provide checks on the simplifying assumptions made.

## III. COMPUTATIONAL DETAILS

In I, results were expressed in terms of summations over directions  $\vec{n}$ . Evaluation of an expression for a given direction  $\vec{n}$  is performed at the center of the element of solid angle  $\Delta\Omega_{\vec{n}}$ . The three components of  $\vec{n}$  are given by

$$n_1 = \sin\theta \cos\phi, \quad (3.1)$$

$$n_2 = \sin\theta \sin\phi, \quad (3.2)$$

and

$$n_3 = \cos\theta; \quad (3.3)$$

furthermore,

$$\Delta\Omega_{\vec{n}} = 2 \sin\theta \sin\left(\frac{1}{2}\Delta\theta\right)\Delta\phi. \quad (3.4)$$

In the above equations  $\theta$  and  $\phi$  are spherical angles and  $\Delta\theta$  and  $\Delta\phi$  are the increments of spherical angle indicated in Fig. 1. By cubic symmetry one need only work with directions in one octant and then multiply the result by eight.  $\Delta\theta$  and  $\Delta\phi$  may be determined for a given direction by dividing an octant of the Debye sphere into a network of nearly equal areas with  $\Delta\theta$  equal to  $(\frac{1}{2}\pi)/m$ , where  $m$  is an integer constant, and  $\Delta\phi$  equal to  $(\frac{1}{2}\pi)/m'$ , where  $m'$  is an integer which varies with  $\theta$ . We choose  $m'$  so as to give areas that are nearly equal by equating  $\Delta A/m'$  as closely as possible to  $\Delta A_{\text{bottom}}/m$ , where  $\Delta A$  is the area of a typical strip of sur-

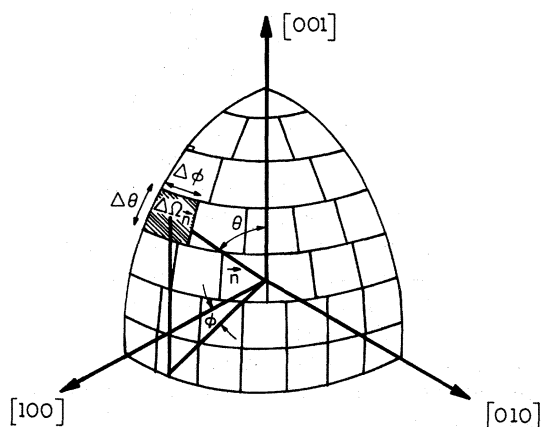


FIG. 1. Network of elements of solid angle  $\Delta\Omega_{\vec{n}}$  over one octant of the Debye sphere.

face elements of constant  $\theta$  in the octant and  $\Delta A_{\text{bottom}}$  is the area of the bottom strip. Then

$$\begin{aligned} m' &\approx m \Delta A / \Delta A_{\text{bottom}} = m \sin \theta / \sin(\frac{1}{2}\pi - \frac{1}{2}\Delta\theta) \\ &= m \sin \theta / \cos(\frac{1}{2}\Delta\theta), \end{aligned} \quad (3.5)$$

where Eq. (3.4) has been used with  $\Delta\phi$  equal to  $\frac{1}{2}\pi$ . Thus  $m'$  is given by  $m \sin \theta / \cos(\frac{1}{2}\Delta\theta)$  rounded to the nearest integer. In the present work  $m$  was chosen to be 24; with this choice there are 366 directions over the octant.

#### IV. ALKALI HALIDES AND $\beta$ -BRASS

In determining the fourth-order elastic constants from the temperature dependence of the second-order elastic constants, the various quantities arising in the expressions given in I must first be evaluated. The notation of I is now adopted. For example, the factor  $N_A/N$  used in the expressions for the low-temperature region is simply  $\frac{1}{2}$  for the alkali halides and  $\beta$ -brass because half of the modes are acoustical modes and the other half are optical. The particle density  $N/V_0$  is  $8/R^3$  in the NaCl structure and  $2/R^3$  in the CsCl structure, where  $R$  is the lattice constant. The mass density  $\rho$  is given by

$$\rho = \frac{M(N/V_0)}{sL}, \quad (4.1)$$

where  $M$  is the molecular weight,  $s$  is the number of different kinds of particles in the crystal, and  $L$  is Avogadro's number.

We now consider the problem of how to evaluate the various quantities for the static lattice, denoted by superscript 0. For the lattice constant this problem is readily solved by making use of the relation, valid to first order in strain,

$$R^0 = R^h(1 - \eta^h) = R^h(1 - \frac{1}{3}\beta^h T), \quad (4.2)$$

where the superscript  $h$  refers to the high-temperature region. In this region the vibrational strain parameter  $\eta$  is proportional to the temperature  $T$  [Eq. (3.5) of I] and the volume thermal expansion  $\beta$ . In practice the room-temperature values for  $R^h$  and  $\beta^h$  ( $T = 300$  K) will be used.

The question of evaluating the static lattice second- and third-order elastic constants is not as straightforward. In principle, these elastic constants can be evaluated by extrapolation of the high-temperature linear region back to 0 K. However, there is considerable uncertainty in determining the high-temperature asymptote. More importantly, experimental data on the temperature dependence of the third-order elastic constants, and even on the room-temperature values of the third-order elastic constants for most materials, are unavailable. In this work experimental room-temperature values for the second-

and third-order elastic constants are used when both are available; when experimental third-order elastic constants are not available (LiBr, RbF), Ghate's calculated 0 K values<sup>19</sup> in conjunction with experimental 0-K second-order elastic constants are used. The justification for this approach is that the expression for the temperature dependence of the second-order elastic constants derived in I involve ratios of the static-lattice third-order and second-order elastic constants. We will assume that the ratios for the static-lattice elastic constants are approximately equal to the ratios for the elastic constants at a given temperature.

Table I lists the structure (NaCl or CsCl), molecular weight  $M$ , room-temperature lattice constant  $R^h$ , room-temperature volume thermal expansion  $\beta^h$ , calculated static-lattice constant  $R^0$ , calculated static-lattice particle density  $N/V_0^0$ , calculated static-lattice mass density  $\rho^0$ , and input second- and third-order elastic constants for LiBi, KCl, RbF, and  $\beta$ -brass.  $\beta$ -brass (Cu-Zn) assumes the CsCl crystal structure and hence may be analyzed by the same approach used for the alkali halides.

Table II, shows how the expressions for the temperature dependence of the second-order elastic constants are linearly related to  $C_{1111}$  and  $C_{1112}$  for LiBr, KCl, RbF, and  $\beta$ -brass (see Sec. II). In these tables  $C'$  is given by

$$C' = \frac{1}{2}(C_{11} - C_{12}). \quad (4.3)$$

$C'$  is a more useful elastic constant for the purpose of comparison with experiment than  $C_{12}^S$  is because it is directly measurable from experiment while  $C_{12}^S$  is found by taking the difference between experimentally measurable quantities which for the alkali halides are usually much larger than their difference.

If data in the low-temperature  $T^4$  regime were available, we would proceed by using these to determine the fourth-order constants. The three measurements for two constants would provide a test of the two fourth-order elastic-constant assumption. The three high-temperature linear coefficients and the three zero-point changes could then be calculated and compared with experiment. This would test the assumption of wavelength independence of the phonon frequencies and their strain derivatives. However, as there are no measurements in the  $T^4$  regime for these materials we simply attempt to see if reasonable values of the two fourth-order elastic constants are obtained when the data are fit in an overall sense to be described.

We will use the following iterative procedure to determine  $C_{1111}$  and  $C_{1112}$  from the linear relations of Table II plus certain experimental information about the second-order elastic constants. First we make an initial estimate of  $dC_{11}^{Sh}/dT$  and  $dC_{44}^h/$

TABLE I. The structure, molecular weight  $M$ , room-temperature lattice constant  $R^h$ , room-temperature volume thermal expansion  $\beta^h$ , calculated static-lattice constant  $R^0$ , calculated static-lattice particle density  $N/V_0^0$ , calculated static-lattice mass density  $\rho^0$ , and input second- and third-order elastic constants ( $10^{10}$  dyn/cm<sup>2</sup>) for three alkali halides and  $\beta$ -brass. [Values for  $M$  were taken from the *Handbook of Chemistry and Physics*, 51st ed. (The Chemical Rubber Co., Cleveland, Ohio, 1970-71).]

Material	Structure	$M$	$R^h$ ( $10^{-5}$ cm)	$\beta^h$ ( $10^{-5}$ /K)	$R^0$ ( $10^{-8}$ cm)	$N/V_0^0$ ( $10^{22}$ /cm <sup>3</sup> )	$\rho^0$ (g/cm <sup>3</sup> )
LiBr	NaCl	86.85	5.49 <sup>a</sup>	15 <sup>b</sup>	5.41	5.05	3.64
KCl	NaCl	74.56	6.28 <sup>a</sup>	11.04 <sup>c</sup>	6.21	3.34	2.07
RbF	NaCl	104.47	5.64 <sup>a</sup>	9.5 <sup>d</sup>	5.59	4.58	3.97
$\beta$ -brass	CsCl	128.91	2.94 <sup>e</sup>	7.8 <sup>e</sup>	2.92	8.03	8.59

Material	$C_{11}$	$C_{12}$	$C_{44}$	$C_{111}$	$C_{112}$	$C_{166}$	$C_{123}$	$C_{144}$	$C_{456}$
LiBr	47.21	15.90	20.52 <sup>f</sup>	-863.8	-71.96	-71.96	28.89	28.89	28.89 <sup>g</sup>
KCl	40.90	7.0 <sup>h</sup>	6.27 <sup>h</sup>	-726	-24	-26	11	23	16 <sup>h</sup>
RbF	65.27	12.55	9.520 <sup>i</sup>	-943.7	-62.11	-62.11	25.86	25.86	25.86 <sup>g</sup>
$\beta$ -brass	124.1	104.2	80.9 <sup>j</sup>	-1252.2	-475.2	-395.6	-466.6	-384.7	-397.8 <sup>j</sup>

<sup>a</sup>See Ref. 20.

<sup>b</sup>See Ref. 21.

<sup>c</sup>See Ref. 22.

<sup>d</sup>See Ref. 23.

<sup>e</sup>See Ref. 12.

<sup>f</sup>See Ref. 24.

<sup>g</sup>See Ref. 19.

<sup>h</sup>See Ref. 25.

<sup>i</sup>See Ref. 26.

<sup>j</sup>See Ref. 6.

$dT$  from the experimental curves. Next we use the appropriate linear relations to find initial estimates for  $C_{1111}$  and  $C_{1112}$ . Then we go through the following series of steps for ten iterations: (i) We calculate the zero-point effect for  $C_{11}$  and  $C_{44}$  from  $C_{1111}$  and  $C_{1112}$  using the appropriate linear relations; (ii) we calculate  $\tilde{C}_{11}^0$  and  $\tilde{C}_{44}^0$  from the zero-point effect plus experimental values for  $C_{11}^{0K}$  and  $C_{44}^{0K}$ ; (iii) we calculate new values for  $dC_{11}^{Sh}/dT$  and  $dC_{44}^h/dT$  from the relation

$$\frac{dC_{ijkl}^{Sh}}{dT} = \frac{C_{ijkl}^{S, 300K} - \tilde{C}_{ijkl}^0}{300} K^{-1}, \quad (4.4)$$

where we use experimental values for the second-order elastic constants at room temperature  $C_{ijkl}^{S, 300K}$ ; and (iv) we calculate new values for  $C_{1111}$  and  $C_{1112}$  using the appropriate linear relations and the new values of  $dC_{11}^{Sh}/dT$  and  $dC_{44}^h/dT$ . It has been found that this process generally reaches the limit values to within 0.1% in less than ten iterations. Once the final values for  $C_{1111}$  and  $C_{1112}$  are found, we may use the linear relations to predict the zero-point effect,  $T^4$  curve, and high-temperature asymptote for all the elastic constants.

Table III lists the final values of  $C_{1111}$  and  $C_{1112}$

TABLE II. Calculated temperature dependence of the second-order elastic constants in terms of  $C_{1111}$  and  $C_{1112}$  ( $10^{10}$  dyn/cm<sup>2</sup>) for LiBr, KCl, RbF, and  $\beta$ -brass.

Elastic constant	Coefficient of $C_{1111}$ (units of $10^{-4}$ )				Coefficient of $C_{1112}$ (units of $10^{-4}$ )				Constant term			
	LiBr	KCl	RbF	$\beta$ -brass	LiBr	KCl	RbF	$\beta$ -brass	LiBr	KCl	RbF	$\beta$ -brass
( $10^8$ dyn/cm <sup>2</sup> K)												
$dC_{11}^{Sh}/dT$	4.19	3.61	3.16	4.29	22.2	33.9	30.0	12.1	-8.63	-6.57	-7.43	-9.71
$dC_{12}^{Sh}/dT$	0	0	0	0	15.3	20.6	18.2	16.4	-1.27	-0.240	-0.590	-4.96
$dC_{44}^h/dT$	0	0	0	0	15.3	20.6	18.2	16.4	-0.809	-0.257	-0.683	-4.95
$ac^h/dT$	2.10	1.80	1.58	2.14	3.46	6.68	5.93	-2.14	-3.68	-3.17	-3.42	-2.38
( $10^{10}$ dyn/cm <sup>2</sup> )												
$\tilde{C}_{11}^0 - C_{11}^{0K}$	-3.45	-3.01	-2.64	-3.08	-19.6	-22.1	-19.5	-16.1	6.76	4.81	5.41	9.14
$\tilde{C}_{12}^0 - C_{12}^{0K}$	0	0	0	0	-13.3	-14.1	-12.4	-19.2	1.02	0.269	0.583	5.67
$\tilde{C}_{44}^0 - C_{44}^{0K}$	0	0	0	0	-13.3	-14.1	-12.4	-19.2	0.642	0.166	0.460	4.63
$\tilde{C}^{0K} - C^{0K}$	-1.73	-1.51	-1.32	-1.54	-3.17	-4.02	-3.55	1.54	2.87	2.27	2.41	1.73
( $10^2$ dyn/cm <sup>2</sup> K <sup>4</sup> )												
$(C_{11}^{0K} - C_{11}^{S1})/T^4$	-2.25	-2.05	-1.83	-5.55	-9.49	-42.3	-38.8	0.454	5.19	5.56	6.96	9.87
$(C_{12}^{0K} - C_{12}^{S1})/T^4$	0	0	0	0	-7.00	-23.2	-21.2	-5.09	0.928	0.230	0.201	1.13
$(C_{44}^{0K} - C_{44}^{S1})/T^4$	0	0	0	0	-7.00	-23.2	-21.2	-5.09	0.479	0.400	0.943	4.10
$(C^{0K} - C^{S1})/T^4$	-1.13	-1.03	-0.917	-2.77	-1.25	-9.54	-8.78	2.77	2.13	2.66	3.38	4.37

TABLE III. Calculated values of  $C_{1111}$  and  $C_{1112}$  ( $10^{10}$  dyn/cm<sup>2</sup>) for three alkali halides and  $\beta$ -brass.

Material	$C_{1111}$	$C_{1112}$	Reference for experimental values used in the calculation
LiBr	12 000 <sup>a</sup>	35.4 <sup>a</sup>	Marshall and Cleavelin (Ref. 24)
KCl	8280 <sup>a</sup>	55.9 <sup>a</sup>	Norwood and Briscoe (Ref. 27)
RbF	6600 <sup>a</sup>	310 <sup>a</sup>	Cleavlin <i>et al.</i> (Ref. 26)
$\beta$ -brass	12 800 <sup>a</sup>	743 <sup>a</sup>	McManus (Ref. 12)
$\beta$ -brass	12 100 <sup>b</sup>	1070 <sup>b</sup>	McManus (Ref. 12)
$\beta$ -brass	15 600 <sup>c</sup>	2390 <sup>c</sup>	Swartz <i>et al.</i> (Ref. 6)

<sup>a</sup>Values found by using  $C_{11}^S$  and  $C_{44}$ .

<sup>b</sup>Values found by using  $C_{11}^S$  and  $C_{12}^S$ .

<sup>c</sup>Swartz *et al.* (Ref. 6).

found by the method described above, for LiBr, KCl, RbF, and  $\beta$ -brass. It also gives values of  $C_{1111}$  and  $C_{1112}$  for  $\beta$ -brass, where we have used  $C_{12}^S$  rather than  $C_{44}$  in the method described above, as well as the Swartz *et al.*<sup>6</sup> values of  $C_{1111}$  and  $C_{1112}$  for  $\beta$ -brass. Figures 2–4 give the theoretical and experimental temperature dependences of  $C_{11}^S$ ,  $C_{44}$ , and  $C'$  for LiBr, KCl, and RbF. In these figures we have fit the theoretical  $T^4$  curves to the 0 K experimental values. Also, the iteration process that we have used forces the high-temperature asymptotes for  $C_{11}^S$  and  $C_{44}$  to pass through the 300 K experimental values.

As expected for a repulsive potential,  $C_{1111}$  and  $C_{1112}$  are found to be positive.  $C_{1111}$  is always much larger than  $C_{1112}$ ; thus nearest-neighbor (nn) inter-

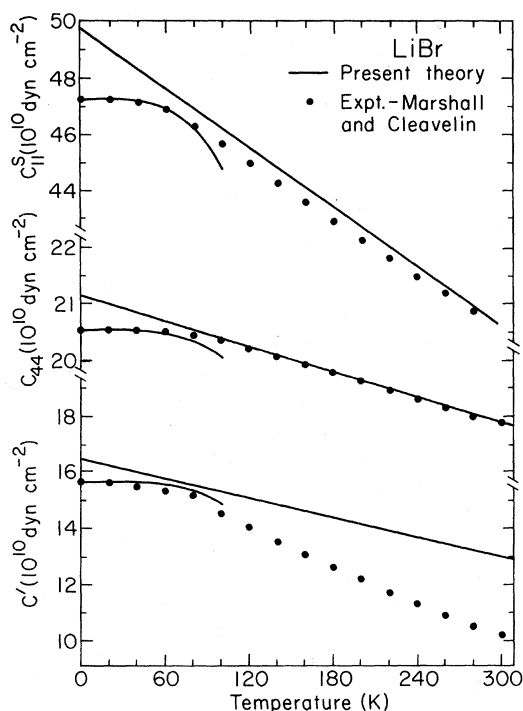


FIG. 2.  $C_{11}^S$ ,  $C_{44}$ , and  $C'$  vs temperature in LiBr.

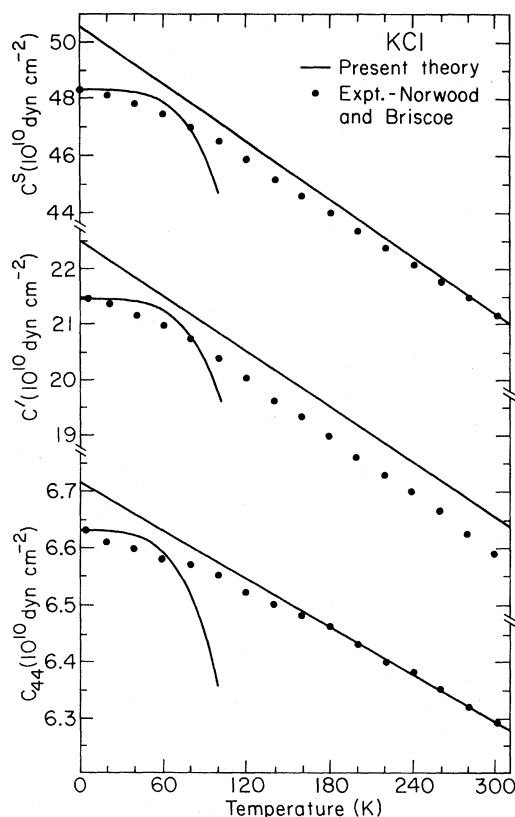


FIG. 3.  $C_{11}^S$ ,  $C_{44}$ , and  $C'$  vs temperature in KCl.

actions predominate for LiBr, KCl, and RbF while next-nearest-neighbor (nnn) interactions predominate for  $\beta$ -brass. That this result is reasonable may be seen by making the relatively crude order of magnitude assumption that the potential is of the form  $1/r^n$  for both the nn and nnn interactions. For the NaCl structure  $C_{1111}^{nn}/C_{1111}^{nnn}$  then becomes  $4(2^{n/2})$ , or 256 if  $n$  equals 12; for the CsCl structure  $C_{1111}^{nn}/C_{1111}^{nnn}$  becomes  $(\frac{4}{81})(\frac{4}{3})^{n/2}$ , or about 0.28 if  $n$  equals 12.  $C_{1111}$  is expected to be approximately an order of magnitude greater than and opposite in sign from  $C_{1112}$ , which is indeed the case. For example, for a potential of the form  $1/r^n$  we have  $C_{1111}/C_{1112}$  equal to approximately  $-(n+6)$  for the NaCl structure and roughly  $-\frac{2}{3}(n+6)$  for the CsCl structure. All of these relationships follow from basic expressions for the third- and fourth-order elastic constants.<sup>1, 17, 19, 28</sup>

Values for  $C_{1111}$  and  $C_{1112}$  by Swartz *et al.*<sup>6</sup> differ from those of the present work mainly because of the differences in the temperature derivatives of the second-order elastic constants which were used.

From Fig. 2 we see that the predicted  $T^4$  dependence of  $C_{11}^S$  and  $C_{44}$  fits in quite well with the experimental results for LiBr. A test of the  $T^4$  temperature dependence cannot be made with these

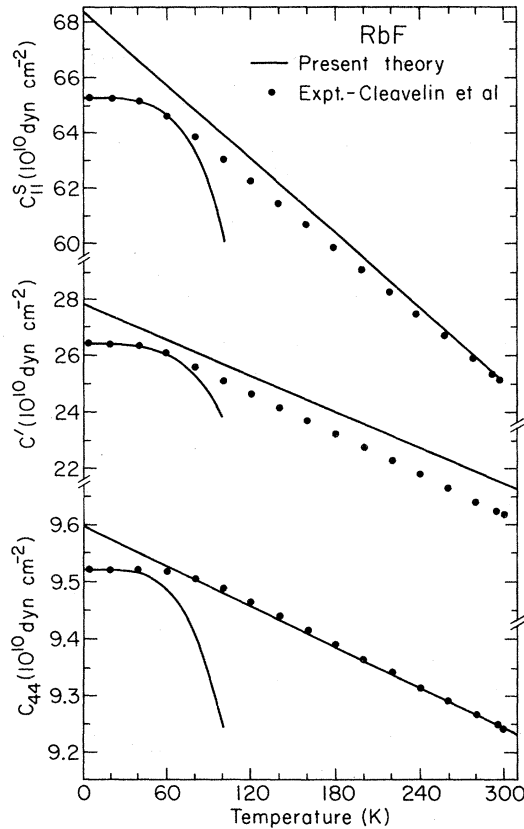


FIG. 4.  $C'_{11}$ ,  $C_{44}$ , and  $C'$  vs temperature in RbF.

data. Such a dependence holds only for the lowest-temperature  $\theta$  range and measurements for changes less than about  $\frac{1}{10}\%$  would be required. However, it would be expected that the data should always be between the  $T^4$  low-temperature and the linear high-temperature asymptotes. In Fig. 2 a much smaller temperature dependence for  $C'$  is predicted than is actually observed in LiBr.

From Fig. 3 we see that the predicted  $T^4$  curves fail to fit the experimental curves for KCl but rather ride well above them. From Fig. 4 we see rather good agreement between theory and experiment in RbF, except perhaps in the high-temperature region for  $C'$ .

In the alkali halides with the NaCl structure, it is found experimentally that  $C'_{12}$  often seems to increase with temperature. This result contradicts the general case illustrated in Fig. 1 of I and is not given by the present theory using the values of the fourth-order elastic constants listed in Table III. The values that we find for  $C_{1111}$  and  $C_{1112}$  if we try to fit the experimental  $dC'_{12}/dT$  do not fit the expected pattern of elastic constants as well as those of Table III;  $C_{1111}$  tends to be too small and/or  $C_{1112}$  too large. For LiBr, KCl, and RbF rough values for  $C_{1111}$  and  $C_{1112}$  are 3800 and

1600, 5800 and 330, and 2300 and 764, respectively (units of  $10^{10}$  dyn/cm<sup>2</sup>).

We note that both  $C'_{12}$  and  $C_{44}$  change very little with temperature in comparison with  $C'_{11}$ , a result which readily follows from the present theory, if it is assumed that nearest-neighbor interactions predominate over next-nearest-neighbor ones in alkali halides with the NaCl structure.

To summarize, the fourth-order elastic constants that we have determined are quite reasonable, but we have failed to predict the increase of  $C'_{12}$  with temperature. Trying to adjust the input values of the second- and third-order elastic constants does not help matters in this regard. Furthermore, this failure cannot be explained by any failure of our assumption about the fourth-order elastic constants, as values for these parameters have been found to be reasonable. Another possible explanation might be that dislocation movements affect the  $C'_{12}$  measurement but not the  $C_{44}$  ones. However, dislocations would also affect the  $C'_{11}$  measurements; no such effect is seen, as the results for  $C'_{11}$  are quite good. The final, and most reasonable, explanation for this failure is the invalidity of the assumption that the strain dependence of the frequencies is independent of wavelength when this assumption is used in the calculation of the  $C'_{12}$  temperature dependence.

Leibfried and Ludwig<sup>29</sup> predict that the temperature-dependent part of the adiabatic second-order elastic constants is proportional to the vibrational energy, and thus the curve of elastic constants vs temperature would have the same shape for all adiabatic elastic constants in a given material. No such prediction is made in the present theory. Thus, it would be of interest to look for materials for which this prediction fails but which can be explained by the present theory. However, more accurate data will be needed to resolve this point.

#### V. NOBLE METALS

The fcc noble metals Cu, Ag, and Au have particle density  $N/V_0$  of  $4/R^3$ , where  $R$  is the lattice constant and the mass density is given by Eq. (4.1). Equation (4.2) is used to determine the static-lattice constant  $R^0$  from the room-temperature lattice constant  $R^h$  and volume thermal expansion  $\beta^h$ . Finally, room-temperature values of the second- and third-order elastic constants<sup>1</sup> are used as input values. The justification for doing so is given in Sec. IV. Table IV lists the molecular weight  $M$ , room-temperature lattice constant  $R^h$ , room-temperature volume thermal expansion  $\beta^h$ , calculated static-lattice constant  $R^0$ , calculated static-lattice particle density  $N/V_0^0$ , calculated static-lattice mass density  $\rho^0$ , and input second- and third-order elastic constants for Cu, Ag, and Au.

TABLE IV. The molecular weight  $M$ , room-temperature lattice constant  $R^h$ , room-temperature volume thermal expansion  $\beta^h$ , calculated static-lattice particle density  $N/V_0^0$ , calculated static-lattice mass density  $\rho^0$ , and input second- and third-order elastic constants ( $10^{10}$  dyn/cm<sup>2</sup>) for Cu, Ag, and Au. [Values for  $M$  were taken from the *Handbook of Chemistry and Physics*, 51st ed. (The Chemical Rubber Co., Cleveland, Ohio, 1970-71). Values for  $R^h$  were taken from Kittel (Ref. 20). Values for  $\beta^h$  were taken from Hiki *et al.* (Ref. 4). The input elastic constants are room-temperature values taken from Hiki and Granato (Ref. 1).]

Material	$M$	$R^h$ ( $10^{-8}$ cm)	$\beta^h$ ( $10^{-5}/K$ )	$R^0$ ( $10^{-8}$ cm)	$N/V_0^0$ ( $10^{22}/\text{cm}^3$ )	$\rho^0$ (g/cm <sup>3</sup> )
Cu	63.54	3.61	4.98	3.59	8.65	9.12
Ag	107.87	4.08	5.67	4.06	5.98	10.70
Au	196.97	4.07	4.26	4.05	6.02	19.68

Material	$C_{11}$	$C_{12}$	$C_{44}$	$C_{111}$	$C_{112}$	$C_{166}$	$C_{123}$	$C_{144}$	$C_{456}$
Cu	166.1	119.9	75.6	-1271	-814	-780	-50	-3	-95
Ag	122.2	90.7	45.4	-843	-529	-637	189	56	83
Au	192.9	163.8	41.5	-1729	-922	-648	-233	-13	-12

Table V gives the temperature dependence of the second-order elastic constants in terms of  $C_{1111}$  for Cu, Ag, and Au (see Sec. II). In this table  $C'$  is given by Eq. (4.3).

In order to determine  $C_{1111}$  we may use the iteration procedure described in Sec. IV. However, in this case we treat the elastic constants  $C_{11}^S$ ,  $C_{44}$ , and  $C'$  separately to yield three different calculated values for  $C_{1111}$ . This process generally reaches the limit values to within 0.1% in less than ten

iterations. Table VI lists the calculated values of  $C_{1111}$  for Cu, Ag, and Au. The three values for each material are considered to be reasonably consistent with each other in consideration of our crude assumption of a single fourth-order elastic constant.  $C_{1111}$  is expected to be approximately an order of magnitude greater than and opposite in sign from  $C_{111}$ , which is in fact the case. For example, for a potential of the form  $1/r^n$  we have  $C_{1111}/C_{111}$  equal to  $-\frac{1}{2}(n+6)$  for the fcc structure in the

TABLE V. Calculated temperature dependence of the second-order elastic constants in terms of  $C_{1111}$  ( $10^{10}$  dyn/cm<sup>2</sup>) for Cu, Ag, and Au.

Elastic constant	Coefficient of $C_{1111}$ (units of $10^{-4}$ )			Constant term		
	Cu	Ag	Au	Cu	Ag	Au
( $10^8$ dyn/cm <sup>2</sup> K)						
$dC_{11}^h/dT$	8.48	9.06	8.99	-12.8	-11.1	-13.5
$dC_{12}^h/dT$	4.24	4.53	4.49	-6.61	-4.17	-6.90
$dC_{44}^h/dT$	4.24	4.53	4.49	-6.78	-6.27	-5.34
$dC'^h/dT$	2.12	2.27	2.25	-3.09	-3.44	-3.32
( $10^{10}$ dyn/cm <sup>2</sup> )						
$\tilde{C}_{11}^0 - C_{11}^{0K}$	-9.38	-6.54	-4.64	13.7	7.03	6.85
$\tilde{C}_{12}^0 - C_{12}^{0K}$	-4.69	-3.27	-2.32	8.04	3.38	3.95
$\tilde{C}_{44}^0 - C_{44}^{0K}$	-4.69	-3.27	-2.32	6.92	3.89	2.45
$\tilde{C}'^0 - C'^{0K}$	-2.35	-1.63	-1.16	2.81	1.83	1.45
( $10^2$ dyn/cm <sup>2</sup> K <sup>4</sup> )						
$(C_{11}^{0K} - C_{11}^{S1})/T^4$	-5.46	-20.8	-61.6	10.1	38.0	10.6
$(C_{12}^{0K} - C_{12}^{S1})/T^4$	-2.73	-10.4	-30.8	2.59	2.78	37.2
$(C_{44}^{0K} - C_{44}^I)/T^4$	-2.73	-10.4	-30.8	5.43	20.9	53.5
$(C'^{0K} - C'^I)/T^4$	-1.36	-5.20	-15.4	3.76	17.6	34.6

TABLE VI. Calculated values of  $C_{1111}$  ( $10^{10}$  dyn/cm<sup>2</sup>) for Cu, Ag, and Au.

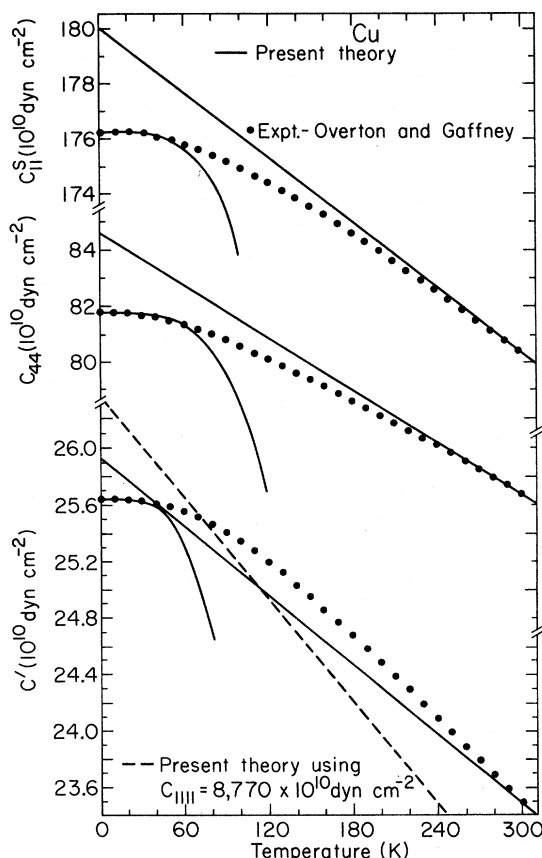
Material	Second-order elastic constant used in the calculation	$C_{1111}$	Reference for experimental values used in the calculation
Cu	$C_{11}^S$	10 500	Overton and Gaffney (Ref. 14)
	$C_{44}$	8770	
	$C'$	10 700	
Ag	$C_{11}^S$	9020	Neighbours and Alers (Ref. 15)
	$C_{44}$	9640	
	$C'$	12 800	
Au	$C_{11}^S$	11 000	Neighbours and Alers (Ref. 15)
	$C_{44}$	9030	
	$C'$	12 800	

nearest-neighbor approximation, as follows from basic expressions for the third- and fourth-order elastic constants.<sup>1,17,19,28</sup>

Figure 5 gives the theoretical and experimental temperature dependence of  $C_{11}^S$ ,  $C_{44}$ , and  $C'$  for Cu. We have fit the theoretical  $T^4$  curves to the 0 K experimental values. For each elastic constant, we have used the value of  $C_{1111}$  determined from that elastic constant by the iteration process, so that the high-temperature asymptotes must pass through the 300 K experimental values. In Fig. 5 for  $C'$  we have also drawn the high-temperature asymptote using the value of  $C_{1111}$  determined from  $C_{44}$ . From Fig 5 we see that reasonably good fits for  $C_{11}^S$  and  $C_{44}$  can be obtained. There is a discrepancy between theory and experiment for  $C'$ ; from Fig 5 and Table V we see that it is impossible to pick a value for  $C_{1111}$  which fits well both the zero-point effect and the high-temperature region. In fact, the iteration technique yields a negative zero-point effect for  $C'$  in both Ag and Au. (The zero-point effect for  $C'$  in Cu is positive but too small.) Thus, although we have obtained reasonable values for  $C_{1111}$ , the zero-point effect is apparently too sensitive to be accounted for by just one fourth-order elastic constant. It can be seen from the tables that the calculated zero-point effect depends on the subtraction of two nearly equal quantities, so that a 25% error in  $C_{1111}$  can cause a much larger error in the calculated zero-point effect.

There is a discrepancy between the calculated results in this work and the measurements of Alers<sup>30</sup> for  $C_{44}$  in Cu in the low-temperature  $T^4$  region in that the coefficient of the  $T^4$  curve using Alers's data is 2.3 times as large as that given in Table V. This discrepancy cannot be explained in terms of error multiplication or with any reasonable value of  $C_{1111}$  and was considered to be very serious because the continuum approach should be valid in the  $T^4$  region. However, while this report was in preparation, measurements of all three

elastic constants in this region were given by Rehn *et al.*<sup>31</sup> These results differ from those of Alers for  $C_{44}$  and are in good agreement with the present results for Cu in the  $T^4$  region; using three of the bottom four relations of Table V they calculated values for  $C_{1111}$  of 12 000 (from  $C_{11}^S$ ), 7000 (from  $C_{44}$ ), and 13 000 (from  $C'$ ), where units are  $10^{10}$  dyn/cm<sup>2</sup>. These values are reasonable (are of about the order of magnitude expected on the nn

FIG. 5.  $C_{11}^S$ ,  $C_{44}$ , and  $C'$  vs temperature in Cu.



assumption used earlier) but differ by amounts that are greater than can be ascribed to the measured third-order elastic constants used in the calculations. We conclude that the one fourth-order elastic-constant approximation is too crude. When compared to the values obtained in Table VI by the fitting process described earlier, these values are seen to be of the same order, but slightly different, suggesting that the wavelength dependence of the strain derivatives of the phonon frequencies may not be strong in Cu.

An example of the usefulness of fourth-order elastic-constant measurements is provided by the example given by Hiki *et al.*<sup>4</sup> in an analysis of high-temperature data. If the fast-changing part of the interatomic potential is described by a Born-Meyer expression of the form

$$w(r) = Ae^{-B(r/r_0^{-1})}, \quad (5.1)$$

where  $w(r)$  is an energy per ion pair and  $r_0$  is the equilibrium separation between nearest neighbors, then the material parameters  $A$  and  $B$  can be determined from the ratio of  $C_{1111}$  to  $C_{111}$  under the assumptions already made. Using the average of the three values of  $C_{1111}$  determined by Rehn *et al.*<sup>31</sup> and the measured value of  $C_{111} = -12.7 \times 10^{12}$  dyn/cm<sup>2</sup> given by Hiki and Granato,<sup>1</sup> one finds  $B = 13.6$  and  $A = 0.06$  eV. These values are close to those which have been found to be most useful in computer simulations of defect properties in Cu by Gibson *et al.*<sup>32</sup> who used  $B = 13.0$  and  $A = 0.051$  eV.

As further measurements become available in the  $T^4$  region in other materials, it may be useful to relax the short-range-interaction assumptions made here. A practical approach may be to use only the Cauchy conditions, which reduce the number of fourth-order constants from eleven to four. As only three independent elastic constants may be measured in the  $T^4$  regime, one further condition is required, but this could be obtained by analysis of pressure-volume data at high pressures. The resulting fourth-order elastic constants could then be examined for inferences about the range of the effective potential. Measurements of the temperature dependence of the elastic constants at high temperature and the zero-point effect could then be used to assess the approximation of wavelength independence of the strain derivatives of the phonon frequencies.

## VI. SUMMARY

A comparison of the theory given in I with experiment has been carried out for several alkali halides,  $\beta$ -brass, and the noble metals Cu, Ag, and Au. The experimentally observed linearity at high temperatures confirms the validity of the quasiharmonic approximation, as a failure of this approximation would give rise to higher-order

terms in the temperature.

In order to carry out the comparison with experiment several assumptions have been made so as to determine values for the static-lattice properties used in the theory. Thus the static-lattice constant was found from the room-temperature lattice constant and thermal expansion. Either room-temperature values of the second- and third-order elastic constants were used, if available, or 0 K values of the second-order elastic constants and theoretical values of the third-order elastic constants (calculated for 0 K) were used. The assumption was made that the ratios of the static-lattice third-order and second-order elastic constants could be approximated by the ratios for the elastic constants at a given temperature. The temperature dependence of the second-order elastic constants, using the above-described inputs, could be expressed as a linear relation in the fourth-order elastic constants, about which additional assumptions were made in order to reduce the number of these to be determined. In particular, the Cauchy relations were assumed to hold for the fourth-order elastic constants. Furthermore, for the alkali halides and  $\beta$ -brass only nearest-neighbor and next-nearest-neighbor contributions were included, requiring just two fourth-order elastic constants, say  $C_{1111}$  and  $C_{1112}$ . For the noble metals only nearest-neighbor contributions were considered, requiring just one fourth-order elastic constant, say  $C_{1111}$ . In either case, the fourth-order elastic constants could be determined from the experimental high-temperature data and 0 K values of the second-order elastic constants by an iteration process using the high-temperature and zero-point linear relations.

There are two aspects to our comparison with experiment: (i) the calculation of values for the fourth-order elastic constants based on our previously described assumptions about these constants and (ii) the matching of theory, using the calculated fourth-order elastic constants, with experiment in the regions where experimental results were not used in the calculation of the fourth-order elastic constants. Overall, the results are more satisfactory in regard to the first aspect than the second. The fourth-order elastic constants were found to have the correct sign and order of magnitude (in relation to each other and to the third-order elastic constants) as predicted by theory for a central potential where each particle is at a center of symmetry (so that the Cauchy relations are valid) and where nearest-neighbor and next-nearest-neighbor contributions are most important. In other words, the calculated fourth-order elastic constants are consistent with the assumptions used in their calculations, and reflect the geometrical aspects of the different structures.

Of the three alkali halides considered, LiBr, KCl, and RbF, it is found that KCl shows by far the worst agreement between theory and experiment in the low-temperature region. The high-temperature results for  $C'$  in all three materials do not agree well with experiment. ( $C_{11}^S$  and  $C_{44}$  were fitted in the high-temperature region.) This problem arises from the fact that  $C_{12}^S$  increases with temperature, a result which is not predicted by theory using the fourth-order elastic constants calculated with the experimental  $C_{44}$ . If the experimental  $C_{12}^S$  is used to calculate fourth-order elastic constants, values are found which are rather different from and not quite as reasonable as those found previously. The most reasonable explanation for this failure is the invalidity of the assumption regarding the independence of the strain dependence of the frequency with regard to wavelength.

For Cu, Ag, and Au experimental data for each elastic constant ( $C_{11}^S$ ,  $C_{44}$ , and  $C'$ ) have been used independently to calculate the single fourth-order elastic constant  $C_{1111}$  by the previously mentioned iteration procedure. The three values of  $C_{1111}$  so calculated for each material are reasonably consistent with each other in consideration of the crude assumption of a single fourth-order elastic

constant. In comparing theory with experiment for Cu overall agreement is found to be reasonable for  $C_{11}^S$  and  $C_{44}$ , but not for  $C'$ . This discrepancy can be explained by the fact that the calculated zero-point effect depends on the subtraction of two nearly equal quantities, so that a 25% error in  $C_{1111}$  can cause a much larger error in the zero-point effect. This problem also occurs for Ag and Au. The assumption of a single fourth-order elastic constant is adequate for an approximate calculation of  $C_{1111}$  but is too crude to account for the zero-point effect in Cu, Ag, and Au.

The region of greatest validity of the present theory is the low-temperature  $T^4$  region. The only pre-existing experimental measurement in this region ( $C_{44}$  in Cu<sup>30</sup>) gives results which disagree with the present theory while very recent measurements<sup>31</sup> show good agreement. From their data, a potential is derived which is in close agreement with one used extensively in point-defect calculations in copper.

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