

ULTRASONIC STUDIES OF THE NONLINEAR PROPERTIES OF DIAMOND LATTICE SOLIDS AT LOW TEMPERATURES¹

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The possibility to begin with fundamental lattice dynamics and include anharmonic terms to calculate the relationship between atomic force constants and elastic constants is examined. The theory of Keating is used to interpret experimental data on diamond lattice solids. Third order elastic constant data on silicon and germanium have been measured between room temperature and liquid helium temperature by use of the harmonic generation technique. These data and the theory of Keating have been used to evaluate a complete set of third order elastic constants over the entire temperature range. Validity of the numerical values of third order elastic constants is examined by calculating the Grüneisen parameter and comparing it with that obtained from thermal expansion data.

1. INTRODUCTION

I should like to discuss the contribution we have made to the understanding of the relationship between lattice dynamics, in which one considers atom-atom interactions in a crystalline solid, and third-order elasticity in which one considers the relationship between a stress and the corresponding deformation in the nonlinear approximation. This subject is not new. Fundamental progress was made in the theory early in the twentieth century by Born and coworkers [1]. Of course they limited themselves to the harmonic approximation and their calculation resulted in a nonphysical negative elastic coefficient, but the basic mathematical approach was correct. Since then so many people have been concerned with the theory and its experimental confirmation that it would be a terrific task just to list all of them. Rather than try to enumerate specific contributions we will focus on only one theory: that of Keating [2], and on only one set of results: ours, realizing that most people in this room at one time

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or another probably have delved more or less deeply into this fundamental subject. The reason I dare discuss this subject at all in the presence of this group of outstanding scientists is that we have a unique means by which we can make measurements that heretofore have been impossible and we now can use both theory and experiment to gain some insight into the fundamental physics. We measure the nonlinear behaviour of crystalline solids by a technique that allows us to express combinations of third-order elastic constants as a function of temperature down to liquid helium temperatures. The third-order elastic constants are determined by lattice anharmonicity. Thus, we have the possibility to compare lattice dynamical theory and experimental results obtained by ultrasonic techniques over a wide range of temperatures, and in detail sufficient to justify inclusion of nonlinear (or anharmonic) terms that until quite recently were ignored because of lack of experimental data.

Speaking of experimental data: If one were to list solids in terms of technological importance, then, of course, such solids as quartz, lithium niobate and the like would come to mind first. We have made some measurements with such materials, but these are not the data I would like to discuss today. The reason is that for the moment I would like to consider nonpiezoelectric materials of simple crystalline symmetry for which one can hope that the lattice dynamical model would work reasonably well when one includes only a finite number of terms in the potential function describing interatomic interactions. If one were to set as his goal the comparison of theory and experiment for some very simple lattice, then probably one would want to begin with a lattice as simple as that of the alkali halides. We considered this possibility recently and began experiments with NaCl. Although the data might be interesting, we have been able to measure NaCl only at room temperature. Study of the behaviour as a function of temperature has not yet been completed because the extremely large thermal expansion coefficient has made difficulty for us in our measurements. We expect soon to have data on the third-order elastic constants over a temperature range in which the thermal expansion coefficient changes to a remarkable degree, but at the moment I will focus on data from other solids of cubic symmetry.

Some time ago we measured the diamond lattice solids germanium and silicon. It is these data I would like to focus on because I believe they are fundamentally interesting. In order to do so it will be necessary to remind you of the basic lattice dynamical theory of Keating [2].

To begin with, central to the theory is the derivation of the lattice strain energy from two different perspectives: that resulting from interatomic interactions and that exhibited as elastic interactions in the solid as a whole. Since the lattice strain energy is fundamental to theories describing such different phenomena as thermal expansion on the one hand and the propagation of an ultrasonic wave in a nonlinear crystalline solid on the other, the derivation can

be very informative about the interrelationship among the various physical quantities. The expression for the elastic strain energy in terms of nuclear displacements resulting from elastic strain has some restrictions placed on it by rotational and displacement invariance, which limits somewhat the number of terms one needs to consider in the series expansion. To describe a crystalline lattice beyond this point one must define the specific lattice of interest. Keating chose to describe the diamond lattice solid. And I am glad he did, for those are the ones we measured. The final expression for the strain energy for diamond lattice solids is assumed by Keating to depend upon only two types of interactions: a nearest-neighbour central term and a noncentral second-neighbour term. This assumption makes the expression for the strain energy tractable, and it is this assumption that we would like to test in our comparison of experimental results. Other possible interactions are: long-range quadrupolar interactions and shell-shell interactions, both of which have been ignored or only partially included in the effective value of the nearest-neighbour interactions.

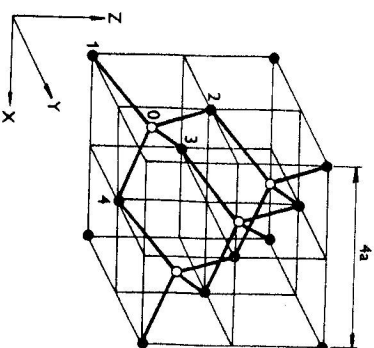


Fig. 1. The crystal model: the open and filled circles represent the atoms on the two different sublattices.

The basic crystalline lattice is shown in Fig. 1. It is a rhombohedron with two atoms (0 and 1) on its major axis which is directed along the [111] direction. The three neighbouring cells of interest contain atoms 2 and 5, 3 and 6, 4 and 7, respectively. It is the interactions among these atoms that must be accounted for in the theory.

II. THE KEATING THEORY

In principle the theory is straightforward: One calculates the strain energy in terms of force constants associated with the chosen atomic interactions, then

calculates the same strain energy in terms of the corresponding elastic strains. A comparison of corresponding terms in the two strain energy expansions allows one to identify lattice parameters on the one hand with second- and third-order elastic constants on the other. Thus, one is making a direct connection between atomic force constants and elastic behaviour of the bulk material. This possibility was interesting to us as a test of some fundamental principles of physics. But our ability to make a relatively complete test depended on a coincidence. The coincidence was that only two harmonic and three anharmonic force constants are necessary to describe the strain energy in the diamond lattice according to the Keating model. The relationships are given in Table I. We could measure velocities and hence calculate all three second-order elastic constants, but we would measure only three combinations of third-order elastic constants. The coincidence that the Keating model required only three anharmonic force constants allowed us to proceed with the experimental test of theory. As you know, cubic lattices such as the diamond lattice require six third-order elastic constants to specify the nonlinear behaviour.

Our procedure, then, to study the anharmonic behaviour of silicon and germanium was to measure three combinations of third-order elastic constants. Then we used this information to calculate the three anharmonic force constants γ , δ and ϵ of the Keating model. From this information the Keating model allows us to calculate all six third-order elastic constants.

The fact that we can measure as a function of temperature to 4 K has made possible a test of the validity of the procedure. Having a complete set of third-order elastic constants allows one to calculate the Grüneisen parameter, which is directly available from thermal expansion data. Comparison parameter independently obtained from thermal expansion data allows us to test the validity of the whole procedure, and make some guesses about where to start to improve the model.

III. CONNECTION BETWEEN THEORY AND EXPERIMENT

To derive the nonlinear wave equation appropriate to the description of ultrasonic wave propagation one expands the elastic potential energy in terms of strains and finds that the coefficients are the elastic constants:

$$\phi(\eta) = \frac{1}{2!} \sum_{ijkl} C_{ijkl} \eta_{ij} \eta_{kl} + \frac{1}{3!} \sum_{ijklmn} C_{ijklmn} \eta_{ij} \eta_{kl} \eta_{mn}.$$

By using the appropriate form of Lagrange's equations and specializing to a

specific orientation of the coordinates with respect to the ultrasonic wave propagation one can write the nonlinear wave equation in the form [3]

$$\rho \ddot{x}_i = \frac{\partial}{\partial a_i} \sum_{k=1}^3 J_k \frac{\partial \Phi(\eta)}{\partial \eta_{ik}}$$

which shows exactly where the strain energy enters into the nonlinear wave equation. We prefer to specialize this equation to propagation in a pure mode direction (for cubic lattices one of the three principal directions). This allows us to write the nonlinear wave equation in the form

$$\rho_0 \frac{\partial^2 u}{\partial t^2} = K_2 \frac{\partial^2 u}{\partial a^2} + (3K_2 + K_3) \frac{\partial u}{\partial a} \frac{\partial^2 u}{\partial a^2}$$

in which K_2 stands for a linear combination of second-order elastic constants and K_3 stands for a linear combination of third-order elastic constants. The expressions for K_2 and K_3 for the pure mode directions in a cubic lattice are given in Table II.

$$u = A_1 \sin(ka - \omega t) - \left[\frac{3K_2 + K_3}{K_2} \right] A_1^2 k^2 a \cos 2(ka - \omega t)$$

contains a second harmonic whose amplitude

$$A_2 = - \frac{3K_2 + K_3}{K_2} A_1^2 k^2 a.$$

The experimental procedure we use is to use the apparatus schematically represented in Fig. 2a with a detector as shown in Fig. 2b to measure the amplitudes of the fundamental and the second harmonic at room temperature. A plot of A_2 vs. A_1^2 has a slope which is proportional to

$$\beta' = - \frac{3K_2 + K_3}{K_2}$$

which we usually call the nonlinearity parameter. A typical plot of the data is shown in Fig. 3. Taking the slope of the curves and knowing $k = 2\pi/\lambda$ and the sample length we can evaluate β' using the expressions given in Table II. Having room temperature values of β' we can evaluate K_3 .

A measurement as a function of temperature of the relative magnitudes of the amplitudes of the fundamental and the second harmonic completes the measurements and allows us to plot K_3 as a function of temperature. A plot of our data on silicon is given in Fig. 4. As can be seen, the data are quite consistent as a function of temperature, but they are not the simplest combinations of third-

-order elastic constants possible. For example, C_{111} appears in all three sets of data. Subtracting out C_{111} and other common constants allow us to plot the three combinations C_{111} , $C_{112} + 4C_{166}$ and $C_{123} + 6C_{144} + 8C_{456}$ given in Fig. 5. For further data interpretation we depend upon the coincidence that only three

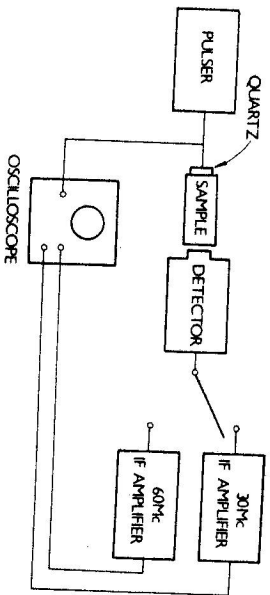
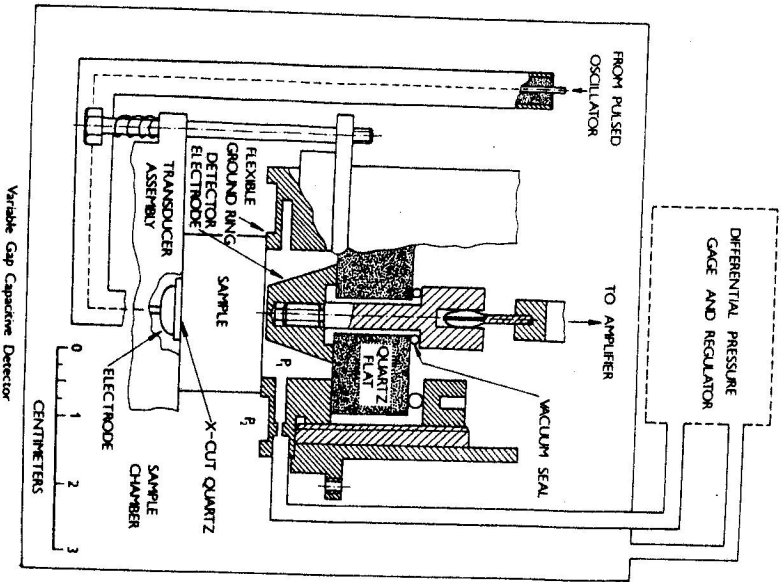


Fig. 2a. Schematic diagram of the apparatus.



2b. Capacitive microphone for measuring ultrasonic wave amplitudes.

interatomic force constants are required by the Keating model and calculate γ , δ and ϵ . Having the Keating anharmonic force constants allows us to calculate all six third-order elastic constants as shown in Figs. 6a and b. Using the same procedure with germanium data, we are able to plot all six third-order elastic constants of germanium as given in Figs. 7a and 7b. The similarity of the behaviour as a function of temperature gives some reassurance of the validity of the data, for all diamond lattice solids should behave in a similar manner.

Fig. 3. Measured second harmonic amplitudes plotted as a function of the square of the fundamental amplitude.

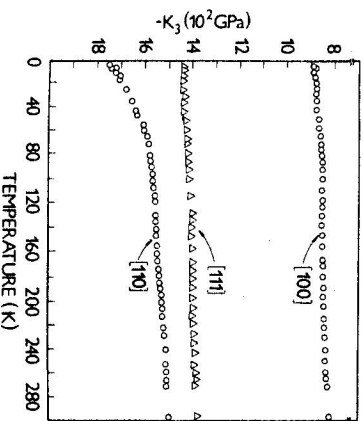
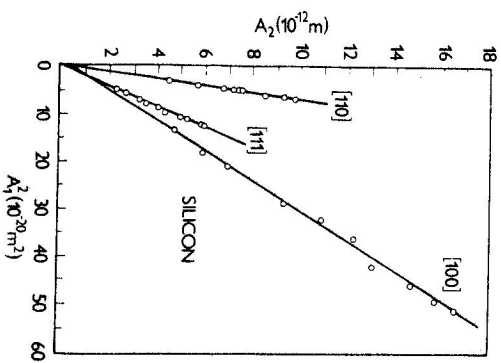


Fig. 4. Values of the parameter K_3 plotted as a function of temperature.

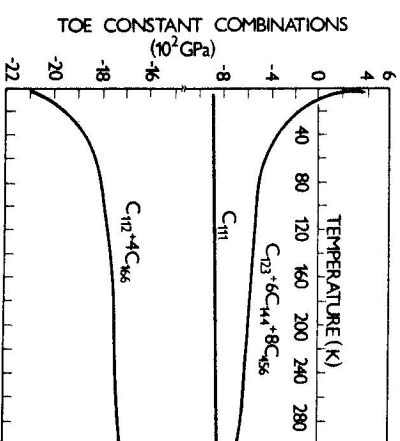


Fig. 5. Three combinations of third-order elastic constants available from K_3 data plotted as a function of temperature.

Now, having all six third-order elastic constants, it is possible to calculate the Grüneisen parameter by making an appropriate average, and it happens that the Grüneisen parameters of diamond lattice solids have a common peculiarity: they go to negative values at approximately one-tenth of their Debye temperature. The ability of the model to predict the Grüneisen parameter in this temperature range should be a good test of the model. Thermal expansion measurements give a Grüneisen parameter for silicon as shown in Fig. 8. Thus,

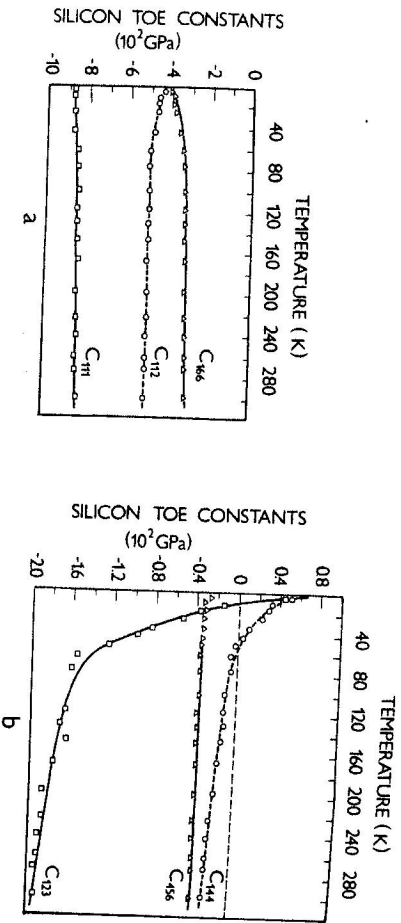


Fig. 8a,b. The six third-order elastic constants of silicon obtained from data in Fig. 5 and the Keating model.

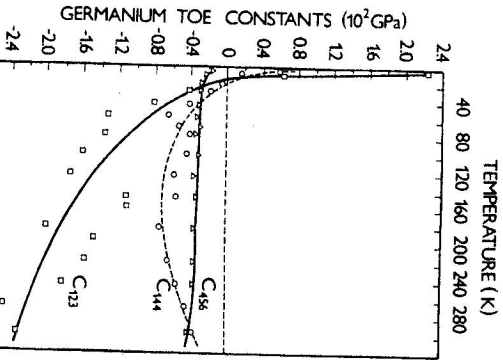
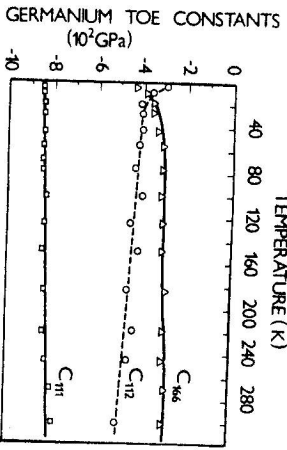


Fig. 7a,b. Third-order elastic constants of germanium.

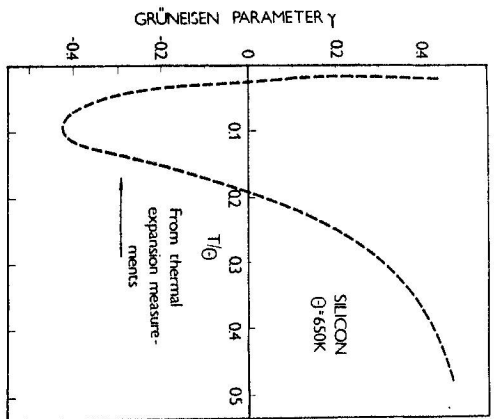


Fig. 8. Behaviour of the Grüneisen parameter of silicon as a function of temperature.

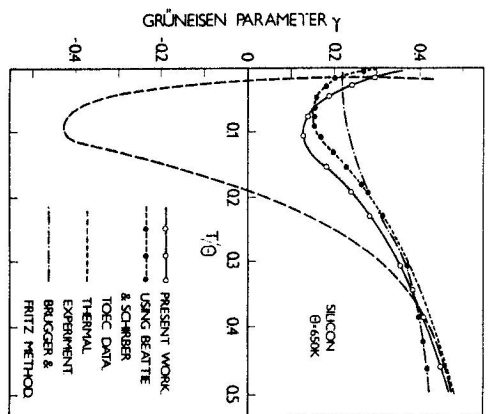


Fig. 9. Silicon Grüneisen parameter data plotted as a function of temperature.

we have results from thermal expansion measurements to compare with the values obtained by acoustical techniques. The comparison is given in Fig. 9. The curve labelled "present work" is to be compared with that labelled "thermal experiment". Several aspects of this comparison are apparent. First, the agreement is not all that good. I think the appropriate response to this observation is that measurement of the temperature dependence of the third-order elastic constants has improved the agreement over that previously obtained by Brugger and Fritz [4] who made a comparison but assumed the third-

Fig. 10. Germanium Grüneisen parameter data plotted as a function of temperature.

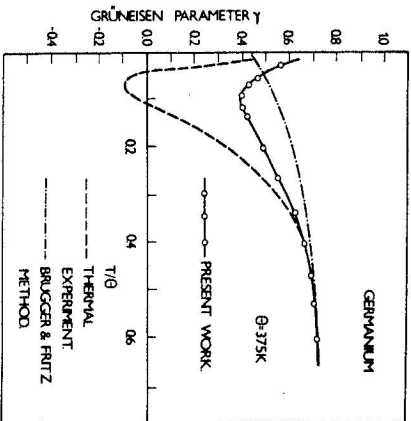


Table 1

Keating model relationships among microscopic coefficients and macroscopic elastic constants for diamond lattice solids

Second-order elastic constants	Third-order elastic constants
$C_{11} = \frac{\alpha + 3\beta}{4\alpha}$	$C_{111} = \gamma - \delta + 9\epsilon$ $C_{112} = \gamma - \delta + \epsilon$
$C_{12} = \frac{\alpha - \beta}{4\alpha}$	$C_{123} = \gamma + 3\delta - 3\epsilon$ $C_{144} = \gamma(1 - \zeta^2) + 8\gamma(1 + \zeta^2) + \alpha(1 + \zeta)(3\zeta - 1) + C_{125}^2$
$C_{44} = \frac{\alpha\beta}{\alpha(\alpha + \beta)}$	$C_{166} = \gamma(1 - \zeta^2) - 8\gamma(1 + \zeta^2) + \alpha(1 + \zeta)(3 - \zeta) + C_{125}^2$ $C_{456} = \gamma(1 - \zeta^3)$
where α is the lattice spacing	Where $\zeta = \frac{\alpha - \beta}{\alpha + \beta}$

Table 11

K_2 and K_3 parameters for the principal directions in a cubic lattice

Wave propagation direction	K_2	K_3
[100]	$\frac{C_{11}}{C_{11} + C_{12} + 2C_{44}}$	$\frac{C_{111}}{C_{111} + 3C_{112} + 12C_{166}}$
[110]	$\frac{C_{11} + 2C_{44}}{2}$	$\frac{4}{9}(C_{111} + 6C_{112} + 12C_{166} + 24C_{166} + 2C_{123} + 16C_{456})$
[111]	$\frac{C_{11} + 2C_{12} + 4C_{44}}{3}$	

-order elastic constants are temperature independent. We used Brugger's and Fritz's method to calculate the Grüneisen parameter from third-order elastic constants but used our measured temperature dependent third-order elastic constants in the calculation.

As an alternative to the Keating theory we have used data from Beattie and Schirber who measured the pressure variation of sound velocity at room temperature, liquid nitrogen temperature and liquid helium temperature along with our measured combinations of third-order elastic constants to get the curve labelled "Using Beattie and Schirber TOEC data". The necessity to interpolate between their measured data evidently is responsible for the shift of the minimum away from the temperature at which it occurs in the thermal expansion data.

Let us now look at the similarities between the curve we obtained using our data and the Keating model. First, the minimum in our data occurs at the proper temperature and the general shapes of the curves are similar. They agree very well at room temperature, but this is true of all of the curves. The corresponding curves for germanium are given in Fig. 10 and show the same general behaviour.

Finally, I would like to speculate that possibly the agreement between the two curves could be improved by a more complete model than that of Keating, one that possibly takes into consideration long-range quadrupolar interactions or shell-shell interactions. Although this speculation may be accurate, it is uncertain whether a more complicated lattice dynamical model would make it possible to improve matters. It is entirely possible that a more complicated model would require more than three anharmonic force constants. If it did, then the coincidence that has allowed us to make the comparison between theory and experiment for silicon and germanium might no longer occur. Possibly the result would be that the insight we have gained through this interpretation of the ultrasonic data would turn out to be qualitatively correct but quantitatively uncertain. Nevertheless, even with the present model we have been able to use the Keating model and our data to obtain a set of all six of the third-order elastic constants of the diamond lattice solids silicon and germanium. By using the third-order elastic constants and the theory of Brugger and Fritz we have been able to calculate the Grüneisen parameters of silicon and germanium between room temperature and 4 K and to use the agreement between the calculated Grüneisen parameter and that calculated from thermal expansion data to define a starting point for further refinement of the theory.

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ИЗУЧЕНИЕ НЕЛИНЕЙНЫХ СВОЙСТВ АЛМАЗНОЙ РЕШЕТКИ ПРИ НИЗКИХ ТЕМПЕРАТУРАХ ПРИ ПОМОЩИ УЛЬТРАЗВУКА

В работе рассмотрена возможность изучения динамики фундаментальной решетки и вхождения ангармонических членов для расчета отношений между постоянными атомного об алмазной решетке использована теория Китинга. При помощи метода гармонического генерирования измерены данные о третьем порядке упругих постоянных, которые получены на кремнии и германии в области от комнатной температуры до температуры жидкого гелия. Эти данные и теория Китинга использованы для вычисления полного набора упругих постоянных в третьем порядке во всей области температур. Подтверждение правильности числовых значений упругих постоянных в третьем порядке теории возмущений проверено на основе расчета параметра Гронейсена и его сравнения со значением, полученным посредством данных о термическом расширении.