Measurement of Higher-Order Elastic Constants, Using Finite Deformations*

B. E. POWELL† AND M. J. SKOVE
Department of Physics, Clemson University, Clemson, South Carolina 29631
(Recieved 17 April 1968)

The deviations from Hooke's law of single-crystal "whiskers" of copper, silver, and iron and fibers of fused quartz have been measured. These deviations are related to the third-order elastic constants. The results are in agreement with third-order elastic constants measured by ultrasonic techniques for copper, silver, and fused quartz. Using the pressure derivatives of the second-order elastic constants of iron as measured by Rotter and Smith and the present results, three of the third-order elastic constants of iron have been determined. The values are (in units of 10^{12} dyn/cm^2) $c_{111}{}^T=-28$, $c_{112}{}^T=-8.0$, and $c_{123}{}^T=-6.1$. For fused quartz, it is possible to make an estimate of a combination of the fourth-order elastic constants: $c_{1111}{}^T-1.4\,c_{1112}{}^T+0.34\,c_{1122}{}^T+0.23\,c_{1123}{}^T=5.5\pm1.5\times10^{14}$ dyn/cm^2.

I. INTRODUCTION

SEVERAL methods of determining the third-order elastic constants have been developed in recent years. These methods use ultrasonic techniques and measure either the adiabatic third-order constants or the "mixed" third-order constants. A different technique uses deviations from linearity in stress-strain curves. These deviations are related to combinations of third-order moduli. The theory for such deviations was reported for isotropic materials by Murnaghan,[1] and extended to materials of cubic symmetry by Seeger and Buck.[2] For cubic crystals, the room-temperature values of the third-order elastic constants can be determined from a knowledge of deviations from linearity and the pressure derivatives of the second-order elastic constants.

A number of deviations from linearity have been reported in the literature. For example, Mallinder and Proctor[3] performed a series of experiments on long fused-silica fibers and soda-glass fibers; their data indicate a dependency of Young's modulus on strain. Brenner[4] reported deviations from Hooke's law at about 2% strain in iron whiskers. Similar deviations have been reported by Cabrera[5] for zinc whiskers and by Gordon[6] for silicon whiskers. Brenner[4] has also found nonlinear results in nickel whiskers ($\epsilon>1.5\%$), Al_2O_3 whiskers ($\epsilon>2\%$), and SiO_2 whiskers ($\epsilon>3.5\%$). Powell and Skove[7] reported deviations from Hooke's law in tin whiskers at strains greater than 2%.

Simple tension experiments, however, do not provide sufficient sensitivity to determine the third-order constants. This article describes a sensitive technique for measuring combinations of third-order constants from finite deformations in fibers, and gives the results of experiments performed on several materials.

II. APPARATUS

In order to eliminate small perturbing effects that mask the small nonlinearities that need to be observed, a differential technique is used to observe the slope of the force-elongation curve. A sensitive tensile apparatus is still used, but a low-frequency, uniaxial, oscillatory force is superposed upon the steady tensile force. The resulting oscillatory displacement produces a small signal in a differential transformer which is analyzed by a lock-in amplifier. The magnitude of this signal as a function of elongation is related to the higher-order elastic constants.

A diagram of the tensile is shown in Fig. 1. The sample is glued between two glass cover slides. The upper mount is movable to permit elongations of the fiber. Although it is stationary during an experiment, the lower mount can be adjusted for differences in whisker lengths. The glass cover slide is attached to a permanent magnet, which can be moved on a flat steel plate. This allows two degrees of freedom for aligning the whisker.

Stress is applied to the sample by turning the micrometer. This stretches the "pulling" spring and applies a known force along the vertical rod to the fiber. The spring is calibrated by hanging known weights from the upper sample mount and observing the subsequent elongation of the spring when the mount is brought back to its equilibrium position. A typical value of the spring constant is 4×10^2 dyn/mm. Since the smallest division of the micrometer is 0.01 mm, force can be applied in increments of 4 dyn.

As force is applied to the vertical rod, the fiber elongates. This elongation is measured by the differential transformer. For small displacements, the changes of output voltage of the differential transformer are linear with displacement. The output voltage of this transformer changes about 4 mV per μ displacement of the

* Work supported by the U. S. Air Force Office of Scientific Research, Grant No. 180-65.
† Present address: Department of Physics, West Georgia College, Carrollton, Ga. 30117.
[1] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951), pp. 1–118.
[2] A. Seeger and O. Buck, Z. Naturforsch. **15a**, 1056 (1960).
[3] F. P. Mallinder and B. Z. Proctor, Phys. Chem. Glasses **5**, 91 (1964).
[4] S. S. Brenner, in *Growth and Perfection of Crystals*, edited by R. H. Doremus, B. W. Roberts, and David Turnbull (John Wiley & Sons, Inc., New York, 1958), p. 157.
[5] N. Cabrera and P. B. Price, in *Growth and Perfection of Crystals*, edited by R. H. Doremus, B. W. Price, and David Turnbull (John Wiley & Sons, Inc., New York, 1958), p. 204.
[6] J. E. Gordon, in *Growth and Perfection of Crystals*, edited by R. H. Doremus, B. W. Roberts, and David Turnbull (John Wiley & Sons, Inc., New York, 1958), p. 219.
[7] B. E. Powell and M. J. Skove, J. Appl. Phys. **36**, 1495 (1965).

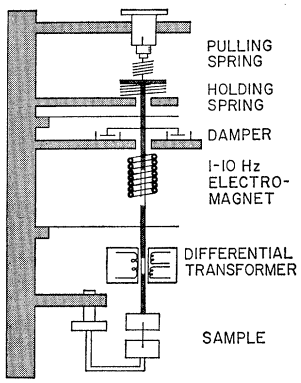

FIG. 1. Tensile apparatus.

core. Since the noise level of the system is approximately 0.1 mV, elongations of about 0.03 μ can be detected by this apparatus.

A small oscillatory uniaxial force is superposed on the much larger spring force by applying low-frequency (1.5–10 Hz) ac voltage to the electromagnet, which alternately attracts and repels the permanent magnet mounted in the vertical rod. This frequency range was chosen to avoid mechanical resonances of the apparatus and to obtain sufficient elongation amplitudes. The oscillatory force produces an oscillatory elongation in the sample and a related oscillation of the core of the differential transformer. The resulting oscillatory signal is superposed on the large dc signal produced by the steady displacement caused by the spring. The elongation produced by the oscillatory force was about 0.01%.

A block diagram of the tensile apparatus and the supporting instruments is shown in Fig. 2. The ac voltage applied to the electromagnet is supplied by the reference output of a lock-in amplifier (Princeton Applied Research Corp. Model JB-5). The output of the transformer is connected to a differential voltmeter (Medistor Model A-75) and to the lock-in amplifier. The changes of the dc signal measured by the voltmeter are used to compute the elongation of the fiber. The lock-in amplifier compares the ac part of the signal with its reference output. The meter on the amplifier thus registers a signal proportional to the amplitude of the oscillatory elongation.

III. THEORY

The Lagrangian strain will be used, in which the strain tensor is given by

$$\eta_{ij}\equiv\tfrac{1}{2}[(\partial u_i/\partial a_j)+(\partial u_j/\partial a_i)+(\partial u_l/a_i)(\partial u_l/\partial a_j)],$$

where a_i and x_i are the unstrained and strained coordinates of a material point fixed in the body and $u_i \equiv x_i-a_i$. Following the notation of Brugger,[8] the elastic constants of order N are defined as

$$c_{ij,kl,mn,\cdots}{}^{T}\equiv\rho_0(\partial^N F/\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn}\cdots)_T, \quad (1)$$

$$c_{ij,kl,mn,\cdots}{}^{S}\equiv\rho_0(\partial^N U/\partial\eta_{ij}\partial\eta_{kl}\partial\eta_{mn}\cdots)_S, \quad (2)$$

[8] K. Brugger, Phys. Rev. **133**, A1611 (1964).

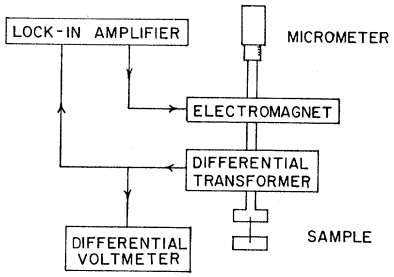

FIG. 2. Block diagram of the apparatus.

where ρ_0 is the initial density, F and U are the Helmholtz and internal energies, and T and S denote isothermal and adiabatic moduli. The "mixed" third-order constants $C_{ij,kl,mn}$ are defined by

$$C_{ij,kl,mn}\equiv[\partial/(\partial^2 U/\partial\eta_{ij}\partial\eta_{kl})_S/\partial\eta_{mn}]_T. \quad (3)$$

Since the strain tensor is symmetric, i.e., $\eta_{ij}=\eta_{ji}$, it is customary to introduce the Voigt[9] notation $11\sim1$, $22\sim2$, $33\sim3$, $23\sim4$, $13\sim5$, $12\sim6$. The definition

$$\eta_{ij}=\tfrac{1}{2}(1+\delta_{ij})\eta_I,$$

where lower-case subscripts running from 1 to 3 and capital subscripts running from 1 to 6 will be used. In this notation

$$c_{IK}\cdots{}^{S}=(\partial^N U/\partial\eta_I\partial\eta_K\cdots)_S,$$

and similarly for the isothermal and mixed constants.

It should be noted that $c_{IKM}{}^{T}$ and C_{IKM} are symmetric with respect to the interchange of any two indices, but C_{IKM} is, in general, symmetric only under interchange of the first two indices.[10]

The relationship between the three types of third-order moduli can be derived from thermodynamics. Brugger[8] has derived a relationship between the adiabatic third-order constants and the mixed constants. The present writers[11] have derived an expression for the difference between the isothermal third-order constants and the mixed constants.

In experiments where the strain cannot be considered infinitesimal, the stress is not linearly related to the strain, nor is the stress a derivative of a thermodynamic potential with respect to the strain, as it is in linear elasticity. For such finite deformations, Murnaghan has derived the relation

$$\sigma^0{}_{ij}=[J(\partial F/\partial\eta)_T]_{ij}, \quad (4)$$

where J is the Jacobian of the initial coordinates with respect to the final coordinates, $(\partial F/\partial\eta)_T$ is the matrix whose ijth component is $(\partial F/\partial\eta_{ij})_T$, and $\sigma^0{}_{ij}$ is a component of the stress tensor, calculated by dividing the applied force by the unstrained area.

[9] W. Voight, *Lehrbuch der Kristallphysik* (B. G. Teubner, Leipzig, 1928).

[10] M. J. Skove and B. E. Powell, J. Appl. Phys. **38**, 404 (1967).

[11] B. E. Powell and M. J. Skove, J. Appl. Phys. **38**, 404 (1967).

Fibers that can sustain large elongations show a nonlinear relation between the applied force and the resulting elongation. The relation between force and elongation can be expressed as

$$\epsilon=(P/E)+\delta(P/E)^2+\zeta(P/E)^3+\cdots, \quad (5)$$

where P is the stress per unit area of the unstrained fiber, E is Young's modulus for the fiber, and δ and ζ are functions of the elastic constants of the fiber material. Murnaghan,[1] using Eq. (5), has derived the relation between δ and the elastic constants of an isotropic substance. Seeger and Buck[2] have derived the relation between δ and the elastic constants of a cubic crystal for single-crystal fibers with axes along the ⟨100⟩, ⟨110⟩, and ⟨111⟩ crystallographic directions. For a fiber with a ⟨100⟩ axis, the result is

$$\delta_{100}=-\tfrac{3}{2}+s_{11}[(\gamma^3-\tfrac{1}{2})c_{111}{}^T+3(\gamma^4-\gamma^2+\gamma)c_{112}{}^T -3\gamma^2c_{123}{}^T], \quad (6)$$

where s_{11} is a component of the second-order compliance tensor and $\gamma=c_{12}{}^T/(c_{11}{}^T+c_{12}{}^T)$. The expressions for δ_{110} and δ_{111} are similar; δ_{110} is a function of all the $c_{IKM}{}^T$ except $c_{456}{}^T$, and δ_{111} is a function of all six of the third-order elastic constants of the cubic material.

It is not possible to determine completely the third-order elastic constants of a cubic material with experiments done with fibers oriented along these directions. These are the only directions which are available. Measurements of the velocity of ultrasound as a function of hydrostatic pressure give three more independent relations among the $C_{IKM}{}^T$, and thus enable the third-order elastic constants to be completely determined.

In this experiment, the lock-in amplifier reading y is proportional to the derivative of the force-elongation curve, since it measures the incremental elongation produced by an incremental force impressed on a much larger constant force. Thus

$$y\propto d\epsilon/d(P/E)=1+2\delta(P/E)+3\zeta(P/E)^2+\cdots. \quad (7)$$

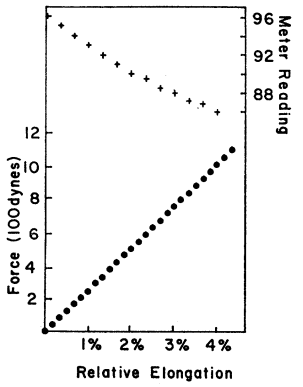

FIG. 3. Results of a typical quartz-fiber experiment. The circles give force (using units on the left-hand ordinate) versus elongation. The crosses give the lock-in-amplifier meter reading (using units on the right-hand ordinate) versus elongation.

TABLE I. Summary of results for quartz fibers.

Fiber number	Diameter (in μ)	δ	ζ
1	1.5	−1.8±0.1	8.8±1.7
2	1.6	−1.7±0.1	10.8±1.2
3	1.9	−2.6±0.1	···
4	2.4	−2.8±0.3	···
5	3.3	−3.2±0.2	···
6	3.3	−2.3±0.2	11.5+1.1
7	2.9	−2.2±0.1	···
8	4.1	−2.7±0.1	18.3±1.5
9	3.6	−1.3±0.1	···
10	2.7	−2.5±0.2	···
11	4.2	−2.3±0.2	17.6±3.7
12	6.0	−3.4±0.1	···
13	5.5	−2.6±0.2	···

The scaled change in the meter reading M can be developed in a power series in ϵ. The result is

$$M\equiv(y-y_0)/y_0=(2\delta)\epsilon+(-2\delta^2+3\zeta)\epsilon^2+\cdots. \quad (8)$$

IV. PROCEDURE

The fused-quartz fibers were prepared by the technique described by Neher.[12] The whiskers of copper, iron, and silver were grown by Brenner's technique.[13] Single-crystal orientations were determined by the rotating-sample x-ray-diffraction method.

A number of glues were used for the various samples. For the quartz fibers, a mixture of epoxies was used. The whiskers were glued with either diphenyl carbazide or sodium silicate.

To determine if the elongations were elastic, the stress was relaxed. If the readings were reproducible as the elongation was decreased, the behavior was taken to be elastic. The sample was then strained until fracture or plastic deformation occurred.

The results of a typical experiment are shown in Fig. 3. The data for each experiment were fitted by a least-squares analysis to a curve of the form $M=K\epsilon+N\epsilon^2$. For each fiber, δ was calculated from the resulting value of K. The uncertainty of the value of δ was calculated from the standard deviation of K obtained from the least-squares fit, since this was the largest source of uncertainty in δ. For fibers having high-yield strains, it was possible to obtain an estimate of the value of ζ from the value of N.

V. RESULTS

A. Fused-Quartz Fibers

A summary of the results is given in Table I. The mean value of δ is −2.4, with a standard deviation of 0.7. This value of δ may be compared with the results of Mallinder and Proctor,[3] who experimented on long fibers of fused silica at −196°C. Their fibers were no smaller than 20 μ in diameter. Their results were reported as a

[12] H. V. Neher, in *Procedures in Experimental Physics*, edited by John Strong (Prentice-Hall, Inc., New York, 1945).
[13] S. S. Brenner, Acta Met. 4, 62 (1956).

change of Young's modulus with strain. Converting their values to a measure of δ, δ ranges from -1.9 to -3.5.

These values of δ may be compared with the work of Bogardus[14] through Eq. (6). The conversion of the C_{IKM} to $c_{IKM}{}^T$ results in a change of less than 0.1% of the C_{IKM} and was neglected. Using the value of the C_{IKM} for fused quartz in Table V and Eq. (6), $\delta=-3.7$ for the bulk samples measured by Bogardus. This bulk value corresponds to δ for the larger fibers used in these tensile tests.

Using the mean value of δ and pressure derivatives of the second-order elastic constants, the isothermal third-order constants for fused silica can be calculated. The elastic constants of bulk samples of quartz have been studied as a function of hydrostatic pressure by a number of investigators.[14–17] For each set of data, combinations of third-order constants were calculated from the pressure derivatives, and were converted to the corresponding isothermal values by formulas given by Barsch.[18] The adiabatic second-order elastic constants were also converted into isothermal constants. Using the three combinations from pressure derivatives (only two are independent) and the three δ's (for isotropic materials, $\delta_{100}=\delta_{110}=\delta_{111}$), the six third-order constants (only three are independent) were calculated, and are shown in Table V. For comparison, the mixed third-order constants reported by Bogardus[14] are also shown in Table V. The values of quantities needed in all of these conversions were obtained from a table prepared by Barsch and Chang.[19]

For the quartz fibers stressed to greater than 2%, enough nonlinearity was observed to estimate ζ. The values listed for a fiber and the error estimate were obtained from a least-squares analysis. The average value of ζ is 13.7, with a standard deviation of 3.7 .

The present authors have derived an expression for ζ valid for materials with cubic or greater symmetry from the theory of Murnaghan. The result is, for the [100] direction,

$$\begin{aligned}\zeta=&-2\delta-s_{11}\{c_{111}{}^T(\sigma^4+2\sigma^2\beta+\delta+\tfrac{1}{2})\\&+c_{112}{}^T[3\sigma^4-2\sigma^3+\sigma^2(2+2\delta+6\beta)\\&-\sigma(4\delta+4\beta+2)+2\beta]\\&+c_{123}{}^T[-2\sigma^3+\sigma^2(2\delta+1)-4\sigma\beta]\\&+c_{1111}{}^T(\tfrac{1}{3}\sigma^4+\tfrac{1}{6})+c_{1112}{}^T\tfrac{4}{3}(\sigma^4-\sigma^3-\sigma)\\&+c_{1122}{}^T(\sigma^4+\sigma^2)+c_{1123}{}^T(2\sigma^2-4\sigma^3)\},\end{aligned}\quad(9)$$

where

$$\sigma=c_{12}{}^T/(c_{11}{}^T+c_{12}{}^T)$$

and

$$\begin{aligned}\beta=&-\tfrac{1}{2}\sigma^2+\sigma-s_{11}(c_{11}{}^T+c_{12}{}^T)^{-1}\\&\times\{\tfrac{1}{2}c_{111}{}^T(c_{11}{}^T\sigma^2-c_{12}{}^T)+c_{112}{}^T[\tfrac{1}{2}c_{11}{}^T(3\sigma^2-2\sigma+1)\\&-c_{12}{}^T(\sigma^2-2\sigma)]-c_{123}{}^T(c_{11}{}^T\sigma+c_{12}{}^T\sigma^2)\}.\end{aligned}$$

By substituting the known values of δ, ζ, and the second- and third-order elastic constants as measured by Bogardus,[14]

$$\begin{aligned}&c_{1111}{}^T-1.37c_{1112}{}^T+0.34c_{1122}{}^T+0.23c_{1123}{}^T\\&\qquad=(5.5\pm1.5)\times10^{14}\ \text{dyn/cm}^2.\end{aligned}$$

There are no experiments with which these results may be compared. When estimates of other combinations of the fourth-order constants become available, it may be possible to calculate the values of the individual fourth-order constants.

Young's modulus E was also calculated for each fiber, using the diameter as measured from an electron micro-

TABLE II. Summary of results for copper whiskers.

Whisker number	Orientation	Diameter (in μ)	δ
1	⟨100⟩	1.8	-3.2 ± 0.3
2	⟨100⟩	1.6	-3.4 ± 0.2
3	⟨100⟩	2.2	-2.9 ± 0.3
4	⟨100⟩	5.9	-4.1 ± 0.2
5	⟨100⟩	2.5	-4.6 ± 0.5
6	⟨100⟩	2.5	-3.1 ± 0.4
7	⟨100⟩	1.6	-3.1 ± 0.3
8	⟨100⟩	5.1	-3.7 ± 0.5
9	⟨100⟩	37	-6.4 ± 0.7
10	⟨100⟩	3.1	-4.6 ± 0.3
11	⟨100⟩	5.7	-3.4 ± 0.3
12	⟨100⟩	2.4	-3.6 ± 0.6
13	⟨100⟩	3.0	-2.8 ± 0.1
14	⟨100⟩	2.3	-1.3 ± 0.6
15	⟨100⟩	2.2	-1.6 ± 0.2
16	⟨100⟩	1.1	-2.2 ± 0.2
17	⟨100⟩	2.1	-2.5 ± 0.2
18	⟨100⟩	3.8	-2.8 ± 0.1
19	⟨100⟩	2.0	-2.0 ± 0.1
20	⟨100⟩	4.9	-1.6 ± 0.1
21	⟨100⟩	5.9	-6.6 ± 0.6
22	⟨100⟩	1.5	-3.0 ± 0.3
23	⟨100⟩	2.3	-3.8 ± 1.4
24	⟨100⟩	2.3	-2.2 ± 0.1
25	⟨100⟩	4.3	-5.5 ± 0.6
26	⟨100⟩	3.1	-4.5 ± 0.6
27	⟨100⟩	3.1	-3.5 ± 0.8
28	⟨110⟩	...	4.4 ± 1.1
29	⟨110⟩	...	3.6 ± 0.5
30	⟨110⟩	...	5.9 ± 0.2
31	⟨110⟩	...	5.0 ± 0.6
32	⟨111⟩	...	2.4 ± 1.3
33	⟨111⟩	...	1.8 ± 0.2
a[a]	⟨100⟩	...	-4.7
b[a]	⟨110⟩	...	10.8
c[a]	⟨111⟩	...	3.8

[a] a, b, c represent δ's calculated from the data of Hiki and Granato (Ref. 21).

[14] E. H. Bogardus, J. Appl. Phys. **36**, 2504 (1965).
[15] L. Peselnick, R. Meister, and W. H. Wilson, J. Phys. Chem. Solids **28**, 635 (1967).
[16] O. L. Anderson, in *Progress in Very High Pressure Research*, edited by F. P. Bundy, W. R. Hibbard, and H. M. Strong (John Wiley & Sons, Inc., New York, 1960), p. 225.
[17] H. J. McSkimin, J. Acoust. Soc. Am. **29**, 1185 (1957).
[18] G. R. Barsch, Phys. Status Solidi **19**, 129 (1967).
[19] G. R. Barsch and Z. P. Chang, Phys. Status Solidi **19**, 139 (1967).

TABLE III. Summary of results for silver whiskers.

Fiber number	Orientation	Diameter (in μ)	δ
1	⟨100⟩	3.9	-4.8 ± 0.3
2	⟨100⟩	3.3	-2.4 ± 0.1
3	⟨100⟩	3.4	-3.8 ± 0.3
4	⟨100⟩	1.0	-0.7 ± 0.1
5	⟨100⟩	2.9	-1.5 ± 0.1
6	⟨100⟩	3.5	-3.0 ± 0.1
7	⟨100⟩	3.8	-4.7 ± 0.3
8	⟨100⟩	4.0	-3.8 ± 0.5
9	⟨100⟩	1.9	-4.2 ± 0.1
10	⟨100⟩	4.4	-5.9 ± 0.3
11	⟨100⟩	3.8	-4.5 ± 0.2
12	⟨100⟩	3.4	-3.8 ± 0.5
13	⟨100⟩	2.4	-2.7 ± 0.3
14	⟨100⟩	3.5	-2.7 ± 0.8
15	⟨110⟩		8.0 ± 1.1
16	⟨110⟩		9.1 ± 0.5

graph. The values of E vary with diameter in a manner similar to that reported by Reinkober.[20]

B. Copper

A summary of the δ's for Cu whiskers is given in Table II. The average values are $\delta_{100}=-3.4$, $\delta_{110}=5.7$, and $\delta_{111}=2.1$; the standard deviation of the average value of δ_{100} is 1.3. The value of ζ was too uncertain to be considered. The values of δ for the three orientations of Cu whiskers may be compared to the δ's calculated from bulk-sample measurements of the C_{IKM} of Hiki and Granato.[21] These calculated values are listed in Table II. The calculations of the δ's are sensitive to small changes of $c_{ij}{}^s$ and C_{IKM}. For example, a 1% change of $c_{ij}{}^s$ causes δ_{100} to change by 10%.

All six of the independent third-order elastic constants of Cu were computed from the experimental δ's and one of three sets of pressure derivatives[21–23] of the second-order constants. They are shown in Table V.

Brenner[4] did not observe nonlinearity in Cu whiskers strained to 2.8% in tension. However, the nonlinearities measured in these experiments would have been difficult to observe in a simple tension experiment.

C. Silver Whiskers

A summary of the values of δ for silver whiskers is given in Table III. The average value of δ_{100} is -3.7 with a standard deviation of 1.2; the average value of δ_{110} is 8.5. The value ζ was too uncertain to be considered. Five of the isothermal third-order elastic constants were calculated from the experimental δ and either of the reported sets of pressure derivatives of the second-order adiabatic constants. The results are shown in Table V.

[20] O. Reinkober, Physik. Z. **32**, 243 (1931); **33**, 32 (1932); **38**, 112 (1937); **40**, 385 (1939).
[21] Y. Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).
[22] D. Lazarus, Phys. Rev. **76**, 545 (1949).
[23] W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958).

TABLE IV. Summary of results for iron whiskers.

Number	Orientation	Diameter (in μ)	δ
1	⟨100⟩	4.4	4.8 ± 0.1
2	⟨100⟩	5.0	4.9 ± 0.1
3	⟨100⟩	3.9	5.0 ± 0.5
4	⟨100⟩	2.3	4.3 ± 0.2
5	⟨100⟩	5.5	4.9 ± 0.4
6	⟨100⟩	2.8	5.5 ± 0.3

D. Iron Whiskers

Only whiskers with axes parallel to the [100] direction were available. A summary of the results is given in Table IV. The average value of δ_{100} is 4.9; the standard deviation of this is 0.4. The value of ζ was too uncertain to be considered.

This δ_{100} may be compared to earlier work with iron whiskers. Brenner[4] observed a decrease in Young's modulus of 15% at an elongation ϵ of 3% and a 40% decrease at $\epsilon=4.9\%$. These results indicate $\delta\simeq2.5$ at 3% strain and $\delta\simeq4$ at 4.9% strain.

From the value of δ_{100} obtained in this study and values of the pressure derivatives of the second-order elastic constants obtained by Rotter and Smith,[24] three of the six independent third-order elastic constants of iron were calculated and are listed in Table V.

VI. DISCUSSION

The variation of the values of δ should be examined. One explanation might be a size dependency of the magnitude of the third-order elastic constants. To investigate this possibility, a least-squares analysis was made using an equation of the form $\delta=aD+b$, where D is the diameter of the fiber. The diameters of the fused-silica fibers were determined from shadow graphs made with an R.C.A. type EMU-2A electron microscope. The cross-sectional areas of the whiskers were calculated from the force-extension data obtained in a tensile test, and the diameter defined as the square root of the cross-sectional area. The results of this analysis for the fused-silica fibers, δ_{100} copper whiskers, and δ_{100} silver whiskers are given in Table VI. Although there may be a size effect, the spread of the values of δ (as indicated quantitatively by the coefficient of correlation between δ and D) precludes a categorical conclusion that δ is dependent on the size of the sample.

An alternative explanation of the variation of δ from whisker to whisker is that the third-order elastic constants are sensitive to impurity concentration. Drabble and Fendley[25] have shown that impurities have an effect on the third-order elastic constants of Ge. An attempt was made to determine the impurity content of the Cu

[24] C. A. Rotter and C. S. Smith, J. Phys. Chem. Solids **27**, 267 (1966).
[25] J. R. Drabble and J. Fendley, J. Phys. Chem. Solids **28**, 669 (1967).

TABLE V. Summary of values of third-order isothermal elastic constants (in units of 10^{12} dyn cm^{-2}).

Material	Supplementary data of	$c_{111}{}^T$	$c_{112}{}^T$	$c_{123}{}^T$	$c_{144}{}^T$	$c_{166}{}^T$	$c_{456}{}^T$
			Isothermal constants				
quartz	Bogardus[a]	3.98	2.90	−0.64	0.97	0.67	−0.75
quartz	Peselnick *et. al.*[b]	3.88	2.85	−0.42	0.83	0.66	−0.69
quartz	Anderson[c]	3.96	2.81	−0.57	0.94	0.68	−0.72
quartz	McSkimin[d]	3.71	2.70	−0.77	0.75	0.66	−0.66
copper	Hiki and Granato[e]	−12.99	−8.11	−1.69	0.87	−7.96	0.70
copper	Lazarus[f]	−14.31	−8.47	−1.24	0.75	−7.50	0.43
copper	Daniels[g]	−12.28	−6.34	0.95	3.20	−5.74	−1.36
silver	Hiki and Granato[e]	−9.59	−4.76	0.99	1.20	−6.73	...
silver	Daniels and Smith[g]	−11.53	−6.85	−1.42	2.18	−6.23	...
iron	Rotter and Smith[h]	−28.29	−8.00	−6.07	...	...	...
			Converted values of mixed third-order constants				
quartz	Bogardus[a]	5.26	2.39	0.54	0.93	0.72	−0.11
copper	Hiki and Granato[e]	−12.82	−8.23	−0.59	−0.03	−7.80	−0.95
silver	Hiki and Granato[e]	−8.58	−5.50	1.68	0.59	−6.34	0.83

[a] Reference 14. [b] Reference 15. [c] Reference 16. [d] Reference 17. [e] Reference 21. [f] Reference 22. [g] Reference 23. [h] Reference 24.

whiskers. The residual-resistance ratios ($\rho_{293°K}/\rho_{4.2°K}$) vary from 50 to 100. A mass-spectrometer test indicated that iron was the dominant impurity, and that its concentration was about 0.1%. Similar impurity concentrations are expected to occur in the Ag and Fe whiskers.

For quartz fibers, some of the variation of δ could be caused by differences in the formation of the fibers. This effect on the reported size dependency of the second-order elastic constants has been discussed by Tighe.[26]

The room-temperature values of the third-order elastic constants determined from measurements of δ and pressure derivatives of the second-order elastic constants are given in Table V.

A detailed error analysis would be extremely laborious, because of the number of terms upon which δ depends. In order to estimate the magnitude of the errors, errors associated with the values of the isothermal third-order constants of copper based on the pressure derivatives of Hiki and Granato[21] were considered. Errors associated with the second-order elastic constants were neglected. The standard deviations of the δ's for the copper whiskers and the probable errors estimated by Hiki and Granato for the C_{ijk}'s were treated as absolute errors and were propagated through the expressions from which $c_{IMR}{}^T$ was calculated according to the usual rules for error propagation, as given by Baird.[27] The magnitude of error estimates are given in parentheses after each of the following constants: $c_{111}{}^T$ (10%), $c_{112}{}^T$ (15%), $c_{144}{}^T$ (300%), $c_{166}{}^T$ (50%), and $c_{456}{}^T$ (100%). The size of the errors estimated for $c_{123}{}^T$, $c_{144}{}^T$, and $c_{456}{}^T$ is the result of each of these constants being the difference of quantities having nearly the same magnitude. The calculated isothermal third-order moduli of copper are within the limits of error of the values of the isothermal constants converted from the values reported by Hiki and Granato.[21]

Errors could be estimated for the other cases in the same manner. The magnitude of the errors for silver and quartz would probably be about the same as those estimated for copper. For iron, the error estimates are $c_{111}{}^T$ (±6%), $c_{112}{}^T$ (±6%), and $c_{123}{}^T$ (±60%). The smaller error limits for the constants for iron results from a smaller standard deviation of δ.

Other reported values of the mixed third-order constants represent experiments performed on a small num-

TABLE VI. Size dependence of δ. The values of δ for quartz fibers, [100] copper whiskers, and [100] silver whiskers were fitted to the function $\delta = aD + b$, where D is the diameter of the fiber. The quantity R is the coefficient of correlation between D and δ, and S is the standard deviation of the slope.

Material	a	b	S	R
quartz fibers	−0.24	−1.6	1.5	−0.44
[100] Cu whiskers	−2.12	−0.61	0.14	0.65
[100] Ag whiskers	−0.06	−1.0	0.3	0.69

[26] Nancy J. Tighe, Natl. Bur. Std. (U. S.) Circ. **569**, 1 (1956).

[27] D. C. Baird, *An Introduction to Measurement Theory and Experiment Design* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962), p. 63.

ber of samples. For example, Hiki and Granato reported measurements on one specimen each of copper and silver. Bogardus's values were obtained from some measurements of sound propagation in certain directions in one sample, and other measurements of sound propagation in different directions of other specimens. While the results of any sample in this work were reproducible, the sample-to-sample variance suggests that the third-order constants may be more structure-sensitive than are the second-order constants.

The magnitude of a combination of fourth-order elastic constants of Cu, Ag, and Fe may be roughly estimated. The coefficient of ϵ^2 in Eq. (8) is less than 20 for these materials. Thus $\zeta=\frac{1}{3}(2\delta^2\pm 20)\simeq 10$.

PHYSICAL REVIEW VOLUME 174, NUMBER 3 15 OCTOBER 1968

Pressure Dependence of Infrared Eigenfrequencies of KCl and KBr†

C. POSTMUS AND J. R. FERRARO
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439
AND
S. S. MITRA*
Department of Electrical Engineering, University of Rhode Island, Kingston, Rhode Island 02881

(Received 6 June 1968)

Pressure dependence of the $\mathbf{k}\sim 0$ TO phonon frequencies of KCl and KBr is reported in the pressure range of 1 to 35 kbar. Using the P-V data, the volume dependence of these modes was determined. The Grüneisen parameters thus obtained compare well with those calculated from Born-Mayer-type potentials. It appears that the temperature dependence of the $\mathbf{k}\sim 0$ TO phonon frequency of KBr can be completely accounted for by its volume dependence. In the temperature range of 5 to 750°K, the "self-energy shift" due to anharmonicity thus seems to be small compared with the thermal-expansion part. The CsCl phase occurs in both KCl and KBr at appropriate pressures. The $\mathbf{k}\sim 0$ TO frequency, as expected, drops by some 10 to 12% at the transition pressure.

I. INTRODUCTION

THE successful incorporation[1,2] of a high-pressure diamond cell[3] into a far-infrared spectrophotometer enabled[4] us to study the effect of pressure on the long-wavelength optic phonons of ionic or partially ionic solids. A similar experiment involving the use of a high-pressure diamond cell in conjunction with a laser-excited Raman spectrophotometer has also been performed.[5] We have previously reported[4] the pressure dependence of the infrared dispersion frequencies of LiF, NaF, and ZnS. In this communication, the effect of pressure on the $\mathbf{k}\sim 0$ transverse optic (TO) modes of KCl and KBr will be described. In both of these solids a phase transition from the NaCl to the CsCl structure is known to occur under application of pressure. Such transitions have been noted in the present study. For KBr, extensive data on the temperature dependence of the TO frequency exist. With the aid of the present data on pressure dependence, the various contributions to the temperature dependence will be discussed.

II. EXPERIMENTAL

Spectrophotometric measurements were made with a Perkin-Elmer Model-301 far-infrared instrument modified for scale expansion[6] to minimize the required attenuation of the reference beam to match the low transmission of the sample beam through the Van Valkenburg high-pressure opposed diamond anvil cell.[3] The 6× beam condenser was modified to accept the high-pressure cell.[1]

To increase the transmission through the cell, necessary for the low wave-number region, the contact area of diamond anvils was increased[2] from approximately 0.3 to 0.75 mm². The actual contact area was determined from microphotographs. The increase in the area reduces the average pressure on the material, defined as the applied force divided by the anvil contact area. The applied force for a given compression of the spring was calibrated against a Dillon force gauge.

Crystals studied were formed from finely powdered materials in the diamond cell by the slow application of relatively low pressure (up to 1–5 kbar) and then

† Based on work performed under the auspices of the U. S. Atomic Energy Commission.
* Supported in part by the U. S. Air Force In-House Laboratory Independent Research Fund under Contract No. AF19(628)-6042.
[1] J. R. Ferraro, S. S. Mitra, and C. Postmus, Inorg. Nucl. Chem. Letters **2**, 269 (1966).
[2] C. Postmus, J. R. Ferraro, and S. S. Mitra, Inorg. Nucl. Chem. Letters **4**, 55 (1968).
[3] C. E. Weir, E. R. Lippincott, A. Van Valkenburg, and E. N. Bunting, J. Res. Natl. Bur. Std. **63A**, 55 (1959). The diamond cell is commercially available from High Pressure Diamond Optics, Inc., McLean, Va.
[4] S. S. Mitra, C. Postmus, and J. R. Ferraro, Phys. Rev. Letters **18**, 455 (1967).
[5] C. Postmus, V. Maroni, J. R. Ferraro, and S. S. Mitra, Inorg. Nucl. Chem. Letters **5**, 269 (1968).
[6] C. Postmus, K. Nakamoto, and J. R. Ferraro, Inorg. Chem. **6**, 2194 (1967).