deformation. The ratio of the production efficiency α_f/α_u decreases with increasing strain.

There is a theoretical possibility and an experimental indication for a larger efficiency to exist during first cycles of cyclic loading than during the initial of unidirectional deformation.

The shear-modulus changes observed during cyclic stressing can be attributed to the formation of dislocation dipoles from dislocations of the initial network.

To detail the exact mechanisms it is necessary to perform resistivity measurements, shear-modulus measurements, and electron-microscopy studies, and correlate these for the same sample.

Third-Order Elastic Constants of Single-Crystal and Polycrystalline Columbium

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The second-order and third-order elastic constants for both single-crystal and polycrystalline columbium were determined at 298°K using an ultrasonic phase comparison method. It is shown that any dislocation contribution to the measurements is negligible with respect to other uncertainties. The third-order elastic constants (Brugger convention) in units of 10^{12} dyn/cm² are

$$c_{111} = -25.64 \pm 0.25; \quad c_{144} = -3.43 \pm 0.10; \quad \nu_1 = -4.8 \pm 1.2;$$
$$c_{112} = -11.40 \pm 0.25; \quad c_{166} = -1.677 \pm 0.05; \quad \nu_2 = -3.70 \pm 0.2;$$
$$c_{123} = -4.67 \pm 0.25; \quad c_{456} = +1.366 \pm 0.05; \quad \nu_3 = +0.75 \pm 0.05.$$

The Grüneisen parameter calculated from these values is 1.511 ± 0.026 for the single crystal, and 1.546 ± 0.092 for the polycrystal, in good agreement with the value 1.52 calculated from bulk-property measurements. The polycrystalline third-order elastic constants are in very good agreement with those calculated from the single-crystal values by the method of Chang.

I. INTRODUCTION

Of the several methods of determining the third-order elastic constants (TOEC) of solids,[1] the one that is proven most useful involves the measurement of the dependence of ultrasonic wave velocities on a static bias stress. Most of the early work in this area is restricted to the use of hydrostatic pressure as the bias stress[2,3] to attain stresses high enough so that the dependence was measurable without introducing plastic flow in the samples. This method cannot provide enough information to obtain all of the TOEC, however. In an elastically isotropic sample, for example, there are only two nondegenerate pure-mode elastic waves which can be propagated, providing two relations involving the three independent TOEC. In crystals of cubic symmetry, there are three pure-mode waves for a given propagation direction and therefore three independent relations among the six independent TOEC. However, the results of these measurements are useful in theoretical studies of those anharmonic properties which are bulk properties in the sense that they do not depend on the crystal orientation, such as thermal expansion (or the Gruneisen parameter) in isotropic

or cubic symmetry crystals.[4] The results of the hydrostatic pressure experiments give just the combinations of TOEC which are required in these studies, but they are limited in that they cannot provide the entire set of TOEC which is required to define completely the anharmonic nature of the sample.

Recent developments of more sensitive experimental methods of determining relative changes in ultrasonic wave velocities have allowed the extension of these methods to include the use of uniaxial bias stresses, as well as hydrostatic pressure.[5] It has been found, however, that in materials with a low yield stress such as pure copper, that at even very low values of uniaxial bias stress, the ultrasonic wave velocity will be affected by a change in the dislocation contribution to the dynamic second-order elastic moduli caused by the applied bias stress.[6] This change in the ultrasonic wave velocity due to dislocations is impossible to separate from the change due to intrinsic lattice anharmonicity, and therefore care must be taken to prevent this effect from occurring. Methods that have been used to pin

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the dislocations and prevent them from contributing to the dynamic elastic moduli are prestraining (Cu, Ag, Au),[7] and pinning with point defects produced by neutron irradiation or by impurity atom doping (Cu).[6]

Complete sets of TOEC have been determined for only those metals mentioned above, all fcc. Other materials for which all the TOEC have been reported are the semiconductors Ge,[8–11] Si,[8–11] GaAs,[12] InSb,[13] the alkali halides NaCl,[14,15] and KCl,[14] and the insulators MgO,[10] quartz,[16] and yttrium iron garnet.[17] Complete sets of TOEC for polycrystalline or amorphous materials that have been reported are for Cu,[1] Fe[1,18] fused silica,[10] pyrex glass and polystyrene,[18] a variety of steels, aluminum alloys, a magnesium alloy, and sintered Mo and W.[19]

Columbium is one of a class of materials, the bcc refractory metals, for which TOEC have not been reported, except for the sintered materials mentioned above. With the growing commercial use of these materials, there has been an increasing interest in their mechanical properties. The contribution of lattice anharmonicity in lattice-defect calculations is one area of theoretical study that is being pursued.[20]

Since the yield points of these metals are considerably higher than those of the fcc metals studied to date, it seems reasonable to expect less of a problem with dislocations when determining their TOEC using a uniaxial bias stress. This expectation was realized as will be seen in the following sections.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

An ultrasonic phase comparison method was used to determine both the values of the pure-mode ultrasonic wave velocities and their dependence on an applied static bias stress, both hydrostatic and uniaxial. An Arenberg PG-650C pulsed oscillator was used as a gated amplifier for pulsing the sample with an rf signal derived from an external cw oscillator whose frequency was continuously monitored by a digital counter. The applied rf pulse length was adjusted twice the round trip transit time of the ultrasonic pulse through the sample so that each echo overlapped one-half the following echo in the pulse-echo train. The frequency of the cw oscillator was then adjusted to obtain an out-of-phase condition between successive echoes so that the overlap regions presented a minimum or null signal level. The overlap region between the 1st and 2nd or 2nd and 3rd echoes was then gated out, amplified, and the unrectified signal displayed on a Hewlett–Packard 175A oscilloscope. The frequency at which the null condition occurs is simply related to the ultrasonic wave velocity in the sample. The null frequency can be determined to one part in 10^6 in the best cases encountered so far even with $\frac{3}{16}$ in. sample lengths. Typically, however, with this size sample, and with a low value of ultrasonic attenuation as experienced with a single crystal, the accuracy is 3–5 parts in 10^6 for shear waves and 3–5 parts in 10^5 for longitudinal waves because of their higher velocities. With larger samples and longer transit times the accuracies for the two types of waves should be the same. A complete description and analysis of the method is given elsewhere.[21]

Quartz crystals of $\frac{1}{8}$ in. diam were bonded to the nominally $\frac{1}{4}$ in. sq sample faces using Nonaq. Both X-cut and AC-cut crystals having 16 MHz fundamental frequencies were used for the single-crystal studies and 5 MHz for the polycrystals. Hydrostatic pressure runs were made with the sample enclosed in a high-pressure chamber pressurized with helium gas. A 16 in. 7500 psi Heise pressure gauge was used to monitor the helium gas pressure to ±0.1% of full scale. The uniaxial stress runs were made with the samples loaded in compression between optically flat stainless steel load platens in an isothermal enclosure on a table model Instron test machine. The load was monitored, by a load cell calibrated to ±0.5% of full scale. The sample temperature was recorded before and after each frequency reading to ±0.025°C using a chromel-alumel thermocouple junction spring loaded to the side of the sample in both test arrangements.

B. Sample Description and History

Two single-crystal columbium samples were used in this study. They were both cut from the same $\frac{5}{16}$ in. diam 3-pass electron-beam zone refined single-crystal rod obtained from Materials Research Corp. A typical analysis for material prepared in this manner is 100 ppm Ta, <30 ppm P, 8 ppm C, 6 ppm W, 4 ppm N, and 23 ppm O, with traces of several other elements. After the initial cutting and lapping stages, special care was taken to alternately etch and polish each of the three pairs of faces of the samples until sharp Laue

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diffraction spots were obtained. The desired crystallographic orientations of the faces were maintained to within 0.5° during these operations. The process of polishing the samples resulted in all six being flat to better than 1λ and each of the three faces parallel to 10 sec of arc.

Sample 1 was nominally $\frac{1}{4} \times \frac{1}{4} \times \frac{3}{16}$ in. with the $\frac{3}{16}$ dimension along [110] and the other two pairs of normal to [1\bar{1}0] and [001]. The second-order constants and their temperature dependences at 25°C were determined for this sample, and then hydrostatic pressure runs made by increasing the pressure in steps to a maximum pressure of 6000 psi, then decreasing the pressure in intermediate steps. Axial stress runs were then made to a maximum of 100 kg or 4800 psi, which is about 55% of the psi yield stress for this material.[22] It was found on some runs at the maximum stress, time-dependent changes in the frequency occurred. This effect was observed at a load of 90 kg or below and so was avoided by staying below this load for most runs. Some were also made by holding the sample at 100 kg until the null frequency stabilized, then decreasing load in steps to zero, and then increasing the load in in steps. No hysteresis was observed during this of run, and no systematic difference was found between these and the runs at the lower stress.

Sample 2 was nominally a $\frac{1}{4}$ in. cube having two pairs {110} faces and one pair of {100} faces. The cube configuration was desired to increase the accuracy of longitudinal wave measurements by obtaining a larger transit time, and to allow both ⟨100⟩ and ⟨110⟩ ultrasonic wave propagation on the same sample. These conditions were obtained at the expense of some more interference in the pulse-echo train from reflection of the divergent ultrasonic beam from the total sides of the sample. The latter was found not to a serious problem, however, since the interference only observed after the 4th or 5th echo and measurements were made on the 1st and 2nd echoes. The experimental procedure for this sample was the same for the first, except that the maximum uniaxial stress used was 1600 psi.

There were also two polycrystalline columbium samples used in this study. Considerable effort was spent in trying to obtain a sample having small, randomly oriented, and equiaxed grains with only partial success. Stock material from several suppliers was cold-worked by different means to produce up to reduction in thickness and then cut into sample blanks. These blanks were then given different recrystallization and anneal heat treatments and their microstructure examined. It was found that this material tends to deform in localized bands during cold-working and most of the specimens only partially recrystallized recrystallized with regions of widely different grain

size.[23] However, two samples were selected from the lot for the ultrasonic study and their surfaces polished as was done with the single-crystal samples.

Sample A was the result of the earlier attempts with sample preparation. It was nominally $\frac{1}{4} \times \frac{1}{4} \times \frac{3}{16}$ in. and had a uniform grain size and shape, but the grains were elongated and more or less aligned in one direction parallel to the $\frac{1}{4} \times \frac{1}{4}$ in. faces of the sample. The size of the grains was about 30 by 75 μ.

Sample B was selected from the later attempts and was nominally $\frac{1}{2} \times \frac{1}{2} \times \frac{3}{16}$ in. In this sample, the grains were equiaxed and averaged 10 μ in size over most of the sample, but there was a region extending along the $\frac{3}{16}$ in. dimension which contained grains of 50 μ size. The ultrasonic measurements on this sample were made with quartz transducer attached in an area containing only 10 μ grains slightly off the center of the $\frac{1}{2} \times \frac{1}{2}$ in. face.

The second-order elastic constants of both samples and their dependence on hydrostatic and uniaxial stress were measured in the same manner as with the single-crystal samples. The density of the samples was determined from weight-volume measurements to be 8.579±0.005 g/cm³ which is, within experimental uncertainty, the same as the single-crystal density of 8.578±0.003 g/cm³ determined previously.[24,25] The latter value was used throughout the elastic constant calculations for both the single-crystal and polycrystalline samples.

C. Dislocation Study

Following the single-crystal measurements, an extensive study was made of the time dependent changes in null frequency observed at the maximum loads for sample 1. It was found that the observed kinetics of this Δf effect could be described at least qualitatively by a dislocation unpinning and repinning model; the net change in frequency was an increase of about 500 Hz on most runs; the effect was absent after cycling the load through zero if it had first been allowed to go to completion, but would reappear after the sample had remained with no load for a period of 24–48 h; the magnitude of Δf decreased on successive runs and finally disappeared; the effect reappeared by activating a different set of dislocation slip systems; and finally, that Δf could be completely suppressed by irradiation of the sample at 1 M rad/h for 46 h with a Co⁶⁰ γ-ray source. Similar studies were made on sample 2, but no Δf effect was seen for this sample even at loads approaching the yield point. Measurements were made

²² T. E. Mitchell, R. A. Foxall, and P. B. Hirsch, Phil. Mag 8, 1895 (1963).

²³ The cold-rolling described here was done in steps of about 10% deformation per pass on a small laboratory rolling machine. Very recent results using a large commerical rolling machine, which produced 50%–60% deformation per pass, produced a more uniform deformation and upon recrystallization a considerable improvement in the polycrystalline grain structure.

²⁴ D. I. Bolef, J. Appl. Phys. 32, 100 (1961).

²⁵ R. J. Wasilewski, J. Phys. Chem. Solids 26, 1643 (1965).

TABLE I. Calculational equations for the uniaxial stress data used with the hydrostatic pressure data to obtain the third order elastic constants of single-crystal columbium. The relation numbers refer to the equations in order in Tables I–III of Ref. 26. The relations at the bottom can be derived from the equations of Ref. 26. The values of the adiabatic second-order elastic constants of columbium used to calculate the constants in these equations are the "best" values listed in Table II. The isothermal elastic constants $C_{11}{}^T$ and $C_{12}{}^T$ needed were determined from $C_{ij}{}^T = C_{ij}{}^S - 0.0161 \times 10^{12}$.

Relation No.	Calculational equation
10	$C_{111} - 3.8597 C_{112} + 2.8597 C_{123} = (+8.7413 m_{10} - 2.2644) \times 10^{12}$
11	$C_{144} - 1.8597 C_{166} \qquad\qquad = (+4.3706 m_{11} + 1.6243) \times 10^{12}$
13	$C_{144} - 0.0754 C_{166} + 8.2754 C_{456} = (-4.7004 m_{13} - 2.9182) \times 10^{12}$
14	$C_{144} - 0.0754 C_{166} - 8.2754 C_{456} = (-4.7004 m_{14} + 1.7822) \times 10^{12}$
16	$C_{111} - 2.0754 C_{112} + 1.0754 C_{123} = (-9.4007 m_{16} - 11.6339) \times 10^{12}$
17	$C_{144} - 0.0754 C_{166} - 8.2754 C_{456} = (-4.7004 m_{17} + 0.6109) \times 10^{12}$

where

$$m_{14} - m_{17} = (1 - A)/2 = 0.2492,$$

$$A = 2C_{44}/(C_{11} - C_{12})$$

$$C_{456} = C_{44}(m_{11} - m_{13} - 1)$$

on sample 1 after irradiation to determine the TOEC for comparison with the previous determination.

There are several significant features of this study with regard to the determination of the TOEC. Assuming the Δf effect observed is due to dislocation motion or rearrangement, it is apparent that this can occur at stresses well below the yield point of this material, and must be prevented in TOEC studies. The magnitude of the time-independent Δf associated solely with lattice anharmonicity in this study ranged from 2 to 35 kHz for a stress of 4800 psi so the 0.5 kHz time-dependent Δf would be significant on some runs. The reason for the different behavior of the two apparently identical samples is not known but may be due to slight differences in impurity levels or in cold-work during preparation, both of which might be methods for controlling the dislocation effect. Other methods for controlling this effect suggested by the dislocation study are preloading or load cycling the sample prior to use, irradiating it, or simply working at lower stresses. These three methods comprise the principle differences in procedure for the three TOEC determinations of the two samples of this study, i.e., (1) preloading of sample 1; (2) irradiating sample 1; (3) using low stress on sample 2.

There is another possible contribution of the dislocations to the change in frequency with applied uniaxial load besides the time-dependent frequency change observed at the higher values of load. This is due to the increase in dislocation loop length as the dislocations bow out with applied stress before break-away occurs. This would cause an apparent reduction in the second-order dynamic elastic moduli, the magnitude of which would depend upon the initial loop length. It is probable that the difference between the behavior of the two samples in the dislocation study described above is due to a difference in loop length along with other factors, and that the loop length in sample 1 was different before and after irradiation.

Therefore, if dislocation bowing in these samples causes an appreciable Δf, systematic differences in the three independent sets of measurements of the uniaxial stress dependences of the ultrasonic wave velocities should be apparent. It will be seen that no such differences were found and that this contribution of the dislocations to the measured frequency change is therefore small.

D. Data Analysis

Analysis of the data to obtain values for the TOEC of columbium was done using the relations given by Thurston and Brugger[26] in their Tables I–III for cubic single crystals and IV for an isotropic medium. These relations will not be repeated here but will be referred to by numbers 1–17 for the single-crystal relations in the order in which they are given, and by $1'$–$5'$ for the isotropic medium relations. These equations relate the stress derivatives of the second-order elastic constants evaluated at zero stress in terms of combinations of second-order and third-order elastic constants. Since these stress derivatives are independent of pressure within the accuracy of the measurements, they are determined by the experimental slopes of the null frequency vs load plots, i.e.,

$$m_n \equiv [(\partial/\partial p)(\rho_0 w^2)_n]_T |_{p=0}$$

$$= [F(C_{ij})_0/\Delta p][2\Delta f/f_0 + (\Delta f/f_0)^2]_n, \quad (1)$$

where Δf is the observed change in frequency for a total pressure or stress change Δp, and $F(C_{ij})$ is the combination of second-order elastic constants for the elastic wave mode associated with relation n in Tables I–IV of Ref. 26. Since the largest $\Delta f/f_0$ value observed was $\sim 10^{-3}$, the $(\Delta f/f_0)^2$ term can be ignored resulting

26 R. N. Thurston and K. Brugger, Phys. Rev. 133, A1604 (1964).

TABLE II. Adiabatic second-order elastic constants of columbium obtained in the present and in previous investigations. The investigators of Refs. 24 and 27 used ultrasonic methods and Refs. 25 and 28 used the resonance method. The values for the present samples listed without parentheses were determined directly from the measured ultrasonic wave velocities and the other values were calculated from them. $C_S' = (C_{11} - C_{12})/2$, $C_L' = (C_{11} + C_{12} + 2C_{44})/2$, $K = (C_{11} + 2C_{12})/3$, and $A = C_{44}/C_S'$.

Present	Temp. (°K)	density (g/cm³)	C_{11} [a]	C_{12} [a]	C_{44} [a]	C_S' [a]	C_L' [a]	K [a]	A
Present
Sample 1	298	8.578	(2.4653)	(1.3335)	0.28368	0.56592	2.1831	(1.7108)	(0.5013)
Sample 2	298	8.578	2.4645	(1.3323)	0.28431	0.56618	2.1828	(1.7098)	(0.5022)
"Best" values	298	8.578	(2.465±0.005)	(1.333±0.007)	0.2840±0.0006	0.5661	2.1829	(1.7102)	(0.5017)
Previous
Ref. 24	300	8.578	2.456±0.0098	1.345±0.014	0.2873±0.0011	0.5604	2.187	1.718	0.5127
Ref. 27	300	8.5605	2.456±0.015	1.387±0.46	0.2930±0.0018	0.5345	2.215	1.743	0.5482
Ref. 25	298	8.578	2.34	1.21	0.2821±0.0004	0.571	2.06	1.59	0.495
Ref. 28	RT	···	2.40±0.11	1.26±0.11	0.2809±0.0007	0.57	2.11	1.64	0.493

[a] Units of 10^{12} dyn/cm².

in the calculational equation

$$m_n = [F(C_{ij})/\Delta p](2\Delta f/f_0). \qquad (2)$$

This equation was used to calculate the value of the slope m for each of the runs. Uncertainty limits for the slopes were established based on the estimated
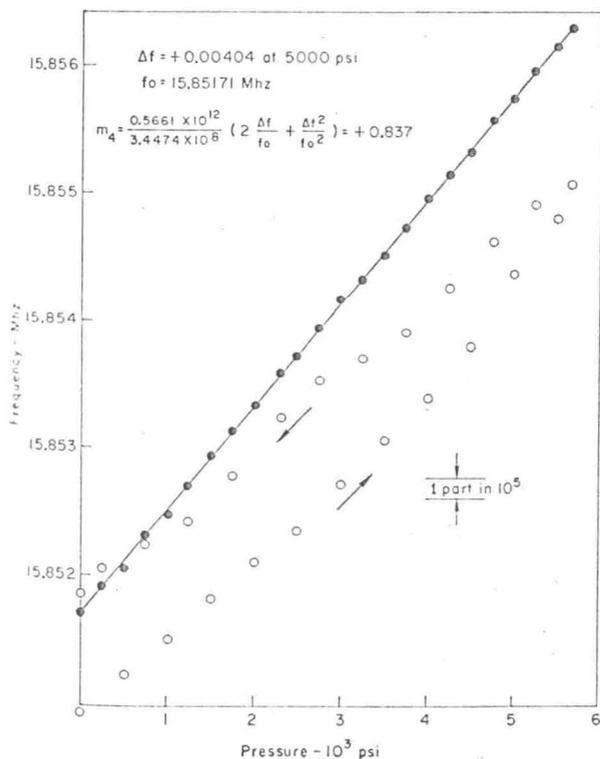

FIG. 1. Example of data for a hydrostatic pressure run. The open circles are data before correcting for temperature changes during the run. The temperatures at the start, middle, and end of the run were about 25.5°, 26.0°, and 25.0°C, respectively. After each 500 psi pressure change, about 15 min was allowed for the temperature to approach equilibrium before frequency readings were taken.

uncertainty in Δf and in the stress, p. Examples of a hydrostatic pressure and a uniaxial stress run are shown in Figs. 1 and 2.

Because of the redundancy in the number of relations available to determine the values of the single-crystal TOEC, and the wide range of uncertainties in the values of m_n, the data analysis from this point is highly subjective. Several procedures were tried with only slightly different results, so only one of these are described. The hydrostatic pressure data was considered the most reliable and was found to have the best internal consistency based on the relations $m_2 \equiv m_5$, and $m_1 + m_2 = m_3 + m_4$, which can readily be shown. The hydrostatic pressure equations were then solved
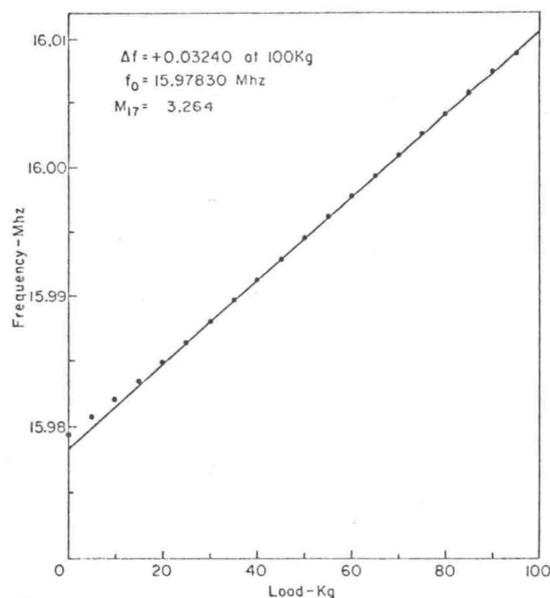

FIG. 2. Example of data for a uniaxial stress run. Some nonlinearity in the stress-frequency dependence at low stresses was often seen.

TABLE III. The measured slopes of the stress dependences of the second-order elastic constants for three independent sets of measure ments and the third-order elastic constants determined from them. The third-order elastic constants listed as "best" values were tained by combining all of the data, and the "best"-value slopes were then calculated from them. The relation numbers refer to relations in order in Tables I–III of Ref. 26.

Relation No.	Sample 2	Sample 1 before irradiation	Sample 1 after irradiation	"Best" values
1	$+7.59\pm0.13$	a	(7.5621 ± 0.13)	$+7.5621$
2	$+0.221\pm0.008$	a	(0.2235 ± 0.006)	$+0.2235$
3	$+6.90\pm0.12$	$+6.95\pm0.32$	(6.9456 ± 0.12)	$+6.9456$
4	$+0.844\pm0.016$	$+0.837\pm0.004$	(0.8400 ± 0.004)	$+0.8400$
5	$+0.232\pm0.008$	$+0.222\pm0.006$	(0.2235 ± 0.006)	$+0.2235$
6	a	a	a	$+0.1138$
7	a	a	a	$+1.6082$
8	a	a	a	-0.4432
9	small pos.	$+0.85\pm0.4$	not meas.	$+0.8891$
10	$+0.856\pm0.013$	$+0.774\pm0.044$	$+0.767\pm0.016$	$+0.8328$
11	-0.446 ± 0.042	-0.475 ± 0.050	-0.442 ± 0.070	-0.4432
12	small neg.	a	a	$+0.1138$
13	-2.34 ± 0.032	a	a	-2.3222
14	$+3.83\pm0.09$	a	a	$+3.4871$
15	small pos.	$+1.2\pm0.7$	not meas.	$+1.4651$
16	-0.49 ± 0.06	-0.54 ± 0.06	-0.502 ± 0.032	-0.4929
17	$+3.20\pm0.07$	$+3.14\pm0.05$	$+3.264\pm0.016$	$+3.2379$
C_{111}	-25.630 ± 0.33 [b]	-25.683 ± 0.66	-25.736 ± 0.26	-25.64 ± 0.25
C_{112}	-11.387 ± 0.27	-11.389 ± 0.60	-11.355 ± 0.24	-11.40 ± 0.25
C_{123}	-4.622 ± 0.33	-4.746 ± 0.65	-4.769 ± 0.26	-4.67 ± 0.25
C_{144}	-3.444 ± 0.11	-3.500 ± 0.13	-3.384 ± 0.17	-3.43 ± 0.10
C_{166}	-1.677 ± 0.06	-1.639 ± 0.065	-1.701 ± 0.09	-1.677 ± 0.05
C_{456}	$+1.360\pm0.16$	$+1.302\pm0.044$	$+1.387\pm0.031$	$+1.366\pm0.05$
$C_{111}+2C_{112}$	-48.404 ± 0.66	-48.460 ± 1.68	not meas.	-48.45 ± 0.66
$C_{144}+2C_{166}$	-6.799 ± 0.040	-6.779 ± 0.030	not meas.	-6.786 ± 0.030
$C_{111}-C_{123}$	-21.008 ± 0.16	-20.937 ± 0.040	not meas.	-20.967 ± 0.040

[a] These values could not be determined because of the crystallographic orientations of the samples.

[b] The units for all the third-order elastic constants are 10^{12} dyn/cm^2.

for the values of the three combinations of TOEC $(C_{111}+2C_{112})$, $(C_{144}+2C_{166})$, and $(C_{111}-C_{123})$, which were considered to be exact within the limits of their uncertainties based entirely on the uncertainties in the values of m_n estimated previously. Of the remaining uniaxial stress data, the data obtained using longitudinal ultrasonic waves were ignored because of their very large uncertainties, and data for relations (6), (7), and (8) could not be obtained because the samples

were not of the right crystallographic orientation. The remaining relations, given in Table I, were then combined with the three relations obtained from the hydrostatic pressure data in such a manner as to obtain the best agreement with all the data taking into account their relative uncertainties.

The data for the polycrystalline samples were analyzed in a similar manner, again relying heavily on the hydrostatic pressure measurements.

TABLE IV. The adiabatic second-order elastic constants of two polycrystalline columbium samples at 298°K. A density of 8.578 g/cm^3 was used. The Voigt–Reuss–Hill average of the single-crystal elastic constants is shown for comparison.

		Sample A elongated $30\times75\ \mu$ grains	Sample B equiaxed $10\ \mu$ grains	Calculated by VRH approx. from single xtal data
$C_{11}=\lambda+2\mu$	10^{12} dyn/cm^2	2.179 ± 0.004	2.203 ± 0.004	2.2113
$C_{12}=\lambda$	10^{12} dyn/cm^2	1.433 ± 0.006	1.453 ± 0.006	1.4597
$C_{44}=\mu$	10^{12} dyn/cm^2	0.373 ± 0.001	0.375 ± 0.001	0.3758
E	10^{12} dyn/cm^2	1.041	1.048	1.0505
G	10^{12} dyn/cm^2	0.373	0.375	0.3758
K	10^{12} dyn/cm^2	1.682	1.703	1.7102
σ — Poisson's ratio		0.397	0.397	0.3977

III. RESULTS

A. Single Crystals

The second-order elastic constants measured for the single-crystal samples are given in Table II along with the values determined for columbium by previous investigators.[24,25,27,28] The values for the present samples having no parentheses were determined directly from the measured ultrasonic wave velocities and are estimated to be accurate to 0.2%, and the values in parentheses were calculated from them. It was considered necessary to determine these values for the present samples because of the rather large disagreement between previously reported values for columbium. Table III lists all the calculated values of the slopes, and their estimated uncertainties for the three independent sets of measurements and the values of the TOEC calculated from them. As described before, sample 1 was run at a maximum uniaxial stress of 4800 psi, both before and after irradiation, and sample 2 at a maximum of 1600 psi. The hydrostatic pressure slopes in parentheses in column 3 were determined as the most probable values from the two samples before irradiation. The uncertainties shown for the TOEC were determined arithmetically as the maximum uncertainties based on the limits estimated for the slopes assuming no contribution from the uncertainties in the second-order elastic constants. In a few cases these uncertainties were increased above their arithmetic value because all of the relations could not be satisfied within the estimated uncertainties of the data.

The excellent agreement and internal consistency between the hydrostatic pressure slopes for the two samples justifies their emphasis in the calculations of the TOEC. Comparing the results of the three sets of measurements, differences in the values of the uniaxial stress slopes which are well outside the uncertainty limits are seen. However, there is no apparent trend between the sets of data, and the TOEC calculated from them agree within their uncertainty limits, so the differences in the slopes were ascribed to random errors brought about possibly by nonuniform stress distribution, interference caused by ultrasonic beam spreading in the small samples, or transducer bond characteristics changing with applied load. There are apparently no systematic differences which could be ascribed to dislocations.

The "best" values listed in the last column of Table III were then determined as the values which would best agree with all of the data. These values of the TOEC are considered the most representative of the two columbium single crystals studied. Their limits are estimated from the arithmetic limits calculated previously for the three sets of data.

[27] K. J. Carroll, J. Appl. Phys. 36, 3689 (1965).
[28] P. E. Armstrong, J. M. Dickenson, and H. L. Brown, Trans. Met. Soc. AIME 236, 1404 (1966).

TABLE V. The measured slopes of the stress dependences of the second-order elastic constants of polycrystalline columbium and the third-order elastic constants calculated from them. The relation numbers refer in order to the equations in Table IV of Ref. 26. The "best"-values slopes were calculated from the third-order elastic constants listed below them.

Relation No.	Sample A elongated $30 \times 75 \mu$ grains	Sample B equiaxed 10 μ grains	
		Experimental	"Best" values
$1'$	$+6.20\pm0.25$	$+7.10\pm0.25$	$+7.098$
$2'$	$+0.273\pm0.04$	$+0.437\pm0.04$	$+0.450$
$3'$	$+1.51\pm1.0$	$+1.3\pm1.3$	$+0.758$
$4'$	-2.79 ± 0.46	-0.828 ± 0.07	-0.858
$5'$	$+4.72\pm0.30$	$+2.182\pm0.07$	$+2.156$
$\nu_1 - 10^{12}$ dyn/cm^2	(see text)		-4.8 ± 1.2
$\nu_2 - 10^{12}$ dyn/cm^2	-4.01 ± 0.3		-3.70 ± 0.2
$\nu_3 - 10^{12}$ dyn/cm^2	$+2.55\pm0.2$		$+0.75\pm0.05$

B. Polycrystalline Samples

The second-order elastic constants measured for the two polycrystalline samples are given in Table IV along with values calculated from the single-crystal constants using the VRH method[29] for comparison. Since the two elastic constants directly determined from the ultrasonic wave velocities, C_{11} and C_{44}, are accurate to about 0.2%, the differences between the two samples are considered to be real and to be caused by the difference in grain structure between the two samples. It is seen that the values determined for the sample having equiaxed 10 μ grains agree within 0.5% of the values calculated from the single-crystal elastic constants.

The TOEC results are shown in Table V. The effect of the grain texture in sample A can be seen by the very different values of the slopes, m_n', measured for the two samples. The internal consistency of the data for sample A is also very poor. The relation

$$m_2' - 2m_4' - m_5' = 0, \qquad (3)$$

which can be readily derived from Thurston and Brugger's equations, is very poorly satisfied by the data for that sample. The values of ν_2 and ν_3 were calculated by adjusting the values of the measured slopes m_2', m_4', and m_5' to satisfy Eq. (3) above, weighting the corrections in proportion to the estimated uncertainties in the measured slopes. However, using these values in relations $1'$ and $3'$ resulted in values of ν_1 of -7 ± 2 and $+17\pm9$, respectively. Other schemes for analyzing the data resulted in slightly better consistency but widely different values for the TOEC and therefore this set of data is considered to be meaningless.

The data for sample B shown in Table V were analyzed in the same manner as described above. For this sample Eq. (3) was very nearly satisfied by the data. The degree of internal consistency of the data may be

[29] R. Hill, Proc. Phys. Soc. Lond. 65, 350 (1952).

TABLE VI. Impurity atom analyses of samples used in second-order elastic constant measurements.

	C_{44} [a]	C_S' [a]	Ta [b]	C	O	N	H	Other
Ref. 28	0.2809	0.57	500	50	50	50	$\cdots$	Other metals present at or slightly above spectroscopic detection limits.
Ref. 25								
low Ta	0.2821	0.571	1175	<20	19	<5	<6	Hf, <80; Ti, Mo, <50 ea.
high Ta	0.2825	0.570	130	<20	19	<5	<6	Ni, Sn, Pb, Zr, Be, V, Cr, Mn, Fe, Co, <15 each.
Present	0.2840	0.5661	100	8	23	4	0.4	P, <30; W, 6
Ref. 24	0.2873	0.5604	1500	$\cdots$	160	110	26	Zr, 100; Fe, 60
Ref. 27	0.2930	0.5345				(No analysis available)		

[a] In units of 10^{12} dyn/cm². [b] In ppm by weight. Ref. 28 does not specify whether by weight or by atom.

seen by comparing the values of the slopes calculated from the TOEC in the last column with the experimental values. The uncertainty limits shown were estimated in the same manner as for the single-crystal data.

IV. DISCUSSION

A. Second-Order Elastic Constants

The second-order elastic constants of Refs. 25 and 28 shown in Table II were measured using the resonant bar method where the elastic compliances S_{ij} are determined directly. These were then used to calculate the elastic constants listed by matrix inversion with a resultant loss in accuracy of C_{11} and C_{12}. However, since $C_{44} = 1/S_{44}$ and $C_S' = \frac{1}{2}(S_{11} - S_{12})$, these elastic constants are accurate enough for comparison with those determined directly by ultrasonic methods by the other investigators.

There seems to be a trend in the values of the second-order shear constants C_{44} and C_S' for columbium. For each set of data if C_{44} is higher than average, C_S' is lower. This follows even for the sample of Ref. 27 which is quoted as having some observable porosity and which has a measured density about 0.2% lower than that of the other samples. Yet its value of C_{44} is the largest of any reported. Also, the values of the constant C_L' and the bulk modulus, K, for this sample are larger than for the other samples which is surprising considering its porosity. Even if this sample is omitted from the comparison the trend still exists, the differences between samples, about 2% for both shear constants, being larger than the reported error limits. This does not appear to be an impurity effect as can be seen by comparing the impurity levels of the different samples as listed in Table VI.

The "best" value second-order elastic constants shown in Table II were used in calculating the TOEC. It can be shown that if the quoted uncertainties in these values are correct, they can be neglected in estimating the uncertainties in the TOEC values as was done in the present study. That this assumption

is valid is supported by the very good agreement between the values for the two samples seen in Table II, and also by the internal consistency of the data for sample 2. For this sample there is a redundancy in the data so that the constant C_{12} can be calculated in two ways, by $C_{12} = C_{11} - C_S' = 1.3321 \times 10^{12}$ and by $C_{12} = 2C_L' - C_{11} - 2C_{44} = 1.3325 \times 10^{12}$. These values are the same within the accuracy of measurements.

B. Third-Order Elastic Constants

The measured stress derivative slopes for the single-crystal samples in Table III are in several instances outside the range of their estimated limits. For example, m_{10} for sample 1 both before and after irradiation is almost 10% lower than the value for sample 2. However, internal consistency requirements with the rest of the data seem to indicate that the value for sample 2 is more nearly correct. This can be seen by the "best" value of m_{10} in the last column and by the close agreement between the values of C_{111}, C_{112}, and C_{123} determined from the three sets of data, and which depend partially on m_{10} along with m_1, m_4, and m_{16}. This indicates the presence of some unknown sources of error in the individual data as mentioned previously. However, the close agreement between the three sets of TOEC calculated from the data suggest that these errors tend to be smoothed out by conditions of internal consistency and that any systematic errors are relatively small.

The trouble experienced in obtaining the TOEC of polycrystalline columbium indicates the importance of having good polycrystalline samples for these measurements. It is seen that the elongated grain structure of sample A resulted in the measured second-order elastic constants being only about 1% lower than for sample B. However, this grain structure was apparently the cause of the very large differences in the measured stress derivatives of the two samples and the lack of internal consistency of the data for sample A.

One check on the reliability of the hydrostatic pressure measurements at least is to compare the values

Grüneisen parameter calculated from the single and the polycrystal TOEC with that calculated bulk data. Using values for the linear expansion ient, $\alpha = 7.02 \times 10^{-6}$ °C^{-1}, and specific heat, 065 cal g^{-1} °C^{-1} obtained from handbooks and density $\rho = 8.578$ g/cm^3, and isothermal bulk mod- $K^T = 1.687 \times 10^{12}$ dyn/cm^2 obtained in the present in the relation

$$\gamma_B = 3\alpha K^T / C_v \rho \qquad (4)$$

the value for the bulk Grüneisen parameter of 1.52. Using the methods of Ref. 4 for obtaining Grüneisen parameter from the elastic constants by aging the contribution of 39 pure-mode phonons at parameter results in values of $\gamma_{SC} = 1.511 \pm 0.026$ $\gamma_{PC} = 1.546 \pm 0.092$ for the single crystal and the crystal, respectively. A useful calculational equa- for the polycrystal Grüneisen parameter which can obtained from the equations of Brugger[4] by imposing ropy conditions is

$$= (K^T m_1' - \Delta K)/6C_{11}{}^S + (K^T m_2' - \Delta K)/3C_{44}{}^S, \qquad (5)$$

re m_1' and m_2' are the measured hydrostatic pres- e slopes for the polycrystal and $\Delta K = K^S - K^T$ is the erence between the adiabatic and isothermal bulk duli.

A second check on the values of the TOEC deter- ed here is to compare the measured polycrystal stants with values calculated from the single- stal constants. Recently, equations permitting this

comparison were derived[30] using strain-energy density considerations with the approximation that a uniform state of strain acting on the surface of a homogeneous, quasi-isotropic, polycrystalline body produces a uniform strain throughout the body. This development, analogous to that of Voigt relating the second-order elastic constants,[31] leads to the following relations between the TOEC:

$$\nu_1 = \tfrac{1}{35}(C_{111} + 18C_{112} + 16C_{123} - 30C_{144} - 12C_{166} + 16C_{456})$$

$$\nu_2 = \tfrac{1}{35}(C_{111} + 4C_{112} - 5C_{123} + 19C_{144} + 2C_{166} - 12C_{456})$$

$$\nu_3 = \tfrac{1}{35}(C_{111} - 3C_{112} + 2C_{123} - 9C_{144} + 9C_{166} + 9C_{456}). \qquad (6)$$

Using the values of C_{ijk} for columbium given in Table III in these equations results in $\nu_1 = -4.59 \pm 0.38$, $\nu_2 = -3.80 \pm 0.15$, and $\nu_3 = +0.78 \pm 0.09$, all in units of 10^{12} dyn/cm^2. These values are seen to be in very good agreement with the values measured for the poly-crystal sample B shown in Table V which provides an indirect check on both sets of TOEC.

ACKNOWLEDGMENTS

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Lithium Niobate: Effects of Composition on the Refractive Indices and Optical Second-Harmonic Generation*

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Crystals of lithium niobate have been grown with varying amounts of Li$_2$O, Nb$_2$O$_3$, and MgO present in the melt. The refractive indices have been measured and the birefringence so obtained correlated with the phase-matching temperature for second-harmonic generation (SHG) and with the composition. The use of optical methods is decribed for the study of compositional uniformity and a method of correcting the effects of uniform composition gradients on SHG described.

I. INTRODUCTION

An extensive literature already exists on lithium niobate with reference to its use in nonlinear optics for mixing or modulating optical beams. It was first proposed in this connection by Boyd et al.,[1] who described

its nonlinear properties and refractive-index data suitable for calculating the details of phase matching. Miller et al.[2] extended this data by pointing out the favorable property of thermally tunable refractive indices present in lithium niobate and showed how this could be used to obtain noncritical phase matching. Hobden and Warner[3] have given extensive details of the wavelength and thermal variation of the refractive

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