

III. RESULTS

A. Single Crystals

The second-order elastic constants measured for the two 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, m_n , 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.

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 30×75 μ grains	Sample B equiaxed 10 μ grains	
		Experimental	"Best" values
1'	+6.20±0.25	+7.10±0.25	+7.098
2'	+0.273±0.04	+0.437±0.04	+0.450
3'	+1.51±1.0	+1.3±1.3	+0.758
4'	-2.79±0.46	-0.828±0.07	-0.858
5'	+4.72±0.30	+2.182±0.07	+2.156
ν_1-10^{12} dyn/cm ²	(see text)		-4.8±1.2
ν_2-10^{12} dyn/cm ²	-4.01 ±0.3		-3.70±0.2
ν_3-10^{12} dyn/cm ²	+2.55±0.2		+0.75±0.05

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 method²⁹ 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

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

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 $+17 \pm 9$, 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

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).

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	...	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	...	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