x-ray diffraction spots were obtained. The desired crystallographic orientations of the faces were maintained to within 0.5° during these operations. The final stage of polishing the samples resulted in all six faces being flat to better than 1λ and each of the three pairs of 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 $\frac{3}{16}$ in. dimension along [110] and the other two pairs of faces normal to [1$\bar{1}$0] and [001]. The second-order elastic constants and their temperature dependences near 25°C were determined for this sample, and then the hydrostatic pressure runs made by increasing the pressure in steps to a maximum pressure of 6000 psi, and then decreasing the pressure in intermediate steps. Uniaxial stress runs were then made to a maximum load of 100 kg or 4800 psi, which is about 55% of the 8650 psi yield stress for this material.[22] It was found that on some runs at the maximum stress, time-dependent changes in the frequency occurred. This effect was never observed at a load of 90 kg or below and so was avoided by staying below this load for most runs. Some runs were also made by holding the sample at 100 kg load until the null frequency stabilized, then decreasing the load in steps to zero, and then increasing the load again in steps. No hysteresis was observed during this type 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 of {110} faces and one pair of {100} faces. The cube configuration was desired to increase the accuracy of the longitudinal wave measurements by obtaining a longer transit time, and to allow both ⟨100⟩ and ⟨110⟩ ultrasonic wave propagation on the same sample. These conditions were obtained at the expense of having more interference in the pulse-echo train from reflection of the divergent ultrasonic beam from the lateral sides of the sample. The latter was found not to be a serious problem, however, since the interference was 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 as 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 85% 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 or 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 $\Delta f$ 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 $\Delta f$ decreased on successive runs and finally disappeared; the effect reappeared by activating a different set of dislocation slip systems; and finally, that $\Delta f$ could be completely suppressed by irradiation of the sample at 1 *M* rad/h for 46 h with a $Co^{60}$ γ-ray source. Similar studies were made on sample 2, but no $\Delta f$ 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 two relations at the bottom can be derived from the equations of Ref. 26. The values of the adiabatic second-order elastic constants for 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 $C_{ij}{}^T = C_{ij}{}^S - 0.0161\times10^{12}$.

| Relation No. | Calculational equation |
| --- | --- |
| 10 | $C_{111}-3.8597C_{112}+2.8597C_{123}=(+8.7413m_{10}-2.2644)\times10^{12}$ |
| 11 | $C_{144}-1.8597C_{166}=(+4.3706m_{11}+1.6243)\times10^{12}$ |
| 13 | $C_{144}-0.0754C_{166}+8.2754C_{456}=(-4.7004m_{13}-2.9182)\times10^{12}$ |
| 14 | $C_{144}-0.0754C_{166}-8.2754C_{456}=(-4.7004m_{14}+1.7822)\times10^{12}$ |
| 16 | $C_{111}-2.0754C_{112}+1.0754C_{123}=(-9.4007m_{16}-11.6339)\times10^{12}$ |
| 17 | $C_{144}-0.0754C_{166}-8.2754C_{456}=(-4.7004m_{17}+0.6109)\times10^{12}$ |
| where | $m_{14}-m_{17}=(1-A)/2=0.2492$, |
| | $A=2C_{44}/(C_{11}-C_{12})$ |
| | $C_{456}=C_{44}(m_{14}-m_{13}-1)$ |

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 $\Delta f$ 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 $\Delta f$ 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 $\Delta f$ 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 breakaway 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 $\Delta f$, 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 $\Delta f$ is the observed change in frequency for a total pressure or stress change $\Delta p$, 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 $\sim10^{-3}$, the $(\Delta f/f_0)^2$ term can be ignored resulting

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