

# Elastic properties of $\text{UO}_2$ at high pressure\*

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The elastic constants of  $\text{UO}_2$  have been measured as a function of pressure up to 20 kbar (2.0 GPa) at 23°C. To within experimental uncertainty, the constants are linear functions of pressure, and no pressure-induced phase transitions occur in this 20-kbar pressure range. The elastic constant data are used to estimate the various polycrystalline elastic moduli and their pressure dependences, and the zero-pressure moduli are compared with data from polycrystalline material. Isothermal moduli are calculated from the adiabatic values. The elastic-constant data are also used to discuss the separation of the 'pure' volume and temperature contributions to the (isobaric) temperature dependences of the elastic constants as well as to estimate the Grüneisen constant, Debye temperature, and equation of state of this material.

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## I. INTRODUCTION

Uranium dioxide,  $\text{UO}_2$ , is a material of considerable technological importance because of its use in reactor fuel cells. Although the physical properties of  $\text{UO}_2$  in both single-crystalline and polycrystalline forms have been quite extensively studied, especially at high temperature, there is little information available about the behavior of this material at high pressure. In particular, it has not been known whether  $\text{UO}_2$  has any pressure-induced phase transitions, similar to those observed in other materials with the same (cubic fluorite) structure. In order to investigate the elastic properties of  $\text{UO}_2$  at high pressure and to look for pressure-induced phase transitions we have made an ultrasonic determination of the pressure dependences of the elastic constants up to 20 kbar at room temperature. No phase transitions were found in this range. In Sec. II of this paper the experimental details of this work are presented. In Sec. III the elastic-constant data are presented and analyzed. In Sec. IV the results of several calculations using the elastic-constant data are discussed. These include the prediction of the elastic properties of polycrystals, the separation of "pure" temperature and volume effects, the transformation from adiabatic to isothermal properties, and estimates of the Grüneisen constant, Debye temperature, and of the equation of state.

## II. EXPERIMENTAL

Since  $\text{UO}_2$  has cubic symmetry, its elastic properties are determined by the three elastic constants  $C_{11}$ ,  $C_{12}$ , and  $C_{44}$ . These three constants may be determined from the velocities of the three acoustic modes propagating along the [110] crystallographic direction. These velocities are given by the relations

$$\rho v_1^2 = C_{44}, \quad (1a)$$

$$\rho v_2^2 = \frac{1}{2}(C_{11} - C_{12}), \quad (1b)$$

$$\rho v_3^2 = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}), \quad (1c)$$

where  $\rho$  is the density,  $v_i$  are the three velocities, and where  $i=1$  represents the shear mode polarized along [001],  $i=2$  represents the shear mode polarized along  $[1\bar{1}0]$ , and  $i=3$  represents the longitudinal mode. The

$\text{UO}_2$  sample utilized in the ultrasonic experiments was prepared with pairs of [110] and [111] faces. The mode velocities along [111] are given by

$$\rho v_4^2 = \frac{1}{3}(C_{11} - C_{12} + C_{44}) \quad (\text{shear}), \quad (2a)$$

$$\rho v_5^2 = \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44}) \quad (\text{longitudinal}). \quad (2b)$$

Measurements of these modes provided cross checks of the data obtained from the [110] orientation.

The  $\text{UO}_2$  crystals used in this work were supplied by H. J. Anderson of the Westinghouse Hanford Company. Crystal growth, impurity analysis, and stoichiometry are exactly the same as described by Wachtman *et al.*<sup>1</sup> The density was determined by weighing in  $\text{CCl}_4$  to be equal to the theoretical x-ray value of 10.97 g/cm<sup>3</sup>. For the sample used in the ultrasonic measurements, the [110] and [111] faces were oriented to within 0.5° by x-ray techniques, and each pair of faces was carefully lapped to be flat and parallel.

All the ultrasonic measurements were made by the pulse-superposition technique of McSkimin.<sup>2</sup> The instrumentation system included a pulse-sequence generator which utilizes logic circuitry to generate a number of sequential applied pulses to the sample at the repetition rate frequency  $f$ , but with a low over-all duty cycle.<sup>3</sup> Also included was a phase-sensitive peak detector with a servo feedback mechanism to automatically follow the superpositioning repetition rate as a function of pressure.<sup>4</sup>

For the measurements of the elastic constants at room temperature, transducers with fundamental frequencies of 10 and 20 MHz operating at either their fundamental or third harmonic frequencies were utilized. The use of these four frequencies plus the technique of McSkimin<sup>5</sup> allowed an unambiguous determination of the correct cycle-for-cycle superpositioning of the ultrasonic echoes. The high-pressure runs were made at 20 MHz, with some of the data checked at 60 MHz. In all cases the transducer-sample bond was phthalic anhydride-glycerin polymer. Hydrostatic pressure was generated by a standard Bridgman press with a 50-50 mixture of pentane and isopentane as the pressure fluid, and pressure was measured to an accuracy of 1% with a calibrated manganin coil.

TABLE I. Single-crystal adiabatic elastic parameters and their pressure and temperature derivatives.

Elastic parameter $Q$	Value of $Q^a$		$\frac{dQ}{dp}^c$	$\frac{dQ}{dT}^{d,e}$
	This work	Wachtman <i>et al.</i> <sup>b</sup>		
$C_{11}$	$3.893 \pm 0.017$	$3.96 \pm 0.018$	$5.35 \pm 0.24$	$-5.2$
$C_{12}$	$1.187 \pm 0.017$	$1.21 \pm 0.019$	$4.35 \pm 0.24$	$-2.3$
$C_{44}$	$0.597 \pm 0.003$	$0.641 \pm 0.0017$	$1.62 \pm 0.03$	$-1.1$
$S_{11}$	$3.00 \pm 0.02$	$2.96 \pm 0.010$	$-0.20 \pm 0.05$	$\dots$
$S_{12}$	$-0.700 \pm 0.012$	$-0.697 \pm 0.008$	$-0.07 \pm 0.01$	$\dots$
$S_{14}$	$16.75 \pm 0.08$	$15.59 \pm 0.041$	$-4.3 \pm 0.1$	$\dots$
$\kappa_V$	$4.79 \pm 0.03$	$4.70 \pm 0.04$	$-1.03 \pm 0.03$	$\dots$

<sup>a</sup> $C_{ij}$  in  $10^{12}$  dyn/cm<sup>2</sup>,  $S_{ij}$  and  $\kappa_V$  in  $10^{-13}$  cm<sup>2</sup>/dyn.

<sup>b</sup>Reference 1.

<sup>c</sup> $dS_{ij}/dp$  in  $10^{-24}$  cm<sup>4</sup>/dyn<sup>2</sup>.

<sup>d</sup> $dC_{ij}/dT$  in  $10^8$  dyn/cm<sup>2</sup>°K.

<sup>e</sup>Reference 13.

### III. RESULTS AND DATA ANALYSIS

#### A. Elastic constants under ambient conditions

The measurements of the repetition rate frequencies at room temperature and atmospheric pressure were reproducible to a few tenths of a percent when different rf frequencies and bonds were used. This slight lack of reproducibility is most likely due to nonideal bonds and is the largest source of error in the measurement of the absolute values of the elastic constants for the mode propagating along [110]. The values of the three elastic constants [determined from Eqs. (1)] and their estimated uncertainties are given in the second column of Table I. Also listed in that column are the derived elastic compliances  $S_{ij}$  and volume compressibility  $\kappa_V$ . All these elastic parameters are adiabatic parameters. The comparison of the present elastic constants with measurements of other workers will be discussed below.

As was already mentioned, the longitudinal and shear modes propagating along [111] were measured as cross checks of the data. It was found that the measured effective elastic constant for the longitudinal mode, Eq. (2b), agreed to within 0.1% with the value predicted using the  $C_{ij}$  obtained from the [110] propagation direction, Table I. The measured shear-mode effective elastic constant, Eq. (2a), however, was about 2% higher than predicted. The exact cause for this discrepancy is not known, but it may be associated with the fact that for this mode the energy flow direction (elastic Poynting vector) is not colinear with the propagation direction. It was noted that the echo pattern was not ideal for this mode and changed somewhat with change in the polarization direction. Therefore, measurements of this mode are probably considerably less reliable than for the other modes. The excellent agreement for the longitudinal mode along [111] indicates that the crystal was accurately oriented and that the correct cycle-for-cycle superpositions were used in the measurements.

#### B. Elastic constants at high pressure

The ultrasonic data for the three modes propagating along [110] are shown in Fig. 1. The quantity plotted is  $[f(p)/f_0]^2$ , where  $f(p)$  is the repetition rate frequency (inverse pulse transit time) and  $f_0$  is the value of  $f(p)$  at  $p=0$ . The relation between the effective elastic con-

stant  $C'(p)$  for a given mode and the repetition rate frequency for that mode is

$$\frac{C'(p)}{C'_0} = \frac{V_0}{V(p)} \left( \frac{l(p)f(p)}{l_0 f_0} \right)^2 = \frac{l_0}{l(p)} \left( \frac{f(p)}{f_0} \right)^2, \quad (3)$$

where  $V$  is the volume of the sample and  $l$  is the ultrasonic path length. Thus the data plots of Fig. 1 represent the reduced effective elastic constants (which are listed on the figure for each mode), but only to the extent that the compression of the sample can be ignored. To extract the pressure dependences of the individual elastic constants a method similar to the method of Cook<sup>6</sup> was used to calculate simultaneously and self-consistently both the dimensional and elastic-constant changes. The resulting pressure-dependent elastic

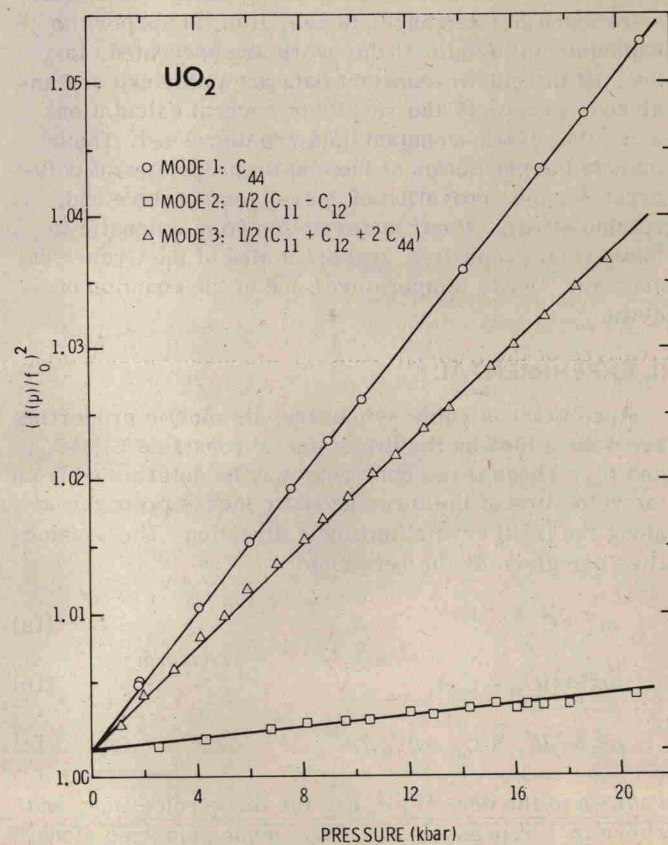


FIG. 1. Repetition rate data plotted as the square of the relative rate versus pressure.