

TABLE VII. Longitudinal elastic constants of lithium niobate.  $\pm$  indicates standard deviation. Units are  $10^{11}$  N/m<sup>2</sup>.

Author	$c_{33}^D$	$c_{33}^E$	$c_{11}^D$	$c_{11}^E$
Warner <i>et al.</i> , 1967 (Ref. 40)	2.52	2.45	2.19	2.03
Korolyuk <i>et al.</i> , 1971 (Ref. 43)	2.51	2.40	2.18	2.02
Chkalova <i>et al.</i> , 1974 (Ref. 42)	2.51	2.38		1.99
Smith and Welsh, 1971 (Ref. 39)	2.495	2.424	2.198	2.030
Nakagawa <i>et al.</i> , 1973 (Ref. 24)	2.51	2.43	2.15	2.0
Present work	2.49 $\pm$ 0.028	2.36 $\pm$ 0.028 <sup>a</sup>	2.21	2.06 $\pm$ 0.03 <sup>a</sup>

<sup>a</sup> Calculated from  $c_{ii}^E = c_{ii}^D - (e_{ii}^2 \epsilon_{ii}^T) / C_{ii}^E$  with  $c_{ii}^D$  and  $e_{ii}$  as determined from the present work.

### B. Shock velocity measurements—Second-order elastic constants

In the present experiments the strains are too small to invoke detectable third-order contributions to wave speed; however, the data are sufficient to determine piezoelectrically stiffened and unstiffened second-order elastic constants.

In the present experimental configuration, in which the electrodes are connected with an effective short circuit, the propagation of the shock wave through the samples is characterized by a jump in strain and an accompanying jump in electric field, each of which is constant in time to a very close approximation (see solutions for the electric fields in Ref. 37). The velocity of the shock wave is

$$\rho_0 U^2 = [T]/[S], \quad (9)$$

where  $\rho_0$  is the initial density,  $U$  is the shock velocity, and  $[ ]$  indicates a jump in the variable across the shock. Based on a constitutive relation such as Eq. (1a), the jump in stress for fixed jump in strain has components of the unstiffened elastic constant  $c^E$  and the jump in electric field which invokes the piezoelectric stiffening. For a constant jump in electric field the wave speed is constant with a magnitude equal to the piezoelectrically stiffened elastic constant  $c^D$ , the constant determined at constant electric displacement. Thus, the shock velocity measurements of the present investigation provide a direct measure of the piezoelectrically stiffened elastic constants. {The same conclusion follows from considering a constitutive relation of the form  $T = \hat{T}(S, D)$  for the case  $[D] = 0$ . }

In prior work on  $X$ -cut quartz<sup>14</sup> the shock velocity measurements could not distinguish between piezoelectrically stiffened and unstiffened wave velocities since the electromechanical coupling is small, such that the velocities differ by only  $\frac{1}{2}\%$ . For lithium niobate, however, the coupling is larger and the stiffening effect is readily apparent. The shock velocity measurements of the present investigation reported in Table IV are in excellent agreement with the ultrasonic wave speeds reported by Smith and Welsh<sup>39</sup> which are determined more accurately than in the present work.

The elastic stiffness constants derived from the present investigation are shown in Table VII and compared to previous work. The agreement between our  $c_{33}^D$  elastic stiffness with that observed by Smith and

Welsh indicates that the larger  $e_{33}$  constant of the present work leads to a lower computed value for  $c_{33}^E$  than that reported by Smith and Welsh.<sup>39</sup>

It should be emphasized that even though the shock velocity measurements of the present work are not as precise as those obtained ultrasonically, the piezoelectric constants observed in the present work are independent of the shock velocity measurements since both the computed piezoelectric polarization and the strain are inversely proportional to the shock velocity.

### C. Electromechanical coupling effect on the current pulses

As indicated in Eq. (6), the current pulse deviates from that predicted from the uncoupled solution, Eq. (3), by a time-dependent factor which depends on the electromechanical coupling factor and the acoustic impedance of the materials in contact with the front and back electrodes. This excess current due to electromechanical coupling is indicated by the  $i_f/i_i$  column in Table I.

Based on Eq. (6) and a model in which the back electrode is in contact with epoxy, the predicted ratio of final current  $i_f$  to initial current  $i_i$  is 8.9% for the quartz impactor experiments and 10.0% for the PMMA impactor experiments. The experimentally observed values are  $7 \pm 1.6$  and  $10 \pm 1.4\%$ , respectively ( $\pm$  indicates standard deviation). The difference between predicted and observed excess current and the scatter observed from experiment to experiment is most likely due to the solder connection to the back electrode which is not of insignificant size and may vary from experiment to experiment.

The excess current observed in the 36°-rotated experiments with the quartz impactors was  $46 \pm 3.5\%$  compared to a predicted value of 58%. This observed excess current is lower than the predicted value as was the case for the  $Z$ -cut samples. For the PMMA impactors, one experiment gave an anomalously large excess current while the other experiment was lower than the predicted value of 66%.

The most unusual and as yet not fully explained observation of the present investigation is the large excess current,  $51 \pm 3.6\%$ , observed in the  $Y$ -cut quartz impactor experiments compared to the computed value of 11% based on the uniaxial longitudinal piezoelectric constant  $e_{22}$ . The much larger than expected excess

current apparently indicates that the electromechanical effects resulting from conditions at the electrodes involve a substantial shear contribution which is not accounted for in the planar uniaxial strain models.

#### D. Threshold for shock-induced conductivity

Shock-induced conductivity observed in *X*-cut quartz has been found to be a consequence of stress-induced dielectric breakdown at the relatively large electric fields, about  $10^8$  V/m, produced by the piezoelectric effect.<sup>36,44</sup> Two factors, sample size and crystallographic orientation, affected the observed thresholds for shock-induced conductivity. Furthermore, the magnitudes of the residual strains within the samples were observed to affect the magnitude of the conductivity.

For *Z*-cut lithium niobate the threshold for conductivity varied from about 0.8 GPa for the thick samples to about 1.2 GPa for the thin samples. These stresses correspond to electric fields of  $2.4 \times 10^7$  and  $4.4 \times 10^7$  V/m, respectively. Whether this thickness dependence is a result of time delays for the initiation of breakdown<sup>5</sup> or lower residual strains in the thin samples which were obtained from smaller-diameter boules is not known.

In a special series of experiments samples were obtained with unusually large internal strain, with normal internal strain, and with unusually low internal strain. Although the thresholds for shock-induced conductivity were not significantly affected by the degree of internal strain, the magnitude of the conductivity was greater for the highly strained material.

The thresholds for shock-induced conductivity for the rotated-cut samples, which were all thick, were 0.8 GPa and a corresponding electric field of  $6 \times 10^7$  V/m.

The threshold for conductivity in thick *Y*-cut samples was 1.8 GPa. Thus, this particular orientation has a much higher threshold than the other orientations. It is not known whether the higher threshold for the *Y*-cut samples is due to improved material quality or due to inherent material properties.

The physical basis for the observed shock-induced conductivity and its dependence on sample size, internal strain, and crystallographic orientation is an important area for further study.

#### VII. CLOSURE

The present investigation has determined three of the four second-order piezoelectric stress constants and two third-order piezoelectric stress constants of lithium niobate. Even though prior work has shown a variation of  $\pm 15\%$  in the value of the  $e_{33}$  constant, the present work demonstrates that material constants of presently available crystals are reproducible to an accuracy of less than 1%. The present value of the  $e_{33}$  constant apparently calls for a downward revision of the  $c_{33}^E$  constant of lithium niobate.

There is no evidence for a change in remanent polarization with strain. The observed sample responses appear to be fully explained by the piezoelectric effect. The present measurements further dem-

onstrate the utility of the impact-loading technique for determination of second- and third-order piezoelectric stress constants. Although this technique has provided the most accurate third-order constant measurements of any technique used to date, it is limited in application since a successful investigation requires a significant number of crystals with diameters of 1 cm or greater and the property of high resistivity at elastic strains of a few percent. In the present investigation the accuracy of the third-order constant measurement is relatively large since the maximum strains were limited to about  $7 \times 10^{-3}$ .

It is worthy to note that lithium niobate is the only piezoelectric single crystal other than quartz with stable reproducible properties at room temperatures and good mechanical strength which is readily available in large sizes in commercial quantities. Since the piezoelectric constants of lithium niobate are an order or magnitude larger than those of quartz, lithium niobate should prove useful for a wide variety of stress transducer applications.

The present investigation shows that the three crystallographic orientations of lithium niobate investigated are well suited for current-mode piezoelectric gauges for time-resolved measurements of wave profiles in shock-loaded solids. The effects of electromechanical coupling on current will cause significant nonlinearities in time but these effects can be accounted for by numerical deconvolution techniques.<sup>46,47</sup>

#### ACKNOWLEDGMENTS

The author is pleased to acknowledge the excellent technical assistance of R. D. Jacobson and review of the manuscript by P. C. Lysne, W. B. Benedick, and L. W. Davison.

#### APPENDIX: HYDROSTATIC PIEZOELECTRIC CONSTANTS OF LITHIUM NIOBATE OBTAINED FROM DIFFERENT COMMERCIAL SUPPLIERS

In order to further investigate the question of reproducibility of piezoelectric constants of lithium

TABLE VIII. Hydrostatic piezoelectric constants of lithium niobate obtained from various suppliers.  $\pm$  indicates standard error.

Supplier	$d_h$ ( $10^{-12}$ CN <sup>-1</sup> )	$d_{hh}$ ( $10^{-2}$ C m <sup>-2</sup> GPa <sup>-2</sup> )
Crystal Technology Composite (see Ref. 16) Range (five samples, seven experiments)	$6.31 \pm 0.014$ 6.23 to 6.38	$0.088 \pm 0.0005$ 0.078 to 0.106
Alpha Company (one sample)	$6.34 \pm 0.044$	$0.085 \pm 0.005$
Harshaw (one sample)	$6.34 \pm 0.035$	$0.088 \pm 0.004$
Isomet (optical grade) (one sample)	$6.34 \pm 0.017$	$0.086 \pm 0.002$
Union Carbide (one sample)	$6.39 \pm 0.012$	$0.086 \pm 0.001$