that the conventional form of the internal-energy function utilized to obtain this identify is thermodynamically inconsistent, it is nevertheless interesting to compare the experimental values obtained in the two experiments. Hruska[46] has obtained a value of $\partial c_{11}/\partial E_1 = 2.6$ with a standard error of about 0.8. Although of limited accuracy, the value is in good agreement with the present value. It would be of considerable interest to accomplish more accurate measurements of the field dependence of the c_{11} constant for comparison with the present value.

Although measurement of piezoelectric constants under hydrostatic compression involves several nonlinear contributions, the results are of interest. Jones[47] measured the pressure dependence of the piezoelectric strain constant d_{11} to 3 kbar and showed that $d_{11}(P) = d_{11}(0)(1+\beta P)$, where P is the pressure in kbar and $\beta = (6.3 \pm 1.1) \times 10^{-3}$ kbar^{-1}. His results indicate a nonlinear dependence which is of the same order of magnitude as that observed for the strain dependence.

The temperature dependence of the nonlinear constant can be estimated from the previous elastic shock-compression measurements[38,39] at elevated and reduced temperatures. Although insufficient data are available to assign accurate values for α needed in the analysis, approximate values can be obtained for the piezoelectric polarization by letting $\alpha = 1.0$ at all strains. The values obtained from an analysis of the elevated and reduced temperature data based on the present model are shown in Table II. At 573 °K, in contrast to the behavior of the linear constant, the nonlinear constant is observed to be little changed from the room-temperature value. The standard error is large enough, however, to permit a significant temperature dependence to exist. At liquid-nitrogen temperature there is a significant decrease in the nonlinear constant even though the linear constant increases in value.

There is presently no basic theory to relate the direct effect nonlinear piezoelectric constant to fundamental properties of the solid. Several authors[4,20] have suggested that Miller's rule[48] relating nonlinear optical properties to susceptibility could be extended to nonlinear piezoelectric constants. However, Miller's rule has been shown to be a specific case of a more general theory based on the ionicity of the crystal lattice.[49] When additional quantitative measurements of nonlinear piezoelectric constants are obtained on other solids, it may be of interest to apply similar theoretical techniques to the study of nonlinear piezoelectric effects.

3. *Strain Dependence of Permittivity*

The electrostatic analysis developed in Sec. IV demonstrates that the ratio of the strained to unstrained permittivity, α, is directly related to the ratio of initial current jump when the shock front first enters the sample to the current when the shock reaches the rear electrode. This electrostatic model, with a correction applied for electromechanical coupling, was utilized to determine values for the strain dependence of α from the experimentally observed current pulses at various strains. Since $\epsilon_{11}^{-1}(\partial\epsilon_{11}/\partial\eta_1) = 1-\alpha$ and $\alpha \approx 1$, the value obtained for the strain dependence of the permittivity is inaccurate but quantitative. The least-squares fit to the data represented by Eq. (28) gives a value of

$$\epsilon_{11}^{-1}\frac{\partial\epsilon_{11}}{\partial\eta_1} = -0.46 \pm 0.13\ ,$$

where the ± indicates the standard error.

Lysne[50] has performed elastic shock-compression experiments with thin X-cut quartz disks subjected to multiply reverberating waves. He utilized a different form for the constitutive relations in order to develop expressions for electromechanical current distortions for many wave reverberations. His data can be analyzed to yield a value $\epsilon_{11}^{-1}(\partial\epsilon_{11}/\partial\eta_1) = -0.5$. This is in good agreement with the present value.

Since the strain dependence of permittivity has not been measured previously, several authors[4,20,44] have applied thermodynamic identities to estimate values for this constant from the photoelastic constant. There appears to be little physical basis for such a calculation since the elasto-optic constants are measured at optical frequencies which yield only the electronic contribution to permittivity. Ultrasonic frequency values, on the other hand, include contributions from electronic and lattice polarizability. Nevertheless, it is of interest to note that the value of the strain dependence of the permittivity deduced from the photoelastic constant is in reasonable agreement with our measurements.

Carr and Slobodnik[44] have related the constants directly through the relation

$$\epsilon_{11}^{-1}\frac{\partial\epsilon_{11}}{\partial\eta_1} = -\frac{\epsilon_1}{\epsilon_0}\,p_{11} \qquad (30)$$

which neglects the frequency difference of the two experiments. McMahon[20] relates the two constants by applying a frequency correction proportional to the square of the ratio of the susceptibilities. When this frequency correction is employed,

$$\epsilon_{11}^{-1}\left(\frac{\partial\epsilon_{11}}{\partial\eta_1}\right) = -\frac{\epsilon_0}{\epsilon_{11}}\,\chi^2\left(\frac{n^2}{n^2-1}\right)^2 p_{11}\ , \qquad (31)$$

where χ is the ultrasonic frequency susceptibility and n is the refractive index. With a value of $p_{11} = 0.138$ (Ref. 30) and $n = 1.5$ (Ref. 51), the strain dependence of the permittivity is calculated to be -0.62 and -1.12 for the directly related and fre-

TABLE III. Elastic constants of X-cut quartz (10^{12} dyn cm^{-2}).

	c_{11}	C_{111}	C_{1111}
McSkimin[a]	0.8680	...	...
Thurston[b]	...	−2.1	...
Fowles[c]	...	...	+160
Present work[d]	0.868 ± 0.0095	-3.0 ± 0.3	$+75\pm25$

[a]Reference 57.
[b]Reference 22.
[c]Reference 15.
[d]± indicates a maximum error based on experimental precision.

quency-corrected calculations, respectively. Thus, it appears that a reasonable estimate for the strain dependence of the permittivity of X-cut quartz can be calculated from the elasto-optic constant if no frequency correction is applied.

A somewhat similar situation obtains for sapphire (α-Al_2O_3). Previously reported measurements[52] of the change in permittivity of sapphire subjected to elastic shock compression along the z axis can be analyzed to show that

$$\epsilon_{33}^{-1}\frac{\partial\epsilon_{33}}{\partial\eta_3}=+2.39\pm0.044\,.$$

This value can be compared to the elasto-optic data with $n=1.768$ (Ref. 53), $p_3=-0.30$ (Ref. 53), and $\epsilon_{33}/\epsilon_0=11.55$ (Ref. 54). Equation (30), which utilizes no frequency correction, predicts a value $\epsilon_{33}^{-1}(\partial\epsilon_{33}/\partial\eta_1)=+3.4$, while Eq. (31), which applies a frequency correction, predicts a value of $+4.2$. Thus it appears that a reasonable estimate of the strain dependence of the permittivity of both X-cut quartz and Z-cut sapphire can be obtained from elasto-optic data on the basis of Eq. (30). This agreement is believed to be somewhat fortuitous and is probably related to the fact that the static and high-frequency dielectric constants for quartz and sapphire are not vastly different. Particularly in view of the increased interest in photoelastic constants,[55] the relationship between elasto-optic constants and the strain dependence of permittivity appears to warrant further investigation.

B. Elastic Constitutive Relation

The elastic constants obtained from the present investigation are compared to values reported by other investigators in Table III. Good agreement for the high-order constants is not achieved between the various investigators.

The fourth-order constant reported by Fowles[15] was obtained from measurements over a limited range of strain. Furthermore, his value was obtained by assuming that the ultrasonic third-order constant was representative of the large-strain response and the question of extrapolating the ultrasonic values to large elastic strains was not critically examined. The experiments also involved inelastic response. For these reasons, the present value is better established and is to be preferred.

The difference between the third-order constant obtained ultrasonically and under elastic shock compression is larger than can be accounted for from the various experimental errors. The two values lead to quite different descriptions for the propagation of a finite-amplitude strain wave. Thurston[56] has pointed out that a linear elastic response is obtained if $c_{111}=-3c_{11}$ and that dispersion in the wave profile will be obtained if $c_{111}<-3c_{11}$. On the basis of the ultrasonic value[57] of $c_{111}=-2.6c_{11}$, a step-function strain wave of 10^{-2} would be expected to disperse to a ramp wave whose rise is about 2 nsec/mm of travel.

The present experiments show that $c_{111}=-3.46c_{11}$ and show no evidence for dispersive behavior even though both the wave transit time and current amplitude measurements are sensitive to wave speed and both are determined with different sample thicknesses. An unrealistically large value for the fourth-order constant would have to be invoked to maintain the steady-wave profile. This large value for the fourth-order constant would cause unrealistic response at the larger strains employed in the elastic shock-compression investigation. Thus there seems to be no way to bring the ultrasonic and elastic shock-compression values into agreement.

It should be noted, however, that Thurston *et al.* used various data-reduction weighting schemes to combine their uniaxial-stress and hydrostatic-pressure measurements. The best fit to their uniaxial-stress data alone shows $c_{111}=-2.6\times10^{12}$ dyn cm^{-2} with a standard error of 0.46. This value is in much better agreement with the present value. Thurston *et al.* also observed similar differences between their uniaxial-stress data and the combined data for the c_{333} constant.

It should be recalled that the elastic constitutive relation was developed with the "weak-coupling" approximation which neglects the piezoelectric contribution to stiffness. Since the nonlinear piezoelectric constants are now known, the piezoelectric stiffening terms for third- and fourth-order can be evaluated. The high-order piezoelectric coupling relations can be readily developed from Eq. (7) by noting that the electric field under open circuit ($D=$ const) conditions is

$$\left(e_{11}+\frac{1}{2}\,\frac{\partial e_{11}}{\partial\eta_1}\,\eta_1\right)\eta_1\left(e_{11}+\frac{\partial\epsilon_{11}}{\partial\eta_1}\,\eta\right)^{-1}.$$

When this value of electric field is substituted into Eq. (7) and the thermodynamic identity $\partial e/\partial E=\partial\epsilon/\partial\eta$ is utilized, it follows that the open-circuit constants c_{11}^D, c_{111}^D, and c_{1111}^D can be expressed in terms of the internally short-circuited constants c_{11}^E, c_{111}^E, and c_{1111}^E as