

$$c_{11}^D = c_{11}^E \left(1 + \frac{e_{11}^2}{\epsilon_{11} c_{11}^E} \right),$$

$$c_{111}^D = c_{111}^E \left[1 + \frac{3e_{11}}{\epsilon_{11} c_{111}^E} \left(\frac{\partial e_{11}}{\partial \eta_1} \right) - \frac{e_{11}^2}{\epsilon_{11} c_{111}^E} \left(\frac{1}{\epsilon_{11}} \frac{\partial \epsilon_{11}}{\partial \eta_1} \right) \right],$$

and

$$c_{1111}^D = c_{1111}^E \left[1 + \frac{1}{\epsilon_{11} c_{1111}^E} \left(\frac{\partial e_{11}}{\partial \eta_1} \right)^2 - \frac{3e_{11}}{\epsilon_{11} c_{1111}^E} \left(\frac{1}{\epsilon_{11}} \frac{\partial \epsilon_{11}}{\partial \eta_1} \right) \left(\frac{\partial e_{11}}{\partial \eta_1} \right) + \frac{e_{11}^2}{\epsilon_{11} c_{1111}^E} \left(\frac{1}{\epsilon_{11}} \frac{\partial \epsilon_{11}}{\partial \eta_1} \right)^2 \right].$$

Substituting values from the present paper into these expressions gives the result that

$$c_{11}^D = c_{11}^E (1 + 0.0084),$$

$$c_{111}^D = c_{111}^E (1 + 0.11 - 0.0011),$$

and

$$c_{1111}^D = c_{1111}^E (1 + 0.023 - 0.0021 + 0.00002).$$

The contribution of piezoelectric stiffening to the third-order constants is calculated to be 11%. This value is large enough such that it should be observable in ultrasonic experiments conducted on low resistivity and open-circuited samples. The contributions to stiffening due to the nonlinear converse-effect constant $[(1/\epsilon)(\partial e/\partial \eta)]$ are noted to be very much less than the contribution of the direct-effect nonlinear constant $\partial e/\partial \eta$.

VII. SUMMARY

The present paper reports the first quantitative experimental measurement of a nonlinear piezoelectric constitutive relation. The measurements yield the most accurate value reported to date for the linear piezoelectric stress constant of X-cut quartz, the first quantitative measurement of a nonlinear piezoelectric constant for the direct effect, and a value for the strain dependence of the

permittivity. The longitudinal finite-strain elastic constitutive relation for x-axis compression was determined with second-, third-, and fourth-order elastic-constant measurements which represent the compression of the solid to compressive strains up to 4.3×10^{-2} . The third-order constant value appears to differ significantly from the value determined from ultrasonic experiments. The technique seems generally applicable to the study of other piezoelectric solids which exhibit large elastic limits under shock-wave loading and should permit nonlinear piezoelectric constants to be studied in some detail.

ACKNOWLEDGMENTS

The author is pleased to acknowledge the unusually competent technical assistance of G. E. Ingram and R. D. Jacobson in carrying out the experimental measurements. Discussions with C. F. Quate, R. B. Thompson, and J. C. Crawford were extremely helpful in relating the present work to microwave acoustics. R. W. Rohde was kind enough to let the author examine his original data. Discussions with P. C. Lysne are also gratefully acknowledged. E. P. Eernisse and P. C. Lysne provided very helpful reviews of the manuscript. Discussions with G. A. Samara provided better insight into the dielectric-constant results.

*Work supported by the U. S. Atomic Energy Commission.

¹For definitions of crystallographic orientations and piezoelectric constants see Proc. IRE 37, 1378 (1949).

²The direct piezoelectric effect causes a piezoelectric polarization upon application of a stress or strain. The converse piezoelectric effect, ordinarily utilized for measurements of piezoelectric constants, causes a strain upon application of an electric field. See, e.g., W. G. Cady [Piezoelectricity (Dover, New York, 1964), Vol. I]. The present experiments provide a measure of the strain dependence of a piezoelectric stress constant. This nonlinear constant will be referred to as the direct nonlinear piezoelectric stress constant to distinguish it from the converse nonlinear piezoelectric constant which describes the change of piezoelectric constant with electric field.

³L. K. Zarembo and V. A. Krasil'nikov, Usp. Fiz. Nauk 102, 549 (1970) [Sov. Phys. Usp. 13, 778 (1971)].

⁴R. B. Thompson and C. F. Quate, J. Appl. Phys. 42,

907 (1971).

⁵P. H. Carr, Phys. Rev. 169, 718 (1968).

⁶P. H. Carr and A. J. Slobodnik, Jr., J. Appl. Phys. 38, 5153 (1967).

⁷J. Holder and A. V. Granato, in Physical Acoustics, edited by Warren P. Mason and R. N. Thurston (Academic, New York, 1971), Vol. 8.

⁸R. A. Graham, J. Acoust. Soc. Am. 51, 1576 (1972).

⁹R. A. Graham, J. Appl. Phys. 32, 555 (1961).

¹⁰F. W. Neilson, W. B. Benedick, W. P. Brooks, R. A. Graham, and G. W. Anderson, Les Ondes de Detonation (Centre National de la Recherche Scientifique, Paris, France, 1962); also available as Sandia Laboratories Report No. SCR-416, 1961 (unpublished).

¹¹R. A. Graham, F. W. Neilson, and W. B. Benedick, J. Appl. Phys. 36, 1775 (1965).

¹²R. A. Graham and W. J. Halpin, J. Appl. Phys. 39, 5077 (1968).

¹³R. A. Graham and G. E. Ingram, J. Appl. Phys. 43,

- 826 (1972).
- ¹⁴J. Wackerle, *J. Appl. Phys.* **33**, 922 (1962).
- ¹⁵R. Fowles, *J. Geophys. Res.* **72**, 5729 (1967).
- ¹⁶R. N. Thurston, in *Physical Acoustics*, edited by Warren P. Mason (Academic, New York, 1964), Vol. IA.
- ¹⁷R. A. Toupin, *J. Ratl. Mech. Anal.* **5**, 859 (1956).
- ¹⁸A. C. Eringen, *Int. J. Eng. Sci.* **1**, 127 (1963).
- ¹⁹H. F. Tiersten, *Int. J. Eng. Sci.* **9**, 587 (1971).
- ²⁰D. H. McMahon, *J. Acoust. Soc. Am.* **44**, 1007 (1968).
- ²¹R. Bechmann, *Phys. Rev.* **110**, 1060 (1958).
- ²²R. N. Thurston, H. J. McSkimin, and P. Andreatch, Jr., *J. Appl. Phys.* **37**, 267 (1966).
- ²³R. A. Graham, *J. Basic Eng.* **89**, 911 (1967).
- ²⁴C. H. Karnes, in *Mechanical Behavior of Materials Under Dynamic Loads*, edited by U. S. Lindholm (Springer-Verlag, New York, 1968).
- ²⁵G. E. Ingram and R. A. Graham, in *Proceedings of the Fifth Symposium on Detonation*, edited by S. Jacobs, also available on request as Sandia Laboratories Report No. SC-R-722722, 1972 (unpublished).
- ²⁶S. Thunborg, Jr., G. E. Ingram, and R. A. Graham, *Rev. Sci. Instr.* **35**, 11 (1964).
- ²⁷See, e.g., G. E. Duvall and G. R. Fowles, in *High Pressure Physics and Chemistry*, edited by R. S. Bradley (Academic, New York, 1963), Vol. II.
- ²⁸M. H. Rice, R. G. McQueen, and J. M. Walsh, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. VI.
- ²⁹W. Herrmann, in *Wave Propagation in Solids* (The American Society of Mechanical Engineers, New York, 1970).
- ³⁰See, R. Bechmann and R. F. S. Hearman, *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, New Series. Group III: Crystal and Solid State Physics* (Springer-Verlag, New York, 1966), Vol. I.
- ³¹Shock-induced conductivity in X-cut quartz has been carefully studied. Descriptions of the previous work are found in Refs. 12 and 13. Except for specific situations mentioned in Sec. V, these studies have shown the conductivity to be zero.
- ³²O. M. Stuetzer, *J. Appl. Phys.* **38**, 3901 (1967).
- ³³M. Redwood, *J. Acoust. Soc. Am.* **33**, 527 (1961).
- ³⁴H. S. Chakraborty, *Czech. J. Phys. B* **19**, 963 (1967).
- ³⁵R. A. Graham and G. E. Ingram, *Bull. Am. Phys. Soc.* **14**, 1163 (1969).
- ³⁶M. Lax and D. F. Nelson, *Phys. Rev. B* **4**, 3694 (1971).
- ³⁷I. Koga, M. Aruga, and Y. Yoshinaka, *Phys. Rev.* **109**, 1467 (1958).
- ³⁸O. E. Jones, *Rev. Sci. Instr.* **38**, 253 (1967).
- ³⁹R. W. Rohde and O. E. Jones, *Rev. Sci. Instr.* **39**, 313 (1968).
- ⁴⁰A. A. Chaban, *Zh. Eksperim. i Teor. Fiz. pis'ma v Redaktsiyu* **6**, 967 (1966) [*Sov. Phys. JETP Letters* **6**, 381 (1967)].
- ⁴¹P. Thery, E. Bridoux, and M. Moriamez, *J. Phys. C Suppl.* **31**, C1-29 (1970).
- ⁴²R. M. White, *Proc. IEEE* **58**, 1238 (1970).
- ⁴³T. C. Lim, E. A. Kraut, and R. B. Thompson, *Appl. Phys. Letters* **20**, 127 (1972).
- ⁴⁴P. H. Carr and A. J. Slobodnik, Jr., *J. Appl. Phys.* **38**, 5153 (1967).
- ⁴⁵W. P. Mason, *Piezoelectric Crystals and their Applications to Ultrasonics* (Van Nostrand, Princeton, N. J., 1950), Appendix A-6.
- ⁴⁶K. Hruska, *IEEE Trans. Sonics Ultrasonics* **SU-18**, 1 (1971). It should be noted that Hruska accomplished the first experimental measurement which involved a non-linear piezoelectric effect. See K. Hruska, *Czech. J. Phys. B* **11**, 150 (1961).
- ⁴⁷M. R. Jones, Ph.D. dissertation (University of Utah, 1970) (unpublished).
- ⁴⁸R. C. Miller, *Appl. Phys. Letters* **5**, 17 (1964).
- ⁴⁹B. F. Levine, *Phys. Rev. Letters* **22**, 787 (1969).
- ⁵⁰P. C. Lysne, *J. Appl. Phys.* **43**, 425 (1972).
- ⁵¹*Handbook of Chemistry and Physics*, edited by C. D. Hodgman (The Chemical Rubber Publishing Co., Cleveland, Ohio, 1962).
- ⁵²R. A. Graham and G. E. Ingram, in *Behavior of Dense Media Under High Dynamic Pressures* (Gordon and Breach, New York, 1968).
- ⁵³T. A. Davis and K. Vedam, *J. Appl. Phys.* **38**, 4555 (1967).
- ⁵⁴R. D. Olt, *Electronics* **32**, 110 (1959).
- ⁵⁵D. F. Nelson and M. Lax, *Phys. Rev. B* **3**, 2778 (1971).
- ⁵⁶R. N. Thurston, *J. Acoust. Soc. Am.* **45**, 1329 (1969).
- ⁵⁷H. J. McSkimin, P. Andreatch, Jr., and R. W. Thurston, *J. Appl. Phys.* **36**, 1624 (1965).