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Ultrasonic Measurement of the Nonlinearity Parameters of Copper Single Crystals*

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The nonlinearity parameters, which are combinations of third-order elastic constants, of neutron-irradiated copper single crystals were determined at room temperature by measuring quantitatively the harmonic distortion of pulsed MHz ultrasonic waves propagating in three crystallographic directions. For this purpose, a capacitive detector was used with which ultrasonic displacement amplitudes of the order of 10^{-10} cm can be detected and measured absolutely. Using the nonlinearity parameters in combination with other data, a complete set of third-order elastic constants for copper is calculated. The experiments represent a new technique for determining third-order elastic constants which is of special interest for measurements on easily deformed metal crystals.

INTRODUCTION

FROM the symmetry properties of a crystal lattice, relations can be found between the coupling parameters of microscopic lattice theory and the elastic constants of macroscopic elasticity theory. For example, the second- and third-order coupling parameters of face-centered cubic crystals have been expressed in terms of the second- and third-order elastic constants, assuming only nearest-neighbor interactions between the atoms.[1,2] Corresponding relations for body-centered cubic lattices with nearest- and next-nearest-neighbor interactions have been obtained, and the case of central forces in the two types of lattices have been investigated.[2] Thus, measurements of elastic constants can yield information about lattice forces.

If only the second-order terms are retained in the elastic energy density and linear elasticity theory is used, a linear relationship between stress and strain results (Hooke's law). This approximation can be used for "infinitesimal" deformations, i.e., when the space derivatives of the displacement vector of a point in the body are small enough that their products and squares may be neglected in relation to the terms themselves. Similarly, lattice dynamics in the harmonic approximation can be used as a first step to describe the mechanical behavior of solids.

However, a large number of important properties depend on the anharmonicity of the lattice potential.[3] For this reason, there has been much interest recently in the experimental determination of third-order elastic constants.

The most precise measurements of elastic constants have been made by dynamic techniques. From the equations of motion for an elastic medium in the linear approximation, one finds the relations between the adiabatic second-order elastic constants and the velocities of ultrasonic waves of different polarizations traveling in various crystallographic directions. Similarly, by extending the calculations to include finite deformations, one obtains relations between the third-order elastic constants and nonlinear effects in sound propagation.

Specifically, there have been a number of measurements of the sound velocity, i.e., of the effective second-order elastic constants, as a function of hydrostatic pressure. Such measurements can be made readily for many solids, even for soft materials which would deform plastically under correspondingly large shear stresses. They cannot, however, yield the complete set of third-

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[1] H. Pfleiderer, Phys. Status Solidi **2**, 1539 (1962).
[2] R. A. Coldwell-Horsfall, Phys. Rev. **129**, 22 (1963).
[3] G. Leibfried and W. Ludwig, Solid State Phys. **12**, 275 (1961).

order elastic constants. In the case of cubic crystals, for example, three combinations of the six third-order constants can be obtained. Thus other techniques are required to isolate all of the constants.

For this purpose the change of sound velocity with uniaxial stress has been measured. Bateman, Mason and McSkimin[4] carried out such experiments on germanium and determined for the first time a complete set of all six third-order elastic constants of a cubic crystal. A similar experiment was done on germanium by Drabble and Gluyas.[5] McSkimin and Andreatch[6] determined the germanium constants with increased accuracy and made measurements on silicon. Using essentially the same technique, Bogardus[7] obtained the third-order elastic constants of germanium, magnesium oxide, and fused silica; Chang[8] obtained those of sodium chloride and potassium chloride crystals; and Thurston, McSkimin, and Andreatch[9] obtained those of quartz.

Until very recently there have been no results for metals because the above technique is difficult to apply to them. Pure metal single crystals are soft and are easily deformed plastically, so that only very small shear stresses can be applied if only elastic deformation is to be obtained. Hiki and Granato[10] have carried out experiments on prestressed single crystals of copper, silver, and gold, using small stresses and a sensitive method of determining ultrasonic velocity changes. Salama and Alers[11] measured the change of sound velocity in neutron-irradiated copper crystals resulting from the application of uniaxial stress.

Because of the difficulty of measurements on metal single crystals, it is of interest to determine their third-order elastic constants by other techniques, preferably ones that do not involve the application of external stresses having shear components. The experiments described here are of that type. They are based on the waveform distortion undergone by ultrasound as it propagates through a solid. After an initially sinusoidal wave is introduced into a specimen, higher harmonics of the fundamental frequency are generated because of the nonlinear properties of the medium.[12] A study of these effects was made by Breazeale and Ford.[13] Their solution of the nonlinear equation for longitudinal plane waves yields a second harmonic term whose amplitude is proportional to the square of the fundamental amplitude, the square of the fundamental frequency, the distance the wave has traveled in the medium, and a constant factor. For single crystals, that constant factor consists of second-order elastic constants and of a combination of third-order constants, designated the nonlinearity parameter, whose exact form depends on the crystallographic direction of propagation. Thus, if the absolute amplitudes of both the fundamental and the second harmonic of a distorted wave can be determined and if the second-order constants of the material are known, the appropriate combinations of third-order constants can be calculated. It turns out that for cubic crystals, experiments with longitudinal waves propagating in the [100], [110], and [111] directions yield three independent combinations of the third-order constants; and that those combinations are in turn linearly independent of the three combinations obtained from the measurement of sound velocity as a function of hydrostatic pressure.

THEORY

The nonlinear equations for particle motion in a cubic crystal can be derived from Murnaghan's theory of finite deformation.[14]

Let a point have the coordinates (a_1,a_2,a_3) in the initial or unstrained state. In the final or strained state, the same point has the coordinates (x_1,x_2,x_3) and the components of the displacement are $u_i=x_i-a_i$. The reference frame with respect to which x_i are measured need not be the same as that to which a_i are referred. Let J be the Jacobian matrix of the transformation from initial to final coordinates. For a rigid displacement $\tilde{J}J$ is the unit matrix E_3, where $\tilde{J}$ is the transpose of J. Thus the strain η, as a measure of the deformation, can be defined as

$$\eta=\tfrac{1}{2}[\tilde{J}J-E_3]. \tag{1}$$

The Langrangian viewpoint is used here, with the initial coordinates the independent variables.

The equation of motion is written simply in terms of Murnaghan's "modified stress tensor," T[15]:

$$\rho\ddot{u}_i=\frac{\partial}{\partial a_k}T_{ik}, \tag{2}$$

where

$$T_{ik}=J_{il}\frac{\partial U}{\partial\eta_{lk}}. \tag{3}$$

ρ is the mass density of the medium in the unstrained state, the dots indicate time derivatives, and U is the elastic-strain energy density. The latter was written by Birch[16] for cubic crystals [Hermann-Mauguin notation $\bar{4}3m$, 432, $(4/m)\bar{3}(2/m)$] in terms of powers of the strain components, including third. The expression is given as Eq. (A1) in Appendix A. The definition of third-order

[4] T. Bateman, W. P. Mason, and H. J. McSkimin, J. Appl. Phys. **32**, 928 (1961).
[5] J. R. Drabble and M. Gluyas, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Ltd., London, 1965), p. 607.
[6] H. J. McSkimin, and P. Andreatch, Jr., J. Appl. Phys. **35**, 3312 (1964).
[7] E. H. Bogardus, J. Appl. Phys. **36**, 2504 (1965).
[8] Z. P. Chang, Phys. Rev. **140**, A1788 (1965).
[9] R. N. Thurston, H. J. McSkimin, and P. Andreatch, Jr., J. Appl. Phys. **37**, 267 (1966).
[10] Y. Hiki and A. V. Granato, Phys. Rev. **144**, 411 (1966).
[11] K. Salama and G. A. Alers, Phys. Rev. **161**, 673 (1967).
[12] M. A. Breazeale and D. O. Thompson, Appl. Phys. Letters **3**, 77 (1963).
[13] M. A. Breazeale and J. Ford, J. Appl. Phys. **36**, 3486 (1965).
[14] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951).
[15] F. D. Murnaghan, *Finite Deformation of an Elastic Solid* (John Wiley & Sons, Inc., New York, 1951), Chap. 6.
[16] F. Birch, Phys. Rev. **71**, 809 (1947).

elastic constants used in Appendix A is consistent with Brugger's thermodynamic definition.[17]

Substituting (A1) into (3) yields the general nonlinear equation for wave propagation in a cubic crystal. The procedure is straightforward but lengthy. Three coupled equations are obtained, one each for particle displacements in the u_1, u_2, and u_3 directions.[18] The equation discussed here can be compared directly with that derived by Seeger and Buck,[19] who considered the case of infinitesimal displacements superimposed on a finite deformation. The two equations are related through the substitution[14]

$$\rho_x/\rho=1/J=1\Big/\left(1+\frac{\partial u_1}{\partial a_1}+\frac{\partial u_2}{\partial a_2}+\frac{\partial u_3}{\partial a_3}\right), \tag{4}$$

where ρ_x is the mass density of the medium in the strained state.

To bring the equations of motion into a form that is useful for determining third-order elastic constants from harmonic generation experiments, they must be specialized to specific propagation directions and wave polarizations and solved for the amplitudes of the fundamental and the second harmonic.

The simplest case to consider is that of a longitudinal plane wave propagating in the [100] direction. Here the equation reduces to

$$\rho\ddot{u}_1-c_{11}\frac{\partial^2 u_1}{\partial a_1^2}=(3c_{11}+C_{111})\frac{\partial u_1}{\partial a_1}\frac{\partial^2 u_1}{\partial a_1^2}. \tag{5}$$

The equation is solved readily by a perturbation technique. The subscripts can be dropped from u and a. The solution is written

$$u=u^{(1)}+u^{(2)}, \tag{6}$$

where

$$u^{(1)}=A\sin(ka-\omega t) \tag{7}$$

and

$$u^{(2)}=-(3c_{11}+C_{111})/8c_{11}A^2k^2a\cos 2(ka-\omega t). \tag{8}$$

Here ω is the angular frequency of the sound wave, k is the magnitude of the wave vector, and A is the initial displacement amplitude of the fundamental frequency.

To treat the cases of plane longitudinal waves propagating in other directions, it is best to rotate the initial coordinate system. For example, for waves propagating in the [110] direction, the coordinates are rotated by 45° about the a_3 axis, so that the new a_1' axis corresponds to the [110] direction. In the new frame, the strain matrix is η'; it is related to η by $\eta=R\eta'R^{-1}$, where R is the rotation matrix and R^{-1} its inverse. The strain energy is now written in terms of the components of η' and the new equation of motion is derived. A similar procedure is followed to align the a_1 axis with the [111] direction.

It turns out that pure longitudinal modes can propagate in the three directions [100], [110], and [111]; and for all three cases, the procedure outlined above leads to a wave equation of the same form as (5). This equation can be written in terms of K_2, a combination of second-order elastic constants, and K_3, a combination of third-order constants called the nonlinearity parameter:[13]

$$\rho\ddot{u}=K_2\left[\frac{\partial^2 u}{\partial a^2}+3\frac{\partial u}{\partial a}\frac{\partial^2 u}{\partial a^2}\right]+K_3\frac{\partial u}{\partial a}\frac{\partial^2 u}{\partial a^2}. \tag{9}$$

By analogy with (7) and (8), the solution of (9) to second order is

$$u=A\sin(ka-\omega t)-[3K_2+K_3]/8K_2A^2k^2a\cos 2(ka-\omega t). \tag{10}$$

The specific combinations K_2 and K_3 for the three directions under consideration are listed in Table I.[13] The K_3 are linearly independent combinations of the third-order elastic constants. They can be calculated from absolute measurements of the amplitudes of the fundamental and the second harmonic components of longitudinal waves traveling in these three directions.

If such results are to be combined with measurements of sound velocity as a function of hydrostatic pressure to isolate all six constants, it must be ascertained that the combinations of constants obtained by the two techniques are linearly independent. That this is actually the case can be seen from the analysis of Thurston and Brugger.[20] For example, the change of velocity with pressure of longitudinal waves in the [100] and [110] directions and of transverse waves in the [100] direction yields the required additional three terms.

In the above analysis, no account was taken of the dissipation of acoustical energy. It is observed, however, that both the fundamental and the second harmonic are attenuated as they propagate in the crystal. An approximate correction can be made by assuming that the attenuation is uniform and that the fundamental and the second harmonic are damped as if each were the

TABLE I. K_2 and K_3 for [100], [110], and [111] directions.

Direction	K_2	K_3
[100]	c_{11}	C_{111}
[110]	$\frac{1}{2}(c_{11}+c_{12}+2c_{44})$	$\frac{1}{4}(C_{111}+3C_{112}+12C_{166})$
[111]	$\frac{1}{3}(c_{11}+2c_{12}+4c_{44})$	$\frac{1}{9}(C_{111}+6C_{112}+12C_{144}+24C_{166})$ $+\frac{1}{9}(2C_{123}+16C_{456})$

[17] K. Brugger, Phys. Rev. **133**, A1611 (1964).
[18] W. B. Gauster, Ph.D. dissertation, The University of Tennessee, Oak Ridge National Laboratory Report No. ORNL-TM-1573, 1966 (unpublished).
[19] A. Seeger and O. Buck, Z. Naturforsch. **15a**, 1056 (1960).
[20] R. N. Thurston and K. Brugger, Phys. Rev. **133**, A1604 (1964).

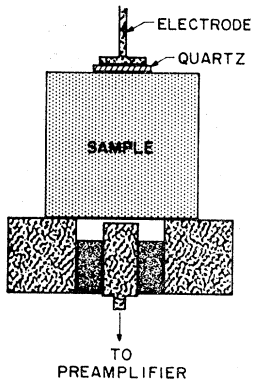

FIG. 1. Schematic representation of capacitive detector.

only wave present.[21] Then the particle displacement is found to be

$$u=A_0e^{-\alpha_1 a}\sin(ka-\omega t)-[3K_2+K_3]/8K_2A_0^2k^2 \times[e^{-2\alpha_1 a}-e^{-\alpha_2 a}]/\alpha_2-2\alpha_1\cos 2(ka-\omega t), \quad (11)$$

where A_0=wave amplitude at $a=0$, α_1=measured attenuation factor for the fundamental frequency f_1, and α_2=measured attenuation factor for a wave of frequency $f_2=2f_1$ traveling alone in the medium.

It is shown in Appendix B that for the samples used, the measured values of α_1 and α_2 were small enough that the error introduced by using Eq. (10) rather than Eq. (11) to analyze the data was smaller than the experimental uncertainty.

EXPERIMENTAL PROCEDURE

Apparatus

For quantitative measurements of the harmonic distortion of ultrasonic waves in solids, one requires a very sensitive detector that can be calibrated for strain-amplitude determinations over a wide frequency range. A number of factors must be considered in the selection of the ultrasonic frequency. First, diffraction of the sound beam introduces an apparent attenuation; the magnitude of this effect depends on the dimensions of the sample in relation to the wavelength of the vibrations. Calculations of diffraction effects[22] indicated that with samples and transducers of convenient size, it was desirable to work at frequencies above 10 MHz. Moreover, Eqs. (10) and (11) indicate that the second harmonic amplitude increases with the square of the frequency, so that again higher frequencies are advantageous. On the other hand, the attenuation becomes greater also. It was verified that in the neutron-irradiated copper samples used, the attenuation increases approximately with the square of the frequency from 30 to 60 MHz. The availability and convenience of handling of fundamental-mode piezoelectric quartz transducers, which were used to generate the ultrasonic waves, provide an upper limit of about 60 MHz. These considerations, together with the ready availability of tuned amplifiers with pass-bands about 30 and 60 MHz, determined the choice of 30 MHz for the fundamental frequency.

The largest ultrasonic displacement amplitudes attained at 30 MHz are on the order of 10 Å. From Eq. (10), using estimated values of third-order elastic constants, it can be calculated that the second harmonic amplitude should then be about 1% of the fundamental. Thus, a detector is needed of sensitivity sufficient to measure displacement amplitudes below 10^{-9} cm.

The capacitive detector developed for that purpose has been described in detail elsewhere.[23] Figure 1 shows schematically the experimental arrangement. Pulses of longitudinal waves at 30 MHz are produced by the piezoelectric quartz transducer that is bonded to the top of the sample. The detector at the bottom is a calibrated capacitance microphone. The preamplifier has a constant response over the frequency range from 5 to 90 MHz. The ultrasonic waves are distorted as they propagate through the sample, so that the detector senses a second harmonic component in addition to the signal at the fundamental frequency. By feeding the signal to high-gain amplifiers with pass-bands about 30 and 60 MHz, respectively (and of width sufficient to amplify the pulsed signals without distortion), it is possible to measure the fundamental and second harmonic components of the ultrasonic displacement amplitude independently.

Sample Preparation

The copper single crystals used in the present experiment were furnished by Young, Jr., Solid State Division, Oak Ridge National Laboratory. They were grown from American Smelting and Refining Company 99.999% copper by a Bridgman technique and were cut to different lengths with an acid saw. Measurements were made on crystals whose faces were perpendicular to the [100], [110], and [111] directions, respectively. One sample each of the first two orientations was used, and three samples of different lengths with faces perpendicular to the [111] direction were available. It was desirable to make measurements on several different specimens of the same orientation in order to check the predicted growth of second harmonic with path length, as expressed by Eq. (10), and to investigate the effect on our results of other length-dependent propagation effects (such as diffraction and attenuation). Further, it could be ascertained in this way that the techniques of sample preparation and handling did not cause noticeable differences in the measurement results from one sample to the next.

To reduce the attenuation of the ultrasonic waves, the copper specimens were irradiated with fast neutrons

[21] A. L. Thuras, R. T. Jenkins, and H. T. O'Neil, J. Acoust. Soc. Am. 6, 173 (1935).

[22] H. Seki, A. Granato, and R. Truell, J. Acoust. Soc. Am. 28, 230 (1956).

[23] W. B. Gauster and M. A. Breazeale, Rev. Sci. Instr. 37, 1544 (1966).

TABLE II. Nonlinearity parameters of copper.

Propagation direction	Sample length (cm)	K_3 (10^{12} dyn/cm^2)	Standard error (10^{12} dyn/cm^2)
[100]	2.86	−14.27	±0.44
[110]	2.72	−32.54	±1.30
[111]	9.00	−26.01	±0.50
	3.97	−24.92	±0.30
	1.38	−26.84	±0.70

which "pin" the dislocations.[24,25] The irradiations were carried out in the Bulk Shielding Reactor at Oak Ridge National Laboratory. The samples were wrapped in cadmium sheet about 1 mm thick to reduce the flux of thermal neutrons. The fast flux was about 4×10^{12} n/cm^2 sec. First the crystals were given a total dose of approximately 4×10^{15} n/cm^2. Then, after the faces of the specimens were lapped flat, they were irradiated again, to a total dose of from 10^{17} to 10^{18} n/cm^2.

It is important to have the end faces of the samples accurately flat in order to be able to define precisely the small gap width in the capacitive detector. For this reason, the sample faces were lapped until deviations from flatness were less than an optical wavelength.

For the attenuation measurements discussed in Appendix B it was necessary to make the sample faces closely parallel and to be able to measure deviations from parallelism. To measure the angle between the faces an autocollimator was used, with which angles as small as 4 sec of arc could be resolved.

The orientations of the crystals were checked by taking Laue back-reflection x-ray patterns. The orientations of the faces were accurate to better than one degree.

RESULTS AND DISCUSSION

Nonlinearity Parameters

In the harmonic generation experiments, a set of fifteen data points was taken for each sample. The generating transducer was reapplied and the specimen aligned in the sample holder assembly three times; each time measurements were taken for five different wave amplitudes. In Fig. 2, the second harmonic is plotted as a function of the square of the fundamental amplitude for two runs on each of three samples. The square dependence is demonstrated clearly.

The nonlinearity parameters K_3 were calculated from the fundamental and second harmonic amplitudes, using the relation indicated in Eq. (10). The values of K_2 used were calculated from the second-order constants given by Hiki and Granato[10] which differ by only about 1 percent from earlier measurements.[26] Table II

[24] D. O. Thompson and V. K. Pare, in *Physical Acoustics*, edited by W. P. Mason (Academic Press Inc., New York, 1966), Vol. III.
[25] G. L. Pearson, W. T. Read, and W. L. Feldman, Acta Met. 5, 181 (1957).
[26] W. C. Overton and J. Gaffney, Phys. Rev. 98, 969 (1955).

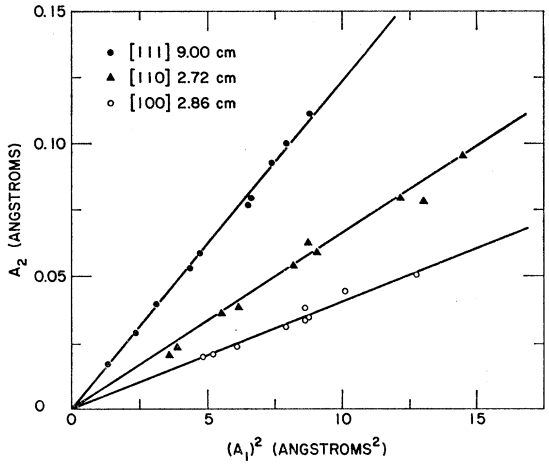

FIG. 2. The second harmonic amplitude versus the square of the fundamental amplitude for measurements on copper crystals in three crystallographic directions.

contains the values of the nonlinearity parameters calculated from the data, together with the root-mean-square deviation or standard error of each set.

The principal sources of error are in determining the gap spacing of the detector and in calibrating the detector and amplifier. The uncertainty of K_3 is less than the inaccuracy of the ratio of the second harmonic amplitude to the square of the fundamental, since K_3 is calculated from that ratio and from values of K_2. The final experimental error of K_3 is estimated to be about 10%, which is considerably more than the standard error.

Another possible source of error is in the effect of attenuation. If this were noticeable, the values of K_3 calculated from measurements on shorter samples (without corrections for attenuation) should be greater than those obtained from longer ones. No such trend is seen in the set of three [111] samples; therefore, no correction for attenuation is applied. (See Appendix B.)

The agreement among the values of K_3 obtained from the three [111] samples of different lengths indicates that the sample preparation and handling did not cause a change in the measured properties from one sample to the next. It also verifies the linear growth of the second harmonic with propagation distance.

The present results can be compared with those of

TABLE III. Comparison of calculated and directly measured nonlinearity parameters of copper in units of 10^{12} dyn/cm^2.

Direction	Present result	Calculated from data of Hiki and Granato[a]	Calculated from data of Salama and Alers[b]
[100]	−14.3	−12.7	−15.0
[110]	−32.5	−32.7	−29.5
[111]	−25.9	−29.5	−27.2

[a] Reference 10. [b] Reference 11.

TABLE IV. Pressure derivatives of effective second-order elastic constants of copper and combinations of third-order constants calculated from them.

	Lazarus[a]	Daniels and Smith[b]	Hiki and Granato[c]	Salama and Alers[d]
$\frac{d}{dp}C_{44}$	0.83	2.35	2.63	2.5
$\frac{d}{dp}\frac{1}{2}(c_{11}-c_{12})$	0.566	0.580	0.375	0.45
$\frac{d}{dp}\frac{1}{3}(c_{11}+2c_{12})$	3.91	5.59	5.44	5.8
$C_{144}+2C_{166}$[e]	−8.18	−14.35	−15.49	−14.25
$C_{111}-C_{123}$[e]	−13.18	−13.29	−11.62	−12.5
$C_{111}+6C_{112}+2C_{123}$[e]	−47.71	−68.17	−66.24	−71.0

[a] D. Lazarus, Phys. Rev. **76**, 545 (1949).
[b] W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958).
[c] See Ref. 10.
[d] Calculated from uniaxial stress data of Ref. 11.
[e] In units of 10^{12} dyn/cm^2.

other experiments. Two sets of measurements of the third-order elastic constants are available.[10,11] In Table III the nonlinearity parameters calculated from the results of Hiki and Granato and of Salama and Alers are given, and it is seen that the agreement with the harmonic generation values is within the experimental uncertainty.

Third-Order Elastic Constants

The nonlinearity parameters can be used together with the pressure derivatives of effective second-order constants to evaluate all six third-order elastic constants. In Table IV, the three sets of pressure derivatives available in the literature are listed, together with the hydrostatic pressure derivatives calculated from the uniaxial stress data of Salama and Alers; and the values of the three combinations of third-order elastic constants calculated from the pressure derivatives are indicated. The terms obtained from the three most recent sets of data are consistent to within 7, 14 and 3%, which is on the order of the experimental uncertainty of the K_3's. Using these numbers and the values of the nonlinearity parameters, the constants listed in Table V are calculated. Each of the constants is expressed in terms of the six measured quantities; and the final error is calculated from the propagation of the experimental uncertainties in evaluating the constants. Rather than the small standard deviations, more realistic measurement uncertainties of 10% for the nonlinearity parameters and of 5% for the pressure derivatives are used. This results in greater percentage-estimated errors, especially for C_{123}, C_{144}, and C_{456}, since the latter are small quantities determined from the differences of large numbers.

For comparison, the complete sets of constants measured by Hiki and Granato and by Salama and Alers are given also in Table V. There is agreement within experimental error among all the sets, with the exception of the constants C_{112}, C_{144} and C_{456} calculated from the data of Lazarus and the present experiments, indicating that the more recent determinations of pressure derivatives are more accurate.

The present results, obtained by a different technique, support the conclusion of Ref. 10 that the closed-shell repulsive interaction between nearest-neighbor atoms is the dominant contribution to the higher-order elastic constants of the noble metals. In that case, the constants should obey approximately the relations

$$C_{111}=2C_{112}=2C_{166},$$
$$C_{123}=C_{456}=C_{144}=0. \quad (12)$$

If these equalities are taken to hold exactly, the K_3's can all be expressed in terms of C_{111} and they become

$$[100]: K_3=C_{111}=-14.3\times10^{12}\ \text{dyn/cm}^2,$$
$$[110]: K_3=(17/8)C_{111}=-30.4\times10^{12}\ \text{dyn/cm}^2,$$
$$[111]: K_3=(16/9)C_{111}=-25.4\times10^{12}\ \text{dyn/cm}^2.$$

From Table II it is seen that the measured values obey the relations very well.

SUMMARY

The experiments described here indicate that meaningful measurements of the amplitudes of the fundamental and the second harmonic of a distorted ultra-

TABLE V. Third-order elastic constants of copper calculated from pressure derivatives and nonlinearity parameters.

	From pressure derivatives and nonlinearity parameters (10^{12} dyn/cm^2)				From hydrostatic and uniaxial stress derivatives (10^{12} dyn/cm^2)	
	Lazarus (1949) and present experiment	Daniels and Smith (1958) and present experiment	Hiki and Granato (1966) and present experiment	Salama and Alers (1967) and present experiment	Hiki and Granato (1966)	Salama and Alers (1967)
C_{111}	−14.27±1.4	−14.27±1.4	−14.27±1.4	−14.27±1.4	−12.71±0.22	−15.0 ±1.5
C_{112}	−5.21±0.7	−8.66±0.8	−7.78±0.8	−8.87±0.8	−8.14±0.09	−8.5 ±1.0
C_{123}	−1.09±1.5	−0.98±1.5	−2.65±1.5	−1.77±1.5	−0.50±0.18	−2.5 ±1.0
C_{144}	+8.54±2.2	+0.64±2.3	−0.06±2.3	−0.63±2.3	−0.03±0.09	−1.35±0.15
C_{166}	−8.36±1.1	−7.49±1.1	−7.71±1.1	−7.44±1.1	−7.80±0.05	−6.45±0.1
C_{456}	−5.47±1.6	+0.44±1.6	+1.17±1.6	+0.66±1.6	−0.95±0.87	−0.16±0.1

sonic wave can be made. For copper, the harmonic generation experiments yield values of the nonlinearity parameters that agree within experimental accuracy with values of third-order elastic constants obtained by other techniques.

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APPENDIX A: ELASTIC ENERGY DENSITY

The elastic strain energy density, to third-order in the strain components, for the most symmetrical classes of cubic crystals, is written in terms of three second- and six third-order elastic constants. With Brugger's definition of the constants,[17] the expression is

$$\begin{aligned}U=&\tfrac{1}{2}c_{11}(\eta_{11}^2+\eta_{22}^2+\eta_{33}^2)+c_{12}(\eta_{11}\eta_{22}+\eta_{22}\eta_{33}+\eta_{33}\eta_{11})\\&+c_{44}(\eta_{12}^2+\eta_{21}^2+\eta_{23}^2+\eta_{32}^2+\eta_{31}^2+\eta_{13}^2)\\&+\tfrac{1}{6}C_{111}(\eta_{11}^3+\eta_{22}^3+\eta_{33}^3)\\&+\tfrac{1}{2}C_{112}[\eta_{11}^2(\eta_{22}+\eta_{33})+\eta_{22}^2(\eta_{33}+\eta_{11})\\&\qquad+\eta_{33}^2(\eta_{11}+\eta_{22})]\\&+C_{123}\eta_{11}\eta_{22}\eta_{33}+C_{456}(\eta_{12}+\eta_{21})(\eta_{23}+\eta_{32})(\eta_{31}+\eta_{13})\\&+C_{144}[\eta_{11}(\eta_{23}^2+\eta_{32}^2)+\eta_{22}(\eta_{31}^2+\eta_{13}^2)\\&\qquad+\eta_{33}(\eta_{12}^2+\eta_{21}^2)]\\&+C_{166}[(\eta_{12}^2+\eta_{21}^2)(\eta_{11}+\eta_{22})+(\eta_{23}^2+\eta_{32}^2)(\eta_{22}+\eta_{33})\\&\qquad+(\eta_{31}^2+\eta_{13}^2)(\eta_{33}+\eta_{11})]. \quad \text{(A1)}\end{aligned}$$

The relations between Brugger's constants C_{ijk} and Birch's C_{ijk}^B are as follows:

$$C_{111}=6C_{111}^B,\quad C_{123}=C_{123}^B,\quad C_{166}=\tfrac{1}{2}C_{166}^B,$$
$$C_{112}=2C_{112}^B,\quad C_{144}=\tfrac{1}{2}C_{144}^B,\quad C_{456}=\tfrac{1}{4}C_{456}^B.$$

APPENDIX B: MEASUREMENT OF ATTENUATION

In Sec. II a simplified analysis was given of the effect of attenuation in harmonic generation experiments. If the attenuation is low enough, its effect on the values of the nonlinearity parameters calculated from amplitude measurements is smaller than the experimental uncertainty and may be neglected.

The attenuation of longitudinal ultrasonic waves at 30 and 60 MHz was measured in a set of [111] Cu crystals irradiated to a fast neutron dose of 10^{18} n/cm^2. The sample lengths were 9.0, 4.0, 1.4, and 0.65 cm. The measurements were made by the pulse-echo technique. An X-cut quartz transducer was bonded to a sample face with polystyrene fluid, and the echo pattern was received at the other end of the specimen by the capacitive detector. An attenuator was inserted between the detector and a tuned amplifier. The amplified pulse-echo pattern was displayed on an oscilloscope screen. The attenuator was set such that the nth pulse produced a given deflection on the oscilloscope screen. Then the attenuation was increased until the first detected pulse produced the reference deflection. The difference in decibels between the two attenuator settings indicated the loss for $n-1$ round trips through the sample.

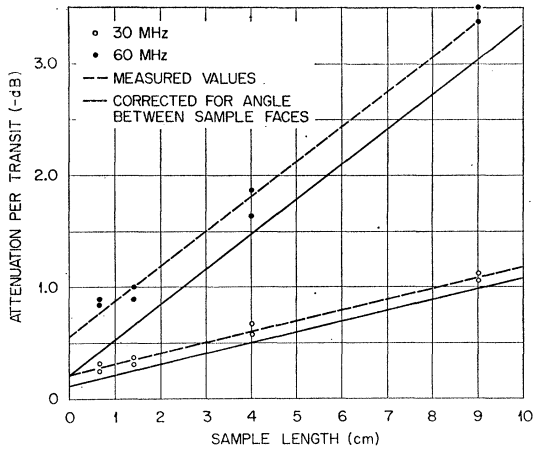

FIG. 3. Attenuation of 30 and 60 MHz ultrasonic waves in the (111) direction of neutron-irradiated Cu crystals of different lengths.

In Fig. 3 the results are indicated. The loss in decibels for one transit and one reflection is plotted as a function of sample length. The fact that the points lie on a straight line indicates that the loss per unit length was very nearly the same in all samples. The slope of the line is the value of the attenuation in decibels per centimeter, and the intercept on the vertical axis gives the loss per reflection.

An approximate correction for one of the reflection effects can be applied. The solid line indicates the damping after subtraction of the contribution due to the nonparallelism of the sample faces, calculated from the analysis of Granato and Truell.[27]

The slopes of the lines indicate values of $\alpha_1=0.096$ dB/cm for 30 MHz and $\alpha_2=0.32$ dB/cm for 60 MHz attenuation.

Comparing Eqs. (10) and (11), one sees that values of $(3K_2+K_3)/8K_2$ calculated without considering attenuation are to be multiplied by a factor which turns out to be 1.035 for the values of α_1 and α_2 given above and a path length of 5 cm. Since the estimated maximum uncertainty of $(3K_2+K_3)/8K_2$ is 20% the correction was not applied.

[27] A. Granato and R. Truell, J. Appl. Phys. 27, 1219 (1956).