Temperature Variation of the Elastic Constants of Cubic Elements. I. Copper

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The ultrasonic pulse technique has been used in conjunction with a specially devised cryogenic technique to measure the velocities of 10-Mc/sec acoustic waves in copper single crystals in the range from 4.2°K to 300°K. The values and the temperature variations of the elastic constants have been determined. The room temperature elastic constants were found to agree well with those of other experimental works. Fuchs' theoretical c_{44} at 0°K is 10 percent larger than our observed value but his theoretical c_{11} , c_{12} , K and $(c_{11}-c_{12})$ agree well with the observations. The isotropy, $(c_{11}-c_{12})/2c_{44}$, was observed to remain practically constant from 4.2°K to 180°K, then to diminish gradually at higher temperatures. Some general features of the temperature variations of elastic constants are discussed.

INTRODUCTION

CCURATE experimental measurements of the elastic constants of single crystals of the metallic elements at temperatures low enough to permit reliable extrapolations to 0°K provide particularly important fundamental quantities. Such values at 0°K are needed in several areas of the solid state theory. They provide a check into the accuracy of the quantum mechanical calculations, such as those due to Fuchs,1 of the elastic constants and the cohesive energy. They permit testing the equations relating the elastic constants at 0°K to the atomic force constants which are used in the calculation of the vibrational spectra and specific heats by the method of Born and von Karman.² If central forces are assumed in a theory of the elasticity of monatomic solids³ the Cauchy relations result but these are not observed experimentally. The deviations from Cauchy relations can be studied in detail with elastic constants at 0°K in view of a recent hypothesis due to de Launay⁴ which takes the electron gas elasticity into account. Both the values at 0°K and the details of the temperature variations of the isothermal elastic constants are needed to test the validity of the Born theory⁵ for these temperature variations.

We are particularly interested in checking the validity of the Born-von Karman theory of specific heat in the case in which only nearest and next-nearest neighbor interactions are considered in the theory.⁶ This requires both experimental elastic constants and experimental specific heat measurements. Calorimetric techniques have improved to the point that some relative experimental uncertainties in specific heats are as small as a few tenths of a percent⁷ at low temperatures and it is expected that the absolute accuracies will ultimately improve to better than one percent. Thus these considerations demand as reasonably good accuracy of measurement of the elastic constants on good quality single crystals as can be obtained by conventional ultrasonic techniques in conjunction with a cryogenic technique suitable for such measurements at liquid helium temperatures.

The measurements on copper crystals reported herein are the first results of a program for the measurement of the elastic constants of crystals of the face-centered and body-centered cubic metallic elements in the range from room temperature to liquid helium temperatures. Because this is the first paper of a series some of the experimental details discussed here will be omitted from later papers. Copper is of interest because of Fuch's theoretical calculations,¹ because its specific heat is reliably known⁸ down to 10°K and because Leighton's theoretical specific heat calculations⁶ were in terms of parameters that differ but little from the experimental parameters for copper.

EXPERIMENTAL METHODS

Well-known results of the theory of plane elastic wave propagation in cubic crystals are the velocities of propagation of one longitudinal and two transverse plane waves in any crystallographic direction. These plane wave velocities, appearing in the elastic theory in the form ρv^2 , are the solutions of a cubic secular determinantal equation. The elements of this determinant are defined by the elastic constants and the direction cosines of the direction of propagation. Thus if the cosines are known and the velocities are measured in a sufficient number of crystallographic directions (sometimes only one direction is required) this is equivalent to the measurement of the fundamental adiabatic elastic constants themselves. It may be shown that it is usually more reliable, from the experimental view-

¹ K. Fuchs, Proc. Roy. Soc. (London) A151, 585 (1935); A153,

¹ K. Fuchs, Proc. Roy. Soc. (London) A151, 585 (1935); A153, 622 (1936).
² M. Born and Th. von Karman, Physik. Z. 13, 297 (1912); Physik. Z. 14, 15 (1913).
³ I. Stakgold, Quart. Appl. Math. 8, 2 (1950).
⁴ J. de Launay, J. Chem. Phys. 21, 1975 (1953).
⁵ M. Born, J. Chem. Phys. 7, 591 (1939); Proc. Cambridge Phil. Soc. 36, 160 (1940); M. Born, Proc. Cambridge Phil. Soc. 39-40, 100 (1943-44); M. Born and M. Bradburn, Proc. Cambridge Phil. Soc. 39-40, 101 (1943-44); M. M. Gow, Proc. Cambridge Phil. Soc. 39-40, 151 (1943-44); M. M. Gow, Proc. Cambridge Phil. Soc. 39-40, 151 (1943-44).
⁶ R. B. Leighton, Revs. Modern Phys. 20, 165 (1948).

⁶ R. B. Leighton, Revs. Modern Phys. 20, 165 (1948).

⁷ J. R. Clement and E. H. Quinnell, Phys. Rev. **92**, 258 (1953). ⁸ W. F. Giauque and P. F. Meads, J. Am. Chem. Soc. **63**, 1897 (1941); S. M. Dockerty, Can. J. Research **15A**, 59 (1937); J. A. Kok and W. H. Keesom, Physica 3, 1035 (1936).

point, to measure the plane wave velocities of waves propagating in crystallographic symmetry directions, such as the [001] and [011] directions. For these two special directions there are five distinct roots of the secular equations for cubic crystals as follows: $\rho v_1^2 = c_{11}$, a longitudinal wave propagating in the [001] direction; $\rho v_2^2 = c_{44}$, two identical roots, corresponding to transverse waves polarized in the [010] and [100] directions propagating in the [001] direction; $\rho v_3^2 = (c_{11}+c_{12}$ $+2c_{44})/2$, a longitudinal wave propagating in the [011] direction; $\rho v_4^2 = c_{44}$, a transverse wave polarized in the [100] direction propagating in the [011] direction; $\rho v_5^2 = (c_{11}-c_{12})/2$, a transverse wave polarized in the [011] direction.

The velocities, v_1 to v_5 , may be determined directly by experiment by measuring the transit time of plane ultrasonic longitudinal or transverse waves in (001) and (011) crystal specimens. To assure that the waves are sufficiently plane it is considered necessary that the diameter of the radiating source be large compared to the wavelength of the sound waves and that the wave front should be small enough in diameter so that it does not suffer appreciable interaction with the walls of the specimen. We have satisfied these requirements sufficiently well in practice by using 2 cm diameter specimens and 2 cm diameter quartz crystals cemented directly to the specimen end faces and excited over 1.4 cm of their diameter at a frequency of 10 Mc/sec. In copper the wave fronts of the propagated waves of 1.4-cm wave-front diameter are about 30 wavelengths across for longitudinal waves and about 50 wavelengths across for transverse waves. It may be shown that these waves are "sufficiently plane" for accurate measurements of the elastic constants. Under these experimental conditions the ultrasonic beam width between halfintensity points is less than 1° in copper so that the wave does not suffer noticeable wall reflections during the time interval of measurement.

We use the following experimental methods for measuring these velocities as functions of temperature (1) the ultrasonic pulse-echo technique for measuring the round trip transit times of 10-Mc/sec longitudinal and transverse waves in the crystal specimens, (2) a cryogenic technique for controlling the temperature between room temperature and 4.2°K, and (3) techniques providing for acoustical coupling over this temperature range between the specimen and the thin wafer quartz crystal which serves as the ultrasonic transducer. All three of these techniques have been discussed previously in detail and so it is only necessary to discuss certain features pertinent to the copper measurements here.

Ultrasonic Technique

The ultrasonic pulse-echo technique as employed in the measurement of the elastic constants of solids has been described in several papers in the literature.⁹ Our electronic equipment is similar to most of those previously described, in that the Du Mont A/R 256-D radar range oscilloscope is employed both for the purpose of triggering the ultrasonic cycle as well as serving as the precision time measuring instrument.

The velocities of longitudinal waves were measured in an (001) copper crystal of length 5.3622 cm at 27.4°C and in an (011) crystal whose length at 20°C was 5.7833 cm. These waves are generated by an X-cut quartz cemented directly to the specimen, the cement providing the acoustical coupling between quartz and specimen. The attenuation of the 10 Mc/sec ultrasonic waves was relatively small in these copper crystals and remained in the neighborhood of 10⁻³ neper per cm over the whole temperature range. Thus very little decay in the sharpness of the leading edges of the echos resulted from attenuation. These specimen lengths were short enough, for longitudinal waves, so that there were always 4 echos of the ultrasonic pulse train in the first 100 microseconds and long enough so that the various end effects, if any, would have a negligible effect on the over-all accuracy of measurement. The most accurate range of the 256-D scope is the delayed-sweep range from 0 to 100 microseconds. In this range the uncertainty in a measurement of the time of arrival of an echo having a rapid rise time can be made as low as about ± 0.02 microsecond, when the manually controlled sweep-delay circuit is properly adjusted and calibrated against calibration markers derived from the 100-kc/sec crystal standard.

The time of arrival of each of the first 4 echos in the train was read 5 times and the 5 readings averaged. Immediately after measuring the arrival times of the echos at each temperature the arrival times of the calibration markers were read. Each calibration marker was also read 5 times to give the average arrival time of each of the 10 markers in the 100 microsecond sweep range. From the latter measurements a calibration correction curve was made by plotting the deviation of the sweep delay dial reading from the (true) time of arrival of the markers. These calibration correction curves always turned out to be smooth and the 256-D scope was adjusted so that the deviations from true time were small (usually less than 0.05 microsecond). Thus the corrections to be applied to the echo arrival times also were usually quite small (in the neighborhood of 0.05 microsecond) and the uncertainty of the corrections were estimated to be no greater than 0.01 to 0.02 microsecond. With this procedure we obtained the corrected time of arrival of each of the first 4 echos in the wave train at each temperature of observation.

To get the round-trip transit times at each temperature the corrected average arrival times were treated by

⁹ D. L. Arenberg, Radiation Laboratory, Massachusetts Institute of Technology Report 932, 1946 (unpublished); H. B. Huntington, Phys. Rev. 72, 321 (1947); D. Lazarus, Phys. Rev. 76, 545 (1949).

least squares. The arrival time, τ , of any echo can be represented by the straight line function, a+tn, where the intercept, a, represents the total electronic delay time after the initiating trigger through the electronic circuits and the crystal transducer, the slope, t, represents the round-trip transit time through the ultrasonic specimen, and n is the integer representing the echo number. Because n is an integer the least-squares determination of the delay, a, and the round-trip transit time, t, from the observed times, τ 's, is arithmetically simple. The delay, a, was about 0.7 microsecond while the desired transit times for both the (001) and (011) crystals ranged between 22 and 25 microseconds. Only the round-trip transit times, t's, are needed in the calculation of the elastic constants.

Transverse wave velocity measurements were made in the manner described above on the (001) copper crystal in the temperature ranges from 4.2°K to 90°K and from 140°K to 300°K. These measurements yielded the temperature variation of the shear elastic constant c_{44} . They were not made as functions of temperature in the (011) crystal because of the difficulty of properly orienting the Y-cut quartz crystal transducer to give the properly polarized shear waves. This difficulty arose because the cementing of the quartz to the specimen had to be done by remote control within the low temperature cryostat at a temperature of about 120°K. However checks at room temperature showed the internal consistency of the elastic constants of the two crystals.

In the transverse wave measurements on the (001)crystal only two echos could be read in the 100 microsecond sweep range of the 256-D scope because of the long round-trip transit time (about 36 microseconds) of the transverse waves. Thus least squares could not be used to adjust the two-echo data. About 75 different transverse wave measurements were taken in the range from 4.2°K to 300°K. A curve was smoothed through the plot of round-trip transit time versus temperature and the residuals, i.e., the deviations of the observed points from the smoothed curve were plotted on probability paper. The standard deviation resulting from this plot was less than ± 0.03 microsecond. This corresponds to a relative error of ± 0.08 percent in the velocity of transverse waves. However the over-all error in the elastic constant c_{44} , has been estimated to be about ± 0.25 percent when other possible sources of error are taken into account.

Transit-Time Correction

In pulse-echo ultrasonic measurements in solids the presence of the cement film bonding the quartz transducer to the specimen solid necessitates a small transit time correction to the observed round-trip transit time through specimen plus film plus quartz. This correction ought to be only the round-trip transit time through the thickness of the cement film only. However, consideration of the various physical factors involved (too detailed to discuss here) shows the possibility of interference among the high-frequency components comprising the leading edges of both the acoustic and electrical pulses impinging on the transducer. The cement film thickness affects the interference pattern and the combined electrical and acoustic effects explain the observed "apparent" delay in "expected" time of arrival of occasional pulses of the echo train.

The magnitudes of these small "apparent" delays (less than 0.1 microsecond at 10 Mc/sec) have been observed experimentally to be temperature dependent. The particular pulses for which the delays are most apparent has also been observed to be temperature dependent. The delays affect the measured average transit time but little while averages of data taken over a temperature range tends to wipe out the effect of the "apparent" delays altogether. On the other hand if the transit time correction is computed from sets of data taken at just one temperature it is likely to be far too large. Thus to get a correct value for the transit time correction by the usual method of measurement on several specimens of different lengths one should perform the measurements at several different specimen temperatures.

We measured transit times on four different specimen lengths [all painstakingly cut from the same (001)copper crystal at 2°K intervals from 290°K to 310°K. These data were treated by least squares and the average correction, computed at 300°K was 0.01 microsecond. In another experiment the transit time through specimen only was measured directly using the liquid acoustic cell technique. Using these data together with the data for the same specimen cemented directly to quartz the computed correction was only about 0.005 microsecond at 300°K. Thus the small corrections which we might make to our copper data are within the usual reading errors (0.01 to 0.02 microsecond). Now the corrections determined, presumably at just one temperature, by Smith et al.¹⁰ range from 0.03 to 0.10 microsecond while those reported by Lazarus¹⁰ range from 0.10 to 0.15 microsecond. We feel that these corrections are too large because they were computed from data taken, presumably, at just one value of the temperature.

Cryogenic Technique

The cryogenic technique used in these experiments is similar to that reported previously.¹¹ The specimen is mounted in a metal holder which surrounds it and tends to maintain a uniform temperature over its length. The metal holder also contains a platinum

 ¹⁰ D. Lazarus, Phys. Rev. 76, 545 (1949); Neighbors, Bratten, and Smith, J. Appl. Phys. 23, 389 (1952); T. R. Long and Charles S. Smith, Office of Naval Research Technical Report No. 12, NR 019201, July, 1953 (unpublished).
 ¹¹ W. C. Overton, Jr., J. Chem. Phys. 18, 113 (1950); thesis, Rice Institute, 1950 (unpublished); W. C. Overton, Jr., and P. T. Swim Phys. Rev. 84, 758 (1051).

R. T. Swim, Phys. Rev. 84, 758 (1951).

resistance thermometer for the temperature range above 20°K and a carbon composition thermometer for the range below 20°K. The temperature of the specimen can be measured to an accuracy of better than 0.1°K at all temperatures. This assembly is supported in the bottom of a Dewar flask by stainless steel support tubes. One of these tubes also serves as a coaxial line down which the 10-Mc/sec rf pulse is fed. The acoustical cement coupling between the quartz crystal and the specimen is made at a temperature of 125°K by using a low melting point cement (5 parts ether, 5 parts isopentane, two parts ethyl alcohol, this mixture abbreviated EPA). This cement is applied on the top face of the thin quartz crystal slab at 125°K as a single tiny drop. The specimen is then lowered onto the quartz thus spreading the drop of EPA into an extremely thin film. On further lowering the temperature to 100°K the EPA film solidifies into a glassy solid thus providing acoustical coupling between quartz and specimen for both longitudinal and transverse waves. It has been found experimentally that no cement applied at room temperature maintains proper acoustical coupling to temperatures below 120°K. Thus it is necessary to have some such technique as here described for cementing at low temperatures in order to attain the still lower temperatures without introducing excessive stresses across the specimen-quartz interface.

Three acoustical bonds were required in order that the whole temperature range below 300°K could be covered. Salol applied at 40°C has been used with success at room temperature as reported in several papers,^{9,11} and we employed it successfully in the range from 300°K down to 210°K for cementing the quartz to copper. We used ordinary stop-cock grease as a cement to cover the range from about 250°K down to 130°K. Both the salol and stop-cock grease cements are applied at room temperature or slightly higher. The cementing technique in which the EPA mixture is used as just described provides acoustical coupling from 100°K to 4.2°K. Few measurements were made in the range from 130°K down to 100°K since a suitable stress-free cement for that range is not presently known.

Temperature control was accomplished by a closed system heat exchanger which could be inserted in the lower part of the cryostat. Liquid nitrogen fed into this heat exchanger provided the necessary refrigeration between 300°K and 90°K. To cool from 300°K to 90°K required a minimum time of 30 minutes but we purposely cooled very slowly to prevent thermal shock and so that the specimen crystal could attain a uniform temperature before taking the ultrasonic measurements. It usually required about 8 hours to cover the temperature range from 300°K to 210°K with a salol cement and a similar period to cover the range from 250°K to 130°K when using stop-cock grease as a binder. Constant attention was required during these periods so that when an equilibrium temperature was reached the ultrasonic measurements could be taken. It was necessary to take data on the "cool-down" so that the onset of excessive stress across the quartz-specimen interface could be detected.

PREPARATION OF SPECIMENS

Crucibles of high purity graphite were designed so that crystals 2 cm in diameter by 5 or 6 cm long of preferred orientation could be grown from 0.5-cm seeds of "nearly" preferred orientation by the Bridgman technique. The crucibles were made in two parts, the upper part being a sleeve to contain the melt, the lower part being a solid cylinder machined with a shoulder over which the upper part fits. The snug fit of the sleeve over the lower part prevents molten metal from leaking past the graphite-graphite joint. In order to obtain a crystal of some desired orientation a 0.5-cm diameter seed of nearly this orientation is selected and a hole to contain it is drilled in the lower part of the crucible at the proper angle. The angle may vary from 0 to 10 degrees, the maximum being determined by the one inch diameter of the crucible and the length of the seed crystal. The proper adjustment of the seed in its hole is facilitated by use of an optical goniometer designed to hold the entire crucible.

With the aforementioned arrangement two large single crystals of copper, 2 cm in diameter by 6 cm long, one with [001] cylinder axis within $\frac{1}{2}$ degree and the other with [011] cylinder axis within one and one half degrees, were grown from seeds of nearly preferred orientation. Melts of Johnson, Matthey, and Company spectroscopic copper (Lab. No. 2804) were lowered through the gradient of a vertical tube furnace in an atmosphere of pure helium. After annealing, a crystal, with seed attached, could be removed from its crucible by simply disassembling the crucible.

A specimen crystal could be separated from its seed by first potting them in a wax matrix, then sawing away the seed with a jeweler's saw. Since the crystal structure is damaged only at the cut, the damage may be removed by acid and the seed may be reoriented in the crucible and used again to grow another large single crystal of preferred orientation.

To prepare a large crystal for ultrasonic measurements, it was waxed into a special thick walled hollow cylinder having flat and parallel end faces closely perpendicular to the cylinder axis. When waxed in, the "growth" and "meniscus" ends of the single crystal protrude beyond the end faces of this cylinder, so that when machined in a lathe these ends develop into flat faces. Care was taken to prevent damage to the crystal structure by machining only 0.002 inch per cut until the "growth" and "meniscus" ends of the crystal were removed and end faces developed. Several cuts of 0.001 inch, then several of 0.0005 inch were taken off these newly developed end faces. Finally about 30 cuts of 0.0001 inch were made so as to remove damage produced by the larger cuts. The crystals were then

carefully hand lapped, tested for parallelism with a Sheffield Style 1000 comparator gauge, and found to be parallel to about ± 0.00005 inch across the 2 cm diameter of the face. The crystal lengths were determined at room temperature to about ± 0.005 percent by comparing against Taft-Pierce gauge blocks.

A spectroscopic analysis of the crystal specimen showed the following impurities: Pb(TR); Fe(FTR); Ag, Ca, Mg(TR); Si(VW). Analysis of the original Johnson, Matthey, and Company copper rods showed: Fe, Ag(TR); Ca, Mg(FTR); Si(VW), Pb not detectable. The symbols denote as follows: (FTR) < 0.0001 percent, 0.0001 percent < (TR) < 0.001 percent, 0.001 percent < (VW) < 0.01 percent. The Pb and slight increases in Ca and Mg impurities evidently were picked up from the low ash content of the graphite crucibles.

EXPERIMENTAL RESULTS

Some 55 measurements of the round-trip transit time for longitudinal waves in the (001) copper crystal were obtained in the manner described above. These constitute the data from which $c_{11} = \rho v_1^2$ versus temperature were calculated. If $t_1(T)$ is the measured transit time at temperature T, then the experimental value of c_{11} at T is obtained conveniently by

$$c_{11}(T) = \rho(T) [v_1(T)]^2$$

$$= \frac{\rho_0 l_{10}^2}{\left(1 + \int_0^T \alpha dT\right)} \times \frac{1}{[t_1(T)]^2}, \qquad (1)$$

where ρ_0 is the density at 0°K and l_{10} is the length of the (001) crystal at 0° K.

Nix and MacNair¹² have measured the linear expansion coefficient of pure copper by an interferometric method from 80°K to about 600°K. They found that the Grüneisen formula, a 10

$$\alpha(T) = \frac{C_{\nu}/Q_0}{\left[1 - \frac{1}{6}(m + n + 3)U/Q_0\right]^2},$$
(2)

fitted their experimental measurements very well with the following parameters: C_v and U determined from the Debye specific heat and energy functions with Debye $\Theta = 325^{\circ}$ K, $Q_0 = 1.2 \times 10^5$ cal-mole⁻¹ (m+n+3)/6=2.8. Using Eq. (2) and these parameters we calculated $\alpha(T)$, determined $\int_0^T \alpha dT$ by graphical integration and prepared a table of $(1 + \int_0^T \alpha dT)$ at 10°K intervals from 0°K to 300°K. The measured values of the length l_1 at room temperature is then easily converted to l_{10} at 0°K.

For density, ρ_0 , we took the product of the x-ray value¹³ for copper at 20°C of 8.9366 g/cm³ with the cube of $(1+\hat{f}_0^{293.2}\alpha dT)$ obtained by interpolation of



FIG. 1. The adiabatic elastic constant c_{11} of copper versus temperature. The points represented by the open circles have been calculated from the measured transit times $(t_1$'s) by means of Eq. (1). The solid curve has been smoothed as described in the text.

the aforementioned table. Such interpolations also give the value of $(1 + \int_0^T \alpha dT)$ to be used in Eq. (1) at each temperature of measurement.

In a similar manner the elastic constant c_{44} was computed by

$$c_{44}(T) = \frac{\rho_0 l_{10}^2}{\left(1 + \int_0^T \alpha dT\right)} \times \frac{1}{\left[l_2(T)\right]^2},$$
(3)

where t_2 is the experimental round-trip transit time for transverse waves in the (001) crystal.

Since the cylinder axis of the (001) crystal deviated by about $\frac{1}{2}^{\circ}$ from the [001] direction the question of a minor correction of the observations to the true [001]direction was considered. The secular determinant was solved for this direction in order to determine this necessary small correction factor, which turned out to be too small, compared to experimental error, to take into account. Thus the actual experimental points of $c_{11}(T)$ and $c_{44}(T)$ shown in Figs. 1 and 2 may be considered as defining the true values and the temperature variation of these elastic constants.

In Fig. 1, in the range from 10°K to 50°K, several experimental points are seen to be higher than the smoothed curve by about 0.4 percent (note the 1 percent bracket). These experimental points were taken on the rapid "warm-up" from 4.2°K, during which time the temperature gradients over the length of the specimen crystal were fairly large. Experimental points taken in this same range on the "cool-down," during which the temperatures were fairly well controlled, are within ± 0.15 percent of the curve. Although the mechanism is not understood it is believed that the deviations are caused by the large thermal gradient, for under isothermal conditions with the specimen in baths of liquid N_2 , O_2 , or He the deviations in the data usually did not exceed about ± 0.1 percent.

The experimental deviations in c_{44} versus T in Fig. 2 average slightly larger than those of c_{11} as may be seen

 ¹² F. C. Nix and D. MacNair, Phys. Rev. **60**, 597 (1941).
 ¹³ M. Straumanis and O. Mellis, Z. Physik **94**, 184 (1935);
 M. Straumanis, Z. Physik **126**, 49 (1949).



FIG. 2. The adiabatic elastic constant c_{44} of copper versus temperature. The points represented by the open circles have been calculated from the measured transit times (t_2) by means of Eq. (3). The solid curve has been smoothed as described in the text.

by referring to the 1 percent brackets. As pointed out previously this is due to the fact that measurements could be made on only two echos in the more accurate 0-100 microsecond delayed sweep range of the 256-D measuring equipment. Nevertheless the standard deviation is still fairly small and the absolute error in c_{44} from all sources is estimated not to exceed ± 0.25 percent, while that for c_{11} is about ± 0.2 percent.

The most accurate measurements obtained were the longitudinal wave measurements on the (011) crystal. Earlier experience gained on the (001) crystal in regard to the preparation of flat and parallel end faces was put to use in preparing the (011) crystal with the result that the probable error of each measurement (based on the least-squares treatment at each experimental point as earlier described) was smaller than the similarly treated longitudinal measurements in the (001) crystal. This may be noted by comparing the spread in the experimental points in Fig. 3 with that in Fig. 1.

The orientation of the cylinder axis of the (011) copper crystal deviated from the true [011] direction by about 1.3°, the direction angles, expressed as spherical coordinates being about 46.2° and 88.7° instead of 45° and 90°. The secular equation solved for this direction of propagation showed that a correction of 1.27 parts in 10,000 should be added to ρv_3^2 . This correction was made to each of the 40 experimental points although it, too, is small compared to the experimental error of ± 0.1 percent. Each experimental point was computed according to

$$\rho v_{3}^{2} = \frac{\rho_{0} l_{30}^{2}}{\left(1 + \int_{0}^{T} \alpha dT\right)} \times \frac{1}{[t_{3}(T)]^{2}}$$
(4)
$$= (c_{11} + c_{12} + 2c_{44})/2,$$

where t_3 is the measured round-trip transit time in the [011] direction and l_{30} is the length of the (011) crystal

at 0° K computed from the room-temperature length as previously described.

Because the temperatures of observation of the experimental points in Figs. 1, 2, and 3 do not coincide, except at some fixed bath temperatures, the calculation of c_{12} , the shear mode, $C' = (c_{11} - c_{12})/2$ and the adiabatic bulk modulus $K = (c_{11}+2c_{12})/3$ from linear combinations of the experimental results must be made from values picked off curves smoothed through the experimental results. Curves were drawn through the experimental points keeping in mind that the variation with temperature should be monotonic and have zero slope at 0°K. These curves were then slightly readjusted to minimize, particularly in those isothermal regions where the measurements are most reliable, the sum of squares of the residuals. From values picked off the smoothed curves of c_{11} , c_{44} , and ρv_3^2 the additional elastic constants were calculated.

Table I summarizes the adiabatic elastic constants c_{11} , c_{12} , the bulk modulus K, the shear mode C', and the crystalline isotropy factor $S = (c_{11}-c_{12})/2c_{44}$. The errors determined from the experimental measurements are c_{11} , ± 0.2 percent; c_{44} , ± 0.25 percent; ρv_3^2 , ± 0.1 percent. Using the standard formulas for the propagation of errors the probable errors in the calculated constants are as follows: c_{12} , ± 0.44 percent; the bulk modulus K, ± 0.34 percent, the shear mode C', ± 1.8 percent; and the crystalline isotropy factor S, ± 1.8 percent.

The isothermal elastic constants, c_{11}^T , c_{12}^T and the isothermal bulk modulus K^T may be calculated from the adiabatic constants in Table I by the thermo-dynamic relationships,

$$c_{11}{}^{T} = c_{11} - K^{s}(\gamma - 1)/\gamma,$$

$$c_{12}{}^{T} = c_{12} - K^{s}(\gamma - 1)/\gamma,$$

$$K^{T} = (1/\gamma)K^{s},$$

(5)



FIG. 3. The combination of adiabatic elastic constants $(c_{11}+c_{12}+2c_{44})/2=\rho v_3^2$ of copper versus temperature. The points represented by the open circles have been calculated from the measured transit times $(t_3$'s) by means of Eq. (4). The solid curve has been smoothed as described in the text.

where $\gamma = C_p/C_v$. By using numerical values of the linear expansion coefficient, density, the adiabatic bulk modulus K^s in Table I and the smoothed values of the specific heat at constant pressure, C_p (Giauque and Meads⁸), in the thermodynamic relation,

$$(\gamma - 1) = 9T\alpha_1^2 K^s / \rho c_p, \tag{6}$$

the value of γ was determined at 10°K intervals below 300°K. These were then used in Eqs. (5) to calculate the isothermal elastic constants and the isothermal bulk modulus shown in Table II. It is to be noted that the thermodynamic formula, Eq. (6), requires the expansion coefficient, $\alpha_1 = dL/LdT$ instead of the $\alpha = dL/L_0dT$ of Eq. (2). If α instead of α_1 is used to calculate first γ and then the elastic constants by Eqs. (5), the latter will sensibly be in error. In the case of copper at room temperature, the isothermal constants would be incorrect by about 0.03 percent.

The number of significant figures in Tables I and II is greater than is warranted by the accuracy of the absolute values. One additional significant figure has been retained for it indicates the smoothness of the

TABLE I. The adiabatic elastic constants, the $[0\bar{1}1](011)$ shear constant $C' = (c_{11}-c_{12})/2$, the reciprocal adiabatic compressibility $K^{s} = (c_{11}+2c_{12})/3$, and the isotropy $S = (c_{11}-c_{12})/2c_{44}$ of copper. The number of significant figures does not indicate the accuracy of the absolute value.

T⁰K	Ac ¢11	liabatic cons c12	stants $\times 10^{-1}$ K^s	1 dyne-cm= <i>c</i> 44	° C'	Isotropy S
0	17.620	12.494	14.203	8.177	2.564	0.314
10	17.620	12.494	14.203	8.176	2.564	0.314
20	17.618	12.492	14.201	8.173	2.563	0.314
30	17.613	12.488	14.196	8.168	2.563	0.314
40	17.605	12.482	14.190	8.160	2.561	0.314
50	17.593	12.475	14.181	8.149	2.559	0.314
60	17.578	12.467	14.170	8.135	2.556	0.314
70	17.560	12.457	14.158	8.118	2.551	0.314
80	17.540	12.447	14.145	8.100	2.546	0.314
90	17.517	12.437	14.130	8.080	2.540	0.314
100	17.493	12.425	14.115	8.059	2.534	0.314
110	17.467	12,414	14.098	8.036	2.527	0.314
120	17.441	12.402	14.081	8.013	2.519	0.314
130	17.412	12.389	14.064	7.990	2.512	0.314
140	17.383	12.377	14.045	7.966	2.503	0.314
150	17.353	12.364	14.027	7.942	2.495	0.314
160	17.322	12.350	14.008	7.917	2.486	0.314
170	17.290	12.337	13.988	7.892	2.477	0.314
180	17.258	12.323	13.968	7.867	2.468	0.314
190	17.225	12.309	13.948	7.841	2.458	0.314
200	17.192	12.295	13.927	7.816	2.448	0.313
210	17.158	12.280	13.906	7.790	2.439	0.313
220	17.123	12.266	13.885	7.763	2.429	0.313
230	17.088	12.251	13.863	7.736	2.419	0.313
240	17.053	12.236	13.842	7.709	2.409	0.313
250	17.018	12.220	13.820	7.681	2.399	0.312
260	16.982	12.205	13.797	7.654	2.389	0.312
270	16.947	12.189	13.775	7.626	2.379	0.312
280	16.911	12.174	13.753	7.597	2.368	0.312
290	16.875	12.158	13.730	7.568	2.358	0.312
300	16.839	12.142	13.708	7.539	2.348	0.312

TABLE II.	The isothe	ermal elastic	c constants	and reciprocal
isothermal co	mpressibility	y of copper.	The numb	er of significant
figures does n	ot indicate t	he accuracy	of the abso	lute value.

	Isotherma	Isothermal constants ×10 ⁻¹¹ dyne-cm ⁻²			
T°K	$c_{11}T$	c_{12}^T	K^T		
0	17.620	12.494	14.203		
10	17.620	12.494	14.203		
20	17.618	12.491	14.200		
30	17.611	12.486	14.194		
40	17.599	12.476	14.183		
50	17.579	12.461	14.167		
60	17.553	12.442	14.146		
70	17.522	12.419	14.120		
80	17.487	12.395	14.092		
90	17.450	12.369	14.062		
100	17.410	12.342	14.031		
110	17 260	10 215	12 000		
120	17.308	12.313	13.999		
120	17.020	12.20/	13.900		
140	17.281	12.239	13.933		
140	17.200	12.230	13.899		
150	17.190	12.201	15.804		
160	17.144	12.172	13.830		
170	17.096	12.143	13.794		
180	17.049	12.114	13.759		
190	17.001	12.085	13.723		
200	16.952	12.055	13.687		
210	16.903	12 025	13 651		
220	16.854	11.995	13.615		
230	16.804	11.965	13.578		
240	16.754	11.935	13.541		
250	16.704	11.905	13.504		
260	16 653	11 974	13 467		
200	16.000	11.0/4	13.407		
210	16 551	11.044	13.430		
200	16 500	11.013	12 255		
290	16.000	11.700	13.333		
500	10.440	11.734	15.517		

elastic constants calculated from the curves smoothed through the experimental data as described previously and, moreover, the relative variations of the elastic constants are known to greater accuracy than the absolute values.

COMPARISON OF RESULTS

In Table III the present measurements on copper are compared with other measurements by the ultrasonic pulse-echo method and by the composite oscillator method. Recently Long^{14} has measured the elastic constants of copper at room temperature and has made preliminary measurements of the temperature variation between 77°K and 300°K. His c_{11} , c_{12} , c_{44} , and K^* agree with the present work within 0.5 percent at 300°K but there is 1.7 percent difference between the $(c_{11}-c_{12})/2$ values. At 80°K the agreement is poorer but this is probably due to differences in cryogenic techniques. Our use of an acoustic cement having a low melting temperature (105°K) in the low-temperature range

¹⁴ T. R. Long (unpublished). We are indebted to Professor C. S. Smith, Case Institute of Technology, and to Mr. Long for their kind permission to use their copper measurements in advance of publication.

TABLE III. Comparison of the present measurements (P) with those of Long (TRL), Goens and Weerts (GW), and with the theoretical calculations of Fuchs (KF). The present data (P) has also been recomputed and denoted by (PC) using Lazarus' large 0.10-microsecond transit-time correction in order to compare the present measurements on the same basis with those of Lazarus (LC).

Obs.	Temp.	C11	C12	C44	$(c_{11} - c_{12})$	K^s
P	300°K	16.84	12.14	7.54	4.70	13.71
TRL	300°K	16.83	12.21	7.54	4.62	13.75
GW	room	16.98	12.26	7.53		
P	80°_{\cdot} K	17.54	12.45	8.10	5.09	14.15
TRL	80°K	17.63	12.59	8.03	5.04	14.27
Р	4.2°K	17.62	12.49	8.18	5.13	14.20
KF	0°K	17.5	12.4	8.9	5.1	14.1
PC	300°K	17.04	12.40	7.58		
LC	room	17.10	12.39	7.56		

below 100°K considerably minimizes stresses between the transducer and specimen. Such stresses would arise from differential thermal contraction if a cement having a high melting temperature were used at low temperatures. Excessive stresses cause distortion of the ultrasonic echos and associated transit time errors and because our cryogenic technique reduces these, we feel that our measurements are quite reliable at low temperatures.

Lazarus' c_{ij} values¹⁰ are denoted in Table III by (LC) and he computed these presumably using 0.10 to 0.15 microsecond transit time connections which, our experiments have shown, are probably far too large. However, to compare our present elastic constants, denoted by (P), with those of Lazarus we have recomputed a set, denoted by (PC), for which we used Lazarus' value of 0.10 microseconds as the transit time correction. The good agreement of (PC) with (LC) (within 0.35 percent) and of (P) with Long's data, (TRL) in Table III, attests to the relative accuracy and reproducibility of the ultrasonic pulse technique. However to obtain reliable absolute values, such as we believe we have in Tables I and II and denoted by (P) in Table III, one must take considerable care in the experimental determinations of the transit time corrections.

The room temperature c_{11} and c_{12} values of Goens and Weerts¹⁵ (GW) in Table III, determined from measurements by a composite oscillator technique, differ from the present data (P) at 300°K by only about 1 percent while the c_{44} values are in very good agreement. Elastic constants determined by this technique should be just as reliable as those obtained by plane wave ultrasonic methods provided the couplings between the various composite oscillator vibrational modes are properly accounted for and corrected.

Fuchs' quantum-mechanical treatment¹ of the copper lattice led to values of the elastic constants and compressibility that are in very good agreement with our present experimental results at 4.2° K except the theoretical c_{44} is about 10 percent larger than the observed value. Fuchs compares his theoretical c_{ij} 's with certain c_{ij} values at 0°K obtained from extrapolating experimental results at and above 80°K. The extrapolated values at 0°K are too large in comparison with our measured values at 4.2°K. At the present time such extrapolations from liquid air temperatures are to be considered unreliable for precision purposes and this lends further emphasis to the need and importance for extending the experimental measurements to liquid helium temperatures.

DISCUSSION

Previously reported linear variations of the elastic constants with temperature, for the temperature range above about Debye $\Theta/3$, are not very much in error because the observed nonlinear monotonic decreasing (or increasing in some cases) elastic constants deviate but little, above $\Theta/3$, from linearity. Below $\Theta/3$, however, the deviations from linearity become important since the c_{ij} vs T should approach 0°K with zero slope. Such is the case for the experimentally observed variations of the elastic constants of copper (Figs. 1, 2, and 3). To see any deviations from linearity above $\Theta/3$ requires accurate experimental observations indeed for in the present measurements one might easily fit the copper data above 110°K by a straight line. It is only the nature of the variation below $\Theta/3$ $(\Theta \approx 325^{\circ} \text{K} \text{ for copper})$ that requires the monotonic variations above this temperature to be nonlinear.

Lazarus¹⁰ has established experimentally for copper, aluminum, and some other solids that the elastic constants must be explicit functions of both temperature and volume. This finding has been further substantiated, using Lazarus' data on the pressure variation of elastic constants, by Long and Smith¹⁰ and independently by Sutton¹⁶ for aluminum. A formula, in which the volume and temperature appear explicitly, for representing the variation of c_{44} of aluminum, used by Sutton is

$$c_{44} = A e^{-B\beta T} R^{-2},$$

where β is the volume expansion coefficient and R is the ratio of volume at temperature T to that at some fixed temperature. We find that a similar relation,

$$c_{44}/c_{44}(0^{\circ}\mathrm{K}) = e^{-B\alpha T} / \left(1 + \int_{0}^{T} \alpha dT\right)^{9},$$

where α is the linear expansion coefficient, represents c_{44} of copper in Table I within 0.2 percent from 0°K to 300°K. In spite of the good fit, these formulas are purely empirical and have no fundamental theoretical basis.

The Born theory⁵ on "The Thermodynamics of Crystal Lattices" provides for the explicit dependence of the elastic constants for face-centered cubic lattices,

¹⁵ E. Goens and J. Weerts, Physik. Z. 37, 321 (1936).

¹⁶ P. M. Sutton, Phys. Rev. 91, 816 (1953).

on both volume and temperature in the form,

$$c_{ij}(V,T) = (a_{ij} + b_{ij}T)/V,$$

where a_{ij} and b_{ij} are explicit functions of the volume, but leads to the Cauchy relations, $c_{12}=c_{44}$, at 0°K. Preliminary attempts to fit Gow's⁵ theoretical calculations to the observed elastic constants of copper have not proved successful, primarily because of the observed deviations from the Cauchy relations.

It is surprising that the elastic constants may also be very closely represented as linear functions of the volume only in the temperature range below Debye Θ . Details of the correlation of the elastic constants of copper and aluminum with thermal expansion data will be discussed in a later paper.¹⁷

It is of interest to note that the isotropy, S $= (c_{11} - c_{12})/2c_{44}$, of copper is constant at 0.314 up to about 180°K, then it gradually decreases to 0.312 (about 1 percent lower) at 300°K (0.2 of the melting temperature). This means that the two shears, c_{44} and $(c_{11}-c_{12})/2$, have the same relative temperature variation up to about one-half Debye Θ , but at higher temperatures $(c_{11}-c_{12})/2$ decreases faster than c_{44} . We note from Sutton's¹⁶ measurements that aluminum has the same behavior, for at 773°K (0.8 of the melting temperature), the isotropy has decreased to a value about 10 percent lower than the 0° K value. In the Born theory⁵ on "The Stability of Crystal Lattices" the vanishing of the shear, c_{44} , is used as an approximate criterion for melting. In view of Sutton's aluminum measurements¹⁶ and our copper data it would appear that $(c_{11}-c_{12})/2$ would disappear at a lower temperature than c_{44} , and so its earlier vanishing would seem to be a more suitable criterion for melting for the monatomic face-centered cubic lattices. Judging from the theoretical graphs of Gow,⁵ however, it appears that the Born theory would have $(c_{11}-c_{12})/2$ and c_{44} vanish at the same temperature.

One of the fundamental problems for which the elastic constants at 0°K are required is the Born-von Karman theory of the lattice specific heat at constant volume. Here the assumed linear atomic restoring force constants needed in the vibrational spectrum calculations may be computed from linear combinations of the elastic constants. The relations used for the face-centered cubic lattice by Leighton⁶ and determined by de Launay⁴ by a phenomenological theory are here considered to be the correct ones. These are $\mu = ac_{44}$, $\sigma = a(c_{11}-c_{12}-c_{44})/4$, where μ is the force constant for nearest neighbor interaction, σ that for next-nearest neighbor interaction, and a is the lattice constant at 0°K.

Using the experimental values of the elastic constants in Table I at 0°K we compute respectively for μ and σ , 2.940×10^4 and 2.742×10^3 dyne-cm⁻¹. Then with the aid of de Launav's¹⁸ theoretical specific heat calculations we find the theoretical Debye Θ of 340.1°K at 0°K. A novel correlation technique¹⁹ for comparing Leighton's theoretical specific heat calculations with experimental specific heats has led to an empirically determined Θ at 0°K of 341±1°K, from raw experimental specific heats. This technique has also led to values of μ and σ which agree within a few percent with those calculated directly from the elastic constants and promises even closer agreement when more theoretical specific heat data become available for the correlation. Thus it appears that a two constant Born-von Karman theory represents fairly accurately the specific heat of copper over our present range (10°K to 100°K for copper) of comparison provided μ and σ are related by the above equations to the elastic constants.

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¹⁸ J. de Launay, J. Chem. Phys. 22, 1676 (1954).

¹⁹ W. C. Overton, Jr., and J. R. Clement, Phys. Rev. **95**, 602 (1954) (to be published in further detail).

¹⁷ de Launay, Clement, and Overton (to be published).