subsidiary loops there is hysteresis and magnetic viscosity without any Barkhausen effect.

According to the domain theory of ferromagnetism a material may change its intensity of magnetization by three different processes: (1) reversal of the saturated magnetization of small domains, (2) reorientation of the magnetization of the domains, (3) increase of size of one domain at the expense of another. The first process is supposed to produce the sudden inductive jumps associated with the Barkhausen effect. The last two processes may take place slowly and continuously, so would not be detected by the use of telephone receivers. It appears, therefore, in view of the experiments just described, that the phenomenon of magnetic viscosity is involved in one or both of the two last named processes, as well as in the first.

It is usually considered that process (2) occurs in strong fields, process (3) in weak fields.[8] For the loop used in the present experiment there is always a demagnetizing field present; however, it seems reasonable to suppose that process (3) is largely responsible for the induction changes of these small loops.

In this case the conclusion to be drawn is that when the boundaries of domains move under the influence of applied fields a certain time is required for equilibrium to be attained after the magnetic field ceases to change. These moving boundaries would be the seat of eddy currents and magnetostrictive strains, so that magnetic viscosity would make its appearance in process (3) as a result of the time required for the disappearance of microscopic temperature gradients and the readjustment of the local strains.

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[8] F. Bloch, Zeits. f. Physik **74**, 333 (1932); R. Becker, Physik. Zeits. **33**, 905 (1932).

AUGUST 15, 1938 PHYSICAL REVIEW VOLUME 54

The Variation of the Elastic Constants of Crystalline Sodium with Temperature Between 80°K and 210°K*

S. L. Quimby and Sidney Siegel
Columbia University, New York, N. Y.

(Received June 20, 1938)

Methods are described for growing single crystals of sodium in the form of rods 4.7 mm in diameter and 10 cm long, for handling the crystals in an atmosphere of helium, and for measuring the principal elastic moduli at low temperatures. Values of the adiabatic and isothermal moduli and constants are tabulated at ten degree intervals between 80°K and 210°K. The value of the Debye characteristic temperature, calculated from the values of the elastic constants at 80°K, is 164°K.

Experimental Method for Measuring the Elastic Constants

A COMPLETE description of the dynamical method employed in this research has appeared in previous issues of this journal.[1] Accordingly, it will suffice here briefly to review its essential features, and their adaptation to the present experimental problem. The specimen is in the form of a right circular cylinder 4.7 mm in diameter and a few centimeters long. The required data are deduced from the observed behavior of a separately excited composite piezoelectric oscillator constructed by cementing to one end of the specimen a suitably cut cylinder of crystalline quartz of identical cross-section. Silver electrodes are chemically deposited in proper position on the quartz, and the oscillator is suspended vertically by delicate supports attached at the middle of the quartz cylinder. One or more harmonic frequencies of free longitudinal or torsional vibration of this system are measured by observing the variation of the electrical impedance of the composite oscillator with the frequency of the applied voltage, and

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* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.

[1] Balamuth, Phys. Rev. **45**, 715 (1934); Rose, Phys. Rev. **49**, 50 (1936); Durand, Phys. Rev. **50**, 449 (1936).

from these the fundamental frequencies, f, of free longitudinal and torsional vibration of the specimen cylinder *alone* are calculated. The latter quantities are related, respectively, to the Young's modulus, E, and the torsion modulus, G, of the specimen material for the direction of the cylinder axis by the formula

$$2fL=(M/\rho)^{\frac{1}{2}}, \tag{1}$$

where L is the length of the specimen cylinder, ρ is the density, and M the elastic modulus. It remains only to relate E and G to the principal elastic moduli and elastic constants of the crystal.

Young's modulus for an arbitrary direction in a cubic crystal is related to the principal elastic moduli by the formula[2]

$$1/E=s_{11}-2s\Gamma, \tag{2}$$

where

$$s=s_{11}-s_{12}-\tfrac{1}{2}s_{44},$$

$$\Gamma=\alpha^2\beta^2+\alpha^2\gamma^2+\beta^2\gamma^2,$$

and α, β, γ are the direction cosines with respect to the principal crystal axes.

When torsional surface tractions are applied across the end faces of a crystalline cylinder, the resultant twist is, in general, accompanied by a bend. This additional strain can be, and in static measurements usually is, prevented by additional contraints, but the relation between the torsion modulus and the principal elastic moduli is quite different according as this is or is not done. If bending is not prevented

$$1/G=s_{44}+4s\Gamma, \tag{3}$$

while if bending is prevented[3]

$$1/G=s_{44}+4s\Gamma-2s^2(\Gamma-4\Gamma^2+3\chi)/(s_{11}-2s\Gamma), \tag{4}$$

where

$$\chi=\alpha^2\beta^2\gamma^2.$$

At first it was thought that the torsional vibration of the specimen cylinder would be governed by the formula (3), and the experimental results on the first three crystals grown were not inconsistent with this view. The results of subsequent experiments, however, showed conclusively that the high frequency[4] torsional vibration of the specimen constituent of the composite oscillator is governed instead by the formula (4). The earlier error arose from the fortuitous circumstance that the cylinder axes of the three crystals lay very nearly in the (100), (110) and (111) directions, for which directions the two formulae are identical.

The elastic moduli and elastic constants are related by the formulae,

$$\begin{aligned} c_{11}&=(s_{11}+s_{12})/(s_{11}-s_{12})(s_{11}+2s_{12}),\\ c_{12}&=-s_{12}/(s_{11}-s_{12})(s_{11}+2s_{12}),\\ c_{44}&=1/s_{44}. \end{aligned} \tag{5}$$

Lastly, the compressibility, κ, is given by the formula,

$$\begin{aligned} \kappa&=3(s_{11}+2s_{12}),\\ &=3/(c_{11}+2c_{12}). \end{aligned} \tag{6}$$

The method yields immediately the adiabatic moduli and constants. These are related to the isothermal quantities by the formulae[5]

$$\begin{aligned} (s_{11})_{\text{ad.}}-(s_{11})_{\text{is.}}&=(s_{12})_{\text{ad.}}-(s_{12})_{\text{is.}}=-T\alpha^2/\rho c_p,\\ (c_{11})_{\text{ad.}}-(c_{11})_{\text{is.}}&=(c_{12})_{\text{ad.}}-(c_{12})_{\text{is.}},\\ &=T\alpha^2/(\rho c_p)(s_{11}+2s_{12})^2, \end{aligned} \tag{7}$$

where T is the absolute temperature, α is the coefficient of linear expansion, c_p is the specific heat at constant pressure, and ρ is the density. The adiabatic and isothermal s_{44} and c_{44} are the same.

To recapitulate: The essential measurements of the method are the fundamental frequencies of the specimen, its length and density, and the orientation of the cylinder axis in the crystal lattice. In addition, the specimen cylinder must be homogeneous and of uniform cross section.

Preparation of the Crystals

The crystals are grown of Mallinckrodt analytic reagent grade sodium triply distilled in vacuum, with the rejection of the first and last quarters of the distillate in the first distillation. The still is constructed of Pyrex glass. Spectroscopic analysis shows the final product to contain traces of copper, vanadium, and aluminum, together with an amount of potassium which defies quantitative chemical analysis. The second distillation leaves the sodium in an ampule, which is sealed off and placed in a Pyrex glass

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[2] Voigt, *Lehrbuch der Kristalphysik*, p. 739.

[3] Goens and Schmidt, Naturwiss. **19**, 520 (1931).

[4] The frequencies employed lie between 28 and 55 kilocycles.

[5] Voigt, reference 2, p. 789.

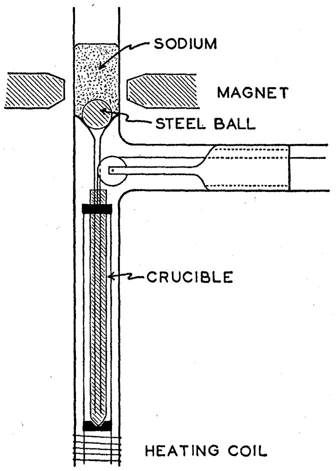

FIG. 1. Cross section of apparatus for growing the sodium crystals.

tube connected with the upper chamber of the apparatus diagrammed in Fig. 1. This apparatus is evacuated and kept at about 125°C with an enveloping furnace which has a glass front.

The ampule is broken in vacuum and the sodium distilled into the upper chamber. The bottom of this chamber is drawn out into a long tube of about 1 mm bore, which projects downward into a crucible and is closed at the top by a nickel plated steel ball. The crucible is made from a very thin walled glass tube, of the sort used for the stems of hydrometer bulbs, carefully selected for uniformity of bore.[6] The interior of the crucible is thinly coated with Socony Super Hecla mineral oil, previously boiled in vacuum in the presence of sodium. The crucible hangs in a nickel frame, suspended by a nickel chain which passes over pulleys to an iron counterweight. The position of the counterweight is controlled by a solenoid, which can be raised or lowered either manually or by a geared down electric motor.

When the distillation into the upper chamber is complete, helium at about 2 mm pressure is admitted above the molten sodium and the steel ball is raised by an electromagnet. The crucible is lowered steadily, by hand, as it fills, so that the bottom of the filling tube remains only a few millimeters below the surface of the sodium. After the crucible is filled it is lowered electrically out of the furnace, past the auxiliary heating coil shown at the bottom of the figure, at the rate of 5 cm per hour. Helium is then admitted to the lower chamber, the apparatus is opened at a ground joint level with the top of the lowered crucible, and the crucible is quickly capped with soft wax in the emerging stream of helium. The yield of good crystals, single over the entire 10 cm of length, is about one in three. The crystals appear to have no tendency to grow in any preferred orientation.[7]

LOCATION OF THE CYLINDER AXIS IN THE CRYSTAL LATTICE

The orientation of the cylinder axis with respect to the principal crystal axes is obtained by the measurement of four Laue x-ray transmission photographs. The diffraction camera has a G. E. Co. model CA 2 molybdenum x-ray tube operated at 35 kv and 20 ma. The specimen-to-film distance is 4.86 cm. Dupont film backed by a Patterson fluorazure screen is used, and the exposure time is 10 minutes.

The crystal, in the crucible, is set with its cylinder axis normal to the x-ray beam, and the pictures are taken after successive 90-degree rotations of the cylinder about its own axis. The spots are identified by comparison with the admirable set of Laue transmission photographs of a body-centered cubic lattice published by Majima.[8] The three direction cosines of each beam with respect to the crystal axes are calculated by the method of least squares from measurements of the radial distances of 8 to 12 spots from the center spot. The specimen-to-film distance used in these calculations is obtained by analysis of a picture taken through a cylinder of crystalline NaCl, in which the cylinder axis coincides accurately with a principal axis.

The four x-ray beams lie on the surface of a cone whose axis is the cylinder axis and the supplement of whose vertex angle is twice the error in setting the cylinder axis normal to the x-ray beam. If the latter were zero, the direction cosines of the cylinder axis would be those of the

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[6] The writers are indebted to the firm of Kessler and Mumberg, of New York, for permission to make this selection directly from their stock.

[7] This method may be compared with that devised independently by Andrade and Tsien, "The Glide of Single Crystals of Sodium and Potassium," Proc. Roy. Soc. **163**, 1 (1937).

[8] Majima, *Scientific Papers of the Institute of Physical and Chemical Research*, Vol. 7, p. 249.

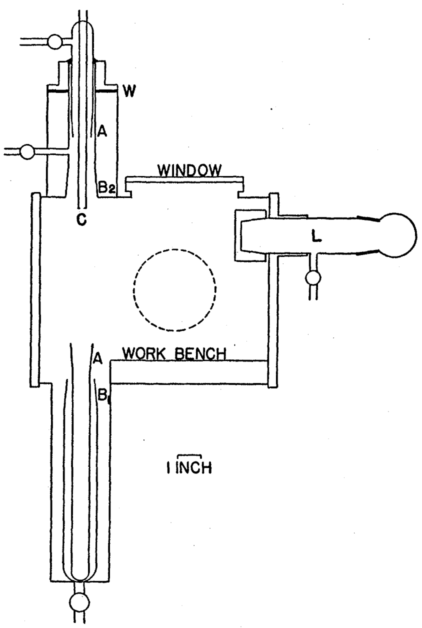

FIG. 2. Cross section of the chamber in which the crystals are handled.

vector cross product of any two mutually perpendicular x-ray beams. The values which are adopted are the arithmetic means of the four corresponding direction cosines obtained from the four possible vector cross products among the four x-ray beams.

The writers were rather surprised to discover that the orientation of the cylinder axis can be obtained in this manner with an accuracy of about five minutes of arc.

HANDLING THE CRYSTALS

After the x-ray analysis the crystal is placed in the handling chamber diagrammed in Fig. 2. The chamber, which is cylindrical in form and built of brass, is evacuated and filled with dry helium at atmospheric pressure. The crystals are handled through opposite holes in the chamber (shown by the dotted lines of Fig. 2), with the hands and arms encased in long obstetrical rubber gloves whose openings are securely clamped about the peripheries of the holes. The auxiliary chamber, *L*, is a lock which permits the introduction of crystals and tools to the chamber with a minimum expenditure of helium.

The crystal is removed from the crucible and cleaned with anhydrous ether kept standing in the presence of sodium. It is then laid in a V block and cut to the desired length with a thin strip of nickel under tension. The strip moves in a transverse slot in the V block. The quartz cylinder is prepared by coating one end with a very thin film of Empire stopcock lubricant,[9] which has been boiled in vacuum immediately before use. The quartz and specimen cylinders are laid end to end in the V block, and the join is made with the specimen held gently in place, by imparting a forward rotatory motion to the quartz.

The quartz cylinder has minute diametrically opposed transverse nicks at its center, and the composite oscillator is mounted by engaging these nicks with the jaws of a clip, shown at *C*, Fig. 2. The jaws are constructed by stretching fine wires horizontally across the forked lower termini of adjacent light vertical strips of spring metal. Two such strips are necessary for a longitudinal and four for a torsional oscillator.

The oscillator is enclosed by joining the glass tubes *AA* (Fig. 2), and the mount lock is closed by joining the glass tube B_1 to the brass tube B_2. Lastly the envelope containing the mounted oscillator is disengaged from the handling chamber at the point *W*, where it rests on a rubber washer, is removed and inserted in a dewar of boiling liquid nitrogen or liquid oxygen, or in the cryostat described in a previous paper.[10]

CALCULATION OF THE ELASTIC MODULI AND CONSTANTS

The quantities which follow immediately from the measurements made in the cryostat are the

TABLE I. *Typical data on a single sodium crystal.*

	Quartz No.	n	f	Velocity $\times 10^{-5}$ cm/sec.
L	I	5	11004	1.443
	II	3	13107	1.468
	I	3	18187	1.472
	II	2	18263	1.478
T	III	2	20237	2.267
	IV	1	27837	2.253

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[9] Empire Laboratory Supply Co., New York.

[10] Siegel and Quimby, Phys. Rev. **54**, 76 (1938). The temperature of this cryostat is measured with a copper-constantan thermocouple, calibrated by comparison with a platinum resistance thermometer certificated by the National Bureau of Standards.

frequencies of longitudinal and torsional vibration of the specimen crystal cylinder. The length of the cylinder at room temperature is measured on a comparator. The value adopted for the density of sodium at 20°C is 0.9712.[11] The lengths and densities at other temperatures are calculated from these numbers and the data on the thermal expansion of crystalline sodium previously published in this journal.[10] Corresponding values of E and G are computed with Eq. (1).

Twelve crystals in all were examined in the course of the present research. Of these, six were investigated very thoroughly at the temperature 79°K, and contributed twenty-four values of E and G at this temperature. Where possible measurements were made with two different longitudinal and two different torsional quartz cylinders, and at two or more different harmonic frequencies. A typical set of data is given in Table I. The first column designates the quartz cylinder by number, the second contains the harmonic numbers, i.e., the approximate number of half-waves of vibration in the specimen cylinder, the third the measured fundamental vibration frequency, and the last the calculated velocity of propagation, $V(=2fL)$.

TABLE II. *Observed and computed values of the longitudinal and torsional velocities in cylinders of crystal sodium at 79°K.*

	Longitudinal Velocity $\times 10^{-5}$ cm/sec.		Torsional Velocity $\times 10^{-5}$ cm/sec.	
Γ	Observed	Computed	Observed	Computed
0.0004	1.399	1.440	2.364	2.423
0.0130	1.465*	1.457	2.260*	2.342
0.1175			1.793	1.833
0.1476	1.795*	1.807	1.656*	1.680
0.1488	1.766	1.812	1.678	1.708
0.2128	2.104*	2.102	1.406*	1.389
0.2286	2.146	2.198	1.259	1.257
0.2491			1.148	1.149
0.2661	2.472	2.492	1.132	1.131
0.2907	2.780*	2.765	1.187*	1.181
0.3044	2.962	2.962	1.073	1.089
0.3145	3.206	3.137		

* Indicates the mean of several observations.

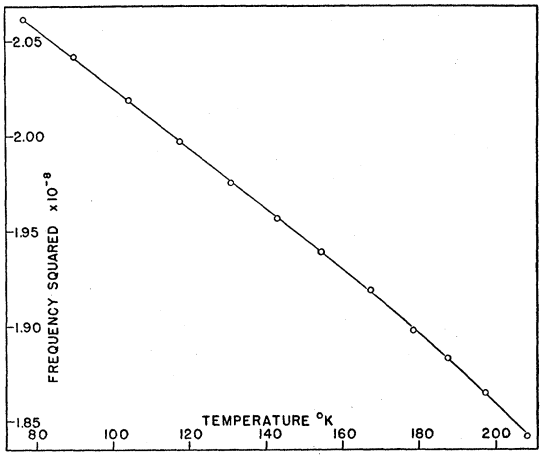

FIG. 3. The variation of f^2 with temperature for the torsional vibration of one of the crystals.

The remaining six crystals contributed ten values of E and G at 79°K,[12] and all of the data which show the variation of the elastic moduli with temperature. The number is adequate, for it is characteristic of the present experimental method that the temperature variation of the several elastic moduli can be measured with considerably greater accuracy than their absolute values. Imperfections in the specimen and other sources of error affect the former measurements less than the latter.

The adiabatic elastic moduli at 79°K were evaluated by solving thirty-four equations of the forms (2) and (4) simultaneously, by the method of least squares, for the three unknown quantities s_{11}, s_{12} and s_{44}. The concordance of the data on all twelve crystals is exhibited in Table II, in which the observed propagation velocities may be compared with those computed from the values of the elastic moduli obtained in this manner. The maximum deviation is 3.6 percent and the average deviation is 1.3 percent. It will be noted that, since the value of the orientation factor, Γ, must lie between 0 and $\frac{1}{3}$, the range of possible values is well covered by the twelve crystals.

The variation of the elastic constants with temperature is obtained as follows: The squares of the observed frequencies, f, of longitudinal and torsional vibration are plotted as functions of the temperature. The observations on the six crystals are thus represented by ten curves, of which that shown in Fig. 3 is typical. Values of f^2 at ten different temperatures between 80°K and 210°K

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[11] Richards and Brink, J. Am. Chem. Soc. **29**, 117 (1907).

[12] Instead of twelve. The occurrence of a parasitic mode of vibration, feebly excited, vitiated the torsional measurements on one of these crystals, and another was, after the removal of a flaw, too short to permit reliable measurement of E. One of the first six crystals was dropped before E was measured.

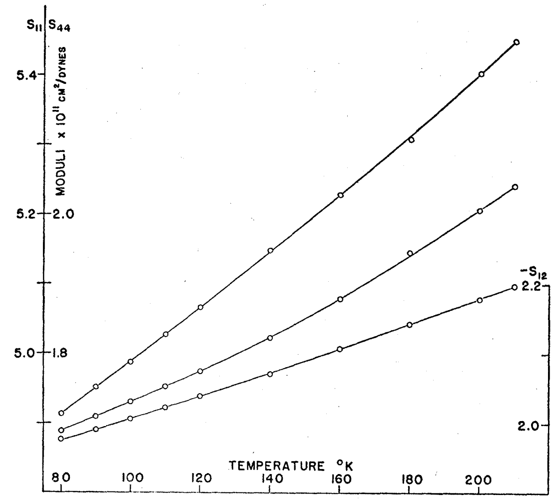

FIG. 4. The variation of the adiabatic elastic moduli of sodium with temperature.

are read from each curve, and corresponding values of E and G are calculated with Eq. (1). These data yield ten sets of ten equations of the forms (2) and (4), each set corresponding to a single temperature. Each set of equations is solved simultaneously, by the method of least squares, for s_{11}, s_{12} and s_{44}. The result of this computation is shown by the curves of Fig. 4.

The absolute values of the elastic moduli at 79°K read from the curves of Fig. 4 differ slightly from those previously computed, since the former are based on ten observations and the latter on thirty-four. Thus the values of s_{11}, $-s_{12}$ and s_{44} at 80°K deduced from all observations are, in units of 10^{-11} cm²/dyne, 4.83, 2.09 and 1.69, respectively, while those deduced from the ten observations alone are 4.91, 1.98 and 1.69. However, these curves are used simply to determine the *ratios* of the values of the moduli at T°K to the values at 79°K. The values hereinafter recorded for the elastic moduli at T°K are obtained by applying the ratios obtained from the curves of Fig. 4 to the values at 79°K deduced from the thirty-four observations at 79°K in the manner previously described. The concordance of the data from which the ratios are evaluated is exhibited in Table III, in which the observed ratios of the velocities at 80°K to those at 210°K for the six crystals may be compared with the ratios computed with the values of the elastic moduli at 80°K and 210°K, thus obtained. The results confirm the remark made above, that the present method yields a more accurate determination of the temperature variation of the elastic moduli than of their absolute values. The maximum deviation in Table III is 1.5 percent and the average deviation is 0.4 percent.

The isothermal moduli and constants are computed from the adiabatic quantities with Eqs. (7), in which, since the difference is small, the values $\rho=1.0$, $c_p=1.1\times10^7$ and $\alpha=6.0\times10^{-5}$ are substituted.

TABLE III. *The observed and computed ratios of the longitudinal and torsional velocities at 80°K to those at 210°K for six crystals.*

LONGITUDINAL		TORSIONAL	
OBSERVED	COMPUTED	OBSERVED	COMPUTED
1.073	1.065	1.060	1.060
1.052	1.053	1.086	1.101
1.072	1.075		
1.061	1.061	1.060	1.064
		1.061	1.059
1.070	1.071	1.086	1.078

RESULTS

The elastic moduli and constants

The adiabatic and isothermal elastic moduli and constants, and the isothermal compressibility, are given as functions of the temperature in Tables IV and V. The estimated uncertainty in the absolute values of s_{11} and s_{44} is about 2 percent and of s_{12} about 3 percent. The precision with which the tabulated values are given is significant only for the calculation of the temperature variation.

Fuchs[13] has given a quantum-theoretical calculation of the quantities $(c_{11}-c_{12})$ and c_{44} for sodium at 0°K, which yields the values 0.141 and 0.58, respectively, in units of 10^{11} dynes/cm². The corresponding experimental values at 80°K are 0.145 and 0.59.

The compressibility

The accuracy of the present measurement of the compressibility is very poor. A significant figure is lost in the evaluation of the difference

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[13] Fuchs, Proc. Roy. Soc. **157**, 444 (1937).

quantity $(s_{11}+2s_{12})$, and the uncertainty in s_{12} is doubled. Thus a change of one percent in the assumed values of s_{11} and s_{12} will, if the errors are additive, change the calculated value of κ from 1.98×10^{-11} to 1.70×10^{-11}. The writers have little doubt that the values given in Table V are high.

Bridgman[14] has measured the variation of the compressibility of polycrystalline sodium with pressure between 2000 and 20,000 kg/cm^2. As the pressure is lowered the compressibility increases toward the (extrapolated) value 1.7×10^{-11} cm^2/dyne at zero pressure and room temperature. If the linear variation of compressibility with temperature here found to hold between 80°K and 210°K be assumed to hold over the entire range from 0°K to 293°K, then Bridgman's value reduces at absolute zero to 1.2×10^{-11}, and the value here found to 1.8×10^{-11}. A quantum-theoretical calculation of the compressibility at 0°K[15] gives $\kappa=1.6\times10^{-11}$.

TABLE IV. *The adiabatic elastic moduli and elastic constants of sodium. The number of significant figures does not indicate the accuracy of the absolute value.*

	ADIABATIC MODULI $\times10^{11}$ cm^2/dyne			ADIABATIC CONSTANTS $\times10^{-11}$ dyne/cm^2		
T°K	s_{11}	$-s_{12}$	s_{44}	c_{11}	c_{12}	c_{44}
80	4.826	2.087	1.685	0.608	0.463	0.593
90	4.861	2.102	1.705	0.603	0.459	0.586
100	4.898	2.118	1.726	0.598	0.456	0.579
110	4.937	2.134	1.747	0.593	0.451	0.572
120	4.975	2.151	1.770	0.589	0.448	0.565
130	5.014	2.168	1.793	0.585	0.445	0.558
140	5.054	2.186	1.818	0.581	0.443	0.550
150	5.094	2.205	1.846	0.579	0.442	0.542
160	5.135	2.224	1.874	0.576	0.440	0.534
170	5.177	2.243	1.904	0.572	0.437	0.525
180	5.220	2.262	1.936	0.568	0.434	0.516
190	5.263	2.281	1.968	0.564	0.431	0.508
200	5.308	2.301	2.002	0.560	0.428	0.499
210	5.354	2.321	2.037	0.555	0.425	0.491

The Debye characteristic temperature

A calculation of the Debye characteristic temperature from the elastic constants requires the evaluation of the reciprocal cubes of each of three propagation velocities, averaged over a unit sphere in the crystal.[16] The latter problem can only be solved by approximate methods, whose difficulty increases enormously when the anisotropy of the crystal is large.[13] In the present instance the averages are calculated by simply evaluating the velocities at 386 points on the sphere and taking the arithmetic means. The result at 0.80°K is, $\Theta_{80}=164$°K. The value obtained from specific heat data is $\Theta=159$°K.[17]

TABLE V. *The isothermal elastic moduli, constants, and compressibility of sodium.*

	ISOTHERMAL MODULI $\times10^{11}$ cm^2/dyne		ISOTHERMAL CONSTANTS $\times10^{-11}$ dyne/cm^2		ISOTHERMAL COMPRESSIBILITY
T°K	s_{11}	$-s_{12}$	c_{11}	c_{12}	κ $\times10^{11}$
80	4.829	2.084	0.601	0.456	1.98
90	4.864	2.099	0.597	0.453	2.00
100	4.901	2.115	0.592	0.449	2.01
110	4.939	2.131	0.586	0.445	2.03
120	4.977	2.147	0.581	0.441	2.05
130	5.018	2.164	0.575	0.436	2.07
140	5.058	2.181	0.571	0.432	2.09
150	5.099	2.199	0.567	0.430	2.10
160	5.140	2.218	0.564	0.428	2.11
170	5.183	2.237	0.560	0.425	2.13
180	5.226	2.256	0.556	0.422	2.14
190	5.269	2.275	0.552	0.419	2.16
200	5.315	2.294	0.546	0.415	2.18
210	5.361	2.313	0.541	0.410	2.20

In conclusion, the writers gratefully acknowledge their indebtedness to Dr. Don Kirkham and Dr. Seymour Rosin for their help in the design and construction of the diffraction camera and handling chamber, and to the Ernest Kempton Adams Fellowship Committee of Columbia University for the financial assistance which made this research possible.

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[14] Bridgman, Proc. Am. Acad. Arts and Sci. **70**, 94 (1935).

[15] Mott and Jones, *The Theory of the Properties of Metals and Alloys*, p. 143.

[16] Reference 15, p. 3.

[17] Simon and Zeidler, Zeits. f. physik. Chemie **123**, 403 (1926).