Variation of the Elastic Constants of Sodium with Temperature and Pressure*

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The variation with temperature and pressure of the velocities of 10-MHz elastic waves propagating in monocrystalline bcc sodium was measured by the phase-comparison technique. At atmospheric pressure, the elastic constants C_{11}, $C' = \frac{1}{2}(C_{11} - C_{12})$, and C_{44} appear to decrease linearly with temperature between 150 and 299°K, while their second temperature derivatives are all negative between 78 and 150°K. At $P = 0$ and $T = 195$°K, the following values of the adiabatic elastic constants were obtained: $C_{11} = 81.3$ kbar, $C' = 6.65$ kbar, $C_{44} = 51.0$ kbar. At $T = 78$°K, 195°K, 273°K, and 299°K, the first two pressure derivatives of the effective elastic constants C_{11}, C', and C_{44} were computed by Cook's method from measurements of the pressure dependence of the transit times extending up to 9 kbar. The pressure derivatives $dC_{11}/dp = 4.17 \pm 0.20$ and $dC'/dp = 0.258 \pm 0.015$ are independent of temperature for 78°K$\leq T \leq 299$°K, while dC_{44}/dp equals 1.74 ± 0.08 for 195°K$\leq T \leq 299$°K, decreasing to 1.17 ± 0.07 at 78°K. The following bounds on the second pressure derivatives of all the elastic constants were established: $-5 \times 10^{-4} \leq C^{-1} d^2 C/dp^2 \leq -2 \times 10^{-4}$ kbar^{-2}. To within experiment alerror, the fractional pressure derivatives of the adiabatic elastic constants decrease linearly with temperature in such a way that at 273°K, $C_{11}^{-1} dC_{11}/dp = 0.054$ kbar^{-1}, $C'^{-1} dC'/dp = 0.042$ kbar^{-1}, and $C_{44}^{-1} dC_{44}/dp = 0.039$ kbar^{-1}, while at 78°K these quantities are equal to 0.049, 0.037, and 0.025 kbar^{-1}, rspectively. Although the absolute values of the isothermal elastic constants $B_T = \frac{1}{3}(C_{11} + 2C_{12})$, C', and C_{44} as well as dB_T/dp and dC_{44}/dp at $T = 78$°K are in good agreement with simple theory, dC'/dp is much larger than expected.

INTRODUCTION

SOME landmarks in the theory of the elastic properties of bcc sodium are the papers by Fuchs[1-3] and by Fuchs and Peng[4] treating the shear elastic constants and the bulk modulus, and Bardeen's 1938 calculation[5,6] of the variation of the compressibility with pressure. The early work represents further development of the Wigner-Seitz theory of metallic cohesion. More recently, refined calculations by Brooks et al.,[7,8] in which the cellular method was also employed, have yielded good agreement with experiment for the cohesive energy, the equilibrium atomic volume, and the P-V relation.

Aspects of the elastic properties of sodium have often been studied in connection with lattice-dynamics investigations and many-body theory. This work will not be reviewed here since no attempt is made in this paper to interpret the experimental results quantitatively in terms of the propagation of phonons.

Fuchs's treatment of the shear elastic constants and bulk moduli of static alkali metal lattices included energy terms arising from short-range (SR) forces due to ion core exchange and polarization phenomena as contributions to the cohesive energy. The resulting SR contributions to the ordinary second-order elastic constants turn out to be small when the magnitude of the SR forces are estimated from ionic-crystal data, as was done by Fuchs. But, because the SR forces presumably vary rapidly with distance, one expects direct ion-ion interaction effects to become important in connection with phase transitions, the P-V relation at very high pressure, and the structure of lattice defects.

Experimental evidence which appeared to be relatively directly related to the size of the SR interaction in metallic sodium was published by Daniels in 1960.[9] Interpreting his room-temperature measurements of the change of the elastic anisotropy with pressure in the framework of Fuchs's theory, Daniels concluded that the SR interaction in metallic sodium was negligibly small. The ratio of the electron number density in the outer part of the Wigner-Seitz cell to the free-electron value (Z_{eff}) was then required to be a sufficiently rapid function of atomic volume (V) to fit the observed pressure derivatives of the shear elastic constants. Both Daniels[9] and Brooks[8] have remarked that the resulting value of $|dZ_{eff}/dV|$ is larger than that expected on the basis of existing band calculations.

In general, the experimental situation so far as the elastic properties of monocrystalline sodium were concerned, seemed at the beginning of this investigation to need clarification since fairly large inconsistencies existed between static measurements of the bulk modulus and dynamic values of the single-crystal elastic constants at low temperatures. Estimates of the pressure derivative of the bulk modulus at room temperature were also in disagreement. As a consequence of recently published ultrasonic measurements of the temperature

[1] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).
[2] K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936).
[3] K. Fuchs, Proc. Roy. Soc. (London) **A157**, 444 (1936).
[4] K. Fuchs and H. W. Peng, Proc. Roy. Soc. (London) **A180**, 451 (1942).
[5] J. Bardeen, J. Chem. Phys. **6**, 367 (1998).
[6] J. Bardeen, J. Chem. Phys. **6**, 372 (1938).
[7] H. Brooks, Nuovo Cimento Suppl. **7**, 165 (1958).
[8] H. Brooks, Trans. AIME **227**, 546 (1963).
[9] W. B. Daniels, Phys. Rev. **119**, 1246 (1960).

variation of the elastic constants below 195°K,[10] and the revision of earlier P-V-T data,[11] the compatibility of elastic-constants data obtained by different experimental methods is now much better than was the case three years ago.

However, the theoretical problems associated with the size of the SR interaction in sodium and the large apparent change of the electronic band structure with pressure implied by Daniels's results have not yet been resolved, nor will they be fully resolved here. The primary purpose of this paper is to present experimental evidence for the proposition that the effects of temperature on the fractional pressure derivatives of the elastic constants $(1/C)dC/dp$ are large in bcc sodium. Measurements of the first two pressure derivatives of three independent combinations of the adiabatic elastic constants are reported. Data were taken at 78, 195, 273, and 299°K. These data are compared with theories of the elastic properties of a static bcc sodium lattice.

Unfortunately, it appears that very little can be concluded firmly regarding the details of the SR interactions in metallic sodium by interpreting measurements of the pressure derivatives of the shear elastic constants made above 78°K in the framework of Fuchs's theory. The strongly anharmonic behavior of some of the lattice-vibration modes is thought to be the main cause of the difficulty. This anharmonicity appears to cause effects which cannot be corrected on the basis of the quasiharmonic approximation.

EXPERIMENTAL PROCEDURE

A. Specimen Preparation

The preparation of good ultrasonic samples of monocrystalline sodium is not easy. For instance, because of the large elastic anisotropy of this material, the crystallographic orientation of the ultrasonically active faces must be controlled relatively precisely if good values of the elastic constants are to be obtained. Since a detailed account of the criteria, which must be met if accurate elastic-wave velocity measurements are desired, is available, along with a description of constraints placed on the experimenter by the reactivity of sodium metal,[12] the following description of the specimen preparation procedures is an outline only.

Single-crystal sodium boules approximately 15 × 2.5 × 3.5 cm in size were grown in a glovebox containing purified helium gas. The starting material used was Mallinckrodt lump sodium of approximately 99.5% purity. The Mallinckrodt sodium was not analyzed chemically. The estimate of purity is based on values quoted in Ref. 13 as being typical of electrolytically

produced sodium metal. The crystals were grown at a controlled rate of 2 cm/hr in a horizontal stainless-steel mold, one end of which was cooled by a nitrogen gas stream.

Rectangular parallelepipeds with faces of the form {110}, {100} were cut from the boules with a string saw after preliminary x-ray studies of each boule had established its approximate orientation. Specimens were taken only from the middle of each boule; the front and rear 2 to 3 cm were discarded because they were likely to be more impure. Precision orientation of the specimens by a diffractometer technique was carried out with the aid of a special two-circle x-ray goniometer, which allowed the preservation of accurate alignment during the final specimen preparation steps. These steps consisted of facing the specimens with a modified American Optical model 820 microtome. Special care was taken to limit the depth of cut to 5μ or less during the final stages of this machining operation which was carried out in a purified helium atmosphere. The acoustic path length was measured with the aid of a Van Keuren "light wave" micrometer having a least count of 10 μin.

Circular X- and Y-cut "doughnut plated" quartz ultrasonic transducers were bonded to the specimens with either U.S.P. mineral oil or General Electric 60 000 centistoke Vicasil which had been heated in the presence of fresh sodium chips for a few hours. The mineral oil bonds were used for experiments from 299 to 195°K, while the Viscasil bonds proved satisfactory down to 77°K.

The end products of these preparation steps were monocrystalline sodium ultrasonic specimens in the form of parallelenineds approximately 1.5 cm on a side, two faces of which were flat and parallel to approximately 0.0005 cm, and coincident with either (100) or (110) planes to 0.1°. The length of the acoustic path was known to 0.001 cm, and the direction of particle motion of the shear-mode transducers coincided with either the [110] or [100] directions to about 3°.

B. Ultrasonic Technique

The elastic-wave velocities were measured by "phase comparison" technique of Williams and Lamb[14,15] except that in the present experiments the same transducer was used both for generating and detecting the elastic waves. For experiments such as the present ones, the phase comparison technique is superior to direct timing methods because of the increased sensitivity available and because the effect of the transducer on the measured time can be corrected.[14]

In the version of the phase comparison technique used for the present experiments, two bursts of phase-coherent 10-MHz rf power are applied to a piezoelectric

[10] M. E. Diederich and J. Trivisonno, J. Phys. Chem. Solids 27, 637 (1966).
[11] C. E. Monfort, III and C. A. Swenson, J. Phys. Chem. Solids 26, 219 (1965).
[12] R. H. Martinson, Ph.D. thesis, Cornell University, 1966 (unpublished).
[13] M. Sittig, Sodium, Its Manufacture, Properties and Uses (Reinhold Publishing Co., New York, 1956).

[14] J. Williams and J. Lamb, J. Acoust. Soc. Am. 30, 308 (1958).
[15] A. Colvin, M.Sc. thesis, Rensselaer Polytechnic Institute, 1962 (unpublished).
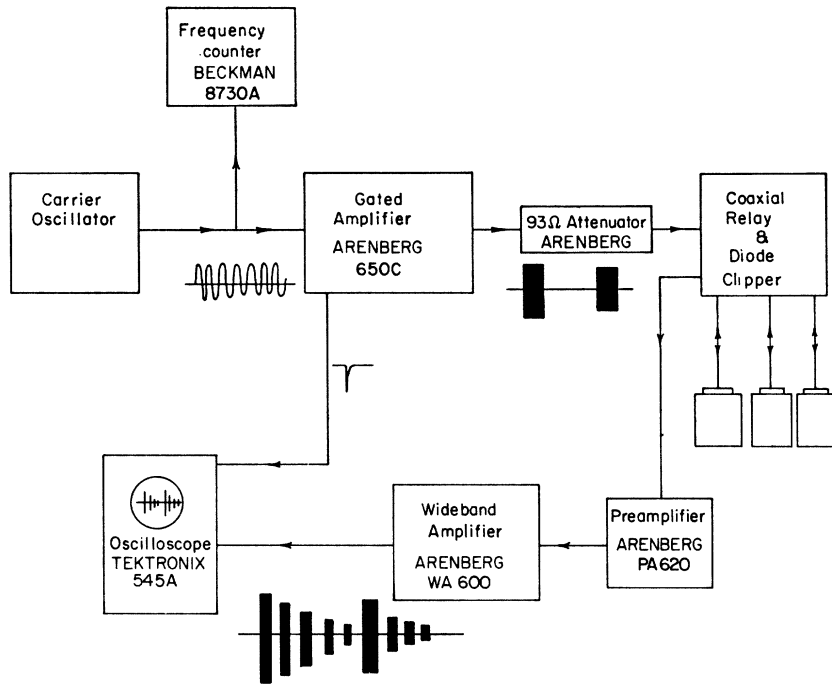
FIG. 1. The ultrasonic system.

transducer bonded to the specimen. The pulses are separated by a variable delay time. Each of these pulses generates its own train of echoes. The two echo

FIG. 2. The pressure vessel and specimen jig.

trains may be brought into time coincidence on an oscilloscope screen by varying the delay time between the exciting pulses, such that the $(n+1)$st echo of the first pulse overlaps the nth echo of the second pulse. If the carrier frequency is now varied, and if the relative amplitudes of the drive pulses are correctly adjusted, complete destructive interference of the echo trains may be obtained. It is shown in Ref. 15 that the transit time is most reliably obtained from measurements of a sequence of null frequencies which bracket the main resonance frequency of the transducer. During measurements of the temperature and pressure variation of the elastic constants, the frequencies of four nulls were followed, and the transit time ratios were computed from means of the null frequencies. No corrections were applied for excess shifts caused by the finite thickness of the acoustic bonds. McSkimin[16] has shown that changes in the acoustic properties of the bond between the transducer and the specimen caused by varying the temperature and pressure may safely be neglected if the bond is sufficiently thin.

The details of the data gathering procedure are described fully in Ref. 12. It is believed that the measured carrier frequencies were converted to transit time *ratios* in a way that is compatible with the sensitivity of the phase comparison technique used—roughly 1 part in 10^6 at 10 MHz. Thus, most of the random scatter in the experimental results is likely to have been caused by uncontrolled fluctuations in the variables P and T.

A block diagram of the ultrasonic system is shown in Fig. 1. An Arenberg 650C pulsed oscillator was con-
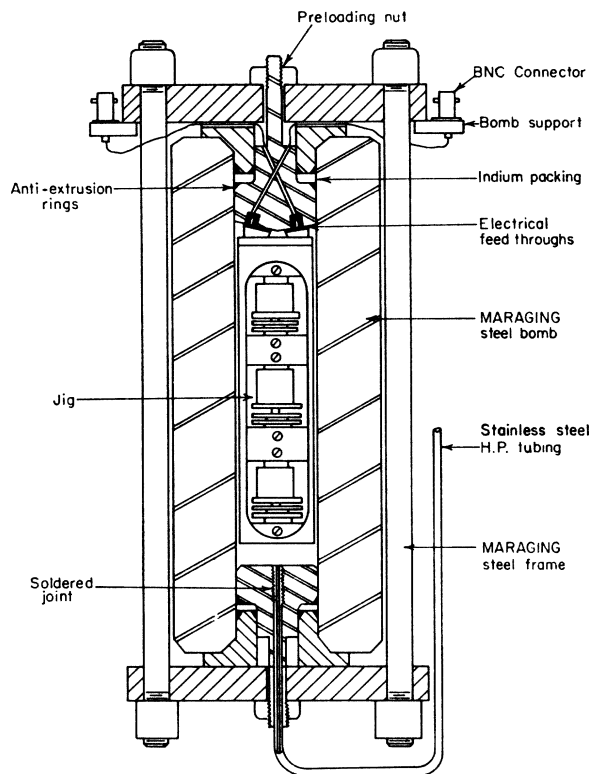
[16] H. J. McSkimin, J. Acoust. Soc. Am. **34**, 609 (1962).

TABLE I. Magnitude of the elastic constants of sodium at 194.7°K, in kilobars (1 kbar = 10^9 dyn/cm²).

Elastic constant	Magnitude (kbar)	Specimen length at 299°K (cm)
C_{11}	81.16	1.8445
	81.30	1.2347
	81.32	1.2405
	mean 81.26	
C_{44}	50.85	1.7259
	51.20	1.2959
	mean 51.02	
$\frac{1}{2}(C_{11}-C_{12})$	6.63	1.2899
	6.64	1.7921
	mean 6.64	

verted by the manufacturer to a gated amplifier capable of providing the phase-coherent variable amplitude rf pulses required. The carrier oscillator consists of a frequency stabilized Signal Corps BC 221 frequency meter and a home made frequency quadrupler. The other instruments are standard commerical items.

C. Pressure System

A gas pressure bench capable of generating up to 15 kbar of gas pressure in a volume of a few cubic centimeters was used in this investigation. This apparatus closely resembles a design which has been described in the literature.[17]

A cross section of the vessel used in the high-pressure experiments is shown in Fig. 2. It is a conventional one-piece design, made entirely of Vacomax 300 vacuum cast maraging steel. The gas inlet tubing is threaded and silver soldered into the lower end plug, while three electrical leads are led out through the upper plug. The end plugs incorporate armoured Bridgman seals with indium packings. It was necessary to develop a special electrical lead to seal the helium gas pressure transmit-

TABLE II. Interpolated values of the adiabatic elastic constants of sodium between 80 and 300°K.

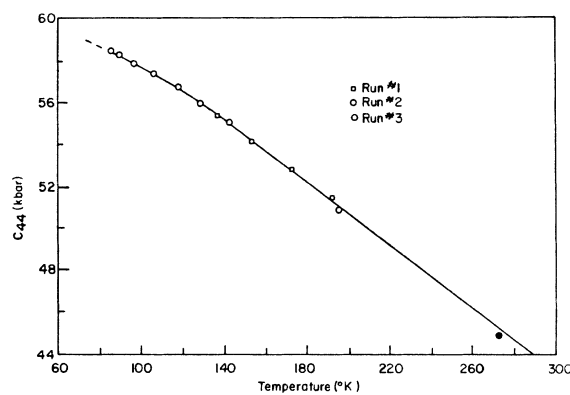| Temperature (°K)	C_{11} (kbar)	C_{44} (kbar)	$\frac{1}{2}(C_{11}-C_{12})$ (kbar)
80	85.7	58.7	7.28
100	85.1	57.7	7.19
120	84.7	56.5	7.09
140	83.2	55.1	6.98
160	82.7	53.7	6.87
180	81.8	52.2	6.76
200	81.1	50.7	6.65
220	80.2	49.2	6.54
240	79.4	47.7	6.45
260	78.6	46.2	6.33
280	77.7	44.6	6.22
300	76.9	43.1	6.11

[17] D. Langer and D. M. Warshauer, Rev. Sci. Instr. 32, 32 (1961).
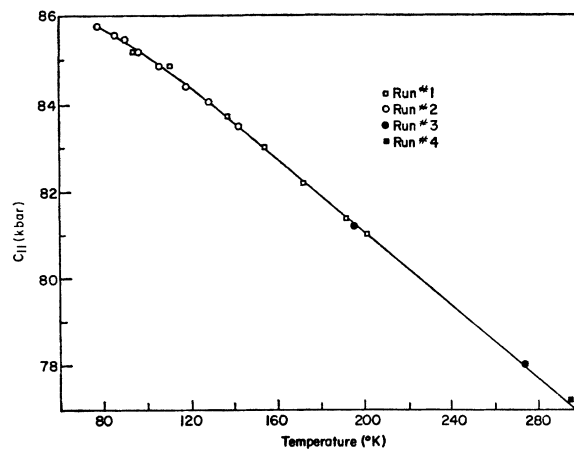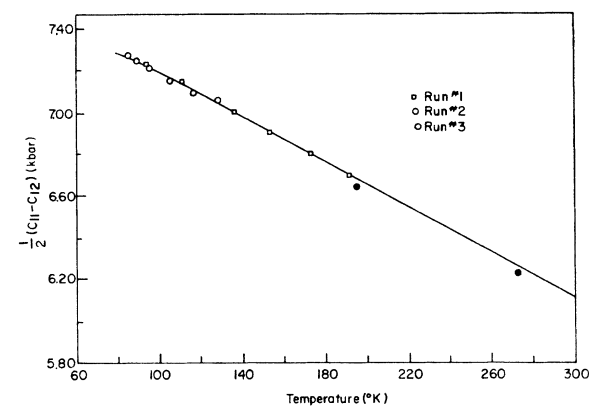
FIG. 3. (a) Temperature dependence of C_{11}; (b) temperature dependence of C_{44}; (c) temperature dependence of C'.

ting medium at low temperature. This seal is described elsewhere.[18]

The pressure was measured with a manganin pressure gauge by the conventional ratio method, using a Guildline six-place potentiometer. The gauge wire was

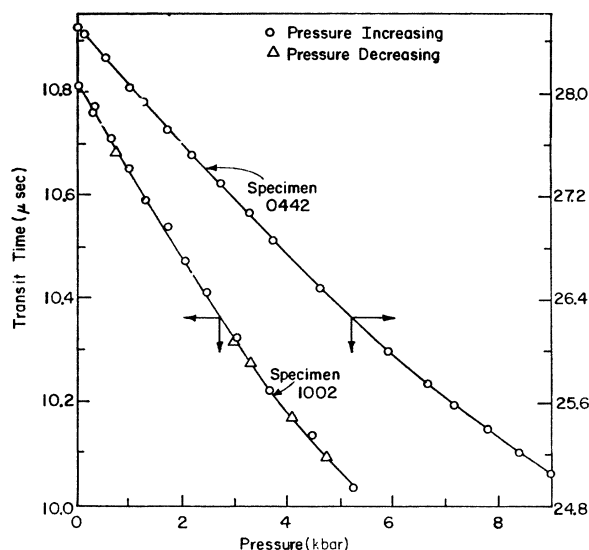[18] R. H. Martinson and R. E. Terry, Rev. Sci. Instr. 38, 1330 (1967).

Fig. 4. Typical transit-time variations with pressure.

calibrated against the freezing point of mercury at 0°C (7565 bars).

The temperature of the pressure vessel was controlled by immersing it in suitable temperature baths. Below room temperature, ice water, solid CO_2, and liquid-nitrogen baths were found to be convenient for this purpose.

During measurements of the temperature dependence of the elastic constants at one atmosphere, the temperature of the specimens was controlled by manually regulating the electrical power delivered to a copper "temperature bomb" which was in loose thermal contact with a liquid-nitrogen bath. The temperature was monitored with two calibrated copper-constantan thermocouples. Data were recorded only at times when the temperature gradient over the 6-cm-long jig supporting the samples was less than 1°C.

EXPERIMENTAL RESULTS

A. Temperature Dependence of the Elastic Constants

To check the reliability of the transmission line theory of the phase comparison method,[14] wave propagation velocities were measured at 194.7°K for two sets of crystals, one of which was approximately 40% longer than the other. The good consistency of the results which are shown in Table I indicates that transducer effects are described quite well by the transmission line theory.

In order to obtain elastic constants from measurements of wave velocities according to the equation $C = \rho v^2$, it is necessary to know the density of the material. I have used the value 0.9725 g/cm³ at 273°K as the reference density[13] and the thermal-expansion data of Quimby and Siegel[12] to correct for the temperature variation of the density.

TABLE III. Some values of the adiabatic elastic constants of sodium in kbar (1 kbar = 10^9 dyn/cm²).

	T = 195°K				T = 299°K			
	a	b	c	d	a	e	f	g
C_{11}	81.3	76.6			76.9		73.8	
C'	6.64	6.30	6.63		6.11		5.85	
C_{44}	51.0	50.0	50.4		43.4		41.9	
B_s	72.5	68.2		71.9	68.8	67.6	66.1	66.5

ᵃ This work.
ᵇ Reference 10.
ᵉ Reference 20.
ᵈ Computed from Table II, Ref. 21, with pressures increased 3% and using $B_s/B_t = 1.0362$.
ᵉ Reference 11.
ᶠ Reference 9.
ᵍ Computed by Daniels (Ref. 9) from measurements made by Bridgman (1935).

The final results of the temperature dependence experiments are shown in Fig. 3 and Table II. These results have been computed from transit time ratios, using absolute wave-velocity measurements at the dry-ice point (194.7°K) as the reference.

In Table III the mean values of the elastic constants at the dry-ice point and at room temperature obtained in this investigation are compared against those proposed by some other workers. Additional data may be found in Ref. 10 and in the other original papers. The degree of over-all agreement between the entries in Table III is somewhat disappointing in view of the care with which all the experiments appear to have been done. No doubt the discrepancies between the recent ultrasonic values reflect the difficulties of doing accurate wave-velocity measurements on a soft, reactive, and highly anisotropic material. It is not obvious which of the sets, (a) or (b), is the more reliable, but because the estimates of the shear elastic constants obtained in the present work agree well with the results of Quimby and Siegel,[20] and since the adiabatic bulk-modulus values seem to be in good agreement with the revised data of Beecroft and Swenson,[11,21] I have used the most recent values of the adiabatic elastic constants [set (a)] in subsequent calculations. This choice does

TABLE IV. Values of the first temperature derivatives of the adiabatic elastic constants of sodium, in kbar (°K)⁻¹.

	a	b	c
$\dfrac{dC_{11}}{dT}$	−0.041	−0.044	−0.040
$\dfrac{dC'}{dT}$	−0.075	−0.071	−0.084
$\dfrac{dC_{44}}{dT}$	−0.0054	−0.0047	−0.0050

ᵃ This work, T > 150°K.
ᵇ Computed from Ref. 10.
ᵉ Computed from Ref. 20.

²⁰ S. Quimby and S. L. Siegel, Phys. Rev. 54, 293 (1938).
²¹ R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 18, 329 (1961).

not materially affect the conclusions reached in this paper.

Three sets of values for the temperature derivatives of three independent elastic constants of sodium are compared in Table IV. Since the experimental methods used in all of these investigations should yield more accurate values for the temperature derivatives of the elastic constants than for their absolute values, the discrepancies in Table IV may reflect real differences in the purity and the state of perfection of the ultrasonic specimens. It seems worthwhile to point out that according to the plots in Ref. 10, the temperature variation of the elastic constants appear to be linear between 78 and 195°K, whereas in the present work a decrease of the first temperature derivative was already detected at about 150°K, where marked nonlinearities in the temperature variation of the thermal expansion coefficient also appear.

B. Pressure Dependence of the Elastic Constants

A plot typical of the observed variation of transit time with pressure is shown in Fig. 4. Since it was intended to study the nonlinearities of the pressure dependence of the transit times in this investigation, the pressure was usually increased until the bond between the specimens and the transducers failed. This occurred quite suddenly in most of the experiments. Thus, it was not always possible to check whether permanent changes of the elastic constants had been caused by the application of the hydrostatic pressure. Accordingly, three experiments were done at 273°K during which the maximum pressure reached was limited to about 5 kbar in order to study this question. Figure 4 also shows the results of one such experiment. One notes that an irreversible change has indeed occurred during the experiment, but that the amount of irreversibility is small compared to the pressure effects. The sign of the irreversible change is consistent with the hypothesis that the specimens were oxidized slightly during the pressure runs by impurities in the helium gas. The initial transit time was recovered to better than 0.2% during these experiments, while the magnitude of the pressure effect on the transit time was approximately 10%. The initial slopes of the graphs of pressure versus transit time may then be in error systematically by about 2% because of oxidation problems.

In pressure experiments like the present ones, a considerable amount of data reduction is required to convert the observed null frequencies to theoretically significant quantities. Since the data reduction problem is not completely straightforward, it will be described in some detail here.

From the measured sequence of four null frequencies at each pressure, mean transit time ratios were hand computed for each specimen. Two kinds of quadratic

polynomials in p, the pressure, were then fitted to the raw data by a least-squares multiple-regression algorithm (MUREG, Cornell University Computing Center). The polynomials were of the following kinds:

$$\text{PA:} \left[\frac{\tau(0)}{\tau(p)}\right]^2 = 1 + a_1 p + a_2 p^2,$$

$$\text{PB:} \frac{\tau(p)}{\tau(0)} = 1 + b_1 p + b_2 p^2.$$

Here $\tau(p)$ is the signal transit time at the pressure p. It is easy to show that the following relations between the coefficients should hold if the data are equally well represented by either PB or PA:

$$a_1 = -2b_1,$$

$$a_2 = 3b_1{}^2 - 2b_2.$$

It was found that on the average the first of these relations was satisfied by the data to about 2% and the second to about 50%. The differences are systematic in sign, and are such that

$$|2b_1| < |a_1|,$$

$$|3b_1{}^2 - 2b_2| < |a_2|.$$

The quantity $1 - r^2$, where r is the multiple correlation coefficient, was found to be about 50% smaller for PA than for PB, and the number of subsequences of equal sign in the ordered sequence of differences between measured and fitted values was approximately 30% greater for PA-type fits. However, the percentage standard errors of estimate of the coefficients in PA tend to be larger than those in PB, negligibly so for the first-order coefficients, but by factors of up to 6 for the quadratic coefficients. Thus, it is not clear which representation of the raw data is the better. Since the results of PB-type fits are available in Ref. 12, and since PA-type fits appear to be more suitable for estimates of the second-order pressure derivatives of the elastic constants, the results of a polynomial representation of type PA will be presented here. The small systematic differences between the first-order pressure coefficients mentioned above do not materially affect the theoretical implications of this paper.

The results of the multiple-regression analysis are summarized in Table V. The mean first-order coefficients a_1 vary systematically with temperature as is shown in Fig. 5. The error bars in Fig. 5 represent ±4%, which seems to be a reasonable uniform bound on the errors. An examination of Table V shows that the data are uneven in quality and that substantially different maximum pressures were attained during the experiments. As a consequence, the uncertainty of the second-order pressure coefficients varies between wide limits. The starred values of a_2 are those which have been used in subsequent calculations.

TABLE V. Results of multiple-regression analysis.

Elastic constant	Run number	No. of observations	Maximum pressure (kbar)	a_1 (10^{-2} kbar^{-1})	$-a_2$ (10^{-4} kbar^{-2})	S.E.a_1[a] (%)	S.E.a_2[a] (%)	$10^4(1-r^2)$[b]	
$\frac{1}{2}[C_{11}+C_{12}+2C_{44}]$	R011	12	7.0	4.85	4.8[c]	2.1	31	2.5	$T=299°$K
C_{11}	R111	14	4.0	4.85	1.9	2.6	150	4.3	
C_{11}	0111	17	8.3	4.82	1.6	1.8	63	1.7	
	0112	18	5.3	4.78	2.7[c]	0.8	28	0.8	
	mean			4.80	2.7	1.4	28		
C_{44}	0442	15	5.3	3.42	5.3[c]	3.3	40	10.7	
	0443	16	5.3	3.24	3.0[c]	2.5	30	4.0	$T=273°$K
	mean			3.33	4.2	2.9	35		
C'	0001	15	8.3	3.67	4.2[c]	1.5	16	1.2	
	0002	17	8.3	3.61	3.8[c]	0.8	9	0.8	
	mean			3.64	4.0	1.2	13		
C_{11}	C112	18	9.0	4.84	5.4	0.8	8	0.4	
C_{44}	C441	8	3.3	3.08	9.5	4.8	450	5.6	$T=195°$K
	C442	16	7.8	2.90	4.0[c]	1.1	10	0.7	
	mean			2.99	4.0	3.5	10		
C'	C001	12	6.5	3.42	2.7	3.0	38	1.4	
	C002	17	9.0	3.58	3.0[c]	1.7	22	1.0	
	mean			3.50	2.9	2.4	30		
C_{11}	N111	8	3.1	4.31	4.3	0.8	460	0.2	
	N112	10	4.3	4.37	1.6	2.2	134	3.4	
	N113	13	4.0	4.29	3.0[c]	2.2	76	3.5	
	mean			4.33	3.0	1.8	76		
C_{44}	N441	13	6.6	1.97	2.5[c]	1.7	14	1.2	
	N443	11	4.0	2.00	3.0[c]	2.5	50	2.7	$T=78°$K
	mean			1.99	2.1	2.1	22		
C'	N001	13	6.6	3.26	3.3[c]	0.7	7	0.4	
	N002	9	3.8	3.20	2.7[c]	2.0	57	2.7	
	N003	13	4.0	3.20	2.9[c]	1.9	50	2.7	
	mean			3.22	2.9	1.6	44		

[a] S.E. is standard error (deviation).   [b] r is correlation coefficient.   [c] These are the values of a_2 which are used in subsequent calculations.

For comparison, two data points from Ref. 9 have been included in Fig. 5. A more complete comparison of the results of the present work with those of Daniels's is carried out in Table VI.

In view of the fact that different methods of data reduction were used in the two investigations, the entries in Table VI must be considered to be in satisfactory agreement. For the elastic constants listed in Table VI, a direct comparison of $(1/\tau)(d\tau/dp)|_{p=0}$, that is, of the results of PB-type fits with Daniels's data yields agreement to within 5%. Daniels has stated that the estimates of $(1/\tau)(d\tau/dp)|_{p=0}$ listed in Ref. 9 are likely to be systematically low, so that the degree of compatibility between the raw data obtained in the two investigations must be good.

To compute the pressure variation of the elastic constants from the transit time variation, a method ori-

TABLE VI. Values of $d/dp[\tau(0)/\tau(p)]_{p=0}^2$ at 299°K. The subscripts refer to the following combinations of elastic constants: 101, $\frac{1}{2}[C_{11}+C_{12}+2C_{44}]$; 100, $\frac{1}{2}[C_{11}-C_{12}]$; 144, C_{44}.

Quantity	This work	Daniels
a_{101}	0.0485	0.0432
a_{100}	0.0372[a]	0.0348
a_{144}	0.0360[a]	0.0348

[a] Extrapolated from 273°K.

ginally proposed by Cook[22] was modified slightly. Here, it is convenient for typographical reasons to denote the general adiabatic elastic constant measured in these experiments by $C_{jj}(p)$ where $j=0$, 1, 4 and to put $C_{00}=C'=\frac{1}{2}(C_{11}-C_{12})$. Letting $\tau_{jj}(p)$ denote the oneway ultrasonic signal transit time associated with $C_j(p)$, one has

$$C_{jj}(p)/C_{jj}(0)=s(p)t_{jj}(p),$$

where $s^3=\rho(p)/\rho(0)$ is the ratio of densities, and, by definition, for PA-type fits

$$t_{jj}=[\tau_{jj}(0)/\tau_{jj}(p)]^2=1+a_{jj}^{(1)}p+a_{jj}^{(2)}p^2. \quad (1)$$

In terms of quantities measured in the present experiments, s is given by

$$s=1+\int_0^p \frac{[1+\delta(p)]dp}{3C_{11}t_{11}-4C_{00}t_{00}}, \quad (2)$$

where $1+\delta(p)$ is the adiabatic-isothermal conversion factor.

Evidently the variation of the $\delta(p)$ with pressure must be known to first order if $C_{jj}(p)$ is desired to second order in the pressure.

[22] R. K. Cook, J. Acoust. Soc. Am. 29, 445 (1957).

From the definition,[22] at any pressure and temperature one has

$$\delta = 9\beta^2 T B_s / \rho C_p, \qquad (3)$$

where β = linear thermal-expansion coefficient, T = the absolute temperature, B_s = adiabatic bulk modulus, ρ = density, C_p = specific heat at constant pressure.

By using standard thermodynamic relations, one can show that to the first order in p

$$\frac{\delta(p)}{\delta(0)} = 1 + \frac{p}{B_T}\left[-1 + \frac{1}{1+\delta_0}\left(\frac{dB_s}{dp}\right) + \frac{2}{3\beta B_T}\left(\frac{dB_T}{dT}\right) \right.$$

$$\left. + \frac{\delta_0}{1+\delta_0}\left(1 + \frac{1}{3\beta^2}\frac{d\beta}{dT}\right) \right], \qquad (4)$$

where all the quantities in parentheses are evaluated at $p = 0$ and at the temperature under consideration. Equation (4) is equivalent in this approximation to an expression derived by Overton.[23]

For sodium, the first-order pressure correction term in

$$\delta(p) \equiv \delta_0 + \delta_1 p$$

is surprisingly large. For example, the thermal-expansion data of Ref. 24 and the specific-heat data of Ref. 25, combined with the present elastic constant data yield $\delta_1 = -5.1 \times 10^{-3}$ (kbar)$^{-1}$ at 299°K, while $\delta_0 = 7.04 \times 10^{-2}$ at this temperature.

The final expressions relating the pressure dependence of the adiabatic elastic constants to the measured transit times are the following:

$$C_{jj}(p)/C_{jj}(0) = 1 + d_{jj}^{(1)}p + d_{jj}^{(2)}p^2, \qquad (5)$$

where

$$S_{jj}^{(1)} = S_1 + a_{jj}^{(1)},$$

$$S_{jj}^{(2)} = a_{jj}^{(2)} + \tfrac{1}{2}Q^{-1}[\delta_1 - Q^{-1}(1+\delta_0)$$

$$\times (3C_{11}a_{11}^{(1)} - 4C_{00}a_{00}^{(1)})] + S_1 a_{jj}^{(1)},$$

$$Q = 3C_{11} - 4C_{00},$$

$$S_1 = (1+\delta_0)Q^{-1}.$$

The coefficients of the polynomial $C(p)/C(0)$ [Eq. (5)] and values of $(dC/dp)|_{p=0}$ computed from them are listed in Table VII.

In view of the sensitivity of the coefficients $a_{jj}^{(2)}$ to the details of data processing procedures, and because the raw data are not of uniform quality, it is impossible to assign a definite common bond to the errors of the absolute values of the coefficients listed in Table VII. I believe that most of the mean coefficients d_1 are not likely to be in error by more than 5%, while the coefficients d_2 should be regarded as preliminary estimates only. A reasonable bound on all of the d_2 appears to be $-5 \times 10^{14} \le d_2 \le -2 \times 10^{-4}$ (kbar)$^{-2}$. In view of this

[22] W. C. Overton, J. Chem. Phys. **37**, 116 (1962).
[24] S. Siegel and S. L. Quimby, Phys. Rev. **54**, 76 (1938).
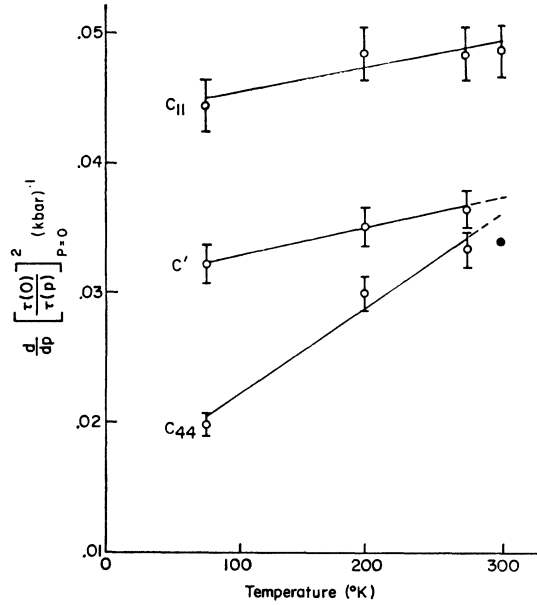[25] T. M. Dauphine, D. K. C. MacDonald, and H. Preston-Thomas, Proc. Roy. Soc. (London) **A221**, 267 (1954).

FIG. 5. Temperature variation of the quantity

$$\frac{d}{dp}\left[\frac{\tau(0)}{\tau(p)}\right]^2_{p=0}.$$

The full circle represents data pertaining to C' and C_{44} obtained from Ref. 9.

uncertainty in the coefficient of p^2, Eq. (5) is clearly not suitable for extrapolation above, say, 20 kbar, without independent confirmation such as may be available from very high-pressure studies.

The temperature dependence of the pressure derivative of the effective elastic constants is shown in Fig. 6. The interpolation line for dC_{44}/dp has been broken at 155°K (the Debye temperature) in an arbitrary way. It is interesting to note that the pressure derivative of the bulk modulus appears to be independent of temperature. This observation confirms earlier experimental work by Swenson et al.[11,21] and the numerical agreement between the two values of dB_s/dp is excellent (3.82 versus 3.85). Since the pressure derivative of the bulk

TABLE VII. Results of pressure dependence experiments. The tabulated coefficients refer to the polynomial $C(p)/C(0) = 1 + d_1 p + d_2 p^2$, where $C(p)$ is the adiabatic elastic constant.

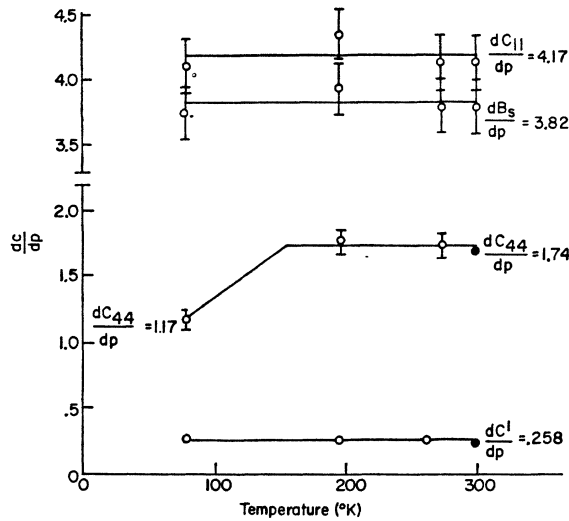| Elastic constant	$T = 299$°K			$T = 273$°K		
	d_1 (kbar)$^{-1}$	$-d_2$ (kbar)$^{-2}$	$\dfrac{dC}{dp}$	d_1 (kbar)$^{-1}$	$-d_2$ (kbar)$^{-2}$	$\dfrac{dC}{dp}$
C_{11}	0.0537	0.0003	4.12	0.0531	0.0002	4.14
C_{44}	0.0390*		1.69	0.0384	0.0003	1.74
C'	0.0390*		0.238	0.0415	0.0003	0.260
B_s			3.80			3.79
	$T = 195$°K			$T = 78$°K		
C_{11}	0.0531	0.0004	4.33	0.0477		4.10
C_{44}	0.0347	0.0004	1.77	0.0243	0.0003	1.17
C'	0.0398	0.0003	0.266	0.0366	0.0003	0.266
B_s			3.96			3.74

* Daniels's data.

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FIG. 6. Variation of the first pressure derivatives of the adiabatic elastic constants with temperature.

modulus plotted in Fig. 6 is computed from the relation

$$\frac{dB_s}{dp} = \frac{dC_{11}}{dp} - \frac{4}{3}\frac{dC'}{dp},$$

the remarkably good agreement with the static measurements provides a valuable check on both dC_{11}/dp and dC'/dp over the whole temperature range $78°K \leq T \leq 299°K$.

Recently, Pastine[26] has stated that some reasons exist for believing that the effect of temperature on $1/C' \times (dC'/dp)$ may be large enough nearly to account for the discrepancies between Daniels's experimental results and the Fuchs's theory. However, Fig. 5 shows that the effect of temperature on the quantity

$$\frac{d}{dp}\left[\frac{\tau_{00}(0)}{\tau_{00}(p)}\right]^2_{p=0},$$

which, apart from a small additive constant, is equal to $(1/C')(dC'/dp)$, is small compared with the effect of temperature on the quantity

$$\frac{d}{dp}\left[\frac{\tau_{44}(0)}{\tau_{44}(p)}\right]^2_{p=0}.$$

The reason for this disagreement between quasiharmonic lattice theory and experiment is not understood at present.

DISCUSSION

It is now customary to discuss pressure experiments like the present ones in terms of "third-order" elastic constants, which are proportional to third derivatives of the Helmholtz free-energy per unit mass F with re-

[26] D. J. Pastine, J. Phys. Chem. Solids **28**, 522 (1967).

spect to Lagrangian strain components.[27] However, the interpretation of the pressure dependence of the shear elastic constants of some metals on the microscopic level is simpler when formulated in terms of certain other quantities (proportional to $d^3F/d\Omega d\gamma^2$, where Ω is the cubic dilation and γ is a parameter describing the shear deformation of the unit cell at constant volume). It seems worthwhile to demonstrate that those combinations of the third-order elastic constants in Brugger's definition[28] which relate to the present experiments are actually linear combinations of such quantities and ordinary second-order elastic constants.

If a cubic crystal in the standard orientation undergoes the homogeneous deformation specified by

$$u_1 = \alpha x_1,$$
$$u_2 = \alpha x_2 + \gamma(1+\alpha)x_3, \tag{6}$$
$$u_3 = \alpha x_3,$$

where the u_i are components of the displacement vector at the point (x_1, x_2, x_3), then the associated nonzero elements of the Lagrangian strain matrix are

$$\eta_{11} = \eta_{22} = \tfrac{1}{2}[(1+\Omega)^{2/3} - 1],$$
$$\eta_{32} = \eta_{23} \equiv \tfrac{1}{2}\eta_4 = \tfrac{1}{2}\gamma(1+\Omega)^{2/3},$$
$$\eta_{33} = \eta_{11} + 2\eta_{23}^2(1+2\eta_{11})^{-1}, \tag{7}$$
$$\eta_{13} = \eta_{12} = 0,$$

where

$$\Omega = (1+\alpha)^3 - 1.$$

For such a deformation, it follows from the strain energy expansion in Ref. 29 that

$$\rho_0 \frac{\partial^3 F}{\partial \eta_1 \partial \eta_4^2} = C_{11} + 2C_{12} + C_{144} + 2C_{166}. \tag{8}$$

Using the two elementary identities

$$\frac{\partial^3 F}{\partial \eta_4^2 \partial \Omega} = \frac{\partial^3 F}{\partial \gamma^2 \partial \Omega} - \frac{4}{3}\frac{\partial^2 F}{\partial \gamma^2}, \tag{9}$$

$$(1+\Omega)^{2/3} = 1 + 2\eta_{11},$$

which follow from Eq. (7), one obtains

$$C_{144} + 2C_{166} = 3\rho_0 \frac{\partial^3 F}{\partial \Omega \partial \gamma^2} - 4C_{44} - (C_{11} + 2C_{12}). \tag{10}$$

Here, F is the Helmholtz free-energy per unit mass and ρ_0 is the density at $p=0$.

Two other identities which are relevant to these experiments may be derived in a similar way:

$$\tfrac{1}{2}(C_{111} - C_{123}) = 3\rho_0 \frac{\partial^3 F}{\partial \Omega \partial \gamma_0^2}$$
$$- 2(C_{11} - C_{12}) - (C_{11} + 2C_{12}), \tag{11}$$

[27] R. N. Thurston, J. Acoust. Soc. Am. **37**, 348 (1965).
[28] K. Brugger, Phys. Rev. **133A**, 1611 (1964).
[29] P. B. Ghate, Phys. Rev. **139A**, 1666 (1965).

$$\tfrac{1}{3}(C_{111}+6C_{112}+2C_{123})=3\rho_0\frac{\partial^3 F}{\partial\Omega^3}+C_{11}+2C_{12}. \quad (12)$$

In Eq. (11), γ_0 denotes the magnitude of the volume-conserving shear strain associated with the shear elastic constant $C'=\tfrac{1}{2}(C_{11}-C_{12})$.

For purposes of discussion, it is convenient to introduce the notation

$$\rho_0\frac{\partial^3 F}{\partial\Omega\partial\gamma^2}=D_{44},$$

$$\rho_0\frac{\partial^3 F}{\partial\Omega\partial\gamma_0^2}=D', \quad (13)$$

$$\rho_0\frac{\partial^3 F}{\partial\Omega^3}=D$$

at this point.[30]

Substituting Eqs. (10)–(12) in the relations between the isothermal derivatives of the effective elastic constants and the third-order constants which are listed in Ref. 29 [Ghate's Eqs. (76)–(78)], one obtains

$$\frac{dC_{44}}{dp}=B_T^{-1}[C_{44}-D_{44}],$$

$$\frac{dC'}{dp}=B_T^{-1}[C'-D'], \quad (14)$$

$$\frac{dB_T}{dp}=-1-B_T^{-1}D.$$

Here, $B_T=\tfrac{1}{3}(C_{11}+2C_{12})_T$ denotes the isothermal bulk modulus.

Fuchs's theory of the shear elastic constants at zero pressure may now be applied to a discussion of their pressure dependence essentially in the same way as was done by Daniels. However, it is first desirable to attempt to correct for lattice-vibration effects, at least in an approximate way.

Recently, Ghate[29] has shown that the third-order elastic constants of the alkali halides should be linear functions of temperature it the lattice-vibration spectrum is a δ function. This should be a good approximation at a sufficiently high temperature. That the second-order elastic constants of sodium are linear functions of temperature above 150°K has been shown already, so that the predictions of quasiharmonic lattice theory seems to be qualitatively well substantiated by experiment in this case. Since the D's defined in Eq. (13) have been shown to be linear combinations of second- and third-order elastic constants, it seems reasonable to expect that the D's should also exhibit a linear temperature dependence above about 150°K.
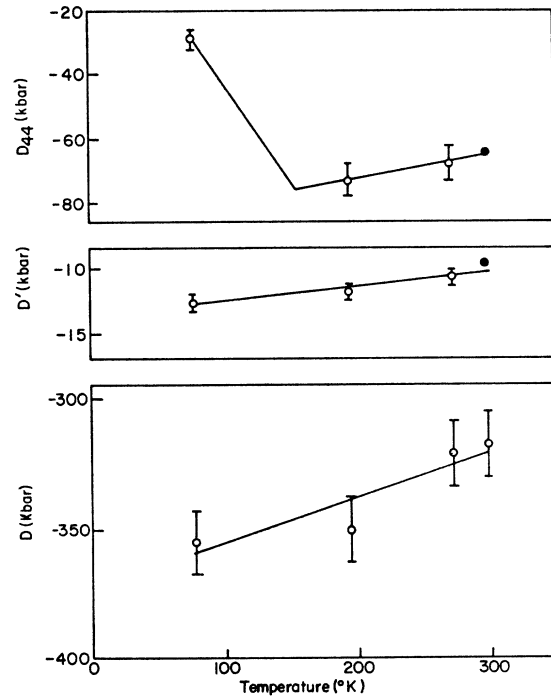

Fig. 7. Variation of third-order elastic constants with temperature. The full circles are data points computed from Daniels's measurements.

The extent to which this prediction is experimentally verified for sodium is shown in Fig. 7. It appears that these data are in qualitative agreement with the predictions of the quasiharmonic approximation. The apparently nonlinear variation of D_{44} with temperature need not, by itself, mean that the quasiharmonic approximation is inapplicable here since 78°K is substantially lower than the Debye temperature of sodium (155°K) and thus qualifies as a "low temperature" from a lattice-dynamics viewpoint. In any case, it is interesting to compare the "athermal"[31] values of the C's and D's, obtained by linearly extrapolating these quantities [Figs. 3(a)–3(c) and 7] to 0°K, the classical theory.

Fuchs showed that a major contribution to the shear constants C' and C_{44} of the static sodium lattice arises from the change with shear strain of the potential energies of valence electron states with $|k|>0$. The SR interactions of the closed shells of core electrons were included in a semiempirical way, using parameters suggested by the work of Born and Mayer. Blume[32] has reexamined the alkali-metal shear-constant problem recently, concluding that the contribution from the kinetic (Fermi) energy of electron states with $|k|\geq0$ is negligible for sodium at an atomic volume $r_s=4$ Bohr

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[30] This somewhat asymmetrical notation is analogous to that now in common use for combinations of the second-order elastic constants of cubic materials.

[31] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12.

[32] M. Blume, Ph.D. thesis, Harvard University, 1959 (unpublished).

Table VIII. Values of the derivatives of $\Gamma(r_s)$ in atomic units.

	Linear interpolation $\dfrac{d\Gamma}{dr_s}$	Quadratic interpolation $\dfrac{d\Gamma}{dr_s}$	$\dfrac{d^2\Gamma}{dr_s^2}$
Reference 32	−0.155	−0.183	0.13
Reference 6	−0.155	−0.155	0

units (B.u.), which he takes to be the equilibrium radius of the s sphere.

Fuchs's results may be expressed in the following way:

$$C' = 2a^{-3}[0.04985f(0)e^2a^{-1} - 1.333x_1W(x_1) + \tfrac{1}{2}W(x_2)(x_2-1)],$$

$$C_{44} = 2a^{-3}[0.3712f(0)e^2a^{-1} + 0.444x_1W(x_1)(x_1-2) - x_2W(x_2)], \quad (15)$$

where

$$W(x) = Ae^{-x},$$

$$x_1 = 0.866a/b,$$

$$x_2 = a/b,$$

a = lattice parameter of the bcc unit cell, e = charge of the electron.

The parameters $f(0)$, A, and b are, respectively, the square of the electron-number density at the boundary of the s sphere, and the Born-Mayer parameters for the sodium ion. The values $A = 2 \times 10^{-10}$ erg and $b = 0.345 \times 10^{-8}$ cm are commonly used for the latter quantities. It is part of the purpose of this work to check whether these values are compatible with experiment.

By differentiating the part of Eq. (15) enclosed in parentheses with respect to Ω, the cubic dilation, one obtains the following estimates of D' and D_{44}:

$$D' = -\tfrac{2}{3}a^{-3}[0.0485e^2a^{-1}g(0) - 1.333x_1W(x_1)(x_1-1) + \tfrac{1}{2}x_2W(x_2)(x_2^2 - 3x_2 + 1)],$$

$$D_{44} = -\tfrac{2}{3}a^{-3}[0.3712e^2a^{-1}g(0) + 0.0444x_1W(x_1) \times (x_1^2 - 4x_1 + 2) - x_2W(x_2)(x_2-1)], \quad (16)$$

where

$$g(0) = f(0) - 3f'(0),$$

$$f'(0) = [df(\Omega)/d\Omega]_{\Omega=0}.$$

The athermal quantities B (the bulk modulus) and D are calculated here with the aid of a simplified theory of the cohesive energy of sodium suggested by the work of Brooks.[7] The SR interaction is included everywhere for consistency.

Let the cohesive energy per valence electron be given by

$$E(r_s) = E_0(r_s) + 2.21r_s^{-2} + 0.284r_s^{-1} + C(r_s) + W(r_s), \quad (17)$$

where $E_0(r_s)$ = the ground-state energy, $C(r_s) = 0.144 + 0.031 \ln r_s + 5 \times 10^{-4}$, $W(r_s)$ = the SR interaction energy, r_s = the correlation energy. Here, r_s and E are measured in Bohr units. The physical significance of the various terms in Eq. (17) has been discussed at length

in the literature.[7,8] The athermal values of B and D may be obtained from Eq. (17) by evaluating the following derivatives:

$$B = 2a^{-3}\frac{d^3E}{d\Omega^2} = 2a^{-3}(r_s/3)^2\frac{d^2E(r_s)}{dr_s^2},$$

$$D = 2a^{-3}\frac{d^3E}{d\Omega^3} = 2a^{-3}(r_s/3)^3\left[-6r_s^{-1}\frac{d^2}{dr_s^2} + \frac{d^2}{dr_s^3}\right]E(r_s). \quad (18)$$

Equation (18) applies to a bcc solid at its equilibrium lattice parameter only since the condition

$$\frac{dE}{dr_s}\bigg|_{r_s=(3/8\pi)^{1/3}a} = 0$$

has been used in deriving these equations. The condition $dE/dr_s = 0$ at $r_s = 3.92$ B.u., which is the athermal equilibrium atomic volume, will be imposed a priori even though this does not follow from Eq. (17). This procedure allows an experimental check to be made of the second- and third-order derivatives of $E(r_s)$ at $r_s = 3.92$ without introducing complications caused by a nonvanishing first derivative. Calculations of the equilibrium atomic volume and the cohesive energy are not, in any case, immediately relevant to the present experiments.

The variation of the ground-state energy E_0 with r_s contribution a major term to both B and D. Derivatives of E_0 may be obtained by the following procedure, which is suggested by Eq. (7.4) of Ref. 7.

It has been shown that

$$\frac{dE_0}{dr_s} = 3\Gamma(r_s)[V(r_s) - E_0]r_s^{-1}. \quad (19)$$

Setting $V(r_s) = -2/r$, differentiating, and successively eliminating dE_0/dr_s by means of Eq. (19), one can obtain relations between the second and third derivatives of E_0, E_0, and derivatives of $\Gamma(r_s)$. In this way existing calculations of $E_0(r_s)$ and $\Gamma(r_s)$ can be used to estimate relatively high derivatives of $E_0(r_s)$ without extensive numerical work. The following values of the first derivative of $\Gamma(r_s)$ at $r_s = 3.92$ which have been obtained from Ref. 6 and 33 by interpolation are listed in Table VIII.

The magnitude of $\Gamma'(r_s)$ is important in the interpretation of all of the present experiments since a good estimate of the parameter $f'(0)$ in Eq. (15) is given by

$$f'(0) = 2\Gamma\Gamma'. \quad (20)$$

The values of $\Gamma = 1$ and $\Gamma' = 0.155$ derived from Ref. 33 by linear interpolation are used here, since the results of the quantum-defect-method investigations of the cohesive energy agree very well with experiment, and

[33] H. Brooks, Phys. Rev. 91, 1027 (1953).

since the variation of Γ with r_s may be other than quadratic.[8] Assuming that $\Gamma(r_s)$ is linear in r_s near $r_s = 3.92$, one obtains the following relations from Eq. (19):

$$\frac{d^2E_0}{d\Omega^2} = \tfrac{1}{3}(GU + \Gamma r_s V'),$$

$$\frac{d^3E_0}{d\Omega^3} = \frac{1}{9}\left\{ -\left[6\Gamma\Gamma' r_s + \Gamma(3\Gamma+8)U + (G-8\Gamma)V'r_s \right. \right. \tag{21}$$
$$\left. \left. + r_s\frac{d}{dr_s}(\Gamma r_s V') \right] \right\},$$

where

$$G = \Gamma' r_s - \Gamma(3\Gamma+1),$$

$$U = V(r_s) - E_0.$$

Here, primes denote derivatives with respect to r_s. In this way one finds that

$$\frac{d^2E_0}{d\Omega^3} = 0.130 \text{ Ry},$$

$$\frac{d^3E_0}{d\Omega^3} = 0.663 \text{ Ry}. \tag{22}$$

For reference, the SR contributions to B and D are listed below:

$$B_{SR} = 2a^{-3}[0.444x_1^2W(x_1) + 0.333x_2^2W(x_2)],$$

$$D_{SR} = -\tfrac{2}{3}a^{-3}[0.444x_1^2W(x_1)(x_1+6) \tag{23}$$
$$+ 0.333x_2^2W(x_2)(x_2+6)].$$

The condition $dE/dr_s|_{r_s=3.92} = 0$ has again been used to derive these results. It should be noted that the SR contributions in Eqs. (16) and (23) do not satisfy a Cauchy relation of the type $C_{12}{}^{SR} = C_{44}{}^{SR}$. The reason for this is, of course, that the lattice is not in equilibrium under the action of the short-range forces alone.

The numerical results of the calculations outlined above are summarized in Table IX and compared with both athermal experimental values and those actually measured at 78°K. The following parameters have been used to generate the theoretical quantities: $a = 4.206 \times 10^{-8}$ cm ($r_s = 3.92$ B.u.), $b = 0.345 \times 10^{-8}$ cm, $A = 2.00 \times 10^{-10}$ erg, $\Gamma(3.92) = 1$, $\Gamma'(3.92) = -0.155$ (B.u.)$^{-1}$, $E_0(3.92) = -0.607$ Ry.

An examination of Table IX shows that the linearly extrapolated athermal experimental values of the elastic constants do not always agree very well with the theoretical values pertaining to a static lattice. The attempt to include the SR forces everywhere consistently is not a success in that agreement with experiment is not always improved by doing so. It has been found that no reasonable values of the SR interaction parameters A and b yield significantly better over-all agreement with experiment than the traditional Born-Mayer

TABLE IX. Comparison of theoretical and experimental values of some of the elastic constants of sodium, in kbar.

Quantity	Long-range forces	SR forces	Total (theory)	Experimental (athermal)	Experimental (78°K)
C'	7.49	−0.105	7.39	7.74±0.30	7.32±0.22
C_{44}	54.7	5.28	60.0	66±3	59.2±1.8
B_T	75.9	8.27	84.2	79±4	73.8±2.2
D'	−3.20	−0.003	−3.20	−13±2	−13±1
D_{44}	−23.9	−14.3	−38.2	−90±20	−30±2
D_T	−386	−46.4	−432	−370±20	−360±10

values. The SR contributions to C' and D' are small because of cancellation effects between first- and second-nearest-neighbor interactions. They are not very sensitive to changes of b while the SR contributions to the other elastic constants vary rapidly with b. Hence, the 300% discrepancy between the observed and calculated value of D' cannot be reduced substantially by adjusting b without spoiling the reasonably good agreement obtained for the other elastic constants.

The work of Blume appears to rule out the possibility that contributions to D_{44} and D' which arise from the nonsphericity of the Fermi-surface sodium are large enough to account for the unexpectedly large value of D'. This is so because from Eq. (24), p. 72 in Ref. 32 one can show that such effects should result in a contribution to D_{44} which is roughly four times as large as that to D'. Since the value of D_{44} observed at 78°K is in good agreement with Fuchs's theory, the "Fermi energy" contribution to D' cannot be large enough to account for a substantial fraction of the 10-kbar discrepancy between the observed and the theoretical value of D'.

I conclude that it does not appear to be possible quantitatively to account for the observed magnitude of $dc'/dp|_{p=0}$ for $T \geq 78°$K in the framework of Fuchs's theory, even though $dc_{44}/dp|_{p=0}$ and $dB_T/dp|_{p=0}$ as well as the zero-pressure values of all the elastic constands of bcc sodium are in good agreement with that theory at 78°K. It is possible that in future experiments $dc'/dp|_{p=0}$ will be found to decrease rapidly with temperature below 78°K in a manner simular to the observed behavior of $dc_{44}/dp|_{p=0}$ below 195°K. The onset of the martensitic phase transformation at about 40°K limits the temperature interval available for the observation of such a decrease to only 40°K, but an exploration of the temperature range $\sim 40°K \geq T \geq 78°$K should produce important information about the bcc sodium lattice.

ACKNOWLEDGMENTS