

*J. Phys. Chem. Solids* Pergamon Press 1966. Vol. 27, pp. 637-642. Printed in Great Britain.

## TEMPERATURE DEPENDENCE OF THE ELASTIC CONSTANTS OF SODIUM

MARY E. DIEDERICH\* and J. TRIVISONNO

John Carroll University, Cleveland, Ohio

(Received 10 July 1965; in revised form 7 October 1965)

**Abstract**—The adiabatic elastic constants of single crystal sodium were measured as a function of temperature from 195°K to 78°K by the ultrasonic pulse-echo technique. In order to eliminate transit time errors a buffer technique was employed. The measured elastic constants at 78°K (in units of  $10^{10}$  dyn-cm<sup>-2</sup>) are as follows:

$$C = 5.78, \quad C' = 0.688, \quad C_n = 13.30, \quad \text{and} \quad B_s = 7.30$$

The notation  $C = C_{44}$ ,  $C' = (C_{11} - C_{12})/2$ ,  $C_n = (C_{11} + C_{12} + 2C_{44})/2$ , and  $B_s = C_n - C - C'/3$  is used. The shear constants  $C$  and  $C'$  are interpreted in terms of Fuchs' electrostatic contribution to the shear stiffness of the alkali metals. The results of this work are in agreement with those of Daniels at 300°K and the shear constants are within 3% of the values computed by Quimby and Siegel. The results are also compared with Bender's value of the elastic constants at 90°K and with Swenson's isothermal compressional data.

### INTRODUCTION

THE single crystal elastic shear constants of sodium were first determined by QUIMBY and SIEGEL.<sup>(1)</sup> They employed a composite oscillator technique over the temperature range 80°–210°K. O. BENDER<sup>(2)</sup> made static measurements on single crystals of sodium at 90°K. In both investigations the elastic compliances were the directly measured quantities and from this data the elastic constants were computed. Since a 15% discrepancy exists in these data and since the elastic constants were not directly determined, it was decided to measure the elastic constants directly by the conventional and more reliable ultrasonic pulse-echo techniques over the temperature range 78°–195°K.

FUCHS<sup>(3)</sup> has calculated the theoretical values of the elastic shear stiffnesses for the alkali metals at absolute zero. He predicts that the main contribution of the shear stiffnesses in these metals arises from the long range electrostatic interaction between ion cores and the valence electrons, which accounts for the large elastic anisotropy observed in the alkali metals.<sup>(4-7)</sup> He also includes a second,

but minor, constituent arising from short range ion core interactions. Since the ultrasonic pulse-echo technique yields directly measured values for the shear constants,  $C = C_{44}$  and  $C' = (C_{11} - C_{12})/2$ , a direct comparison with Fuchs' theoretical values of these constants can be made.

### EXPERIMENTAL PROCEDURE

The procedure for crystal growth, orientation, and preparation of the acoustic specimens was the same as described in a paper by DANIELS<sup>(8)</sup> and similar to the techniques employed on potassium presented in a recent publication from this laboratory.<sup>(7)</sup>

For a cubic material all three independent elastic constants can be obtained by the ultrasonic pulse-echo technique if the appropriate wave is propagated along the [110] direction. Generation of longitudinal, fast shear, and slow shear waves was straightforward once the proper handling techniques were perfected. Because of the high anisotropy of sodium, generation of slow shear waves caused the most difficulty and proved quite sensitive to crystal orientation and to proper positioning of the polarization direction of the Y-cut transducer. Two crystals oriented in the [110] direction

\* NSF Undergraduate Research Participant. Presently NSF Graduate Fellow at University of Chicago.

were used to obtain elastic constant measurements as a function of temperature. A third crystal oriented along [100] was used to measure the elastic constant  $C_{11}$  directly.

The elastic constants were measured by a buffer technique.<sup>(7)</sup> Adoption of the buffer technique eliminates both the transit time error and the necessity of applying a transducer directly on the soft metal. According to this method the transducer and sample are cemented at opposite ends of a buffer rod. A pulse propagated through the rod is partially reflected and partially transmitted at the buffer-specimen interface. The transit time measured is then the true transit time. In this work magnesium served quite well as the buffer due to the desirable acoustic impedance reflection and transmission coefficients which exist between a magnesium-sodium interface.

A silicone release agent, Dow Corning 7 Compound, was used as a bond between both the quartz and magnesium and the magnesium and sodium. This seal, which does not react with sodium, was fluid at temperatures below that of the melting point of sodium so that thin seals could be made without introducing distortions, glassy at low temperatures to compensate for the relative thermal expansion differences involved, and rigid enough to provide good acoustic coupling for shear waves at the temperatures desired.

Transit time measurements for all three wave propagations were taken at liquid nitrogen and dry ice temperatures. In addition, measurements were taken at 20° temperature intervals between 78°K and 195°K. These intermediate temperatures were determined by placing an iron-constantan thermocouple in good thermal contact with the aluminum cartridge which contained the buffer assembly. About 2 hr were required to go from 78° to 195°K. The round trip transit times measured were of the order of 6, 10 and 28  $\mu$ sec for longitudinal, fast shear, and slow shear waves respectively for a 1 cm sample.

At 295°K sample 1 had a length of 1.34 cm and sample 2 a length of 1.05 cm. The sample lengths were measured at room temperature with a micrometer and corrections appropriate to the measuring temperature were made using the thermal expansion data of QUIMBY and SIEGEL.<sup>(9)</sup>

The elastic constants were calculated from the density, transit time, and sample length and plotted

as a function of temperature. From these graphs a set of elastic constants were chosen for each 20°K temperature interval. The temperatures selected were those for which a complete set of measurements as described was obtained for the two [110] samples. In addition, new seals were placed on each of these crystals and the measurements repeated. The velocities obtained in various runs always agreed within 1%. A third crystal was measured at 78°K and the results also agreed with the data reported here. In addition, longitudinal velocities were measured as a function of temperature on a crystal oriented along [100] and are reported in the next section.

### RESULTS

The elastic constants are related to the acoustic wave velocities in the [110] direction by the following equations:

$$\begin{aligned} C_n &= (C_{11} + C_{12} + 2C_{44})/2 = \rho v_2^2 \\ C &= C_{44} = \rho v_5^2 \\ C' &= (C_{11} - C_{12})/2 = \rho v_4^2 \end{aligned} \quad (1)$$

where  $\rho$  is the density,  $v_2$  is the longitudinal velocity,  $v_5$  is the fast shear velocity with particle motion in the [001] direction, and  $v_4$  is the slow shear velocity with particle motion in the [110] direction. The adiabatic bulk modulus,  $B_s$ , and the stiffness  $C_{11}$  and  $C_{12}$  can be obtained by combining the directly measured quantities in the following way:

$$\begin{aligned} B_s &= \rho v_2^2 - \rho v_5^2 - \rho v_4^2/3 = (C_{11} + 2C_{12})/3 \\ C_{11} &= \rho v_2^2 - \rho v_5^2 + \rho v_4^2 \\ C_{12} &= \rho v_2^2 - \rho v_5^2 - \rho v_4^2 \end{aligned} \quad (2)$$

The elastic constants shown in Table 1 have been calculated using equations (1) and (2).

Table 2 lists the adiabatic bulk modulus  $B_s$ , along with the isothermal bulk modulus  $B_T$ . The latter was computed from  $B_s$  using the approximate relation

$$B_T \approx B_s \left( 1 - \frac{TV\beta^2 B_s}{C_p} \right)$$

where  $V$  is the molar volume,  $\beta$  is the volume coefficient of expansion and  $C_p$  is the molar heat capacity. The values of  $V$  and  $\beta$  were obtained

Table 1. Values of the adiabatic elastic constants, the elastic anisotropy, and the density of sodium. Elastic constants in units of  $10^{10}$  dynes-cm<sup>-2</sup> and the density in g-cm<sup>-3</sup>

Temp. (°K)	Sample	C	C'	C <sub>n</sub>	C <sub>11</sub>	C <sub>12</sub>	A	ρ
78	1	5.78	0.680	13.26	8.15	6.79	8.50	1.010
78	2	5.77	0.695	13.34	8.26	6.87	8.30	1.010
115	1	5.53	0.665	12.85	7.98	6.65	8.31	1.006
115	2	5.53	0.673	12.94	8.08	6.74	8.21	1.006
155	1	5.27	0.650	12.41	7.78	6.48	8.11	0.999
155	2	5.27	0.652	12.50	7.88	6.58	8.09	0.999
195	1	5.00	0.634	11.97	7.61	6.34	7.89	0.991
195	2	4.99	0.630	12.07	7.71	6.45	7.92	0.991
300	Daniels	4.19	0.585	11.01	7.41	6.24	7.16	0.970

Table 2. Values of the adiabatic and isothermal bulk moduli of sodium in units of  $10^{10}$  dynes-cm<sup>-2</sup>

Temp. (°K)	B <sub>s</sub> (a)	B <sub>T</sub> (b)	B <sub>T</sub> (c)
78	7.30	7.29	7.09
115	7.14	7.10	6.99
155	6.97	6.74	6.92
195	6.82	6.50	6.72
300 (Daniels)	6.61	6.16	6.33

- (a)  $B_s = C_n - C - C'$ .  
 (b) Computed from  $B_s$ .  
 (c) Swenson.

from SWENSON<sup>(10)</sup> and the values of  $C_p$  were obtained from MARTIN.<sup>(11)</sup> Swenson's values of  $B_T$  are also listed and the agreement is well within experimental error of either measurement.

The values of the adiabatic elastic constant  $C_{11}$  obtained from direct measurement of the longitudinal wave velocity on a crystal oriented along [100] are shown in Table 3. The values of  $C_{11}$  obtained in this manner agree well with indirect determination of this quantity.

Table 4 includes the experimental values of the shear constants  $C_{44}$ ,  $C'$  and the elastic anisotropy at 78°K along with FUCHS<sup>(3)</sup> theoretical values at 0°K. The theoretical values take into account only the electrostatic contribution to the elastic constants. Also included in the tables are the experimental values of these quantities at 80°K determined by QUIMBY and SIEGEL<sup>(1)</sup> and the experimental values of BENDER<sup>(2)</sup> at 90°K. Daniels' values at 300°K are also listed.

The values of the elastic constants obtained in this work have a calculated precision of 2-3% when one includes errors in length measurements, transit time, and density. The internal consistency appears to be better than this, as can be seen in Figs. 1 and 2.

Table 3. Values of the adiabatic elastic constant  $C_{11}$  obtained from velocity measurements in [100] direction

Temp. (°K)	C <sub>11</sub>
78	8.46
115	8.29
155	8.11
195	7.93
300 (Daniels)	7.38

The elastic constants  $C_{44}$ ,  $C'$  and the elastic anisotropy plotted as a function of temperature are shown in Fig. 1. Daniels' values of these quantities at 300°K and the data of Quimby and Siegel at 80°K and 200°K are also shown. Since sodium undergoes a low temperature martensitic transformation from a b.c.c. structure to an h.c.p. structure,<sup>(12)</sup> no low temperature data were obtained. The values of the elastic constants at 0°K can be obtained by extrapolating the present data and breaking the curve at about 20°K so that the slope is zero at 0°K.

ure. From these graphs a ere chosen for each 20°K ne temperatures selected complete set of measure- btained for the two [110] ew seals were placed on and the measurements obtained in various runs %. A third crystal was e results also agreed with In addition, longitudinal as a function of tempera- ed along [100] and are ion.

#### ULTS

are related to the acoustic [110] direction by the

$$(C_{11} + 2C_{44})/2 = \rho v_2^2 \quad (1)$$

$$C_{12}/2 = \rho v_4^2$$

,  $v_2$  is the longitudinal shear velocity with particle motion, and  $v_4$  is the slow particle motion in the [110] direction.  $B_s$  and  $C_{11}$  can be obtained by measured quantities in the

$$C_{11} = (C_{11} + 2C_{12})/3 \quad (2)$$

shown in Table 1 have equations (1) and (2).

adiabatic bulk modulus  $B_s$ , isothermal bulk modulus  $B_T$ . The values of  $B_T$  using the approximate

$$B_T = \frac{TV\beta^2 B_s}{C_p}$$

volume,  $\beta$  is the volume expansivity, and  $C_p$  is the molar heat capacity. The values of  $V$  and  $\beta$  were obtained

Table 4. Comparison of the shear constants  $C_{44}$ ,  $C' = 1/2(C_{11} - C_{12})$ , and the elastic anisotropy. Elastic constants in units of  $10^{10}$  dyn-cm $^{-2}$

Temp. (°K)	$C_{44}$	$C'$	$A$	Source
0	5.32	0.715	7.44	Theory
78	5.78	0.688	8.40	Present
80	5.93	0.725	8.18	Quimby and Siegel
90	6.18	0.830	7.45	Bender
300	4.19	0.585	7.16	Daniels

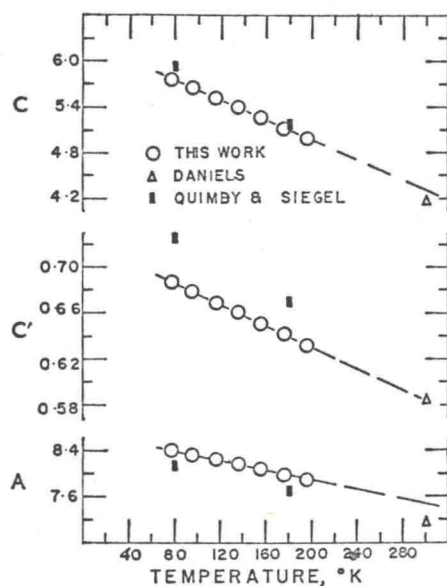


FIG. 1. The elastic constants  $C = C_{44}$  and  $C' = 1/2(C_{11} - C_{12})$  and the elastic anisotropy  $A = C/C'$  plotted as a function of temperature. Elastic constants in units of  $10^{10}$  dynes-cm $^{-2}$ .

The values of the shear constants obtained in the present study are in substantial agreement with the values of these quantities obtained by Quimby and Siegel. This experiment, like that of Quimby and Siegel yields more accurately the temperature variation of the elastic constants rather than the absolute value of the elastic constants themselves. The agreement here is excellent as can be seen in Fig. 1. This experiment also yields values of  $C_n$ ,  $C_{11}$ , and  $B_s$  and their temperature dependence, which were either unknown or unreliable before the present study was completed. Figure 2 shows the elastic constants  $C_n$ ,  $C_{11}$ , and the

adiabatic bulk modulus as a function of temperature. The  $C_{11}$  data is taken from measurements on an acoustic specimen oriented along [100].

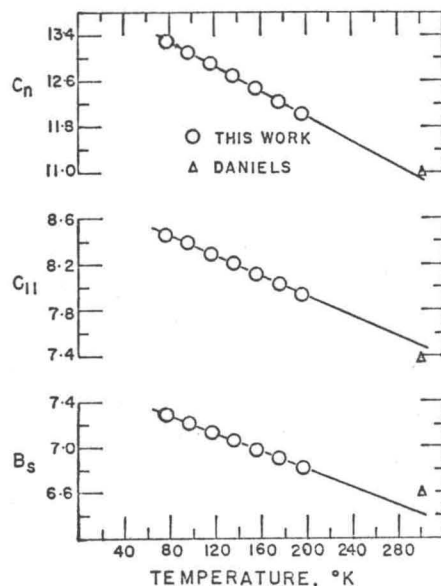


FIG. 2. The elastic constants  $C_n$ ,  $C_{11}$  and  $B_s$  plotted as a function of temperature. Units are  $10^{10}$  dynes-cm $^{-2}$ .

The observed temperature coefficients at constant pressure of the elastic constants were obtained from Figs. 1 and 2; these are related to the pressure variation of the elastic constants by the thermodynamic relation,

$$\left(\frac{d \ln C}{dT}\right)_P = \left(\frac{d \ln C}{dT}\right)_V + \alpha \left(\frac{d \ln C}{d \ln r}\right)_T \quad (3)$$

where  $\alpha$  is the coefficient of linear expansion at 300°K and the quantity  $(d \ln C/d \ln r)_T$  can be obtained from the pressure measurements of

Daniels. The constant volume temperature coefficient obtained from equation (3) is of theoretical interest, and numerical values of this quantity are shown in Table 5. The constant volume temperature coefficient of the adiabatic bulk modulus is positive for sodium while this same coefficient is negative for the shear constants, a result similar to that found in Cu, Ag, Au, LiF, NaF and more recently in potassium.

78°K is 8.4 and is slightly higher than the theoretical value of this quantity. It should be noted that the experimental values of  $C$ ,  $C'$ , and  $A$  cannot be brought into detailed agreement by using a value of  $Z_{\text{eff}}^2$  different from one as was done in the case of potassium.

Fuchs, in his original work, included a second contribution to the shear stiffnesses arising from short range repulsive interactions of ion cores. If

Table 5. Temperature coefficients of the elastic constants of sodium. Units are  $10^{-4} \text{ deg}^{-1}$  and the temperature is  $300^\circ\text{K}$

Constant	$[(d \ln C)/dT]_p = [(d \ln C)/dT]_V + \alpha[(d \ln C)/(d \ln r)]_T$		
$C$	-16.70	-11.70	-5.00
$C'$	-8.03	-3.07	-4.96
$B_s$	-5.90	+1.10	-7.00

INTERPRETATION OF RESULTS

The values of the shear constants obtained in this work at  $78^\circ\text{K}$  can be compared with Fuchs' theoretical values of these constants. The results obtained by Fuchs for the electrostatic contribution to the shear constants of b.c.c. metals with one valence electron per atom are the following:

$$C_E = 0.7422(e^2/a^4)Z_{\text{eff}}^2$$

and

$$C'_E = 0.0997(e^2/a^4)Z_{\text{eff}}^2$$

where  $e$  is the electronic charge,  $a$  is the lattice constant at  $0^\circ\text{K}$ , and  $Z_{\text{eff}}$  is a parameter which takes into account the deviation of the actual charge density at the boundary of the atomic polyhedron from the value  $e/\Omega$  which one would get if the charge were distributed uniformly over the volume  $\Omega$  of the atomic cell. The results obtained by Fuchs for sodium with  $Z_{\text{eff}} = 1$  are, in units of  $10^{10} \text{ dyn-cm}^{-2}$ ,  $C_E = 5.32$  and  $C'_E = 0.715$ . The corresponding experimental values are  $C = 5.78$  and  $C' = 0.688$ .

The agreement, although not perfect, indicates that the major contribution to shear constants of sodium arises from the long range Coulomb interaction, a result previously noted in lithium, potassium, and sodium by other investigators. The experimental elastic anisotropy  $A = C/C'$  at

$w(r)$  is the energy of a pair of ions a distance  $r$  apart, it is easily shown that the following contributions to the elastic constants arise from nearest and next nearest neighbor interactions for a body-centered crystal:

$$C_I = 4/9\Omega^{-1}[r_0^2 w''(r_0) + 2r_0 w'(r_0)] + \Omega^{-1} \delta w'(\delta)$$

$$C'_I = 4/3\Omega^{-1} r_0 w'(r_0) + 1/2\Omega^{-1} [\delta^2 w''(\delta) + \delta w'(\delta)]$$

where  $r_0$  is the nearest neighbor distance,  $\delta$  is the next nearest neighbor distance, and the primes signify derivation with respect to  $r$ . This gives a value of  $C_I > 0$  and  $C'_I \approx 0$ . In order to explain the experimental values of  $C$ ,  $C'$ , and  $A$  based on a two constituent model consisting of an electrostatic stiffness and an ionic stiffness, it is clear that  $C_I/C'_I$  must have a value different from  $C_E/C'_E$ .

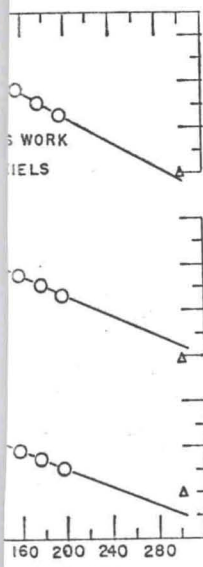
This additional term could account for the observed values of the elastic shear constants and the elastic anisotropy. The pressure derivative experiment of Daniels shows that

$$\frac{d \ln C}{d \ln r} = \frac{d \ln C'}{d \ln r}$$

a result which he states rules out any ionic contribution to the stiffness. However, Smith has pointed out that it rules out only a contribution for which  $(d \ln C_E/d \ln r)$  differs appreciably from

$-C_{12}$ , and  
 $\text{cm}^{-2}$   
 source  
 by and Siegel  
 er  
 is

as a function of tempera-  
 en from measurements on  
 ented along [100].



Units are  $10^{10} \text{ dynes-cm}^{-2}$ .

temperature coefficients at con-  
 stic constants were obtained  
 these are related to the pres-  
 elastic constants by the

$$\left(\frac{d \ln C}{dT}\right)_V + \alpha \left(\frac{d \ln C}{d \ln r}\right)_T \quad (3)$$

ent of linear expansion at  
 ty  $(d \ln C/d \ln r)_T$  can be  
 pressure measurements of

( $d \ln C_I/d \ln r$ ). For sodium ( $d \ln C_E/d \ln r$ ) has a value of 7.3 while ( $d \ln C_I/d \ln r$ ) cannot be directly determined. If one assumes ( $d \ln C_I/d \ln r$ ) is equal to 17 as is the case for Cu, Ag, and Au, then the pressure experiment rules out an ionic contribution. It should be emphasized that the major contribution to the elastic constant is the electrostatic stiffness which accounts almost entirely for the observed value of  $C'$  and 90% of the value of  $C_{44}$  if one adjusts  $Z_{\text{eff}}^2$  to a value of 1.1. It is not clear why the observed anisotropy is high in sodium while in potassium its value is almost equal to the electrostatic value.

Another possible contribution to the elastic constants can arise from the Fermi energy. BLUME<sup>(13)</sup> has included a Fermi contribution to the shear stiffnesses of lithium. The results of his calculation yielded values of  $C_F$  and  $C'_F$  which are both negative. These values were consistent with the observed elastic constants and the high anisotropy of lithium. The Fermi surface of sodium, however, is very nearly spherical and lies well within the Brillouin zone so that the Fermi contribution to the elastic constants is negligible for this metal.

*Acknowledgments*—The authors are indebted to Dr. EDWARD F. CAROME of the John Carroll Physics Department and Professors CHARLES S. SMITH and DONALD E.

SCHUELE of the Case Institute of Technology for many valuable discussions. We are also indebted to Professor SCHUELE for his computer program used to make the orientation and perturbation corrections of the elastic constants. This work was supported in part by the United States Air Force Office of Scientific Research.

#### REFERENCES

1. QUIMBY S. L. and SIEGEL S., *Phys. Rev.* **54**, 293 (1938).
2. BENDER O., *Ann. Phys.* (5) **34**, 359 (1939).
3. FUCHS K., *Proc. R. Soc.* **A153**, 622 (1936); **A157**, 444 (1936).
4. NASH H. C. and SMITH C. S., *J. Phys. Chem. Solids* **9**, 113 (1959).
5. SMITH P. A. and SMITH C. S., *J. Phys. Chem. Solids* **26**, 279 (1964).
6. TRIVISONNO J. and SMITH C. S., *Acta Met.* **9**, 1064 (1961).
7. MARQUARDT W. R. and TRIVISONNO J., *J. Phys. Chem. Solids* **26**, 273 (1964).
8. DANIELS W. B., *Phys. Rev.* **119**, 1246 (1960).
9. SIEGEL S. and QUIMBY S. L., *Phys. Rev.* **54**, 76 (1938).
10. BEECROFT R. I. and SWENSON C. A., *J. Phys. Chem. Solids* **18**, 329 (1960).
11. MARTIN D. L., *Proc. R. Soc.* **A254**, 433 (1960).
12. BARRETT C. S., *Acta Crystallogr.* **9**, 671 (1956).
13. BLUME M. S., Doctoral Thesis, Harvard University (1959).