

Pressure Variation of the Elastic Constants of Sodium

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The pressure variation of the single crystal elastic constants of sodium has been measured using a modified ultrasonic pulse echo method. The values found for the pressure derivatives of the elastic constants are:

$$dC_{44}/dP=1.63, \quad dC'/dP=0.226, \quad dB_s/dP=3.60.$$

The notation $C' = (C_{11} - C_{12})/2$ and $B_s = (C_{11} + 2C_{12})/3$ has been used. The experimental observation that the elastic anisotropy ratio C'/C' ($C = C_{44}$) does not depend on pressure indicates that one can positively neglect interaction of ion cores as a contribution to the elastic stiffness of sodium. The results are interpreted in terms of Fuchs' theoretical calculation of the Coulomb contribution to the shear stiffnesses of the alkali metals. The interpretation indicates that as sodium is compressed, the value of the electronic wave function at the boundaries of the atomic polyhedra increases more rapidly than $\Omega^{-1/3}$, where Ω is the volume of the atomic polyhedron. The volume variation of the value of the wave function of the lowest electronic state at the boundaries of the atomic polyhedra is found to be:

$$\left[\frac{d \ln \mu_0(r_s)}{d \ln \Omega} \right]_{\Omega=\Omega_0} = -0.27.$$

INTRODUCTION

AS Benedek and Kushida¹ have shown, it is possible to evaluate the volume dependence of the electronic wave function of a solid at the position of the atomic nucleus, using the pressure variation of the Knight Shift. However, as far as cohesive properties of a solid are concerned, one is considerably more interested in the volume dependence of the value of the wave function at the boundaries of the atomic polyhedra. Fuchs² has shown for the case of the alkali metals, where one can neglect ion core interactions and Brillouin zone effects which contribute to the stiffness of multivalent metals, that the elastic shear stiffnesses are proportional to the square of the electronic charge density at the boundaries of the atomic cells. We have measured the pressure variation of the single crystal elastic constants of sodium and have computed from these data the volume dependence of the value of the electronic wave function at the boundaries of the atomic polyhedra.

EXPERIMENT

High-Pressure System

The high-pressure system has been described in detail in a recent article,³ and needs little further elaboration here except for mention of the modifications of technique necessitated by the mechanical softness and high chemical reactivity of sodium.

The sample mount must be designed such that the crystal is not subjected to even moderate nonhydrostatic stresses; venting of the regions near the crystal helps

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¹ G. B. Benedek and T. Kushida, *J. Phys. Chem. Solids* **5**, 241 (1958).

² K. Fuchs, *Proc. Roy. Soc. (London)* **A153**, 622 (1936); **A157**, 444 (1936).

³ W. B. Daniels and C. S. Smith, *Phys. Rev.* **111**, 713 (1958).

to ensure that large viscous forces will not be applied to the sample during pressure changes. The mount design problem is further complicated by the large compressibility of sodium because a change of sample dimensions must not cause the electrode on the quartz transducer to lose contact with the rf input lead. In the present experiment these problems were met by resting the crystal on a long coil spring of very low stiffness, which maintained electrode contact but exerted only very small forces on the sample. Electrical contact to the crystals proper was made by pushing a 0.04-cm diameter wire a short distance into the sodium in a region outside the acoustic path. Octoil *S*, previously used as the pressure transmitting fluid, is unsatisfactory for use with a material as reactive as sodium. It was found that about a 50-50 mixture of mineral oil and isopentane performed satisfactorily in this respect if kept in the presence of sodium shavings for a week or so before use.

The high pressure fixed point used to calibrate the Manganin wire hydrostatic pressure gage was the freezing pressure of mercury at 0°C, taken to be 7640 kg/cm² following Bridgman.⁴

Sample Preparation

The chemical activity, the mechanical softness and the low melting temperature of sodium force the experimenter to exercise caution in manipulating the material, particularly in single crystal form.

The sodium used was Mallinckrodt Analytical Reagent. The exact purity is not known, but a cooling curve run for the material gave a sharp transition at the freezing point.

Single crystals 0.75 inch in diameter and 5 inches long were grown by a modified Bridgman technique.

⁴ P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1952).

A mild steel crucible as shown in Fig. 1 was used. It was made in two pieces to facilitate removal of the crystals. The entire sample was immersed in mineral oil during the growing process, but it was found unnecessary to keep the entire setup in a controlled atmosphere. By heating the top of the crucible and cooling the bottom, an initial temperature gradient of about 100 centigrade degrees over the 5 inch length was set up from bottom to top of the melted sample of sodium and the freezing took place from the bottom of the melt as the power to the heating coils at the top of the crucible was reduced. The large contraction of the sodium on freezing and cooling to room temperature made the removal of the grown boule very easy. There was no tendency of the sodium to wet the steel through the protective layer of mineral oil. The yield was four randomly oriented single crystals obtained in six growing attempts. For easy handling of the grown boules, a screw eye was threaded into the top of each. This end of the crystal was later discarded.

The chemical activity of sodium made it necessary to use rather extreme tactics to etch the boule to look for grain boundaries. At room temperature, the methanol etch followed by a rapid quench in xylene, which was successful in the case of lithium,⁵ could not be applied to sodium because the action was far too rapid. We finally used as an etchant a mixture of roughly half and half commercial diethyl ether and methanol cooled to nearly liquid nitrogen temperature. Increased methanol content in the etchant gave faster action, less gave better etch pits. The procedure followed was to lower the test tube containing the etchant part way into a Dewar of liquid nitrogen, then to lower the boule into the mix. This etching process gave brilliant crystallographic blaze planes and a very bright metallic luster to the surface of the sample, on which grain boundaries were clearly visible.

Since all these observations had to be made while the sample was immersed and at low temperature, orientation of the crystals using the blaze plane optical reflections was not convenient. Once the boule was observed to consist of a single crystal, it was oriented using transmission Laue x-ray photographs of the

crystal with the aid of the set of transmission Laue photographs of a body-centered cubic lattice published by Majima.⁶ In addition, the high intensity of thermal diffuse scattering (TDS) simplified the analysis of the transmission Laue photographs of sodium. The blackening of the photographic film due to TDS traced out a geometrical figure with the same symmetry as that of the crystal relative to the x-ray beam.

To prepare a specimen for the x-ray photography, a shim about a millimeter thick was cut off the boule using a string saw charged with a methanol-water mixture. It was possible to cut through the 0.75-inch diameter of the boule in about five minutes. While somewhat faster cutting can be done by charging the saw with pure water, it has been found that the addition of about 10 percent of methanol resulted in formation of a coating on the cut surface of the sodium which proved to be remarkably resistant to further corrosion by the air. With a little practice, it was possible to make cuts whose surface was flat to about 0.005 inch. The thinness of the x-ray specimen resulted in transmission Laue spots which were quite sharp and easy to locate.

Once the orientation of the crystallographic axes of the specimen was known relative to the boule axes, an acoustic specimen could be cut from the boule with any desired orientation. The advantage of growing large diameter single crystal boules is that one can cut reasonably sized oriented acoustic specimens from a single crystal boule of any orientation. The acoustic specimens were all about 2 cm in diameter and ranged in length from 0.9 to 3 cm.

We have found that sodium remains relatively unattacked if kept in contact with pure paraffinics, e.g., isopentane, mineral oil, Vaseline and paraffin, which have been treated by exposure to freshly cut sodium shavings. For example, holding the sample in the string saw mount is done by embedding the bulk of the crystal in Vaseline which has proven stiff enough to keep it in place for the cutting operation.

After cutting the crystal to proper orientation and approximate final size, it was cemented into an aluminum lapping ring³ with pure paraffin. The flattening and polishing of the acoustic faces of the specimen were carried out using as a lap a piece of fine cotton sheeting moistened with methanol and stretched over a piece of plate glass. A final polish was imparted to the surface using mineral oil soaked cotton sheeting on plate glass. These techniques yielded acoustic faces parallel to about 0.001 cm in 1.6 cm. Samples which have been prepared, then stored long enough for a thin layer of oxide to appear on the acoustic faces can be cleaned up by stroking the crystal very lightly over mineral oil soaked cotton sheeting.

For the measurements to be made at high pressures, the quality of the mechanical bond between the quartz

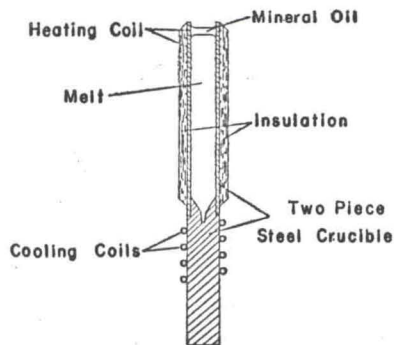


FIG. 1. Crucible for growing sodium crystals.

⁵H. C. Nash and C. S. Smith, *J. Phys. Chem. Solids* 9, 113 (1959).

⁶M. Majima, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* 7, 259 (1927).

transducer and the sample crystal is critical. It must be completely free from gas bubbles as well as provide good acoustic coupling. If any gas bubbles are present at atmospheric pressure, at high pressure the sodium flows into the bubble space with accompanying distortion of the crystal. Early attempts, using paraffin as a cement, failed because there were reactive materials left in the paraffin to react with the sodium producing small bubbles in the bond. The procedure finally adopted was to maintain the crystal and transducer in a bath of the melted paraffin under a fore pump vacuum for several hours at a temperature of 70°C. After this time, the transducer was positioned on the crystal while both were in the bath. Then, both were removed from the hot paraffin bath and a small weight placed on the quartz to hold it in place while the crystal cooled and the paraffin seal froze. This treatment yielded consistently good bubble free bonds, and in addition annealed the sodium crystal before measurement. The paraffin seal will not transmit shear waves into stiff materials such as copper, but it apparently matches the acoustic impedance of sodium well enough to transmit both shear and longitudinal waves. The rf electrode was then painted directly onto the surface of the transducer with duPont 4817 silver paint. The sodium and/or paraffin deforms so easily that the quartz transducer does not break in spite of the large compressibility difference between quartz and sodium.

Measurements

For each crystal, appropriate longitudinal and transverse wave velocities, as well as the change of the velocities with pressure, were measured using the ultrasonic pulse echo method.⁷⁻⁹ The details of technique for measuring the pressure derivatives are described in a recent article.³ It will suffice to say here that the change of acoustic wave velocity as a function of pressure was measured as directly as possible, as the pressure was cycled up, then down several times. A typical raw data plot is shown in Fig. 2, giving the difference between time of arrival of a pulse echo of the C' wave,

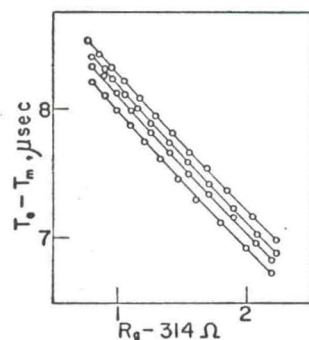


FIG. 2. Typical raw data plot showing difference between time of arrival of a pulse echo of the C' wave in a sodium crystal and a nearby time marker vs the pressure gage coil resistance. Four runs are shown; they have been separated slightly for clarity.

⁷ H. B. Huntington, Phys. Rev. 72, 321 (1947).

⁸ J. R. Neighbours and C. S. Smith, J. Appl. Phys. 21, 1338 (1950).

⁹ J. R. Neighbours, F. W. Bratten, and C. S. Smith, J. Appl. Phys. 23, 389 (1952).

and a nearby calibration time marker, as a function of the change of the pressure gage coil resistance. The pressure range indicated is about 2000 bars.

We are interested in the initial slope of a curve such as Fig. 2. For the stiff materials copper, silver, gold,³ aluminum and magnesium,¹⁰ the curves plotted for change of transit time with pressure did not differ sensibly from a straight line, probably because the fractional change of volume of those materials was small over the 10 000 bar maximum pressure range used. The volume change of very compressible materials such as sodium is comparatively quite large over the same pressure range, so that appreciable changes in slope of such a plot may be expected. In practice the initial slope is difficult to obtain accurately from the data since the curve is not fitted well by a parabolic expression. In the interest of simplicity of data reduction and consistency of procedure from measurement to measurement, the data taken to obtain the initial or nearly initial slope of transit time with pressure,

TABLE I. Analysis and comparison of the values of the elastic constants of sodium. (Units are 10^{10} dyne cm^{-2}). The sample crystal orientation is listed after each value.

	$C=C_{44}$	$C'=(C_{11}-C_{12})/2$	C_{11}^a	$B_s=(C_{11}+2C_{12})/3$
Present	4.204[110]	0.587[110]	7.38[100]	6.62[110]
	4.190[100]	0.586[110]	11.01[110]	6.60[100]
	4.192[110]	0.586[110]		
Average	4.19	0.585		6.61
Fuchs Theo. ($T=0^\circ\text{K}$)	5.36	0.719		
Quimby and Siegel ^b	4.17	0.600		4.41
Bridgman ^c		6.65
Swenson ^d		7.25

^a $C_{11}^a = \rho v_{\text{long}}^2$ see reference (8).

^b Extrapolated by us to 300°K from data taken over the range 80°K to 210°K.¹¹

^c B_s computed by us from isothermal dilatometric data and converted to B_s .¹²

^d Computed from dilatometric data taken at 4.2°K.¹³

are restricted to a large number of points taken over the small pressure range 0–2000 bars. The procedure followed to estimate the initial slope was to make a least squares fit to a straight line covering data taken in the 0–2000 bar range. Thus the results obtained for the pressure derivatives are slightly lower than the true initial slopes. The systematic error is less than 5% in any case.

RESULTS

The room temperature values of the adiabatic elastic constants of sodium¹¹⁻¹³ are given in Table I. This table includes an analysis of the measurements made on each crystal in the present work, the elastic constants of sodium found by Quimby and Siegel¹¹ (which have been extrapolated by us to 300°K), and the value of the adiabatic bulk modulus derived from Bridgman's¹²

¹⁰ R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids 9, 100 (1959).

¹¹ S. L. Quimby and S. Siegel, Phys. Rev. 54, 293 (1938).

¹² P. W. Bridgman, Proc. Natl. Acad. Sci. U. S. 21, 109 (1935).

¹³ C. A. Swenson, Phys. Rev. 99, 423 (1955).

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isothermal measurements of the change of volume of sodium with pressure at 273°K and Swenson's¹³ measurements at 4.2°K.¹⁴ The agreement of the presently found values of the shear constants with the extrapolation of the results obtained by Quimby and Siegel is considered within the error of the extrapolation. The value of B_s found by us is less than 1% lower than the value we obtain from Bridgman's data. We do not know the explanation of the very large difference between the Quimby and Siegel value of B_s and that found by other investigators. The theoretical values of C and C' due to Fuchs' for 0°K are also presented.

An analysis of the present measurements of the pressure variation of the adiabatic elastic constants of sodium at room temperature is given in Table II, together with results obtained from data by Bridgman¹² and Swenson.^{13,14} Note that the result for dC_{44}/dP is based on three crystals of two different orientations, [110] and [100] and the result for dC'/dP is based on

TABLE II. Analysis of the pressure derivative data for sodium. [The quantity $(1/T)(dT/dP)$ is the fractional change of transit time of an acoustic pulse echo per unit pressure change. The units are 10^{-11} cm² dyne⁻¹. These are the results closest to the original measurements and are presented for comparison].

	$(1/T)(dT/dP)$	dC/dP
C	1.74[100]	1.63
	1.65[110]	
	1.67[110]	
C'	1.65[110]	0.226
	1.69[110]	
	1.70[110]	
C ₁₁ ^a	0.216[110]	5.30
Present B_s		3.60
Bridgman ^b		3.30
Swenson ^c		4.13

^a $C_{11}' = \rho v_{long}^2$.

^b dB_T/dP derived from dilatometric data.¹²

^c From dilatometric data taken at 4.2°K.¹⁴

three [110] crystals of different lengths. The measurements of dB_s/dP are derived from four runs made on a single [110] crystal. More extensive measurements of dB/dP were not made at this time because it is intended to repeat all measurements of the pressure variation of the elastic constants of sodium at several temperatures below 300°K in order to estimate the error in assuming the results to apply at 0°K. It should

¹⁴ The dilatometric data by Bridgman¹² and Swenson¹³ are $\Delta V/V_0$ vs pressure. We found the compressibility and its pressure derivative at zero pressure by plotting $(1/P)(\Delta V/V_0)$ from their data and drawing a smooth curve through to points thus obtained. The intercept of this curve on the $P=0$ ordinate is the initial compressibility, $\chi_T = (1/V)(dV/dP)_T$ and the initial pressure derivative of the compressibility may be found using the relation: $dB_T/dP = 2a_2/a_1^2 - 1$ where a_2 is the initial slope and a_1 the intercept of the curve. Then using the relation

$$B_s = B_T(1 + TV\beta^2 B_T/C_P)$$

we have computed a value of B_s from the Bridgman data. At temperatures as low as 4.2°K, the difference between B_s and B_T is negligible.

be mentioned here that the nature of the ultrasonic pulse echo method is such that the variation of the shear constants is measured directly; i.e., each is independent of measurements made on the other, while in general, determination of the variation of B_s involves use of measurements of the variation of both C_{44} and C' as well as the longitudinal data.³

Room temperature for all of these measurements is $299^\circ\text{K} \pm 1^\circ\text{K}$.

INTERPRETATION OF RESULTS

The elastic constants of a crystal can be expressed as the second derivatives of the crystal binding energy with respect to the appropriate strain. The conventional model¹⁵ on which elastic constant calculations are based considers that the only important contributions to the elastic constants arise from (1) a long range Coulomb interaction between the charged particles making up the crystal, (2) the Fermi energy, and (3) a short range repulsive interaction between closed shell ion cores.

The pressure variation of the elastic constants of copper, silver and gold,³ and of aluminum and magnesium¹⁰ have been interpreted in these terms. In the series of monovalent noble metals copper, silver and gold, the ion core term (3) predominates, while in the polyvalent metals aluminum and magnesium, the Fermi term (2) represents an important contribution to both the shear elastic constants and the bulk moduli, as well as to their pressure derivatives.

In the case of the alkali metals on the other hand, the ion cores are so widely spaced relative to their diameters that the contribution their interaction makes to the elastic constants may be neglected. Also, the alkali metals are monovalent; one expects the Fermi surface to be nearly spherical, to lie entirely inside the first Brillouin zone, and to remain unchanged by elastic distortions which do not change the volume of the crystal. Thus one can neglect the contribution (2) to the elastic shear constants of this series of metals. The Fermi energy will, of course, contribute to the bulk moduli of these materials, and is in fact the major contributor to it. This leaves only the contribution (1) due to the long range Coulombic interactions to account for the values of the elastic shear constants of the alkali metals.

Fuchs² has calculated the Coulomb contribution to the elastic shear stiffnesses of the alkali metals of 0°K on the basis of a model consisting of a lattice of positive point charges at atom sites, imbedded in a uniform sea of electronic charge. Since a number of investigators¹⁶ have shown that the electronic wave function is constant over most of the volume of the alkali metal crystals,

¹⁵ N. F. Mott, *Progress in Metal Physics*, edited by Bruce Chalmers (Interscience Publishers, Inc., New York, 1952), Vol. 3, pp. 90-94.

¹⁶ See for example F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. X.

one expects this model to produce reasonable results for their shear elastic constants. The results obtained by Fuchs for the Coulomb contribution to the shear stiffnesses of body-centered cubic metals with one valence electron per atom are:

$$C \equiv C_{44} = Ke^2/\Omega^{\frac{1}{2}}, \quad C' \equiv \frac{1}{2}(C_{11} - C_{12}) = K'e^2/\Omega^{\frac{1}{2}}, \quad (1)$$

where e is the electronic charge, Ω is the atomic volume and K and K' are constants. In addition, Fuchs presents a modification to the above results to take into account the difference of the electron charge density at the surfaces of an atomic polyhedron, from the value e/Ω which would obtain if the electron charge were distributed uniformly over the volume Ω of the cell. The modification to C and C' consists of adding a multiplicative factor Z^2 , where Z represents the ratio of the actual charge density at the cell boundary to the value e/Ω , yielding:

$$C = Z^2Ke^2/\Omega^{\frac{1}{2}}, \quad C' = Z^2K'e^2/\Omega^{\frac{1}{2}}. \quad (2)$$

If one represents the valence electronic wave function in the crystal by

$$\psi_0(\vec{r}) = [\mu_0(\vec{r})/\Omega^{\frac{1}{2}}] \exp i\vec{k} \cdot \vec{r},$$

where $\mu_0(\vec{r})$ is the wave function of the lowest electronic state, normalized over the volume of the atomic polyhedron, Z is given by: $Z = |\mu_0(\vec{r}_e)|^2$ where \vec{r}_e is the position vector of any point on the cell boundary. If one examines the wave function in the approximation that the atomic polyhedron has been replaced by a sphere of equal volume, as has been done by Wigner and Seitz and others, the expression for Z becomes $Z = |\mu_0(r_s)|^2$ where r_s is the radius of the "S" sphere with volume Ω . That is, $\frac{4}{3}\pi r_s^3 = \Omega$. This yields for C and C' the results:

$$C = |\mu_0(r_s)|^4 Ke^2/\Omega^{\frac{1}{2}}, \quad C' = |\mu_0(r_s)|^4 K'e^2/\Omega^{\frac{1}{2}}. \quad (3)$$

Measurements of the elastic constants of the alkali metals lithium,⁵ sodium,¹¹ and potassium¹⁷ have been made over a range of temperatures. Results of these measurements are shown in reference (5), where the experimental values of C and C' are plotted as a^4C/e^2 and a^4C'/e^2 versus temperature in order to compare them with the corresponding Fuchs theoretical result which is indicated on the $T=0^\circ\text{K}$ ordinate. a is the lattice parameter and is proportional to $\Omega^{\frac{1}{3}}$. Bender's measurements on potassium were made only at 78°K and are marked by triangles. It may be seen that the agreement at 0°K is not perfect, but that it predicts the large anisotropy ratio C/C' which is observed in these materials. The results for the shear elastic constants are discussed in greater detail in reference (5).

It is possible to extend the theoretical results for the shear constants of the alkali metals to obtain a prediction of their pressure (or better, volume) variation.

¹⁷ O. Bender, Ann. Physik 34, 359 (1939).

Using the unmodified equation (1),

$$d \ln C / d \ln \Omega = d \ln C' / d \ln \Omega = -\frac{1}{2}.$$

An experimentally determined value of each of $d \ln C / d \ln \Omega$ and $d \ln C' / d \ln \Omega$ can be found from the corresponding pressure derivatives, using the relation $d \ln G / d \ln \Omega = -B_T(dG/dP)$ where G may be any quantity. This with values of dC/dP and dC'/dP from Table II yields the results: $d \ln C / d \ln \Omega = -2.4$, $d \ln C' / d \ln \Omega = -2.4$, which are nearly a factor of two larger than the prediction. Possibly the most remarkable observation to be made about these experimental results is the indication they give that the elastic anisotropy is essentially independent of the compression of the crystal (at 299°K at least). *This observation rules out in the practical sense any interaction between neighboring ion cores of the crystal because the nearest neighbor ion core interactions in a low density bcc metal would be expected to increase C and decrease C' from their respective values without ion core interaction, with rapidly increasing effect as the pressure was applied, contrary to the observations.* The indication is then that the electronic charge density at the boundary of the atomic polyhedron is changing with volume faster than $1/\Omega$, or in other words, $\mu_0(r_s)$ as defined earlier is increased as Ω is decreased. Using the equations (3) together with $d \ln C / d \ln \Omega$ and $d \ln C' / d \ln \Omega$, we obtain the result:

$$\left. \frac{d \ln C}{d \ln \Omega} \right|_{\Omega=\Omega_0} = -\frac{1}{2} + 4 \left(\frac{d \ln \mu_0(r_s)}{d \ln \Omega} \right)_{\Omega=\Omega_0} = -2.4, \quad (4)$$

where Ω_0 is the equilibrium zero pressure atomic volume. Whence:

$$\left(\frac{d \ln \mu_0(r_s)}{d \ln \Omega} \right)_{\Omega=\Omega_0} = -0.27. \quad (5)$$

The work of various theoretical investigations¹⁸⁻²⁰ indicates values of $[d \ln \mu_0(r_s) / d \ln \Omega]_{\Omega=\Omega_0}$ at $T=0^\circ\text{K}$ which lie between -0.08 and -0.13 .

Interpretation of the pressure variation of the elastic constants of Aluminum¹⁰ by Schmunk and Smith, required an assumption that the electrostatic contribution to the shear elastic constants varied as r^{-8} instead of r^{-4} .

Bulk Modulus

We consider now the more difficult question of interpretation of the value of the bulk modulus and its variation with volume. Interpretation of the elastic constants appropriate to strains which involve a volume change is, in general, more difficult and more susceptible to error than interpreting shear elastic constants and their volume variation. Since some of the contributions to the cohesive energy of the crystal may

¹⁸ H. Brooks, Phys. Rev. 112, 344 (1958); 91, 1028 (1953).

¹⁹ E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933) 46, 1002 (1934).

²⁰ J. Bardeen, J. Chem. Phys. 6, 367 (1938).

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be considered to depend on volume only, they give no contribution to the pure shear elastic constants.

Bardeen²⁰ and others^{19,21,22} have deduced pressure-volume relations for the alkali metals and compared the results with experimental *p-V* relations. Bardeen used Bridgman's²³ values of $\Delta V/V_0$ vs pressure for the alkali metals, making an extrapolation to 0°K of measurements made at 293°K. Since that time, compression measurements on the alkali metals have been made by Swenson¹³ at 4.2°K, and measurements on single crystals of sodium by the present author give values of the adiabatic bulk modulus and its pressure variation at room temperature more directly. The question arises then, which data to use in this interpretation.

Comparison of the results derived from Bridgman's compression data for sodium taken at 293°K and from Swenson's data taken at 4.2°K and shown in Tables I and II indicates that the initial bulk modulus increases about 15% in going from 293° to 4.2°, but that the initial values of dB/dP are essentially the same for the two temperatures. The low-temperature value of compressibility of sodium calculated from Swenson's data is about 15% above the 0°K value computed by Bardeen by theoretical extrapolation from the high temperature Bridgman data and displayed in Bardeen's Fig. 2.²⁰ Examination of the results obtained by Quimby and Siegel¹¹ for the adiabatic bulk modulus of sodium obtained over the range 80 to 210°K indicates an expected change of about 18% in going from 293°K to 4°K. However, their absolute values of B_0 are out of line with those found by other investigators as shown in Table II.

We have chosen to apply the initial value of B_T derived from Swenson's low temperature data and our own value of dB_0/dP measured at room temperature on single crystals.

The bulk modulus B and its variation with volume $dB/d \ln \Omega$ may be written in terms of the cohesive energy per atom as follows:

$$\begin{aligned} \Omega_0 B &= \Omega^2 \frac{\partial^2 E}{\partial \Omega^2} \Big|_{\Omega = \Omega_0}, \\ \Omega_0 \frac{dB}{d \ln \Omega} &= \Omega^2 \frac{\partial^2 E}{\partial \Omega^2} + \Omega^3 \frac{\partial^3 E}{\partial \Omega^3} \Big|_{\Omega = \Omega_0}. \end{aligned} \quad (6)$$

The cohesive energy per atom may be written as the sum of the energy of the lowest electronic state plus the average Fermi energy, i.e., $E_c = E_0 + E_F$. Following Fröhlich²¹ and Bardeen,²⁰ we take as an approximate expression for E_0 applicable to atomic volumes near the equilibrium volume;

$$E_0 = \frac{A}{(\Omega/\Omega_0)} - \frac{C}{(\Omega/\Omega_0)^3}, \quad (7)$$

and for E_F we take the expression $E_F = B/(\Omega/\Omega_0)^{1/2}$. These expressions are only approximate in that they assume (1) that the values of the wave function near the boundaries of the atomic polyhedra do not differ appreciably from the free electron value, and (2) that the average effective mass of the electrons does not depend on the atomic volume for values near the equilibrium volume. The results given in this paper in the section concerned with volume variation of the shear elastic constants already indicates failure of these assumptions. Let us proceed with the approximate expressions, however, using experimental data to evaluate the constants A , B , and C , then to examine directly the effects of the failures of the assumptions by comparison of A , B , and C with the theoretically expected values. The experimental data used are:

1. The sum of the atomic heat of sublimation and the ionization potential.
2. The lattice parameter.
3. The bulk modulus.

All are to be taken at 0°K and evaluated at $P=0$. In order, these three conditions yield the following equations in terms of the constants A , B , and C of the equation of state,

$$E_c = \frac{A}{(\Omega/\Omega_0)} + \frac{B}{(\Omega/\Omega_0)^{1/2}} - \frac{C}{(\Omega/\Omega_0)^3}; \quad (8)$$

$$10.04 \times 10^{-12} \text{ erg atom}^{-1} = A + B - C,$$

$$0 \text{ erg atom}^{-1} = -3A - 2B + C,$$

$$24.66 \times 10^{-12} \text{ erg atom}^{-1} = 18A + 10B - 4C.$$

Simultaneous solution of these yields:

$$A = 2.29 \times 10^{-12} \text{ erg atom}^{-1},$$

$$B = 5.46 \times 10^{-12} \text{ erg atom}^{-1},$$

$$C = 17.79 \times 10^{-12} \text{ erg atom}^{-1}.$$

The value of

$$\Omega \frac{dB}{d \ln \Omega} \Big|_{\Omega = \Omega_0},$$

predicted by these equations and called the "empirical" value is given by:

$$\begin{aligned} \Omega \frac{dB}{d \ln \Omega} \Big|_{\Omega = \Omega_0} &= -4A - \frac{50}{27}B + \frac{16}{27}C \\ &= -8.73 \times 10^{-12} \text{ erg atom}^{-1}. \end{aligned}$$

Table III contains these values, and for comparison, a theoretical value for B from the free electron equation for the Fermi energy with $m^* = m$, and a theoretical value for C equalling the electrostatic energy of a uniform sphere with volume Ω of one electronic charge surrounding a positive ion, omitting the electrostatic self energy of the electron.²¹

¹⁹ H. Fröhlich, Proc. Roy. Soc. (London) A158, 97 (1937).

²⁰ T. S. Kuhn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950).

²¹ P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 207 (1938).

TABLE III. Calculation of the parameters in the semiempirical equation of state of sodium^a

Atomic volume Ω_0^b	37.8
Ionization potential ^c	1.81
Heat of sublimation ^d	8.23
$-E_c$	10.04
ΩB_0^e	2.74
A (empirical)	2.29
B (empirical)	5.46
B (theoretical)	3.11
C (empirical)	17.79
C (theoretical)	16.6
$-\Omega dB/d \ln \Omega$ (empirical)	8.73
$-\Omega dB/d \ln \Omega$ (experimental)	8.80

^a All entries except the atomic volume are in units of 10^{-12} erg atom⁻¹, Ω_0 is in units of 10^{-24} cm³ atom⁻¹.

^b From x-ray data corrected using S. L. Quimby and S. Siegel thermal expansion data, Phys. Rev. **54**, 70 (1938).

^c F. Seitz, see reference 10.

^d American Institute of Physics Handbook (McGraw-Hill Book Company Inc., New York, 1957).

^e B_0 at 4.2°K from C. A. Swenson, Phys. Rev. **99**, 423 (1955).

In addition, the experimental value of $\Omega dB/d \ln \Omega$ is given to compare with the value calculated from the

equation of state. The atomic volume at 0°K is also given in Table III.

B (empirical) and B (theoretical) do not agree especially well, at least in part due to the structure of the equations, a small error in the bulk modulus results in large errors in B . The values of C (emp) and C (theo) agree quite well, the empirical value of $\Omega dB/d \ln \Omega$ is surprisingly near the experimental value. One would have expected the breakdown of the assumptions regarding the Frohlich-Bardeen equation of state to have yielded an empirical value appreciably less than the experimental value.²²

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~~Crystal Structure of Ferroelectric $\text{LiH}_3(\text{SeO}_3)_2$~~

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~~The structure of the room-temperature ferroelectric $\text{LiH}_3(\text{SeO}_3)_2$ has been determined by x rays, using the heavy atom method, and refined on the IBM 704. The crystals are monoclinic, with space group Pn and $a=6.25$ Å, $b=7.88$ Å, $c=5.43$ Å, $\beta=105.2^\circ$. Fairly strong O-H...O bonds with distances 2.52, 2.56, and 2.57 Å are found, nearly perpendicular to the polar direction. The O-Se-O angles in one of the two selenite ions are rather similar; in the other ion these angles are unequal, as in the structure of H_2SeO_3 . Possible positions for the Li ions are given based on crystal-chemical considerations.~~

I. INTRODUCTION

FERROELECTRICITY is observed in lithium trihydrogen selenite, $\text{LiH}_3(\text{SeO}_3)_2$, over the temperature range from -196°C to 90°C .¹ The spontaneous polarization is the largest yet observed in a water-soluble crystal: $15 \mu\text{coul}/\text{cm}^2$. The coercive field, 1400 volts/cm, is disadvantageously high when compared to that of $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$: 220 volts/cm.²

A recent structure analysis of $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$, utilizing both x-ray³ and neutron⁴ diffraction and the x-ray anomalous dispersion method⁵⁻⁷ for establishment

* This analysis has been supported by contracts with the Air Force Office of Scientific Research, Air Research and Development Command and with the U. S. Atomic Energy Commission.

¹ R. Pepinsky and K. Vedam, Phys. Rev. **114**, 1217 (1959).

² B. T. Matthias, C. E. Miller, and J. P. Remeika, Phys. Rev. **104**, 849 (1956).

³ S. Hoshino, Y. Okaya, and R. Pepinsky, Phys. Rev. **115**, 323 (1959).

⁴ S. Hoshino, Mitsui, Y. Okaya, and R. Pepinsky (to be published).

⁵ Unterleitner, Y. Okaya, and R. Pepinsky (to be published).

⁶ R. Pepinsky and Y. Okaya, Proc. Natl. Acad. Sci. U. S. **42**, 286 (1956).

of the absolute configuration of the polar crystal, has permitted assignment of a polarization and switching mechanism for that ferroelectric.

The x-ray analysis reported here is a first step in the development of similar understanding of the polarization and switching mechanism in $\text{LiH}_3(\text{SeO}_3)_2$. No attempt has been made in this study to locate hydrogen atoms, which would be very difficult if not impossible in the presence of the heavy selenium atom. A neutron analysis at the Brookhaven reactor, and an anomalous dispersion study similar to that accomplished for $(\text{glycine})_3 \cdot \text{H}_2\text{SO}_4$, are in progress.

II. EXPERIMENTAL

The crystals of $\text{LiH}_3(\text{SeO}_3)_2$ used in the present x-ray study were grown from aqueous solution of lithium hydroxide or lithium carbonate and selenious acid in stoichiometric ratios. These crystallize in the monoclinic system, with space group Pn and cell dimensions

⁷ R. Pepinsky, Record Chem. Progr. Kresge-Hooker Sci. Lab. **17**, 145 (1956).

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O2	0
O3	0
O4	0
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