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Report

AD No 205-944

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Single Crystal Elastic
Constants of Lithium

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H. C. NASH
CHARLES S. SMITH

Office of Naval Research
Technical Report No. 24

Contract Nonr - 114103

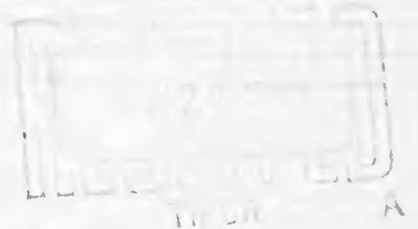
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SINGLE CRYSTAL ELASTIC CONSTANTS OF LITHIUM

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Case Institute of Technology, Cleveland, Ohio



ABSTRACT — The elastic constants of single crystal lithium have been measured by the ultrasonic pulse-echo technique. The results in units of 10^{11} dyne cm^{-2} are;

Temperature, °K	C_{44}	$(C_{11}-C_{12})/2$	B_s
78	1.08	0.116	1.33
155	1.00	0.111	1.25
195	0.96	0.109	1.20

where B_s is the adiabatic bulk modulus. These results are compared with Fuchs' theoretical calculation of the Coulomb contribution to the shear stiffness of the alkali metals, which in lithium is the only significant contribution. Extrapolation of the experimental values to absolute zero gives values for both C_{44} and $(C_{11}-C_{12})/2$ which are lower than the corresponding theoretical values. The extrapolated anisotropy, $C_{44}/(C_{11}-C_{12})/2$, is higher than the value predicted by the theory.



INTRODUCTION

Fuchs¹ has calculated theoretical values for the shear elastic constants of the alkali metals lithium, sodium, and potassium. In these calculations the dominant term is the long-range electrostatic, or Coulomb, stiffness. Since this same physical term occurs as a contribution to the stiffness of all metals, it is desirable to verify these calculations experimentally to the fullest extent possible. Lithium is most suitable for this purpose because the electrostatic stiffness is relatively a more important contribution in lithium than in any other metal; all other contributions to its shear constants are small. Other investigators^{2,3} have measured the single crystal elastic constants of sodium and potassium. One of these, O. Bender³, attempted to produce single crystals of lithium, but the various methods he employed were unsuccessful. This paper describes a method of growing single crystals of lithium, and the results of elastic constant determinations at three temperatures by the ultrasonic pulse-echo technique.

EXPERIMENTAL PROCEDURE

Lithium single crystals were grown from a melt of commercial grade lithium in a crucible of special design shown in Figure 1. The unusual feature of this crucible is that the nucleation tip is formed at the top of the melt, and solidification proceeds downward from the surface of the melt. This crucible form was developed when attempts to produce single crystals with crucibles of the usual shape were unsuccessful. The usual crucible shape has a small diameter nucleation tip at the apex of a conical bottom, and is suitable for growing crystals of many metals by freezing upward from the bottom. However, the high surface tension and low density of lithium do not allow it to flow into a bottom nucleation tip when the ingot is melted. Also, some of the surface contamination on the ingot settles to the bottom of the melt, producing spurious nucleations. With the crucible of special design, impurities which tend to settle are at the end of the melt which solidifies last, and therefore have no effect on the part of the crystal to be used. Impurities which rise to the surface are skimmed off before crystal growth begins.

The entire growing process was carried out in an argon atmosphere. The sample and all surfaces touching it were lightly coated with petroleum jelly. This coating was found necessary to control chemical reactions at the surface of the sample.

Briefly, the growing procedure was the following: The lithium stock was melted and cast into a cylindrical ingot. This ingot was

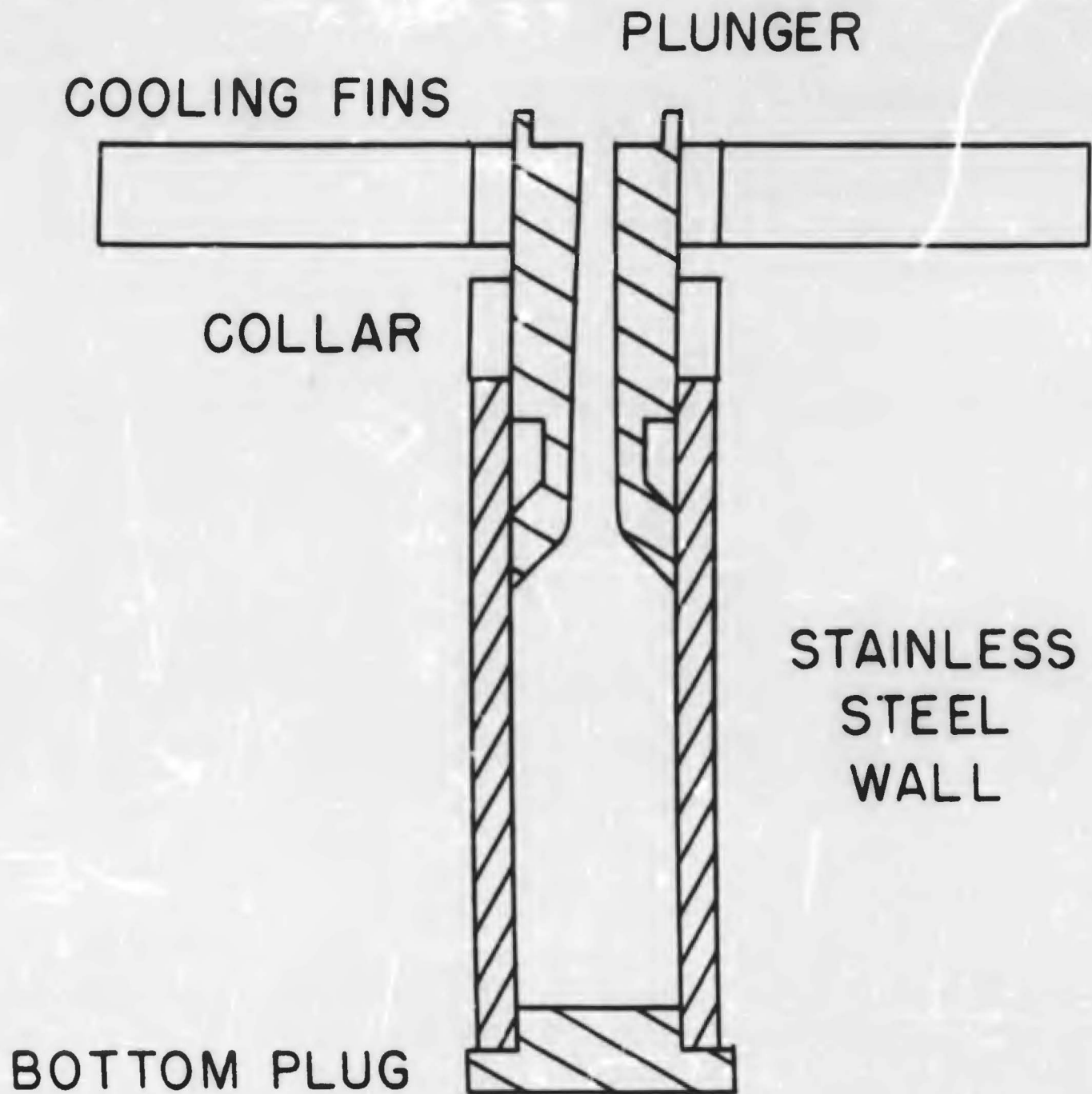


Fig. 1. Crucible used in growing lithium crystals. The crucible is heated by a hot plate at the bottom and nucleation starts at the top.

melted in the cup of the growing crucible and heated at 315°C for one hour on a hotplate. The plunger, preheated to 315°C , was then lowered into the crucible, forcing the molten lithium up through the center channel, until a bead of lithium formed at the top. The adjustable collar held the plunger at this position while the bead of molten lithium with any surface contamination was removed. Next the cooling fins were attached to the top of the plunger. By manual control, the hotplate temperature was lowered at a rate of 30°C per hour until solidification was complete.

Under these conditions the crystal nucleated at the top of the plunger bore, and growth continued downward. A large temperature gradient, initially about 20°C per centimeter, was produced by the combined effect of the controlled hotplate at the bottom, the copper cooling fins at the top, and a stainless steel crucible wall. The crucible bottom plug and the plunger were made of mild steel.

After cooling, the sample was examined for grain boundaries. The coating of petroleum jelly remaining after the growing process was removed by rinsing the sample in xylene. Methanol proved to be a suitable etchant. Best results were obtained by etching for a few seconds and then rinsing in xylene, repeating this process four or five times. If either the sample or the etchant became too warm, the resulting vigorous etching action led to poor grain-boundary definition. This operation and all succeeding ones were carried out in air, protecting the sample with a coating of petroleum jelly except when etching. (The re-

action of the air with the sample between etching in methanol and rinsing in xylene is an essential part of the etching technique. Attempts to follow the same procedure in an argon atmosphere were completely unsuccessful. A white crust covered the sample as soon as it was removed from the methanol. This crust was not soluble in xylene.)

If no grain boundaries were brought out by the etching, the sample was examined by x-ray diffraction techniques. The back-reflection Laue diffraction method used on the heavier metals is not applicable to lithium because of the low scattering power of lithium atoms and the effects of thermal agitation. However, transmission Laue diffraction patterns can be observed directly on a fluorescent screen. These have been observed satisfactorily through the four centimeter length of a single crystal specimen. The x-ray examination of the sample was performed by placing the sample on a traveling stage and translating it through the x-ray beam in such a way that the orientation of the sample with respect to the x-ray beam did not change. In this way each sample was examined throughout its volume. Whenever the x-ray beam crossed a grain boundary, easily observable changes in the diffraction pattern occurred.

The crystal growing method which has been described was used until a sufficient stock of single crystals was in hand. Roughly 50 per cent success was encountered. The crystals were free from mosaic structure as judged by visual examination of the etched crystals and of the Laue patterns. The ingots showed no evidence of frozen out impurities and spectroscopic analysis of the crystals showed no major impurities. Sol-

uble magnesium in particular analyzed at 0.01 per cent.

In measuring the elastic constants of a cubic material by the ultrasonic pulse-echo technique, it is advantageous to have the direction of wave propagation along a $[110]$ direction.⁴ It is then possible to determine each of the elastic shear constants by an independent measurement. In lithium the anisotropy of the shear constants is large (approximately 9). Because of this, the experimental measurement of both shear constants on one single crystal sample is feasible only for propagation directions very close to $[110]$.

Each single crystal sample was cut to produce two parallel faces perpendicular to a $[110]$ direction. To accomplish this, the sample was mounted in a two-circle goniometer in the x-ray beam, and the angle between the sample axis and the nearest $[110]$ direction was measured by rotating the sample until a $[110]$ Laue pattern was observed on the fluorescent screen. A lapping ring was made to hold the sample at this angle. The specimen ends were cut off parallel to the lapping ring faces by means of a string saw charged with methanol; about two hours were required for one cut through a one-half-inch diameter sample. The surfaces obtained were somewhat irregular and therefore the cut was positioned to leave about 0.05 inches of material to be removed by lapping. The faces of the sample were finished by lapping them flat and coincident with the lapping ring faces. The lap used consisted of paper toweling placed on a plate glass backing and moistened liberally with methanol.

A transmission Laue diffraction photograph taken with the sample face perpendicular to the x-ray beam provided the orientation of the

finished sample. All samples were within two degrees of $[110]$. The proper polarization directions for the slow and fast shear waves were also noted from this film to facilitate positioning of the shear wave transducers.

The elastic constants were measured by the ultrasonic pulse-echo method. The appropriate 10 megacycle quartz transducer was cemented to one end of the single crystal sample. At 195°K and 155°K , petroleum jelly was a suitable cement. The transducer was attached to the single crystal sample at room temperature with a thin layer of petroleum jelly. The sample was enclosed in an aluminum cartridge and cooled to the measuring temperature. When cooled, the cement transmitted both shear and longitudinal waves satisfactorily. Attempts to use this cement at 78°K were unsuccessful because the quartz transducers cracked. A small amount of rubber dissolved in the petroleum jelly produced a cement which was satisfactory at this temperature if the sample was not cooled too rapidly.

The electronic equipment used to produce the pulses and measure the transit times has been described previously.⁵

RESULTS

The primary data are the transit time measurements. The longitudinal and the two transverse acoustic-wave velocities propagated in the $[110]$ direction as found from these transit times are shown in Table 1 for the lithium crystal designated as "I" below. To obtain these values, the length of the sample was measured at 298°K , and the lengths at the measuring temperatures were calculated with aid of Pearson's measurements of the lattice parameter of lithium at these temperatures.⁶ The lattice parameter values used were: 3.510 Å, 3.494 Å, 3.489 Å, and 3.482 Å at 298°K , 195°K , 155°K , and 78°K respectively.

The single crystal adiabatic elastic constants of lithium were calculated from the velocity data. These constants at 195°K are shown in Table 2 where Zener's notation for the two shear constants $C = C_{44}$ and $C' = (C_{11} - C_{12})/2$ has been used, and B_s denotes the adiabatic bulk modulus, $(C_{11} + 2C_{12})/3$. Table 2 also compares the results for three samples of different lengths and slightly different orientations as measured at 195°K . The agreement of the three specimens is seen to be good. Crystal I was considered to be the most reliable of the three for experimental reasons; the results for it are quoted in the remainder of the paper.

The lengths of the three crystals are also given in Table 2. The range of lengths used is not large but there appears to be no systematic dependence of elastic constant on length such as would arise if a "transit time error"⁵ were present. This error would not be expected to be large since the acoustic mismatch between lithium and the quartz transducers is large. Extensive experiments with dummy transducers showed no error from this source.

Table 1. Acoustic-wave velocities in the $[110]$ direction. Results are expressed in units of 10^5 cm sec^{-1} and are for Li crystal I.

TEMPERATURE, $^{\circ}\text{K}$	SLOW SHEAR	FAST SHEAR	LONGITUDINAL
78	1.46	4.44	6.69
155	1.43	4.29	6.50
195	1.42	4.22	6.37

Table 2. Comparison of the elastic constants of three lithium samples at 195°K . Results are expressed in units of $10^{11} \text{ dyne cm}^{-2}$.

SAMPLE	C'	C	B_s	Length (Cm)
I	0.1086	0.960	1.197	1.11
II	0.1054	0.969	1.205	0.98
III	0.1064	0.959	1.193	1.40
Ave.	0.1068	0.963	1.198	

The results for the three measuring temperatures are given in Table 3. Also shown in this table are the values of the density which have been used in the calculation of the elastic constants. The densities were obtained from Pearson's lattice parameter measurements⁶ and Hutchison's atomic weight determination.⁷

The values shown in Tables 2 and 3 have been corrected for the difference between the actual direction of propagation of the acoustic waves and the $[110]$ direction. This difference was only a few degrees in the worst case, and less than one-half degree for Crystal I. Perturbation corrections⁴ are zero for the $[110]$ direction and were found to be negligible for the actual orientations.

Because Barrett⁸ has reported that β transformation from BCC to FCC can be induced in lithium at 78°K by plastic deformation, the elastic constants were measured at 195°K both before and after the measurements at 78°K . No change in the elastic constants was observed.

Finally in Table 4 are given the adiabatic stiffnesses, C_{ij} and compliances, S_{ij} for the 195°K temperature. Isothermal quantities have not been computed owing to the lack of specific heat data at this temperature.

Table 3. Values of the adiabatic elastic constants of lithium and of the density. Elastic constants expressed in units of 10^{11} dyne cm^{-2} , and the density in gcm^{-3} .

TEMPERATURE, $^{\circ}\text{K}$	C'	C	B_s	ρ
78	0.116	1.08	1.33	0.5454
155	0.111	1.00	1.25	0.5421
195	0.109	0.96	1.20	0.5398

Table 4. The values for lithium of the measured adiabatic elastic stiffnesses C^s , and the computed adiabatic compliances S^s . Units are 10^{11} dyne cm^{-2} for C and 10^{-11} cm^2 dyne $^{-1}$ for S .

T	C_{11}	C_{12}	C_{44}	S_{11}	S_{12}	S_{44}
78	1.481	1.248	1.077	2.948	-1.348	0.929
155	1.401	1.179	0.997	3.094	-1.414	1.003
195	1.342	1.125	0.960	3.162	-1.442	1.042

DISCUSSION

This problem was undertaken to test the validity of the Fuchs theory¹ of the electrostatic shear stiffness. In the one previous case where a comparison can be made, that of sodium, the calculated values of C and C' at absolute zero are lower than the extrapolated experimental values.⁹ But since the exact form of the extrapolation is somewhat uncertain, it is difficult to evaluate the degree of disagreement.

The Fuchs theory gives the electrostatic contribution to the shear constants of the alkali metals in the form:

$$C = 0.7422 \frac{e^2}{a^4}, \quad C' = 0.0997 \frac{e^2}{a^4}, \quad (1)$$

where "a" is the cubic lattice constant and "e" is the electronic charge. The theory can conveniently be compared with the experimental values by plotting the dimensionless quantity $a^4 C / e^2$ vs. temperature, placing the common theoretical value for all alkali metals at $T = 0^\circ\text{K}$ and the experimental values of individual metals at the measurement temperatures. The reader may then make his own extrapolation.

Figure 2 presents the experimental findings of this work, those of Quimby and Siegel² for sodium, and a single point for potassium due to Bender³, together with the theoretical values of Fuchs, for the two shear constants C and C' . (The lattice constant of potassium has been estimated rather crudely from the room temperature values to be 5.248 Å at 78°K.) It is seen that there is rough agreement between the experimental values for these three alkali metals and those calculated from Equations (1).

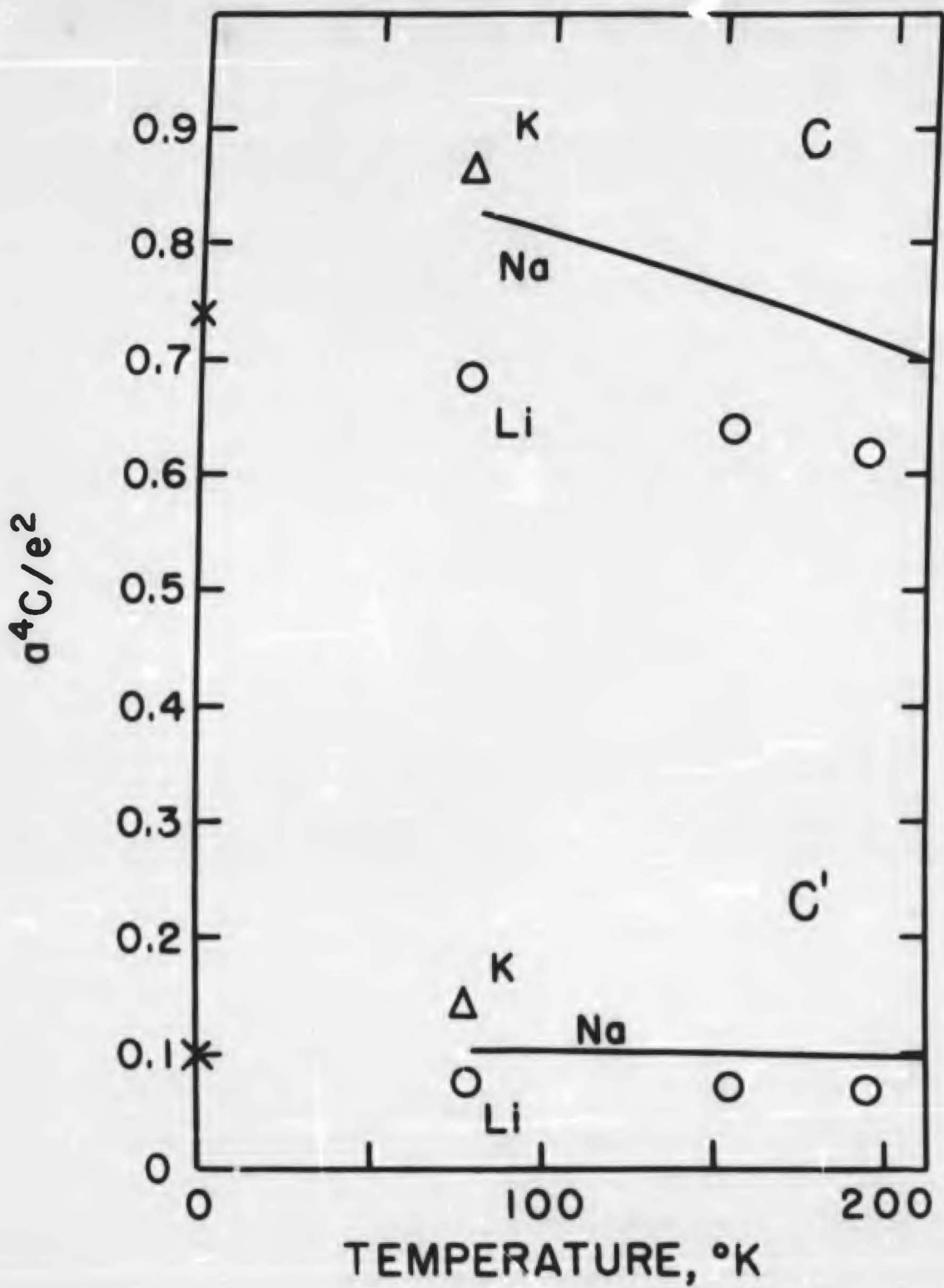


Fig. 2. The elastic shear constants C and C' , expressed in the dimensionless form a^4C/e^2 , plotted as a function of temperature for Li, Na and K. The crosses at $T = 0$ are the theoretical values of the Coulomb contribution.

The experimental values for both C and C' for lithium increase as the temperature decreases, but the increase is not sufficient to bring the extrapolated values up to the predictions of Eqs. (1). On the other hand, the experimental values for sodium at 80°K are already higher than the theoretical values, and extrapolation increases the discrepancies. The same statement holds for potassium if a curve similar to those for lithium and sodium is passed through the single point which is available.

The elastic shear constants of Li, Na, and K fall in a monotonic sequence in Fig. 2 which is the same as their sequence in the periodic table. The number of nodes in the actual "s" wave function for the three metals follows the same sequence. In Fuchs' calculations the effect of shear strain on the wave function in the region of these nodes is neglected, Eqs. (1) being obtained by considering a constant valence electron charge density. These two facts taken together suggest that a more sophisticated treatment of the "electrostatic" term may be all that is necessary to bring about more detailed agreement between theory and experiment for all the alkali metals. However, we consider here some other possibilities.

As Fuchs points out, Equations (1) may be modified on reasonable grounds by the introduction of a common factor " f^2 " on the right side of each, " f " being physically the electron density at the boundary of the unit polyhedron in the metal. Fuchs gives the factor " f " as unity in the case of sodium and potassium. Its value is uncertain for lithium.

Because of the uncertainty in the " f " value for lithium, the theory and experiment can better be compared by inspecting the anisotropy, C/C' , in the elastic constants, which is independent of the value of " f ". The anisotropies have been plotted in Fig. 3. Again there is basic agreement with the theoretical values, but detailed disagreement in a monotonic sequence

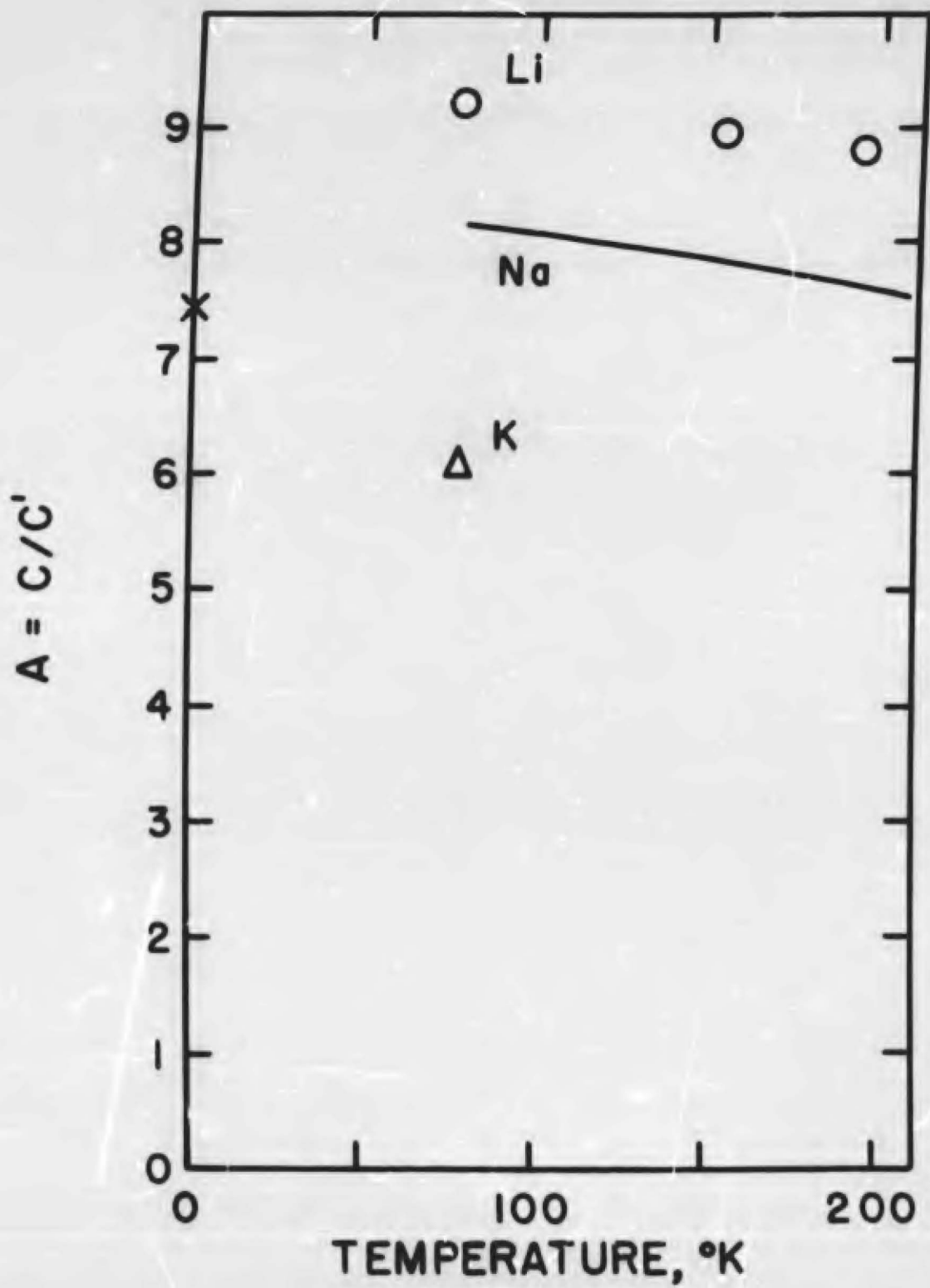


Fig. 3. The elastic anisotropy C/C' plotted as a function of temperature for Li, Na and K. The cross at $T = 0$ is the theoretical anisotropy.

as noted in connection with Fig. 2. We note that the small uncertainty in the lattice constant of potassium present in Fig. 2 has also cancelled out in the anisotropy. It is apparent that the differences between experiment and Eqs. (1) shown in these two figures cannot be resolved by the simple device of introducing "f".

In addition to the electrostatic contribution to the shear constants, Fuchs in his original papers includes a term for the repulsive interaction of the closed-shell ion cores, and a van der Waals term. We regard the theoretical values of these terms as exceedingly questionable, but the effect of introducing them may be considered in empirical terms. For this purpose the van der Waals term may be grouped with the repulsive interaction since both are short range and operate only between nearest neighbor ions. If $W(r)$ is the short-range interaction energy per ion pair, or "bond" (such that $\frac{1}{2}W(r)$ is the energy per atom in these BCC metals), the contribution of W to the shear constants may be written:

$$\Omega C_R = \frac{4}{9} r_0^2 W'' + \frac{8}{9} r_0 W', \quad \Omega C'_R = \frac{4}{3} r_0 W'. \quad (2)$$

where Ω is the atomic volume, r_0 is the equilibrium separation of the nearest neighbors, and differentiation with respect to r is indicated by a prime. For a net repulsive interaction we have $W'' > 0$, and $W' < 0$ and for a short range interaction $|r_0^2 W''| \gg |r_0 W'|$. Thus these contributions to the theoretical values will be positive for C , and negative and smaller in magnitude for C' . Inspection of Figures 2 and 3 shows that the agreement of theory and experiment for lithium cannot be improved for both C and C' by the introduction of such a term alone. The theory and experiment can be brought into detailed agreement in the case of lithium by assuming reasonable

values for C_R and C_R' and combining these with a suitable value of f^2 , but this process amounts to satisfying two experimental numbers by three free parameters and we do not feel justified in pursuing the point.

Bardeen¹⁰ has calculated the bulk modulus of lithium at absolute zero. This value is shown in Table 5 together with the values determined in the present work. The order of magnitude agreement is good. Also shown in this table is the room temperature adiabatic bulk modulus obtained from Bridgman's data by the following approximate relation:

$$B_S \cong B_T \left(1 + \frac{9T\alpha^2 B_T}{\rho C_p} \right)$$

where $\rho = 0.532 \text{ gm cm}^{-3}$, and $\alpha = 46.6 \times 10^{-6} \text{ deg}^{-1}$ were taken from Pearson⁶, $C_p = 0.816 \text{ cal gm}^{-1} \text{ deg}^{-1}$ (11), and $B_T = 1.127 \times 10^{11} \text{ dyne cm}^{-2}$ (12).

The agreement is considered satisfactory, considering the inherent difficulties in Bridgman's method of measuring B_T of lithium.

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Table 5. Experimental and theoretical values of the adiabatic bulk modulus of lithium. Results are expressed in units of 10^{11} dyne cm^{-2} .

TEMPERATURE, °K	B_s	SOURCE
0 Theoretical	1.19	Bardeen ¹⁰
78 Experimental	1.33	This paper
155 Experimental	1.25	This paper
195 Experimental	1.20	This paper
303 Experimental	1.17	Bridgman ¹²

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