

# Pressure Dependence of the Elastic Shear Constants of Li

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The elastic shear constants  $C=C_{44}$  and  $C'=\frac{1}{2}(C_{11}-C_{12})$  of lithium have been measured as a function of pressure at room temperature. The measured values of  $d \ln C/d \ln r$  and  $d \ln C'/d \ln r$  are  $-4.1$  and  $-2.8$ , respectively. This inequality of the two pressure variations is contrary to the situation found in sodium, where the two coefficients were equal. Theoretically, the two coefficients are expected to be the same, if only the electrostatic interaction between the electrons and the ions is responsible for the elastic stiffness of metal. The different behavior in lithium can be understood in terms of the extra contribution to the shear constants arising due to the change in the Fermi energy of the electrons on shearing.

## INTRODUCTION

IN monovalent metals, there are generally two important contributions to the elastic stiffness of the crystal. First is the long-range electrostatic stiffness which arises due to the change in the electrostatic energy of the positive ions immersed in a negative sea of electrons. The other contribution comes from the change in the short-range repulsive interaction of the ion cores. For alkali metals, Fuchs<sup>1</sup> has shown theoretically that the electrostatic stiffness is the dominant one and the short-range contribution is extremely small in comparison. Recent measurements of the pressure dependence of the elastic constants of sodium by Daniels<sup>2</sup> appear to rule out the possibility of any short-range contribution. Since the ratio of the ionic radius to the nearest neighbor distance is even less for lithium than for sodium, we expect a negligible contribution due to the short-range interaction in lithium also. However, the measurements by Nash and Smith<sup>3</sup> indicate that in addition to the dominant contribution due to the Coulomb interaction there is another small contribution, but again the results cannot be satisfactorily accounted for in terms of the short-range interaction.

A third possible source of the shear stiffness can be the change in the Fermi energy of the electrons in a metal on shearing. For a spherical Fermi surface lying wholly inside the Brillouin zone, the shearing of the lattice does not change the Fermi energy and the contribution to the shear constants due to this cause is zero. However, a Fermi surface which has been distorted due to its closeness to the Brillouin zone planes can lead to a finite contribution to the elastic stiffness of a metal. In lithium, Cohen and Heine<sup>4</sup> have recently discussed the experimental evidence which indicates that the Fermi surface in lithium bulges out towards the Brillouin zone planes in the  $[110]$  directions. The

shearing of the crystal raises the energy at some points in  $k$  space while depresses at the others resulting in a net decrease of the Fermi energy which gives rise to the negative contribution in the shear constants  $C=C_{44}$  and  $C'=\frac{1}{2}(C_{11}-C_{12})$ . Thus by the addition of the Fermi energy effect to the electrostatic contribution, it is possible to account for the observed magnitudes of both  $C$  and  $C'$ .

The pressure dependence of the shear constants can further be used to investigate into the nature of the various effects constituting them. In sodium, Daniels observed that the pressure coefficients of  $C$  and  $C'$  are equal, which would be expected only if the electrostatic interaction is considered responsible for the elastic stiffness of the metal. The presence of any other contribution to  $C$  and  $C'$  would most likely lead to the inequality in their pressure coefficients. The present measurements of the shear constants of lithium as a function of pressure were undertaken to make a further investigation of the possibility of the Fermi energy effect.

## EXPERIMENTAL PROCEDURE

Single-crystal specimens of lithium suitable for acoustic measurements were prepared in this laboratory

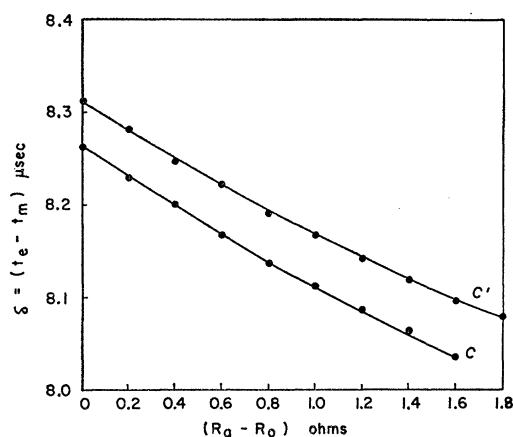


Fig. 1. Typical raw data plot of the difference between the arrival time of a particular echo and a nearby time marker vs the pressure gauge resistance ( $1 \text{ ohm} = 1.389 \times 10^9 \text{ d cm}^{-2}$ ). The total transit times are  $24.82$  and  $43.74 \text{ } \mu\text{sec}$  for  $C$  (5th echo) and  $C'$  (3rd echo), respectively.

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<sup>1</sup> K. Fuchs, Proc. Roy. Soc. (London) **A153**, 622 (1936); **A157**, 444 (1936).

<sup>2</sup> W. B. Daniels, Phys. Rev. **119**, 1246 (1960).

<sup>3</sup> H. C. Nash and C. S. Smith, J. Phys. Chem. Solids **9**, 113 (1959).

<sup>4</sup> M. H. Cohen and V. Heine, *Advances in Physics* edited by N. F. Mott (Taylor and Francis, Ltd., London, 1958), Vol. 7, p. 395.

by J. Trivisonno using the techniques described previously.<sup>5,6</sup> The acoustic faces of the samples were the (110) crystallographic planes and were parallel to about 0.001 cm in a one-cm long sample.

For acoustic measurements a  $\frac{1}{2}$ -in. diam X- or Y-cut quartz transducer was attached to one of the surfaces using paraffin wax which does not react with lithium. The wax was outgassed before use by melting it under vacuum. This procedure gave an airfree seal between the transducer and the lithium sample.

In order to determine the elastic constants, the propagation velocities of the two shear and one longitudinal waves were measured using the conventional method of sending a 10-Mc/sec pulse of 1  $\mu$ sec duration and measuring the time between the arrival of successive echoes. The high-pressure system and the method of measuring the elastic constants as a function of pressure have already been described by Daniels and Smith.<sup>6</sup> The fluid used for transmitting pressure in the high-pressure system was a mixture of isopentane and mineral oil in equal proportions. The common method to determine the change in the elastic constants with pressure is to note the shift of a particular echo relative

TABLE I. Values of the shear constants of lithium and their pressure derivatives. Shear constants denoted by  $X$  are expressed in units of  $10^{11}$  d cm<sup>-2</sup> and  $(1/X)dX/dP$  in units of  $10^{-11}$  cm<sup>2</sup> d<sup>-1</sup>.

	$C$	$C'$	$B_T$
$X$ (300°K)	0.88	0.102	1.17
$X$ (0°K)	1.15	0.121	...
$(1/X)dX/dP$ (300°K)	1.17	0.79	...
$d \ln X / d \ln r$ (300°K)	-4.1	-2.8	...

to a nearby time marker on the cathode ray oscilloscope as the pressure is cycled up and down. The range of pressure used in the present experiment was from 0 to 2000 atm. The data were taken at an interval of about 200 atm. A typical data plot of the difference between the arrival time of a pulse echo and a nearby time marker is shown as a function of pressure in Fig. 1. Both plots for  $C$  and  $C'$  show some nonlinear effects in the high-pressure region. In order to determine the initial slope of the transit time vs pressure plot, a least-squares analysis of the entire data was made.

## RESULTS

The values of the shear constants of lithium expressed as  $C = C_{44}$  and  $C' = \frac{1}{2}(C_{11} - C_{12})$  are given in Table I for 0°K and room temperature. The values at 0°K are obtained by extrapolation of the shear constants data<sup>3,5</sup> at intermediate temperatures. The shear constants data reported for 300°K were obtained by attaching the transducer directly on one of the faces of the

TABLE II. Analysis of the pressure derivative data for two samples of lithium. Both  $(1/t)dt/dP$  and  $(1/X)dX/dP$  are expressed in units of  $10^{-11}$  cm<sup>2</sup> d<sup>-1</sup>.

$X$	Sample	$\frac{1}{t} \frac{dt}{dP}$	$\frac{1}{X} \frac{dX}{dP}$
$C$	Li A	-0.47	1.16
		-0.44	
		-0.44	
	Li B	-0.44	1.19
		-0.46	
		-0.45	
		-0.46	
$C'$	Li A	-0.24	0.77
		-0.25	
		-0.24	
		-0.25	
	Li B	-0.26	0.81
		-0.26	
		-0.27	
		-0.26	

sample and agreed to within 0.5% with the measurements<sup>5</sup> made on the same samples using a buffer quartz between the transducer and the sample.

The behavior of the shear constants at high pressures has been expressed in terms of the fractional rate of change of the shear constants with pressure which has been calculated from the pressure derivative of the transit time using the expression:

$$\frac{1}{C} \frac{dC}{dP} = \frac{1}{3B_T} - \frac{2}{t} \frac{dt}{dP}. \quad (1)$$

The results of the least-squares analysis of the transit time versus pressure data are given in Table II for two samples for several pressure runs made on each sample. For the simplicity of discussion, the pressure derivatives of the two shear constants  $C$ ,  $C'$  have been expressed in terms of the dimensionless quantity  $\pi$ , defined by

$$\pi = (d \ln X / d \ln r) = -(3B_T/X)(dX/dP), \quad (2)$$

where  $X$  stands for either of the shear constants  $C$  and  $C'$ .

The pressure derivatives of the two shear constants and hence the quantities  $\pi$ ,  $\pi'$  were found reproducible to within 3%. Room temperature for all the measurements was  $(300 \pm 2)^\circ\text{K}$ .

## INTERPRETATION

According to the theoretical calculations by Fuchs,<sup>1</sup> the dominant contribution to the shear constants for lithium arises due to the change in the electrostatic energy of the positive ions immersed in a negative sea of electrons. The two shear constants for the electro-

<sup>5</sup> J. Trivisonno and C. S. Smith, Acta Met. (to be published).

<sup>6</sup> W. B. Daniels and C. S. Smith, Phys. Rev. **111**, 713 (1958).

static interaction alone are given by

$$\begin{aligned} C_E &= 0.7422\delta^2 e^2/a^4, \\ C_E' &= 0.0997\delta^2 e^2/a^4, \end{aligned} \quad (3)$$

where  $a$  is the lattice constant and  $(\delta e)$  is the effective charge density at the boundary of the atomic polyhedron. If the electronic charge is distributed uniformly around the positive ions in the atomic polyhedron, then  $\delta$  is unity. For lithium, however, theoretical estimates by Brooks<sup>7</sup> indicate  $\delta > 1$ .

When a metal is subjected to higher pressures, both  $C_E$  and  $C_E'$  are changed because of the change in  $a$  as well as in  $\delta$ . An increase in  $\delta$  on increasing pressure has clearly been demonstrated by the measurements of the shear constants<sup>2</sup> of sodium at high pressures and is in qualitative agreement with the theoretical estimates.

As regards the short-range interactions, we can assume them to be unimportant for the following reasons. If  $w(r)$  is the interaction energy per ion pair,  $r_0$  the nearest neighbor distance, and  $r_d$  the next neighbor distance, then the analytic expressions for the shear constants are:

$$\begin{aligned} C_{sr} &= \left( \frac{4}{9} r^2 w'' + \frac{8}{9} r w' \right)_{r=r_0} + (r w')_{r=r_d}, \\ C_{sr}' &= \left( \frac{4}{3} r w' \right)_{r=r_0} + \frac{1}{2} (r^2 w'' + r w')_{r=r_d}. \end{aligned} \quad (4)$$

It is seen from these expressions that the significant contribution to  $C_{sr}$  can arise from the nearest-neighbor interactions only since  $|(4/9)r^2 w''|_{r=r_0} \gg |r w'|_{r=r_d}$  while in the expression for  $C_{sr}'$  the effect due to the nearest-neighbor interaction is almost completely cancelled out by that due to the next-neighbor interactions because of  $|(4/3)r w'|_{r=r_0} \sim |\frac{1}{2}r^2 w''|_{r=r_d}$ . Therefore the short-range contribution to  $C$  can be positive and finite while to  $C'$  it will almost be zero. Since in lithium the ions are small and are well separated from each other, we will assume that  $C_{sr}$  is also quite small in comparison with  $C_E$ . The pressure dependence of the shear constants of sodium is already a strong support for this assumption.

Therefore, in addition to the electrostatic interaction, the only other effect need to be considered is the Fermi energy effect which arises due to the deviations from a spherical Fermi surface. Cohen and Heine<sup>4</sup> have shown that the Fermi surface of the electrons in lithium bulges out towards the (110) Brillouin zone planes. Several anomalous properties of lithium can be explained in terms of this distortion of the Fermi surface from sphericity. When a shearing strain is applied to such a crystal, the energy is raised at some of the

symmetry points within the Brillouin zone while depressed at the others. The shearing of the crystal, therefore, results in a rearrangement of the electrons in  $k$  space and in a depression of the net Fermi energy which gives a negative contribution to the shear constants of the crystal. This contribution to the shear constants can be calculated approximately by using Jones' method of calculating similar constants for  $\beta$ -brass with necessary modifications required to take into account the fact that the Fermi surface in lithium lies entirely within the first Brillouin zone. Following Jones,<sup>8</sup> we treat the distortion of the Fermi surface by one pair of Brillouin zone planes. We may represent the energy function for this case by

$$\epsilon = \alpha[k^2 - k_z^2 + p_n^2 F(z)]. \quad (5)$$

Here  $p_n = \sqrt{2}\pi/a$  is the perpendicular distance from the center of the zone to the (110) faces.  $\alpha$  is the ratio of the free electron mass to the average effective mass and  $F(z)$  is a nondimensional function of  $z = k_z/p_n$ . For simplicity of calculations, the  $z$  axis has been taken along the [110] direction. The function  $F(z)$  is so chosen that near the center of the Brillouin zone  $F(z) \rightarrow z^2$  which corresponds to the spherical constant energy surfaces, while at the (110) planes of the Brillouin zone  $F'(1) = 0$ .

Since the Fermi surface lies entirely inside the Brillouin zone, we can denote the maximum value of the Fermi momentum in the  $z$  direction by  $k_f$  so that  $z_f = k_f/p_n \leq 1$ .  $z_f = 1$  will correspond to the situation when the Fermi surface actually makes contact with the (110) planes in the  $k$  space. Since for a spherical Fermi surface  $z_f = 0.878$ , we would expect  $0.878 \leq z_f \leq 1$  for an arbitrarily chosen distorted Fermi surface. For a given distortion, it can easily be shown that the total number of electrons  $N$  and the Fermi energy  $W$  both taken per unit volume are given by

$$2\pi^2 N/p_n^3 = z_f F(z_f) - U_1, \quad (6)$$

and

$$4\pi^2 W/p_n^5 = z_f F^2(z_f) - U_2, \quad (7)$$

where

$$U = \int_0^{z_f} F(z) dz \quad \text{and} \quad U_2 = \int_0^{z_f} F^2(z) dz.$$

Under a pure shear the value of  $p_n$  is changed while the atomic volume remains constant. Thus we can calculate the change in  $W$  on shearing keeping the total number of electrons/unit volume constant. Therefore, for pure shear  $dN=0$  and in that case Eq. (6) gives

$$\left( \frac{dz_f}{dp_n} \right)_{N=\text{const}} = - \frac{6\pi^2 N}{p_n^4 z_f} F'(z_f). \quad (8)$$

<sup>7</sup> H. Brooks, (private communication). M. Blume, Ph.D. thesis, Harvard University, Cambridge, Massachusetts, 1959 (unpublished).

<sup>8</sup> H. Jones, Phil. Mag. **43**, 105 (1952).

According to Jones' model<sup>8</sup> the total change in the Fermi energy resulting from a shear is obtained by adding the individual contributions from all the six pair of (110) Brillouin zone planes. He has shown that the shear constants  $C_f$  and  $C_f'$  may, then, be written in terms of the first and second derivatives of the function  $W$  defined above with respect to  $p_n$ . For a body-centered cubic lattice, they are given by

$$\begin{aligned} C_f &= C_{44} = \frac{1}{2} p_n W'' + \frac{3}{2} p_n W', \\ C_f' &= \frac{1}{2} (C_{11} - C_{12}) = \frac{1}{4} p_n^2 W'' + (7/4) p_n W'. \end{aligned} \quad (9)$$

Substituting for  $W'$  and  $W''$  from Eq. (7) and using Eq. (8) in these expressions leads to the following expressions for  $C_f$  and  $C_f'$ :

$$\begin{aligned} \frac{C_f}{\alpha K} &= -\frac{\nu^2}{4z_f} + \frac{4\nu U_1}{z_f} - \frac{35}{4} \left( U_2 - \frac{U_1^2}{z_f} \right), \\ \frac{C_f'}{\alpha K} &= -\frac{5\nu^2}{8z_f} + \frac{4\nu U_1}{z_f} - \frac{55}{8} \left( U_2 - \frac{U_1^2}{z_f} \right), \end{aligned} \quad (10)$$

where  $K = p_n^5 / 2\pi^2 \text{ ry} / A \text{ H}^3$  and  $\nu = 2\pi^2 N / p_n^3$ .

For lithium  $N = 4.75 \times 10^{22} / \text{cc}$  and the lattice constant at  $T = 0^\circ \text{K}$  is  $a = 3.4795 \text{ \AA}$ .<sup>9</sup> This gives  $\nu = 0.4501$  and  $K = 10.47 \times 10^{11} \text{ dynes/cm}^2$ . The values of  $U_1$  and  $U_2$  can be determined if the form of the function  $F(z)$  is known. Jones assumed a form

$$F(z) = z^2 - \lambda z^{2/\lambda},$$

where  $\lambda \ll 1$ . Using this form of  $F(z)$ , one can easily evaluate the expressions for  $N$  and  $W$  from Eqs. (6) and (7) in terms of the distortion parameters  $z_f$  and  $\lambda$ . By using the number of electrons/unit volume as known,  $\lambda$  can be calculated numerically as a function of  $z_f$ . The final figures for  $C_f$  and  $C_f'$  can then be

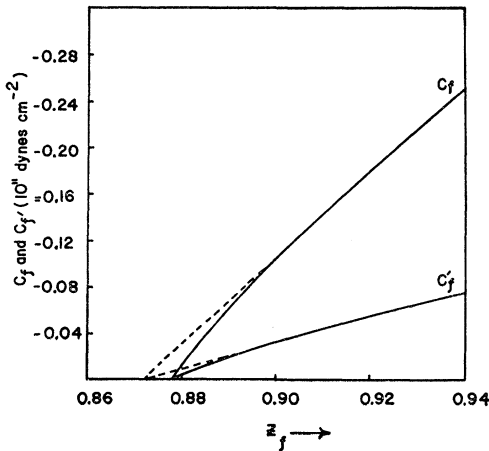


FIG. 2. Fermi energy contributions  $C_f$  and  $C_f'$  plotted as a function of the Fermi surface distortion parameter  $z_f = k_f / p_n$ . Both  $C_f$  and  $C_f'$  are negative and are in units of  $10^{11} \text{ d cm}^{-2}$ .

<sup>9</sup> W. B. Pearson, Can. J. Phys. 32, 708 (1954).

TABLE III. Magnitude of the various effects constituting the shear constants of lithium. (Shear constants are expressed in units of  $10^{11} \text{ d cm}^{-2}$ .)

Electrostatic effects		
Shear constants	$C_E = 1.33$ ;	$C_E' = 0.18$
Pressure coefficients	$\pi_E = \pi_E' = -4.7$	
Fermi energy effect		
Shear constants	$C_f = -0.18$ ;	$C_f' = -0.058$
Pressure coefficients	$\pi_f = \pi_f' = -8.7$	

obtained as a function of  $z_f$  alone. The results of these calculations are shown in Fig. 2 where  $C_f$  and  $C_f'$  are plotted as a function of the single distortion parameter  $z_f$  using an average effective mass  $m = 1.38m_e$  for the electrons. It is easily seen from the graph that above  $z_f = 0.90$  both  $C_f$  and  $C_f'$  can be approximated by the linear relations:

$$\begin{aligned} C_f &= -3.75(z_f - 0.872) \times 10^{11} \text{ d cm}^{-2}, \\ C_f' &= -1.2(z_f - 0.872) \times 10^{11} \text{ d cm}^{-2}. \end{aligned} \quad (11)$$

The variation of  $C_f$  and  $C_f'$  with volume is, then, given by

$$\pi_f = \pi_f' = -5 + d \ln(z_f - 0.872) / d \ln r. \quad (12)$$

Therefore, if we consider that only the electrostatic interaction and the Fermi energy effect are responsible for the shear constants of lithium and also assume that  $\pi$  and  $\pi'$  are independent of temperature, we can write

$$\begin{aligned} C_{\text{meas}} &= C_E + C_f, \\ (C')_{\text{meas}} &= C_E' + C_f', \\ \pi_{\text{meas}} &= (\pi_E C_E + \pi_f C_f) / C_{\text{meas}}, \\ (\pi')_{\text{meas}} &= (\pi_E C_E' + \pi_f C_f') / (C')_{\text{meas}}. \end{aligned} \quad (13)$$

Substituting for  $C_E$ ,  $C_E'$ ,  $C_f$ ,  $C_f'$  from Eqs. (3) and (11), using the values of  $C_{\text{meas}}$  and  $(C')_{\text{meas}}$  extrapolated to  $0^\circ \text{K}$  and  $\pi_{\text{meas}}$  and  $(\pi')_{\text{meas}}$  at room temperature from Table I, the four Eqs. (13) are sufficient to determine the four unknown quantities  $\delta^2$ ,  $z_f$ ,  $\pi_E$ , and  $\pi_f$ . The solution of the first two of the Eqs. (13) gives  $\delta = 1.07$  and  $z_f = 0.92$ . The final results are given in Table III.

Brooks and Blume<sup>7</sup> have calculated the magnitude of the various effects constituting the shear constants in lithium on slightly different theoretical basis and have obtained  $C_E = 1.34$ ,  $C_E' = 0.18$ ,  $C_f = -0.16$  and  $C_f' = -0.037$  in units of  $10^{11} \text{ d cm}^{-2}$ . The sign and the general magnitude of these theoretical results are in good agreement with the values given in Table III.

A value of  $\pi = -4.7$  gives  $d \ln \delta / d \ln r = -0.35$  which indicates that the electronic charge density at the boundary of the atomic polyhedron in lithium increases with decreasing volume. Such variation has already been observed in sodium though on a rather large scale. The value  $z_f = 0.92$  means that the Fermi surface

bulges out about one third the distance between the free-electron sphere ( $z_f=0.878$ ) and the Brillouin zone planes ( $z_f=1.0$ ). Also using  $\pi_f=-8.7$  in Eq. (12) leads to  $z_f \sim r^{-0.2}$ , which suggests an increase in the distortion of the Fermi surface on decreasing volume. Both these results for the distortion of the Fermi surface are in agreement with the theoretical predictions by Ham.<sup>10</sup> Furthermore,  $z_f=0.92$  corresponds to a  $\lambda=0.194$  which, when used in Eq. (5), gives 0.064 ry for the depression of the energy at the (110) planes from the free-electron value. On Cohen and Heine's model,<sup>4</sup> this gives an energy gap of 0.128 ry across the (110) planes which can be compared favorably with the theoretical estimates<sup>10</sup> ranging from 0.153 to 0.228 ry.

In conclusion, the shear constants of lithium and their pressure coefficients can be explained in terms of the electrostatic interaction and the change in the Fermi energy on shearing, provided a proper dependence

<sup>10</sup> F. S. Ham, Proceedings of the International Conference on Fermi Surface, Cooperstown, 1960 (unpublished).

of the Fermi surface distortion and the electron charge density on volume is taken into consideration. It must be pointed here that although the model, which has been used in the analysis of the present experimental data, gives the variation of the above-mentioned quantities with volume in the direction predicted by theory, their exact numerical magnitudes are to be accepted with some reservations because of the nature of the assumptions involved in the calculation of the Fermi energy effect.

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