

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°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°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°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

( $d \ln C_I/d \ln r$ ). 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.

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