

Pressure Dependence of the Hall Constant of the Alkali Metals*

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The pressure dependence of the Hall constant of the five alkali metals has been measured to 15 000 kg/cm² at room temperature. The purpose of the measurements was to investigate the effect of lattice constant on the warping of the Fermi surface. The Hall constant R is written as $1/Neen^*$, where N is the number of carriers/cc and n^* expresses the deviation from the free electron value of the Hall constant. In all the alkalis except cesium, n^* decreases monotonically with increasing pressure; the decreases range from 5% in 15 000 kg/cm² for lithium to 8% in 15 000 kg/cm² for rubidium. In the case of cesium, n^* passes through a minimum at 5000 kg/cm² and rises to a value of 1.2 at 15 000 kg/cm². The change of n^* between room and liquid nitrogen temperatures was measured and is less than 3% for all the alkalis except lithium. In lithium, n^* decreases about 25% between room and liquid nitrogen temperature. The sign of the pressure dependence of n^* , as well as its magnitude, can be reconciled with recent band structure calculations by Ham only if highly anisotropic scattering times are considered. The pressure results are explained in a semiquantitative manner using a scattering time, τ , that varies by a factor of 3 over the Fermi surface. Consideration of the factors determining the scattering time indicates the both umklapp processes and the large elastic anisotropy of the alkalis contribute to the anisotropy of τ . A crude calculation shows that the present results can be explained by the effects of umklapp processes alone.

THE Fermi surface in metals has recently been extensively investigated, theoretically and experimentally. The alkali metals are of special interest, for they are expected to conform closely to a free electron model, in which the electron energy E is proportional to the square of the electron wave number k , and in which the Fermi surface is consequently a sphere in k space. Furthermore, there have been some calculations which allow the shape of the Fermi surface to be determined. The recent calculations by Ham¹ of the band structure of the alkali metals are of particular importance for several reasons. They provide curves of E vs k in the three principal directions in k space and allow the deduction of an approximate shape for the Fermi surface. They are made for the entire alkali series, using the same method in each case, and should give a qualitative picture of the change in the shape of the Fermi surface as one progresses through the series. They have been carried out for several values of lattice constant and provide a guide to how the Fermi surface should change under pressure.

Despite the fact that there has been considerable progress made in experimental techniques for studying the Fermi surface, the methods that proved very successful in investigating the noble metals, de Haas-van Alphen measurements using pulsed magnetic fields² and measurements of acoustic attenuation in magnetic fields have not been applied to the alkali metals. This is in large part because of the difficulty of growing and measuring single crystals of these very reactive metals.

These techniques for determining the shape of the Fermi surface are quite difficult, one can attempt

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* S. Ham, *Proceedings of the Fermi Surface Conference* (Wiley & Sons, Inc., New York, 1960), p. 9.

† H. von Hoerner, *Phil. Mag.* 5, 105 (1960).

† A. Morse, A. Myers, and C. T. Walker, *Phys. Rev. Letters* 1, 105 (1960).

to glean some information from measurements of the transport properties. In particular, it would be interesting to make such measurements as a function of lattice constant by performing them under pressure. The alkalis are particularly attractive for such measurements, since they are highly compressible; the linear contraction of potassium, for example, is 9% in 15 000 kg/cm². In order to take advantage of the pressures available in the laboratory, the experiment should be done at room or liquid nitrogen temperatures, since at liquid helium temperature the pressure transmitting fluid would freeze at relatively low pressures.

The simplest transport property to measure is the conductivity; Bridgman has measured the resistance of all five alkali metals as a function of pressure.⁴⁻⁶ For a metal having a spherical Fermi surface the conductivity, σ , is given by

$$\sigma = Ne^2\tau/m^*, \quad (1)$$

where N is the number of electrons/cc, e is the electronic charge, τ is an isotropic scattering time, and m^* an effective mass.

For a nonspherical Fermi surface this expression is multiplied by a factor that depends upon the distortion of the surface. Olson and Rodriguez⁷ give this factor for a particular type of warping. Since the conductivity depends upon the magnitude of the scattering time and upon the effective mass, both of which may have strong pressure dependences, Bridgman's data are difficult to interpret. Furthermore, since more detailed study shows the conductivity is relatively insensitive to distortion of the Fermi surface, these data are not useful for studying the pressure dependence of the surface.

On the other hand the expressions for the magneto-

⁴ P. W. Bridgman, *Phys. Rev.* 27, 68 (1926).

⁵ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* 72, 176 (1938).

⁶ P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* 81, 184 (1952).

⁷ R. Olson and S. Rodriguez, *Phys. Rev.* 108, 1212 (1957).

resistance of a metal with a warped Fermi surface obtained by Olson and Rodriguez show that this property is quite sensitive to the shape of the surface. Unfortunately the size of the magnetoresistance effect depends on the square of the mobility and becomes extremely small at room temperature. Measurements by Kapitza⁸ on sodium and lithium using pulsed magnetic fields of 300 kgauss at room temperature showed resistance changes of less than 2%; since the effect goes as the square of the magnetic field ordinary dc magnetic fields of 10 kgauss would produce resistance changes of 0.002%, too small to be useful.

The Hall effect is another transport property that can be studied. The Hall constant, R , is defined by

$$E = RJH, \quad (2)$$

where E is the electric field in the y direction produced in a sample in which a current of density J flows along the x direction and which is subject to a magnetic field H along the z direction. The Hall constant, in units of (volt-cm)/(ampere-gauss), may be written as

$$R = 1/Necn^*, \quad (3)$$

where c is the velocity of light in cm/sec and n^* , which we shall refer to as electrons/atom, is a factor which is unity if the expression for R is derived for the case of free electrons or for any spherical Fermi surface. More accurate treatments of the Hall effect involve solving the Boltzmann transport equation for specific forms of the energy, $E(\mathbf{k})$, and the scattering time $\tau(\mathbf{k})$. The Hall constant is then given as the quotient of two integrals involving the scattering time and energy derivatives taken over the Fermi surface⁹; n^* is then obtained as a factor which depends only on the anisotropy of $\tau(\mathbf{k})$ and $E(\mathbf{k})$, and is independent of the magnitude of τ .

Cooper and Raimes have carried out such a calculation for the case of anisotropic scattering times and warped Fermi surfaces that are described by Kubic harmonics.^{10,11} They express the length of the wave vector of an electron on the Fermi surface as:

$$k = k_0[1 + AY_4(\theta, \phi) + A_1Y_6(\theta, \phi)]. \quad (4)$$

Similarly they write

$$\left(\frac{\partial k}{\partial E}\right)_{E=E_f} = k_0'[1 + BY_4(\theta, \phi) + B_1Y_6(\theta, \phi)]; \quad (5)$$

the derivative is taken at the Fermi energy E_f . The scattering time is also expanded in Kubic harmonics;

$$\tau = \tau[1 + CY_4(\theta, \phi) + C_1Y_6(\theta, \phi)]. \quad (6)$$

The Kubic harmonics $Y_4(\theta, \phi)$ and $Y_6(\theta, \phi)$ are combinations of spherical harmonics having cubic symmetry;

⁸ P. Kapitza, Proc. Roy. Soc. (London) A123, 292 (1929).

⁹ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), p. 226.

¹⁰ J. R. A. Cooper and S. Raimes, Phil. Mag. 4, 145 (1959).

¹¹ J. R. A. Cooper and S. Raimes, Phil. Mag. 4, 1149 (1959).

they are given by¹²

$$Y_4(\theta, \phi) = 5/2(x^4 + y^4 + z^4 - 3/5),$$

and

$$Y_6(\theta, \phi) = 231/2(x^2y^2z^2 - Y_4(\theta, \phi)/55 - 1/105)$$

where $x = \sin\theta \cos\phi$, $y = \sin\theta \sin\phi$ and $z = \cos\theta$. In the principal directions the values of the Kubic harmonics are:

$$Y_4(100) = 1, \quad Y_4(110) = 1/4, \quad Y_4(111) = 1/4 \\ Y_6(100) = 1, \quad Y_6(110) = -13/8, \quad Y_6(111) = 1/4$$

By evaluating the expression for the Hall constant using the above forms for the scattering time and the energy surfaces Cooper and Raimes obtain an expression for n^* ;

$$n^* = 1 + 4/21[9A^2 - 18A(C-B) - (C-B)^2] \\ + 8/13[20A_1^2 - 40A_1(C_1-B_1) - (C_1-B_1)^2]$$

As expected, n^* is unity for spherical surfaces at isotropic scattering times.

Except for the direct volume dependence of pressure dependence of R comes from n^* . Changes in n^* reflect changes in the anisotropy of the Fermi surface and/or the anisotropy of the scattering time. If a measurement of the pressure dependence of the Hall constant is performed in the impurity scattering range the anisotropy of the scattering time is directly related only to the anisotropy of the Fermi surface, the effect of the measurement can be interpreted in terms of changes of the anisotropy of the Fermi surface. In a room temperature measurement lattice scattering is dominant and the possibility of anisotropy of scattering time arising from the elastic anisotropy of the crystal must be considered.

In addition to sensitivity of the Hall effect to the anisotropy of the Fermi surface and of the scattering time there are some experimental advantages to this measurement. It can be performed at room temperature, single crystal samples are not necessary, and if the scattering is dominated by the lattice small concentrations of impurities are not important.

EXPERIMENTAL¹³

The electrical measurements were performed in a dc system using a Rubicon No. 2767 μV potentiometer with a galvanometer amplifier as a detector. The galvanometer amplifier employed a simple optical system to focus the light reflected by the mirror of the potentiometer onto two selenium photocells which were connected so that their voltages opposed each other. One of the pair fed a secondary galvanometer amplifier which had a sensitivity of

¹² F. C. von der Lage and H. A. Bethe, Phys. Rev. 68, 103 (1947).

¹³ The experimental setup is described in Gordon McKay Laboratory Technical Report HP-6, Gordon McKay Laboratory, Massachusetts, 1960 (unpublished).

secondary galvanometer deflection, making it possible to resolve 10^{-8} v. The sample current was 3 amp. The magnet was of laboratory design, with 7-in. pole pieces and a 2-in. gap. After initial checks on the linearity of Hall voltage vs magnetic field, all measurements were made by reversing a fixed field of 6310 gauss.

The samples were placed in a beryllium-copper bomb, which was connected by $\frac{1}{8}$ -in. flexible stainless steel tubing to the piston and cylinder arrangement used to generate the pressure. The bomb has been described in detail elsewhere.¹⁴ The electrical leads were brought out through a four terminal plug of beryllium copper. The pressure was determined by measuring a bridge the change of resistance of a manganin wire which was calibrated by assuming the freezing pressure of Hg at 0°C to be 7640 kg/cm^2 . Pentane was used as the pressure transmitting fluid.

Sample preparation and handling presented some difficulty, since the alkali metals are highly reactive. The usual technique for making and preserving alkali metal samples for electrical measurements is to freeze the metal in glass capillaries or ampules. This is not suitable for measurements under pressure because the contraction of the glass is to generate nonhydrostatic strains in the sample. The sample holder finally developed, shown in Fig. 1, incorporates several compromises. In order to expose the metal to the pressure fluid we had to tolerate some surface oxidation. While it is desirable to have the sample completely free to contract under pressure, it was necessary to constrain it somewhat in order to make reliable contacts and to keep the sample orientation fixed. The relatively small hysteresis found in curves of Hall voltage vs pressure, of the order of 1%, and the agreement of the pressure dependence of the resistance of rubidium with the data of Bridgman on free samples to at least 10%, indicates that the sample is behaving as if it were unconstrained.

The samples of lithium, sodium, and potassium were cleaned under Deo Base, a light mineral oil, by rolling the sheet of the metal to a thickness ranging from 0.007 to 0.050 in. and trimming it to the shape shown while it was on the sample holder. In the case of rubidium and cesium, it was necessary to cool the oil to approximately 5°C in order to reduce the oxidation and, in the case of cesium, to prevent melting. The Deo Base and the pentane pressure transmitting fluid were purified by reacting them with alkali chips and ampules of molten sodium-potassium alloy.

The lithium, from Fairmount Chemical Company, and the potassium from Mallinckrodt Chemical Company, were cleaned by heating to above the melting point under forepump vacuum. The sodium, from Rock and Company, was cleaned by melting under vacuum. The object of the cleaning process was to produce microscopically homogeneous specimens, not to remove

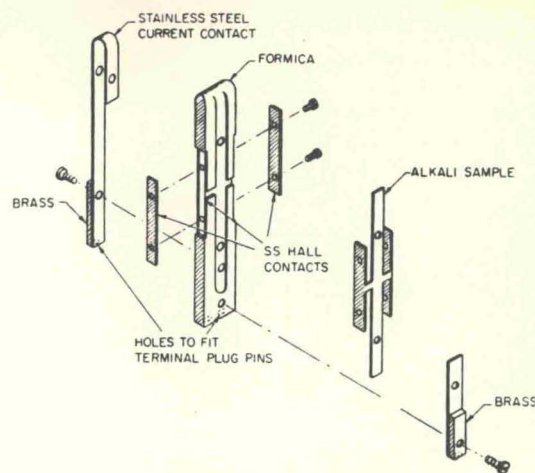


FIG. 1. Sample holder and sample.

impurities which were found not to be important in the lattice scattering range, as would be expected. The rubidium and cesium were obtained from MacKay and from Fairmount Chemical; they had already been distilled into glass vials and no attempt was made to clean them further.

Although the primary interest was in relative changes of the Hall constant, thickness measurements were made on lithium, sodium, and potassium using a 0.001-in. dial comparator with an accuracy of 0.001 in.

Temperature measurements on lithium were performed using a sample holder similar to that used in the pressure experiments. The sample holder and an associated heater were enclosed in a glass tube filled with helium exchange gas and the entire assembly was placed in a nitrogen Dewar; temperatures below 77°K were obtained by pumping on the liquid nitrogen and measured using a copper-constantan thermocouple. Rubidium and cesium were protected from accidental exposure to air by enclosing the sample holder in a formica tube filled with mineral oil.

RESULTS

Figure 2 shows the results of the pressure measurements on typical samples of lithium, sodium, and rubidium, in terms of the normalized Hall voltage at fixed field V_H vs pressure. As an indication of the kind of reproducibility achieved, in a total of five runs on two different samples of rubidium the decrease in V_H in $15\,000 \text{ kg/cm}^2$ was between 12% and 13% for four of the runs and 9% in the fifth run.

In contrast to the pressure results on the other alkalis, the results for different potassium samples did not agree. Figure 3 indicates this difference and the approximate range of the value of V_H at $15\,000 \text{ kg/cm}^2$. The resistance vs pressure curve for potassium was anomalous insofar as it consistently differed from the data of Bridgman.⁵ Our value of 0.4 for the normalized resistance at $15\,000 \text{ kg/cm}^2$ is in sharp disagreement

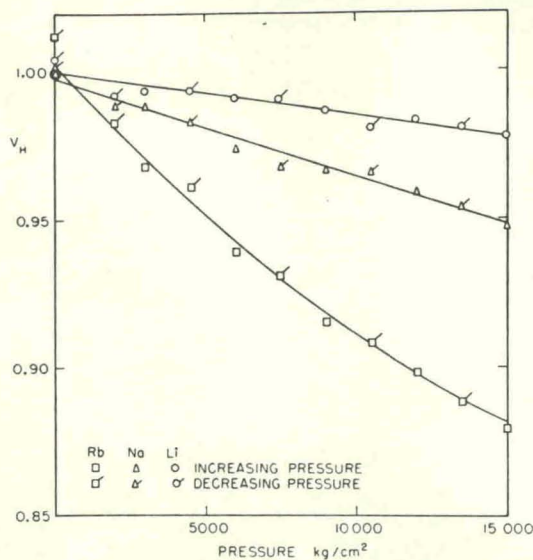


FIG. 2. Normalized Hall voltage vs pressure for lithium, sodium, and rubidium.

with Bridgman's value of 0.22. Because we suspected that our sample holder might be acting as a constraint we repeated Bridgman's experiment, which used a free wire of potassium. Although difficulties with the contacts caused sample current fluctuations and made it impossible to get accurate curves, the value of the normalized resistance at 15 000 kg/cm², 0.4, was confirmed.

Figure 4 shows a typical Hall voltage curve for cesium; this measurement was made at approximately 14°C. The reproducibility was good; the value of V_H at 15 000 kg/cm² was between 0.61 and 0.64 for six runs on two different samples.

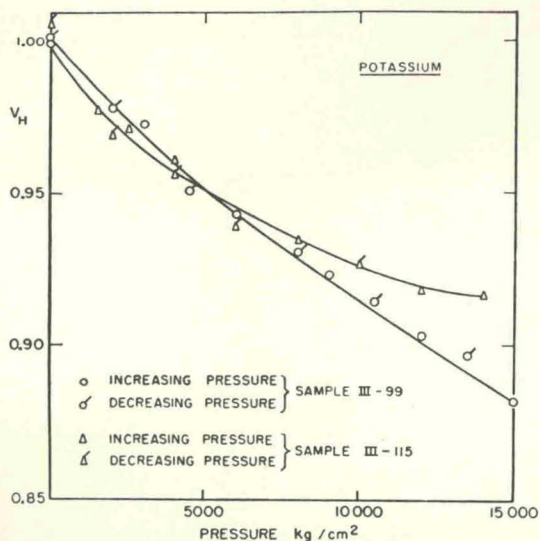


FIG. 3. Normalized Hall voltage vs pressure for two different potassium samples.

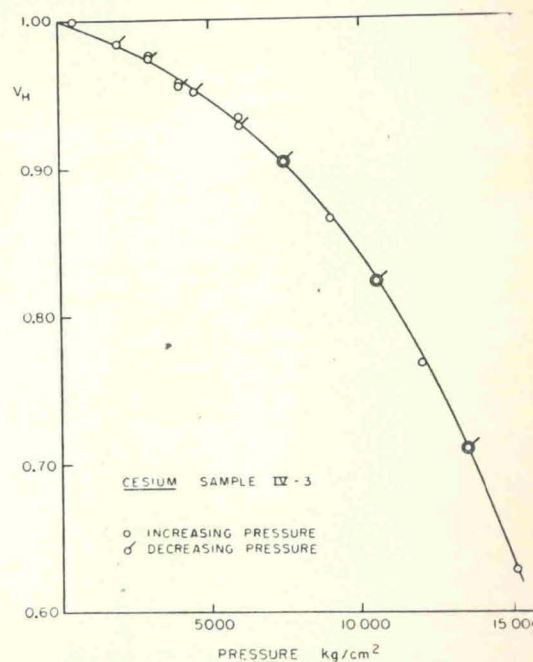


FIG. 4. Normalized Hall voltage vs pressure for cesium

Since the Hall voltage is

$$V_H = RHI/t = HI/Necn^*t,$$

where t is the thickness of the sample and I the sample current two dimensional corrections must be applied to obtain n^* . These give

$$n^* = V(P)/V_H(P)t(P),$$

where $t(P)$ is the thickness as a function of pressure and $V(P)$ the volume. $V(0) = t(0) = 1$. The values of $V(P)$ and $t(P)$ are obtained from Bridgman's compressibility data.^{4,15} n^* was arbitrarily normalized to unity at atmospheric pressure. The resulting curves of n^* vs pressure for the alkalis are shown in Figs. 5 and

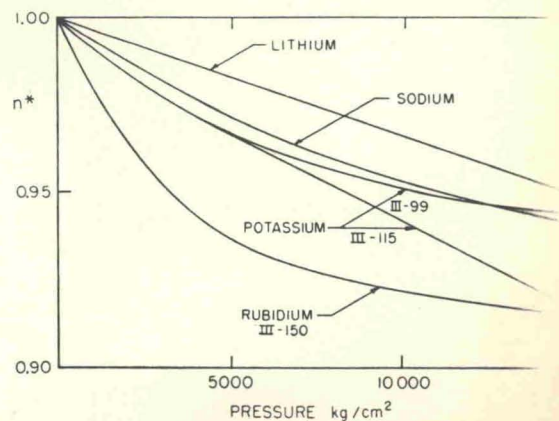


FIG. 5. n^* , normalized electrons/atom vs pressure for lithium, sodium, potassium, and rubidium.

¹⁵ P. W. Bridgman, Proc. Am. Acad. Arts Sci. 70, 93 (1940).

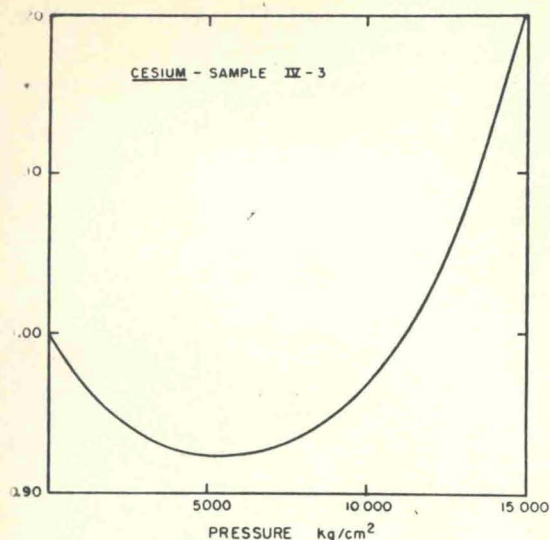


FIG. 6. n^* , normalized electrons/atom vs pressure for cesium.

The curves for lithium and sodium, where the pressure effect was both small and linear, were computed from the average of the least square slopes of V_H vs pressure for two lithium samples and four sodium samples. The curves for potassium, rubidium, and cesium were obtained from the values of V_H read from curves for specific samples which, except for potassium, were well reproducible. Since we were interested in fitting the shape of the n^* vs pressure curve the extra precision to be gained by doing a least squares fit of all the data to a quadratic curve was not needed.

Figure 7 shows n^* vs temperature for lithium. The values of n^* are computed from the measured values of R using Bridgman's values of the thermal expansion. Table I shows the values of V_H and n^* at room and liquid nitrogen temperatures for sodium, potassium, rubidium, and cesium; n^* is not given for cesium because no value of the thermal expansion coefficient is available.

In the course of interpreting the results we became interested in the absolute value of n^* ; in particular we noticed that the literature values of the Hall constant

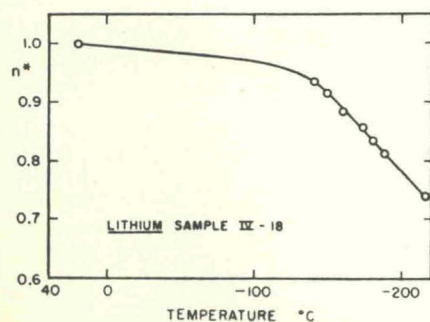


FIG. 7. n^* , normalized electrons/atoms vs temperature for lithium.

TABLE I. Hall voltages of four alkali metals at room and liquid nitrogen temperatures.

| Metal | Temp. | V_H | |
|-----------|-------|------------|------------------|
| | | Normalized | n^* Normalized |
| Cesium | R.T. | 1.000 | |
| | 77°K | 0.973 | |
| Rubidium | R.T. | 1.000 | 1.00 |
| | 77°K | 0.971 | 1.00 |
| Potassium | R.T. | 1.000 | 1.00 |
| | 77°K | 0.981 | 0.98 |
| Sodium | R.T. | 1.000 | 1.00 |
| | 77°K | 1.000 | 0.97 |

for sodium and potassium¹⁶ gave n^* greater than unity. As we expected, for reasons that will be given in the discussion, that n^* should be less than unity we decided to compute the absolute value of the Hall constant from our data where possible. Figure 8 shows $2V_H$ vs the reciprocal of sample thickness for sodium, lithium, and potassium; the slopes of these plots were used to obtain the Hall constants. Table II lists the values of R and n^* obtained, along with values of R calculated on a free electron basis and values of n^* calculated from published data on lithium,¹⁷ rubidium,¹⁸ and cesium.¹⁶

The electrical portion of the measurement is accurate to better than 2%, since the accuracy of the voltage measurement is about 1% and the current and magnetic field measurements are each accurate to better than 1/2%. The thickness measurement, accurate to 0.001 in., gives a 10% error on (0.010 in.) samples and an error of less than 5% on the thicker (0.020 in. to 0.050 in.) samples. Since the latter were favored in fitting straight lines to the points shown in Fig. 8, we estimate the error due to the thickness measurement is 5%. The over-all accuracy of the measurement is 7%. The accuracy of the previous Hall measurements is given as 6% for sodium and 5% for potassium,¹⁶ so that the disagreement falls outside of experimental error.

TABLE II. Hall constants of the alkali metals.

| | Li | Na | K | Rb | Cs |
|---|------|------|------|------|------|
| $R_{calc} \times 10^{13}$ volt-cm amp-gauss | 13.5 | 24.5 | 46.5 | | |
| $R_{exp} \times 10^{13}$ volt-cm amp-gauss | 15.5 | 25.8 | 49.0 | | |
| n_{exp}^* | 0.87 | 0.95 | 0.95 | | |
| n^* from literature values of R | 0.79 | 1.17 | 1.11 | 0.94 | 0.98 |

¹⁶ F. J. Studer and W. D. Williams, Phys. Rev. **47**, 291 (1935).

¹⁷ A. v. Ettingshausen and W. Nernst, Ann. Physik **29**, 343 (1886).

¹⁸ E. Krautz, Z. Naturforsch. **5a**, 13 (1958).

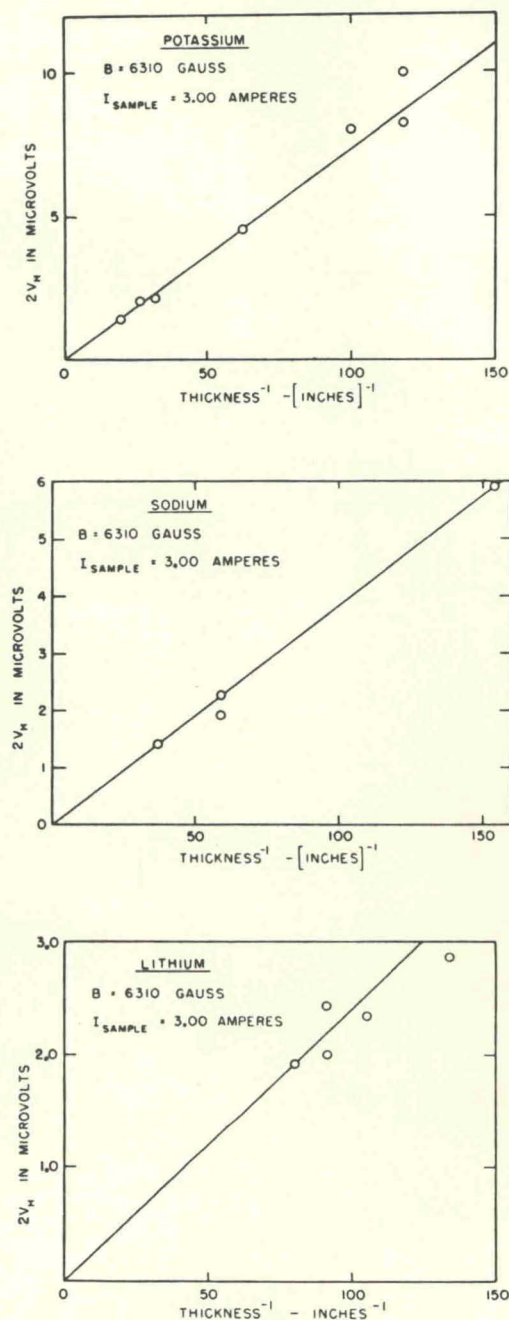


FIG. 8. $2V_H$ vs reciprocal thickness for sodium, lithium, and potassium.

DISCUSSION

The results of the pressure measurements show two important features. First, for the elements lithium, sodium, potassium, and rubidium the value of n^* decreases as the pressure increases. Second, in cesium n^* goes through a minimum as the pressure increases.

Equation (9) for n^* contains too many parameters to allow any conclusions to be drawn from the experimental data alone. However the computations of Ham

can be used to obtain those parameters which describe the warping of the Fermi surface as a function of pressure; we shall see that not even the direction of the experimental effect can be explained on the basis of a pressure dependent warping of the Fermi surface alone and that the scattering time must also be highly anisotropic.

Ham's data give electron energy vs $ka/2\pi$, where a is the lattice constant, for the [100], [110], and [111] directions. If the Fermi energy is known, the length of the k vector to the Fermi surface can be obtained for the three principal directions and Eq. (4) used to compute k_0 , A , and A_1 . The Fermi energy may be obtained from the requirement that the volume in k space enclosed by the Fermi surface contain exactly one electronic state per atom. Using an expression for the volume enclosed by a surface of the form given by Eq. (4) one can show that for the values of the warping coefficients encountered in the alkalis the enclosed volume is, to better than 2%, just that of a sphere of radius k_0 . The condition on the enclosed volume yields the requirement

$$k_0 a / 2\pi = 0.62. \quad (12)$$

The Fermi energy was obtained simply by picking an energy for which the computed value of k_0 satisfied Eq. (12). The results of this procedure are given in Table III along with the values of $ak/2\pi$ for the three principal directions; the last figure on the values of A and A_1 is not justified by the precision of the fit but is given to avoid obscuring some of the changes in the warping parameters. In Table IV we give the warping parameters for lattice constants corresponding to atmospheric pressure and to 15 000 kg/cm², as obtained by a linear interpolation using the data in Table III.

The coefficients B and B_1 are not independent of A and A_1 , but depend upon them through some rather cumbersome algebraic expressions. Table III shows that the k vectors for the [100] and [111] directions

TABLE III. Warping parameters for alkali metals computed from data of Ham.

| Metal | a atomic units | $\frac{ak_{100}}{2\pi}$ | $\frac{ak_{110}}{2\pi}$ | $\frac{ak_{111}}{2\pi}$ | A | A_1 |
|-------|------------------------|-------------------------|-------------------------|-------------------------|--------|--------|
| Li | 8.11 | 0.613 | 0.623 | 0.613 | -0.002 | -0.000 |
| | 6.65 | 0.607 | 0.634 | 0.613 | -0.011 | -0.011 |
| | 5.34 | 0.575 | 0.665 | 0.590 | -0.031 | -0.031 |
| Na | 10.04 | No anisotropy | | | | |
| | 8.11 | No anisotropy | | | | |
| | 6.65 | No anisotropy | | | | |
| K | 11.46 | 0.625 | 0.640 | 0.625 | -0.003 | -0.003 |
| | 10.05 | 0.620 | 0.620 | 0.620 | 0 | 0 |
| | 8.11 | 0.585 | 0.675 | 0.575 | -0.013 | -0.013 |
| Rb | 12.57 | 0.611 | 0.629 | 0.611 | -0.004 | -0.004 |
| | 10.74 | 0.605 | 0.627 | 0.605 | -0.005 | -0.005 |
| | 9.05 | 0.560 | 0.680 | 0.560 | -0.028 | -0.028 |
| Cs | 13.35 | 0.600 | 0.655 | 0.600 | -0.013 | -0.013 |
| | 11.46 | 0.580 | 0.670 | 0.580 | -0.021 | -0.021 |
| | 10.04 | 0.495 | 0.655 | 0.495 | -0.041 | -0.041 |

are usually equal; in this case Eq. (4) leads to the condition $A=0.47A_1$. We used this relation to compute B and B_1 for values of A_1 between 0.00 and -0.08 ; the result can be expressed as

$$B/A = B_1/A_1 = 3.3 - 60A_1, \text{ for } A_1 < 0. \quad (13)$$

Before attempting to fit the curves of n^* vs pressure it is useful to notice that the terms arising from the sixth order Kubic harmonics dominate the expression for n^* , Eq. (9); if $C=0$ and $|A| \leq 0.03$ the terms in A and B contribute only about 1% to n^* . We can simplify the fitting of the data with no significant error by considering only the contribution of terms in A_1 , B_1 , and C_1 to n^* ; the expression for n^* then becomes:

$$n^* = 1 + 12.3A_1^2 - 24.6A_1(C_1 - B_1) - 0.615(C_1 - B_1)^2. \quad (14)$$

Examination of this expression together with Eq. (13) and Table IV shows that if the scattering time is taken to be isotropic, that is if $C_1=0$, the predicted change in n^* will be an increase as the pressure increases. In order to obtain a decrease in n^* with an increase in A_1 a non-zero value of C_1 must be considered. In Fig. 9 we give some curves of n^* vs A_1 obtained using Eqs. (13) and (14) and various forms of C_1 . $C_1 = -0.3$ and $C_1 = -0.4$ represent the simplest nonzero C_1 's whose magnitudes give values of n^* at $A_1=0$ that are in the same range as the observed values. The other forms of C_1 were chosen because they give a steeper initial slope of the n^* vs A_1 curve.

The experimental data can be semi-quantitatively fitted using non-zero C_1 's of the form shown in Fig. 9; that is the change in n^* produced by changes in A_1 of the magnitude indicated in Table IV is consistent with the size of the observed effect. Furthermore the value of n^* passes through a minimum and then rises rapidly; no additional assumptions need be introduced to account for the observed minimum of n^* in cesium. However a quantitative fit does not seem feasible at this stage; some theoretical guidance as to the form of C_1 is needed. It is perhaps worth noting that while the consideration of nonzero C_1 's was forced upon us by the direction of the change in n^* , it is also needed to account

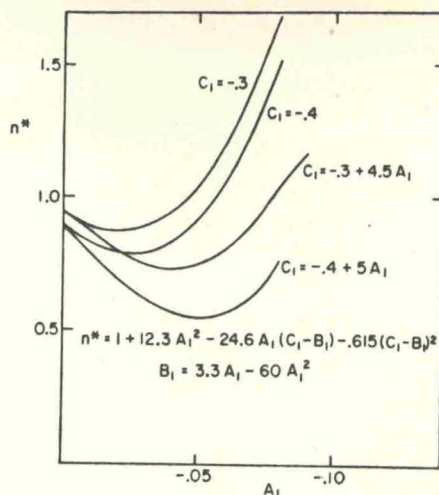


FIG. 9. n^* vs A_1 for various values of C_1 .

for the magnitude of the change in n^* in sodium and lithium, where the predicted change in A_1 is small.

Several difficulties with the fit should be considered. Ham's data, in Table IV, indicate the warping in sodium is zero both at atmospheric pressure and at 15 000 kg/cm², making it impossible to attribute the change in n^* to the pressure dependence of A_1 . However the existence of a low temperature magnetoresistance in sodium implies that there is a small anisotropy of the Fermi surface although this effect might conceivably be connected with the martensitic transition that sodium undergoes above hydrogen temperature or with anisotropic scattering times. If A_1 is nonzero for sodium we expect it to change with pressure and if C_1 is large enough the observed effect could still be accounted for.

The calculated change in A_1 for lithium is small (0.004); in order to account for the observed 5% change in n^* we chose a value for C_1 of $-0.4 + 5A_1$ to obtain a sufficiently steep initial slope on the n^* vs A_1 curve. The value of n^* for lithium at atmospheric pressure obtained from this curve is 0.78, in agreement with the fact that the absolute value of n^* for lithium is substantially less than one (Table II). By contrast the absolute values of n^* are much closer to unity for the other alkalis; this suggests that the value of C_1 for lithium should be different from that for the other alkalis.

In order to account for the observed minimum in n^* for cesium it is necessary to postulate that the atmospheric pressure value for A_1 is approximately -0.02 indicating considerably less warping than Ham's calculations, which give -0.045 . With this assumption about A_1 , the cesium data can be explained by the curve for $C_1 = -0.3 + 4.5A_1$. If one accepts Ham's value of $A_1 = -0.045$ the curve for $C_1 = -0.4 + 5A_1$ will produce a minimum in n^* with further warping, but this curve also implies an unreasonably low value of n^* at atmospheric pressure (0.6). Alternatively, since the work

TABLE IV. Warping parameters of alkali metals at two pressures, computed from data of Ham.

| Metal | Pressure kg/cm ² | a atomic units | A | A_1 |
|-------|-----------------------------|------------------|--------|--------|
| Li | 1 | 6.64 | -0.011 | -0.011 |
| | 15 000 | 6.42 | -0.015 | -0.015 |
| K | 1 | 9.85 | -0.001 | -0.003 |
| | 15 000 | 9.00 | -0.007 | -0.026 |
| Rb | 1 | 10.64 | -0.006 | -0.015 |
| | 15 000 | 9.55 | -0.021 | -0.047 |
| Cs | 1 | 11.44 | -0.021 | -0.045 |
| | 15 000 | 10.01 | -0.041 | -0.088 |

of Ham indicates that the Fermi surface nearly touches the zone boundary, it is possible that the drastic change in the behavior of n^* vs pressure is due to the beginning of contact with the zone face.

Another result of anisotropic scattering times is that the values of n^* for $A_1=0$ are always less than one. As Ham's calculations indicate the Fermi surface for sodium is spherical the value $n^*=1.17$ obtained from previous measurements¹⁶ seems unreasonable, as does the value for $n^*=1.11$ for potassium. If we accept our values for sodium and potassium, the atmospheric pressure value of n^* is less than one for all the alkalis; the proposed explanation for this is the existence of a non-zero C_1 .

The pressure data and the changes in the warping parameter A_1 obtained from Ham's calculation agree semiquantitatively if we consider anisotropic scattering times with values of C_1 of about -0.3 . We shall indicate possible sources of the proposed anisotropy and make an estimate of its order of magnitude.

Mott and Jones¹⁹ have obtained an expression for an isotropic scattering time assuming a spherical Fermi surface and isotropic transition probabilities; that is $P_{kk'}dS'$, the probability per unit time of an electron making a transition between two states k and k' both lying on the same constant energy surface is assumed to be independent of the original state k and to be a function of the angle θ between k and k' only. dS' is an element of area on a constant energy surface about the state k' . If we follow their derivation and let the electric field (z axis) lie along the direction \mathbf{k} for which we wish to compute $\tau(\mathbf{k})$, but do not assume isotropic scattering times or isotropic transition probabilities we obtain:

$$\frac{1}{\tau(\mathbf{k})} = \int_{\text{Fermi sphere}} \left[1 - \frac{\cos\theta\tau(\mathbf{k}')}{\tau(\mathbf{k})} \right] P_{kk'}dS'. \quad (15)$$

Since Eq. (15) is an integral equation for $\tau(\mathbf{k})$ we shall set $\tau(\mathbf{k}')/\tau(\mathbf{k})=1$ inside the integral in order to estimate the anisotropy of $\tau(\mathbf{k})$. This may be regarded as the first step of an iteration procedure for finding τ . With this assumption Eq. (15) can be written as

$$\frac{1}{\tau(\mathbf{k})} = k_s^2 \int_0^\pi d\phi \int_0^{2\pi} [1 - \cos\theta] |\sin\theta| P_{\mathbf{k},\phi}(\theta) d\theta; \quad (16)$$

ϕ is the angle between the plane of k and k' and the zx plane and k_s the radius of the Fermi sphere. These limits on θ and ϕ , rather than the more conventional ones in which θ goes from 0 to π and ϕ from 0 to 2π , are chosen because of the possibility that $P_{\mathbf{k},\phi}(\theta) \neq P_{\mathbf{k},\phi}(-\theta)$. This possibility arises because for an arbitrary direction of k the section of the phonon Brillouin zone centered on the tip of the k vector is not

¹⁹ N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Dover Publications, New York, 1958), p. 259.

symmetrical about the line $\theta=0$. The absence of a sign on $\sin\theta$ is used because of the limits on θ .

Perturbation theory gives

$$P_{\mathbf{k},\phi}(\theta) = \frac{1}{4\pi^2\hbar} \frac{|U_{kk'}|^2}{|\nabla_k E|_k}, \quad (17)$$

where $U_{kk'}$ is the matrix element of the perturbing potential U taken between the initial electron state ψ_k and the final state $\psi_{k'}$; unit crystal volume is assumed. Only the perturbation due to the lattice vibrations is considered, since these dominate the scattering of electrons at room temperature. We write

$$U(\mathbf{r}) = \sum_l V[\mathbf{r}-\mathbf{l}-\mathbf{R}(\mathbf{l})] - V(\mathbf{r}-\mathbf{l}) \\ = -\sum_l \mathbf{R}(\mathbf{l}) \cdot \nabla V(\mathbf{r}-\mathbf{l}); \quad (18)$$

where $V(\mathbf{r}-\mathbf{l})$ is the contribution to the potential at \mathbf{r} associated with the ion at lattice point \mathbf{l} and $\mathbf{R}(\mathbf{l})$ is the displacement of the ion at \mathbf{l} . $V(\mathbf{r}-\mathbf{l})$ includes both the potential due to the ion core and to the electrons that shield the core. This is a refined "rigid ion" model in which a neutralizing charge distribution which moves with the ion core has been introduced.

The wave functions are written in the Bloch form

$$\psi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_k(\mathbf{r}). \quad (19)$$

By changing the origin to the lattice point at \mathbf{l} so that $\mathbf{r}'=\mathbf{r}-\mathbf{l}$ the matrix element may be written as

$$U_{kk'} = -\sum_l \mathbf{R}(\mathbf{l}) \exp[-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{l}] \\ \times \int_{\text{crystal}} \psi_{k'}^*(\mathbf{r}') \nabla V(\mathbf{r}') \psi_k(\mathbf{r}') d\mathbf{r}'. \quad (20)$$

Bailyn²⁰ has computed the integral in Eq. (20) in a calculation that uses the Hartree-Fock equation for the electrons. In his notation

$$\int_{\text{crystal}} \psi_{k'}^*(\mathbf{r}') \nabla V(\mathbf{r}') \psi_k(\mathbf{r}') d\mathbf{r}' = \mathcal{S}[JS], \quad (21)$$

where $\mathcal{S}=\mathbf{k}-\mathbf{k}'/|\mathbf{k}-\mathbf{k}'|$. J denotes the contribution to the matrix element of the ion core alone and S denotes a shielding factor which includes the effect of the electron cloud about the core and the exchange hole. Normalizing factors have been dropped.

If we now express the displacement $\mathbf{R}(\mathbf{l})$ in terms of lattice waves we have,

$$\mathbf{R}(\mathbf{l}) = \sum_p \sum_q \hat{e}_{\mathbf{q},p} a_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{l}}, \quad (22)$$

where $\hat{e}_{\mathbf{q},p}$ is a unit vector which depends on \mathbf{q} , the lattice vibration or phonon wave number and the po-

²⁰ M. Bailyn, Phys. Rev. 120, 381 (1960).

polarization p . a_q is the amplitude of the vibration. Then

$$U_{k,k'} = -\sum_q \sum_p \exp[-i(\mathbf{k}-\mathbf{k}'+\mathbf{q})\cdot\mathbf{l}] a_{q,p} \sum_p \hat{e}_{q,p} \cdot \hat{s} [JS]. \quad (23)$$

The sum over \mathbf{l} yields the condition

$$\mathbf{k}-\mathbf{k}'+\mathbf{q}=\mathbf{K}, \text{ a reciprocal lattice vector, } \text{or}=0, \quad (24)$$

and a value N , the number of ions. Since \mathbf{k} and \mathbf{k}' are specified and we have restricted \mathbf{q} to the first Brillouin zone, \mathbf{q} is specified and the sum over \mathbf{q} reduces to a single term. a_q is obtained from the matrix element for a phonon annihilation or creation operator and is given by

$$a_{q,p} = \left[\frac{\hbar}{2NM\omega_{q,p}} \right]^{\frac{1}{2}} \times \begin{cases} [\bar{n}_{q,p}]^{\frac{1}{2}} & \text{annihilation} \\ \text{or} \\ [\bar{n}_{q,p}+1]^{\frac{1}{2}} & \text{creation,} \end{cases} \quad (25)$$

where M is the mass of the ion and $\omega_{q,p}$ the angular frequency of the phonon \mathbf{q} .²¹

$\bar{n}_{q,p}$ the equilibrium number of phonons is given by the factor;

$$\bar{n}_{q,p} = \frac{1}{\exp(\hbar\omega_{q,p}/kT) - 1}. \quad (26)$$

In the high temperature limit $\hbar\omega/kT \ll 1$ and $a_{q,p}$ becomes

$$a_{q,p} = \left[\frac{\hbar}{2NM\omega_{q,p}} \frac{kT}{\hbar\omega_{q,p}} \right]^{\frac{1}{2}} = \frac{B^{\frac{1}{2}}}{N\omega_{q,p}}. \quad (27)$$

The constants have been lumped into B ; the $1/N$ cancels the N from the sum in Eq. (23).

Then by substituting Eq. (27) into Eq. (23) for $U_{k,k'}$ and dropping the sum over p with the understanding that we will consider the polarization that gives the largest contribution to $U_{k,k'}$ we obtain

$$P_{k,\phi}(\theta) = \frac{B}{4\pi^2\hbar} \frac{[\{JS\}(\theta)]^2 (\hat{e}_{q,p} \cdot \hat{s})^2}{|\nabla_k E|_{k'} \omega_{q,p}^2}. \quad (28)$$

When all the constants are included in D and Eq. (28) is substituted into Eq. (16) we obtain

$$\frac{1}{\tau(\mathbf{k})} = D \int_0^\pi d\phi \int_0^{2\pi} d\theta \times \frac{(1-\cos\theta) |\sin\theta| [\{JS\}(\theta)]^2 (\hat{e}_{q,p} \cdot \hat{s})}{\omega_{q,p}^2 |\nabla_k E|_{k'}}. \quad (29)$$

We can now consider the sources of anisotropy in $\tau(\mathbf{k})$. The density of states factor is, strictly speaking, isotropic since a spherical constant energy surface was assumed in obtaining Eq. (15). If Eq. (15) is still assumed valid for a warped Fermi surface, then

TABLE V. Velocity of sound in potassium. Numerical values are for potassium in units of dynes/cm² × 10⁻¹⁰.

| Direction of polarization | Values of $\rho c_{q,p}^2$ | | |
|---------------------------|----------------------------|--|---|
| | 100 | Direction of propagation | |
| | | 110 | 111 |
| Longitudinal | $c_{11}=4.2$ | $\frac{1}{2}[c_{11}+c_{12}+2c_{44}]=6.4$ | $\frac{1}{3}[c_{11}+2c_{12}+4c_{44}]=7.1$ |
| Transverse [001] | $c_{44}=2.6$ | $c_{44}=2.6$ | — |
| [110] | — | $\frac{c_{11}-c_{12}}{2}=0.41$ | $\frac{c_{11}-c_{12}+c_{44}}{3}=1.15$ |

$1/|\nabla_k E|_{k'}$ acts as a weighting factor in Eq. (29). The variation of this factor with direction can be estimated using Eq. (5); for a warping typical of the alkali metals, $A_1 = -0.02$, $B = B_1 = -0.09$, the value of the density of states factor varies by about $\pm 20\%$ from its average value. This is a relatively weak weighting factor, compared with the effect of $\omega_{q,p}^2$.

We now write

$$\omega_{q,p} = c_{q,p} q, \quad (30)$$

and chose for $c_{q,p}$ the velocity of sound in the elastic limit (small q).

Although this is incorrect for large q , we are only concerned with indicating the relative importance of the longitudinal and transverse branches of the phonon spectrum and of the different directions of the same branch. In Table V, we list expressions for the velocity of sound squared times the density for the three principal directions²² and evaluate these expressions using the published values of the elastic constants for potassium.²³ The table indicates how bad the assumption of an elastically isotropic solid, usually made in computing τ , is for the alkali metals. Since $c_{q,p}^2$ is substantially larger for the longitudinal modes than for the transverse ones the contribution of the transverse phonons to the integral Eq. (29) is weighted more strongly than that of the longitudinal ones. Likewise certain transitions, namely those using [110] phonons polarized 110 will be weighted much more strongly than others. The anisotropy in the sound velocity is averaged in Eq. (29), since transitions from a given initial state \mathbf{k} to those states for which the transition probability is large involve many different phonon directions. Since the angular terms in the integral Eq. (29) weight certain values of the scattering angle, θ , heavily and since the phonon direction for fixed θ depends on the initial state \mathbf{k} we do not expect averaging to be complete, although we expect the anisotropy of $\tau(\mathbf{k})$ to be considerably less than that of $c_{q,p}^2$.

Another source of anisotropy is the term $1/q^2$ in Eq. (29). For a normal (N) process, in which $K=0$, \mathbf{q} depends only on the angle θ between \mathbf{k} and \mathbf{k}' ; how-

²² Jules de Launay, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), p. 267.

²³ *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), pp. 3-81.

²¹ J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), p. 181.

ever for an umklapp (U.K.) process in which $K \neq 0$, \mathbf{q} depends not only on θ , but also on the particular reciprocal lattice vector \mathbf{K} used. The latter depends on the initial state \mathbf{k} .

Figure 10 shows a cross section of the Brillouin zone for a bcc lattice, taken in a [001] plane. The circles are cross sections of the Fermi surface and the dashed square is a zone for phonons, centered on the state \mathbf{k} . The U.K. processes are those for which the final state \mathbf{k}' lies on that portion of the circle centered at 0 which is outside the dashed square. The dependence of $|\mathbf{q}|$ on the initial state \mathbf{k} can be most easily seen by taking $\theta = 180^\circ$ and \mathbf{k} first in the [100] and then in the [110] direction. For the latter direction $|\mathbf{q}|$ is about $\frac{1}{2}$ as large as for \mathbf{k} in the [100].

Normal processes must use longitudinal phonons, at least for those directions in which a separation into longitudinal and transverse modes is possible, because the term $\hat{\epsilon}_{\mathbf{q},p} \cdot \mathbf{s}$ becomes $\hat{\epsilon}_{\mathbf{q},p} \cdot \mathbf{q}$ and this is zero for a transverse mode. For a U.K. process \mathbf{s} is not parallel to \mathbf{q} and transverse phonons participate; indeed the small sound velocity for transverse phonons emphasizes those U.K. processes which use transverse phonons.

We should like to obtain the anisotropy of $\tau(\mathbf{k})$. To do this accurately one would need to choose a direction \mathbf{k} , compute \mathbf{q} , $c_{\mathbf{q},p}$, and $\hat{\epsilon}_{\mathbf{q},p}$ for a large number of points \mathbf{k}' on a Fermi sphere and evaluate Eq. (29). This is a major computational task; a simpler but considerably less accurate procedure is to consider only scattering in two dimensions and evaluate the θ integral in Eq. (29) for fixed ϕ . Some of the loss of accuracy comes from the fact that for some \mathbf{k} directions the θ integral depends strongly on the value of ϕ chosen. For example, if one chose \mathbf{k} in the 110 direction and replaced the Brillouin zone for phonons by a sphere of equal volume, there is ϕ symmetry in the sense that $|\mathbf{q}|$ for fixed θ is independent of ϕ , although $c_{\mathbf{q},p}$ and $\hat{\epsilon}_{\mathbf{q},p} \cdot \mathbf{s}$ are not; on the other hand for \mathbf{k} in a 111 direction this is not true.

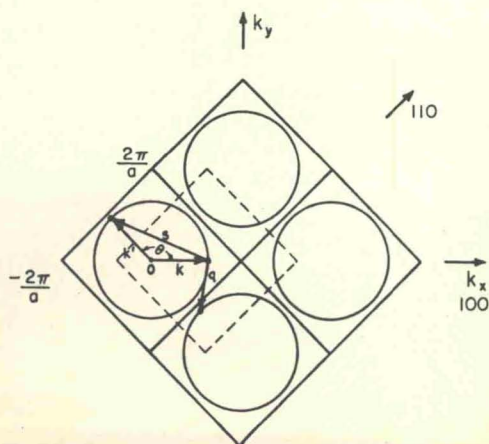


FIG. 10. Cross section, in [001] plane, of Brillouin zones for bcc metal.

We estimated the anisotropy in $\tau(\mathbf{k})$ by evaluating

$$I(\mathbf{k}) = \int_0^{2\pi} \frac{(1 - \cos\theta) |\sin\theta| [JS(\theta)]^2 d\theta}{|\mathbf{q}|^2} \quad (31)$$

for \mathbf{k} in the [100], [110], and [111] directions. This is a very crude procedure, which not only replaces the three dimensional integral in Eq. (29) by a two dimensional one, but also considers the velocity of sound, the polarization factor $\hat{\epsilon}_{\mathbf{q},p} \cdot \mathbf{s}$ and the density of states as constants. The calculation will underestimate the anisotropy in τ since it ignores the anisotropy of the velocity of sound (Table V).

We obtained the values of $(JS)^2$ from Bailyn²⁰; in Table VI we list his values of $u^2(JS)^2$ vs $u = \sin\theta/2$ for potassium and lithium. Potassium was chosen as representative of all the alkalis except lithium, which differs from the others in that $(JS)^2$ goes through a zero near

TABLE VI. Scattering functions for K and Li using Bailyn's values of $u^2(JS)^2$.

| $u = \sin\theta/2$ | θ degrees | $(1 - \cos\theta) \times \sin\theta$ | $u^2(JS)^2$ for K | $u^2(JS)^2$ for Li | $F(\theta)$ for K | $F(\theta)$ for Li |
|--------------------|------------------|--------------------------------------|-------------------|--------------------|-------------------|--------------------|
| 0.00 | 0 | 0 | 0 | 0 | 0.00 | 0.00 |
| 0.10 | 11.5 | 0.004 | 0 | 0 | 0.00 | 0.00 |
| 0.20 | 23 | 0.03 | 0.005 | 0.005 | 0.02 | 0.02 |
| 0.30 | 35 | 0.10 | 0.035 | 0.035 | 0.13 | 0.13 |
| 0.40 | 47 | 0.23 | 0.090 | 0.090 | 0.32 | 0.32 |
| 0.50 | 60 | 0.43 | 0.190 | 0.190 | 0.65 | 0.65 |
| 0.60 | 74 | 0.70 | 0.315 | 0.265 | 1.02 | 0.86 |
| 0.65 | 81 | 0.83 | 0.345 | 0.275 | 1.04 | 0.83 |
| 0.70 | 89 | 0.98 | 0.375 | 0.265 | 1.07 | 0.76 |
| 0.75 | 97 | 1.11 | 0.393 | 0.220 | 1.03 | 0.58 |
| 0.80 | 106 | 1.22 | 0.400 | 0.125 | 0.95 | 0.30 |
| 0.85 | 116 | 1.30 | 0.385 | 0.025 | 0.82 | 0.05 |
| 0.90 | 128 | 1.28 | 0.340 | 0.010 | 0.60 | 0.02 |
| 0.95 | 144 | 1.07 | 0.305 | 0.025 | 0.38 | 0.03 |
| 0.97 | 152 | 0.88 | 0.300 | 0.033 | 0.29 | 0.03 |
| 0.98 | 157 | 0.70 | 0.296 | 0.035 | 0.23 | 0.03 |
| 0.99 | 164 | 0.54 | 0.293 | 0.040 | 0.17 | 0.02 |
| 1.80 | 180 | 0.00 | 0.290 | 0.042 | 0.00 | 0.00 |

$\theta = 120^\circ$. We also tabulate

$$F(\theta) = (JS)^2 (1 - \cos\theta) \sin\theta, \quad (32)$$

for potassium and lithium. Values of \mathbf{q} as a function of θ for \mathbf{k} in the [100], [110], and [111] directions were obtained by measuring on a diagram such as that in Fig. 10, the integral of Eq. (31) plotted as a function of θ , and $I(\mathbf{k})$ evaluated graphically. The results are shown in Table VII; we have also evaluated $I(\mathbf{k})$ counting U.K. processes only. This takes account of the large velocity of sound for the longitudinal phonons by not counting these processes at all.

As pointed out before the integration for $\mathbf{k}(111)$ is unrepresentative since the possible scattering processes depend strongly on the particular great circle on the Fermi sphere for which we have chosen to do the θ integration; because of the strong ϕ dependence no two dimensional integration will give a very meaningful

TABLE VII. $I(\mathbf{k})$, [see Eq. (31)], for various conditions.

| Quantity $1-0.3Y_6$ | Direction of \mathbf{k} | | |
|--|---------------------------|--------------|--------------|
| | [110] 1.5 | [111] 0.5 | [100] 0.7 |
| Using potassium matrix element | | | |
| (a), N and U.K. processes-arbitrary units $[\tau(\mathbf{k})]^{-1} \times 100$ proportional to $\tau(\mathbf{k})$ | 46 | 48 | 57 |
| (b), U.K. processes only $[\tau(\mathbf{k})]^{-1} \times 100$ U.K. only | 2.2 | 2.1 | 1.8 |
| (c), U.K. processes only $[\tau(\mathbf{k})]^{-1} \times 100$ U.K. only | 26 | 34 | 44 |
| (d), U.K. processes only $[\tau(\mathbf{k})]^{-1} \times 100$ U.K. only | 3.8 | 2.9 | 2.3 |
| Using lithium matrix element | | | |
| (a), N and U.K. processes-arbitrary units $[\tau(\mathbf{k})]^{-1} \times 100$ | 58 | 62 | 71 |
| (b), U.K. processes only $[\tau(\mathbf{k})]^{-1} \times 100$ U.K. only | 1.7 | 1.6 | 1.4 |
| (c), U.K. processes only $[\tau(\mathbf{k})]^{-1} \times 100$ U.K. only | 25 | 28 | 40 |
| (d), U.K. processes only $[\tau(\mathbf{k})]^{-1} \times 100$ U.K. only | 4.0 | 3.6 | 2.5 |

mate of $\tau(111)$. On the other hand Eq. (31) can give a meaningful estimate of $\tau(100)$ and $\tau(110)$ in the case of the weak ϕ dependence.

The results show a difference of about 20% in the values of $I(\mathbf{k})$ for the [110] and [100] directions counted both N and U.K. processes and using either the sodium or the potassium matrix element. If only U.K. processes are counted the difference becomes nearly 50% using the potassium matrix element and 60% using the lithium matrix element.

We have also tabulated $1-0.3Y_6$ for the three principal directions. This gives the dependence of $\tau(\mathbf{k})$ on the sixth order Kubic harmonic with $C_1 = -0.3$. It should be pointed out that we have no way of knowing whether there is no reason for C and C_1 to be simply related the way A and A_1 were for certain shapes of the E curves. In addition, even though the influence of n^* may be small because of the smaller size of the coefficients arising from the fourth order Kubic harmonic its influence on τ is not. It is interesting to note that both matrix elements give $\tau(110) > \tau(100)$ as would be the case if τ were proportional to $1-0.3Y_6$.

We conclude that if the matrix elements obtained by Flynn are correct, then the geometry of the U.K. processes alone is sufficient to produce appreciable anisotropies in τ for both potassium and lithium. The velocity of sound is also highly anisotropic in the alkalis and may produce further anisotropy in τ ; like the geometrical factor ($1/q^2$) it is most significant in the clapp region.

The highly anisotropic $\tau(\mathbf{k})$ for lithium is in line with the large deviation of n^* from unity for this metal noted in Table I; however it is not clear why the same deviation does not occur in the case of potassium where the anisotropy is also large. The form of $F(\theta)$ for lithium suggests a possible explanation for the strong temperature dependence of n^* shown in Fig. 7. $F(\theta)$ is much

more sharply peaked in the case of lithium than in the case of potassium and although the peak is at $\theta = 75^\circ$ scattering processes at $\theta = 90^\circ$ are still quite heavily weighted. The wave vectors for phonons involved in scattering from $k(110)$ at $\theta = 90^\circ$ are quite large [approximately 50% large than for $k(111)$ or $k(100)$ and $\theta = 90^\circ$]; as the temperature is lowered some of these phonons are no longer excited and the scattering should be changed severely. The high Debye temperature, $\theta_D = 430^\circ\text{K}$, suggests that there should actually be "freezing out" of phonons at nitrogen temperature even though we are interested in the Debye temperature for transverse phonons which will be lower than the specific heat θ_D . There is, however, also the possibility that the change in n^* may be connected with the martensitic transition occurring near 77°K .²⁴

The small changes in n^* with temperature for sodium and potassium may also be due to the beginning of the "freezing out" of some phonons. However, the scattering function $F(\theta)$ is much less sharply peaked in the case of potassium than in the case of lithium and so the total scattering is much less sensitive to the freezing out of large q phonons. In addition the Debye temperatures are lower for these metals. Both factors should decrease the temperature effect in sodium and potassium.

CONCLUSIONS

The observed pressure effects in the alkalis require the assumption of an anisotropic scattering time, $\tau(\mathbf{k})$, in order to explain how relatively small increases in the warping parameters which describe the Fermi surface cause n^* to decrease. The assumption of anisotropy in $\tau(\mathbf{k})$ is required both by the sign of the pressure effect, and, in the case of sodium and lithium, by its magnitude. The anisotropy in the shape of the Fermi surface is small, except possibly in the case of cesium, while the anisotropy in τ , is large. The anisotropy in τ comes from: (1) the fact that $1/|q|^2$ occurs as a \mathbf{k} dependent weighting factor in the expression for τ and (2) the fact that $1/c_{q,p}^2$ occurs as a highly anisotropic weighting factor in the same expression.

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²⁴ C. S. Barrett, Phys. Rev. 72, 245 (1948).