

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 k for which we wish to compute $\tau(k)$, but do not assume isotropic scattering times or isotropic transition probabilities we obtain:

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

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

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

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 $P_{k,\phi}(\theta) \neq P_{k,\phi}(-\theta)$. 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

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

Perturbation theory gives

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

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 \mathcal{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,

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

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

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

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