Electrical and Thermal Resistivities and the Fermi Surface of Monovalent Metals

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Crude information about the nature of the Fermi surface in alkalis and noble metals is derived from the ratio of low-temperature electrical and thermal resistivities. The values of the characteristic temperatures occurring in electrical and thermal resistivities are evaluated through the use of Houston's method. The inferences regarding the Fermi surface are found to be consistent with recent refined measurements.

CRUDE information about the grosser features of the Fermi surface can be obtained through the study of transport properties like electrical and thermal resistivities. The ratio of low-temperature electrical and thermal resistivities can give broad indications about the nature of the Fermi surface.[1-5] The comparison of the observed low-temperature Lorentz ratio with the predictions of the free electron model, and the explanation of the discrepancy in terms of Umklapp processes was first made by Klemens[1] and he drew conclusions concerning the Fermi surface of monovalent metals which are considered to be substantially correct. The quantity

$$D = \frac{64.0}{497.6} \frac{\Theta_\rho{}^6}{\Theta^4{}_W} \frac{\rho_i(T)}{LW_i(T)T^3} \tag{1}$$

should exceed unity for a spherical Fermi surface and should increase with the distortion of the Fermi surface. Here $\rho_i(T)$ is the ideal electrical and $W_i(T)$ the ideal thermal resistivity in the temperature range where they are proportional to T^5 and T^2, respectively, Θ_ρ and Θ_W are the respective characteristic temperatures and L is the Lorentz number. Cohen and Heine[4] first calculated the quantity

$$D' = \frac{64.0}{497.6} \frac{\Theta^2{}_D}{L} \frac{\rho_i(T)}{W_i(T)} \frac{1}{T^3}, \tag{2}$$

which depends only on the measured quantities, and then estimated the ratio

$$D'/D = \Theta^4{}_W \Theta^2{}_D / \Theta_\rho{}^6. \tag{3}$$

Here Θ_ρ and Θ_W are computed from the knowledge of the respective average velocities of sound c_ρ and c_W. A reasonable method of defining c_ρ and c_W would be[4,6]

$$\left(\frac{1}{c_\rho}\right)^6 = \int \frac{d\Omega}{4\pi} \sum_i \frac{(\mathbf{q}_j \cdot \mathbf{u}_j)^2}{c_j{}^6}, \tag{4a}$$

and

$$\left(\frac{1}{c_W}\right)^4 = \int \frac{d\Omega}{4\pi} \sum_i \frac{(\mathbf{q}_j \cdot \mathbf{u}_j)^2}{c_j{}^4}. \tag{4b}$$

Here $\mathbf{q}$ is a unit vector in the direction of the propagation vector and $\mathbf{u}$ is the polarization vector of the normal mode, the integration is over all the directions of $\mathbf{q}$, and the summation is over three polarizations for each $\mathbf{q}$. Cohen and Heine obtained the estimates of (4) by separately averaging $(\mathbf{q}_j \cdot \mathbf{u}_j)^2$ and $c_j{}^{-n}$. This method was considered by them to be very rough at best. We have calculated Θ_ρ and Θ_W by an alternative method due to Houston,[7] which is more reliable and has been successfully applied to the calculations of Debye temperatures,[8-11] the coefficients of thermal expansions,[12] and the vibrational spectra of solids.[13-15] Houston's method gives proper weight to each reciprocal lattice point and is inherently preferable to one that relies merely on taking a very large number of points in the reciprocal space.

We briefly summarize the results of the method. To evaluate

$$J = \int I(\theta,\phi)d\Omega, \tag{5}$$

where the integrand, like those occurring in Eqs. (4), is invariant under the operations of the complete cubic symmetry group, we will require the value of $I(\theta,\phi)$ in the following six directions: $A[100]$, $B[110]$, $C[111]$, $D[210]$, $E[211]$, and $F[221]$. These will be written I_A, I_B, etc. The expansion of the integrand in cubic harmonics retaining four, five, and six terms leads to the following expressions for J:

$$J_4 = (4\pi/945)[45I_A + 32I_B + 243I_C + 625I_D], \tag{6a}$$

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TABLE I. Physical constants of various materials considered.

Element	Density g/cm³	Elastic constants (10^{11} dyne/cm²)			Temp. (°K)	Source	D' (Cohen and Heine[f])	Θ_D (°K)	Θ_ρ (°K)	Θ_W (°K)	D	
		c_{11}	c_{12}	c_{44}							Calculated	Cohen and Heine[f]
Li	0.545	1.481	1.248	1.077	78	a	19.3	369[g]	447	591	9.3	⋯
Na	0.997	0.945	0.779	0.618	90	b	3.1	158[g]	215	265	2.5	2.8
K	0.893	0.457	0.374	0.263	83	b	6.8	89[g]	129	156	6.7	4.3
Rb	1.619	0.330	0.286	0.196	0	c	14.2	61[h]	77	92	11.1	⋯
Cs	1.986	0.245	0.208	0.159	0	c	15.7	44[h]	57	67	13.8	⋯
Cu	9.021	17.620	12.494	8.177	0	d	6.4	344[i]	518	590	8.7	6.0
Ag	10.654	13.149	9.733	5.109	0	e	4.4	226[j]	365	418	6.7	3.7
Au	19.320	20.163	16.967	4.544	0	e	4.3	165[i]	320	370	9.1	3.1

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$$J_5 = (4\pi/10\ 395)[1197I_A + 1456I_B + 729I_C$$
$$+ 3152I_D + 3888I_E], \quad (6b)$$

$$J_6 = (4\pi/1\ 081\ 080)[117\ 603I_A + 76\ 544I_B + 17\ 496I_C$$
$$+ 381\ 250I_D + 311\ 040I_E + 177\ 147I_F]. \quad (6c)$$

From the knowledge of the average velocities thus evaluated, Θ_ρ, Θ_W, and D values for the alkali and noble metals are calculated. The results along with the elastic constants and D' values (same as those used by Cohen and Heine) are presented in Table I. For all the metals the values of the characteristic temperatures were calculated from the four-, five-, and six-term approximations and these showed an excellent convergence, resulting from the less anisotropic behavior of the quasi-longitudinal waves considered here, as compared to quasi-transverse modes. In the table we only give Θ_ρ and Θ_W values obtained from the six-term approximation. It may be incidentally pointed out that the values of Θ_ρ and Θ_W obtained here are in remarkably close agreement with the values of these parameters for alkali metals estimated by Collins and Ziman[16] in a roundabout way from the experimental data.

D is a valuable index of the distortion of the Fermi surface. Klemens[3] suggests that if the Fermi surface touches the nearest zone faces, the D value is increased by a factor of 10 for body-centered cubic metals and 5 for face-centered cubic metals. It appears from the inspection of the values of D that the Fermi surface of Na is nearly isotropic, that of K is somewhat distorted, that of Li rather more so but may not be in contact with the zone boundary. In Rb and Cs the Fermi surface is in considerable contact with the zone surfaces. The values of D for Rb and Cs may not be very reliable as the elastic constant values are approximate ones. Many band-structure calculations and the experimental

results show[17-20] a trend in Fermi surface distortion like that found here. Luthi,[20] from his magnetoresistance work, finds that the low-temperature modification of Li approximates to the free electron model and the Fermi surface is closed. In the case of noble metals, from the D values shown in Table I it appears that for all these metals the Fermi surface touches the zone boundary. The distortion appears to be least in case of Ag and the relative amount of zone boundary touching in copper and gold is nearly the same. Cohen and Heine, at the time they wrote their review article, believed that the case of Ag or Au, or both, differed from that of copper, and hoped that such a difference would appear from a proper treatment of D. The present paper does not confirm this supposition and our conclusions are in surprisingly good agreement with the conclusive evidences on the shape of Fermi surface obtained through various recent experiments.[17,21,22]

The present calculations are based on a model according to which the electrons interact only with the longitudinal polarization component (dilation) of a lattice wave. The calculated values of D for Au, Ag, and Cu are larger than D', which corresponds to interaction with all polarization components on more or less equal footing. Which of these models is more appropriate is still an open question, though Klemens[3] argues for the latter model from lattice thermal conductivity data. For the alkali metals such data do not exist, but there is evidence for the former model in case of potassium from measurements of the lattice component of the thermoelectric power of potassium alloys.[23] Since the

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present calculation gives comparable values of D' and D for the alkali metals, it is quite possible that the former model applies to them. We are inclined to believe that this difference in behavior between the alkali metals and noble metals may be due to the reason that at low temperatures the interaction of long-wavelength phonons with electrons involves only the longitudinal modes if the Fermi surface is a sphere, but a multiply-connected surface which the noble metals have, should be much more sensitive to shear strains in the lattice, and there should be strong interaction with the transverse phonon modes,[24] especially in the neck regions.

Our conclusions about the Fermi surface, though in qualitative agreement with experiments, are weakened by the findings of Bailyn[25,26] that the Umklapp processes

dominate the electrical resistivity at all temperatures down to a few degrees Kelvin, and that these are dominated by scattering involving transverse phonons of large wave vector. As a consequence the scattering is affected moderately by whether or not the Fermi surface comes close to Brillouin zone surface. The whole problem of transport properties is of extreme complexity, for it involves almost all the basic properties of the metals, both the electronic band structure and the dynamical properties of the lattice.

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Nuclear Magnetic Resonance of Tc99 in Tc Metal and Tc99 and V51 in Tc-V Alloys*

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The nuclear magnetic resonance of Tc99 has been observed in Tc metal and its Knight shift measured relative to a solution of CsTcO4. The Tc99 and V51 resonances have been studied in 50–50 at. % TcV and TcV3 alloys as a function of field and temperature. The Tc99 resonance curves in TcV and TcV3 have a Lorentzian shape while V51 is Gaussian in TcV and Lorentzian in TcV3. Probable causes for the shape changes and excess widths encountered are discussed.

NUCLEAR magnetic resonance (NMR) measurements of Tc99 in Tc metal and Tc99 and V51 in Tc-V alloys have been made with a Varian, model V4200, wide-line nuclear magnetic resonance spectrometer and a Varian, model V4012A, electromagnet. The frequency was accurately measured by means of a Beckman/Berkeley model 7175 frequency meter. Temperature-dependent measurements of the line parameters were made by means of a gas-flow Dewar system through which the temperature could be varied from −150 to 300°C.

Technetium metal has the hexagonal close-packed crystal structure with lattice parameters $c_0 = 4.400 \pm 0.001$ A, $a_0 = 2.743 \pm 0.001$ A, and $c/a = 1.604$ and the Tc99 nucleus has a nuclear spin $I = 9/2$. Figure 1 shows a typical recording trace of Tc99 in Tc metal where the central line and its eight satellites are clearly observed. The first reported resonance of Tc99 was in an aqueous

solution of NH_4TcO_4.[1] A detailed description of the quadrupole interactions and isotropic and anisotropic Knight shifts of Tc99 in Tc metal have been given by Jones and Milford.[2] The isotropic Knight shift is $(0.61 \pm 0.02)\%$ relative to a 350-μg/ml solution of $CsTcO_4$. No chemical shift was observed between the $CsTcO_4$ solution and a 35-mg/ml solution of NH_4TcO_4. Table I gives the central line width versus field strength from which the anisotropic Knight shift and quadrupole effects are calculated. An analysis of the data shows that the anisotropic Knight shift is small. The quadrupole coupling constant e^2qQ/h evaluated from the satellites and central line width are, respectively, 5.05 and 5.15 Mc/sec. Operating in the U mode, the Tc99 in the $CsTcO_4$ solution gave rise to the so-called "m" curve and using the theory developed by Hubbard and Rowland[3]

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