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OF TUNGSTEN

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Effect of Surface Condition on the Transport Properties
of Tungsten^{*}

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Abstract

Measurements are presented of the low-temperature electrical and thermal resistivities, ρ and W , of several high-purity, single-crystal tungsten rods of various orientations for which the electron mean-free path λ is larger than the sample diameter d . For the highest purity samples oriented with a $\{110\}$ direction parallel to the rod axis, we observe several effects of surface condition on the electron transport properties. Firstly, both the electrical and thermal resistivities are increased substantially by sandblasting or electroetching the surface, and reduced correspondingly by electropolishing the surface. Secondly, the temperature dependent part of the electrical resistivity $[\rho - \rho_0]$ is reduced by sandblasting or electroetching the surface, and increased by electropolishing the surface. The corresponding effect is not observed for the thermal resistivity. Thirdly, the Lorenz number extrapolated to $T = 0$ K, $L(T \rightarrow 0) = (\rho/WT)_0$, is found to equal the standard

value $L_0 = 2.445 \times 10^{-8} \text{ } \Omega/\text{K}^2$ for the sandblasted or electro-etched surface, but is reduced significantly (up to 18%) below this value for the electropolished surface. In the latter case, application of a longitudinal magnetic field strong enough to prevent many of the conduction electrons from striking the surface is observed to increase $L(T \rightarrow 0)$ to L_0 , confirming that this is, indeed, a surface effect.

I. Introduction

It is well known that when the mean-free path of conduction electrons in a metal becomes comparable to specimen size, the surfaces can have an important effect on the transport properties. These size effects are conveniently divided into two regimes. The first is the classical size-effect regime in which the electron mean-free path ℓ is larger than the smallest specimen dimension d , but much larger than the electron wavelength λ . The second is the quantum size-effect regime in which d is comparable to λ . This paper deals with classical size effects, which include: the enhancement of resistivity with decreasing specimen size, the change in temperature dependence of the resistivity with specimen size, and the decrease of the longitudinal magnetoresistance with increasing magnetic field. The literature on these effects is very extensive and has been reviewed recently by Chambers¹, Brändli and Olsen², and Larson³.

The usual theoretical treatments of classical size effects are semiclassical treatments based on the Boltzmann equation. Within this framework the electron wavefunctions are assumed to be essentially unperturbed by the presence of the surfaces, so that the surfaces act only to scatter the incident electrons. The nature of this scattering enters the theory as a boundary

condition on the solution of the Boltzmann equation. Although simple in principle, a realistic solution of this equation is generally difficult in practice for two reasons. First, the detailed nature of the surface scattering is not known, and second, even if it were, the problem of solving the Boltzmann equation for a given bulk scattering mechanism and Fermi surface would be exceedingly complicated except under special circumstances. Thus, it has been customary to assume that the surface scattering is either diffuse or specular or a mixture of each. Diffuse scattering refers to an event in which the incident electron has equal probability of being scattered into any state which carries the electron into the metal. Specular scattering, on the other hand, refers to an event in which the component of wavevector parallel to the surface is conserved. (Umklapp processes, which are determined by the translational symmetries of the surface, are also possible.)

It has been customary, since the original work of Fuchs,⁴ to describe the relative amounts of diffuse and specular scattering by the specularity parameter p with $p = 0$ corresponding to completely diffuse scattering and $p = 1$ to specular scattering. Even with this simplification of the surface scattering, it usually has been necessary to assume that the bulk scattering can be described by a relaxation time and

that the Fermi surface is spherical, to make the solution of the Boltzmann equation feasible.

The results of many size-effect experiments have supported the view that for metals the surface scattering is mainly diffuse.¹ However, there is evidence that specular scattering can be important. Studies of the electrical resistivity of thin films and whiskers³ and of the optical reflectivity of thin films⁵ have strongly supported the existence of specular scattering under certain conditions. The most direct evidence is provided by the observation of magnetic surface states⁶; these states could not exist if the surface scattering were entirely diffuse. However, in several investigations^{5,7,8} negative values of p have been obtained, suggesting that under some circumstances the description of scattering at the surface in terms of the specularity parameter p may be too great a simplification.

We have undertaken this study to explore in greater detail the effect of surface scattering on electron transport properties.⁹ Since one expects the extremes of diffuse and specular scattering to correspond to very rough and very smooth surfaces, respectively (a more quantitative criterion for smoothness will be given later), we were led to investigate the effects of these two extremes of surface condition on the electrical resistivity, the thermal resistivity, the Lorenz number, and

the longitudinal magnetoresistance of tungsten single crystals. Tungsten was chosen because it could be obtained in oriented single-crystal rods of high purity and with polished surfaces. Furthermore, previous measurements on tungsten¹⁰ indicated that the transport properties could be influenced by the condition of the surface.

There has been very little previous investigation of the effect of surface condition on transport properties. In fact, on at least one occasion when the surface condition was deliberately changed during the course of a size-effect experiment, it was reported that no concomitant change in the resistivity had occurred¹¹. However, we note that Schwarz¹² has reported a change in the resistivity of a sample of cadmium after etching the electropolished surface. Bennett et al.⁵ have studied the optical reflectivity of thin films of silver of known surface roughness and have concluded that for roughness less than $45\text{\AA}$ rms the scattering is predominately specular, while for greater degrees of roughness the scattering is predominately diffuse. Finally, Koch and Murray¹³ have investigated the effect of surface condition on magnetic surface states.

II. Experimental Details

Measurements were made on variously oriented single-crystal tungsten rods ranging from 0.13 mm to 3 mm in diameter. These included measurements of the longitudinal magnetoresistance (LMR) at 4.2 K and the electrical and thermal resistivities, ρ and W , as a function of temperature from 1.5 to 5.5 K. The LMR measurements were useful primarily in indicating the amount of surface scattering present. The resistivity data, while also of considerable intrinsic interest, were used to calculate the Lorenz number, $L = \rho/WT$, as a function of temperature. The value of the Lorenz number extrapolated to zero temperature $L(T \rightarrow 0)$ was also of interest and was computed from the extrapolated values of ρ and WT . For one sample the longitudinal thermal magnetoresistance was measured in addition to the electrical magnetoresistance. The surfaces of several of the samples were altered by plating, etching, sandblasting, and electropolishing, and the effects of the surface condition on the above measurements were noted.

The LMR measurements were made in a superconducting solenoid whose field was homogeneous to about 0.1% over the sample volume. The samples were aligned in the field to about 1.5° ; the alignment was not critical for measurements below about 500 G, but at higher fields the LMR normally increased with

field at a rate that depended strongly on sample alignment. This was presumably due to a small admixture of the larger transverse component of magnetoresistance, which increases quadratically with magnetic field.

The possible existence of anomalous LMR behavior due to current jetting^{14,15} was investigated by adding two extra voltage leads to the sample, so that the voltage could be measured across three sections of the sample. We found that the measured LMR was qualitatively the same across all three sections and that the measured voltage across two individual sections added to give the measured voltage across both sections together. Therefore, we could find no evidence that current jetting was playing any significant role in these measurements.

The electrical and thermal resistivities were measured in the manner described by Wagner et al.¹⁰. As much care as possible was taken to avoid strain on the smaller samples, although some was unavoidable and its effects were seen on the smallest sample. The precision of the measurements was essentially the same as given in Ref. 10, being about $\frac{1}{2}\%$ for the electrical measurements and 1% for the thermal measurements.

We have attempted to observe the effects of our treatment on the tungsten surface by means of an optical microscope and a scanning electron microscope (SEM). Table I lists observed surface characteristics as viewed by the naked eye,

by the optical microscope, and by the SEM. The resolution of the scanning electron microscope was slightly better than 300Å. One should note, however, that the scale of surface roughness that is important for determining characteristics of surface scattering is probably at least an order of magnitude smaller. Nonetheless, the SEM pictures, as shown in Figs. 1 and 2, are useful in showing the drastic differences in the sample surfaces produced by our treatments of the surface.

The characteristics of each sample with the surface in a given condition are listed in Table II. It is important to note that some of the treatments of the surface were incomplete. For example, the H_2O_2 etch attacked specific planes on the sample surface and left a larger fraction of the surface unaffected. In these cases we have denoted the state of the surface as "selectively etched." As one would expect, these samples exhibited characteristics that were intermediate between those exhibited when the surface was polished and those exhibited when the surface was uniformly etched.

III. Experimental Results

One problem inherent in dc size-effect studies is the determination of the relative purities of different samples of varying size. For bulk samples the residual resistance ratio, $r_R = \rho(299 \text{ K})/\rho(0 \text{ K})$, is a good indicator of purity. However, when the electron mean-free path is size-limited, r_R is affected by both bulk impurity scattering and surface scattering and is no longer a useful indicator of purity. Several methods¹⁶⁻¹⁸ have been used to surmount this difficulty, but none of them is completely satisfactory. Perhaps the simplest is that suggested by Berthel.¹⁷

According to this method, the quantity r_R/d is used, rather than r_R , to characterize purity in the regime $\ell \gtrsim d$. This approach can be illustrated by assuming that the resistivity is given by the Nordheim expression, which can be written

$$r_R/d = (r_R/\ell)_{\text{bulk}} \frac{\ell}{\ell+d} \cdot \quad (p = 0) \quad (1)$$

Since $(r_R/\ell)_{\text{bulk}}$ is a constant of the material in this model, it is seen that for $\ell \gtrsim d$, r_R/d depends much more weakly on d than does r_R . Also for a given value of d , r_R/d is an increasing function of ℓ which saturates at the value $(r_R/\ell)_{\text{bulk}}$ as ℓ becomes much larger than d . For these reasons we have found the quantity r_R/d to be a useful although relatively crude indicator of sample purity.

We would like to emphasize that it is not useful to attempt to refine this method until the nature of the scattering at the surface and the actual Fermi surface are taken into account. In support of this we note the following: According to Eq. (1) the maximum value of r_R/d is $(r_R/l)_{\text{bulk}}$, which is given by

$$(r_R/l)_{\text{bulk}} = \rho(299 \text{ K}) \left[\frac{e^2}{2\pi^3 \hbar} S_F \right], \quad (2)$$

where S_F is the total Fermi surface area and e is the electronic charge. For tungsten¹⁹, $(r_R/l)_{\text{bulk}}$ has the value of $58,000 \text{ mm}^{-1}$. Referring to Table II, which summarizes the characteristics of the tungsten specimens, we note that for sample W-16, oriented with a [111] direction parallel to the rod axis, the measured value of r_R/d is $110,000 \text{ mm}^{-1}$. This is nearly twice the maximum value predicted by Eq. (1). One might first suppose that this discrepancy could be resolved by assuming that specular scattering is present ($p \neq 0$). However, it is more likely that this large value of r_R/d reflects the fact that, for the [111] orientation, the velocities of a large number of electrons on the octahedral hole sheet of the tungsten Fermi surface are nearly parallel to the rod axis. Since these electrons carry a disproportionate share of the transport current for $l \gg d$, it can be expected that the resistivity for this orientation would be anomalously low.

We conclude, as does Larson³, that the Nordheim formula and similar, more exact treatments,^{20,21} which assume an isotropic electron gas, can be misleading when applied to metals like tungsten which have a very anisotropic Fermi surface. Because of the strong influence of sample orientation on r_R/d , this quantity should be used as an indicator of sample purity only among specimens having the same orientation.

Better estimates of the bulk electrical resistivity can be obtained by measuring the reduction of the resistivity in a longitudinal magnetic field. As the cyclotron radii of the carriers become smaller than the sample diameter, the effect of surface scattering is greatly reduced and the resistivity approaches the value it would have in a bulk sample in the same longitudinal magnetic field. When the bulk magnetoresistivity is taken into account, one can estimate the zero-field bulk resistivity, and hence the mean-free path λ . By using the sample W-7 (the largest sample) as a gauge, we estimate that the bulk resistivity is increased approximately 20% by a longitudinal magnetic field. Using this value and the method outlined above, we estimate the mean-free path of sample W-12 to be about 1.8 mm.

Among samples of similar size and the same orientation, there appear to be two principal types of LMR behavior as shown in Fig. 3. The first (marked I on the graph) consists

of a decrease (occasionally preceded by a small increase) in the resistivity with increasing field, the minimum resistivity of the sample being 50% to 60% of the zero-field value. The second (marked II on the graph) consists of an increase in the resistivity of about 10% and then a decrease to approximately the zero-field value at higher fields. Of the samples having a [110] orientation, those exhibiting the first type of LMR behavior appear to be the purest, since these samples have the largest values of r_R/d . The two different types of behavior can be understood qualitatively by a very simple model which is outlined in the next section. As one would expect, both behaviors show that the smaller the sample, the slower the decrease in resistivity with increasing field.

Figure 4 focuses on the LMR of sample W-12 for various surface conditions and demonstrates that the zero-field electrical resistivity can be changed reversibly by altering the condition of the sample surface. The LMR is shown for the initial polished state, after etching, after repolishing, and after sandblasting. By roughening the surface, the zero-field electrical resistivity is increased, while by repolishing the surface the zero-field resistivity is decreased.²² In all cases, however, the resistivity approaches essentially the same value as the magnetic field increases. Because the fraction of the electrons striking the surface decreases with

increasing longitudinal magnetic field, this observation suggests that the bulk properties of the specimens have not been altered by our treatment of the sample surface.

Of the samples measured in this study and in the previous study by Wagner, et al.¹⁰, samples W-8 and W-12 exhibit characteristics that clearly set them apart from the others. The temperature dependence of the electrical resistivity of these two samples is larger than normal, as can be seen by referring to Fig. 5 and Ref. 10. Moreover, their Lorenz numbers extrapolated to zero temperature $L(T \rightarrow 0)$ are substantially lower than L_0 when their surfaces are in the polished condition. With the surfaces in the etched condition, these samples exhibit the normal behavior with $L(T \rightarrow 0)$ essentially equal to L_0 . From the behavior of the LMR of these samples (see Fig. 3) and their large values of r_R/d , these two specimens appear to be the purest. Because of their anomalous behavior, most of our attention has been devoted to these samples, particularly to W-12.

It is important to mention that samples W-8 and W-12 are essentially no different than the other samples in one respect: The temperature dependence of WT for these two samples is nearly identical to that of the other samples, as shown in Fig. 6 and Ref. 10.²³

Figure 7 shows the temperature dependence of the electrical

resistivity of sample W-12 for various conditions of the surface. From this figure it can be seen that the magnitude and temperature dependence of the resistivity change with surface condition. Roughening the surface increases the electrical resistivity while polishing the surface decreases it as observed previously in Fig. 4. The thermal data, seen in Fig. 8, also show an increase after the surface is roughened and a decrease after the surface is repolished. A careful look at the temperature dependences of the electrical and thermal resistivities shows, however, some differences in the effect of the surface on electrical and thermal conduction. It is observed from Fig. 9 that sandblasting the surface decreases the temperature dependence of the electrical resistivity relative to the initial polished state, while repolishing the surface increases the temperature dependence to nearly that of the original polished sample. In all cases the temperature dependence of the electrical resistivity of this sample is greater than that of a typical 'bulk' sample. In contrast, Fig. 10 shows the temperature dependent part of WT, and it is noted that surface condition plays little, if any, role in the temperature dependence of this quantity.²⁴

The Lorenz number, $L = \rho/WT$, is also found to depend upon the surface condition of the sample. Figure 11 shows the Lorenz number of sample W-12 as a function of temperature for

various surface conditions. It is seen from the figure that the Lorenz number is depressed by electropolishing the surface and is increased by sandblasting the surface. In particular, the Lorenz number extrapolated to zero temperature $L(T \rightarrow 0)$ is depressed below L_0 for the polished surface and is increased to nearly L_0 for the sandblasted surface.

Further evidence that the condition of the surface is responsible for this effect is provided by measurements of the electrical and thermal resistivities of the repolished sample (W-12G) in a longitudinal magnetic field strong enough to remove most surface scattering. The results of this measurement are plotted in Fig. 12. From the graph it can be seen that at a field of 480 G, $L(T \rightarrow 0)$ has a value of nearly L_0 , while at zero field it approaches a value about 10% lower. Since it is well known for a bulk metal that the Lorenz number will equal L_0 if scattering is elastic (this is also valid in a longitudinal magnetic field), these results demonstrate directly that the observed deviations from the Wiedemann-Franz law must be ascribed to the polished condition of the surface. The data also show a decrease in the thermal magnetoresistivity with increasing field similar to that observed in the electrical case.

We have also experimented briefly with another treatment of the surface. By plating the surface of sample W-12G, both the

electrical and thermal resistivities are increased proportionally, so that the Lorenz number is not significantly changed. Apparently, the increased surface scattering due to the gold plating affects the thermal conduction to the same degree as the electrical conduction.

The dependence of the Lorenz number on surface condition exhibited by sample W-12 contrasts with that exhibited by sample W-15, a smaller sample with the same orientation and a slightly lower value of r_R/d . The Lorenz number of sample W-15 shows no significant dependence on surface condition, although the temperature dependence of the electrical resistivity is decreased by sandblasting just as for sample W-12. One should note that the temperature dependence of ρ and WT for sample W-15A is larger than that of more 'typical' samples, such as samples W-4 or W-7 (see Figs. 5 and 6). We believe that this is due to strain and have observed similar, more exaggerated behavior in a small, badly strained specimen (W-14). This illustrates one of the difficulties in making meaningful measurements on very fine specimens.

We have observed aging effects in samples W-8 and W-12. Such effects have also been observed by Walsh²⁵ in tungsten. Over a period of six months, during which the samples were kept at room temperature, the electrical resistivity of W-12 in the initial polished condition was observed to increase

about 15% while the surface condition was not deliberately altered. We also made new measurements on sample W-8B a year and a half after the initial measurements had been made.⁹ In the original measurement $L(T \rightarrow 0)$ was found to be essentially equal to L_0 , while in our subsequent measurement on the sample we found that it had decreased well below L_0 . Sandblasting the surface of this sample produced only very slight changes in the electrical and thermal resistivities, in marked contrast to results on other samples. This suggests that a surface layer may have formed on the sample. After removing 0.3 mm from the diameter of W-8B by electropolishing, this sample was observed to behave as it did originally. We have looked for aging effects in some of our other samples, but have not found any nearly as large as those shown by W-8 or W-12.

IV. Discussion

The longitudinal magnetoresistance measurements reported here are similar to those that have been made in other metals.² For samples of the same size and orientation we find two characteristic types of LMR behavior determined largely by sample purity. This behavior can be explained with the modified Kohler's rule proposed by Olsen,²⁶ or perhaps more simply by assuming that the LMR consists of three components: a constant term corresponding to the zero-field value of the resistivity, a negative term due to the decreasing effect of surface scattering as the magnetic field is increased, and a positive term corresponding to the bulk magnetoresistance.

If one uses the calculation by Chambers²⁷ for the size-effect term and assumes that the bulk LMR saturates at a field inversely related to the mean-free path, one can roughly account for the two behaviors observed. As l is varied from $l < d$ to $l > d$, the shape of the LMR curve changes slowly from a small rise followed by a small decrease (curve II) to a very small rise followed by a large decrease (curve I). The character of the LMR behavior depends, therefore, on sample purity. This analysis is consistent with earlier comments in this paper that samples W-8 and W-12 are purer than other samples and therefore have the longest mean-free paths. This simple model ignores orientation effects.

The LMR measurements have established that significant surface scattering is present in the samples, and also have indicated to some extent the relative amounts of such scattering among the samples. These measurements also have been useful in establishing that the surface treatment changes the zero-field resistivity, while not significantly changing the bulk resistivity. Thus, we conclude that our treatment of the surface has not significantly altered the interior of the sample. Our observation that the resistivity can be appreciably affected by treatment of the surface contrasts sharply with the results of Startsev et al.¹¹, who observed no dependence on surface condition in their size-effect study on tungsten.

The dependence of the resistivity on surface condition implies that by changing the surface one has changed the nature of the surface scattering. In the simplest model, one might assume that the proportion of diffuse and specular scattering has been changed or, for example, that the specularity parameter p is decreased by roughening the surface. Way and Kao²⁸ have calculated the LMR of thin films for different values of p , and their results could be used to infer the existence of specular scattering in our samples. However, even if we assume that these results would be similar to those for a wire, one must still keep in mind that there are important differences in the nature of specular scattering for a metal

with a very anisotropic Fermi surface (such as tungsten) and for the free electron gas assumed in the calculations of Way and Kao²⁸. For a metal with an anisotropic Fermi surface, the angle of incidence will not necessarily equal the angle of reflection, and furthermore, an electron may scatter to more than one location on the Fermi surface^{29,30}. If one includes umklapp processes, the number of such possibilities can become very much greater³¹, especially if the surface does not lie in a major crystallographic plane.

The separation of surface scattering into a specular component and a diffuse (or random) component is probably a rather drastic simplification of the problem in most situations. R. F. Greene²⁹ has formulated in general terms the surface boundary condition for electron-surface scattering using current conservation at the surface in the usual semiclassical theory. The resulting boundary condition is equivalent to the assumption of a specularity parameter p only in special cases, and even for these cases p will generally depend upon the electron distribution function. Thus, p will be different for different transport processes. However, the general boundary condition is difficult to apply, so it has usually proven convenient to assume that a specularity parameter exists, keeping in mind the possible limitations.

One obvious consideration is that the nature of the surface

scattering should depend upon the angle at which the electron collides with the surface, and various workers have investigated theoretically the dependence of p upon the scattering angle.^{3,31} In particular, Soffer³² has shown by simple diffraction considerations for a surface with uncorrelated irregularities, that the specularity parameter p is given by

$$p(\cos\theta) = \exp[-(4\pi h \cos\theta/\lambda)^2] , \quad (3)$$

where θ is the angle of incidence, h is the rms roughness, and λ is the deBroglie wavelength of the electrons. From this formula one can see that p is appreciable only for glancing angles of incidence even if the surface is atomically smooth. For example, if $h = \lambda$ (in a metal this corresponds to an atomically smooth surface), then $p > \frac{1}{e}$ only for angles of incidence greater than 85° . In most size-effect phenomena, the electrons travelling nearly parallel to the surface (with large angles of incidence) play an important role. In the dc size effect, $\cos\theta$ is roughly d/l or less for the electrons which transport the bulk of the current. In the anomalous skin effect, the important electrons are the effective ones for which $\cos\theta < \delta/l$, where δ is the skin depth. For magnetic surface states, $\cos\theta$ is about $2\sqrt{2}z_1/R$ where z_1 is the maximum depth achieved by the ground state trajectory and R is its radius of curvature. In the latter case $\cos\theta$ is typically 0.01, which corresponds

to a value of p of 0.99 for an atomically smooth surface. In the case of dc transport, values of d/l appreciably less than unity can be obtained only in very fine specimens at low temperatures. Thus, it seems from these simple considerations that specular scattering should be completely dominant for magnetic surface states, but diffuse scattering should be predominant for dc transport phenomena.

Greene³³ has argued that, for a degenerate system, p might be greater than one would expect from simple diffraction considerations. His argument is based on the observation that for diffuse scattering the initial and final occupation factors must be included, while for specular scattering they need not be, since specular scattering is simply a way of constructing the standing wave states required by the presence of the boundary. Because quantitative calculations based on these arguments require detailed knowledge of transition probabilities, it is not known whether such a mechanism can produce the large value of p necessary to make specular scattering in dc transport processes more plausible from a theoretical point of view.

In spite of the theoretical difficulties, there is considerable experimental evidence for specular scattering in dc transport phenomena, as we discussed in the introduction. It is tempting to view many of our results in terms of specular

and diffuse scattering, but we have had difficulty understanding them consistently in these terms, as we discuss later in this section.

Other experimenters have noted the effect of chemical coatings^{8,34} on the resistivity of metals. The surfaces of our samples were not ultra-clean, so such effects could be important. In general, the changes we observe in the resistivity due to changing the surface condition are larger than those produced by coatings.^{34,35} A very simple view of the possible effects of chemisorbed atoms allows the electron density of the metal and the surface scattering to change. For a compensated metal, such as tungsten, a small change in the electron density would produce little change in the resistivity, but would cause a larger change in the Hall voltage such as observed by Bastl³⁵. A change in surface scattering could increase the resistivity, and we may have observed this effect when the sample had aged and possibly when the sample was gold plated.

An increase in the temperature dependence of the electrical resistivity has been observed by many others in size-effect studies in several metals.² Although these results are usually called deviations from Mattheissen's rule,³⁶ Ehrlich³⁷ and Boughton and Neighbor³⁸ point out that these increased temperature dependences are to be expected from a careful analysis of the conventional size-effect theory. The mechanism

proposed by Olsen²⁶ to explain the increased temperature dependence of the resistivity of small wires has been shown by Boughton and Neighbor³⁸ to be largely unnecessary, but could still be present. Such a mechanism would, however, predict an increased temperature dependence for a roughened surface compared to a smooth surface, in contrast to our results. Although Boughton and Neighbor have not investigated the role of specular scattering in their model, a standard treatment ascribing very little, if any, temperature dependence to the specular parameter p would give, for a sample with p nearly equal to unity, a temperature dependence similar to that of a bulk sample. This would contrast with our results, in which the smoothest sample (that most likely to have large amounts of specular scattering) had the largest temperature dependence, while the roughest sample (that most likely to have large amounts of diffuse scattering) had a temperature dependence more nearly like that of a bulk sample. If, as others have suggested³⁹, the specular parameter has a large temperature dependence (p decreasing with increasing temperature), this could qualitatively explain our observations.

Another interesting aspect of the data is the observation that, although the temperature dependence of the electrical resistivity changes with surface condition, that of the thermal resistivity does not change. This is most certainly related

to the fact that the electron mean-free path for thermal conduction is shorter than that for electrical conduction in the temperature range of our measurements. On this basis one expects that the thermal resistivity would be less sensitive than the electrical resistivity to the presence of the surfaces, and this is consistent with all our observations.

We now turn to a discussion of the Lorenz number measurements. Normally in a bulk metal the Lorenz number is a good indicator of the amount of small-angle inelastic scattering present. Such scattering (e.g. scattering by phonons at low temperatures) has the effect of reducing the Lorenz number L below the standard value $L_0 = 2.445 \times 10^{-8} \text{ W}\Omega/\text{K}^2$. (Electron-electron scattering can also cause such behavior.) At even lower temperatures these processes become less important than the temperature-independent elastic processes, such as scattering by defects, impurities, etc., and L returns to the value L_0 . However, this pattern is not followed by samples W-8 and W-12 when their surfaces are in the electropolished state; their values of $L(T \rightarrow 0)$ are less than L_0 , as discussed in Sec. III. The significance of this result depends upon two considerations. First, does the extrapolation to $T = 0 \text{ K}$ actually reflect the real situation or are the extrapolations misleading? Second, if the extrapolations do reflect the true situation at $T = 0 \text{ K}$, how can this result be explained?

We cannot rule out the possibility that the extrapolations might be misleading. However, in order for the Lorenz number to approach L_0 at $T = 0$ K, the character of the temperature dependence of the resistivities would have to change dramatically below 1.5 K. Such a change might be produced by the freezing out of some inelastic surface scattering mechanism, and would be of considerable interest for its own sake. Clearly, measurements at lower temperatures would be helpful in clarifying this point.

However, if our extrapolations do reflect the true behavior of the Lorenz number, then this presents serious problems that are difficult to resolve by conventional treatments of dc size effects. One might attempt to resolve the problem by postulating two different specularly parameters, one for electrical conduction and one for thermal conduction. Then the deviation of $L(T \rightarrow 0)$ from L_0 would be attributable to the difference between the two parameters. However, this flexibility does not exist when all scattering mechanisms are elastic, and we show in an appendix that one expects $L(T \rightarrow 0)$ to equal L_0 for elastic bulk and surface scattering mechanisms. Consequently, we do not have a satisfactory explanation for these deviations from the law of Wiedemann and Franz.

V. Conclusion

In this study we have shown that for very pure, single-crystal tungsten rods, oriented with the rod axis parallel to a [110] direction, the condition of the surface can markedly affect the magnitudes of the electrical and thermal resistivities, the temperature dependence of the electrical resistivity, and the value of the Lorenz number extrapolated to zero temperature $L(T \rightarrow 0)$. Furthermore, these effects are observed to be reversible -- that is, they can be restored by appropriate treatment of the surface. We believe this to be the first detailed study of the effects of surface condition on the dc transport properties of a pure metal.

Clearly, there is much work left to be done on this subject. For example, future work in tungsten should deal with the role played by crystal orientation. An effort must be made to quantify surface roughness, and to prepare and maintain surfaces of known condition. The techniques developed in the field of surface physics should be extremely useful in this regard. It is possible that future systematic studies of the effects of surface condition on transport properties could be important in elucidating the interaction of conduction electrons with the metallic surface.

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APPENDIX: Proof of the Validity of the Wiedemann-Franz Law
in the Classical Size-Effect Regime for Elastic Scattering.

Consider a cylindrical conductor oriented with the cylinder axis along the z direction. We apply an electric field E_z or a thermal gradient $\nabla_z T$ to the conductor which perturbs the equilibrium Fermi distribution function f_0 by the amount $eE_z \eta_E$ in the electrical case, and by $(-k_B \nabla_z T) \eta_T$ in the thermal case (e is the electronic charge and k_B is Boltzmann's constant). The quantities η_E and η_T are determined by the Boltzmann equation, which can be written in each case as

$$\vec{v} \cdot \vec{\nabla}_r \eta_E = \left(-\frac{\partial f_0}{\partial \mathcal{E}} \right) v_z + W(\eta_E) \quad (A1)$$

and

$$\vec{v} \cdot \vec{\nabla}_r \eta_T = \left(-\frac{\partial f_0}{\partial \mathcal{E}} \right) u v_z + W(\eta_T) \quad (A2)$$

where $\vec{\nabla}_r$ is the transverse (radial) gradient operator, $u = (\mathcal{E} - \mu)/k_B T$, $\mathcal{E}$ is the electron energy, μ is the chemical potential, $\vec{v}$ is the electron velocity, and $W(\eta)$ is the collision integral which will be defined shortly. For simplicity we have considered only one band, but the following arguments can be readily generalized to include several bands. Both η_E and η_T are functions of wavevector $\vec{k}$ and radial position r .

The boundary condition for scattering from the surface can be written in at least two equivalent ways.^{39,40} The condition used by Greene is based on the requirement that the net current through a given point on the surface be zero.

That condition is

$$v_n(\vec{k}^+) \eta_E(\vec{k}^+) = - \int d\vec{k}^- v_n(\vec{k}^-) \eta_E(\vec{k}^-) w(\vec{k}^-, \vec{k}^+) \quad (A3)$$

for each point on the boundary and each state $\vec{k}^+$. A similar condition exists for the thermal case with η_E replaced by η_T . v_n is the component of velocity normal to the surface, $\vec{k}^-$ represents the wavevector of a state with velocity incident on the surface, and $\vec{k}^+$ represents a state with velocity directed away from the surface. $w(\vec{k}^-, \vec{k}^+)$ is the probability for scattering at the surface from state $\vec{k}^-$ to $\vec{k}^+$.

For bulk impurity scattering the collision integral can be written as

$$W(\eta) = - \frac{1}{k_B T} \frac{1}{4\pi^3} \int d\vec{k}' (\psi - \psi') P(\vec{k}, \vec{k}'),$$

where $P(\vec{k}, \vec{k}')$ is the equilibrium transition rate between states $\vec{k}$ and $\vec{k}'$ and ψ is defined by $\eta = \left(- \frac{\partial f_0}{\partial \mathcal{E}} \right) \psi$. For elastic scattering $P(\vec{k}, \vec{k}') = \delta(\mathcal{E} - \mathcal{E}') P'(\vec{k}, \vec{k}')$ and with this form for $P(\vec{k}, \vec{k}')$ it can be readily shown that

$$W(u\eta_E) = u W(\eta_E)$$

Thus, if η_E is the solution to the first Boltzmann equation (A1), then $\eta_T = u\eta_E$ is a solution of the second (A2), provided the boundary condition (A3) is also met. We have assumed that $\vec{\nabla}_r u = 0$, or equivalently that there is no radial variation in the chemical potential μ or temperature T ; we believe this to

be a sound assumption.

To show that the boundary condition is satisfied, we note that for elastic scattering $w(\vec{k}, \vec{k}^+) = \delta(\xi^+ - \xi^-) w(\vec{k}, \vec{k}^+)$. Using this form for $w(\vec{k}, \vec{k}^+)$, it is easy to show that if η_E satisfies the boundary condition for electrical conduction, $\eta_T = u\eta_E$ will satisfy the boundary condition for thermal conduction.

To compute the Lorenz number L , one needs to calculate the electrical and thermal currents, or equivalently the electrical and thermal conductivity tensor elements σ_{zz} and κ_{zz} which are given by

$$\begin{aligned}\sigma_{zz} &= \frac{e^2}{4\pi} \int d\vec{k} v_z \eta_E \\ \kappa_{zz} &= \frac{k_B^2 T}{4\pi} \int d\vec{k} u v_z \eta_T \\ &= \frac{k_B^2 T}{4\pi} \int d\vec{k} u^2 v_z \eta_E\end{aligned}$$

By writing the integral over wavevector as an energy and surface integral in the usual manner one has

$$\frac{\kappa_{zz}}{\sigma_{zz} T} = \left(\frac{k_B}{e}\right)^2 \frac{\int_{-\infty}^{\infty} du u^2 \operatorname{sech}^2 \frac{u}{2}}{\int_{-\infty}^{\infty} du \operatorname{sech}^2 \frac{u}{2}} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 = L_0$$

to order $\left(\frac{k_B T}{\mu}\right)^2$. This completes the proof. It is important to mention at this point that the measured Lorenz number is

$\rho_{zz}/W_{zz}T$ and that this is equal to $\kappa_{zz}/\sigma_{zz}T$ provided that one neglects thermoelectric effects and provided that the cylinder axis is along an axis of twofold or higher symmetry. The latter condition is satisfied for all our specimens.

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Figure Captions

- Fig. 1: Photograph of polished surface at x 10,000 on scanning electron microscope. Etch pits are used to help focus microscope.
- Fig. 2: Photograph of sandblasted surface at x 5,000 on scanning electron microscope.
- Fig. 3: Longitudinal magnetoresistance as a function of magnetic field for various samples. All samples have a [110] orientation parallel to rod axis except W-16 and W-17, which have [111] and [100] orientations, respectively. All data were taken at 4.2 K except as otherwise indicated.
- Fig. 4: Longitudinal magnetoresistivity as a function of magnetic field at 4.2 K for various conditions of sample surface.
- Fig. 5: Variation of the temperature dependent part $[\rho - \rho_0]$ of the electrical resistivity with temperature for various samples.
- Fig. 6: Variation of temperature dependent part $[WT - (WT)_0]$ of the thermal resistivity multiplied by temperature for several samples.
- Fig. 7: Electrical resistivity ρ as a function of temperature for various surface conditions.

Fig. 8: Thermal resistivity multiplied by temperature WT as a function of temperature for various conditions of sample surface.

Fig. 9: Variation of the temperature dependent part $[\rho - \rho_0]$ of the electrical resistivity with temperature for various conditions of sample surface compared to a typical bulk sample.

Fig. 10: Temperature dependent part $[WT - (WT)_0]$ of the thermal resistivity multiplied by temperature as a function of temperature for several surface conditions of sample W-12.

Fig. 11: The Lorenz number as a function of temperature.

Fig. 12: Temperature dependence of the electrical and thermal resistivities of sample W-12G at zero field and in a longitudinal magnetic field. The circled and square data points were taken in the same experiment. The data points indicated by triangles were taken in a separate experiment.

Table 7 Surface characteristics of tungsten samples for different treatments

<div>treatment</div> <div>probe</div>	Electropolished	Etched	Sandblasted
eye	Surface is mirror smooth.	Etching attacks different planes preferentially, often leaving some of the surface mirror-like and some matt.	Surface appears uniformly dull.
Optical Microscope x 420	Surface is smooth with some random imperfections like etch pits.	Both mirror and matt portions of surface are present.	Surface has a sandpaper-like finish.
Scanning Electron Microscope x 5,000 x 10,000	Etch pits present, but most of the surface is smooth.	Both mirror and matt portions of surface are present.	Surface appears very rough like mossy zinc.

Table II: Characteristics of the Tungsten Samples

Sample	Orientation	d [mm]	r_R	$\frac{r_R}{d}$ [mm ⁻¹]	(WT) ₀ [10 ⁻² K ² -cm/W]	ρ_0 [10 ⁻¹⁰ Ω -cm]	$L(T=0) = \frac{\rho_0}{(WT)_0}$ [10 ⁻⁸ W- Ω /K ²]	Surface Treatment	Surface Condition
W-4	[110]	1	30,000	30,000	.721 $\pm$.005	1.780 $\pm$.004	2.47 $\pm$.02	electro- etched	matt
W-7	[110]	3	96,000	32,000	.214 $\pm$.01	.566 $\pm$.004	2.64 $\pm$.11	electro- polished	mirror
W-8	[110]	1.5	75,000	50,000	.319 $\pm$.002	.695 $\pm$.006	2.18 $\pm$.02	"	"
W-12A	[110]	.9	57,000	63,000	-----	.94 $\pm$.005	-----	"	"
W-12B	"	.9	52,000	57,000	.495 $\pm$.004	1.04 $\pm$.015	2.10 $\pm$.05	"	"
W-12C	"	.9	38,500	43,000	.663 $\pm$.005	1.395 $\pm$.005	2.10 $\pm$.025	H ₂ O ₂ etched	slightly and selec- tively etched
W-12D	"	.8	47,500	59,000	.555 $\pm$.006	1.13 $\pm$.005	2.03 $\pm$.025	electro- polished	mirror
W-12E	"	.8	42,000	52,000	.601 $\pm$.004	1.275 $\pm$.006	2.12 $\pm$.025	electro- etched	selectively etched
W-12F	"	.8	30,000	37,500	.750 $\pm$.005	1.790 $\pm$.007	2.39 $\pm$.025	sand- blasted	matt
W-12G (H = 0)	"	.74	43,000	58,000	.569 $\pm$.004	1.260 $\pm$.005	2.21 $\pm$.025	electro- polished	mirror
W-12G (H = 480G)	"	.74	-----	-----	.285 $\pm$.005	.690 $\pm$.005	2.42 $\pm$.05	"	"
W-12H	"	.74	37,000	51,000	.657 $\pm$.005	1.445 $\pm$.066	2.20 $\pm$.025	gold- plated	gold
W-12J	"	.5	17,000	35,000	1.31 $\pm$.01	3.12 $\pm$.02	2.38 $\pm$.035	sand- blasted	matt
W-14	[100]	.13	6,300	48,500	3.55 $\pm$.04	8.61 $\pm$.05	2.43 $\pm$.03	electro- polished	mirror
W-15A	[110]	.28	15,000	50,000	1.57 $\pm$.01	3.85 $\pm$.01	2.46 $\pm$.03	"	"
W-15B	"	.28	9,000	32,142	2.27 $\pm$.01	5.66 $\pm$.015	2.49 $\pm$.03	sand- blasted	matt
W-16	[111]	.23	23,000	110,000	1.07 $\pm$.006	2.62 $\pm$.005	2.45 $\pm$.01	electro- polished	mirror
W-17	[100]	.6	18,000	30,000	1.23 $\pm$.01	3.03 $\pm$.005	2.46 $\pm$.02	"	"
W-19	[110]	.6	~28,000	~46,000	-----	-----	-----	"	"
W-20	[110]	1.0	~40,000	~40,000	-----	-----	-----	"	"

FIGURE 1

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Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11