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Electronic relaxation rates of copper, aluminum, and potassium determined from the temperature dependence of the anomalous surface impedance

David P. Love,* Craig T. Van Degrift,† and W. H. Parker
Department of Physics, University of California, Irvine, California 92717

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Changes in frequency of an extremely stable isothermal *LC* oscillator are associated with the temperature dependence of the surface impedance of a thermally isolated metallic sample placed within the inductor. Even in the anomalous skin-effect regime, where the electronic mean free path is much greater than the rf skin depth, there is a small yet measurable temperature dependence to the surface impedance. The formulas for the surface impedance (valid for the anomalous through classical skin-effect regimes) by Reuter and Sondheimer are used to extract, from the changes in frequency of the oscillator, information related to electronic relaxation rates. The electronic relaxation rates determined in this way are compared to relaxation rates obtained from published dc electrical resistivity data. Cu, Al, and K have yielded consistent temperature dependencies with respect to the dc measurements in certain temperature ranges. A comparison of dc electrical conductivity and surface-impedance measurements is also made through the use of the theoretical work of Manz, Black, Pashaev, and Mills, who find, for the temperature-dependent surface impedance in the extreme anomalous limit, a new relaxation rate different from that in the relaxation-time approximation. This new relaxation rate in certain limits is predicted to be proportional to that characterizing the dc electrical resistivity. The results obtained from copper are the best verification of this prediction. Data from aluminum are about a factor of 5 greater than the model-dependent prediction of Manz *et al.* Difficulty in achieving a high residual resistance ratio in potassium prevents a comparison through the theory of Manz *et al.* However, a T^2 dependence observed with potassium at low temperatures is about 150 times greater than that observed in recently reported dc electrical resistivity data. A further theoretical investigation by Black and Mills examined the contribution of electron-electron normal scattering processes to surface impedance in the extreme anomalous limit. Their findings suggest that these electron-electron *N* processes may fully contribute to the surface-impedance relaxation rate. Our copper and potassium data qualitatively support this suggestion.

I. INTRODUCTION

The behavior of conducting media at ordinary temperatures exposed to electromagnetic radiation is well understood. Here, the mean free path of the conduction electrons is much less than the penetration depth of the ac fields. This is the realm of the classical skin effect where local electrodynamics apply. With the advent of microwave generators, a sufficiently pure metallic sample at low temperatures was shown to exhibit nonlocal electrodynamics. This occurs when the mean free path of the conduction electrons becomes greater than the penetration depth of the ac fields. Historically, this regime has become known as the anomalous skin-effect regime.

The surface impedance is defined to be the ratio of the electric field (assumed parallel to the surface) at the surface of the metal to the depth integral of the induced current density. The surface impedance of a metal occupying the half-space $z \geq 0$ is defined as

$$Z_s = \frac{E(0)}{\int_0^\infty J(z)dz} \ . \tag{1.1}$$

When local electrodynamics are appropriate, *J* and *E* are often simply related through a scalar quantity σ, the electrical conductivity. Reuter and Sondheimer[1] obtained two expressions for the nonlocal situation appropriate for a simple metal using the linearized Boltzmann equation within the relaxation-time approximation.

Two formulas are obtained in the two limits of either specular or diffuse scattering at the surface. There is no simple way to treat an intermediate surface scattering character. Historically, p denotes the fraction of electrons scattered specularly. Thus $p=1$ represents a purely specular surface and $p=0$ represents a purely diffuse surface.

Early results for the surface impedance by Pippard[2] and more complete results by Chambers[3] are in very good agreement with the Reuter-Sondheimer formula for $p=0$. A more recent study verified the $\omega^{2/3}$ frequency dependence of the anomalous surface impedance[4] predicted by Reuter and Sondheimer. Recently, a description of an analog network that models the Reuter and Sondheimer formulas was reported.[5]

Chambers measured the temperature dependence of the surface impedance to map out the transition regime between the anomalous and classical regimes. Measurements involving the temperature dependence within the transition region were reported by Daybell and co-workers.[6]

Most of the above-mentioned measurements involve the real part of the surface impedance. However, this paper deals with the imaginary part. By varying the temperature of a thermally isolated sample within the inductor of an isothermal, stable, tunnel-diode driven LC oscillator, changes in frequency can be related to changes in the surface impedance of the sample.

It can be shown from the Reuter and Sondheimer theory that a change in impedance can be related to a change in the relaxation rate of the conduction electrons in the sample. Within the assumptions of Reuter and Sondheimer, this relaxation rate can also be related to the electrical resistivity.

A recent theoretical investigation concerning electron-phonon contributions by Manz *et al.*[7] indicated that the relaxation rate obtained from a measurement of the temperature dependence of the surface impedance near the extreme anomalous limit does not equal, although in certain limits may be proportional to, the relaxation rate obtained from dc electrical resistivity. Further theoretical work by Black and Mills[9] showed that for a simple metal in the extreme anomalous limit the electron-electron normal processes may fully contribute to the temperature dependence of the surface impedance.

A more thorough theoretical discussion appears in Sec. II. A description of the experimental apparatus and data analysis are in Sec. III. Section IV describes the nature of our metallic samples: copper, aluminum, and potassium. Section V presents a discussion of the results. The final section, Sec. VI, presents our concluding remarks.

II. THEORY

This section proceeds from a simple phenomenological explanation for the anomalous behavior in the surface impedance due to Pippard[8] to a short discussion of the Reuter-Sondheimer[1] theory. A summary of recent reports involving electron-phonon interactions by Manz *et al.* on the temperature dependence of the surface impedance in the extreme anomalous limit is presented, followed by a discussion of the Black and Mills[9] report concerning the electron-electron normal process contribution to the surface impedance.

In the extreme anomalous skin effect, the mean free path Λ of the conduction electrons is much greater than the rf skin depth δ. Pippard[10] inferred that not all the conduction electrons were able to respond to the incident rf fields. This discussion is well known, but is presented to introduce some useful parameters.

Consider an electron traveling toward the surface from a depth Λ. It will experience the exciting field only within a distance δ of the surface. Thus, over the majority of its mean free path, this electron does not experience the electric field. Hence it is ineffective in absorbing rf energy. However, an electron traveling parallel to the surface and within a depth δ of the surface will be accelerated by the electric field over its entire mean free path. Thus, this electron will absorb more rf energy. Such an electron is called an effective electron. The effective electrons travel within an angle δ/Λ of the surface. The number density of effective electrons is then $n'=n\delta/\Lambda$, where n is the total number density. The effective rf conductivity is similarly reduced, resulting in a mean-free-path—independent skin depth and hence a temperature-independent surface impedance (classically proportional to δ).

The Reuter and Sondheimer[1] calculation of the anomalous surface impedance is based on certain simplifying yet reasonable assumptions: (1) The depth of field penetration is small compared with linear dimensions of the sample (thus it becomes permissible to treat the sample as a semi-infinite slab). (2) The conduction electrons are described by an isotropic effective mass m^*. (3) A single relaxation time, τ, completely describes the collision mechanism. The time τ is assumed to be identical to the relaxation time in the dc electrical conductivity. It is further assumed that a fraction p of the electrons scatter specularly and $1-p$ diffusely from the surface of the metal.

Through the use of Maxwell's equations (neglecting the displacement current) and the linearized Boltzmann equation, Reuter and Sondheimer[1] find the surface impedance for $p=1$ and $p=0$ to be[11]

$$Z_s^{p=1}=-j\frac{2\omega v_F\mu\tau}{\pi}\int_0^\infty \frac{d\eta}{\eta^2-j\left[\dfrac{3\eta e^2\omega v_F^2\mu\tau^3}{2m^*}\right]\left[\left[\dfrac{1}{\eta}+\dfrac{1}{\eta^3}\right]\tan^{-1}\eta-\dfrac{1}{\eta^2}\right]}$$
$$=-j\left[\frac{16m^*\omega^2 v_F\mu^2}{3ne^2\pi^3}\right]^{1/3}\lambda^{1/3}I_1(\lambda) \qquad (2.1)$$

and[12]

$$(Z_s^{p=0})^{-1}=\frac{j}{\pi\omega v_F\mu\tau}\int_0^\infty \ln\left\{1-j\frac{3\eta e^2\omega v_F^2\mu\tau^3}{2m^*\eta}\left[\left[\frac{1}{\eta}+\frac{1}{\eta^3}\right]\tan^{-1}\eta-\frac{1}{\eta^2}\right]\right\}d\eta$$
$$=j\left[\frac{3ne^2}{2m^*\omega^2 v_F\mu^2\pi^3}\right]^{1/2}\lambda^{-1/3}I_0(\lambda)\,, \qquad (2.2)$$

where $j=\sqrt{-1}$, v_F is the Fermi velocity, μ is the magnetic permeability of the metal (very close to μ_0), e is the charge on an electron, ω is the angular frequency of the incident fields, and $\lambda=3\Lambda^2/\delta^2$. The classical skin depth

$$\delta=(2m^*v_F/ne^2\mu\omega\Lambda)^{1/2}\ .$$

The forms for the surface impedance in the extreme anomalous limit are found by letting $\tau\rightarrow\infty$. The result for specular scattering is

$$Z_\infty^{p=1}=\frac{8}{9}\left[\frac{\sqrt{3}\omega^2\mu^2\Lambda}{16\pi\sigma}\right]^{1/2}(1-j\sqrt{3})\ . \qquad (2.3)$$

where $\sigma=ne^2\Lambda/m^*v_F$ is the dc electrical conductivity. Similarly, one finds for diffuse scattering

$$Z_\infty^{p=0}=\tfrac{9}{8}Z_\infty^{p=1}\ . \qquad (2.4)$$

These expressions are the temperature-independent limits of the surface impedance in the extreme anomalous limit.

For a finite relaxation time there is a small, yet finite, temperature-dependent contribution to Z that we call ΔZ. An analytical expression for the first temperature-dependent correction term can only be found for the specular case. Dingle has shown[13]

$$\Delta Z=\frac{8}{27\pi}\left[\frac{729\sqrt{3}\mu\omega^2m^*v_F}{2ne^2}\right]^{1/3}\frac{\delta'}{\Lambda}\left[1+\frac{j}{\sqrt{3}}\right], \qquad (2.5)$$

where δ' is an appropriate skin depth in the anomalous regime.[14]

Figure 1 depicts the total surface impedance from numerical integration of Eq. (2.1) for specular scattering. Also shown are the surface impedance obtained from the classical skin effect and that obtained from the first-order correction to the $\tau=\infty$ limit [Eq. (2.3)].

Values of ΔZ for both specular and diffuse reflection found numerically are depicted in Fig. 2. Note that the diffuse reflection case has a linear dependence on $\lambda^{-1/3}$ (and therefore is proportional to $1/\tau$) for large λ similar to that found analytically for the specular case. This implies that ΔZ is linearly dependent on the relaxation rate near the anomalous limit.

We now review the recent investigations by Manz *et al.*[7] concerning the contribution to ΔZ from electron-phonon interactions. They find that the temperature dependence of the surface impedance in the extreme anomalous limit is characterized by a new effective relaxation time for the electron-phonon system, different from that used in the relaxation time approximation. Throughout

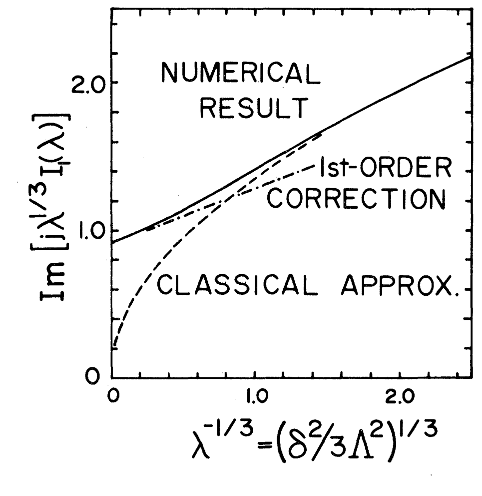

FIG. 1. Imaginary part of the Reuter-Sondheimer anomalous surface impedance for specular reflection integrated numerically vs a parameter proportional to $1/\tau$, the relaxation rate of the conduction electrons. Also shown for comparison are the first-order correction terms obtained analytically and the surface impedance from the classical skin effect. In the figures δ is the classical rf skin depth and Λ is the mean free path of the electrons.

their investigations they assume the metal has a spherical Fermi surface, and the phonon system is described by a Debye spectrum of phonons with only longitudinal phonons involved in the scattering process.

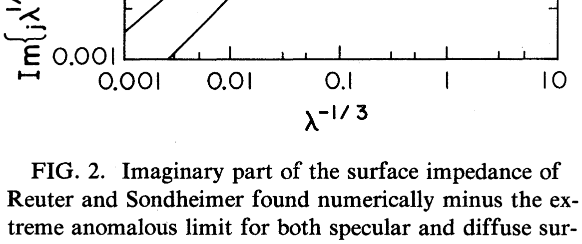

FIG. 2. Imaginary part of the surface impedance of Reuter and Sondheimer found numerically minus the extreme anomalous limit for both specular and diffuse surface reflection vs a parameter proportional to $1/\tau$, the relaxation rate of the electrons. Note that any change in impedance requires a larger $1/\tau$ for the specular case than diffuse case in the anomalous limit, $\lambda \gg 1$.

An important dimensionless parameter evolves from their analyses. This parameter is the ratio of two characteristic angles. The first angle θ_E is the ratio of the rf skin depth at $T=0$ to the impurity-limited mean free path δ/Λ_I. Thus $\theta_E \ll 1$ in the extreme anomalous limit. θ_E is the angle on the Fermi surface that contains Pippard's effective electrons. The second angle, θ_p, is the ratio of Q_T, the wave vector of a phonon of energy $\sim k_B T$, to the Fermi wave vector. With c_s denoting an average sound velocity, $Q_T = k_B T/c_s$. For the temperature range of interest within this theory, $\theta_p \ll 1$.

The magnitude of the ratio

$$r = \theta_p/\theta_E = Q_T \Lambda_I/(k_F \delta)$$

plays a key role in their discussions. If $r \ll 1$, a limit achievable at sufficiently low temperatures for any sample, the angular deflection of an electron upon emission or absorption of a thermal phonon is very much smaller than θ_E. This implies that an effective electron before the interaction remains effective afterwards. When $r \gg 1$, which occurs for samples of high purity at temperatures well below the Debye temperature, an effective electron that emits or absorbs a phonon is scattered out of the effective electron belt on the Fermi surface as long as the phonon is not traveling parallel ($\pm\theta_p$) to the surface of the sample.

In both limits ($r \ll 1$, $r \gg 1$) Manz *et al.* find the first temperature-dependent correction term to the surface impedance to be proportional to T^5 as $T \rightarrow 0$, with differing coefficients. In order to analytically make connection with the form of ΔZ seen in the relaxation-time approximation [see Eq. (2.5)], Manz *et al.* assume the sample is in the extreme anomalous limit where $\Lambda_I/\delta \rightarrow \infty$.

In this limit, the electron-phonon relaxation rates from surface-impedance measurements, $1/\tau_z$, in the two extreme limits of r are determined and compared with the relaxation rate $1/\tau_p$, calculated from the dc electrical resistivity involving the same electron-phonon interaction.[15] Their results with $T \rightarrow 0$ are

$$\frac{1}{Z_z} = \frac{5}{12}\frac{1}{\tau_p}, \quad r \ll 1 \tag{2.6}$$

and

$$\frac{1}{\tau_Z} = \frac{1}{6}\frac{1}{\tau_p}, \quad r \gg 1 \tag{2.7}$$

each having a T^5 temperature dependence.

As pointed out by Manz *et al.*, in order to make a connection between their calculated ΔZ and that determined phenomenologically through the relaxation-time approximation, they must assume $\Lambda_I/\delta \rightarrow \infty$. In a strict sense they cannot define a simple effective relaxation rate. However, they have carried out lengthy numerical studies to determine the relation between $1/\tau_z$ and $1/\tau_\rho$ as a function of temperature. Figure 3 reproduces their results in the limit $r \gg 1$. This figure displays τ_z/τ_ρ as a function of reduced temperature $t=T/T_0$, where $T_0 = c_s k_F/k_B$. T_0 is a temperature near the Debye temperature for a simple metal. (Note that the curve approaches the $r \ll 1$ limit at high temperature.)

It should be emphasized that $1/\tau_z$ reflects an average over the entire Fermi surface. Surprisingly, this theory contains a geometrical factor $1-(\sin\theta)/\theta$ which at small angles is equivalent to the usual $1-\cos\theta$ term in dc transport phenomena. This then is the source of the predicted T^5 temperature dependence.

The contribution to the surface-impedance relaxation rate of electron-electron momentum conserving (normal or N process) scattering processes has been treated by Black and Mills.[9] They find that in the extreme anomalous limit the surface-impedance relaxation rate τ_z is directly proportional to an electron-electron N process scattering rate $1/\tau_N$. At sufficiently low temperatures where $1/\tau_N$ is proportional to T^2, electron-electron scattering dominates electron-phonon scattering, which is proportional to T^5.

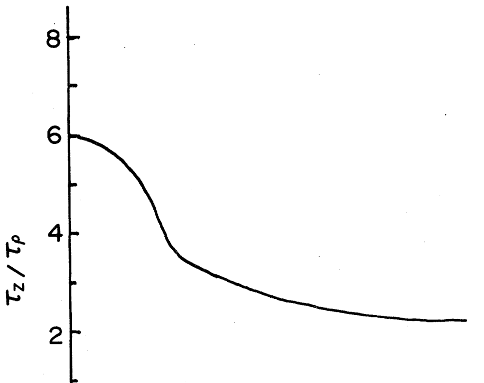

FIG. 3. Ratio of the relaxation time τ_z determined from surface impedance and relaxation time τ_ρ determined from dc electrical resistivity vs temperature in the limit $r \gg 1$. T_0 is approximately the Debye temperature in simple metals.

Somewhat surprisingly, their findings show that $1/\tau_z$ is directly proportional to $1/\tau_N$ with a *negative* coefficient. This follows from the result that electron-electron scattering increases rather than decreases the wave-vector–dependent conductivity at large wave vectors.

III. EXPERIMENTAL METHOD AND DATA ANALYSIS

The experimental apparatus is thoroughly described elsewhere,[16] thus only an abbreviated discussion is presented here. A circuit schematic for the low-temperature tunnel-diode oscillator is shown in Fig. 4. The fractional frequency stability of this oscillator at 4.2 K with $Q=620$ was $\Delta f/f = 1.4\times10^{-10}$ short term and 7.5×10^{-10} in 12 h operating near 1.4 MHz. The frequency counter averaging time was $\sim$8 sec.

The oscillator was contained within a vacuum can surrounded by a regulated liquid-helium bath. Extreme care was necessary to reduce to tolerable levels the dependence of the frequency of the oscillator on the helium-bath pressure and temperature. The inductor of the oscillator consisted of 166 turns of 0.025-cm-diam. Cu (99.999% purity) wire

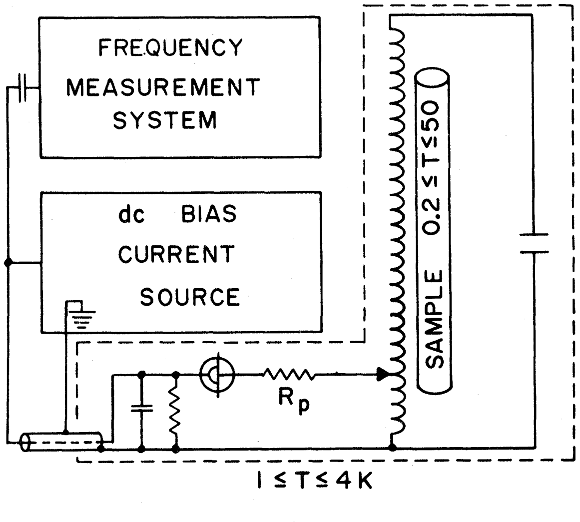

FIG. 4. Block diagram of experimental apparatus and electronics. Temperature of the sample is varied while that of the oscillator is held at the temperature of the liquid-helium bath. dc bias current source biases the tunnel diode at a point of minimum negative resistance. Frequency-measurement system includes amplifiers, a frequency synthesizer, a mixer, an oscillator phase-locked to the mixer output, and a frequency counter.

wound at a uniform pitch of 22.0 turns/cm on a helically grooved 1.27-cm-diam. single-crystal sapphire tube. The 440-pF capacitor was coaxial with the coil and consisted of a central cylinder supported within an annulus by six 0.16-cm-diam. sapphire spheres. A tiny lever could be adjusted when the apparatus was at room temperature to securely connect R_P to any turn on the coil. R_p is a parasitic suppression resistor that lowers the Q of the potential oscillation consisting of the junction capacitance of the tunnel diode and the lower portion of the coil. The appropriate turn of the coil for the attachment of R_P is determined by proper impedance matching. The circuit normally oscillated at 1.4 MHz, but the frequency could be varied by changing the spacing of the capacitor. The problem of separating the temperature dependence of the sample from that of the oscillator circuit components was overcome by thermally isolating the sample from the oscillator. The effect of mechanical vibrations was made negligible by the appropriate use of rigid graphite and stainless-steel supports to reduce the relative motion of the sample and coil.

The room-temperature electronics include a dc bias current source for the tunnel diode and a frequency measurement system. Only about 0.1-μV rms of the oscillator signal appears at the input to the frequency measurement system.

The temperature sensor is either a calibrated Ge or C (for $T \lesssim 0.5$ K) resistor. The C resistor was calibrated against the Ge thermometer each successive cool-down. The resistance measurement is made by the usual four-lead dc method. The uncertainty of the temperature measurement is less than 0.1% throughout the temperature range examined in this paper.

In order to determine the residual resistivity ratio ($\mathscr{R}$) of the metal samples, a contactless eddy-current decay method was employed. It has been shown[17] that if R is the radius of the sample in cm and the resistivity ρ given in Ω cm, the time constant τ_R of the exponential decay of the voltage in a coil surrounding the sample after removal of a uniform magnetic field is

$$\tau_R \cong 2.17 R^2 \times 10^9/\rho \,. \qquad (3.1)$$

This time constant is detected by the method of Le Page *et al.*[18] with a commercial logarithmic amplifier.[19] A protected operational amplifier eliminated the need of a shorting switch.

The uncertainty of this method of determining $\mathscr{R}$ is estimated to be 10%. This uncertainty is not serious due to the insensitivity of the anomalous surface impedance to $\mathscr{R}$ once $\mathscr{R}$ is sufficiently large.

In order to obtain values of the electronic relaxation time as a function of temperature from the measurement of the oscillator frequency as a function of sample temperature, we used the Reuter-Sondheimer formulas. A list of values of surface impedance obtained from the Reuter-Sondheimer formulas expressed in an appropriate parametrized form is used in a computer routine to create a simulated data set for each experiment of oscillator frequency versus a convenient parameter λ, given below. The actual experimental data of oscillator frequency versus temperature are compared to this computed data set to determine the temperature dependence of the appropriate parameter which is proportional to the relaxation rate of the conduction electrons. This process is explained in greater detail in the following paragraphs.

We begin by recalling Eqs. (2.1) and (2.2) in parametrized form, using

$$\lambda = 3\Lambda^2/\delta^2 \qquad (3.2)$$

to have

$$Z_s^{p=1} = -j\left[\frac{16 m^* \omega^2 v_F \mu^2}{3ne^2\pi^3}\right]^{1/3} \lambda^{1/3} I_1(\lambda) \qquad (3.3)$$

and

$$(Z_s^{p=0})^{-1} = j\left[\frac{3ne^2}{2m^*\omega^2 v_F \mu^2 \pi^3}\right]^{1/3} \lambda^{-1/3} I_0(\lambda)\,, \qquad (3.4)$$

where

$$I_1(\lambda) = \int_0^\infty \frac{d\eta}{\eta^2 - j\lambda\left[\left(\frac{1}{\eta}+\frac{1}{\eta^3}\right)\tan^{-1}\eta - \frac{1}{\eta^2}\right]} \qquad (3.5)$$

and

$$I_0(\lambda) = \int_0^\infty \ln\left\{1 - j\frac{\lambda}{\eta^2}\left[\left(\frac{1}{\eta}+\frac{1}{\eta^3}\right)\tan^{-1}\eta - \frac{1}{\eta^2}\right]\right\} d\eta \,. \qquad (3.6)$$

A tabulation of the functions $\lambda^{1/3} I_1(\lambda)$ and $\lambda^{-1/3} I_0(\lambda)$ as a function of λ is generated by a Simpson's-rule integration scheme on a digital computer. Approximately 600 entries are computed to an accuracy of one part in 10^6 for the range

$10^{-3} \le \lambda \le 10^9$. This first table (surface impedance versus λ) is used in a later step of the analysis.

The experimental data of oscillator frequency versus sample temperature are fitted to a simple formula by a least-squares method to determine the extrapolated oscillator frequency at $T=0$, f_0. From this, a list of fractional frequency shift, $(f-f_0)/f_0$, versus sample temperature is determined.

The next step is to generate a second table, this time of frequency shift versus λ from Eqs. (3.3) and (3.4). The necessary inputs are $\mathscr{R}$, f_0, a filling factor, and the oscillator Q. The filling factor is not simply a ratio of the sample volume to the coil volume because the filling factor must be adjusted for the shielded environment of the inductor. (The volume available to the field even with the coil empty is reduced from that of a coil in free space.) The entries in this frequency shift versus λ table are calculated using the values of the surface inductance L_s [$L_s = \mathrm{Im}(Z_s/\omega)$] from the first table. The oscillator Q is obtained from the values of the real part of the surface impedance and $\mathscr{R}$. The frequency shift resulting from a change in Q is obtained from an analytic expression derived elsewhere.[20] Thus, a final tabulation produces a numerical simulation of a "Reuter-Sondheimer metal" located within an inductor of an oscillator whose frequency is dependent upon the Q of the oscillator.

Each data point from the actual experiment (frequency shift and temperature) is analyzed in a four-point Lagrangian interpolation within the table just described to determine the value of λ associated with the temperature of that data point. The temperature-dependent electronic relaxation rate is found by subtracting the relaxation rate at $T=0$ determined by $\mathscr{R}$. That is,

$$1/\tau(T) = 1/\tau - 1/\tau(T=0) \ . \qquad (3.7)$$

Here again, the uncertainty in $\mathscr{R}$ is not serious because the simulated oscillator is insensitive to the exact value of $\mathscr{R}$ in the anomalous limit.

The quantitative accuracy of $1/\tau(T)$ is not good. Owing to the uncertainty of the effects of the shielded environment and approximately a factor of 2.5 difference between the specular and diffuse analyses, we can claim only precision in the temperature dependence. Of course at the higher temperatures when the sample resides in the classical skin-effect regime, our results should match those of dc electrical resistivity measurements.

Figure 2 indicates that for a given change in surface impedance, diffuse surface scattering results in a smaller value of the parameter $\lambda^{-1/3}$ than specular surface scattering. We have found that diffuse surface scattering generally yields better quantitative agreement with dc data. All the analyses of data presented below assumed diffuse scattering.

IV. SAMPLE DESCRIPTIONS AND PREPARATIONS

In this section we present descriptions of the copper, aluminum, and potassium samples examined. The sample descriptions include dimensions, residual resistance ratios ($\mathscr{R}$), purities, and crystalline character. The sample preparations include heat treatments and chemical polishing of surfaces. A summary of sample characteristics appears in Table I.

A. Copper

Four different copper samples have been examined. They are denoted as OFHC (for oxygen-free, high conductivity) copper, Schriempf's copper sample, Cu-100, and Cu-111.

The OFHC copper sample, a 0.48-cm-diam. polycrystalline commercially acquired rod of at least 99.9% purity, had an original $\mathscr{R}$ of only 50 determined using a four-terminal dc measurement. The surface was electropolished as described by Tegart.[21] Upon oxygen annealing the $\mathscr{R}$ of this sample increased to 180 as measured in an eddy-current decay method of Le Page *et al.*[18] This sample was again electropolished but in a different and improved method described by Powers.[21]

TABLE I. Summary of sample properties.

Sample label	$\mathscr{R}$	Λ/δ (at $T=0$)	T (in K) at which the Manz *et al.* parameter $r=1$
		Copper	
OFHC	50	0.3	>1000
O_2-annealed			
OFHC	180	2	~ 150
Schriempf	1500	50	14
Cu-100	5600	390	4
Cu-111	2150	290	10
		Aluminum	
Al-100	2500	40	27
		Potassium	
K-3	300	1.8	38

Schriempf's copper sample, a 0.18-cm-diam. polycrystalline rod previously oxygen annealed by him, had an $\mathscr{R}$ of 1500. The sample was electropolished by the method of Tegart before any surface-impedance data was obtained. dc electrical resistivity measurements were taken with this sample,[22] and these are compared to the results obtained from the surface-impedance measurement. This sample was subsequently oxygen annealed in this laboratory and electropolished by the Powers method. $\mathscr{R}$ was found to be unchanged through a four-terminal dc measurement.

Two high-purity (99.999%) oriented single-crystal ([100] and [111] directions along the rf magnetic field) copper samples were obtained from Materials Research Corporation.[23] Each had a diameter of 0.63 cm. The sample Cu-100 had an $\mathscr{R}$ of 5600 and Cu-111 had an $\mathscr{R}$ of 2150 after oxygen annealing. These $\mathscr{R}$'s were determined by the eddy-current decay technique. Cu-100 was electropolished by the Tegart technique, and Cu-111 was electropolished by the Powers technique.

B. Aluminum

A 0.63-cm-diam. single crystal of high-purity (99.9999%) aluminum oriented with the [100] direction along the rf magnetic field was purchased from Aremco Products.[24] Some cold working was required to straighten the sample. After a subsequent vacuum annealing, an $\mathscr{R}$ of 2500 was determined using the eddy-current decay method. This sample was electropolished as described by Tegart.[25]

C. Potassium

High-purity (99.95%) potassium was obtained from MSA (Ref. 26) in high-purity Spectrosil-A quartz[27] ampoules filled under a flowing argon atmosphere and sealed about 4–5 cm above the metal. The magnetic susceptibility of the quartz added a temperature dependence to the oscillator frequency unrelated to the surface impedance of the potassium. This addition is due to paramagnetic impurities in the quartz. A test with a similar quartz tube containing ^{4}He for thermal equilibration found this contribution to be proportional to $1/T$ and only significant below 2 K. Thermal time constants due to the quartz were found not to be serious in any of the measurements.

Voids would form between the quartz and the metal when attempts were made to grow single crystals of K within the ampoule.[28] The sample discussed in the next section contained three such voids ($\sim$1-mm diam.). These were later determined to be due to trapped Ar. It should be emphasized that there was no control of the surface character of the potassium sample because of the quartz container.

We have found the quartz container to be a serious problem in trying to obtain a high $\mathscr{R}$ sample. $\mathscr{R}$ of the sample discussed in the next section was only 300 as measured by the eddy-current decay method. This low value is not due to impurities—it is an indirect effect of the quartz. The potassium adheres to the quartz resulting in stresses in two fashions. First, the volume reduction of the potassium upon solidification of the molten metal is at least 2.5%.[29] This we believe to be about 50% of the problem because after five weeks' storage at room temperature, $\mathscr{R}$ increased to 600. Another source of stress is due to the differential thermal contraction between the metal and the quartz upon cooling the sample. This results in a negative hydrostatic pressure upon the metal.[30] The sample is cooled to 77 K in time intervals $\gtrsim 4$ h when making $\mathscr{R}$ measurements and $\gtrsim 18$ h when making rf measurements in an attempt to minimize this problem. Rapid cooling to 77 K (on the order of minutes) is known to be detrimental to attaining high-$\mathscr{R}$ samples. A free-standing sample of potassium was formed from the metal of one of the ampoules and its $\mathscr{R}$ was found to be greater than 1500. The uncertainty is due to surface contamination affecting the cross-section area of metal. This sample also had a great deal of cold working. The argon was removed from another ampoule while the potassium was heated above the melting point. Later, $\mathscr{R}$ was measured to be only 300. No voids were observed in this sample. Thus we believe the low $\mathscr{R}$ is not due to impurities (Ar included), but due to stresses in the metal caused by the quartz container.

V. RESULTS AND DISCUSSION

Results for the copper, aluminum, and potassium samples are presented in this section. The deduced surface-impedance relaxation rates are compared to dc relaxation rates calculated from dc electrical resistivity data. These comparisons of different experimental methods are used to examine the validity of the theoretical works of Black and Mills and co-workers.[7,9] A summary of sample characteristics appears in Table I.

A. Copper

Surface-impedance relaxation rates versus temperature for the OFHC copper sample without heat treatment (open circles) and after oxygen annealing (solid circles) are presented in Fig. 5 along with dc relaxation rates (triangles) calculated from the classic dc electrical resistivity data of White and Woods.[31] The qualitative consistency is quite good as is the quantitative agreement when one considers the uncertainties in determining the filling factor of the sample within the coil. This agreement is not a test of the anomalous skin-effect calculations since the ratio of the electron mean free path to the rf skin depth is only about 0.3 for the unannealed case and only 2 for the oxygen-annealed case. From this comparison we are able to conclude that our analysis routines are correct in the high-temperature and/or low-$\mathscr{R}$ classical skin-effect regime.

The rapid temperature dependence below 10 K for the "as-received" sample and that below 6 K for the oxygen-annealed case are both due to a Kondo-type resistivity minima at about 4 K. The magnetic impurity responsible for this is unknown, but is probably Mn or Cr.

Schriempf's copper sample has a Λ/δ ratio of about 50 at $T=0$. Therefore this sample is in the anomalous regime below about $T=15$ K. The deduced relaxation rates versus temperature are presented in Fig. 6, where the open circles are the results from the sample without additional heat treatment, the solid circles are those after the sample was oxygen annealed in this laboratory, and the triangles are dc relaxation rates calculated from the dc electrical resistivity data obtained on this sample by Schriempf.[22]

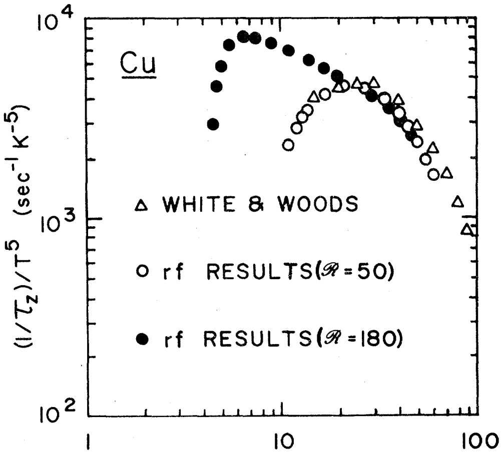

FIG. 5. Comparison of surface-impedance results from commercial grade OFHC copper to results from dc electrical resistivity data of White and Woods. The higher-$\mathscr{R}$ data are obtained after oxygen annealing.

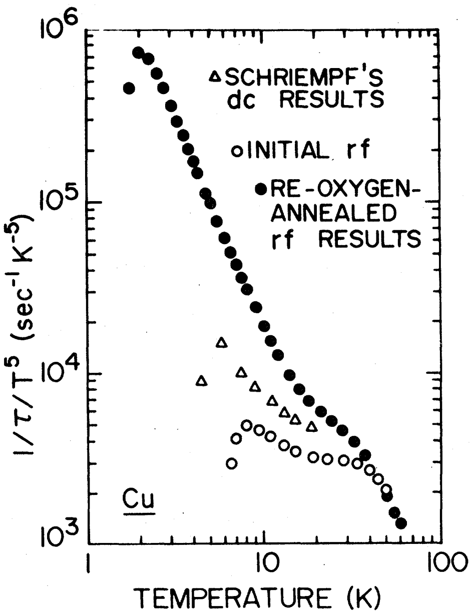

FIG. 6. Comparison of rf and dc results from a high-purity polycrystalline sample of copper. Reasonable quantitative and qualitative agreement are found between Schriempf's dc electrical measurements and the initial rf measurement. Higher-temperature data correspond with those of Fig. 5. The re-oxygen-annealed rf results indicate a dramatic T^2 dependence below 10 K.

We first discuss the qualitative features. The high-temperature ($T>30$ K) rf data are seen to overlap the oxygen-annealed OFHC copper sample and the White and Woods dc data of Fig. 5. The lowest-temperature data for all three cases of Fig. 6 are indicative of Kondo-type resistivity minima at differing temperatures. This shift in the Kondo temperature probably results from the measurement technique that probes different fractional volumes of the sample. The dc measurement probes 100% of the sample. The first rf measurement probed roughly a 3-μm surface layer and the second rf measurement probed a similar 3-μm layer after removal of a surface layer of material by electropolish. In the intermediate-temperature range ($8 \lesssim T \lesssim 30$) we see good qualitative agreement between the dc results and the rf results in the untreated case. The re-oxygen-annealed results are indicative of a T^2 dependence below $T=15$ K in contrast to the other data.

Quantitative comparisons can be made through the use of the theoretical investigations of Manz *et al.*[7] Their dimensionless characteristic parameter r is found to be equal to one at a temperature of about 15 K. If we assume $r \ll 1$ (the low-temperature limit), then Manz *et al.* predict $1/\tau_z$ to be about 0.4 times $1/\tau_p$. The experimental data suggest a ratio of about 0.6 in this case. The difference is not a serious discrepancy due to the model-dependent nature of the theory. It is also noted that the theoretically predicted T^5 variation in both $1/\tau_z$ and $1/\tau_p$ as $T \rightarrow 0$ is not observed in the surface-impedance or in other dc measurements which indicate either T^3 (Ref. 32) or T^4 (Ref. 33) dependencies.

The re-oxygen-annealed data show a striking T^2 dependence from about 1.5 to 15 K. The coefficient of the T^2 here is about 10^7 $\text{sec}^{-1}\,\text{K}^{-2}$. Black and Mills[9] showed that the relaxation rate due to electron-electron N processes may appear in the surface-impedance relaxation rate without any fractional umklapp scattering parameter. Lawrence[34] calculated the contribution of electron-electron scattering to the dc electrical resistivity of copper. He finds $\rho_{ee}/T^2 = 7.6 \times 10^{-14}$ $\Omega\,\text{cm}\,\text{K}^{-2}$ with an umklapp effectiveness parameter $\Delta = 0.79 \pm 30\%$, which translates into a full electron-electron relaxation rate of $1.36 \times 10^6 T^2$ sec^{-1} by removing the dependence on Δ as suggested by Black and Mills.[9] We therefore see that the theoretical prediction is about a factor of 7 below our observed coefficient of T^2. A recent observation of a T^2 dependence in a dc measurement on polycrystalline copper[33] is about a factor of 2 below the dc prediction of Lawrence. The reported coefficient of T^2 equates to a relaxation rate of 5.4×10^5 $\text{sec}^{-1}\,\text{K}^{-2}$, nearly a factor of 20 below our value. Further comments on electron-electron scattering and contributions to the surface-impedance relaxation rate are found at the end of this section.

Further work with high-$\mathscr{R}$ single-crystal samples of copper gave results not consistent with theory for $T \lesssim 20$ K. For example, data from the Cu-100 sample after the first oxygen annealing and electropolishing displayed a T^2 contribution proportional to 3×10^7 $\text{sec}^{-1}\,\text{K}^{-2}$ in the temperature range $3 < T < 15$. Further measurements after the second oxygen annealing and electropolishing found the T^2 behavior only between 6 and 15 K of magnitude, approximately 10^8 $\text{sec}^{-1}\,\text{K}^{-2}$. Data between 0.5 and 4 K on this sample yielded a relaxation rate proportional to T^3 with a coefficient of about 7×10^6 $\text{sec}^{-1}\,\text{K}^{-3}$. The Cu-111 sample yielded data with a T^3 dependence below 6 K proportional to about 4×10^6 $\text{sec}^{-1}\,\text{K}^{-3}$ and lacked a pure T^2 at intermediate temperatures. However, between 8 and 18 K a power of T between 2 and 3 is observed. For comparison, one should note that a T^3 component in the dc electrical resistivity has been observed in copper by Rumbo.[32] His T^3 coefficient translates into a relaxation rate coefficient of 0.3×10^6 $\text{sec}^{-1}\,\text{K}^{-3}$, at least an order of magnitude smaller than reported here.

B. Aluminum

The measured relaxation rates from a single-crystal aluminum sample (Al-100) versus temperature are presented in Fig. 7. It is observed that in the temperature range $3 \lesssim T \lesssim 15$ K, the temperature dependence of $1/\tau_z$ is in qualitative agreement with the inverse scattering time calculated from the dc electrical resistivity data of Ekin and Bringer.[35] At the higher temperatures (above 35 K), the sample is in the classical skin-effect regime. At these temperatures, the temperature dependence (the slope) is not in complete agreement with the dc data. This may be due to an error in determining the filling factor. If the rf data of Fig. 7 were increased by a factor of about 1.15, then it appears that the curves might meet with equal slopes.

The uncertainty in the filling factor has been found to be at least 15%.[20] This is determined by calculating the inductance of the coil in this shielded geometry (with some simplifications) and comparing this to the inductance determined from the reasonant frequency and the known capacitance

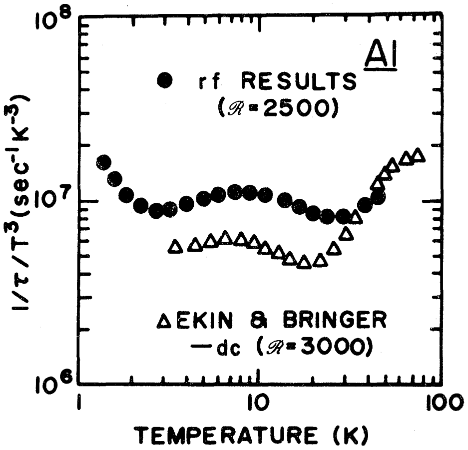

FIG. 7. Comparison of relaxation rates obtained from rf surface impedance and dc electrical resistivity for aluminum.

measured at room temperature.

The Manz *et al.* parameter r for this aluminum sample is found to equal one at 27 K. Again, Manz *et al.* predict the rf results should be 0.4 of the dc results. However, the data of Fig. 7 show the ratio of rf to dc to be about 2, nearly a factor of 5 greater than predicted. This is not considered a serious error due to the very model-dependent calculation of Manz *et al.*

C. Potassium

The surface-impedance results of potassium sample K-3 in a quartz ampoule are presented as $\log_{10}(\rho-\rho_0)/T$ vs $1/T$ in Fig. 8 with the effects due to the quartz removed. The dc resistivity results of Ekin and Maxfield[36] are presented as open triangles, and those of van Kempen *et al.*[37] are presented as filled triangles. The low $\mathscr{R}$ of 300 in this sample is due to stresses and not impurities as discussed in Sec. IV. This sample lies in the crossover regime between the anomalous and classical skin-effect regimes with $\Lambda/\delta\approx 1$ at low temperature.

The data follows the form

$$\rho(T)=\rho_0+AT^2+BTe^{-\Theta/T}$$

as seen by other investigators[36–39] with $\Theta=20$ K, in agreement with the dc data. The departure from the exponential dependence at about 4 K is the result of the T^2 contribution. It is observed that this T^2 dependence is at least 2 orders of magnitude greater than that observed in dc resistivity measurements, regardless of any error in filling factor noted at the higher temperatures. The coefficient of the T^2 term here is 27 pΩ cm K^{-2} and is on the order of that predicted for the full electron-electron scattering rate calculated by Kukkonen and Wilkins.[40]

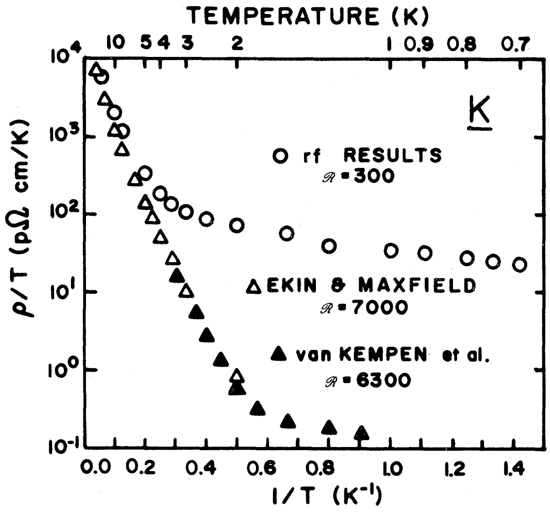

FIG. 8. Comparison of rf and dc results for high-purity potassium. The low $\mathscr{R}$ for the rf sample is not due to impurities (see text). The departure from exponential behavior at lower temperatures is indicative of a T^2 dependence. Our coefficient of the T^2 term is at least 2 orders of magnitude greater than that observed in dc measurements.

Kukkonen and Wilkens actually calculate the electron-electron contribution to the thermal resistivity. Within the relaxation-time approximation, the relaxation time for the electrical resistivity is the same as that for the thermal resistivity. Within this assumption the prediction of Kukkonen and Wilkins corresponds to a T^2 coefficient for the full electron-electron scattering contribution to electrical resistivity of 14.5 pΩ cm K^{-2}, nearly a factor of 2 below our observation. We therefore find reasonable consistency between our coefficient of T^2 and the full electron-electron relaxation rate predicted by Kukkonen and Wilkins. This supports the contention of Black and Mills[9] that the full electron-electron scattering rate contributes to the surface impedance *only* in magnitude but not with respect to the sign of the contribution. If there were full agreement between theory and experiment, then the impedance (proportional to relaxation rate) would be observed to *decrease* as T^2. Actually, the impedance is observed to *increase* as T^2. We have no explanation of this discrepancy.

VI. CONCLUSIONS

In copper, we first observe that the electronic relaxation rates determined from the surface impedance at temperatures within the classical skin-effect regime agree with the rates obtained from dc resistivity measurements to within the accuracy of the geometric filling factors. It should be noted that the analysis of our data employed the Reuter-Sondheimer formulas and not explicitly the simple classical skin-effect expression. In this limit the analysis is independent of the character of the surface scattering (specular or diffuse). This agreement provides evidence for the validity of the analysis routine.

This technique of measuring the surface impedance has the demonstrated resolution to measure the temperature-dependent contribution to the surface impedance in the anomalous limit. Since the temperature-dependent contribution in the anomalous limit is dependent upon an appropriate electronic relaxation rate, this technique is capable of measuring that rate. As pointed out in theoretical papers, this relaxation rate is not identical to, but related to, the relaxation rate associated with dc resistivity.

Surface-impedance measurements on a pure polycrystalline copper sample ($\mathscr{R}=1500$) yielded qualitative and quantitative agreements with dc measurements on the same sample. The theoretical analysis of Manz *et al.* was used to relate the surface-impedance relaxation rate to the dc resistivity relaxation rate. For this sample, the mean free path divided by the rf skin depth is approximately 50 at $T=0$. This agreement is observed for temperatures greater than 6 K. Below this temperature a Kondo-type anomaly prevents a detailed comparison. In order to obtain this quantitative agreement, diffuse surface scattering had to be assumed.

Studies of high-purity single-crystal copper samples gave inconsistent results, dependent upon the treatment of the surface for temperatures below 20 K. Within an intermediate temperature regime typically $7<T<18$ K a T^2 temperature dependence was observed. The coefficient of this term varied by a factor of 3, increasing with further heat treating. Below 5 K, typically a T^3 dependence appeared. The coefficient of this term varied by a factor of 3 between two samples. Measurements on the pure polycrystalline sample after an additional oxygen annealing gave a T^2 dependence between 1 and 15 K. We believe we have ruled out any possible magnetic impurity effects that might produce such a temperature dependence.[41] The magnitude of the coefficient of this T^2 term is a factor of 3 less than the smallest T^2 coefficient in the single-crystal copper data.

Published dc resistivity data do not show these dependencies of comparable magnitude in the same temperature ranges. A T^2 dependence was reported in the low-temperature limit (below 2 K) rather than the intermediate-temperature regime with a coefficient about 1 order of magnitude smaller than observed here. A T^3 dependence reported in dc resistivity in the intermediate-temperature range is at least 1 order of magnitude smaller than seen here.

Surface-impedance measurements on a single-crystal aluminum sample gave qualitative but not quantitative agreement with published data for the resistivity of aluminum of comparable $\mathscr{R}$. The ratio of the mean free path to the rf skin depth is approximately 40 at $T=0$. This qualitative agreement was observed in the temperature range from the superconducting transition temperature to the upper limit of our measurements, 40 K. Again, diffuse surface scattering at the surface was required to give the closest quantitative agreement.

Surface-impedance measurements on a pure but greatly stressed potassium sample yielded relaxation rates consistent both qualitatively and quantitatively with an exponential temperature dependence above 5 K as observed by others in the dc measurements. Below 4 K the coefficient of a T^2 term observed here is at least 2 orders of magnitude greater than that observed in dc measurements. This coefficient is, however, within a factor of 2 of the predicted full electron-electron scattering rate including the normal scattering processes. Presently, there is no convincing theoretical basis to claim that our observed behavior is due to electron-electron scattering.

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[†] Permanent address: National Bureau of Standards, Washington, D. C. 20234.

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