PHYSICAL REVIEW B, VOLUME 64, 233106

Residual resistivity for alkali and noble metals at 0 K

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(Received 29 May 2001; published 27 November 2001)

A derivation of the decay rate of electrons in emission of acoustic phonons in single-crystal pure alkali and noble metals at 0 K is obtained that leads to an expression for the residual resistivity for this class of metals at 0 K given by (cgs)

$$\rho(0)=\frac{mW_0q_c^3}{3ne^2k_F}f(x_F)=\frac{2\pi}{3}\frac{mE_1^2\sqrt{15Mm}}{e^2\rho_M\hbar E_F}\propto\frac{M^{1/2}E_F}{n_i}$$

where $f(x_F)$ is a known positive definite function of the parameter $x_F\equiv 2k_F/q_c$, q_c is a characteristic wave number, k_F is the Fermi wave number, W_0 is a known parameter, e is electronic charge, E_1 is the deformation-potential constant, and E_F is the Fermi energy. The right side of the above relation shows the dependence of $\rho(0)$ on electron-ion masses (m,M), ion mass density ρ_M, and the Fermi energy. A plot of the proportionality form on the right of the preceding relations against ion number density (with related values for Li and Cs varied for consistency) shows nearly parallel behavior with measured residual resistivity of pure alkali metals.

DOI: 10.1103/PhysRevB.64.233106 PACS number(s): 72.15.Eb, 72.10.−d, 05.20.Dd

I. INTRODUCTION

This paper addresses residual resistivity at 0 K in pure alkali and noble metals. In a previous work,[1] employing the quantum Boltzmann equation, it was found that in addition to Bloch's T^5 component, residual electrical resistivity exists at 0 K for this class of single-crystal metals void of impurities. Bloch's electrical resistivity temperature dependence was found to enter at $T\gtrsim\Theta/5$, where Θ is the Debye temperature. In a more recent study,[2] an expression for thermal conductivity was derived for this class of metals that includes an analysis of the decay rate of electrons in emission of acoustic phonons at 0 K. In the present work, an alternative derivation of residual resistivity in a pure metal is given that stems directly from the latter property. The decay rate so derived is a positive definite form that implies residual resistivity for this class of metals. Plotting the proportionality form of the resulting formula against ion number density shows, apart from anomalous behavior of Cs and Li, nearly parallel behavior with measured residual resistivity of pure alkali and noble metals.

II. PERTURBATION

The perturbation Hamiltonian describing the deformation potential interaction is given by[3,4]

$$H'=iE_1\sum_{\mathbf{kq}}(\hbar/2M_T\omega_{\mathbf{q}})^{1/2}|\mathbf{q}|(a_{\mathbf{q}}-a^{+}_{-\mathbf{q}})c^{+}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}. \tag{1}$$

In this expression, $a_{\mathbf{q}},a^{+}_{\mathbf{q}}$ and $c_{\mathbf{k}},c^{+}_{\mathbf{k}}$ are phonon and electron annihilation and creation operators, respectively, $\hbar\omega_{\mathbf{q}}$ is phonon energy, E_1 is the deformation-potential constant (with dimensions of energy), and M_T is mass of the sample. The term at the far right in Eq. (1) is equivalent to $-a^{+}_{\mathbf{q}}c^{+}_{\mathbf{k}-\mathbf{q}}c_{\mathbf{k}}$ and represents phonon emission, whereas the second term from the right represents phonon absorption. The Hamiltonian (1) assumes a spherical energy surface.[4,5]

The probability per unit time that an electron with momentum $\mathbf{k}$ decays in emission of a phonon with momentum $\mathbf{q}$ in a metal with phonon population $n_{\mathbf{q}}$ is given by

$$W=\frac{2\pi}{\hbar}|\langle\mathbf{k}-\mathbf{q};n_{\mathbf{q}}+1|H'|\mathbf{k},n_{\mathbf{q}}\rangle|^2\delta(E_{\mathbf{k}}-\hbar\omega_{\mathbf{q}}-E_{\mathbf{k}-\mathbf{q}}). \tag{2}$$

As noted previously,[1] this decay may be attributed to a process "induced" by zero-point ion oscillations. With Eq. (1) we obtain

$$|\langle\mathbf{k}-\mathbf{q};n_{\mathbf{q}}+1|H'|\mathbf{k},n_{\mathbf{q}}\rangle|^2=(E_1^2\hbar q/2M_Tc_s)(n_{\mathbf{q}}+1), \tag{3}$$

$$c_s^2=\frac{m}{15M}v_F^2=\frac{2}{15M}E_F=\frac{(\hbar k_F)^2}{15\,Mm},\quad \omega_q=c_sq, \tag{4a}$$

$$E_F=\frac{\hbar^2}{2m}(3\pi^2n)^{2/3},\quad k_F^2=(3\pi^2n)^{2/3}, \tag{4b}$$

where c_s is sound speed, (M,m) are ion and electron effective mass, respectively, and v_F, k_F, and E_F are Fermi speed, wave number, and energy, respectively. At 0 K, $n_{\mathbf{q}}=0$, and only the first term on the far right of Eq. (1) representing phonon emission is relevant.

III. DECAY RATE

The total decay rate becomes (including a tacit integration over volume)

$$W=[E_1^2/4\pi c_s]\int_{-1}^{1}d\cos\theta\int_0^{q_m}dq\,q^3\delta(E_{\mathbf{k}}-\hbar\omega_{\mathbf{q}}-E_{\mathbf{k}-\mathbf{q}})$$

$$=W_0\int_{-1}^{1}d\cos\theta\int_0^{q_m}dq\,q^3\delta(2\mathbf{k}\cdot\mathbf{q}-q^2-qq_c), \tag{5a}$$

$$W_0\equiv\frac{mE_1^2}{2\pi c_s\rho_M\hbar^2},\quad \hbar q_c\equiv 2mc_s. \tag{5b}$$

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The coefficient W_0 has dimensions of c_s/k, $\rho_M = M_T/V$ is ion mass density, and V is the volume of the metal. The upper limit q_m in Eq. (5a) represents the radius of a sphere in $\mathbf{q}$ space chosen so that the number of enclosed modes equals the number of atoms in the sample. In obtaining Eq. (5a), it was noted that $\hbar^2/2m$ is a common factor in the argument of the delta function. As q is written for the magnitude of $\mathbf{q}$ both in the volume element $dq\, q^2$ and in the linear factor in H', it follows that the domain of q in the present study is $q \geqslant 0$. Developing the δ function in Eq. (5a) gives

$$\delta(2\mathbf{k}\cdot\mathbf{q} - q^2 - qq_c) = \delta[q(q-\overline{q})] = \frac{\delta(q) + \delta(q-\overline{q})}{|\overline{q}|}, \tag{5c}$$

$$\overline{q} \equiv 2k\mu - q_c, \quad \mu \equiv \cos\theta = \frac{\mathbf{k}\cdot\mathbf{q}}{kq}. \tag{5d}$$

In developing the second δ function Eq. (5c), one notes that $\overline{q}$ values are in the domain of q. It follows that $\overline{q}$ values likewise satisfy the condition $\overline{q} \geqslant 0$, which, with Eq. (5d), gives $k_{\min} = q_c/2$. With these observations and the property $\overline{q} = |\overline{q}|$, one writes

$$W = W_0 \int_{-1}^{1} d\mu\, \overline{q}^2 \frac{\overline{q}}{|\overline{q}|} = W_0 \int_D d\mu\, \overline{q}^2, \tag{6}$$

where D is the domain $\overline{q} \geqslant 0$. To evaluate this integral we transform variables of integration from μ to $\overline{q}$. There results

$$W = W_0 \int_D d\mu\, \overline{q}^2 = W_0 \frac{1}{2k} \int_0^{2k-q_c} d\overline{q}\, \overline{q}^2$$
$$= \frac{W_0 (2k)^2}{3} \left(1 - \frac{q_c}{2k}\right)^3, \tag{7}$$

which has the dimensions of inverse time. This positive decay rate illustrates that electron decay in a metal with emission of a phonon persists at $T = 0$ K. It is noted that neglecting $q_c/2k$ in Eq. (7) returns previously obtained high-k estimates of W.[3,4] Note that

$$k_{\min} = \frac{q_c}{2} = \frac{mc_s}{\hbar} \tag{8a}$$

is the minimum value of k for which the argument of the δ function on the left of Eq. (5c) vanishes[4] and corresponds to $q = 0$. This minimum k value is consistent with the positive quality of W, Eqs. (8). It is noted that

$$k_{\min}^2 = \frac{m}{30M} k_F^2 \ll k_F^2 = (2\pi^2 n)^{2/3}. \tag{8b}$$

We note further that in the absence of an applied field, the electron-phonon scattering matrix element in Eq. (2) vanishes at 0 K because conduction electrons are contained within the Fermi sphere and the interaction cannot conserve energy.[6] However, with an electric field present, electrons displaced from the Fermi surface are made available and the scattering matrix in Eq. (2) does not vanish at 0 K.

IV. RESISTIVITY

To obtain an expression for resistivity in the present case, we recall the canonical form for the current density:[7]

$$J = \frac{ne^2 \tau E}{m} = \frac{1}{\rho} E, \tag{9a}$$

where E is the applied electric field, n is the conduction-electron number density, ρ is the electrical resistivity, and at finite temperatures, τ^{-1} is the electron-phonon collision frequency. At 0 K this interpretation of τ^{-1} is not appropriate. Instead, it is given by the decay-rate integral

$$\frac{1}{\tau} = \frac{1}{k_F} \int_{\min}^{k_F} W\, dk > 0 \tag{9b}$$

The integral in this expression may be reduced as follows. Changing the variables to

$$x \equiv \frac{2k}{q_c} \geqslant 1$$

gives

$$\frac{1}{\tau} = \frac{W_0 q_c^3}{3k_F} \int_1^{x_F} \frac{1}{x} (x-1)^3 dx > 0, \tag{9c}$$

TABLE I. Parameters for the alkali and noble metals including measured residual resistivity $\rho(0)$ and proportionaliy factor $\tilde{\rho}(0)$, both in relative units. Correction factors are shown also.

Metal	$n_i \times 10^{-22}$ (cm^{-3})	$\rho(0) \times 10^2$	M (amu)	E_F (eV)	$\tilde{\rho}(0) \times 10^{22}$
Cs	0.905	(4)16	133	1.58 (5 K)	(3)20.13
Rb	1.15	33.5	85.5	1.85 (5 K)	14.88
K	1.40	14	39	2.12 (5 K)	9.457
Na	2.65	0.40	23	3.23 (5 K)	5.845
Li	4.7	3.25	6.9	4.7 (78 K)	(2) 2.627
Ag	5.85	2.86	108	5.48 (300 K)	3.245
Au	5.90	1.67	197	7.00 (300 K)	4.37
Cu	8.45	0.781	63.6	5.48 (300 K)	2.202

$$x_F \equiv \frac{2k_F}{q_c} = \frac{v_F}{c_s} = \frac{k_F}{k_{\min}} > 1. \tag{9d}$$

The preceding integrates to give

$$\frac{1}{\tau} = \frac{W_0 q_c^3}{3k_F}\left(\frac{x_F^3}{3} - \frac{3x_F^2}{2} + 3x_F - \ln x_F\right) \equiv \frac{W_0 q_c^3}{3k_F} f(x_F), \tag{10}$$

where $f(x_F)$ is as implied. Thus our expression for the resistivity of a pure single crystal at 0 K is given by (we recall that in cgs, $[\rho]=\text{time}$)

$$\rho(0) = \frac{mW_0 q_c^3}{3ne^2 k_F} f(x_F) > 0. \tag{11a}$$

As

$$x_F = \left(\frac{15M}{m}\right)^{1/2} \gg 1,$$

it follows that $f(x_F) \approx x_F^3/3$ so that

$$\rho(0) \cong \frac{mW_0 q_c^3 x_F^3}{9ne^2 k_F} = \frac{8mW_0 k_F^2}{9ne^2}. \tag{11b}$$

Combining Eq. (11b) with Eq. (5b) gives

$$\rho(0) = \frac{2\pi}{3}\,\frac{mE_1^2\sqrt{15Mm}}{e^2 \rho_M \hbar E_F}. \tag{12}$$

The deformation potential constant E_1 corresponds to the change in system energy $\varepsilon(\mathbf{k})$ due to a small uniform static deformation. Thus,

$$\varepsilon(\mathbf{k}) \cong \varepsilon_0(\mathbf{k}) + E_1 \Delta, \tag{13a}$$

where $\varepsilon_0(\mathbf{k})$ is unperturbed energy and Δ is dilation. For a free-electron gas, $E_1 = \partial\varepsilon(0)/\partial\Delta$, and one obtains[4] $E_1 = -(2/3)E_F$. Ion oscillations remain at low temperatures and tend to diminish the dilation energy. To incorporate these effects into the deformation potential constant, we divide it by $\hbar\omega$ where $\omega \propto M^{-1/2}$ is the ion frequency. In dimensionless form one obtains

$$E_1 = -\frac{2}{3} E_F \left(\frac{M}{m}\right)^{1/2}. \tag{13b}$$

Substituting this expression into Eq. (12) gives

$$\rho(0) = \left(\frac{2}{3}\right)^3 \frac{\pi E_F M^{3/2}\sqrt{15}}{e^2 \rho_M \hbar}, \tag{14}$$

which gives the following dependence on material properties:

$$\rho(0) \propto \frac{M^{1/2} E_F}{n_i} \equiv \tilde{\rho}(0). \tag{15}$$

V. COMPARISON WITH EXPERIMENT

In the classic experiments of MacDonald and Mendelssohn[8] (MM), residual resistivities were found in highly purified samples of the alkali metals: lithium, sodium, potassium, cesium, and rubidium. In each such measurement, $\rho(0)$ has a zero slope with respect to temperature and rises as T^s, where $s \approx 4.85$.[9,10] The Fermi surface of Li is not known due to martinsitic transformation to a mixture of crystalline phases at 77 K. Sodium likewise has a martinsitic transformation at 23 K, but with care a low-temperature Fermi energy may be

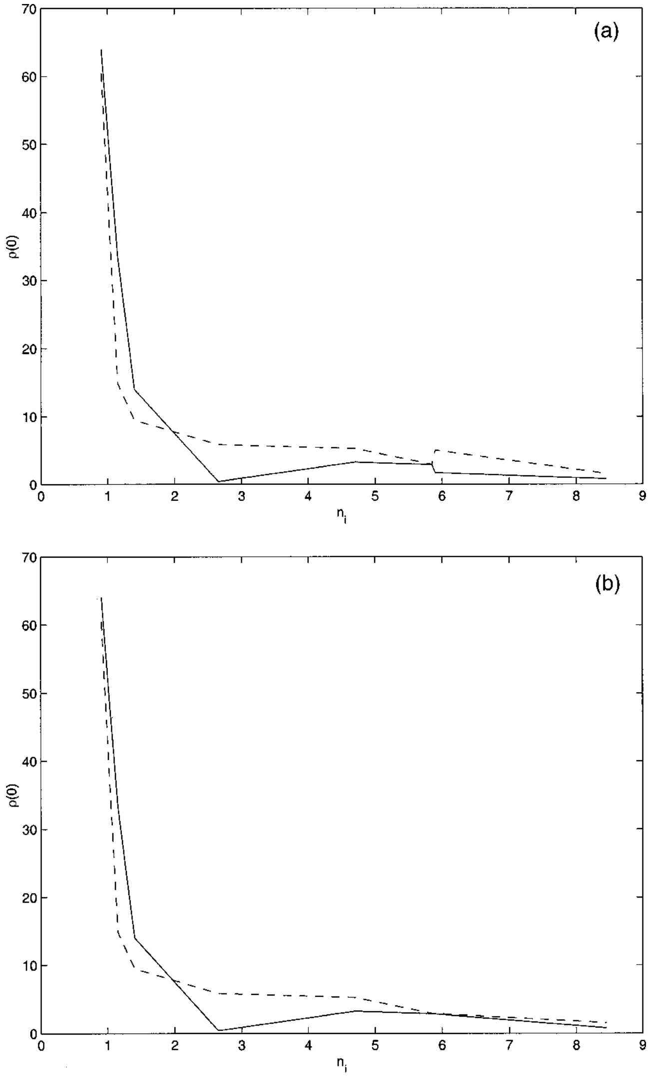

FIG. 1. (a) Proportionality factor $\tilde{\rho}(0)$ (dashed curve) and experimental residual resistivity (solid curve) of the alkali metals, Eq. (15), and noble metals, Eq. (16), vs ion number density with values of Cs and Li as well as the deformation potential constant of the noble metals, varied for consistency. Values of the ion number density are $n_i \times 10^{-22}\,\text{cm}^{-3}$. Values of $\tilde{\rho}(0)$ (relative units) were multiplied by 10^{22}. The singular behavior of gold is attributed to its anomalous electronic structure. (b) Same curves as in lacking data for gold, showing smoother behavior.

obtained. Thus the Fermi energy for lithium in the present work is evaluated at 78 K, whereas for the remaining alkali metals it is evaluated at 5 K and for the noble metals at 300 K. It is found that a correction factor of 2 in the proportionality form $\tilde{\rho}(0)$ for lithium gives a smoother curve of this parameter versus ion density. Furthermore, regarding the element cesium, MM say, ‘‘ . . . the unusual behavior of the metal, in particular at very low temperature, leading to uncertainty in the true value of residual resistivity . . . ’’ This property may be attributed in part to the very strong affinity of cesium for oxygen. With this description, correction factors of 4 on $\rho(0)$ and 3 on $\tilde{\rho}(0)$ for cesium were found to give a closer dependence of these parameters on ion-number density. Data for the noble metals silver and copper were obtained from the experiments of Rumbo.[11] Data for gold were obtained from Hall.[12] It is noted that data in MM are given by $10^q R/R_{290\ \mathrm{K}}$, where $q=2$ or 3. Data in Rumbo and Hall were revised to be in accordance with MM. Anomalous behavior for the noble metals (all, fcc) is attributed to the fact that the free-electron sphere bulges out in the $\langle 111 \rangle$ directions where contact is made with hexagonal zone faces. To incorporate these metals into the analysis, we note that the relation (13b) for the deformation potential constant is relevant to spherical energy surfaces. For the noble metals we write

$$E_1 = -\lambda E_1^{(s)},$$

where $E_1^{(s)}$ relates to a spherical energy surface and the dimensionless parameter $\lambda \cong 1$. Numerical work suggests the value $\lambda \cong 1/\sqrt{3}$. With Eq. (12) we note that $\rho(0) \propto E_1^2$, so that for this class of metals Eq. (15) is rewritten

$$\tilde{\rho}(0) \cong \frac{1}{3} \frac{M^{1/2} E_F}{n_i}. \tag{16}$$

Relevant data and values of $\tilde{\rho}(0)$ and measured values of $\rho(0)$ are listed in Table I. The residual resistivity $\rho(0)$ of these measurements and the proportional factor $\tilde{\rho}(0)$ in relative units (with corrections cited) are plotted together in Fig. 1(a) against ion number density. The resulting curves exhibit a nearly parallel behavior for the alkali metals with a jump in values for the noble metals. These same curves, lacking data for gold, are plotted in Fig. 1(b) and are noted to be free of the said singularity. This singular behavior may be attributed in part to the atomic structure of gold that has an additional $4f^{10}$ electronic shell outside a closed [Xe] core that causes, for example, gold to be less electropositive than the other noble metals.

VI. CONCLUSIONS

In conclusion, expressions for the electrical resistivity of single-crystal pure alkali and noble metals at 0 K were derived in terms of the total rate of electron decay in the emission of acoustic phonons. Due to anomalies in the low-temperature properties of Cs and Li, correction factors were introduced for the residual resistivity of these elements. For the noble metals, a correction factor was introduced for the corresponding deformation potential constant. When plotted together with the measured values of this parameter, as functions of ion number density, respectively, the resulting curves show nearly parallel behavior for the alkali and noble metals, with better comparison resulting when gold is omitted.

ACKNOWLEDGMENTS

Fruitful discussions of these topics with my colleagues Peter Krusius, Lou Hand, Dieter Ast, Jack Freed, Brian Ridley, Bruce Green, X. Liu, J. Chan, Ali Alvi, and Young Chul are gratefully acknowledged.

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