Theory of Thermal Relaxation of Electrons in Metals

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If electrons in a metal are heated to a temperature T_e greater than the lattice temperature T_L, the electron-phonon interaction causes temperature relaxation $dT_e/dt=\gamma_T(T_L-T_e)$ which is rapid for $T_L>\theta_D$. A formula $\gamma_T=3\hbar\lambda\langle\omega^2\rangle/\pi k_B T_e$ is derived, where $\lambda\langle\omega^2\rangle=\eta/M$ is an important parameter in the theory of superconductivity. Quantitative agreement with recent experiments is good.

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Recent developments in ultrafast laser pulses have opened a new field of time-resolved spectroscopy.[1] Several groups[2-4] have reported time-resolved observations of the thermal relaxation of hot electrons in metals. In these experiments, a laser pulse of $\simeq$50–300 fs (1 fs $=10^{-15}$ s) duration created a nonequilibrium electron distribution, leaving the lattice temperature $T_L\simeq 300$ K essentially unchanged. Then, over a time scale of a few picoseconds (10^{-12} s) the electrons were observed to return to a local equilibrium at a somewhat elevated temperature, with electron-phonon interactions causing an equilibrium distribution of the excess energy between the electronic and lattice subsystems in a time equal to a few phonon oscillation periods. Finally, a slower relaxation process dominated by heat diffusion returned the system to the ambient temperature.

As pointed out by various authors[2-5] the rate of return to local equilibrium is governed solely by electron-phonon processes, unlike steady-state transport experiments which always measure a combined rate caused by all available relaxation processes. In this paper I derive a simple formula for the thermal relaxation rate, namely $\gamma_T=3\hbar\lambda\langle\omega^2\rangle/\pi k_B T$. The factor $\lambda\langle\omega^2\rangle$ is of great interest in the theory of the superconducting transition temperature[6] T_c, both because of the central role of λ in determining[7] T_c and because the relative simplicity[6-8] of the product $\lambda\langle\omega^2\rangle=\sum_a \eta_a/M_a$ (where the sum is over atoms a of mass M_a in the unit cell, and η_a is a Fermi-surface average scattering of atom a per unit displacement) has made possible many microscopic calculations.[8] No other experiment is known which directly probes $\lambda\langle\omega^2\rangle$, and few experiments so nicely separate electron-phonon from other effects.

The rates of change of electron and phonon distributions F_k and N_Q due to electron-phonon collisions are given by standard Bloch-Boltzmann-Peierls formulas[9]:

$$\left(\frac{\partial F_k}{\partial t}\right)_{ep}=-\frac{2\pi}{\hbar N_c}\sum_Q |M_{kk'}|^2\{F_k(1-F_{k'})[(N_Q+1)\delta(\epsilon_k-\epsilon_{k'}-\hbar\omega_Q)+N_Q\delta(\epsilon_k-\epsilon_{k'}+\hbar\omega_Q)]$$
$$-(1-F_k)F_{k'}[(N_Q+1)\delta(\epsilon_k-\epsilon_{k'}+\hbar\omega_Q)+N_Q\delta(\epsilon_k-\epsilon_{k'}-\hbar\omega_Q)]\}, \quad (1)$$

$$\left(\frac{\partial N_Q}{\partial t}\right)_{ep}=-\frac{4\pi}{\hbar N_c}\sum_k |M_{kk'}|^2 F_k(1-F_{k'})[N_Q\delta(\epsilon_k-\epsilon_{k'}+\hbar\omega_Q)-(N_Q+1)\delta(\epsilon_k-\epsilon_{k'}-\hbar\omega_Q)], \quad (2)$$

where k and Q are short for the electron or phonon quantum numbers $(\mathbf{k},n)$ and $(\mathbf{Q},j)$, respectively, and $\mathbf{Q}$ is always $\pm(\mathbf{k}-\mathbf{k}')$. N_c is the number of cells in the sample; the electron-phonon matrix element $M_{kk'}$ is normalized to the unit cell and has magnitude $(E_F\hbar\omega_D)^{1/2}$. The extra factor of 2 in Eq. (2) accounts for electron-spin degeneracy. It is easily verified that the rates (1) and (2) conserve total energy:

$$2\sum_k \epsilon_k\left(\frac{\epsilon F_k}{\partial t}\right)_{ep}+\sum_Q \hbar\omega_Q\left(\frac{\partial N_Q}{\partial t}\right)_{ep}=0. \quad (3)$$

If the distributions $F_k(t)$ and $N_Q(t)$ are known at $t=0$, then Eqs. (1) and (2) determine their evolution at all future times provided (1) diffusion driven by spatial inhomogeneity is negligible; (2) acceleration due to both external and internal (space-charge) fields is negligible; and (3) no other collision processes are important. The model used in this paper is as follows: (a) Other collision processes such as electron-electron (Coulomb) and phonon-phonon (anharmonic) are active in keeping the distribution F_k and N_Q equal to local equilibrium distributions $\{\exp[(\epsilon_k-\mu)/k_B T_e(t)]+1\}^{-1}$ and $\{\exp[\hbar\omega_Q/k_B T_L(t)]-1\}^{-1}$ characterized by separate electron and lattice temperatures T_e and T_L which depend on time; (b) diffusion is negligible because of the short time scale and constrained geometry; (c) the laser driving field has disappeared by $t=0$ leaving the electrons at an elevated temperature $T_e(0)$ and the lattice essentially undisturbed. Under these assumptions, Eqs. (1) and (2) completely govern the subsequent energy redistribution. The assumption that the distributions F and N are always thermal is of course incorrect at some level, possibly only

in detail or possibly more seriously. However, experimental monitors[2-4] are so far consistent with the notion that even if F and N are athermal, they are still adequately characterized by a thermal distribution at equivalent energy. In other words, deviation of F and N from local thermal populations may not in fact have much influence on the energy relaxation described by Eqs. (1) and (2).

Now calculate the rate of energy exchange:

$$E_e = 2\sum_k \epsilon_k F_k \approx E_0 + \tfrac{1}{2} T_e^2, \tag{4}$$

$$E_L = \sum_Q \hbar\omega_Q N_Q \simeq 3N_a k_B T_L, \tag{5}$$

$$(\partial E_e/\partial t)_{ep} = (4\pi/\hbar N_c)\sum_{kk'} \hbar\omega_Q |M_{kk'}|^2 [S(k,k')]\delta(\epsilon_k - \epsilon_{k'} + \hbar\omega_Q). \tag{6}$$

The electron thermal energy is governed by the linear heat-capacity coefficient $\gamma = \pi^2 N_c N(\epsilon_F) k_B^2/3$, where $N(\epsilon_F)$ is the density of state of both spins per unit cell, and the electron-phonon enhancement factor $(1+\lambda)$ is intentionally omitted because the temperatures are all assumed comparable to or greater than the Debye temperature.[10] The thermal factor in Eq. (6) is

$$S(k,k') = (F_k - F_{k'})N_Q - F_{k'}(1 - F_k). \tag{7}$$

Equations (6) and (7) require some relabeling of dummy variables to derive. Next, three factors of 1 are inserted into Eq. (6), namely $\int d\epsilon\, \delta(\epsilon_k - \epsilon)$, $\int d\epsilon'\, \delta(\epsilon_{k'} - \epsilon')$, and $\int d\Omega\, \delta(\omega_Q - \Omega)$. Then Eq. (6) can be rewritten[6] in terms of the "electron-phonon spectral function" $\alpha^2 F$,

$$\alpha^2 F(\epsilon, \epsilon', \Omega) \equiv [2/\hbar N_c^2 N(\epsilon_F)] \sum_{kk'} |M_{kk'}|^2 \delta(\omega_Q - \Omega)\delta(\epsilon_k - \epsilon)\delta(\epsilon_{k'} - \epsilon'). \tag{8}$$

This function has Ω variation on a scale of ω_D but ϵ and ϵ' variation only on a much larger energy scale, $1/N(\epsilon_F)$. Therefore, inside Eq. (6), it is legitimate and customary[6] to neglect the ϵ and ϵ' dependence of $\alpha^2 F$, with use of the value $\alpha^2 F(\epsilon_F, \epsilon_F, \Omega) \equiv \alpha^2 F(\Omega)$. Then Eq. (6) becomes

$$\frac{\partial E_e}{\partial t} = 2\pi N_c N(\epsilon_F) \int_0^\infty d\Omega\, \alpha^2 F(\Omega) \hbar\Omega \int d\epsilon\, d\epsilon' \{[f(\epsilon) - f(\epsilon')]N(\Omega, T_L) - f(\epsilon')[1 - f(\epsilon)]\} \delta(\epsilon - \epsilon' + \hbar\Omega), \tag{9}$$

where $f(\epsilon)$ is the Fermi-Dirac function at $T = T_e$, and $N(\Omega, T_L)$ is the Bose-Einstein distribution at $T = T_L$. Now the ϵ and ϵ' integrals in Eq. (9) can be done, yielding

$$\frac{\partial E_e}{\partial t} = 2\pi N_c N(\epsilon_F) \int_0^\infty d\Omega\, \alpha^2 F(\Omega) (\hbar\Omega)^2 [N(\Omega, T_L) - N(\Omega, T_e)]. \tag{10}$$

This formula translates the free-electron gas Eq. (6) of Kaganov, Lifshitz, and Tanatarov[5] into modern terminology appropriate to arbitrary electronic spectra.

The high-T limit of Eq. (10) has a particularly simple form in terms of the moments of $\alpha^2 F(\Omega)$ appearing in superconductivity theory:

$$\lambda\langle\omega^n\rangle = 2\int_0^\infty d\Omega\, [\alpha^2 F(\Omega)/\Omega]\Omega^n, \tag{11}$$

where the coupling constant λ which determines T_c is the same as $\lambda\langle\omega^0\rangle$. If we make a Taylor expansion of Eq. (10) in terms of $\hbar\Omega/k_B T$, the result is

$$\partial E_e/\partial t = \pi\hbar N_c N(\epsilon_F)\lambda[\langle\omega^2\rangle - \hbar^2\langle\omega^4\rangle/12 k_B^2 T_e T_L + \ldots] k_B (T_L - T_e). \tag{12}$$

Now use Eq. (4) to convert this into a temperature relaxation rate:

$$\partial T_e/\partial t = \gamma_T (T_L - T_e), \tag{13}$$

$$\gamma_T = (3\hbar\lambda\langle\omega^2\rangle/\pi k_B T_e)(1 - \hbar^2\langle\omega^4\rangle/12\langle\omega^2\rangle k_B^2 T_e T_L + \ldots). \tag{14}$$

Equation (14) includes a first thermal correction factor, which is likely to be quite small under most experimental conditions.

An alternative version of Eqs. (10), (12), and (14) follows from the identity[11]

$$\alpha^2 F(\Omega) = [2\pi\hbar N_c N(\epsilon_F)]^{-1} \sum_Q (\Gamma_Q/\omega_Q)\delta(\omega_Q - \Omega), \tag{15}$$

where Γ_Q is the electron-phonon part of the phonon "quasiparticle" relaxation time which governs the return to equilibrium of a small disturbance,

$$\Gamma_Q (4\pi\omega_Q/N_c) \sum_k |M_{k,k+Q}|^2 \delta(\epsilon_k - \epsilon_F)\delta(\epsilon_{k+Q} - \epsilon_F). \tag{16}$$

Γ_Q is also the electron-phonon part of the half-width at half maximum of the neutron-scattering cross section $S(Q,\omega)$. With use of Eq. (15), Eqs. (10) and (12) become

$$dE_e/dt = \sum_Q \Gamma_Q \hbar\omega_Q [N(\omega_Q, T_L) - N(\omega_Q, T_e)] \tag{17}$$

$$\sim (\sum_Q \Gamma_Q) k_B (T_L - T_e) = \bar{\Gamma}[E_L(T_L) - E_L(T_e)], \tag{18}$$

where Eq. (18) is the high-T limit and $E_L(T)$ is the lattice energy $3\nu N_c k_B T$ in the high-T limit, ν is the number of atoms per cell, and $\bar{\Gamma}$ is the Q average of Γ_Q. Since $dE_e/dt = -dE_L/dt$, Eq. (18) defines the lattice energy relaxation rate $\Gamma_{L,E} = -(dE_L/dt)/\Delta E_L = \bar{\Gamma}$. The energy relaxation rate of the lattice is the same as the quasiparticle relaxation rate of the lattice, at least at high T. Curiously, the same is not true for the electrons. If we define an electron energy relaxation rate by $\Gamma_{e,E} = -(dE_e/dt)/\Delta E_e$, the high-$T$ result is $3\hbar\lambda\langle\omega^2\rangle/\pi k_B T_{av}$, identical to the leading term of (14) except with $T_{av} = (T_e + T_L)/2$ in place of T_e. The quasiparticle relaxation rate for electrons is $2\pi\lambda k_B T_L/\hbar$. This is faster at high T_e than γ_T by a factor $2\pi^2 k_B^2 T_e T_L/3\hbar^2\langle\omega^2\rangle$. Electron energy loss at high T by phonon emission is a multistep process.

This theory can now be used to extract values of $\lambda\langle\omega^2\rangle$ for Cu (Ref. 3), Au (Ref. 4), and W (Ref. 2). Elsayed-Ali *et al.*[3] quote a value for Cu of $G = 1\times10^{17}$ W/m^3 K, where G is the coefficient of $T_L - T_e$ in Eq. (12). With use of the experimental value of γ to eliminate $N_c N(\epsilon_F)$, $\lambda\langle\omega^2\rangle$ is 61 meV^2. Khan *et al.*[12] have calculated $\lambda\langle\omega^2\rangle$ for Cu to be 43 meV^2 which is within the $\pm 50\%$ implied accuracy of the measurement of G in Ref. 3. The value of Ref. 11 corresponded to the separate parts $\lambda = 0.111$ and $\langle\omega^2\rangle = 387$ (meV)^2.

For gold, the data of Figs. 2 and 3 of Ref. 4 were analyzed under the assumptions that the vertical axis, $\Delta R/R$, is proportional to T and that the peak temperature, as estimated, is 10^3 K. Then the temperature relaxation rate at both $t = 1$ and 2 ps corresponds to $\gamma_e T_e = 4\times10^{14}$ K/s, which yields $\lambda\langle\omega^2\rangle = 24$ meV^2. Given that θ_D for Au is about one-half of θ_D for Cu, this result is consistent with a λ value somewhat larger in Au than in Cu. This is consistent with other estimates[13] which give $\lambda \approx 0.15$ for Au.

For W, Fujimoto *et al.*[2] estimate a value $C_e\gamma_e = (0.5-1)\times10^{12}$ W/cm^3 K, which translates into $\lambda\langle\omega^2\rangle = 100-200$ meV^2. One expects $\lambda\langle\omega^2\rangle$ to be about 3 times larger for W than Cu because λ is $\simeq 0.3$ (Ref. 7) and θ_D values are very similar. Thus for all three metals, $\lambda\langle\omega^2\rangle$ has been extracted to 50% accuracy. Improvements in ultrafast spectroscopy should make possible absolute measurements of $\lambda\langle\omega^2\rangle$ to significantly better accuracy, and would provide a valuable probe of electron-phonon coupling strengths.

Equation (10) is valid for all T_e and T_L given the accuracy of the underlying assumptions. There have recently been several elegant ultralow-temperature measurements[14,15] of thermal relaxation in metals. In pure metals, α^2F has the form $\lambda^*(\omega/\omega_D)^2$ at small ω, where λ^* has no uniform relation to λ but has the same expected magnitude. Then at very low T, Eq. (10) becomes [see Ref. 5, Eq. (8)]

$$\frac{dE_e}{dt} = \frac{48\pi\zeta(5) N_c N(\epsilon_F) \lambda^* k_B^5}{\hbar^3 \omega_D^2} (T_L^5 - T_e^5), \tag{19}$$

which yields an energy relaxation rate

$$\Gamma_{e,E} = \frac{288\zeta(5)}{\pi} \frac{\lambda^*}{1+\lambda} \left(\frac{k_B T_e}{\hbar\omega_D}\right)^3 \omega_D \left[\frac{1-(T_L/T_e)^5}{1-(T_L/T_e)^2}\right]. \tag{20}$$

This can be compared with the quasiparticle relaxation rate averaged by $-\partial f/\partial\epsilon$ over states near the Fermi energy,[16]

$$\bar{\Gamma}_e = 24\pi\zeta(3) \frac{\lambda^*}{1+\lambda} \left(\frac{k_B T_e}{\hbar\omega_D}\right)^3 \omega_D. \tag{21}$$

The rates (20) and (21) agree to 5% if $T_L/T_e \ll 1$ but energy relaxation is faster by 2.62 if $|T_e - T_L| \ll T_e$. Energy relaxation rates proportional to T^n with $n \approx 3$ have been measured in several metals.

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