

# Two-temperature Heat Conductivity of Gold

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**Abstract**— Heat transfer by electrons has a significant influence on the heating of the metal target under the action of ultrashort laser pulses. Therefore, in problems of laser ablation of metals it is important to know the value of the electronic thermal conductivity. We made calculations and present analytical expressions of the electronic thermal conductivity of solid and liquid gold in the important for the interaction of femtosecond laser pulses with metals state with unequal electron and ion temperatures in a wide range of temperatures and densities.

## 1. INTRODUCTION

When considering the problem of interaction of femtosecond laser pulses with metals we often use the system of equations describing the hydrodynamical motion of metal target under the laser pulse action. These equations take into account heat transfer by electrons. Thus electron thermal conductivity becomes a very important kinetic coefficient governing the dynamics of heating of a target, temperature and pressure distribution in a heating layer of a target. The peculiar feature of the interaction of femtosecond laser pulses with metals is the occurrence of nonequilibrium state with large difference between electron ( $T_e$ ) and ion ( $T_i$ ) temperatures. Therefore we need the knowledge of electron thermal conductivity in such two-temperature states [1–5]. Difference between electron and ion temperatures can achieve several electron Volts. Furthermore, when considering ablation under the laser irradiation, we have a strong expansion of matter and thermal conductivity therefore must be calculated at differing values of density. In addition laser ablation is accompanied by phase transitions of a target matter which also must be taken into account. We calculate electron thermal conductivity of gold in a wide range of electron and ion temperatures in the absence of equilibrium between them and in dependence on the density with taking into account phase transition between solid and liquid state.

## 2. CONTRIBUTION OF ELECTRON-ELECTRON COLLISIONS INTO THE THERMAL CONDUCTIVITY

As we consider electron temperatures up to several eV, electron-electron collisions contribute to a significant extent to the electron relaxation time at large electron temperatures. In a noble metal such as gold we are interesting in the scattering of conduction electrons ( $s$ -electrons) by the same  $s$ -electrons and  $d$ -electrons. According to the Matthiessen's rule the thermal conductivity  $\kappa_{se}$ , due to the scattering of  $s$ -electrons by other electrons satisfies the condition given by  $\kappa_{se}^{-1} = \kappa_{ss}^{-1} + \kappa_{sd}^{-1}$ , where  $\kappa_{ss}$  and  $\kappa_{sd}$  present contributions of  $s$ - $s$  and  $s$ - $d$  collisions. By solving the kinetic equation for the electron-electron scattering by the method of [3, 6] we have calculated the thermal resistivity  $\kappa_{se}$  due to  $e$ - $e$  collisions. The two-parabolic model of the electron spectrum [3, 6] with the Thomas-Fermi screening was used. Parameters of parabolic electron bands — the bottom of the  $s$ -band  $E_s = -9.2$  eV, the bottom of the  $d$ -band  $E_1 = -6.8$  eV and the top of the  $d$ -band  $E_2 = -1.7$  eV, measured from the Fermi level, were found by using the density functional theory in the VASP package [7]. Our band structure calculations [8] carried out using the VASP package [7] show that in gold Fermi energy is proportional to the compression  $x = \rho/\rho_0$  to the first degree:  $E_F = xE_{F0}$ , and is not proportional to  $x^{2/3}$ . Here  $\rho_0 = 19.5$  g/cm<sup>3</sup> is the density at zero temperature and pressure,  $E_{F0}$  is the Fermi energy at  $x = 1$ .

$$\kappa_{se}(T_e, x) = 1.076 \cdot 10^{-5} x^{4/3} \left( 1/t + b_0/\sqrt{t} + b_1 + b_2 t \right) \quad (1)$$

(in units of W/(m · K)), where  $b_0 = 0.03$ ,  $b_1 = -0.2688$ ,  $b_2 = 0.9722$  and the normalized temperature  $t = 6k_B T_e / E_F(x) = 6k_B T_e / (xE_{F0})$ , where  $k_B$  is the Boltzmann constant,  $E_F$  — Fermi energy, is used. We neglect the dependence of  $\kappa_{se}(T_e, x)$  on the ion temperature  $T_i$ , since in noble metals it is weak [6, 9, 10]. At a fixed concentration of ions electronic spectrum rather weakly depends on the phase (solid or liquid) of the metal. Therefore, we use the approximation (1) in solid and liquid phases alike.

### 3. THERMAL CONDUCTIVITY OF GOLD IN THE SOLID PHASE

Thermal conductivity  $\kappa$ , associated with the electron-phonon interaction in the solid phase can be written as  $\kappa_{si} = c_e v \lambda_{si} / 3$  with the electronic heat capacity per unit volume  $c_e$ , average speed of electrons  $v$  and the mean free path length  $\lambda_{si} = 1 / (n \Sigma_{si})$ , where  $n$  is the concentration of atoms and  $\Sigma_{si}$  is the effective cross section of the electron-phonon interaction. For the effective cross section we have  $\Sigma_{si} \propto u_0^2 (T_i / \theta)$ ,  $u_0 \propto \hbar / (M k_B \theta)^{1/2}$ , where  $u_0$  is the amplitude of zero-point vibrations of the atom with mass  $M$ ,  $\theta = \hbar c_s k_D / k_B$  is the Debye temperature,  $c_s$  — sound velocity,  $k_D = (6\pi^2 n)^{1/3}$  — Debye wave number. Then  $\lambda_{si} \propto \theta^2 / (n T_i)$ . Thus, when calculating the mean free path and transport characteristics the dependence of the Debye temperature  $\theta$  on the dimensionless density  $x$ , defined above becomes important.

To analytically describe the effect of tension and compression, we need a cold-pressure dependence on the density. We represent it as the sum of the attractive and repulsive parts

$$p_c = A n_0 x (x^a - x^b), \quad (2)$$

where  $n_0$  is a concentration of atoms in equilibrium at  $T = 0$ ,  $p = 0$ . Parameters in the expression (2)  $A = 14.6 \text{ eV/atom}$ ,  $a = 3.92$ ,  $b = 1.95$  are defined to reproduce reference value of the bulk modulus of gold  $K = 220 \text{ GPa}$  (Wikipedia) under normal conditions, cohesive energy  $3.78 \text{ eV/atom}$  [11] and the reference value  $14.2 \cdot 10^{-6} \text{ K}^{-1}$  of the thermal expansion coefficient under normal conditions [12]. For these values of the parameters ( $A$ ,  $a$ ,  $b$ ) minimal pressure on the cold curve (2) is equal to  $p_{\min} = -26.0 \text{ GPa}$ . at the expanding ratio  $x_{\min} = 0.77$ . Present values are consistent with the commonly used data ( $x_{\min} = 0.74$ ,  $p_{\min} = -21 \text{ GPa}$ ) [13, 14]. When making a binomial formula (2) for cold pressure the expression for the Debye temperature has the form

$$\theta(x) = (\hbar / k_B) c_{s0} k_{D0} x^{1/3} y^{1/2}(x), \quad y(x) = [(a+1)x^a - (b+1)x^b] / (a-b), \quad (3)$$

where  $y \propto K = \rho dp_c / d\rho$ ,  $K$  — bulk modulus, and cold pressure  $p_c$  is given by (2); the speed of sound  $c_{s0}$  is averaged over directions by using the relation  $3/c_{s0}^3 = 1/c_{l0}^3 + 2/c_{t0}^3$  with longitudinal  $c_{l0}$  and transverse  $c_{t0}$  sound velocities taken at  $x = 1$  as well as the Debye wave number  $k_{D0} = k_D(x = 1)$ . To avoid the difficulties associated with the negative values of  $y(x)$  at small  $x$  and to describe moderate (tens of percent) density variations around the equilibrium value, we use the function

$$\bar{y}(x) = (1 + c_{ab})x^\alpha / (1 + c_{ab}x^\beta), \quad \alpha = 2a + 1, \quad \beta = a + 1, \quad c_{ab} = (a - b) / (b + 1) \quad (4)$$

instead of the function  $y(x)$ . Parameters of the function  $\bar{y}(x)$  (4) are chosen so that the functions  $\bar{y}$  and  $y$  are close to each other near the equilibrium density  $x = 1$ . As it can be seen, when  $x \rightarrow 0$ , the function  $\bar{y}(x)$  (4) remains positive. The thermal conductivity in the solid phase can be written as  $\kappa_{sol} = \kappa_{se} \kappa_{ei}^{sol} / (\kappa_{se} + \kappa_{ei}^{sol})$  with the electron-electron contribution to the thermal conductivity  $\kappa_{se}$  given by (1). Index “ $se$ ” denotes the  $s$ -electron scattering on the  $s$ - and  $d$ -electrons.

Coefficient of thermal conductivity due to electron-phonon collisions in a solid phase  $\kappa_{si}^{sol}$  is calculated by the formula

$$\kappa_{si}^{sol} = (1/3) c_e v \lambda_{si} = (1/3) n k_B C(t) v_F \lambda_{si}, \quad (5)$$

In the formula (5) a dimensionless factor  $C(t)$ ,  $t = 6k_B T_e / (xE_{F0})$  comprises the dependence of heat capacity and average speed of  $s$ -electrons  $v = v_F ((1 + 3k_B T_e / (2xE_{F0}))^{1/2})$  on the electron temperature  $T_e$  (and  $x$ ). Fermi velocity  $v_F = v_{F0} x^{2/3}$ , when  $E_F = E_{F0} x$ . Other multipliers in (5) don't depend upon  $T_e$ . The heat capacity of the  $s$ -electrons is calculated in the framework of the two-parabolic approximation of the electron spectrum [3] and significantly differs from the total electron heat capacity of gold.

Replacing  $y(x)$  by  $\bar{y}(x)$  in (3), we obtain  $\theta^2(x) = \theta^2(1) x^{2/3} \bar{y}(x)$ . Then  $\lambda_{si} \propto [\bar{y}(x) / x^{1/3}] (1/T_i)$ . Entering the value  $\kappa_0(t) = (1/3) n_0^{2/3} k_B C(t) v_{F0}$ , having the thermal conductivity dimension, we get from (5)  $\kappa_{si}^{sol} \propto \kappa_0(t) x^{4/3} \bar{y}(x) / T_i$ . The function  $\kappa_0(t)$  was calculated for solid gold at  $x = 1$ . Results can be approximated by the expression

$$\kappa_0(t) = 131 \frac{t(1 + 3.07t^2)}{(1 + 1.08t^{2.07})}$$

(in units of W/(m·K)). We denote  $x_{rt} = 19.3/19.5$  relative density of gold on the sublimation curve at room  $T_{rt} = 0.293$  kK temperature. Together with the experimental value of the thermal conductivity under these conditions 318 W/(m·K), we obtain

$$\kappa_{si}^{sol}(T_e, T_i, x) = 318 \left( \frac{x}{x_{rt}} \right)^{4/3} \frac{\bar{y}(x)}{\bar{y}(x_{rt})} \frac{T_{rt}}{T_i} \frac{\kappa_0(t)}{\kappa_0(t_{rt})}, \quad (6)$$

in units of W/(m·K), where  $t_{rt} = 6k_B T_{rt}/(x_{rt} E_{F0})$ .

#### 4. THERMAL CONDUCTIVITY OF GOLD IN THE LIQUID PHASE

Electron-electron contribution into the thermal conductivity of molten gold is still given by (1). Assuming that in the liquid phase electron mean free path  $\lambda_l$  due to the electron-ion scattering can be, as in the solid phase, written in factorized form  $\lambda_l = n_0^{-1/3} W(T_i) x^\beta$ , and again using the value  $\kappa_0(t(T_e, x))$ , we have for the coefficient of thermal conductivity

$$\kappa_{ei}^{liq}(T_e, T_i, x) = \kappa_0(t) \cdot x^{5/3} W(T_i) x^\beta.$$

Drude formula for resistivity gives

$$r(T_i, x) = \frac{\rho_F}{ne^2 \lambda_l} = \frac{r_0}{W(T_i) x^{\beta+2/3}}.$$

Here  $r_0 = (3\pi^2)^{1/3} R_0 / (2\pi) n_0^{-1/3} = 3254$  nOhm·m. According to quantum molecular dynamics calculations [15] we take  $\beta = 4/3$ . Function  $W(T)$  can be found by the use of known experimental dependence  $r_l(T)$  of the resistivity of gold [12] on the temperature on the boiling curve  $x_l(T)$  of phase diagram, so that

$$W(T) = \frac{r_0}{r_l(T) x_l^{\beta+2/3}(T)}$$

Boiling curve [16] for the temperature  $T$  in kK can be approximated as  $x_l(T) = 0.8872 - 0.03283(T - 1.337) - 0.003098(T - 1.337)^2 - 0.0001649(T - 1.337)^3$  with a resistivity in the units of nOhm·m on it  $r_l(T) = 148.5 + 119.3 * T * 15.337 / (14 + T)$ , which coincides with the known experimental data and tends to the minimum metallic conductivity in strongly disordered ion system at high ion temperatures.

Then we obtain the coefficient of thermal conductivity in the liquid phase due to electron-ion collisions in the form

$$\kappa_{ei}^{liq}(T_e, T_i, x) = \kappa_0(t) \frac{r_0}{r_l(T_i)} x \left( \frac{x}{x_l(T_i)} \right)^{\beta+2/3}. \quad (7)$$

The thermal conductivity coefficient in liquid phase is entirely calculated with taking into account  $\kappa_{se}$ , so that the thermal conductivity is  $\kappa_{liq} = \kappa_{se} \kappa_{ei}^{liq} / (\kappa_{se} + \kappa_{ei}^{liq})$ .

In Fig. 1 the electron thermal conductivity of gold in dependence on the temperature for single-temperature situation in the thermal equilibrium state on the binodal curve including the sublimation and boiling curve, as well as on the normal density isochore is presented. Phase transition between solid and liquid states is manifested in a jump in the thermal conductivity on the binodal and slightly more smooth transfer from its value in the solid state to the value in the molten state on the isochore. Fig. 2 presents results of calculation of thermal conductivity in dependence on the relative density  $x$  at three values of equilibrium temperature  $T = 1000$  K, 1337 K and 1800 K. Influence of liquid-solid phase transition onto the thermal conductivity can be seen.

In Fig. 3 electronic thermal conductivity in the nonequilibrium two-temperature case, interesting for the interaction of ultrashort laser pulses with metals, is shown in dependence on the electron temperature for several values of the ion temperature in both the solid and liquid phases for the density  $\rho = 19.5$  g/cm<sup>3</sup> (density at  $T = 0$ ,  $p = 0$ ). The nonmonotonic behaviour of the coefficient of thermal conductivity in the solid phase at relatively low ion temperatures is due to significantly weaker increase of the electron-electron collisions as the electron temperature increases above 10 kK, than at lower temperatures of the electrons, whereas the continuing increase in the heat capacity  $s$ -electrons and their average velocity takes place.

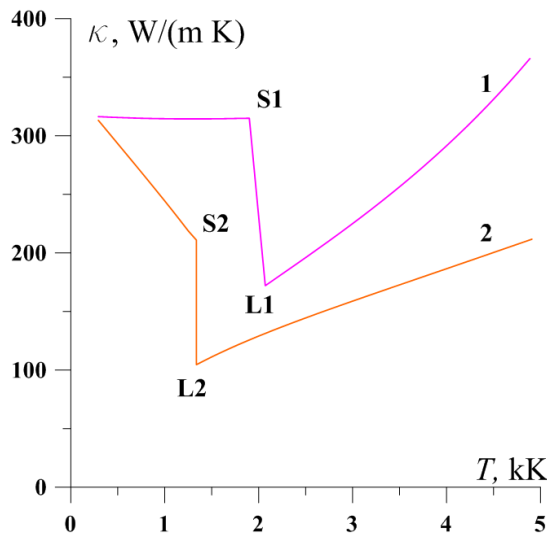


Figure 1: Dependence of the electron thermal conductivity of gold on the temperature  $T$ , the same for ions and electrons. 1 — on the isochore of  $19.3 \text{ g/cm}^3$  density; 2 — on the binodal curve consisting of sublimation and boiling curve. S1L1 and S2L2 segments contain liquid-solid phase transition region.

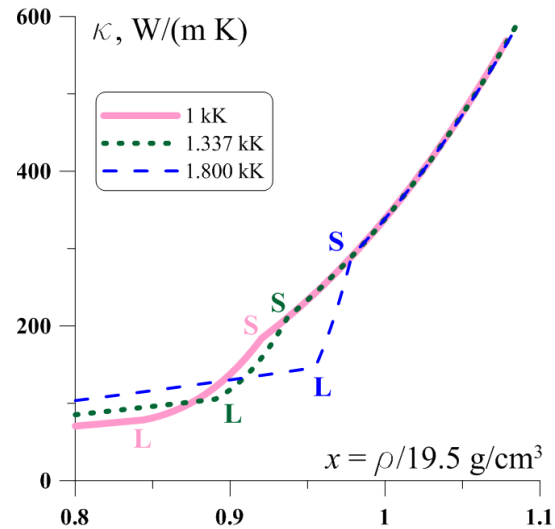


Figure 2: Electron thermal conductivity coefficient of gold in dependence on the relative density  $x$  at three values of temperature  $T$ , equal both for electrons and ions. 1 —  $T = 1000 \text{ K}$ ; 2 —  $T = 1337 \text{ K}$ ; 3 —  $T = 1800 \text{ K}$ . SL segments indicate the regions of liquid-solid phase transition.

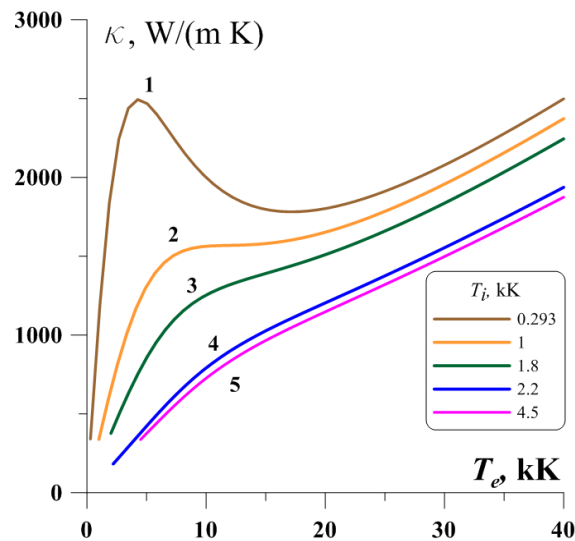


Figure 3: Electron thermal conductivity coefficient of gold in dependence on the electron temperature  $T_e$  in the  $2T$ -case. Curves 1, 2, 3 refer to the solid phase (1 — at ion temperature  $T_i = 0.293 \text{ kK}$ , 2 — at  $T_i = 1 \text{ kK}$ , 3 — at  $T_i = 1.8 \text{ kK}$ ), curves 4 and 5 refer to the liquid phase (4 — at  $T_i = 2.2 \text{ kK}$ , 5 — at  $T_i = 4.5 \text{ kK}$ ). Relative density  $x = x_{rt} = 1$ .

## 5. CONCLUSION

We present analytical expressions of electron thermal conductivity coefficient of gold in dependence on the electron and ion temperatures and density within the range, characteristic for the interaction of femtosecond laser pulses with metals. In calculations the electron-electron as well as electron-ion scattering is taken into account with  $s$ - and  $d$ -electrons of gold under consideration as well as in the solid phase and in the melt, with taking into account the jump at the phase transition. These analytical expressions can be used in two-temperature hydrodynamic and molecular dynamics codes to study problems of laser ablation of metals.

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