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## On the temperature dependence of the electronic thermal conductivity in metals when the electron and phonon subsystems are not in local equilibrium

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**Abstract.** The knowledge of the temperature dependence of the thermal conductivity is necessary in many aspects. It is required, for example, as an important input parameter for the calculation of temperature distributions in metals after interaction with laser pulses. Although extensive compilations exist on this subject they may be of limited value because the data were obtained under steady state conditions where the electrons and phonons are described by a single common temperature. At short laser pulses, however, the electron and phonon subsystems are not in local thermal equilibrium and have to be characterized by different temperatures. It is shown that the validity of the often used linear dependence of the thermal conductivity on the electron temperature is limited to some few thousand kelvin and becomes definitely wrong at higher temperatures. A formula including the thermoelectric effects is derived that is valid throughout the whole temperature range as well as for the case of local thermal equilibrium and nonequilibrium.

The electronic thermal conductivity in metals is about one to two orders of magnitude higher than for the corresponding phonon contribution. It is a well known quantity and tabulated in many compilations or textbooks (e.g. Weast 1982). For temperatures above the Debye temperature the thermal conductivity is almost constant in metals. This property, however, is measured under steady state conditions and for solids, therefore, the temperatures are restricted to values below the melting point or for liquids to values below the evaporation point. Due to the steady state condition, the electron and phonon subsystems are in local thermal equilibrium and, hence, characterized by a common temperature. From a theoretical point of view, as a result, higher order corrections in Sommerfeld's expansion (see e.g. Ashcroft and Mermin 1976) can be neglected since they are proportional to  $(k_B T / \mu_0)$  where  $\mu_0$  is the Fermi energy at zero temperature. On short time scales, however, which, for example, become important for the interaction of short laser pulses with metals, this is not longer true and one has to consider separate temperatures for the electrons and phonons. These can be very different. Under such conditions, the use of the experimentally determined standard values becomes questionable. In the case of two different temperatures a first and commonly used approach for modelling the following relation can be derived for the thermal conductivity from the simple gas equation

$$\lambda(T_e, T_0) = \lambda(T_0) T_e / T_0 \quad (1)$$

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where  $T_0$  represents the steady state temperature at which the conductivity was measured. To obtain this expression the following assumptions have been made: first, the electronic specific heat is proportional to the electron temperature  $T_e$  and, second, the scattering time depends, in essence, only on the number of phonons and, therefore, on their temperature.

Below we will show that this predicted linear dependence on the electron temperature is restricted to fairly low electron temperatures up to some few thousand kelvin. For higher values the behaviour is completely different, and the thermal conductivity decreases roughly with the inverse of the electron temperature. This is worth noting since the thermal conductivity is an important input quantity for the calculation of the temperatures inside a metal after an interaction with a short laser pulse (Anisimov and Rethfeld 1996, Hüttner and Rohr 1996, 1998) where for short periods of time the electron temperatures can rise up to some few electron volts while the phonon temperature stays almost constant. In these cases the use of (1) would lead to serious errors for the thermal diffusivity and, consequently, wrong values would be predicted for the electron and phonon temperatures. The mentioned nonlinear behaviour becomes especially important for metals with a comparatively small coefficient of heat exchange and, therefore, long relaxation times, for example gold, silver or lead that are frequently used in short time experiments e.g. by Fann *et al* (1992) or Wang and Downer (1992).

In the semiclassical theory of conduction in metals the electronic thermal current density is defined by

$$q = \sum_{\mathbf{k}} [E(\mathbf{k}) - \mu(T_e)] v(\mathbf{k})^2 \tau(E(\mathbf{k})) \frac{\partial f_{\mathbf{k}}^0}{\partial T_e} (-\nabla T_e) \quad (2)$$

where for the sake of a simpler notation we have assumed that the heat is carried by the electrons in only a single band. In the following we will restrict ourselves to the free electron model. This simplification does not affect the general validity of our physical statement below since the consideration of a real band structure would only make the derivation more complicated. Another important point is worth noting: a linear relation between the flux and the force as in (2) implies that from the point of view of thermal dynamics the temperature is a well defined quantity (de Groot 1952). In our final discussion below we will stress this point once more.

As all abbreviations hold their usual meaning (2) is quite general. It is important to indicate that only electron properties are involved. Therefore,  $T_e$  is the temperature of the electrons described by the Fermi–Dirac distribution. Within the frame of the relaxation time approximation possible interactions with other subsystems, which may have different temperatures, are only included in the electron lifetime  $\tau(E)$ . In the standard theory one inserts into (2) the electron–phonon scattering time represented by Drude’s scattering time. This time is proportional to the inverse of the phonon temperature. The corrections caused by the electron–electron interaction are usually neglected in the case of local thermal equilibrium because they are assumed to be small. The situation is different, however, if the electrons possess a much higher temperature than the phonons. Utilizing the Fermi liquid theory one obtains for the electron–electron scattering time

$$\tau_{e-e}^{-1} = \tau_T^{-1} + \tau_E^{-1} = 4\pi^2 \beta k_B^2 T_e^2 + \beta (E - \mu)^2 \quad (3)$$

where  $\beta$  is an experimental parameter (Parkins *et al* 1981). Combining this relation with the Drude time  $\tau_D$  the complete electron lifetime can be written as

$$\tau(T_e, T_{ph}) = \frac{\tau_D(T_{ph})}{1 + z(T_e, T_{ph}) + \beta (E - \mu(T_e))^2} \quad (4)$$

with the abbreviation  $z(T_e, T_{ph}) = \tau_D/\tau_T = \tau_D 4\pi^2 \beta k_B^2 T_e^2$ . After expansion of the chemical potential up to the second order

$$\mu(T_e) = \mu_0 \left( 1 - \frac{\pi^2 k_B^2 T_e^2}{12 \mu_0^2} - \frac{7\pi^4 k_B^4 T_e^4}{360 \mu_0^4} \right) \quad (5)$$

and insertion of equations (3)–(5) into (2), the electronic thermal conductivity is given by

$$\lambda = \sum \frac{[E - \mu(T_e)]^2}{T_e} \frac{v^2 \tau_D}{(1 + z + \beta(E - \mu(T_e))^2)} \times \left( \frac{E - \mu_0}{k_B T_e} - \frac{\pi^2 k_B T_e}{12 \mu_0} - \frac{7\pi^4 k_B^3 T_e^3}{120 \mu_0^3} \right) \left( -\frac{\partial f^0}{\partial E} \right). \quad (6)$$

For reason of simplification the index  $k$  is omitted. For evaluating (6) the sum is replaced by an integral over the wave vector  $k$ . After integration over the angles the remaining integral is rewritten as an energy integral. Applying Sommerfeld's expansion up to the second order then yields

$$\lambda = \lambda_{LTE} \frac{T_e G(T_e)}{T_{ph}(1 + z(T_e, T_{ph}))} \left\{ 1 + \frac{1}{G(T_e)^2} \left[ \frac{\pi^2 k_B^2 T_e^2}{24 \mu_0^2} + \frac{7\pi k_B^4 T_e^4}{480 \mu_0^4} \right] \right\} \quad (7)$$

where we have suppressed all terms higher than the fourth order in  $k_B T_e/\mu_0$ . The function  $G(T_e)$  is defined up to the same order by

$$G(T_e) = \sqrt{1 - \frac{\pi^2 k_B^2 T_e^2}{12 \mu_0^2} - \frac{7\pi^4 k_B^4 T_e^4}{360 \mu_0^4}}. \quad (8)$$

For a more correct notation we have changed the index '0' from (1) for the index 'LTE' emphasizing that this is the conductivity related to the case of local thermal equilibrium ( $T_e = T_{ph}$ ) without the contribution of the electron–electron scattering. As a result of the integration its explicit form is

$$\lambda_{LTE} = \frac{\pi^2 k_B^2}{3 e^2} T_{ph} \sigma_D. \quad (9)$$

This is nothing else but the Wiedemann–Franz law with  $\sigma_D$  as the Drude dc electrical conductivity. Although (9) is based on a highly oversimplified model, it captures the correct trend of the temperature dependence (Pinski *et al* 1981). A more realistic calculation beyond the free electron approach requires the determination of  $(n/m)_{eff}$  from band theory as proposed by Allen *et al* (1986). Furthermore, for some transition metals with low lying d bands the electron density of states can vary significantly within an energy interval  $\pm k_B T_e$ . This may have a substantial effect on the magnitude of the effect calculated here, but should not change its qualitative features.

Assuming for a moment  $z \ll 1$  and  $k_B T_e/\mu_0 \ll 1$  one can recognize that (7) reduces to (1). By this way we have confirmed this simple equation on a more fundamental basis. We also identify that this expression includes only the electron–phonon contribution to the thermal resistivity.

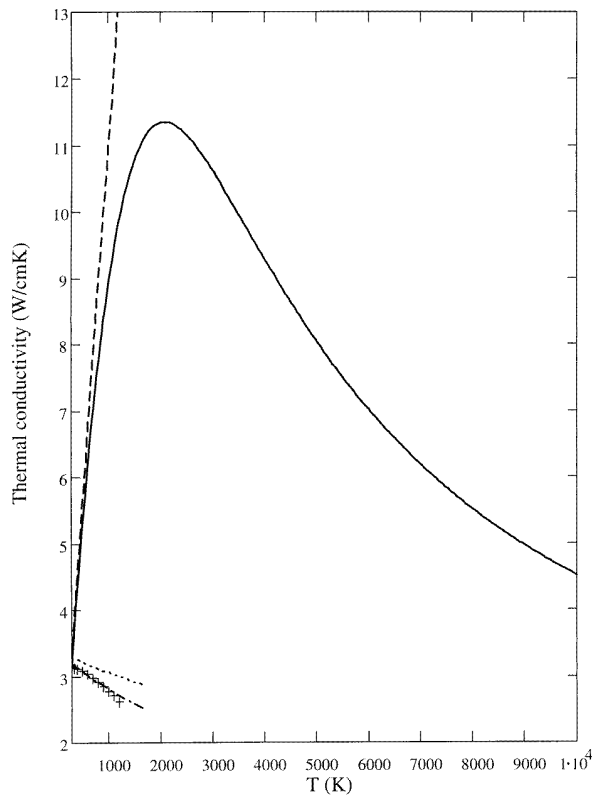
In general, it follows from (7) that for electron temperatures not too high the thermal conductivity is proportional to  $(T_e/T_{ph})$  as given by (1). But for higher values a dependence on roughly the inverse electron temperature becomes dominant because  $z$  is proportional to the square of the electron temperature. Obviously, the location of the turning point depends on the value of the constant  $\beta$ . For the noble metals this quantity is in the order of  $10^{13}$  (s eV<sup>2</sup>)<sup>-1</sup> (Parkins *et al* 1981). An estimate of the leading factor in front of the opening

curly bracket in (7) predicts for gold ( $\beta = 2.4 \times 10^{13} \text{ s}^{-1} \text{ eV}^{-2}$  and  $\lambda_{LTE} = 3.2 \text{ W cm}^{-1} \text{ K}^{-1}$ ) at  $T_{ph} = 300 \text{ K}$

$$\frac{\lambda_{LTE} T_e}{T_{ph}(1 + \tau_D(T_{ph})4\pi^2 \beta k_B^2 T_e^2)} \cong \begin{cases} 0.03 & \text{for } T_e = 300 \text{ K} \ll 1 \\ 0.3 & \text{for } T_e = 10^3 \text{ K} \approx 1 \\ 30 & \text{for } T_e = 10^4 \text{ K} \gg 1. \end{cases}$$

From these values we conclude that also under steady state conditions the electron–electron scattering becomes important at higher temperatures and that in the general case it even is dominant at high electron temperatures.

These statements are corroborated by figure 1 where the electronic thermal conductivity of gold is plotted. The full curve represents the electronic short-time temperature dependence as a function of the electron temperature at a fixed phonon temperature of  $T_{ph} = 300 \text{ K}$ . A deviation from the linear increase predicted by (1) (dashed curve) can be recognized around 1000 K and for temperatures above about 2000 K a completely different behaviour appears. The assumed constancy of the phonon temperature should be correct for gold up to about one picosecond, as shown by Juhasz *et al* (1992). The rise of the electron temperature may be caused by the interaction with a fs laser pulse. (7) is, of course, more general and not restricted to a constant phonon temperature. The dash–dotted curve is the calculated thermal



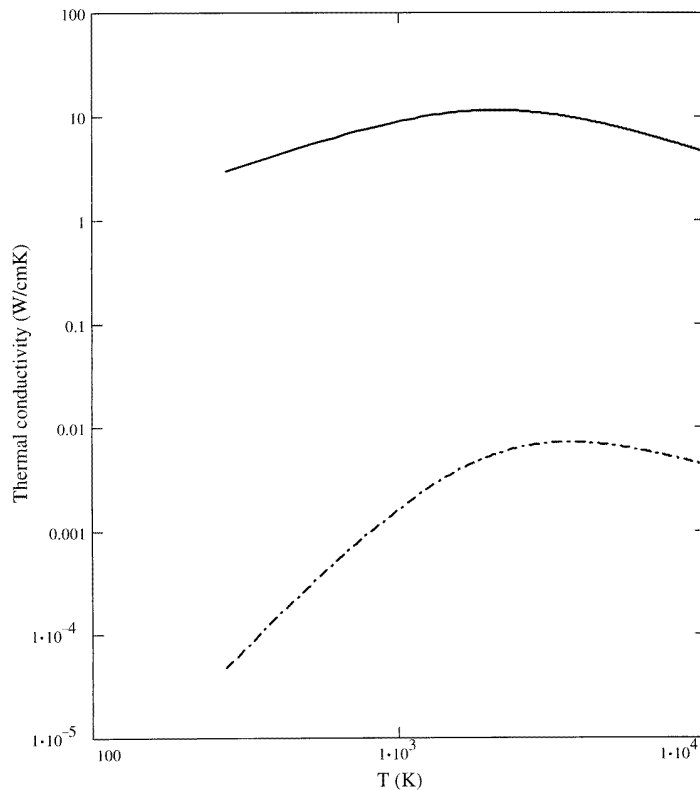
**Figure 1.** Thermal conductivity of Au, upper curves for the non-equilibrium state as a function of  $T_e$  at a fixed  $T_{ph} = 300 \text{ K}$ ; (7), full curve; (1), dashed; lower curves for the case of local thermal equilibrium ( $T = T_e = T_{ph}$ ); (7) dash–dotted curve; (7) without  $G(T_e)$ , i.e. without electron–electron scattering, dotted; +, experimental values taken from Weast (1982).

conductivity if both temperatures are equal as happens during measurements under steady state conditions. The good agreement with the experimental values (+) taken from Weast (1982) confirms the correctness of the constant  $\beta$  and underlines the necessity of already including the electron–electron scattering in the case of local thermal equilibrium. A further improvement of the agreement between the experimental points and the theoretical curve could be achieved if the thermal expansion were taken into account. We have neglected this aspect because it was not our goal to give an as good as possible a description of the thermal conductivity for the steady case but to work out the principally distinct behaviour for different electron and phonon temperatures. We also have not distinguished, therefore, between the solid and liquid phase. Consequently, above the melting point the curves can be regarded only as an approximation. Considering electron–phonon scattering only, one obtains the dotted curve where values for the thermal conductivity are too large.

Up to this point we have ignored thermoelectric effects. In the steady state this contribution is usually neglected because the deviations from the thermal conductivity are of the order of  $(k_B T / \mu_0)^2$  which is much smaller than unity. Since in the general case the electron temperature can be much higher than the phonon temperature one has to recalculate the thermoelectric corrections. Following Ashcroft and Mermin (1976) this contribution is defined by

$$\lambda_{TE} = -\frac{e^2}{T_e} \left[ \sum v^2(\mathbf{k}) \tau(E) (E(\mathbf{k}) - \mu(T_e)) \left( -\frac{\partial f^0}{\partial E} \right) \right]^2 \left[ \sum v^2(\mathbf{k}) \tau(E) \left( -\frac{\partial f^0}{\partial E} \right) \right]^{-1} \quad (10)$$

with  $e$  as the electronic charge and ‘TE’ as an abbreviation for the thermoelectric effect.



**Figure 2.** Full curve: thermal conductivity of gold according to (7); dash-dotted curve: (11), absolute value of thermoelectric correction.

Evaluating equation (10) as done above we find after the integrations

$$\lambda_{TE} = -\lambda_{LTE} \frac{T_e}{T_{ph}} \frac{\pi^2 k_B^2 T_e^2}{12\mu_0^2(1+z(T_e, T_{ph}))G(T_e)^{3/2}}. \quad (11)$$

Since this result is similar to (7), however additionally weighted by the ratio  $(k_B T_e / \mu_0)^2$  we expect only small contributions as in the standard theory. Figure 2 shows a double-logarithmic plot of the thermal conductivity as given by (7) and the absolute value of the thermoelectric correction. Summarizing our results, we find that (1) can be used as an approximation for moderate electron temperatures. For higher temperatures, however, it becomes definitely wrong and (7) must be applied. This point of view is especially important for the modelling of the electron and phonon temperature distribution in metals during and after interaction with short laser pulses. A good match to this equation is already obtained by the expression in front of the opening curly bracket.

The application of our theory takes for granted the establishment of an electron temperature and is, therefore, restricted to not too short time scales. A few scattering events must occur for this reason. A further limitation of the above derivation is related with the validity of the Boltzmann theory. Allen and coworkers (1986) have shown that this theory is accurate if the mean free path is larger than about five interatomic spacings.

Finally, however, one should keep in mind that a nonequilibrium electron distribution is found in the experiments (e.g. Fann *et al* 1992). One possibility to describe such behaviour is to expand the Boltzmann equation up to the second order. Under these conditions the heat flow is given by an expression similar to the Maxwell–Cattaneo equation which corresponds to (2), but with an additional term  $\tau_{relax} \partial q / \partial t$  on the left-hand side (Jou *et al* 1993). Nevertheless, one can still identify the expression before the temperature gradient with the thermal conductivity even if some higher order corrections appear due to the nonequilibrium electron distribution function. From this point of view we can regard (7), on the one hand, as an improvement of the standard theory and, on the other hand, as an approximation to a nonequilibrium theory still to be developed.

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