

# Time-resolved thermorefectivity of thin gold films and its dependence on the ambient temperature

T. Juhasz

*Department of Physics, University of California, Irvine, California 92717*

H. E. Elsayed-Ali

*Laboratory for Laser Energetics, University of Rochester, Rochester, New York 14623*

X. H. Hu and W. E. Bron

*Department of Physics, University of California, Irvine, California 92717*

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The dependence on the ambient temperature of the transient thermorefectivity of single-crystal thin gold films has been determined experimentally. We assume the existence of an effective electron temperature throughout the experiment, and demonstrate that it is possible to transform the temporal evolution of the thermorefectivity to the temporal evolution of the effective electron temperature, and to determine the dependence of the decay of the effective electron temperature on the ambient temperature.

Time-resolved thermomodulation has attracted considerable recent attention and has been widely used to study the dynamics and transport of optically excited electrons in normal metals and in superconductors.<sup>1</sup> In the present experiment a modulated ultrashort-duration laser pulse train is used to generate (pump) excited electrons. The transient change in the reflectivity,  $(\Delta R/R)(t)$  of the sample is determined by appropriately delayed (probe) laser pulses. Figure 1 displays a typical transient thermorefectivity measurement obtained from a single crystalline gold film of  $\sim 200$  Å thickness held at an ambient temperature of 100 K. The film is exposed, starting at  $t=0$ , by a  $\sim 150$  fs duration pulse of 615-nm wavelength<sup>2</sup> and with  $40\text{-}\mu\text{J}/\text{cm}^2$  laser fluence per pulse. Similar results were obtained at ambient temperatures from 5 to 300 K.

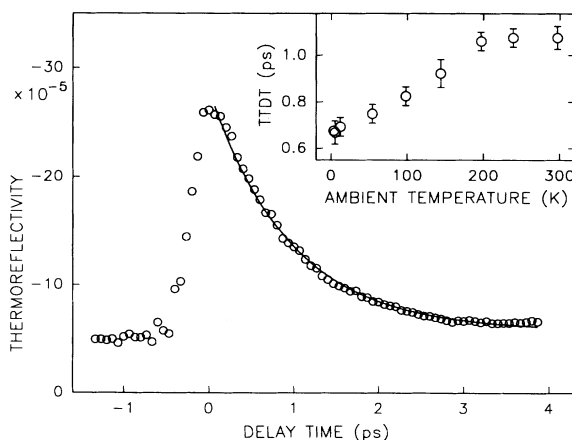


FIG. 1. Typical transient thermorefectivity taken at an ambient temperature of 100 K and laser fluence of  $40\text{ }\mu\text{J}/\text{cm}^2$ . The solid line displays the result obtained by fitting the function  $a\exp(-t/\tau)+b$  to the data. Inset: The dependence of the transient thermorefectivity decay time (TTDT) on the ambient temperature.

Further details of the measurements are as follows. The pump and probe beams are each nearly at normal incidence and focused to a measured beam diameter of  $15 \pm 1\text{ }\mu\text{m}$ . We have assumed that the  $200\text{-}\text{\AA}$  sample is heated uniformly across its thickness since the film thickness is comparable to the laser skin depth ( $150\text{ }\text{\AA}$ ) and since electron transport is expected to quickly ( $\sim 100$  fs) smooth any effective gradient in the electron temperature across the thickness of the film. The single-crystal gold films are fabricated by epitaxial growth on heated NaCl crystals and then transferred to sapphire substrates.<sup>3</sup> (We have previously reported comparisons of the response between single-crystal and polycrystalline gold films.<sup>3</sup>) Experimental observations for each ambient temperature were repeated 4–6 times. The experimentally determined absorptivity of the laser pulse by the film was determined through measurements of the reflectivity and the corresponding transmissivity and found to be  $\sim 5\%$  at room temperature and to decrease slowly and smoothly to  $\sim 4.2\%$  at 3 K. The decay of  $(\Delta R/R)(t)$  for each ambient temperature is shown to fit a function of the form  $a\exp(-t/\tau)+b$ , in which  $a$  is the magnitude of the thermorefectivity at  $t=0$ ,  $\tau$  is the decay time ( $1/e$  point) of the exponential component of  $(\Delta R/R)(t)$ , and  $b$  is the residue after the exponential decay. The dependence of  $\tau$  on the ambient temperature is shown in the inset to Fig. 1. (Each error bar reflects the standard deviation.) Strictly speaking, the measured thermorefectivity represents a temporal convolution of the probe pulse with that of the transient thermorefectivity. The results of this convolution affect primarily the values at the peak of the thermorefectivity<sup>4,5</sup> and amounts to approximately 10% in the present case. Since this is comparable to the uncertainty of the absorption measurement itself, we have not treated the effects of the convolution beyond this point.

It has generally been assumed, to within the temporal resolution of the experiment, that the excited electronic distribution thermalizes, i.e., that a local electron temperature,  $T_e$ , can be determined even though  $T_e$  may differ

considerably from the ambient temperature  $T_a$ . The dynamics of such a two-temperature system is then described by the following coupled nonlinear diffusion equations:<sup>6</sup>

$$C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla \cdot (\kappa \nabla T_e) - G(T_e - T_l) + P(z, t), \quad (1a)$$

$$C_l \frac{\partial T_l}{\partial t} = G(T_e - T_l). \quad (1b)$$

In Eq. (1a)  $C_e(T_e)$  is the heat capacity of the excited electrons (usually assumed to vary linearly with  $T_e$ ),  $\kappa$  is the electron thermal conductivity,  $G$  is the electron-phonon coupling parameter, and  $P(z, t)$  is the spatial and temporal evolution of the power density of the exciting laser pulses. In Eq. (1b)  $C_l$  is the lattice heat capacity. No diffusion term is present in Eq. (1b) as the result of the much slower diffusion of energy among phonons as compared to that among the electrons in metals.

The application of Eqs. (1a) and (1b), and the concept of effective local temperatures, have not, however, been free from concern. For example, the following questions arise: (i) Is the electron heat capacity,  $C_e$ , linear for all excited electronic excursions? (ii) Is  $G$  a constant for all  $T_e - T_l$ , which is known not to be the case for  $T_e$  and  $T_l$  less than the Debye temperature?<sup>6-8</sup> The equations should hold for small excursions of  $T_e$ . But what is small enough, and is the resultant concentration of excited electrons large enough for them to reach a local equilibrium within the temporal resolution of the experiment?

Unfortunately, our understanding of some of these factors is limited. In order to proceed beyond this point it is necessary to introduce a number of simplifications. For example, we will follow the usual assumption that under the conditions of the experiment both  $T_e$  and  $T_l$  are well-defined effective, local temperatures and that they remain so throughout the excitation of the electrons and phonons and their subsequent interaction. We also neglect the electron diffusion terms in Eq. (1a) since our films were purposely limited to a thickness of  $\sim 200$  Å, i.e., of the order of the skin depth of gold. Thus only a small concentration gradient occurs across the small dimension of the film. In addition, the relatively large focal diameter of the laser beam, means that only a very small portion of the excited film can support a concentration gradient in the plane of the film.

It is known that the electron-phonon coupling,  $G$ , is not always independent of the temperature. An *a priori* calculation of  $G(T)$  is, however, not easy to achieve. In order to circumvent this problem we adopt an empirical approach and solve for  $T_e$  and  $T_l$ , in restricted regimes, without direct knowledge of  $G$ . For this purpose we replace the term containing  $G$  in Eq. (1a) by Eq. (1b) and integrate the result from the ambient temperature  $T_a$  to  $T_e$  and  $T_l$  such that

$$\int_{T_a}^{T_e} C_e(T_e) dT_e + \int_{T_a}^{T_l} C_l(T_l) dT_l = \int_0^t P(z, t) dt. \quad (2)$$

Equation (2) simply states that the absorbed laser energy density (per pulse) is distributed, in general, among the electrons and the phonons. At this point we assume that the maximum value of  $\Delta R/R$  (see  $t=0$  in Fig. 1) corre-

sponds to purely electronic excitation because the phonons have not had the time to interact with the electrons.<sup>9</sup> Thus the second term on the left side of Eq. (2) vanishes for  $t \approx 0$ , and it becomes possible to recover  $T_e(t \approx 0) \equiv T_e^{\max}$  from the empirically determined laser energy absorbed and  $C_e(T_e) = 66T_e$  J/m<sup>3</sup>K.<sup>10</sup> Similarly, we may assign special meaning to that part of Fig. 1 for which  $\Delta R/R$  does not vary much with  $t > 0$ . In this "minimum" of  $\Delta R/R$  we assume that the electrons and phonons have reached the same effective local temperature  $T_e^{\min} = T_l^{\min}$ . The system, however, is not in absolute thermal equilibrium at this stage in the cooling of the electrons, since  $T_e^{\min}$  remains higher than the ambient temperature,  $T_a$ .

Therefore, in the regime of the minimum, the limits of the integration on the left-hand side of Eq. (2) are both from  $T_a$  to  $T_e^{\min}$ . Since  $C_l(T_l)$  can be obtained through interpolations of published values,<sup>11</sup> it becomes possible to also determine  $T_l^{\min}$  and  $T_e^{\min}$  from Eq. (2).

We now have  $(\Delta R/R)(t)$  for all time, and we have  $T_e$ , at various ambient temperatures, but only at specific times in the evolution of  $(\Delta R/R)(t)$ ; namely, at the times at which  $T_e^{\max}$  and  $T_e^{\min}$  are defined. At this point we define  $\Delta T_e^{\max} = T_e^{\max} - T_a$  and  $\Delta T_e^{\min} = T_e^{\min} - T_a$ . The dependence of these parameters on  $T_a$ , are shown in the inset to Fig. 2. The fact that  $\Delta T_e^{\max}(T_a)$  is, in general, greater than  $\Delta T_l^{\min}(T_a)$  simply reflects the lower  $C_e(T_e)$  relative to  $C_l(T_l)$ .

From time to time it has been reported that the temporal profile of  $T_e$  follows directly that of  $(\Delta R/R)(t)$ . We now demonstrate that (i) this is in general not so, even if  $(\Delta R/R)(t)$  decays exponentially, (ii) the function which describes the difference in these profiles can be recovered from the experimental results, and (iii) moreover, an iteration of the inverse of this function can be used to recover  $T_e(t)$ .

We take note that the magnitude of the thermoreflectivity reflects the thermal smearing of the Fermi surface caused by the excited electrons. Assuming that the

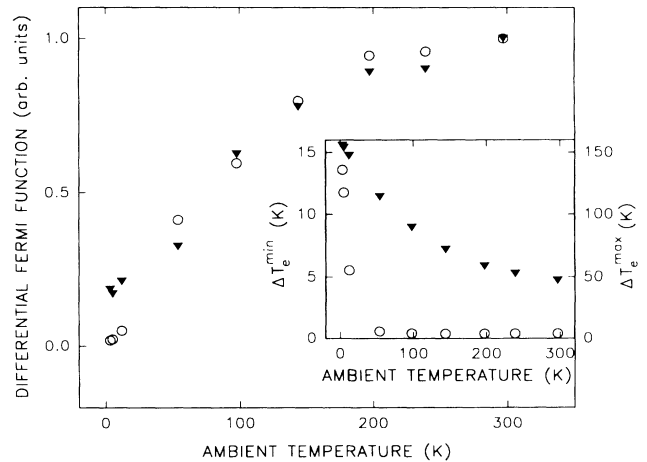


FIG. 2. The differential Fermi function determined at  $\Delta T_e^{\min}$  (open circles) and at  $\Delta T_e^{\max}$  (solid triangles) as a function of the ambient temperature. Inset: Dependence of  $\Delta T_e^{\min}$  (open circles) and  $\Delta T_e^{\max}$  (solid triangles) on the ambient temperature, and at a constant laser fluence of  $40 \mu\text{J}/\text{cm}^2$ .

lattice contribution is negligible, and assuming that the  $d$  band of gold is flat, then the transient thermorefectivity can be approximated as<sup>12,13</sup>

$$\frac{\Delta R}{R}(t) \propto \frac{df(h\nu, T_e(t))}{dT_e} \Delta T_e(t), \quad (3)$$

where  $f(h\nu, T_e)$  is the Fermi distribution and  $\Delta T_e = T_e - T_a$ . Since  $f(h\nu, T_e)$  is a nonlinear function of  $T_e$ , it is clear from Eq. (3) that the temporal profiles of  $(\Delta R/R)(t)$  and  $T_e(t)$  are, in general, different from each other. The differences among the temporal profiles depend also on the ambient temperature. An *a priori* evaluation of Eq. (3) requires a more complete description of the Fermi function, and its temperature derivatives, than is readily available. Moreover, the details of the actual electronic transitions are complicated by the fact that our laser excitation is not resonant with the top of the  $d$  band to the Fermi level, but rather with transitions from an absorption tail.<sup>14</sup>

In order to circumvent this problem, we again adopt an empirical approach and solve Eq. (3) for  $df/dT_e$  in terms of the experimental values of  $\Delta R/R$  and  $\Delta T_e$  at the special values of  $\Delta T_e^{\max}$  and  $\Delta T_e^{\min}$ . For convenience we refer to  $df/dT_e$  as the "differential Fermi function,"  $\xi(T, t)$ . Clearly, this function yields the change in the thermomodulation per unit change in  $T_e$ . Figure 2 is a compilation of the normalized  $\xi(T, t)$  functions evaluated at  $\Delta T_e^{\max}$  and  $\Delta T_e^{\min}$  as a function of  $T_a$ . As can be observed from Fig. 2, the two sets of normalized values for  $\xi(T, t)$ , show agreement despite the difference in their origin.

We assume that the above analysis is most appropriate if the temperature excursions are such that  $\Delta T_e \ll T_a$  for all ambient temperatures. Near  $\Delta T_e^{\max}$  this restriction is not obeyed for  $T_a \leq 100$  K and may be the source of the higher values of  $\xi(T, t)$ , at the lower temperatures, than is obtained using  $\Delta T_e^{\min}$ .

The discrepancy can be decreased by using  $\Delta T_e^{\min}$ . In this case, however, the thermomodulation signal can be influenced by several effects other than smearing of the Fermi distribution. For example, lattice expansion and Fermi level shifting may be present.<sup>9,10</sup> However, these effects are small compared to those associated with  $\Delta T_e^{\max}$ . Therefore, we limit further evaluations to the case of  $\Delta T_e^{\min}$ .

The temperature dependence of the differential Fermi function (for a spherical Fermi surface) is in qualitative agreement with the changes in the electron occupancy among the states in the monitored energy range ( $\sim 2$  eV). The effect is small at low temperatures, since the electron occupancy changes significantly only near the Fermi energy (2.4 eV). At higher ambient temperature the "smearing" of the electron occupancy is more pronounced and results in a larger occupancy change per degree of heating even in the 2-eV region. Thus this analysis of the results is in qualitative agreement with Fig. 2.

We now turn to the original task; namely, to recover  $T_e(t)$  from the empirical values of  $(\Delta R/R)(t)$  and the differential Fermi function. For this purpose we perform an iteration of the time coordinate starting at the "maximum" and proceeding to the "minimum." Specifically, we calculate

$$\Delta T_e(t_n) = c(\Delta R/R)(t_n) [\xi(T_e(t_{n-1}))]^{-1} \quad (4)$$

where  $t_n$  is the delay time of the  $n$ th data point away from the "maximum." We denote  $\Delta t = t_{n+1} - t_n$ . Here  $n$  is a positive integer and  $\Delta t$  is required to be small. In the present experiment  $\Delta t$  is 64 fs. Lowering this time interval any further does not appreciably alter the result. The iteration process proceeds as follows. A polynomial is fit to  $\xi(T_e, t)$  to permit interpolation between experimental points. A value of  $c$  is calculated by setting the right-hand term of Eq. (4) to the empirical value of  $(\Delta R/R)(t)$  and  $\xi(T, t)$  to the corresponding value at the peak as displayed in the inset to Fig. 2. At this point all the independent values of  $t_0$  are set to zero which is the temporal delay at the "maximum." Equation (4) is then applied to obtain  $\Delta T_e(t_1)$  from  $(\Delta R/R)(t_1)$  and  $[\xi(t_0)]^{-1}$ . This process is repeated until the other end point is reached. Figure 3 is a comparison between a  $(\Delta R/R)(t)$  determined at  $T_a \sim 12$  K and the corresponding values of  $T_e(t)$ . Note from Fig. 3 that the observed minimum electron temperature ( $\sim 18$  K) is in agreement with the sum of  $\Delta T_e \sim 6$  K at  $T_a \sim 12$  K as obtained from the inset to Fig. 2. Similar agreement is found for all other  $T_a$ . Although this agreement does not entirely rule out cumulative errors in the iteration, it does imply that such errors are small. The decay of  $T_e(t)$  [defined similarly to the decay of  $(\Delta R/R)(t)$ ] as a function of  $T_a$  is displayed in the inset to Fig. 3. As can be seen, the decay time is essentially constant from 300 to 150 K and increases slightly at lower temperatures. This result is consistent with observation by others<sup>8</sup> that the electron-phonon coupling parameter decreases with decreasing ambient temperature. However, the exact form of the  $G(T)$  is not readily available and no attempt has been made to recover it from our results. A typical value for the decay time of the effective electron temperature is found to be 1 ps.

We have demonstrated that an empirically derived

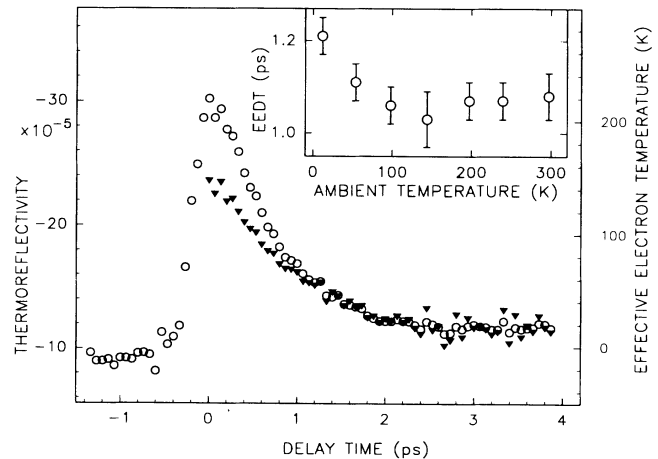


FIG. 3. The temporal dependence (ps) of the thermorefectivity (open circles) and the correspondent transient effective electron temperature (solid triangles) at 12-K ambient temperature. Inset: The dependence of the decay time of the excited electrons on the ambient temperature. EEDT stands for the excited electron decay time.

differential Fermi function can be used to transform the thermomodulation into an effective excited electron temperature. Since the differential Fermi function depends nonlinearly on temperature, the temporal dependence of the effective electron temperatures need not, in general, be the same as that of the thermorefectivity. This is clearly demonstrated in Fig. 3. Note that  $(\Delta R/R)(t)$  and  $T_e(t)$  cannot be linearly scaled into each other under the conditions of the present experiment. A similar conclusion can be reached by comparing the temperature dependences of the transient thermorefectivity decay time (see inset to Fig. 1) and that of the excited electron decay time (see inset to Fig. 3).

The central assumption of the present analysis of the thermorefectivity is that it requires that the excited electrons (and the excited phonons) exist at a local thermal equilibrium; i.e., that an effective electron (and phonon) temperature can always be defined. Such equilibria would be present if the thermomodulation process produces only excursions which are not far from true thermal equilibri-

um; i.e., for small transfer of energy from the incident laser field to the metallic thin film.

In summary, time-resolved thermomodulation experiments have been conducted on  $\sim 200\text{-\AA}$ -thick, single-crystal gold films. The films are attached to a heat sink with variable temperatures from  $\sim 5$  to 300 K. We establish relations between the observed thermorefectivity and an effective, local, electron temperature. This temperature can be determined from experimental observations, the heat equation, and an empirically obtained differential Fermi function. This relation is, in general, nonlinear in the effective electron temperature, so that the temporal evolution of the thermorefectivity and that of the effective electron temperatures generally need not be the same.

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<sup>9</sup>The validity of this assumption has been verified at room temperatures by solving Eqs. (1a) and (1b) (see first citation in Ref. 1). The solutions indicate that the lattice temperature at  $t=0$  is approximately 0.1% of that of the electrons, and moreover that this ratio does not change markedly near the maximum.

<sup>10</sup>*American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray (McGraw-Hill, New York, 1972).

<sup>11</sup>*CRC Handbook* (CRC Press, Boca Raton, FL, 1990), p. D-94.

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