

Direct measurement of nonequilibrium electron-energy distributions in sub-picosecond laser-heated gold films

W.S. Fann ^{a,*}, R. Storz ^b, H.W.K. Tom ^c and J. Bokor ^d

^a *Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan, ROC*

^b *AT&T Bell Laboratories, Holmdel, NJ 07733, USA*

^c *Department of Physics, University of California, Riverside, CA 92521, USA*

^d *Department of Electrical Engineering, University of California, Berkeley, CA 94720, USA*

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The electron-energy distribution in a gold film was measured with ~ 700 fs time-resolved photoemission spectroscopy following laser heating by a 400 fs visible laser pulse. The measured distribution can be fit by the Fermi–Dirac function at an elevated temperature except within 800 fs of the heating pulse (time-resolution limited), when a reproducible departure is observed. As a result, the relaxation of nonequilibrium electrons was found to be inadequately described by the standard electron–phonon coupling model.

The fact that the electron–phonon relaxation time in metals is on the order of picoseconds has led to many investigations with sub-picosecond lasers. Model calculations suggest that it should be possible to heat the electron gas to a temperature, T_e , of up to several thousand K for a few ps while keeping the lattice temperature, T_l , relatively cold [1,2]. The observation of the subsequent equilibration of the electronic system with the lattice affords the possibility of directly studying electron–phonon coupling under various and unusual conditions [3]. Detailed understanding of the electron–electron (e–e) and electron–phonon relaxation mechanisms should also provide greater insight into chemical reactions [4] and phase transitions [5] induced by ultrashort laser pulses. Several groups have undertaken such investigations by relating dynamic changes in the optical constants (reflectivity, transmissivity) to relative changes in electronic temperature [6–10]. However, no direct measurement of electron temperature has been reported so far. More importantly, the fact that T_e is a valid concept only if the electron gas is fully thermalized has often

been ignored. Direct measurement of the dynamics of the electron distribution by photoemission spectroscopy provides a much more detailed picture of the mechanisms of relaxation of such highly nonequilibrium systems. Not only are difficulties of relating the dynamic changes of the optical constants to the electron temperature removed but the energy distribution could also reveal how well the electron gas is described by the Fermi–Dirac distribution. It is of interest to note that the Anisimov et al. [2] originally proposed the measurement of photoelectric emission in order to study the dynamics of picosecond laser-heated metals.

We have directly measured the electron-energy distribution in gold films using sub-picosecond laser photoemission spectroscopy. A 674 nm wavelength (1.84 eV photon energy) pump pulse of 400 fs duration was used to excite a 300 Å thick polycrystalline gold film. The heating pulse fluence varied from 0.4 to 1.6 mJ/cm² and 15% of the light was absorbed. The laser system consists of a dual-jet synchronously pumped dye laser amplified to 200 μJ/pulse by a 100 Hz excimer laser-pumped dye amplifier system. The 225 nm probe pulse (5.52 eV photon energy) was pro-

* To whom correspondence should be addressed.

duced by first frequency doubling the 674 nm amplified dye laser output in a potassium dihydrogen phosphate (KDP) crystal and subsequently frequency mixing the 674 nm radiation with the 337 nm second harmonic radiation in a beta-barium borate (BBO) crystal. The probe pulse duration was measured to be 700 fs by cross-correlation with the visible 674 nm pulse. The photoemission spectrum of the laser-heated sample produced by the probe pulse was measured by the time-of-flight technique. Special time-of-flight signal processing electronics were used which allowed for the independent processing of multiple electron counts for each laser shot. All spectra were taken in the normal emission direction with an angular acceptance of $\pm 4^\circ$.

Extreme care was exercised to eliminate space-charge effects on the photoemission spectra. A relatively large probe beam spot size, on the order of 1 mm^2 , was found to be effective in eliminating space-charge broadening of the spectrum while maintaining an adequate photoelectron count rate. Since the work function of gold is 5.1 eV, the 5.52 eV probe photons produce photoelectrons by single-photon photoemission. However, at the pump intensity required to produce substantial electron heating, multiphoton photoemission from the pump pulse could not be completely avoided. The single-photon probe spectrum was recovered by subtracting the spectrum taken with the pump alone from the raw spectrum taken with both the pump and probe. The photoemission spectra are plotted as electron counts per unit energy, $dN(E)/dE$ versus energy E .

Fig. 1 also shows the best fit of the Fermi-Dirac function multiplied by the free-electron density-of-states, ie: $n^*(E) = E^{1/2}/\{\exp[(E - \mu)/kT_e] + 1\}$ to the spectra. The fit was obtained with a nonlinear least-squares fitting routine. In these fits the chemical potential, μ , electron temperature T_e and an overall vertical scale factor are used as fitting parameters. The random variation of the best-fit value of μ (nominally $\mu = E_F \approx 5 \text{ eV}$) for spectra taken at different intensities and time delays is around 10 meV. The fitted temperature for the $t = -0.8 \text{ ps}$ spectrum is 360 K, which is higher than the actual substrate tem-

perature, 300 K. The lowest fitted temperatures, even for spectra taken for unheated samples, were consistently in the 330–380 K range, and this is defined by energy resolution limit of the time-of-flight electron spectrometer. Due to the typical signal/noise ratio and the details of the data analysis procedures, the temperature accuracy for all fits was determined to be $\pm 30 \text{ K}$. The best fit temperatures are indicated in the caption to fig. 1. The quality of the fits, particularly in the edge-region, is quite good for the $t = -0.8$ and $+1.2 \text{ ps}$ spectra. In fact, for all time delays $> 0.8 \text{ ps}$, the spectra are well fit by the Fermi-Dirac distribution.

On the other hand, there is a reproducible and significant deviation from a simple Fermi-Dirac

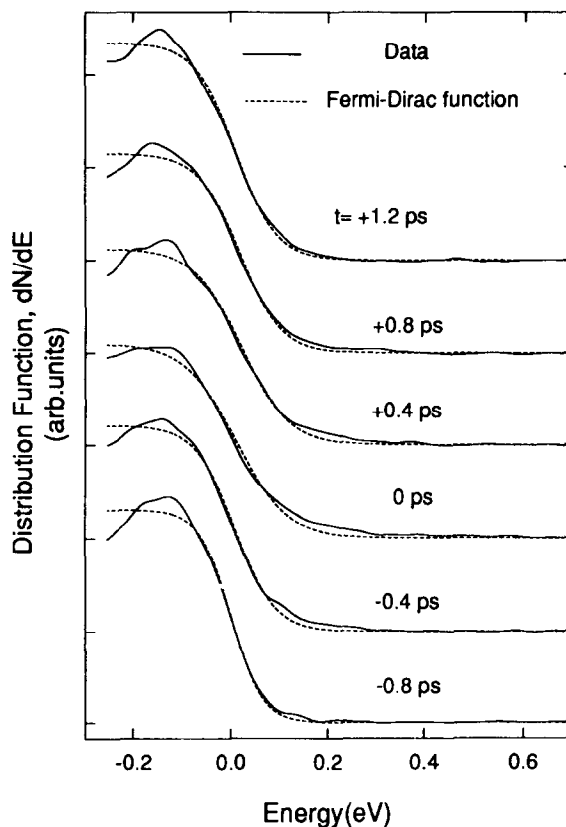


Fig. 1. Photoelectron spectra and least-squares best fits to the Fermi-Dirac function for several different time delays. The fits correspond to electron temperatures of 380, 483, 625, 582, 508, and 490 K for $t = -0.8, -0.4, 0.0, +0.4, +0.8,$ and $+1.2 \text{ ps}$, respectively.

distribution for the $t = 0, \pm 0.4$ ps spectra. For example, the best fit temperature at $t = 0$ ps is 625 K, but there is a distinct difference from 0 to +0.4 eV. We believe this deviation is due to the finite time required for the “nascent” electrons to equilibrate to a Fermi–Dirac distribution and shall refer to it as a “hot tail”. By nascent, we mean the energy distribution as created by the direct absorption from the photons prior to any scattering. We rule out the possibility that the hot tail is a density-of-states effect because, as mentioned above, gold is free-electron-like near the Fermi-level so that the density-of-states is fairly flat. A very large peak (of order 100% variation) in the density-of-states from 0 to +0.4 eV would be required to cause the deviation shown in fig. 1. We do observe (10–15)% departure from the fit in the -0.2 to -0.1 eV range. This is perhaps due to density-of-states effects. Second, it was found that, if a long laser pulse (1 ps) was used to produce a distribution with the same fitted peak temperature, the hot tail virtually disappears. We also rule out the possibility that the hot tail came from the laser pulse-to-pulse energy fluctuations, which in our experiment were about $\pm 25\%$, by explicitly simulating the spectrum which would be obtained by summing different Fermi–Dirac functions at different temperatures with a weighting function given by our measured laser pulse energy distribution. The fact that the laser pulse distribution is quite symmetric about the mean lead to a simulated spectrum which was itself extremely well fit by a simple Fermi–Dirac function with a temperature equal to that of the center of the distribution. We also rule out the possibility that the hot tail is related to inhomogeneities in the laser beam profile by carefully producing a nearly flat-topped beam profile. Finally we rule out the coherent effect because if it were the case the hot tail should extend 1.84 eV above the Fermi energy. We therefore conclude that the hot-tail is genuinely a signature of non-thermalized electrons.

We now examine the relaxation dynamics of the electron temperature and how well it can be described by the usual electron–phonon coupling model [1,2]. Since the electron gas is not fully thermalized for $t < 800$ fs, one should keep in

mind the temperature is not exactly a good parameter to characterize the system in this time scale. In this model one describes the metals as two coupled subsystems, one for the electrons and one for the phonons. Each subsystem is in local equilibrium so the electrons are characterized by a Fermi–Dirac distribution at temperature T_e and the phonon distribution is characterized by a Bose–Einstein distribution at the lattice temperature T_l . The coupling between the two systems occurs via electron–phonon interaction, characterized by an exchange of energy at a rate proportional to $T_e - T_l$. The time-evolution of the energies in the two subsystems are given by the coupled differential equations:

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

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

In eqs. (1a) and (1b), T_e and T_l are the electron and lattice temperatures, $C_e(T_e)$ is the temperature dependent electronic heat capacity, C_l is the lattice heat capacity, κ is the thermal conductivity, G is the electron–phonon coupling constant, and $P(x, t)$ is the energy density per unit time absorbed from the incident laser beam.

In fig. 2 we show the electron temperature (obtained by the best fit with the photoemission spectra) versus time delay for measured absorbed laser fluences of 0.09 ± 0.03 , 0.16 ± 0.03 , and 0.2 ± 0.06 mJ/cm². In addition, we show the calculated electron temperatures obtained by numerically solving eqs. (1). For gold $C_e = \gamma T_e$ with $\gamma = 71.5$ J m⁻³ K⁻², $C_l = 1$ K⁻¹. $P(x, t)$ was proportional to the laser intensity pulse shape and to the exponential depth dependence of the optical absorption. The equations were solved in one dimension and with the boundary conditions appropriate for the thin film. The absorbed fluences used in the calculations were adjusted to fit the data. Due to difficulties in experimentally determining the precise location of $t = 0$ ps (perfect overlap of the pump and probe pulses), the time axis was artificially adjusted for both the data and the calculations such that $t = 0$ ps corre-

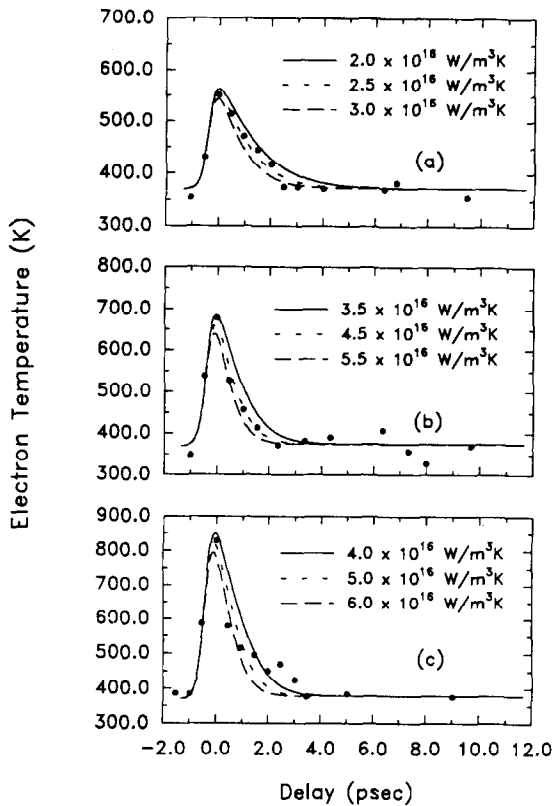


Fig. 2. Time dependence of best-fit electron temperature for three heating laser pulse fluences. Fits used the values of G shown and heating laser fluences of (a) 0.10 mJ/cm^2 , (b) 0.21 mJ/cm^2 , (c) 0.37 mJ/cm^2 .

sponds to the point where the temperature reaches its maximum.

As one sees immediately, there is no single value of G that fits all three sets of data. Best fits are obtained for values from $(2.5\text{--}6) \times 10^{16} \text{ W m}^{-3} \text{ K}$. In particular, for the highest fluence (fig. 2c), the early part of the curve requires $G \approx 6 \times 10^{16} \text{ W m}^{-3} \text{ K}$ and a much lower value for the later part of the curve. Also, the value of absorbed fluence needed to fit the data in figs. 2b and 2c is higher than the measured fluence. However, once the Fermi–Dirac distribution is obtained (in these experiments $t > 800 \text{ fs}$) then a single value of $G = (3.0 \pm 0.5) \times 10^{16} \text{ W m}^{-3} \text{ K}$ can be used to fit all of the data.

This is not a completely surprising result since eq. (1a) does not properly take into account (1) the finite time for the nascent electrons to relax to the Fermi–Dirac distribution, and (2) the possibility of an increased rate of energy transfer to the lattice when the electron energy distribution is non-Fermi–Dirac. In order for eqs. (1) to be valid, the time required to relax to the Fermi–Dirac distribution must be much faster than the time required for electron–phonon scattering so no energy is transferred to the lattice. This assumption is clearly not valid for our experimental conditions. The rapid drop of the “best fit” Fermi–Dirac temperature from 830 to 580 K within 500 fs in fig. 2c directly shows that a substantial amount of energy is transferred from the electron subsystem to the lattice subsystem during the transition from the nascent to Fermi–Dirac distribution. On the other hand, once the system is thermalized, the relaxation dynamics is well described by the coupling model and single value of G could be used to fit all the data.

In summary, we have demonstrated that photoemission spectroscopy could be used to measure the electron energy distribution in laser heated metals on a sub-picosecond time scale. It was confirmed that the coupling between the electrons and lattice is weak on this time scale, hence it is possible to highly excite the electron gas while keeping the lattice relatively cold. However, the hot electron spectra could not be fit by a Fermi–Dirac distribution at the earliest times indicating a finite relaxation time for the electrons from their nascent distribution to Fermi–Dirac. As a result, an electron temperature cannot be defined in this phase of the process and hence the electron–phonon coupling model of Anisimov et al. [2] commonly used to analyze laser heating experiments, fails on the sub-picosecond time scale. The detailed dynamics of the relaxation of the nascent distribution to Fermi–Dirac were not resolved and improved time resolution will be required in order to do so.

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References

- [1] M.I. Kaganov, I.M. Lifshitz and L.V. Tanatarov, *Zh. Eksp. Teor. Fiz.* 31 (1956) 2232 [*Sov. Phys. JETP* 4 (1957) 173].
- [2] S.I. Anisimov, B.L. Kapeliovich and T.L. Perelman, *Zh. Eksp. Teor. Fiz.* 66 (1974) 776 [*Sov. Phys. JETP* 39 (1979) 375].
- [3] P.B. Allen, *Phys. Rev. Lett.* 59 (1987) 60.
- [4] J.A. Prybyla, T.F. Heinz, J.A. Misewich, M.M.T. Loy and J.H. Glowonia, *Phys. Rev. Lett.* 64 (1990) 1537; F. Budde, T.F. Heinz, M.M.T. Loy, J.A. Misewich, F. de Rougemont and H. Zacharias, *Phys. Rev. Lett.* 66 (1991) 30241.
- [5] C.V. Shank, R. Yen and C. Hirlimann, *Phys. Rev. Lett.* 50 (1983) 454; 51 (1983) 900; H.W.K. Tom, G.D. Aumiller and C.H. Brito-Cruz, *Phys. Rev. Lett.* 60 (1988) 1438.
- [6] H.E. Elsayed-Ali, T.B. Norris, M.A. Pessot and G.A. Mourou, *Phys. Rev. Lett.* 58 (1987) 1212.
- [7] R.W. Schoenlien, W.Z. Lin, J.G. Fujimoto and G.L. Eesley, *Phys. Rev. Lett.* 58 (1987) 1680.
- [8] S.D. Brorson, J.G. Fujimoto and E.P. Ippen, *Phys. Rev. Lett.* 59 (1987) 1962.
- [9] H.E. Elsayed-Ali, T. Juhasz, G.O. Smith and W.E. Bron, in: *Ultrafast Phenomena VII*, Eds. C.B. Harris, E.P. Ippen, G.A. Mourou and A.H. Zewail (Springer, Berlin, 1990).
- [10] S.D. Brorson, A. Kazeroonian, J.S. Moodera, D.W. Face, T.K. Cheng, E.P. Ippen, M.S. Dresselhaus and G. Dresselhaus, *Phys. Rev. Lett.* 64 (1990) 2172.