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## Effect of a nonthermal electron distribution on the electron-phonon energy relaxation process in noble metals

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We show experimentally that the electron distribution of a laser-heated metal is a *nonthermal* distribution on the time scale of the electron-phonon ( $e$ -ph) energy relaxation time  $\tau_E$ . We measured  $\tau_E$  in Ag and Au films as a function of lattice temperature (10–300 K) and laser-energy density (0.3–1.3 J cm<sup>-2</sup>), combining femtosecond optical transient-reflection techniques with the surface-plasmon polariton resonance. Calculations support the experimental result that the nonthermal distribution leads to a *slower*  $e$ -ph energy relaxation process below room temperature, compared to the thermalized limit.

Dynamical aspects of the interaction between electrons and phonons play a crucial role in many properties of metals. A widely used technique to study the dynamics of highly excited electrons in thin metal films is femtosecond pump-probe spectroscopy. It provides a unique way to measure the electron-phonon ( $e$ -ph) energy relaxation time  $\tau_E$  ( $\sim 1$  ps), from which  $e$ -ph interaction-related properties can be derived (e.g., coupling parameters in superconductors<sup>1</sup>). Numerous optical studies have been made of metals like Au,<sup>2</sup> Cu,<sup>3,4</sup> Ag,<sup>5</sup> W,<sup>6</sup> and [high- $T_c$  (Ref. 7)] superconductors.<sup>8</sup> A demonstration of the heat transport<sup>9</sup> by hot electrons was given, and effects of lattice imperfections on the energy relaxation process<sup>10</sup> were seen.

The search for the ( $e$ - $e$ ) dynamics *within* the electron gas in a laser-heated metal is a real challenge. The extremely small  $e$ - $e$  collision time ( $\sim 10$  fs), associated with the highly nonthermal electron distribution during excitation, makes direct observation difficult. Investigations<sup>2,4</sup> of the wavelength-resolved transient reflectivity, which is related to the change of the distribution around the Fermi level, did not reveal a nonthermal distribution of the electron gas. A recently reported room-temperature photoemission experiment<sup>11</sup> on Au showed that electron thermalization is established within 500 fs.

We present here experimental evidence of the  $e$ - $e$  dynamics in a laser-heated metal. We observed its direct effect on the  $e$ -ph energy relaxation process for Ag and Au in the regime of low temperature and low laser-energy density. We theoretically show that the incomplete thermalization makes the  $e$ -ph energy relaxation process significantly *slower* below room temperature, and nearly *insensitive* to the deposited laser-energy density, as com-

pared to the thermalized limit. In recent preliminary experiments,<sup>12</sup> a temperature dependence of the  $e$ -ph relaxation time in Au was observed, but the results were interpreted without considering  $e$ - $e$  dynamics.

Our experimental technique<sup>5</sup> combines the merits of the surface-plasmon polariton (SPP) resonance<sup>13</sup> of a thin metal film with femtosecond pump-probe spectroscopy. The SPP is a coupled excitation of the electromagnetic field and the surface-plasmon mode. The pump pulse and the time-delayed probe pulse each excite SPP's. The SPP's of the pump pulse decay into hot electron-hole pairs, which redistribute the excess energy by  $e$ - $e$  collisions. The electron gas transfers energy to the lattice by  $e$ -ph collisions and returns to thermal equilibrium in a typical time  $\tau_E$ : the  $e$ -ph energy relaxation time ( $\sim 1$  ps at 300 K). The electron gas and lattice remain at a slightly higher temperature, until equilibrium with the rest of the sample is established by lattice heat conduction<sup>14</sup> in  $\sim 100$  ps. The induced change of the dielectric constant of the metal shifts the SPP-resonance conditions of the probe pulse and is detected as a change of reflectivity  $\Delta R(t)$  at consecutive time delays  $t$  between pump and probe. The part of the dielectric constant  $\epsilon$  that is most sensitive to the distribution of electrons is related to the interband transitions from the filled  $d$  band to the empty states above the Fermi level. Using the model of Rosei,<sup>15</sup> it can be shown that  $\Delta\epsilon$  is proportional to the total excess energy contained in the electron gas, provided that the energy of individual excitations (electrons and holes) and the photon energy (2 eV) is much smaller than the energy of interband transitions (Au: 2.5 eV, Ag: 4 eV).<sup>15</sup> As this inequality holds at any time ( $> 150$  fs) when measurements are performed, it is concluded that, by recording the change of reflectivity, the

energy relaxation of the electron gas is measured.

The experimental setup<sup>5</sup> is based on a colliding-pulse mode-locked (CPM) laser, which delivers 150-fs pulses with a center wavelength of 630 nm (2 eV) at a repetition rate of 95 MHz. The laser beam is split in two. The pump beam is doubly (8 MHz  $\otimes$  500 Hz) amplitude modulated so that influence of noise is suppressed by the synchronous detection. The weak probe beam passes a time delay stage. Resonant excitation of SPP's occurs when the focused laser beams are *p* polarized and internally reflected from the hypotenuse face of a transparent prism, on which the metal film of suitable thickness has been coated. At a critical angle of incidence, the SPP-resonance angle  $\Phi_{\text{SPP}}$ , a sharp minimum in the reflectivity  $R(\Phi)$  is found. Tuning the angle of incidence of the pump to  $\Phi_{\text{SPP}}$  ensures an efficient excitation of hot electron-hole pairs. By tuning the probe angle to one of the two steep sides of  $R(\Phi)$  [where  $dR(\Phi)/d\Phi$  is extremal], a maximal sensitivity to the hot electron induced shift of  $\Phi_{\text{SPP}}$  is attained. The laser-energy density, deposited by the pump pulse, is estimated  $U_\ell = 1.3 \text{ J cm}^{-3}$ . The Ag films (45 nm thick) were evaporated on a substrate in a standard vacuum chamber at  $10^{-6}$  Torr. Under these circumstances the films are known<sup>16</sup> to be polycrystalline. The substrates were single-crystal, optically polished quartz plates, glued on the hypotenuse of a quartz prism. The 30-nm Au films were epitaxially grown in a molecular-beam epitaxy chamber on the freshly air-cleaved hypotenuse of a single-crystal NaCl prism. The crystallinity of the Au films was checked by reflection high-energy-electron diffraction (RHEED) during growth. The NaCl prism or the quartz plate was thermally anchored to the cold finger of a He flow cryostat.

The measured signal ( $\Delta R \approx 10^{-4}$ , see inset of Fig. 1) shows a subpicosecond decay. After a few picoseconds, a small contribution remains, which is attributed to the heating of the lattice. On the latter contribution, we observed slow oscillations (Ag: period of 25 ps), which were interpreted<sup>17</sup> as traveling acoustic strain waves, bouncing up and down in the metal film. The signal within

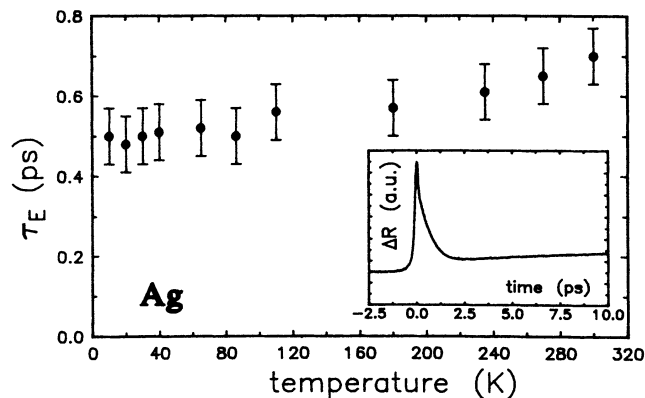


FIG. 1. Experimental electron-phonon energy relaxation time (averaged between  $t = 0.25$ – $1.25$  ps) as a function of lattice temperature for Ag. The inset shows a typical measurement of the reflectivity  $\Delta R(t)$  vs time delay  $t$ .

the time interval of 4–10 ps was found to have a small constant slope and was used as a reference level for the subpicosecond decay. This fast decay is due to the cooling of the electron gas and appeared to be slightly nonexponential. The effective relaxation times (averaged over a time interval 0.25–1.25 ps) of Ag and Au have been plotted as a function of the lattice temperature in Fig. 1 and Fig. 2, respectively. We observe a slowly decreasing relaxation time (710–530 fs for Ag, 830–530 fs for Au) as temperature is decreased from 300 to 10 K. At several temperatures we measured the relaxation curve at a pump power reduced by a factor of four and asserted that the signal scaled linearly (within 5%) with the power. The temperature dependence of the resistivity of the films (Ag:  $\rho = 0.8$ – $2.4 \mu\Omega \text{ cm}$  between 4–300 K) shows that elastic scattering is weak.

We will show that the generally accepted two-temperature model (TTM) fails to explain our experimental results. In this model, the hot electron gas is characterized by a temperature  $T_e$ , which is higher than the lattice temperature  $T_i$ . The underlying assumption in the TTM is that the electron and phonon subsystems are each maintained in a thermalized state by (Coulomb) *e-e* and (anharmonic) *ph-ph* interaction, respectively. The time evolution of  $T_e$  and  $T_i$  is given by<sup>18</sup>

$$\gamma T_e \frac{dT_e}{dt} = -H(T_e, T_i) + P(t), \tag{1}$$

$$C_i(T_i) \frac{dT_i}{dt} = H(T_e, T_i),$$

where  $P(t)$  is the amount of laser power ( $\text{W m}^{-3}$ ) that is dissipated in a unit volume of the electron gas,  $H(T_e, T_i)$  is the rate of energy transfer from electrons to the lattice, and  $\gamma T_e$  and  $C_i(T_i)$  are the specific heats of electrons and lattice, respectively. We may neglect the variation of  $T_i(t)$  with time, since  $C_i(T_i)$  is at least ten times larger than  $\gamma T_e$  for  $T_i > 8 \text{ K}$ .

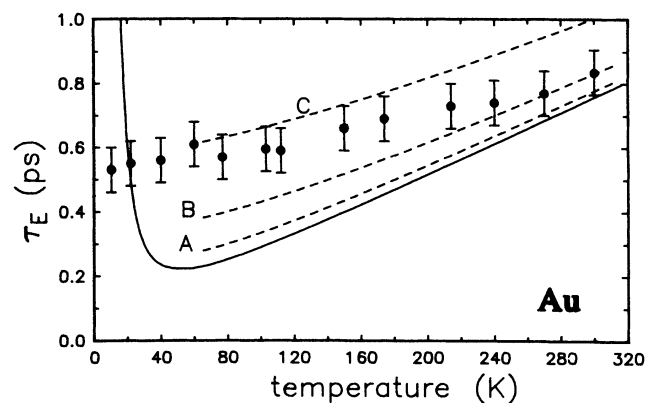


FIG. 2. Comparison between experimental data and the calculated electron-phonon energy relaxation time  $\tau_E$  in the two-temperature model vs temperature for various amounts of deposited laser-energy density  $U_\ell$ . Solid line: infinitesimally small  $U_\ell$ . Dashed lines A, B, C:  $U_\ell = 0.3, 1.3, 5.2 \text{ J cm}^{-3}$ , respectively. Dots: experimental data for Au.

The energy transfer rate  $H(T_e, T_i)$  has been calculated<sup>19</sup> by summing over all elementary one-phonon emission and absorption processes involving acoustic phonons with a Debye spectrum.<sup>20</sup>  $H(T_e, T_i)$  can be written as  $H(T_e, T_i) = f(T_e) - f(T_i)$ , where

$$f(T) = 4g \left( \frac{T}{\Theta_D} \right)^5 \int_0^{\Theta_D/T} \frac{x^4}{e^x - 1} dx. \quad (2)$$

Here,  $\Theta_D$  is the Debye temperature [170 (210) K for Au (Ag)] and  $g$  is the electron-phonon coupling constant. The quantity that can be most easily related to the experiment is the instantaneous energy relaxation time, defined as

$$\tau_E(T_e, T_i) \equiv \frac{(U_e(\infty) - U_e)}{(dU_e/dt)} = \frac{\gamma(T_e^2 - T_i^2)}{2H(T_e, T_i)}, \quad (3)$$

where  $U_e = U_e(t) = \frac{1}{2}\gamma T_e(t)^2$ ;  $U_e(\infty) \approx \frac{1}{2}\gamma T_i^2$  and  $T_e = T_e(t)$ . The important experimentally accessible control parameter is the deposited laser-energy density  $U_\ell = \int P(t)dt$ , that brings the electron gas to the initial peak temperature  $T_e(0) = \sqrt{T_i^2 + 2U_\ell/\gamma}$ . We have calculated the effect of laser energy on the energy relaxation time, using Eqs. (2) and (3). In Fig. 2, the initial relaxation time  $\tau_E(T_e(0), T_i)$  is plotted as a function of lattice temperature  $T_i$  for various values of  $U_\ell = 0.3$ – $5.2$  J cm<sup>-3</sup>.

We will compare our experimental results with the predictions of the TTM. The lattice temperature  $T_i$  can be approximated by the substrate temperature, due to the low deposited laser energy. At  $T_i = 300$  K, the relaxation time of the TTM can be made to match the corresponding experimental data point (taking  $g = 2.7 \times 10^{16}$  and  $3.1 \times 10^{16}$  W m<sup>-3</sup>K<sup>-1</sup> for Au and Ag, respectively). However, at lower temperatures a significant discrepancy arises: the experimental slope of the relaxation time versus  $T_i$  is 2–3 times smaller than predicted by the TTM (Fig. 2). One might argue that the deposited energy must have been higher at low temperature so that the slope is effectively decreased, but in that case we should have observed a large (30%) decrease in the relaxation time upon a (4 times) reduction of the laser energy. Instead, we found the relaxation time to be almost independent from laser energy. Both the observed small slope  $\tau_E(T_i)$  and the *independence* from laser energy are in striking contradiction with the TTM.

These observations can be readily understood as a consequence of a nonthermal distribution of quasiparticles (electrons and holes). Let us consider the process by which the hot quasiparticles redistribute their energy by  $e$ - $e$  collisions. The  $e$ - $e$  collision rate  $\tau_{e-e}^{-1}$  is proportional to the quasiparticle energy:<sup>21</sup>  $\tau_{e-e}^{-1} = K(E - E_F)^2$ . Accordingly, the most energetic quasiparticles ( $|E - E_F| \approx 2$  eV) are the first ones to transfer their energy by exciting new quasiparticles out of the Fermi sea. Roughly speaking, in a single collision the hot electron (or hole) cloud will half its energy, while the number of hot quasiparticles is doubled. The first steps of thermalization take as little as a few femtoseconds [ $K = 0.3$  ( $\pm 50\%$ ) fs<sup>-1</sup>eV<sup>-2</sup> for Au,  $K = 0.2$  ( $\pm 50\%$ ) fs<sup>-1</sup>eV<sup>-2</sup> for Ag, see references in Kaveh and Wiser<sup>22</sup>]. However, the time for a single elec-

tron to cool from initial energy  $E(0)$  down to  $E(t_{th})$  of about 0.05 eV is  $t_{th} \approx 1/(2K)[E(t_{th})^{-2} - E(0)^{-2}] = 700$  fs, which is already of the order of the  $e$ -ph energy relaxation time  $\tau_E$ . At the time ( $t \approx 150$  fs) we start measuring  $\tau_E$ , the average energy of the hot-electron cloud will certainly be larger than  $k_B\Theta_D$  ( $\approx 0.02$  eV), in which case each electron has a nearly constant phonon emission rate. The amount of phonon-emitting electrons is doubled in each step of thermalization. Therefore, the energy relaxation rate to the lattice increases as the thermalization within the electron gas progresses. Thus, we conclude that incomplete thermalization reduces the  $e$ -ph energy relaxation rate of laser-heated electrons. The thermal excitations ( $k_B T_i$ ) of quasiparticles, so far neglected in this paragraph, enhance the  $e$ - $e$  collision rate. The characteristic temperature  $T_{e-e, e-ph}$  for which the thermally excited quasiparticles make the  $e$ - $e$  collision time equal to the  $e$ -ph energy relaxation time is

$$T_{e-e, e-ph} = \left( \frac{g}{K\gamma\pi^2 k_B^2} \right)^{1/3}, \quad (4)$$

which is of the order of 300–600 K. Below  $T_{e-e, e-ph}$ , effects of  $e$ - $e$  nonthermalization on the  $e$ -ph energy relaxation are present.

We performed an extensive numerical calculation of the energy relaxation process of a nonthermal electron distribution using a Boltzmann equation that incorporated a two-particle  $e$ - $e$  collision integral and a one-phonon one-electron  $e$ -ph collision integral,<sup>23</sup> but neglects, e.g., multiphonon processes. In the calculation, a thermal phonon distribution with constant temperature  $T_i$  and an initially nonthermal electron distribution  $n(E) = n_{T_i}(E) \pm \Delta n(E)$ , which consists of a Fermi distribution  $n_{T_i}$  at temperature  $T_i$  and a small Gaussian electron (and hole) distribution  $+(-)\Delta n(E)$

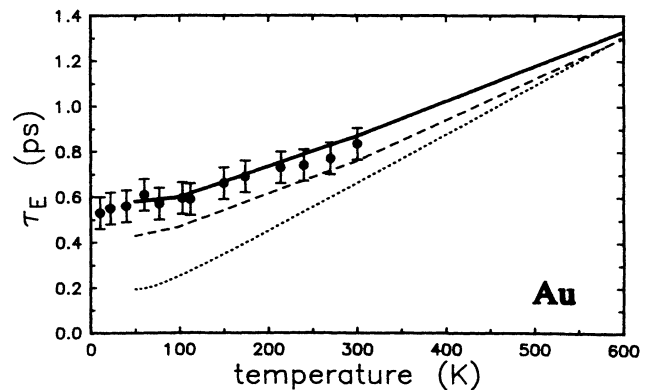


FIG. 3. Comparison between experimental data and the calculated average electron-phonon energy relaxation time  $\tau_E$  using the Boltzmann equation, which accounts for both electron-electron and electron-phonon scattering. Electron-electron scattering rate: solid line  $K = 0.1$  fs<sup>-1</sup>eV<sup>-2</sup>, large dashes  $K = 0.2$  fs<sup>-1</sup>eV<sup>-2</sup>, and small dashes  $K = \infty$  (thermalized limit). The electron-phonon coupling constant is  $g = 3.0 \times 10^{16}$  W m<sup>-3</sup>K<sup>-1</sup> for all curves. Dots: experimental data for Au.

centered at  $+(-) 0.3$  eV, was taken. The chosen energy is high enough to mimic the distribution after laser excitation. An in-depth analysis of the influence of the various model parameters was made. The calculated energy relaxation time, averaged over the time interval 0.25–1.25 ps is shown in Fig. 3 for different temperatures  $T_i$  and values of  $K$ . The influence of the  $e$ - $e$  dynamics confirms the above qualitative picture. The  $e$ -ph energy relaxation rate increases when the  $e$ - $e$  collision rate is increased for a constant  $e$ -ph coupling  $g$ . The consequences of nonthermalization becomes much more important at lower temperatures. The results given in Fig. 3 were obtained for  $U_\ell = 1\text{--}5$  J cm $^{-3}$ . Varying  $U_\ell$  in this regime led to nearly identical results, in agreement with the experimentally found insensitivity of  $\tau_E$  to  $U_\ell$ . The experimental data can be fitted well with  $g = 3.5(5) \times 10^{16}$  W m $^{-3}$ K $^{-1}$  for Ag and  $g = 3.0(5) \times 10^{16}$  W m $^{-3}$ K $^{-1}$  for Au. For both metals we found the value  $K = 0.1$  ( $\pm 50\%$ ) fs $^{-1}$ eV $^{-2}$ . The estimated values of  $K$  compare well with data<sup>22</sup> from

resistivity measurements.

We have experimentally shown that the electron distribution of a laser-heated metal is a nonthermal distribution on the time scale of the  $e$ -ph energy relaxation process. We discovered that the finite thermalization time of electrons has a large effect on the temperature dependence and deposited laser-energy-density dependence of the measured  $e$ -ph energy relaxation time. It leads to a slower energy relaxation process below room temperature, as compared to the thermalized limit.

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