Thermal Response of Metals to Ultrashort-Pulse Laser Excitation

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Both electron thermal conductivity and thermal exchange with the lattice can cool an electron distribution initially heated on a metallic surface with an ultrashort laser pulse. The interplay between the two processes allows the electron-lattice coupling parameter to be determined. We report measurements of optical damage to molybdenum and copper. Damage caused by pulses have a duration $\tau_L \lesssim 1$ nsec can be understood only with a two-temperature model of metals.

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A reliable value of the electron-phonon coupling constant g in metals[1] has wide implications, perhaps even in the field of superconductivity.[2] Recent investigations[3-6] have deduced or inferred experimental values of g. However, a large uncertainty remains because of the difficulty in firmly relating observations to theory. The experimental approach has been to diagnose the electron temperature either by photon-assisted electron emission[4] or by the change in reflection[3,6] (or transmission[5]) of visible light near the d-state resonance. These processes are all limited to relatively weak excitation, the former because of space-charge effects and the latter because of nonlinear saturation processes.[5] Moreover, in the case of thick samples, the initial reduction of the electron temperature that is measured at the surface is mainly due to the fast electron diffusion process,[7] and unless correctly treated leads to an incorrect value of g. Thin samples, on the other hand, can have anomalously fast electron cooling due to electron-impurity and electron-surface scattering.

This paper reports a new method of determining g. It relies on competition between two fast processes: electron-lattice energy exchange and electron thermal conduction. The former cools electrons heated with an ultrashort 10-μm pulse (penetration depth ~200 Å) by transferring their heat to the lattice. The latter removes energy from the surface.

The paper has a second purpose. A theory is developed to describe the pulse-duration dependence of optical damage to metals, and experimental results are presented in support of the theory.

The heat transport inside the metal can be described with the following one-dimensional, two-temperature model[8]:

$$C_e \frac{\partial}{\partial t} T_e = \frac{\partial}{\partial x} \kappa \frac{\partial}{\partial x} T_e - g(T_e - T_i) + A(x,t) \qquad (1)$$

and

$$C_i \frac{\partial}{\partial t} T_i = g(T_e - T_i) \,, \qquad (2)$$

where x is the direction perpendicular to the surface. The electron heat capacity C_e is given by $C_e = C_e' T_e$, C_e' being a constant,[9] and κ is the heat conductivity. According to Sommerfeld's model,[9] $\kappa \propto T_e/\nu$, where $\nu = \nu_{ee} + \nu_{ei}$ and ν_{ee} and ν_{ei} are the electron-electron and electron-phonon collision frequencies, respectively. T_e and T_i are, respectively, the electron and lattice temperatures and C_i is the lattice heat capacity. $A(x,t)$ is a source term and g is the electron-phonon coupling constant.[1]

As a guide, we will derive some approximate scaling laws for the response of a metal to an ultrashort pulse. These scaling laws have two essential roles. First, they allow quantities that are necessary to understand the following measurements to be introduced. Second, they provide an analytic theory of short-pulse damage to metals.

We assume that the heat is initially deposited into the electrons at the surface at $x=0$. For t smaller than some relaxation time τ_R, the heat will diffuse without being absorbed by the lattice. To enable us to obtain analytic expressions, we will assume $\nu = \nu_{ei} \propto T_i$. Computer simulations, using the more complete expression[10] for ν, indicate that the following equations will be modified by only a small amount with this assumption. In Eq. (1), only the first term on the right-hand side is important and T_e^2 is the solution of the usual diffusion equation,

$$T_e^2 = (A_0/2)(C_e' T_i/\kappa_0 \pi t)^{1/2} \times \exp(-C_e' T_i x^2/4\kappa_0 t) \,, \qquad (3)$$

where $A_0 = 4E_{\mathrm{abs}}/C_e'$ and E_{abs} is the fluence absorbed at the surface. In Eq. (1) we have treated T_i as a constant in κ. The diffusion length for T_e^2 is given by $x_D = (2\kappa_0 t/C_e' T_i)^{1/2}$. The surface electron temperature as a function of x_D becomes

$$T_e = (8/\pi)^{1/4}(E_{\mathrm{abs}}/x_D C_e')^{1/2} \,. \qquad (4)$$

To derive Eqs. (3) and (4) we required $t < \tau_R$, which we estimate by keeping only the second term on the right-hand side of Eq. (1) and neglecting T_i in that term.

We obtain

$$\tau_R = C_e' T_e / g \,. \tag{5}$$

We can now define a heat deposition depth x_R as the diffusion length x_D at $t = \tau_R$:

$$x_R = \frac{1}{\sqrt{2}} \left[\frac{64}{\pi^{1/2}} \frac{\kappa_0^2}{T_i^2} \frac{E_{\text{abs}}}{g^2 C_e'} \right]^{1/5} . \tag{6}$$

One simple means of measuring the surface lattice temperature is to observe optical damage. If the damage threshold is given by the absorbed fluence E_{th} necessary for the lattice to reach the melting point, then

$$E_{\text{th}} \simeq C_i (T_{im} - T_{i0}) x_R \,, \tag{7}$$

where T_{i0} and T_{im} are the initial and melting temperatures, respectively. Neglecting T_{i0} and assuming that T_i in Eq. (6) is T_{im} and that $E_{\text{abs}} = E_{\text{th}}$, one obtains

$$x_R = \left[\frac{128}{\pi} \right]^{1/8} \left[\frac{\kappa_0^2 C_i}{T_{im} g^2 C_e'} \right]^{1/4} . \tag{8}$$

Equation (8) shows that the distance the electrons penetrate before coupling to the lattice depends strongly on g. Moreover, this value of x_R, which is several thousand angstroms thick in metals of interest, exceeds by a large factor the value of the heat deposition depth that would be predicted by a one-temperature model (the laser skin depth in the very-short-pulse case). Taken together, Eqs. (7) and (8) imply very high damage thresholds for metals irradiated with ultrashort pulses.

The large heat deposition depth x_R results in E_{th} being nearly independent of the laser pulse duration for very short pulses. One can assume a delta function at $t = 0$ for the energy deposition at the surface if the laser pulse is shorter than

$$\tau_R = (8/\pi)^{1/4} (C_e' C_i T_{im})^{1/2} / g \,, \tag{9}$$

as obtained from Eqs. (4), (5), and (7).

For a laser pulse duration τ_L longer than τ_R, our scaling laws retain their validity. The heat diffusion depth x_R, as well as the damage threshold fluence E_{th}, is reduced by a small factor $(\tau_L/\tau_R)^{1/5}$ since the term E_{abs} appearing in Eq. (6) should be replaced by the absorbed fluence per unit of time τ_R. Thus for an intermediate range, the surface temperature is only weakly dependent on the pulse duration.

For pulses much longer than some critical time τ_c, the diffusion of the lattice temperature becomes important. For lattice-temperature diffusion depth x_{Di} larger than x_R, the damage threshold E_{th} will scale[11,12] as $\tau_L^{1/2}$. One can find τ_c by using a one-temperature model.[11] The one-temperature model is obtained from Eqs. (1) and (2) by our letting g go to infinity, i.e.,

$$C_i \frac{\partial T}{\partial t} \simeq \kappa_0 \frac{\partial^2}{\partial x^2} T + A(x,t) \,, \tag{10}$$

where $T_e = T_i = T$ and C_e is neglected since $C_e \ll C_i$. The solution of Eq. (10) has a diffusion depth $x_{Di} = (2\kappa_0 t / C_i)^{1/2}$ and τ_c is given by $\tau_c = \frac{1}{2} C_i x_R^2 / \kappa_0$, or

$$\tau_c = (8/\pi)^{1/4} (C_i^3 / C_e' T_{im})^{1/2} / g \,, \tag{11}$$

which is larger than τ_R by a factor $C_i / C_e' T_{im}$. The critical time τ_c is inversely proportional to g and provides a new method of measuring g. Equation (11) is also an important result for optical damage. It gives the time at which the $\tau_L^{1/2}$ scaling of the damage threshold (typical of long pulses)[12,13] changes to pulse-duration-independent damage (typical of ultrashort pulses).

For our experiment, we chose multishot optical damage as a method of measuring the surface temperature. For long pulses it is well established that the damage threshold is determined by surface melting.[13] For shorter pulses this is also true although superheating may have to be considered.[14] We have used the criterion of multishot damage (number of shots > 100) to ensure that defects have an adequate chance to propagate, thereby minimizing superheating.

We experimentally investigated the response of metal mirrors to normally incident ultrashort pulses. Copper and molybdenum were illuminated with 9.3-μm pulses[15] of 2.5-psec, 50-psec, 15-nsec, or 80-nsec duration. Previously published results on Mo and Cu have established the long-pulse ($\tau > 1.7$ nsec) damage behavior of these metals.[12]

The 9.3-μm beam was focused with a ZnSe lens to a focal spot having $\omega_0 = 80$ μm, where ω_0 is the radius at which the electric field is $1/e$ of its maximum value. (Because $\omega_0 \gg x_R$ our assumption of a one-dimensional model is justified.) A Gaussian beam profile was confirmed by our moving a 50-μm aperture through the beam and also by measuring the energy transmitted through apertures 50, 100, and 200 μm in diameter.

Both the input and reflected energy were monitored. Damage was assessed by (1) observing changes in mirror reflectivity as a function of the number of shots; (2) observing visible sparks on the mirror surface in a darkened room; and (3) observing the mirror under an optical microscope with ~ 1-μm resolution.

All measurements were performed in a 10^{-6}-Torr vacuum with standard laser mirrors. Laser mirrors were used because electron-surface scattering is a major contributor to energy absorption in metals. Mirror surfaces, because of their flatness, minimize these losses.

Figure 1(a) shows the results obtained for all four pulse durations. Two experimental points are plotted for each investigated pulse duration. These bracket the multishot damage threshold. The 15- and 80-nsec data are consistent with previous optical damage measurements.[12] We have included the experimental points from Ref. 12 (without error bars) for comparison.

The experimental results are consistent with the scaling predictions. For both Cu and Mo there are two dis-

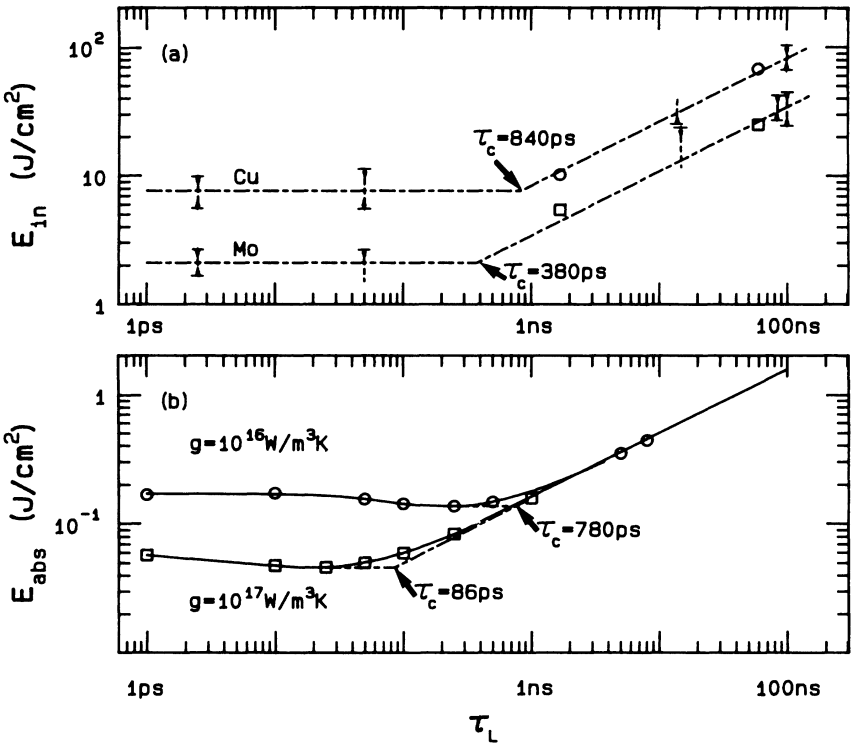

FIG. 1. (a) Incident fluence at damage threshold as a function of τ_L. The horizontal bars are experimental points where damage does and does not occur. Circles and squares are data reproduced from Ref. 12 for Cu and Mo, respectively. (b) Absorbed fluence at damage threshold as a function of τ_L. The circles and squares are obtained from our numerical model for Cu, with $g=1.0\times10^{16}$ W/m^3 K and $g=1.0\times10^{17}$ W/m^3 K, respectively. The solid curves are meant only as a guide. The dashed lines in (a) and (b) determine τ_c.

tinct regions. The short-pulse ($\tau_L \lesssim 500$ psec) region has a damage threshold that is independent of the pulse duration. For longer pulses ($\tau_L \gtrsim 1$ nsec) the damage threshold scales with $\tau_L^{1/2}$ as noted by many previous authors.

In order to have a better comparison with the experiment, Eqs. (1) and (2) are solved numerically with an explicit finite-difference scheme for the case of Cu. We use[3] $C_e'=96.6$ J/m^3 K^2, $C_i=3.43\times10^6$ J/m^3 K, and $\kappa_0=401$ W/mK. The absorbed fluence, which is assumed to be Gaussian in time, is introduced through $A(x,t)$ in Eq. (1), at the surface $x=0$. The metal temperature for $x \gtrsim 0$ is initially set at $T_i=300$ K. The electron-electron collision frequency has also been included by use of

$$\nu=\nu_0[T_i(1-\alpha)+\alpha T_e^2(300\text{ K})]/(300\text{ K}),$$

where $\alpha=\nu_{ee}/\nu_{ei}$ at room temperature. From Ref. 10, we obtain $\alpha=0.53\%$ for Cu.

In Fig. 1(b), the upper curve (circles) is the damage threshold computed for $g=1.0\times10^{16}$ W/m^3 K plotted as a function of τ_L. The value of τ_c is in good agreement with the experimental value of $\tau_c=840$ psec shown for Cu in Fig. 1(a). The absorbed fluence is also found to be consistent with the experimental results of Fig. 1(a), if we assume 2% absorption for Cu. The value of g is, however, 10 times smaller than the previous measurement[5] and 20 times smaller than the calculation in Ref. 1. For comparison, the damage threshold is also computed for $g=1.0\times10^{17}$ W/m^3 K (as obtained in Ref. 5), and is shown by the lower curve (squares) in Fig. 1(b). The value of $\tau_c=86$ psec is incompatible with the experimental results. With $g=10^{17}$ W/m^3 K only 0.6% of the incident energy is required for surface melting. Absorption of 0.6% is much less than that expected for Cu. Note in Fig. 1(b) that $\tau_c \propto 1/g$ in agreement with Eq. (11).

Further evidence for a small value of g comes from the Mo data. With appropriate changes in the material parameters, we determine that $g=2\times10^{16}$ W/m^3 K.

The above approach for the measurement of g has advantages over previous techniques. It can be used with many metals. It is not sensitive to surface contamination since the heat deposition depth is ~ 1 μm. It is compatible with other techniques for measurement of the lattice temperature. Two aspects, however, require further discussion.

Equation (11) indicates that τ_c is only weakly dependent on the temperature at which damage occurs. However, the lower curve (squares) would look like the upper curve (circles), if both the melting temperature were 3 times higher than T_m until $t=86$ psec and then, the melting temperature decreased to T_m in the interval 86 psec $<t<780$ psec. It is essential to question whether superheating could account for such a temperature dependence of the melting threshold. Superheating has not been investigated in Cu or Mo. In the case of aluminum,[14] single-shot melting occurs in less than 20 psec if the lattice temperature exceeds the melting point by a factor of 2.6. We expect superheating to be considerably reduced in the multishot case since nucleation theory suggests that defects should propagate some distance on each shot. Thus, we expect superheating to play a limited role in this experiment.

The electronic heat capacity of Cu is significantly altered by the d state (2 eV below the Fermi level) for electron temperatures greater than approximately 0.4 eV. An electron temperature of 0.4 eV is undoubtedly reached for the 2.5-psec pulse. The 50-psec data are barely, if at all, affected by the d state. The enhanced heat capacity above $T_e \sim 0.4$ eV will play only a minor role in the determination of the heat deposition depth, and therefore g, for reasons similar to those outlined after Eq. (9). This is confirmed by the Mo data which give a similar value of g. (The density of states is not a strong function of the electron energy for Mo.)

The reason that our value of g differs from the previous measurement is primarily the thickness of the samples. Thin samples have additional relaxation pathways due to impurity and surface scattering which will enhance electron-lattice coupling. These scattering rates can far exceed the electron-phonon scattering rate and will modify the energy relaxation process.

In conclusion, in bulk metal experiments it is essential to fully consider thermal transport in any analysis. Transport will dominate for $t<\tau_R$. In the limit of weak excitation $\tau_R \sim 400$ fsec if $g=10^{17}$ W/m^3 K and $\tau_R \sim 4$ psec if $g=10^{16}$ W/m^3 K [τ_R is still given by Eq. (5) but with T_e = room temperature]. In this limit thermalization among the electrons is not assured. ($\nu_{ee}<\tau_R^{-1}$ for both values of g.[9,10]) Since both photoemission and thermoreflection measurements are sensitive to the electron distribution, they are unreliable in this limit. For stronger excitation the electron distribution will thermalize; however, thermal conduction is more important since τ_R is larger.

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