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Electron diffusion in metals studied by picosecond ultrasonics

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We have studied the ultrasonic pulses that are generated when a picosecond light pulse is absorbed in a metallic film. The pulse shape is influenced by the distance that the hot electrons diffuse before losing their energy to the lattice. We show that this method can be used to test theories of the electron-phonon and electron-electron scattering rates. The results are in excellent agreement with a calculation in which the nonthermal character of the electron distribution is taken into account.

I. INTRODUCTION

Electron-scattering processes play a crucial role in the transport properties of metals, such as electrical and thermal conductivity. The development of ultrafast pulsed-laser techniques has enabled time-resolved investigations of electron diffusion and thermalization. In these experiments the electron gas is optically excited by a picosecond laser pulse that creates an electron distribution out of equilibrium with the lattice. A variety of optical techniques have been developed to study the subsequent equilibration. These include time and wavelength-resolved measurements of optical reflectivity and transmissivity,[1-5] transient photoemission spectroscopy,[6-8] heat transport studies,[9] and surface-plasmon experiments.[10] Nondiffusive, ballistic propagation of hot electrons has also been reported[11] in thin gold films.

Several of these experiments[2-7,9,11] have been analyzed in terms of a two-temperature model. The electrons are taken to have a Fermi-Dirac distribution with temperature T_e and the phonons have a Planck distribution with temperature T_l. The model includes the effects of the electron-phonon interaction which transfers energy from the electron system to the phonons and eventually makes T_e and T_l become equal. In addition, except for experiments with very thin films, it is necessary to include the effect of electron diffusion, i.e., the transport of energy away from the surface layer where the light is absorbed. Recently, the use of the two-temperature model to analyze these experiments has been criticized.[8,10] It has been argued that the electron distribution function cannot be approximated by a Fermi-Dirac distribution, and so it is necessary to consider a nonthermal electron distribution.

In this article we describe a method for the study of hot-electron diffusion, and we present a detailed analysis of the experiment in terms of the effect of electron-electron and electron-phonon scattering on the electron distribution. In the experiment a light pulse is absorbed in a metallic film and hot electrons are produced in a thin layer near the front of the film. These electrons diffuse into the interior of the film, losing energy to the lattice as they propagate. The increase in temperature of the lattice sets up a thermal stress which launches an elastic wave. By detecting this elastic wave we are able to study how far into the film the electrons diffuse before they lose their excess energy to the lattice. This, in turn enables us to test theories of the electron-electron and electron-phonon scattering rates.

II. GENERATION OF SOUND WAVES

Picosecond ultrasonics has been used in several experiments to study sound velocity and attenuation at high frequencies in metals and semiconductors,[12-14] dielectrics,[14-16] and multilayer structures,[14,17] and to detect thin interfacial layers.[14,18] As a starting point we describe the sound generation process from a *macroscopic* point of view, and then show the shortcomings of this approach. Consider an ultrashort light pulse of duration τ and energy Q directed onto an area A of the surface of a metallic film which has been deposited on a substrate. Let the absorption length for the light be ζ, and assume that ζ is much less than the film thickness d. The temperature rise at a distance z into the film is then

$$\Delta T(z)=\frac{(1-R)Q}{CA\zeta}\exp(-z/\zeta)\ , \tag{1}$$

where R is the optical reflectivity, and C is the specific heat per unit volume of the film. Thus, the temperature profile inside the film is as shown by the solid curve in Fig. 1. This temperature rise sets up an isotropic thermal stress σ given by

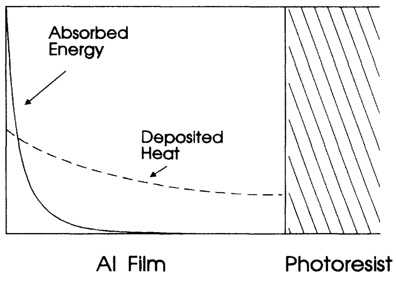

FIG. 1. Qualitative form of the temperature rise of the lattice as a function of distance into the metal film. The solid curve shows the temperature profile when electron diffusion is negligible. The dashed curve indicates the temperature profile when some electrons are able to diffuse all the way through the film before losing their energy to the lattice.

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$$\sigma = -3B\beta\Delta T(z)\,, \tag{2}$$

where β is the linear-expansion coefficient and B is the bulk modulus. This stress launches longitudinal acoustic waves into the film. From each point z strain waves are launched in the positive and negative directions. The negative-going pulse is reflected at the free surface of the film with a sign change. After a time long compared to the time ζ/v_s (v_s = sound velocity) for sound to propagate through a distance equal to the absorption length, the form of the strain pulse inside the film is given by[12,19]

$$\eta(z,t) = -\frac{3(1-R)Q\beta B}{2AC\zeta\rho v_s^2} \times \exp[-(z-v_s t)/\zeta]\,\mathrm{sgn}(z-v_s t)\,. \tag{3}$$

This pulse will be partially reflected and transmitted at the interface between the film and the substrate as discussed later. The above calculation ignores the finite duration τ of the light pulse, but it is straightforward to correct for this.

The calculation of the strain profile can also be corrected to allow for the diffusion of the heat deposited by the laser. The inclusion of this effect modifies the pulse shape. The importance of heat diffusion is determined by the relative magnitudes of two characteristic times. The time for the acoustic wave to leave the region that is heated by the light pulse is $\tau_{\mathrm{ac}}\zeta/v_s$. The time for a significant fraction of the heat to diffuse out of this region is $\tau_{\mathrm{diff}} = \zeta^2/D$, where D is the thermal diffusivity equal to κ/C, with κ the thermal conductivity. Thus, if τ_{diff} is comparable to or less than τ_{ac}, the temperature distribution will change significantly while the strain pulse is leaving the region of generation and so the pulse shape will be modified from the form given by Eq. (3). Therefore, according to this approach the effect of heat diffusion is important if

$$D \geq \zeta v_s\,. \tag{4}$$

For a typical metal D is of the order of 1 $\mathrm{cm}^2\,\mathrm{sec}^{-1}$ at room temperature, v_s is around 5×10^5 $\mathrm{cm\,sec}^{-1}$, and ζ is 100 to 200 Å for visible light. As a result, D and ζv_s are comparable and an appreciable modification of the pulse shape is predicted to occur.[12]

The approach just described is entirely macroscopic, i.e., it is assumed that the material can be described by a temperature and that energy transport can be calculated from the macroscopic thermal conductivity. In the present context this is a poor approximation. The energy of the light pulse is at first given to the electrons, leaving the temperature of the lattice unchanged. These electrons will diffuse into the interior of the film while losing energy to the lattice via phonon emission. The electron diffusion coefficient is

$$D_e = \kappa/C_e\,, \tag{5}$$

where C_e is the electronic contribution to the specific heat, and the lattice contribution to the thermal conductivity has been assumed to be negligible. Since C_e is typically 100 times smaller than the total specific heat, the electron diffusion coefficient is 100 times larger than the macroscopic diffusion coefficient D. Thus, if the electrons are able to diffuse for a time of 1 ps, for example, before losing their energy to the lattice, they will be able to carry their energy about 1000 Å into the film. This will modify the shape of the strain pulse, and the detection of this change in shape is the goal of the experiments reported here. If the electron diffusion is sufficiently rapid, the heating of the lattice will extend all the way through the film, as shown qualitatively by the dashed curve in Fig. 1. This gives a qualitative change in the acoustic response, because there is now a discontinuity in thermal stress at the interface between the film and the substrate. We consider the theory of this in more detail in Sec. IV.

III. EXPERIMENTAL TECHNIQUE

In this type of experiment several factors have to be considered in the choice of metal and substrate. One possibility would be to use a metal film epitaxially grown onto a crystalline substrate. However, many of the metal-substrate combinations that are readily available have the disadvantage that the acoustic impedances of the metal and substrate lie in the same general range, resulting in a small acoustic reflection at the metal to substrate interface. This makes it difficult to observe acoustic echoes in the metal film. To get around this difficulty we have instead used a metal film evaporated onto a thick layer (4 μm) of photoresist which had been deposited onto a silicon wafer. Photoresist was chosen because its acoustic impedance is much lower than that of most metals, thereby giving a large acoustic reflection. A disadvantage of an amorphous material such as photoresist is that the metal film will normally be polycrystalline. For most metals the velocity of sound is anisotropic and so for a polycrystalline film there will be scattering at grain boundaries. In addition, if the grain size is comparable to the film thickness, the sound velocity will be different in different regions of the film according to the dominant orientation of the grains in a particular region. To overcome this problem we decided to study aluminum films in these experiments. The velocity of longitudinal sound varies by less than ±3% between different crystallographic directions in Al, and hence these anisotropy effects are unimportant. Of course, the hot electrons may be scattered at the grain boundaries.

The metal films had a thickness in the range 500–1200 Å and were evaporated in a vacuum of better than 10^{-6} torr. The electrical resistivities of the films were measured by the four-point probe method, and were found to be roughly twice of the bulk values for pure aluminum at room temperature.

The schematic diagram of the experimental setup is shown in Fig. 2. The light pulses used in these experiments were produced by a hybrid mode-locked dye laser operating at 6320 Å. The pulse duration was 0.2 ps full width at half maximum, the repetition rate was 76 MHz, and the energy of the light pulses used to generate the sound was 0.5 nJ. The light was focused onto a region of the metal film approximately 20 μm diam. In terms of the macroscopic approach to heat flow and sound genera-

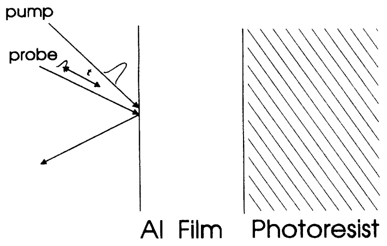

FIG. 2. Schematic diagram of the experiment. The samples were metal (Al) films deposited on thick photoresist substrate in order to create a large acoustic mismatch at the interface.

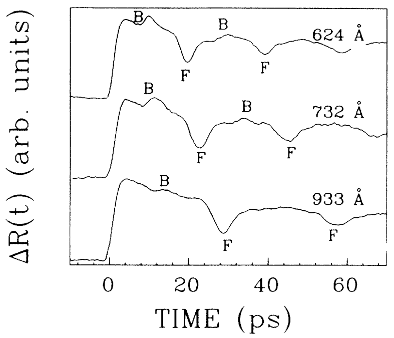

FIG. 3. The change $\Delta R(t)$ in optical reflectivity as a function of time for Al films of thickness (a) 624 Å, (b) 733 Å, (c) 933 Å, deposited onto a thick layer of photoresist. The echoes labeled F and B arise from strain pulses produced by the thermal stress discontinuities at the front and back side of the films, respectively.

tion described in the previous section, this would give a transient temperature rise within the absorption length of the light of a few degrees K, and a sound pulse with strain amplitude of the order of 10^{-5}.

The strain pulses were detected by the following method. The acoustic pulse in the film causes a change in the optical parameters n and κ of the film, and hence the optical reflectivity undergoes a small change $\Delta R(t)$. For small values of the strain the changes in n and κ at a distance z into the film will be proportional to the strain $\eta(z,t)$ at that point. Consequently, it is possible to write the change in the reflectivity in the form

$$\Delta R(t)=\int f(z)\eta(z,t)dz \ , \tag{6}$$

where $f(z)$ is a "sensitivity function" which has been discussed previously,[12,16] and describes how much the reflectivity of the surface is changed by an elastic strain a distance z below the surface. The function $f(z)$ is appreciable for a distance into the film of the order of the optical-absorption length ζ. Thus, the reflectivity change is primarily due to the strain in the part of the film very close to the free surface. To measure $\Delta R(t)$, and hence to detect the strain pulses, a probe pulse was used which was time delayed with respect to the generating pulse ("pump"). The probe-pulse energy was about ten times less than that of the pump. The magnitude of $\Delta R(t)$ was about 10^{-5}.

IV. ANALYSIS

The results of measurements of the reflectivity change as a function of time for 624-, 732-, and 933-Å thick Al films on photoresist are shown in Fig. 3. These data were taken at room temperature. The results for $\Delta R(t)$ show a pattern of echoes arising from the ultrasonic pulse bouncing back and forth in the metal film, superimposed on a background contribution. This background component consists of a jump at zero time followed by a slow decrease. The background arises because, in addition to the change in reflectivity due to the strain [Eq. (6)], there is a contribution to $\Delta R(t)$ from the change in temperature of the metal film. The temperature undergoes a sudden jump when the pump pulse is absorbed and then the film slowly cools via heat conduction into the substrate.

The acoustic contribution to the response is simplest to understand for the thickest sample. There is a series of echoes (labeled F) that are spaced by a time interval equal to one acoustic round trip in the sample (i.e., 29 ps). These originate from the strain pulse launched from the free surface of the film as described approximately by Eq. (3). For the two thinner samples there are additional echoes (labeled B) that appear half way between the main echoes. These features arise from strain waves launched from the surface of the metal film that is in contact with the photoresist substrate, and indicated that some of the hot electrons are able to diffuse through the film before losing their energy to the phonons, as discussed at the end of Sec. II. The decrease in the amplitudes of successive front or back (F or B) echoes is in reasonable agreement with expectations based on the calculated reflection coefficient at the Al-photoresist interface. From literature values for the density and sound velocity this reflection coefficient is calculated to be 0.56.

It is clear that the experimental data cannot be understood in terms of the diffusion of heat as governed by the macroscopic diffusion coefficient. For the three aluminium samples the thermal conductivities as estimated from the electrical resistivity via the Wiedemann-Franz law[20] were 0.99, 1.18, and 1.13 W K^{-}1 cm^{-1} for the 624-, 732-, and 933-Å films, respectively. Thus, the average thermal diffusivity was 0.45 cm^{2} sec^{-1}. The time constant for the temperature to become uniform inside a film of thickness d is

$$d^2/\pi^2 D \ . \tag{7}$$

For a 900-Å film this time is 19 ps. This is comparable to the time (15 ps) for the sound to traverse the sample and so cannot explain the existence of a fairly sharp echo arriving from the back of the sample. Thus it is necessary to consider a theoretical mode that allows for some form of hot-electron diffusion.

A. Two-temperature model

We first consider a widely used[1–7,9,11] model of hot-electron diffusion in which it is assumed that the electron distribution can be described by a temperature T_e, which is different from the lattice temperature. It is assumed that after the energy of the laser pulse is given to the electrons, the electron gas very quickly comes to internal equilibrium via electron-electron collisions. The energy is then transferred to the lattice, leading to a cooling of the electron gas. This approach was developed by Kaganov, Tanatarov, and Lifshitz[21] who were primarily concerned with the explanation of experiments that studied deviations from Ohm's law for large current densities. According to this model the electron temperature T_e and the lattice temperature T_l evolve with time according to the equations[6]

$$C_e(T_e)\frac{\partial T_e}{\partial t}=\frac{\partial}{\partial z}\left[\kappa_e(T_e)\frac{\partial T_e}{\partial z}\right]-G(T_e-T_l)+S(z,t)\ , \tag{8}$$

$$C_l\frac{\partial T_l}{\partial t}=G(T_e-T_l)\ , \tag{9}$$

where C_e and C_l are the specific heats of the electrons and of the lattice, $S(z,t)$ is the source term describing the local rate of energy input into the electron system due to the laser pulse, and G is the energy-transfer coefficient from electrons to the lattice. The thermal conductivity κ_e of the electron gas when its temperature is the same as the lattice is taken to be equal to the macroscopic thermal conductivity. For T_e significantly larger than T_l the conductivity is assumed to be enhanced by a factor T_e/T_l, i.e., it is assumed that the diffusivity of the electrons is determined by the lattice temperature. The thermal conductivity due to phonons is neglected.

The energy-transfer coefficient G has been related to the electron-phonon coupling constant by Allen.[22] It is predicted to be independent of temperature for T_e and T_l greater than or comparable to the Debye temperature $\Theta_D^{21,22}$. The Debye temperature for Al is 420 K so it is probably a reasonable approximation to take G independent of temperature, at least for temperatures of 300 K and above. Allen's theory relates G to the electron-phonon coupling parameter λ entering into the theory of superconductivity via the expression

$$G=\frac{3\hbar\lambda\langle\omega^2\rangle\gamma}{\pi k_B}\ , \tag{10}$$

where $\langle\omega^2\rangle$ is the average of the square of the phonon frequency, and γ is the coefficient of the linear term in the electronic specific heat. For Al,[23] $\hbar\langle\omega^2\rangle^{1/2}=330$ K, $\gamma=9.2\times10^{-5}$ J cm^{-3} K^{-2}, and $\lambda=0.38$. Using these values one obtains the result $G=4.9\times10^{11}$ W cm^{-3} K^{-1}. In related calculations Allen has used the same general theoretical approach to calculate the electron-phonon scattering rate associated with electrical resistance in terms of λ, and has achieved good agreement with experiment.

These equations are nonlinear because the specific heat and the thermal conductivity of the electrons vary with temperature. In our measurements it is always a good approximation to assume that the change in the lattice temperature is small. However, the initial change in temperature of the electron gas near the free surface is several hundred K, and thus cannot be treated as a small quantity. Consequently, we are forced to solve these equations numerically. The lattice heat capacity of Al is 2.44 J cm^{-3} K^{-1}, and the thermal conductivity κ_e was calculated using the procedure already described. For the source term the following form was used:

$$S(z,t)=\frac{(1-R)Q}{\zeta A}\exp(-z/\zeta)I(t)\ . \tag{11}$$

The pulse energy Q was 0.5 nJ, the reflectivity R was 0.93, and the absorption length ζ was 64 Å. The function $I(t)$ describing the time profile of the laser pulse was taken as

$$\frac{1}{2\tau_L\cosh(1.76t/\tau_L)^2} \tag{12}$$

with $\tau_L=0.14$ ps. The area was taken to be a circle of radius 10 μm. Equations (8) and (9) were integrated numerically to obtain T_e and T_l as a function of time and position in the film.

From these temperatures it was possible to calculate the thermal stress in the Al film. The stress inside the film may be considered to have two independent contributions. The first σ_e is due to the pressure of the free-electron gas[12,24] and is given by

$$\sigma_e=-\tfrac{2}{3}C_e(T_e)\Delta T_e=-\tfrac{2}{3}\Delta E_e\ , \tag{13}$$

where ΔE_e is the change in energy of the electrons. The second contribution σ_l is the thermal stress due to the temperature rise in the lattice as given previously by Eq. (2). To compare the magnitudes of the electronic and the lattice stress note that the lattice stress can be written as

$$\sigma_l=-\gamma_l C_l\Delta T_l=-\gamma_l C_l\Delta E_l\ , \tag{14}$$

where ΔE_l is the energy transferred to the lattice, and γ_l is Grüneisen's constant. For Al γ_l is 2.16 at room temperature,[25] and so one can see from Eqs. (13) and (14) that once the electron and lattice temperatures have become equal the main contribution to the stress comes from the lattice.

We have listed the main parameters for Al in Table I. For the sensitivity function $f(z)$ we used the results described previously.[12,16]

Based on these inputs the results of a calculation of the expected $\Delta R(t)$ for a 732-Å aluminum film are shown in Fig. 4(b). To compare these with the experimental data we made a fit to the background contribution to the data (arising from thermal rather than acoustic effects), and then subtracted this background. The result is shown in Fig. 4(a). It can be seen that the back echoes are essentially absent from the theoretical curve, i.e., the theory appears to greatly underestimate the distance that electrons are able to diffuse before they lose their energy.

We have investigated whether the discrepancy between the experimental result and the theory could be associated with the uncertainties in some of the parameters. It is clear that the precise form of the sensitivity function does not strongly affect the ratio of the strength of the back to the front echoes. In addition, we were able to show that errors in the energy of each laser pulse, the optical

TABLE I. Parameters of aluminum used in the analysis of the experimental results.

Sound velocity v_s	6.42×10^{5} cm s^{-1}
Average phonon energy $\hbar\langle\omega^2\rangle^{1/2}$	330 K
Electronic specific-heat coefficient γ	9.2×10^{-5} J cm^{-3} K^{-2}
Electronic heat capacity as 300 K C_e	0.028 J cm^{-3} K^{-1}
Lattice heat capacity C_l	2.443 J cm^{-3} K^{-1}
Grüneisen constant γ_l	2.16
Electron-phonon coupling constant λ	0.38
Electron-phonon coupling parameter G [Eq. (10)]	4.9×10^{11} W cm^{-3} K^{-1}
Fermi energy E_F	11.7 eV
Plasma frequency ω_p	2.4×10^{16} sec^{-1}

reflectivity, or the spot size were unimportant.

We then performed a series of simulations with different choices of the electron-phonon coupling parameter G. The best fit is shown as Fig. 4(c). This fit uses a value of G of 8×10^{10} W cm^{-3} K^{-1}, i.e., about five times smaller than the theoretical value. Given the fact that Allen's theory gives a good description of the electron-phonon scattering associated with the temperature dependence of the electrical resistance it is hard to believe that the value of G can be five times smaller than theory.

B. Nonthermal model

We now consider the possibility that the discrepancy between theory and experiment has its origin in the use of the two-temperature model. For simplicity, we begin with a discussion of the basic features of hot-electron relaxation in a metal for a system that has been excited *uniformly* in space. Thus we begin by neglecting the effect of diffusion.

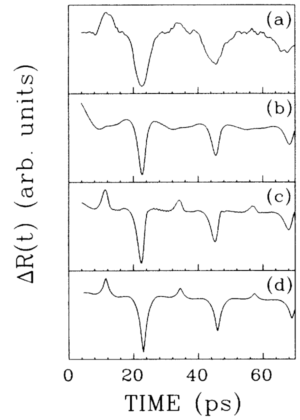

FIG. 4. Acoustic echoes for the 733-Å sample. (a) shows the experimental data after the background has been subtracted. (b) is the result of a computer simulation using the two-temperature model together with the theoretical value of the electron-phonon coupling parameter G. (c) is the result from the two-temperature model that is obtained from G is adjusted to give the best fit to the data. (d) shows the calculated shape of the acoustic echoes using the nonthermal model. This calculation has no adjustable parameters.

The basic assumption of the two-temperature model is that the electron-electron scattering is a very fast process compared to electron-phonon scattering. If one considers first an electron gas in the *absence* of any electron-phonon interactions, the sequence of relaxations is as follows:

(1) The absorption of the pump pulse creates an electron-hole distribution of the form shown qualitatively in Fig. 5. The distribution extends to an energy of $h\nu$ above and below the Fermi level (ν=frequency of pump light), and within the nearly-free-electron approximation will be almost flat since $h\nu$ is considerably less than E_F.

(2) These excited electrons then scatter off the electrons below E_F. The electron-electron scattering time for an excitation of energy E above or below the Fermi energy is[26]

$$\tau_{e-e}=\tau_0\left[\frac{E_F}{E}\right]^2 , \tag{15}$$

where

$$\tau_0=\frac{128}{\pi^2\sqrt{3}\omega_p} , \tag{16}$$

and ω_p is the plasma frequency. This expression for τ_0 was derived by Quinn and Ferrell[27] for an electron gas in the limit of high density; attempts to correct this result for screening at metallic densities have been reviewed by Penn.[28] The scattering time given by Eq. (15) is correct if the density of electron (and hole) excitations is very low so that we can consider that the excitations scatter off a Fermi sea at zero temperature, and that collisions *be-*

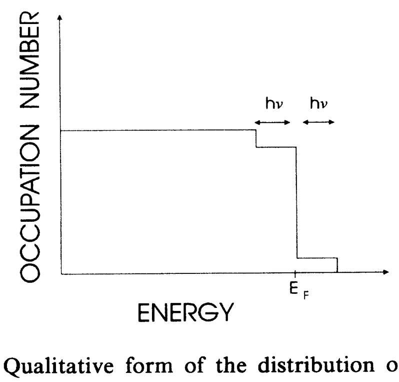

FIG. 5. Qualitative form of the distribution of excitations produced by the pump light pulse.

tween excitations are unimportant. This is a good approximation in our experiments since the density of electron-hole excitations initially produced by the pump pulse is of the order of 5×10^{19} cm^{-3}, which is much less than the electron density of 2×10^{22} cm^{-3} in the range between $E-h\nu$ and E. After each scattering event there are three new excitations. The probability for any one of the new excitations to have an energy lying in the range between E' and $E'+dE'$ from the Fermi energy has been calculated by Ritchie,[29] and is

$$P(E',E)=\frac{2(E-E')dE'}{E^2} \ . \tag{17}$$

It follows from Eqs. (15)–(17) that the number of excitations $n(E)$ changes with time according to

$$\frac{dn(E,t)}{dt}=-\frac{n(E,t)}{\tau_0}\frac{E^2}{E_F^2}+6\int_E^\infty\frac{dE'}{E_F}\frac{(E'-E)}{E_F}\frac{n(E',t)}{\tau_0} \ . \tag{18}$$

Note that in our experiment the number of holes at energy E below E_F is the same as the number of electrons at energy above E_F. Using Eq. (18) we have calculated the distribution in energy of the excitations as a function of the time after the system is excited. The Fermi energy of Al is 11.7 eV and the plasma frequency[30] is 2.4×10^{16} sec^{-1}. The result of the calculation is shown in Fig. 6 (solid lines). The excitation distribution relaxes towards the Fermi energy ($E=0$), and after a few collisions have taken place the distribution assumes a scaling form. To derive this let us introduce into Eq. (18) the substitution

$$n(E,t)=g(u,t)/E^2 \ , \tag{19}$$

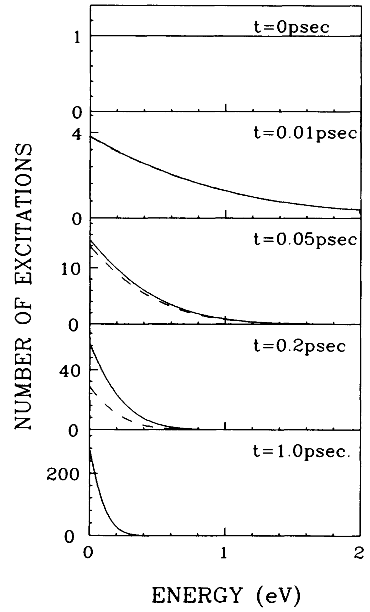

FIG. 6. Relaxation of the distribution of excitations. The solid lines show the electron distribution that would exist if the only electron interactions were electron-electron collisions. The dashed curves show the effect of including the electron-phonon interaction.

where the variable $u\equiv E^2t/E_F^2\tau_0$. Then we obtain the equation for g

$$\frac{\partial g(u,t)}{\partial \ln T}=-u\frac{\partial g}{\partial u}-ug+3\int_u^\infty du'g(u',t)\left[1-\left[\frac{u}{u'}\right]^{1/2}\right]\frac{u}{u'} \ . \tag{20}$$

After several decays g tends to a value that is independent of t (except for the implicit dependence through the variable u). Thus, dropping the time argument of g (i.e., the second argument) we have

$$n(E,t)\approx g(E^2t/E_F^2\tau_0)/E^2 \ . \tag{21}$$

The form of the function g as calculated from Eq. (20) is shown in Fig. 7. By integration of Eq. (20) one finds that in this scaling regime the average energy per excitation is

$$\langle E\rangle=0.38E_F\left[\frac{\tau_0}{t}\right]^{1/2} \ . \tag{22}$$

This result holds regardless of the initial energy spectrum of the excitations, but assumes that several collisions have taken place. In this scaling regime the total number of excitations per unit volume is therefore

$$n_{\text{tot}}=2.7\frac{E_V}{E_F}\left[\frac{t}{\tau_0}\right]^{1/2} \ . \tag{23}$$

(3) The above equations hold provided that the number of excitations in any energy range is small compared to the number of available energy states, i.e., it assumes that the occupation numbers for the excitations are much less than unity. It is when the occupation numbers become of the order of unity that it becomes possible to describe the electron distribution by a temperature. From Eqs. (22) and (23) the number of excitations per unit energy range is of the order of

$$\frac{E_V}{E_F^2}\left[\frac{t}{\tau_0}\right] \ . \tag{24}$$

The density of states per unit energy range is $\frac{3}{2}n_0E_F^{-1}$, where n_0 is the number of free electrons per unit volume. Thus the time τ_T at which the electron system begins to

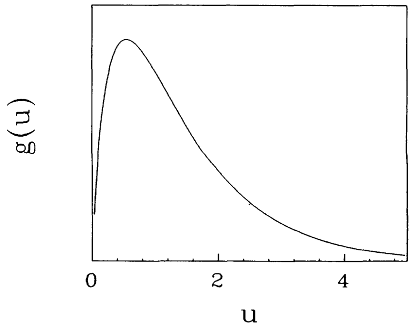

FIG. 7. The scaling function g calculated from Eq. (20).

have a distribution that can be described by a temperature is

$$\tau_T \approx n_0 \tau_0 \left[\frac{E_F}{E_V} \right] . \tag{25}$$

After this time, in the absence of electron-phonon interactions that transfer energy from the electron system to the lattice, the electron distribution becomes stationary.

From this analysis one can see that the two-temperature model will be a reasonable approximation if the electron-phonon interaction has little effect on the electron distribution before the electron system is thermalized, i.e., before the system has reached stage 3 as described above. We now investigate the effect of the electron-phonon interaction on the relaxation of the electron system. For an electron whose energy exceeds E_F by an amount that is large compared to both $k_B\theta_D$ and k_BT_l, but small compared to E_F, the rate of energy loss $\dot{q}$ can be calculated classically by considering the work that the electron does on the lattice as it passes through it. The electron radiates phonons in a process similar to Cherenkov radiation. For an electron in an elastic continuum this calculation has been performed by Buckingham[31] and by Kaganov, Lifshitz, and Tanatarov.[21] They show that for an electron with excess energy in the range specified above, $\dot{q}$ is independent of the electron energy and the lattice temperature. They derive an explicit expression for $\dot{q}$ using a simple model of the electron-phonon interaction in which the electrons only interact with longitudinal phonons and these phonons have a linear dispersion relation.

For our purposes it is convenient to relate the rate of energy loss to Allen's calculation of the electron-phonon energy transfer G defined earlier. Consider an electron gas in which the electron distribution is described by a temperature T_e which is much larger than θ_D and T_l. The total number of electrons and holes is then $2\ln(2)\rho(E_F)k_BT_e$, where $\rho(E_F)$ is the density of states at the Fermi energy. Using these conditions each excited electron or hole will lose energy at the same rate $\dot{q}$. Thus, the total rate of energy transfer to the phonon system is

$$2\ln(2)\rho(E_F)k_BT_e\dot{q} \ . \tag{26}$$

This must be equal to GT_e [see Eqs. (8) and (9)]. It then follows from Allen's expression for G [Eq. (10)] that

$$\dot{q} = \frac{\pi\hbar\lambda\langle\omega^2\rangle}{2\ln 2} \ . \tag{27}$$

For Al this gives $\dot{q} = 1.05\ \text{eV psec}^{1-}$.

The rate at which energy is transferred to the lattice at any instant is thus simply the number of excitations times $\dot{q}$. If there were no electron-electron scattering, the effect of the electron-phonon interaction would be to relax all excitations back toward the Fermi energy at a constant rate. Thus the rate of energy transfer to the lattice per unit volume at a time t after the exciting pulse would be

$$\begin{aligned} \dot{Q} &= E_V \left[1 - \frac{\dot{q}t}{h\nu} \right], \quad t < h\nu/\dot{q} \\ &= 0, \quad t > h\nu/\dot{q} \ . \end{aligned} \tag{28}$$

In our experiment $h\nu$ is 2 eV and so the energy transfer would take 2 psec. It is clear that the effect of electron-electron scattering is to greatly increase the rate at which energy is transferred to the lattice. This is because each scattering process between the electrons creates three new excitations which can each lose energy at the rate $\dot{q}$ by the electron-phonon interaction.

The combined effect of electron-electron and electron-phonon interactions on the excitation energy distribution is shown by the dashed lines in Fig. 6. It is clear from these results that the two-temperature model is not valid in the present context. The electron-phonon interaction causes a substantial change in the electron distribution at times as early as 100 fsec, and at this time the electron system has definitely not thermalized. This is most clearly seen by a calculation of the rate of energy transfer $\dot{Q}_l$ to the lattice as a function of time (Fig. 8). For electron-phonon scattering alone, $\dot{Q}_l$ decreases monotonically with time [see Eq. (28)]. When electron-electron scattering is included, $\dot{Q}_l$ initially increases because of the increase in the number of excitations with time. The time for all of the energy to be transferred to the lattice is considerably reduced by the electron-electron scattering. For comparison we have also shown the time dependence of Q_l according to the two-temperature model. This depends on the total amount of energy deposited by the laser. The two curves plotted are for energy inputs that correspond to initial temperatures of the electron gas by 400 and 1000 K. The lattice temperature is taken to be 300 K.

We now use the nonthermal model to calculate the expected acoustic response. To perform this calculation it is necessary to know not only the rate at which energy is transferred to the lattice, but also the rate at which the hot electrons diffuse through the sample. When the electron and phonon systems are in equilibrium and have

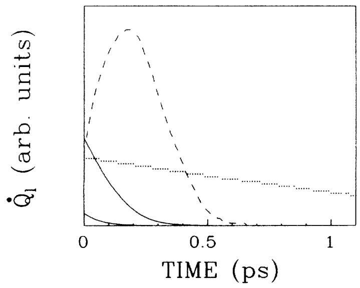

FIG. 8. Rate $\dot{Q}_l$ at which heat is transferred to the lattice as a function of the time after laser excitation. The dotted curve shows $\dot{Q}_l$ calculated when electron-electron scattering is ignored, and the dashed curve shows $\dot{Q}_l$ when the electron-electron scattering is included. The two solid curves are the results obtained from the two-temperature model for initial temperatures of the electron gas of 400 and 1000 K.

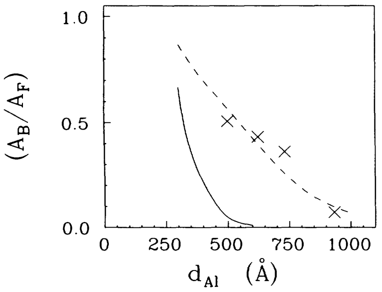

FIG. 9. Ratio of the size of the back echo to the front echo as a function of the thickness of the aluminum film. The experimental data are denoted by ×; the solid curve shows the result obtained from the two-temperature model, and the dashed curve shows the result obtained from the nonthermal model.

nearly the same temperature, the diffusion coefficient of the electrons is simply the thermal conductivity κ_e divided by the electron contribution C_e to the specific heat. The diffusion coefficient of electrons is limited by defect scattering (including impurities, grain boundaries, etc.) and by the electron-phonon interaction. Since the resistivity of our samples is approximately twice that of bulk Al, the defect-scattering rate must exceed the electron-phonon scattering. This defect scattering is unlikely to be strongly dependent on the excess energy of the electrons. In addition, it is straightforward to show that if $T > \theta_D$ the electron-phonon scattering rate depends only weakly on electron energy when $|E| \ll E_F$. Thus, it is reasonable to assume that the diffusion coefficient of the electrons is independent of energy, and hence can be taken to be κ_e/C_e. The calculation of the acoustic response is then straightforward. The results of the calculation for the 733-Å sample are shown in Fig. 4(d). The agreement with experiment is very good.

As an additional test of the model we have calculated the ratio of the back to the front echo height as a function of the thickness of the Al film. This is compared to the experimental results in Fig. 9. We have included data from four films with thicknesses ranging from 500 to 933 Å. The agreement between theory and experiment is excellent.

The above analysis has shown that the experimental data are in agreement with theory when we use the electron-phonon and electron-electron scattering times as calculated by Allen and by Quinn and Ferrell, respectively. One can also ask a different question, namely whether the data can be used to *extract* values of these relaxation times. To investigate this we first kept $\tau_{\text{el-ph}}$ fixed at its theoretical value and studied how the fit to the data shown in Fig. 9 was changed as $\tau_{\text{el-el}}$ was varied. We found that an increase or decrease of $\tau_{\text{el-el}}$ by more than about 30% lead to a significant deterioration of the fit. Thus, we can consider that the experiment confirms Quinn and Ferrell's theory for $\tau_{\text{el-el}}$ with an uncertainty of about 30%. A similar investigation of the change in the fit produced by a variation of $\tau_{\text{el-ph}}$ while holding $\tau_{\text{el-el}}$ constant at the theoretical value led to the conclusion that the uncertainty in the determination of $\tau_{\text{el-ph}}$ was around 20%. It may of course, also be possible to make a good fit to the data by making a simultaneous variation of $\tau_{\text{el-ph}}$ and $\tau_{\text{el-el}}$ away from their theoretically predicted values; we have not made a study of this.

V. SUMMARY

In this paper we have presented a method for the study of the rate at which hot electrons lose energy to the lattice. A laser pulse is used to generate hot electrons in the region near to the free surface of a metal film. These electrons diffuse into the sample while losing their energy. We are able to use the picosecond ultrasonic technique to determine the distance into a sample at which the energy is transferred to the lattice. We have compared the experimental data with a calculation based upon a model in which the electrons and phonons are assumed to have thermalized distributions with different temperatures. This "two-temperature" model is shown to lead to results which are in disagreement with the experiment. By considering the theory of electron-electron and electron-phonon scattering we showed that the underlying assumptions of the two-temperature model are not justified in this experiment. We then performed a calculation in which the nonthermal distribution of the electrons was taken into account. This calculation, which contains no adjustable parameters, is in excellent agreement with the experimental results.

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