Observation of Nonequilibrium Electron Heating in Copper

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Picosecond laser pulses are used to sequentially heat and probe the thermally induced reflectivity transients in copper, and the nonequilibrium heating of electrons to a temperature above that of the lattice is observed. The ability to temporally resolve electronic and lattice heating contributions is of considerable significance to thermomodulation spectroscopy of solids.

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Thermomodulation spectroscopy is an important method for studying the critical points associated with the interband optical absorption in solids.[1] The early work of Scouler[2] demonstrated the significance of this technique to band-structure studies in metals, and the use of this technique continues through the present day.[3]

The traditional approach to a thermomodulation measurement is to pass a low-frequency (~50 Hz) alternating current through an optically thin (~40 nm) sample film, and synchronously detect the corresponding heating-induced reflectivity change as a function of optical wavelength. Temperature changes of ~10 K result in reflectivity changes on the order of $\Delta R \sim 10^{-4}$. A variety of effects contribute to the reflectivity change, including thermal expansion, electron-photon interactions, and shifting of the Fermi level.[4] Scouler[2] and Rosei and Lynch[4] were the first to observe a sign reversal of ΔR when the photon energy was tuned through the d-band to Fermi-level interband transition energy of Au and Cu. This unique feature was interpreted as the result of Fermi distribution smearing, i.e., a heating-induced increase in unoccupied states below the Fermi level and a decrease in unoccupied states above the Fermi level.[1] However, other mechanisms influence the thermomodulation spectrum in this energy range, and the detailed contributions are not readily separated by use of the traditional measurement method.

In this work, I demonstrate the use of picosecond lasers to sequentially heat and probe the thermally induced reflectivity transients of Cu in the vicinity of the d-band edge. I observe an anomalous rapid heating and cooling component in the reflectivity change, which I believe can be attributed to the initial heating of electrons above the lattice temperature. The phenomenon of inequality between the electron temperature and the lattice temperature is referred to as nonequilibrium heating,[5] and to my knowledge, it has not previously been observed in metals. Observation of this phenomenon results from the ability to temporally resolve the electronic and lattice contributions to the reflectivity change and to show their different spectral behavior. By electronic contributions I mean changes resulting from hot electrons alone, whereas by lattice contributions I mean changes resulting from a hot lattice in equilibrium with the electrons.

The apparatus used for transient thermomodulation spectroscopy (TTMS) consists of a mode-locked argon-ion laser which synchronously pumps two ring dye lasers at a pulse repetition rate of 246 MHz. The heating dye laser is fixed in wavelength at 645 nm (1.92 eV), with an average output power of 140 mW and a pulse intensity autocorrelation of 8 psec [full width at half maximum (FWHM), as measured by second-harmonic generation]. The probing laser is tuned to a variety of wavelengths between 572 and 610 nm for the TTMS measurements, and after attenuation the average probe power at the sample is $\lesssim$2 mW. The probe-pulse autocorrelation FWHM is nominally 8 psec with an additional 1-psec broadening at the tuning extremes.

The temporal cross correlation of the heating pulse with the probing pulse is measured by two-photon absorption in GaP.[6] The cross-correlation FWHM is nominally 12 psec at a probe wavelength of 590 nm, and 1 psec wider at the wavelength extremes. The GaP was placed in the sample position so that these measurements also provided the zero-time-delay position of the optical delay line.

An optical schematic of the TTMS experiment is shown in Fig. 1. The heating laser passes through an electro-optic amplitude modulator driven by a 10-MHz sine wave, and is focused to a beam diameter of ~30 μm. The heating laser is polarized parallel to the plane of incidence. The probe laser passes through a variable optical delay line, a polarization beam splitter, and a

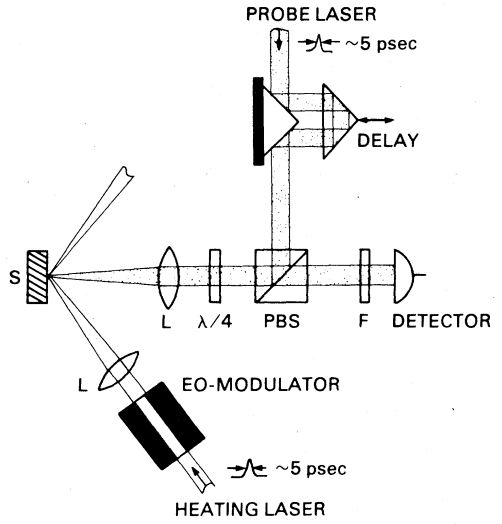

FIG. 1. Optical schematic of the transient thermomodulation spectroscopy apparatus. L: lens; F: filter; PBS: polarization beam splitter; λ/4: quarter-wave plate.

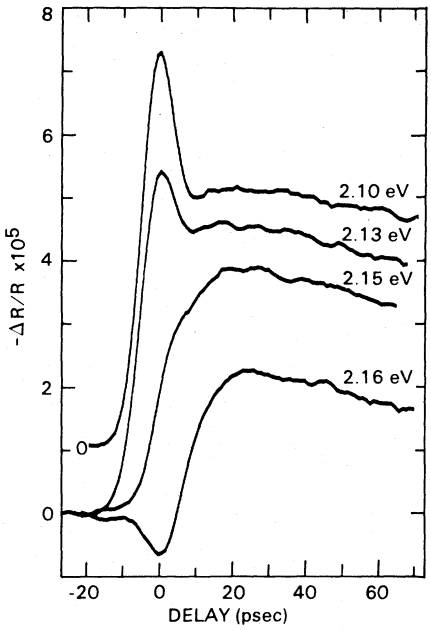

FIG. 2. Time-resolved $-\Delta R/R$ transients for copper. Each curve is labeled by the probe photon energy and the horizontal axis is the delay of the probe pulse relative to the heating pulse. The 2.10-eV data are offset for clarity.

quarter-wave plate prior to being focused to a beam diameter of ~30 μm at the sample. After passing through the quarter-wave plate again, the retroreflected probe-light polarization is rotated by 90° relative to the incoming light and thus exits through an orthogonal port on the beam splitter. The reflected probe light is transmitted through a short-pass dichroic mirror (to reject scattered heating laser light) and is detected by an avalanche photodiode. The heating-induced modulation of the probe photocurrent is measured by a lock-in amplifier tuned to the 10-MHz modulation frequency.

The transient thermomodulation spectrum is obtained by fixing the probe wavelength and scanning the optical delay line. This procedure is repeated at several different probe wavelengths, with the delay scanning and data accumulation controlled by computer. All of the following data result from an average of four temporal scans at each probe wavelength, using a lock-in time constant of 0.5 sec. The measured signal from the lock-in is divided by the photodiode dc signal to yield the normalized change in reflectivity, $\Delta R/R$.

The sample consists of a 400-nm-thick Cu film which was argon-ion sputtered onto a commercial gold-plated CuZr mirror substrate. The sample was not contained in vacuum for the $\Delta R/R$ measurements, which were completed within 3 h after the film was sputtered. Measurements of Cu oxidation in pure oxygen would indicate that after 3 h, less than 10 nm of oxide is present.[7] Only after approximately 24 h did oxidation noticeably affect the relative $\Delta R/R$ amplitudes at different probe wavelengths.

I note that for the time delays used in this experiment, the laser focal diameters are large enough such that heat diffusion into the sample dominates over radial diffusion out of the illuminated area.[8] Also, the optical skin depth in Cu at the probing wavelengths is approximately one-tenth of the total film thickness.[9]

The unusual TTMS temporal features observed from Cu are shown in Fig. 2. I have plotted temporal delay scans of $-\Delta R/R$ at four selected probe photon energies. The rapid transient which occurs at zero time delay is followed by a relatively slow (~200 psec) decay of $\Delta R/R$. The rapid and slow decay components of the data in Fig. 2 are separated by scaling and subtracting the 2.15-eV data from all other delay scans at different probe photon energies. (The reason for this will become apparent.) The result is a peak whose shape is nearly identical to the cross correlation of the heating pulse with the probing-laser pulse. This suggests that the rapid component of the data is a result of direct electron heating and cool-

ing on a time scale of a few picoseconds, as would be expected. Although the electron-phonon collision time in Cu at room temperature is 2 $\times 10^{-14}$ sec, the large energy mismatch between the hot electron (2 eV) and a phonon (~0.15 eV) requires a few hundred collisions for energy relaxation.[5,9,10]

The polarity reversal of the 2.16-eV data is easily understood by considering the heating-induced change in unoccupied electronic states near the Fermi level. These states are probed by monitoring the change in metal reflectivity at photon energies ($\hbar\omega$) which induce the transition of electrons from the upper edge of a filled d band (energy E_d) to the Fermi level (E_F). When the conduction-electron temperature increases during the heating-laser pulse, the Fermi distribution of unoccupied states,

$$\rho = 1 - 1/\{1 + \exp[-(E_F - E_d - \hbar\omega)/kT]\},$$

increases slightly for $\hbar\omega < E_F - E_d$. That is, $\partial\rho/\partial T > 0$, and more d-band electrons absorb probe photons resulting in the reflectivity decrease ($\Delta R/R < 0$). At the same time, however, there is a decrease in the number of unoccupied states above E_F and thus $\Delta R/R > 0$ for $\hbar\omega > E_F - E_d$. For $\hbar\omega = E_F - E_d = 2.15$ eV in Cu, there is no temperature modulation of the unoccupied states sampled, because to first order $\partial\rho/\partial T = 0$. This is the justification for subtracting the 2.15-eV data of Fig. 2 from all other data scans to retrieve the rapid Fermi-smearing component alone.

The 2.15-eV data display the qualitative temporal behavior for transient lattice heating and cooling of metals described by the heat-conduction equations.[5,8,10] A rough estimate of the lattice temperature can be made by comparing our $\Delta R/R$ transient amplitude to that measured by Rosei and Lynch.[4] In their work, they estimate a temperature rise of ~12 K for $\Delta R/R \sim 10^{-3}$; thus our lattice transients of $\sim 5 \times 10^{-5}$ would imply a $\Delta T \sim 1$ K.

The importance of the time-resolved information obtained using TTMS now becomes apparent. In Fig. 3(a) I have plotted the peak height of the rapid Fermi smearing component versus photon energy. In Fig. 3(b) I have plotted an average of the $\Delta R/R$ signal between delay times of 39 to 42 psec, versus photon energy. These data are representative of the lattice contribution to $\Delta R/R$, which includes not only expansion-induced changes band structure and increased electron-phonon interactions, but also includes Fermi smearing of electronic states in equilibrium with the lattice. Thus, the spectrum of Fig. 3(b) results from the same heating-induced changes as the conventional thermomodulation spectrum which is dominated by Fermi smearing in this energy range.[4] The fact that the rapid transient data of Fig. 3(a) reverse polarity prior to Fig. 3(b) indicates that the *ratio* of the Fermi-smearing contribution to the other contributions is larger during the heating pulse than it is 40 psec later. This implies that the electron temperature during the heating pulse exceeds the lattice temperature during the heating pulse. I believe that this is the first reported observation of nonequilibrium electron heating in metals.

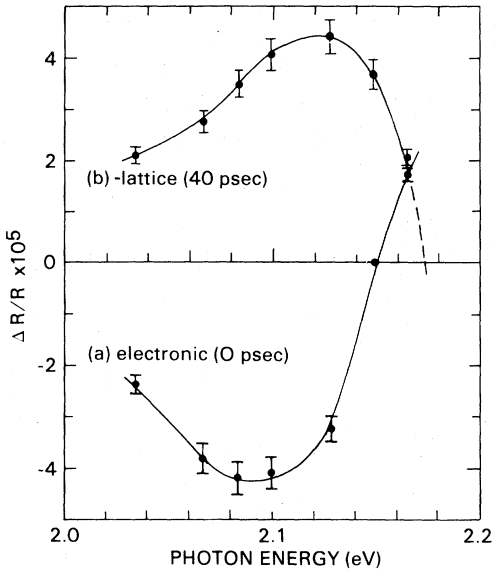

FIG. 3. Transient thermomodulation spectra of copper: (a) peak height of the rapid contribution to the data in Fig. 2 (minus the 2.15-eV data); (b) $-\Delta R/R$ at ~40-psec delay. Dashed line indicates the expected behavior for larger photon energies.

The ability to resolve the initial electron heating contribution to $\Delta R/R$ in these experiments is afforded by the coincidence between probe photon energy and the d-band to Fermi-level transitions. I have observed qualitatively similar $\Delta R/R$ transients from Au films, where $E_F - E_d = 2.4$ eV. As a result of the relatively large energy gap in Ag ($E_F - E_d = 4$ eV), no Fermi-smearing transients are observed using ~2-eV photons.

In addition to the normal-incidence optical configuration used here, I have also done TTMS in the ellipsometric configuration discussed in Ref. 11. In this case, the probe laser is incident on the sample at an angle of 70° and is polarized at

45° to the plane of incidence. The anisotropy in the $\Delta R/R$ transients for the tangential and normal field components results in a probe polarization rotation. By use of optical heterodyne detection, it is possible to retrive the Fermi-smearing signal alone. This can be achieved because of the different phases of the optical signals produced by the "resonant" electronic and "nonresonant" lattice mechanisms.

In conclusion, I have demonstrated a new method for performing thermomodulation spectroscopy of solids. The picosecond time resolution of this method permits the separation of electronic and lattice contributions to the heating-induced reflectivity change. Extension of the technique into the femtosecond regime should provide the capability to measure directly hot-electron relaxation times as a function of probe photon energy and as a function of both the transient and the equilibrium sample temperatures. From the above considerations, I believe that transient thermomodulation spectroscopy can yield significant new information about metallic band structure at critical points. Since the heating is produced optically, thick films and single crystals can also be studied.

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