Time-Resolved Infrared Spectroscopy on the U12IR Beamline at the NSLS

J.D. LaVeigne[‡], G.L. Carr[†], R.P.S.M. Lobo[‡], D.H. Reitze[‡], and D.B. Tanner[‡]

† National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973

‡ Physics Department, University of Florida, Gainesville, FL 32611

email: carr@bnl.gov

Abstract

A facility for performing time-resolved infrared spectroscopy has been developed at the NSLS, primarily at beamline U12IR. The pulsed IR light from the synchrotron is used to perform pump-probe spectroscopy. We present here a description of the facility and results for the relaxation of photoexcitations in both a semiconductor and superconductor.

Keywords: time-resolved spectroscopy, synchrotron radiation, infrared spectroscopy

INTRODUCTION

Synchrotron radiation has been used as an infrared light source for more than 10 years. The advantages over traditional thermal sources, such as higher brightness and more far infrared power, are well known[1,2]. The pulsed nature of synchrotron radiation is another advantage over a thermal source. When combined with a suitable pump source, synchrotron radiation may be used to perform subnanosecond pump-probe spectroscopy.

The U12IR beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Lab (BNL) was recently completed and commissioned. Its key purposes are for time-resolved and far infrared spectroscopies. In conjunction with a mode-locked Ti:sapphire laser as a pump, the beamline is capable of performing time-resolved spectroscopy over a frequency range from 2 - 10,000 cm^{-1}.

EXPERIMENT

The experiments described here were conducted on the U12IR beamline of the National Synchrotron Light Source (NSLS) VUV ring at Brookhaven National Laboratory. This beamline has two end stations which can be used for infrared (IR) spectroscopy[3]. One is a commercial Bruker IFS 113v spectrometer, suitable for the spectral range from 20 cm^{-1} to 10,000 cm^{-1}. The other is a lamellar grating interferometer that spans the 2-100 cm^{-1} spectral range[4].

The time-resolved experiments make use of a pulsed laser synchronized with the IR pulses from the synchrotron storage ring (the NSLS VUV ring) to perform pump-probe spectroscopy. The pump-probe technique uses a short pulse of light (the pump pulse) to excite a specimen. Then, at an arbitrary but selectable time later, a second light pulse (the probe) senses the specimen's spectral properties at an instant of time during the relaxation process. To generate a full decay measurement, spectra are collected over a range of relative times between the pump and probe pulses.

In our experiments, a mode-locked Ti:sapphire laser serves as the pump while the synchrotron infrared is used for the spectroscopic probe. Depending on the operating conditions for the storage ring, synchrotron pulses are produced at pulse repetition frequencies (PRFs) of 5.88MHz, 17.6MHz or 52.9MHz and with durations ranging from 0.2ns to 2ns. The laser is a custom Mira 900P from Coherent Inc. Laser Group,

producing ~2ps duration pulses at a PRF of 105.8 MHz, twice that of the VUV ring. In order to reduce the laser PRF to match the maximum for the synchrotron, an electro-optic "pulse-picker" is used to deflect every other pulse. The rejected pulses are optically delayed and then re-injected into the beam path next to the following pulse. This allows most of the power that would be lost in the rejected pulses to be recovered. When needed, a subsequent pulse picker is used to match the laser PRF to the two other available PRFs for the synchrotron. The maximum measurable decay time (without gating the spectrometer's detector) is determined by the time between two successive pump pulses, which is 170 ns when the system is operated at 5.88MHz. Lastly, the time resolution is determined by the cross-correlation between the pump and probe pulses, which is limited by the minimum synchrotron pulse duration to ~200ps.

Laser pulses are maintained at a selectable time relative to the synchrotron pulses using a standard "Synchro-Lock" electronics package provided by Coherent. Under software control, the user can select any desirable pump-to-probe delay time. There is also a provision for modulating (f~100Hz) the laser arrival time by nearly 1ns, making "dithered" measurements possible. In this case lock-in detection can be employed and the signal is the response time derivative. This is well-suited to a step scan interferometer such as the lamellar grating spectrometer. Derivative spectra are taken at a range of arrival times and then integrated to give the time dependent response of the sample to the pump pulse. Spectrally averaged measurements may also be conducted on the lamellar by keeping the grating at a fixed position (typically at zero path difference) and making derivative measurements in the same fashion as above. Such measurements are routinely performed prior to collecting full spectra in order to survey signal levels and gauge the overall relaxation time.

The Bruker 113v is a rapid scan instrument where the interferometric modulation can extend from a few Hz to 10s of kHz, making it incompatible with the dithered technique as used with the lamellar. Instead, with the rapid scan interferometer, complete spectra are collected at two different pump pulse arrival times. In order to reduce the effects of long term drifts and changes in number of stored electrons in the synchrotron, a series of interleaved spectra with the two delay times are taken, then separated and averaged.

TIME-RESOLVED MEASUREMENTS OF MCT

As a test of the experiment setup, a sample consisting of a $Hg_xCd_{1-x}Te$ (MCT) epilayer on a Cd(Zn)Te substrate was measured using both the lamellar and Bruker 113v. The MCT epilayer composition places the band gap near 0.37eV, corresponding to the energy of ~3000 cm^{-1} photons. When electrons are promoted from the valence band to the conduction band, there is an increase in far IR absorption from mobile charge carriers (intraband transitions). There is also a corresponding decrease in absorption very near the gap frequency due to a reduction in both filled valence band states and empty conduction band states (interband transitions).

Given the laser power, spot size and repetition rate, a calculation can be made of the expected number of carriers generated by each pump pulse. The laser has a repetition rate of 53 MHz, with an average output power of 300 mW at the sample when operated at 800 nm wavelength. This leads to approximately 2.3×10^{10} photons per laser pulse. Most of this falls into a 0.5 cm diameter spot, reasonably well-matched to the sample aperture. Thus, the photon fluence is approximately 10^{11} cm^{-2}.Taking reflectance losses at the surface into account (a factor of 2), the induced electron density immediately after a laser pulse is ~ 5×10^{10} cm^{-2}.

Because the synchrotron light spans a wide spectral range, the probe pulses can also excite carriers. This would lead to a "DC shift" in the measured time dependent response of the sample, since the synchrotron pulse is always coincident with itself. This effect may be estimated by calculating the incident power on the sample above the bandgap of the MCT (~ 3000 cm^{-1}). The lamellar grating instrument uses brass waveguide and thick polyethylene windows that sharply reduce the intensity of the light above a few hundred wavenumbers, effectively eliminating the problem. For the mid IR measurements, the average power below the cutoff of the spectrometer's Ge:KBr beamsplitter (7000 cm^{-1}) and above the MCT gap

(3000 cm^{-1}) is about 20 mW at an average beam current of 600 mA. This level is further reduced by reflection losses at windows and the beam splitter, leading to an estimate of 10 mW for synchrotron power available for carrier generation. This is less than 5% of the laser power, and more or less negligible in this experiment. Since our experiments involve derivative measurements, we are actually insensitive to DC shifts of this nature.

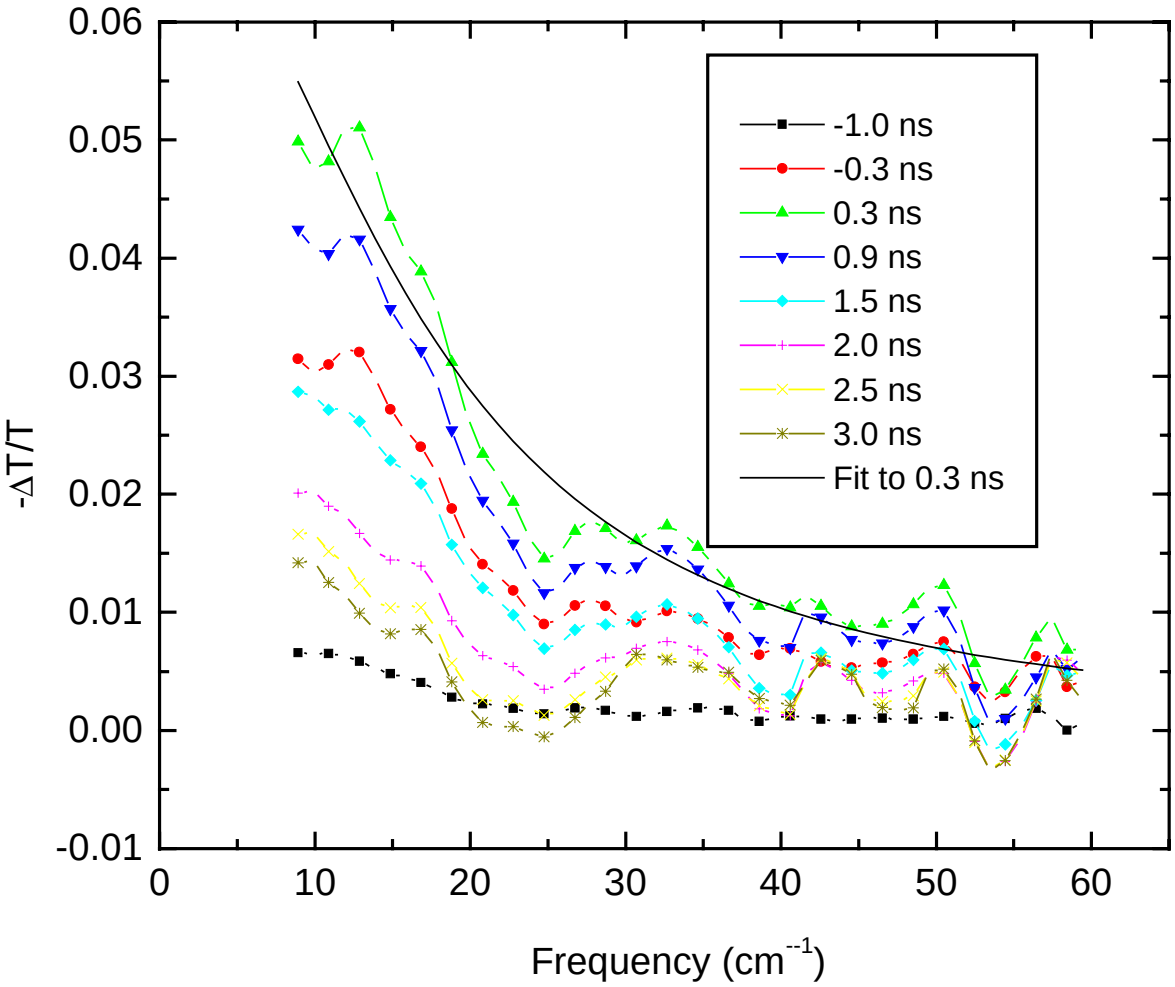

Figure 1. Far IR time-resolved photoinduced absorption of the MCT film at 5 K. The solid line is a fit based on a Drude model with a single type of carrier.

Time resolved spectroscopy measurements were conducted on the MCT sample using the lamellar grating and Bruker 113v spectrometers. For the measurements using the lamellar grating, differential spectra taken by modulating the arrival time of the pump pulse were collected and then integrated. The integrated responses were then divided by the unexcited transmission to give the photoinduced absorption spectrum $-\Delta T/T$ as a function of time. Figure 1 shows time-resolved spectra in the far IR region for the MCT sample at T = 5 K. The data are well described by a Drude model with fixed scattering rate, which is interpreted as a single type of carrier being responsible for the observed change in transmission. The scattering rate in the fits is 17 cm^{-1}, consistent with the mobility of electrons in MCT. Thus the photogenerated response is attributed exclusively to electrons. This is the expected result, since the holes carry much less oscillator strength due to their larger effective mass. The film thickness is approximately 15

μm, an order of magnitude larger than the penetration depth of the laser light (~ 1 μm). For this analysis, the carriers were assumed to have a uniform distribution throughout the film. It is noted that at the long wavelengths used here, the far IR probe is sensitive only to the sheet resistance of the carriers and the meaningful quantity extracted is the number of carriers per unit area. The oscillator strengths from the Drude analysis of the transmission data are fit with a convolution of the probe pulse with a biexponential decay. A plot of the oscillator strengths with the fit is shown in Figure 2. The fit yields a maximum oscillator strength (proportional to the carrier density) of 890 cm^{-2} immediately following the pump pulse. Assuming an effective mass $m^*=0.07\ m_e$, the carrier density is 2.6×10^{10} cm^{-3}, in reasonable agreement with the predicted value of 5×10^{10} cm^{-2}.

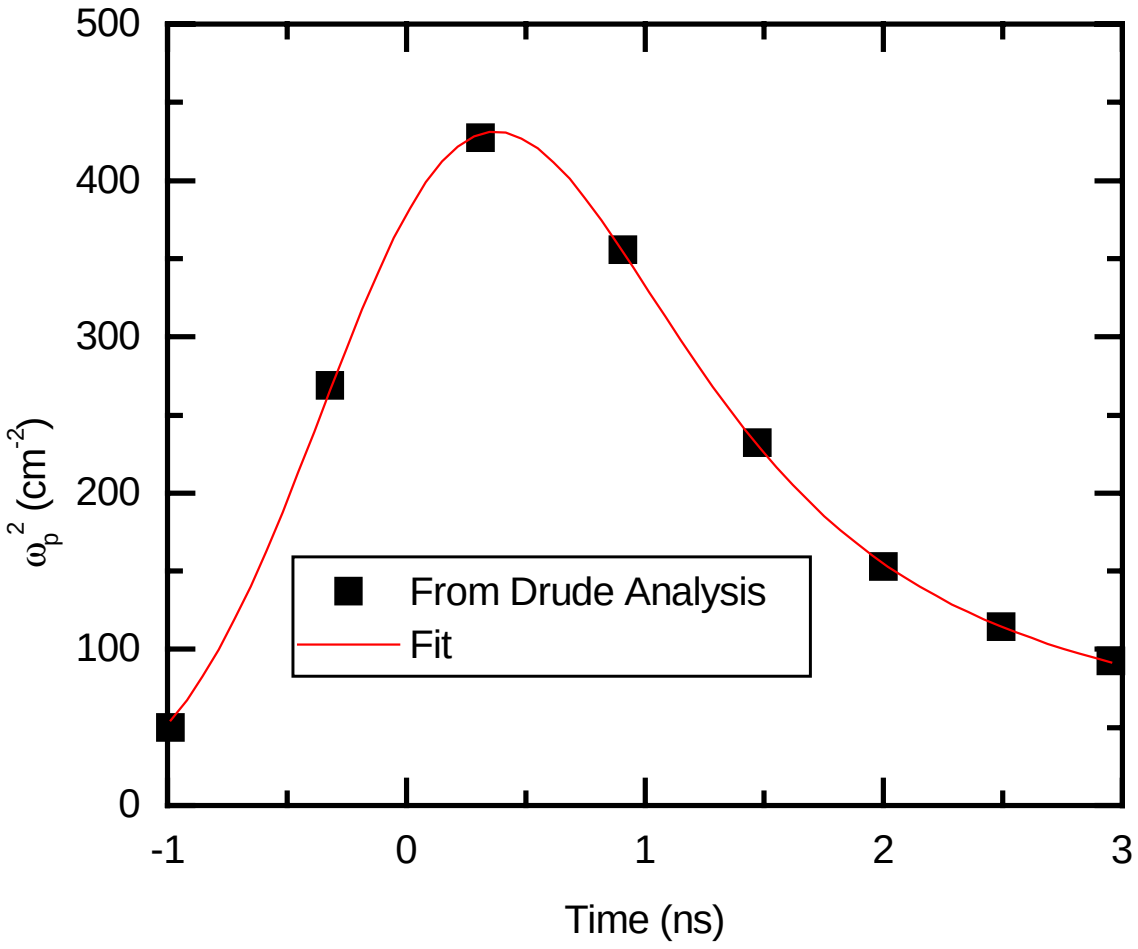

Figure 2. Oscillator strengths from the Drude model fits to the far IR photoinduced absorption. The line is a fit based on a convolution of a Gaussian probe pulse with a biexponential decay.

Measurements in the mid-infrared range were carried out on the Bruker 113v. The resulting spectra, shown in Figure 3, reveal photoinduced bleaching near the gap edge. This is attributed to a reduction in available states for absorption as some of the electrons are promoted from the valence band to the conduction band. The sum rule for oscillator strengths states that an increase in oscillator strength in one spectral range must be compensated by an equal reduction in oscillator strength elsewhere. To compare the

oscillator strength in the far and mid infrared measurements, we integrate the photoinduced absorption over frequency at each delay for the two ranges. These integrals are plotted in Figure 4. The plot shows that the sum rule is semi-quantitatively satisfied, with the oscillator strength gained in the far IR region being removed from the gap edge. The local laser intensity was not accurately measured in each case, leading to the possibility of substantial error bars in the overall magnitude. The time dependence of the excitations is not in good agreement. We speculate that this may be due to processes occurring above the gap which are not observable in the mid infrared transmission measurement.

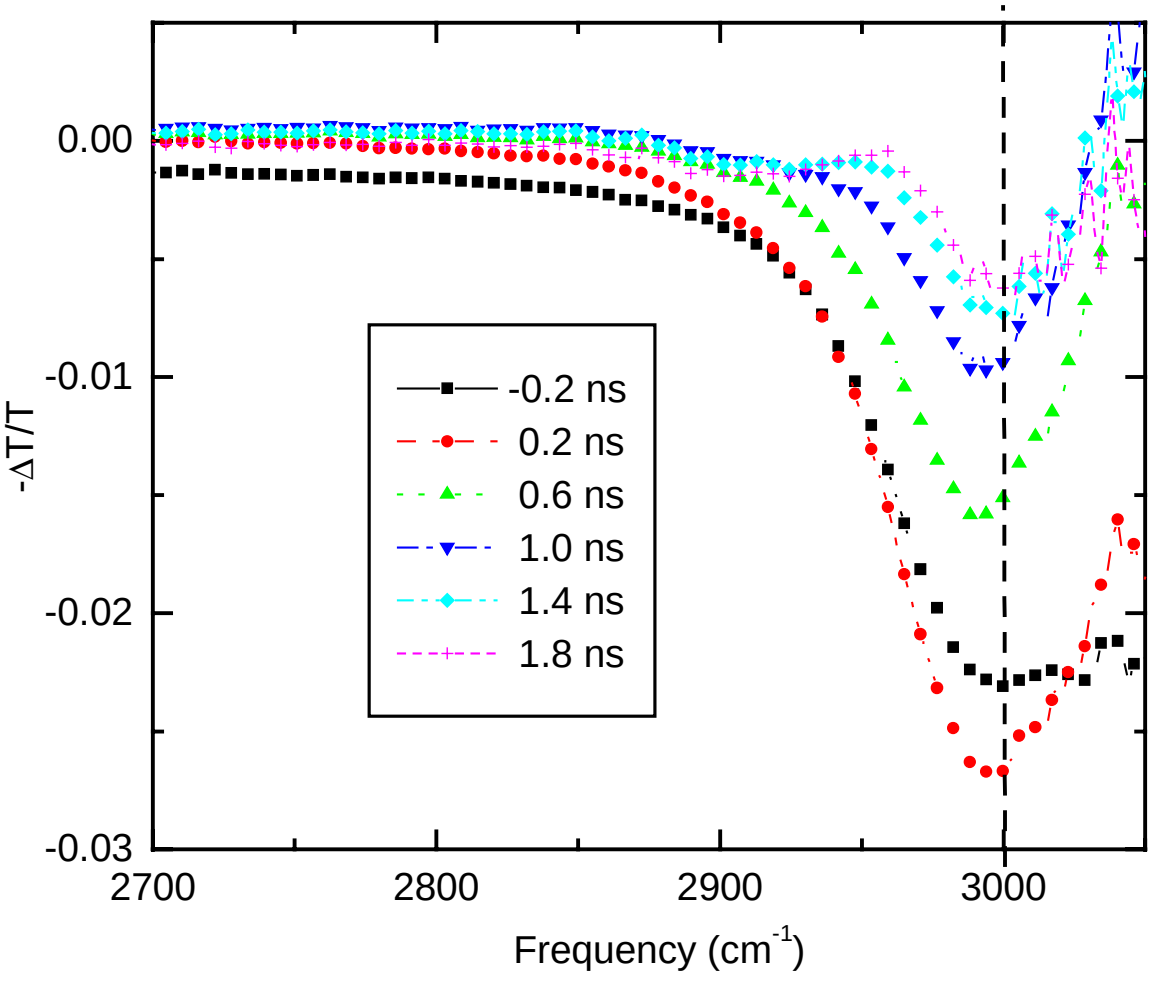

Figure 3. Mid IR time-resolved photoinduced absorption in an MCT film. The dashed vertical line at 3000 cm^{-1} marks the location of the gap.

TIME-RESOLVED MEASUREMENTS OF SUPERCONDUCTING Pb FILMS

Time-resolved measurements were also conducted on superconducting Pb films. Paired electrons can be broken by incident photons of sufficient energy. This results in an excess density of unpaired "quasiparticle" excitations. As shown by Owen and Scalapino[5], excess quasiparticles reduce the superconducting gap. Far IR transmission experiments are sensitive to this gap change and can be used to follow the superconducting state as the quasiparticles recombine into Cooper pairs.

Thin films of lead were grown *in situ* on a sapphire substrate in a He-tran cryostat used for the optical measurements. The substrate was clamped to the cold finger with indium foil gaskets to insure high thermal conductivity. The Pb was evaporated from a tungsten basket heater onto the substrate held at T = 80 K. Based on previous experiments with a similar technique, film thicknesses were estimated to be approximately 100 angstroms. The film thickness was not measured because the apparatus has no *in situ* thickness monitor and the films did not survive being warmed to room temperature; thus, external measurements were also not possible.

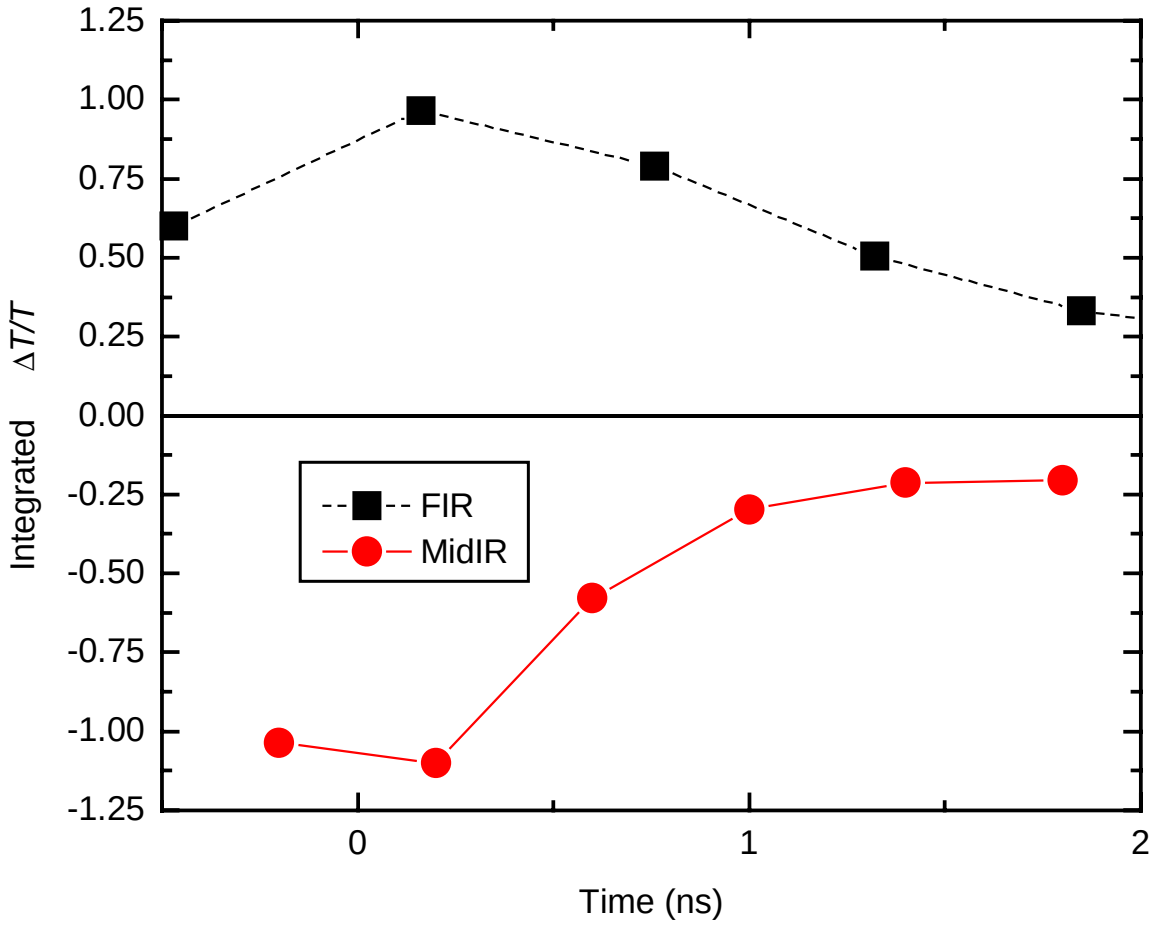

Figure 4. Integrated photoinduced absorption for the MCT film in the far and mid infrared regions.

In the time-resolved measurements reported here, the lamellar interferometer was fixed at zero path difference (ZPD) and the laser delay was dithered. The detector signal then is the spectrally averaged differential transmission, as described above. A typical dither amplitude was between 200 and 600 ps. The laser power was kept low (~ 20mW or less) to limit sample heating and maintain a linear response. Since the transmission of the sample is temperature dependent below T_c, the average signal at the detector may be used as a thermometer to determine the amount of sample heating. The temperature rise for a film with a 10% transmission in the normal state was 0.15 K at 3.5K.

The differential (dithered) photoinduced signal was acquired at pump-to-probe delay values spanning the entire 18.9ns time interval between pulses, and then integrated to give the time-dependent response.

Figure 5 shows a plot of the integrated response of a 10% transmitting Pb film for temperatures between 3.75 K and 6 K. The results indicate a two component decay, similar to that observed by Johnson in transient electrical current experiments on Nb films[6]. The magnitude of the slow component is constant with temperature. The slow decay shows little or no curvature over the 18.9 ns between pulses, suggesting a lifetime longer than 18.9 ns. The fast response increases with reduced temperature and is too fast to be resolved by the particular synchrotron probe pulses used for this measurement.

A second experiment on a film with a 30% transmission in the normal state was performed using shorter synchrotron probe pulses. Figure 6 shows the results of the integrated response of this film. The shorter bunches allow the resolution of the decay at 3.75 K yielding a lifetime of 200 ps.

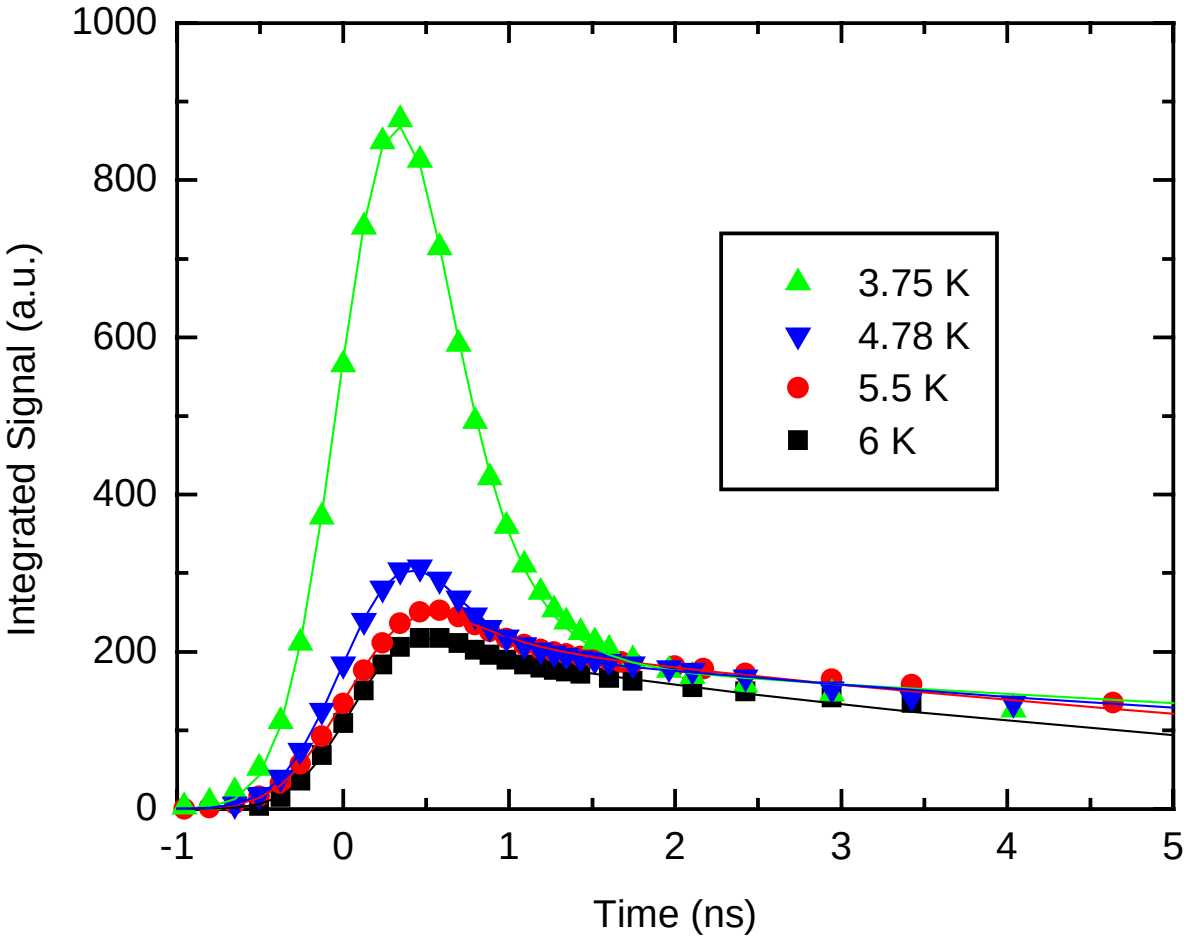

Figure 5. Frequency averaged change in transmission for a Pb film with a 10% transmission in the normal state. The fits give a pulse width of ~500 ps, which is too wide to resolve the fast decay.

SUMMARY

These experiments demonstrate the capabilities of the U12IR beamline for use in measuring time-resolved spectra in the far and mid infrared regions. The pump-probe method is effective with both step scan and rapid scan instruments, covering a range from 2 cm^{-1} to 10,000 cm^{-1} with a maximum time resolution of 200 ps. The investigations of quasiparticle recombination in Pb films resulted in the direct

measurement of the quasiparticle lifetime. The time-resolved, frequency averaged response showed a two component decay similar to that reported in transient electrical measurements of Nb films. The fast response varied strongly with temperature and was ascribed to the recombination of excess quasiparticles. The slow response was nearly constant over the range of temperatures measured and was ascribed to sample heating. A maximum time resolution to date was achieved with probe pulse widths of ~300 ps.

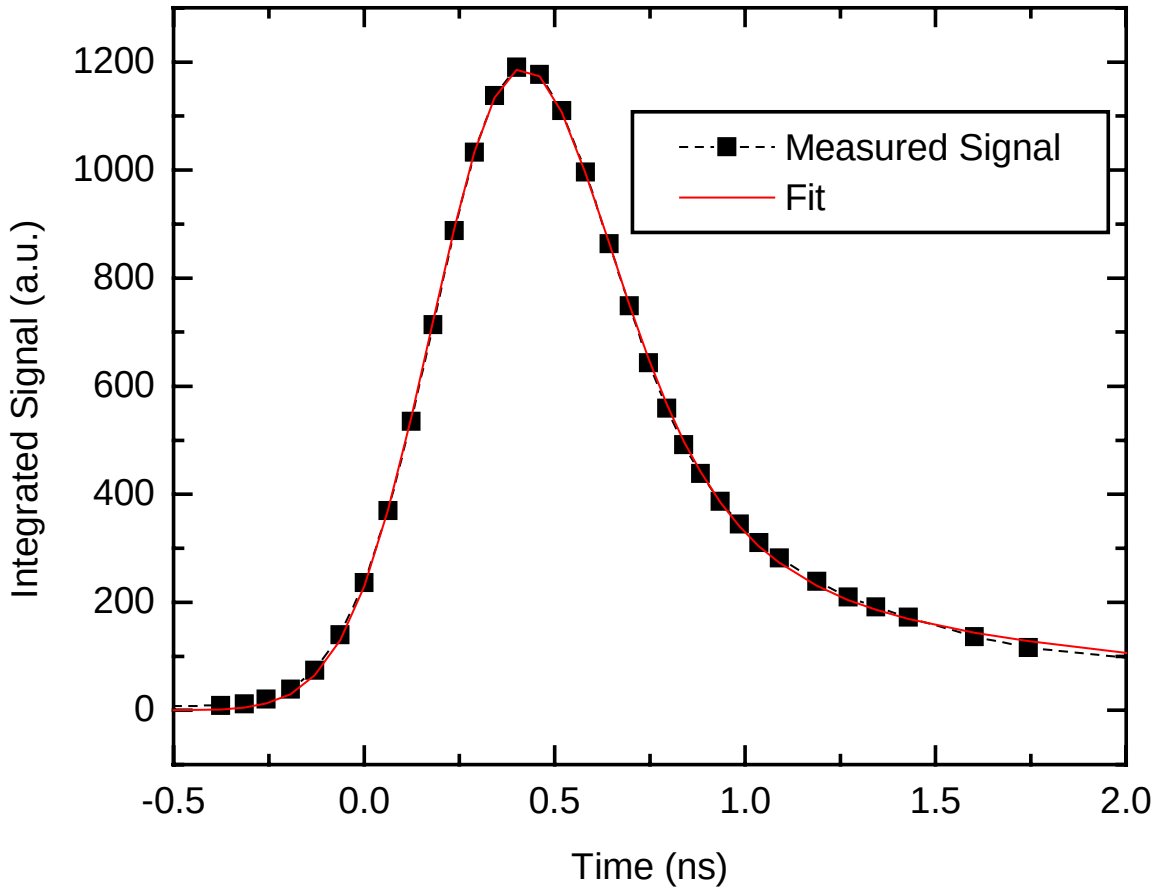

Figure 6. Time-resolved change in frequency averaged transmission for a Pb film at 3.75 K. The film has a 30% transmission in the normal state. This measurement was taken with a short bunch synchrotron lattice yielding a pulse width of 270 ns. The fit gives a recombination time of 200 ps.

In sum, the U12IR beamline has proved to be a useful tool for sample characterization and the investigation of some of the fundamental phenomena of solid-state physics. The broad frequency and time scale ranges allow the study of a host of systems. Current experiments are limited to temperatures above 3 K and sample heating by the laser has proved to be a concern in some instances. The addition of an immersion cryostat, presently being commissioned, will allow lower temperatures and higher fluences while at the same time reducing sample heating effects.

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