Delay of laser excited electron/hole interaction with germanium lattice

Edward A Stern\textsuperscript{1} and Dale Brewe\textsuperscript{2}

\textsuperscript{1}Physics Department, University of Washington, Seattle, WA 98195-1560, USA

\textsuperscript{2}Advance Photon Source Bldg. 435, Argonne National Laboratory, Argonne, IL 60439, USA

E-mail: stern@phys.washington.edu

Abstract. Laser pump/XAFS probe study of Ge using the high efficiency facility at PNC/XOR CAT at sector 20 of the Advanced Photon Source (APS) has discovered some surprising results of how the excited electrons/hole (e/h) decay. The 200 femtosecond (fs) pulse laser is triggered at the frequency of the APS ring so as to use the x-rays of one pulse of the 24 singlet mode at 100\% efficiency. The higher efficiency of the use of the ring’s x-rays (about two orders more efficient than usual) allowed the measurement of XAFS spectra at a large number of delay times between laser pump and x-ray probe and at different laser powers. The XAFS data determined the time dependence of the relative distances and their vibration amplitudes of the first and second Ge neighbors. The laser pulse excites a classical long wavelength optical mode that within 0.1 picoseconds (ps) or so excites only the vibrations of the 1st neighbor while to excite the second neighbor requires decay of the excited e/h through coupling with incoherent phonons. The surprising result is that this decay is delayed 11 ps, independent of the laser power as it is increased by a factor of two.

1. Introduction
The time response of the Ge lattice after femtosecond (fs) pulsed laser excitation has attracted much interest [1-5]. In all cases where x-rays probe the lattice response the method of choice was diffraction which measures the average periodic structure [6,7]. Here we probe the time response of the lattice using X-ray Absorption Fine Structure (XAFS) which, as we discuss in greater detail below, gives a complementary new insight into the lattice response. XAFS determines the local structure which measures the actual distance between neighbors. When local disorder is present the actual distance between neighbors may differ from that determined by diffraction [8]. In addition, there is an important difference between the atomic vibration amplitudes as measured by diffraction and XAFS. For solids in thermal equilibrium diffraction measures the vibration about the crystal \textit{lattice} site while XAFS measures, whether it is or out of thermal equilibrium, the \textit{relative} vibration between an atom and its neighbors. Phonons are characterized in terms of relative vibrations, not vibrations about lattice sites. For example, a long wavelength acoustic mode will cause atoms to vibrate about their lattice sites as per the mode amplitude, while the relative vibration amplitude is small so that the force between neighboring atoms is small leading to a low phonon frequency. When the semiconductor Ge is pumped by a fs pulsed laser, electrons and their holes (e/h) are excited by bonding electron states vacated, and anti-bonding states filled. This generally creates within a hundred or so fs a long
wavelength optical mode [1] consisting of multiple coherent phonons forming a classical macroscopic optical mode vibration. Such a phenomenon is the solid state analog of the Franck-Condon effect in molecules. For diamond structures such as Ge this optical mode produces vibrations between first neighbor basis atoms (NN1) only, while the second neighbor atoms (NN2), being at the primitive lattice constant distance, are not excited. The NN2 will be excited only when the excited e/h start to interact with the lattice and produce incoherent phonons, and when the classical mode starts decaying because of anharmonic coupling between phonons. We find that the dominant mechanism for exciting the second shell is by incoherent phonon production as discussed in section 4, but surprisingly, this mechanism is delayed by about 11 picoseconds (ps) after laser excitation.

XAFS contributes new insights to time resolved measurements of Ge in addition to distinguishing between the classical vibration mode and incoherent phonons excitations. These include determining directly changes in nearest neighbors’ relative distances even if the excitation introduces local disorder that typically is invisible to diffraction such as not changing the average structure. XAFS can directly measure the laser energy absorbed by the sample which, generally, differs from the incident laser energy because of reflection from and transmission through interfaces. The absorbed energy is monitored by the changes in NN relative vibration amplitudes after equilibrium is reached, and is calibrated by measuring the equilibrium vibration amplitudes as a function of temperature and knowledge of its specific heat. XAFS adds the better criterion for thermal equilibrium that both the NN1 and NN2 should have vibration amplitudes corresponding to the same temperature. Since phonons are characterized by relative vibrations XAFS is more physically connected to lattice properties that depend on phonons, namely, lattice energy, entropy and specific heat. This physical connection is based on the fact that the frequency of phonons is determined by the force between neighbors which depends on relative vibrations, not vibrations about lattice sites.

2. Experimental details
The Ge sample was a 100nm polycrystalline film that was deposited on a fused SiO₂ disk by sputtering, and annealed to crystallize the as-deposited amorphous Ge structure. The Ge film was sandwiched between 50nm sputtered silicon nitride films for protection from the atmosphere and substrate. The sample disk was spun during measurements at approximately 2600RPM using a precision spinner designed for CD/DVD disk testing. Spinning the sample eliminated temperature buildup due to incomplete cooling between shots by providing a new location for each shot, and eliminated sample damage by spreading the excitations over a much larger area.

The sample was excited using an 800nm Ti-sapphire laser system with 200fs pulse width and 272KHz repetition rate, matching the bunch repetition rate of the Advanced Photon Source storage ring. The laser system was synchronized to the storage ring using an 88MHz RF signal derived from the synchrotron beam position monitors to drive a feedback system controlling the laser oscillator serving as the source of laser pulses to the main re-gen amplifier, which was triggered by the 272KHz clock signal from the ring.

The laser was focused to a spot size of 120µm diameter and the x-rays were focused to a spot size of ~5µm diameter using a Kirkpatrick-Baez mirror system. The laser and x-ray beams were incident onto the sample at approximately 45°. The beams were aligned to be nearly collinear to reduce potential dynamic misalignments between the beams produced by wobble during spinning. This was accomplished by passing the x-ray beam just over the top of a semicircular mirror that was used to steer the laser beam onto the sample.

3. Experimental measurements, analysis and results
XAFS data were collected at a series of relative time delays between the laser pulses and x-ray bunches separated by approximately 18ps. One XAFS scan was collected at each time delay and statistics were improved by cycling repeatedly through the entire range of time delays used in the experiment. This was done to reduce the possibility of systematic drifts that might occur if all data at each time delay were collected at once. Typically 10-12 scans were collected at each of 15 time delays
and completed in 12 hours. Several such cycles were recorded to increase statistics and check for stability of the apparatus. This procedure was repeated at a series of three laser fluencies. All data were analyzed using FEFF and FEFFIT programs. The energy origin $E_0$ and amplitude factor $S_0^2$ were found by analyzing a collection of room-temperature data and then fixed during analysis of the time-dependent data, while bond length $R$ and Debye-Waller factor $\sigma^2$ were allowed to vary. The value of $\sigma^2$ at a given delay time was obtained as the average of the results for individual scans, and the uncertainty was estimated from standard calculations of variance of a quantity with random errors.

The time dependence of $\sigma^2$ for the first and second coordinated shells were modeled by simple step functions convoluted with the x-ray bunch time profile as measured with a streak camera. The FWHM of the x-ray bunches at the APS is approximately 90ps. The value of $\sigma^2$ before laser excitation was fixed at the value obtained from analysis of the room-temperature data. The final value of $\sigma^2$ and $t_0$, the time delay when the sample responded to the laser, were varied. As discussed in the introduction the first shell responds within a hundred or so fs and compared to the one ps time resolution we find in our analysis we consider as the zero of the delay time scale when the first shell responds. The bunch width was also allowed to vary to account for the possibility of jitter in the synchronization, possible systematic errors in time calibration, and deviations of the sample response from a simple step function. The best fit was typically obtained with a contraction of the bunch width that averaged 16%.

It is important to note that jitter and errors in time calibration do not enter into the comparison of the time response between the first and second shells, because they come from the same data set and therefore represent exactly the same time.

Results of the analysis are reported in the table, and plotted in figures 1 and 2 for the A and C of the three laser fluence values, respectively. The most striking result is the $\Delta t_0$ delay between 1st and 2nd shells of 11 ps.

**Table** The delay time dependent $\sigma^2$ for excitation of three different fluences. $\Delta \sigma^2$ refers to the change in $\sigma^2$ as a result of laser excitation. $T_{\text{final}}$ refers to the temperature reached after the sample equilibrated; estimated by comparison with the measured temperature dependence of $\sigma^2$ as a function of temperature in bulk Ge. A value is given for both the first and second shells, as well as an average for both shells. Agreement between the two shells confirms that the sample may be reaching local equilibrium after excitation. $\Delta t_0$ refers to the difference in the time at which the first and second shells initially responded to the laser excitation in our simple step-function model.

| Data Set | Fluence (mJ/cm²) | 1<sup>st</sup> shell $\Delta \sigma^2$ (10<sup>-3</sup>Å<sup>2</sup>) | 1<sup>st</sup> shell $T_{\text{final}}$ (K) | 2<sup>nd</sup> shell $\Delta \sigma^2$ (10<sup>-3</sup>Å<sup>2</sup>) | 2<sup>nd</sup> shell $T_{\text{final}}$ (K) | Avg. $T_{\text{final}}$ (K) | $\Delta t_0$ between 1st and 2nd Shell (ps) |
|----------|-----------------|--------------------------|-------------------|--------------------------|-------------------|------------------|------------------|
| A        | 8.0             | 3.56 ± 0.08              | 628 ± 6           | 11.22 ± 0.59             | 606 ± 12          | 617              | 11.2 ± 1.5       |
| B        | 5.3             | 2.14 ± 0.08              | 518 ± 7           | 6.97 ± 0.36              | 511 ± 9           | 515              | 11.2 ± 1.7       |
| C        | 4.0             | 1.63 ± 0.08              | 472 ± 8           | 5.29 ± 0.37              | 468 ± 10          | 470              | 10.5 ± 2.3       |
Figure 1. Plot of time dependence of the response of Ge 1st and 2nd shells after laser excitation by the A fluence of the table.

Figure 2. Plot of time dependence of the response of the 1st and 2nd shells after laser excitation by the C fluence of the table.
4. Discussion

The new most important result discovered by our time-resolved XAFS measurements is the laser-power-independent 11ps time delay before the excited e/h start decaying by interacting with incoherent phonons. It is generally assumed that this interaction starts immediately after excitation at temperatures well above the critical temperature of 6K for formation of e/h droplets [9]. The condensation of excited e/h from a gaseous to a droplet fluid state below 6 K was discovered in the 1960’s when the exciting laser’s power was above a threshold value sufficient to produce enough density of the e/h [9], to allow the condensation. Such a threshold is a signature of the first order transition from gas to fluid. In the fluid state the e/h are bound and do not interact with the incoherent phonons. We decreased our laser power by a factor of 2 in an unsuccessful attempt to detect a threshold. Thus we could not prove nor disprove that a metastable droplet state is the cause of the decay delay. Whatever is the metastable binding mechanism between electrons and holes, our measurements show that such an effect is present.

The fluence independence of the delay time indicates that anharmonic coupling in not involved as cause of the delay since its coupling increases as the fluence to the 3/2 power. Measurements of optical mode lifetime broadening indicate a room temperature lifetime of 4ps dominated by anharmonic coupling [4]. The decay of the classical mode does not have a significant effect on exciting the second neighbor atoms. The remaining dominant mechanism exciting the second shell atoms is the excitation of incoherent phonons by the delayed decay of the bound e/h states.

This result has important consequences to the interpretation of time-resolved diffraction results. For laser fluence below 50mJ/cm² (the threshold for thermal melting) any excited changes in Ge measured by diffraction prior to 1ps must be produced by the classical optical mode only. Even at powers above the threshold the classical mode is excited and can affect the diffraction signal. One such possible example [6] after excitation by a laser fluence of 200mJ/cm² is a decrease to 0.8 in the diffraction peak amplitude within a hundred or so femtoseconds, the same time for creation of the optical mode. This decrease was suggested to be an “electronic melting” of part of the Ge layer. A subsequent much slower decrease over several tens of ps was attributed to rapid thermal melting. The optical mode excitation explains the initial very rapid decrease of the diffraction signal as due to the relative vibration $\sigma^2_{cl}$ between the basis atoms and can be used to measure its value from the equation

$$G^2\sigma^2_{cl} = -3\ln \Delta I$$

where $\Delta I$ is the remaining fraction of the diffraction peak intensity and G is the magnitude of the reciprocal vector of the (111) Bragg peak. From the equation, $\sigma^2_{cl} = 0.030a^2$ where $a$ is the nearest neighbor distance in Ge. This large initial vibration amplitude is 0.17 of the nearest neighbor distance and will propagate a large perturbation in the solid due to strong anharmonic coupling, as was observed, and it also explains why the Bragg peak did not disappear in the 170nm thick Ge film during the “electronic melting”.

5. Concluding remarks

At first glance it may seem surprising that a pulse of 90ps FWHM can measure to 1ps a time delay between the 1st and 2nd shells. However, figures 1 and 2 clearly show that is possible when the delay persists for a sufficient number of delay points. The delay in the e/h interaction with incoherent phonons indicated that there is a surprising metastable binding between electrons and holes when they are initially excited. This perplexing result is revealed by XAFS since it can distinguish between the incoherent and coherent phonons production initiated by femtosecond laser pulse width excitation. Such a binding occurs below 6K where excited electrons and holes condense into a liquid state when their density is above a critical value [9]. In the case of our experiment the binding occurs at room temperature before any heating of the lattice occurs. Concomitant with the e/h excitation is the formation of the classical long wavelength optical mode. Since the optical mode has a shorter lifetime than the lifetime of the bound e/h it is hard to believe that it is involved in the binding. This
phenomenon of metastable e/h binding at room temperature warrants further investigation which may give more insight into the highly excited e/h state in semiconductors.

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