Chapter 8

Time resolved x-ray diffraction studies using K-α radiation

Time resolved x-ray diffraction (TXRD) measurements for studying the dynamics in solids have evoked considerable interest in the recent years [10, 72-77, 210]. In particular, this technique has been used for studying the lattice response of shocked crystals for a variety of research investigations such as phase transition [6,211], strain propagation [210, 212-213] etc. This technique provides the time resolved information on the lattice level, which is important for understanding the mechanisms governing the lattice response and the structural changes under shock propagation [213-215] which cannot be retrieved from conventional measurements. The origin of the shock wave is the ablation of the solid surface irradiated by focussing a laser pulse of short duration (sub-nanosecond) at intensity ≥10^9 W cm^{-2} on the sample. The absorption of the laser energy at the sample surface generates plasma, which while expanding outwards drives a shock wave into the sample. Many theoretical and experimental investigations have indicated that the induced shock pressure is related to the laser and target parameters [216].

The generated shock wave has a profile which changes rapidly with propagation distance [217]. The propagation of the shock wave inside the crystal changes the inter-planar spacing, leading to shift or broadening of the diffracted Bragg peak [215,218-220]. Thus, time resolved monitoring of the rocking curve evolution provides direct insight of the lattice response to the external / transient strain propagation inside the bulk material.

TXRD experiments are usually carried out utilizing pump-probe setup, wherein an ultra-short duration optical pump laser synchronized with an x-ray probe is used to perturb the sample. The x-ray probe pulse can be synchrotron radiation [9, 11] or high brightness x-ray free electron laser [9] from a large scale central facility. On the other hand, a small scale
laboratory based laser plasma x-ray source offers jitter free (between the laser pump and the x-ray probe) x-ray pulses of sub-picosecond duration, with moderate brightness. In a typical TXRD setup using laser plasma x-ray source, a major part of the laser beam energy is focussed on to a solid target to generate an efficient, high brightness, sub-picosecond x-ray source of K-\(\alpha\) radiation. The K-\(\alpha\) line radiation is used as a monochromatic x-ray probe for probing the transient structural modifications in a crystalline sample, induced by the remaining fraction of the laser beam (referred to as the pump laser). The rocking curve widths of the sample are recorded for different time delays between the pump and the probe pulse. Mostly, the experiment is performed in Bragg geometry and the dynamics of the lattice deformation is studied from the shift / broadening of the diffracted x-ray peak and the change in the reflectivity of the sample.

The recorded high resolution x-ray diffraction spectrum in such a setup is the integral of the diffraction from the lattice planes along the x-ray penetration depth in the sample, having contribution of both shocked and unshocked lattices. The studies reported earlier for strain - depth analysis utilizing TXRD setup observed the x-ray diffraction pattern for a particular photon energy. However, this method only gives information about the characteristics of the sample averaged over the penetration depth for that photon energy. For instance, the studies published in refs 215, 219 have used TXRD to investigate the strain – depth profile induced in silicon crystal under pulsed-laser irradiation, using characteristic K-\(\alpha\) lines of Cu and Fe respectively as the probe x-ray pulse. In this work, the use of x-ray probe of different photon energies (6 – 8 keV) is shown to yield information about the strain over a greater crystal depth for similar shock wave propagation. The simplest approach of depth analysis is to record the x-ray diffraction pattern using the probing x-rays of different photon energies. The earlier studies [215, 219] have been extended here to bring out the role of depth of penetration of the probe x-rays by using characteristic K-\(\alpha\) x-ray lines of three different target materials (titanium, iron, and copper) as the probe, whereas the irradiation parameters
of the laser used to compress the sample are same. The use of x-ray probe of different photon energies yields information about the strain over a greater crystal depth for similar shock wave propagation. Such measurements are also of interest for shock wave propagation studies, where the x-rays are interacting with the shocked as well as the undistorted crystal (at longer depth). It is useful for better understanding of the x-ray diffraction and for refining analytical approach for modelling the data.

The work presented in this chapter is focussed on the lattice modification by shock wave propagation in silicon crystal under laser excitation. The origin of the shock wave and x-ray diffraction are described in section 8.1. The description of the experiment is given in section 8.2. Section 8.3 describes the studies on shock wave propagation in silicon crystal under laser excitation, probing of strain propagation in laser shocked crystal with K-α x-ray probe of different photon energies and measurements on deformation in laser irradiated silicon crystal.

8.1 X-ray diffraction from compressed sample

Most of our knowledge on the structures of crystal at the atomic length scale originates from x-ray-diffraction experiments. In this method, the periodic structure of crystal causes a beam of x-rays to diffract in specific directions. The angles and intensities of these diffracted beams depend on the density of electrons within the crystal and the angle/s subtended with the crystal plane/s. The measurement gives the interplanar spacing/s as well as information about any disorder present in the crystal structure.

A schematic diagram of the basic concept of Bragg reflection from the crystal planes is shown in the Fig. 8.1. Bragg diffraction occurs when electromagnetic radiation or subatomic particle waves with wavelength comparable to atomic spacing, incident upon a crystalline sample, are scattered in a specular fashion by the atomic planes in the system, and undergo constructive interference in accordance to the Bragg's law. For a crystalline solid, the
waves are scattered from lattice planes separated by the interplanar distance d. Where the scattered waves interfere constructively, they remain in phase since the path length of each wave is equal to an integral multiple of the wavelength. The path difference between two waves undergoing constructive interference is given by $2dsin\theta$, where $\theta$ is the angle between the x-rays and the crystal plane. This leads to Bragg's law $2d(hkl) sin \theta = n\lambda$, which describes the condition for constructive interference from successive crystallographic planes (h, k, and l, as given in Miller notation) of the crystalline lattice. Here ‘d’ is the separation between parallel reflecting planes of the crystal, n is the order of reflection ($n=1,2,3,\ldots$), $\theta$ is the Bragg angle. Moreover, the condition that the angle of incidence equals the angle of reflection should also be satisfied.

A diffraction pattern is obtained by measuring the intensity of scattered waves as a function of the scattering angle. Very strong intensities known as Bragg peaks are obtained in the diffraction pattern when scattered waves satisfy the Bragg condition. It should be taken into account that if only two planes of atoms were diffracting, as shown in the pictures, then the transition from constructive to destructive interference would be gradual as the angle is varied. However, since many atomic planes are interfering in real materials, they result in very sharp peaks surrounded by mostly destructive interference.

Fig. 8.1: A schematic diagram of the basic concept of Bragg reflection from the crystal planes.
When a polychromatic parallel beam of x-rays is incident on a crystal at an angle $\theta_o$, x-rays of wavelength $\lambda_o = 2d \sin \theta_o$ and its sub harmonics i.e. $\lambda_o/2, \lambda_o/3, \ldots$ etc. are reflected. On the other hand, when a diverging polychromatic beam is incident on the crystal, subtending a certain range of angles, then the x-rays of different wavelengths, incident at appropriate angles from maximum of $\theta_1$ and $\theta_2$ satisfying the Bragg conditions are reflected as shown in Fig. 8.2. For the latter case, the spectral range and spectral resolution depend upon the crystal used (2d as well as size), the distance between the source and the detector (via crystal), and the orientation of the detector with respect to the x-rays incident on it.

![Fig. 8.2: Diverging polychromatic beam incident on the crystal, subtending a certain range of angles, then the x-rays of different wavelengths satisfying Bragg condition is recorded on detector.](image)

The origin of the shock wave is the ablation of the solid surface irradiated by focusing a laser pulse of short duration (sub-nanosecond) at intensity $\geq 10^9 \text{ W cm}^{-2}$ on the sample. The absorption of the laser energy at the sample surface generates plasma, which while expanding outwards drives a shock wave into the sample. Many theoretical and experimental investigations have indicated that the induced shock pressure is related to the laser and target parameters [216]. The generated shock wave has a profile which changes rapidly with propagation distance [217]. The propagation of the shock wave inside the crystal changes the inter-planar spacing. This can be probed by simple Bragg or Laue diffraction showing the shift or broadening of the diffracted Bragg peak [215,218-220]. Time resolved x-ray diffraction measurement monitoring of the rocking curve evolution provides direct insight of the lattice response to the external / transient strain propagation inside the bulk material.
The diffraction of the x-rays takes place in a finite volume inside the crystal and the observed diffraction pattern is a weighted sum of the diffraction data from different depths over which the analysis is performed [4]. The schematic diagram shown in Fig. 8.3 shows the basic concept of diffraction from the lattices along the x-ray penetration depth in the sample, having contribution of both shocked and unshocked lattices. When the lattice spacing is such that the Bragg condition is satisfied at a particular angle, the x-ray beam is diffracted from the sample within a thin layer of the crystal. The different layers, strained to different extents under the influence of the compression wave, will diffract at slightly different angles leading to the broadening. On the other hand, if uniform compression is applied than a shift of the Bragg angle will occur. Besides this, thermal wave propagation occurs in a long laser pulse excitation, which leads to the expansion of lattice and diffraction occurs at a lower Bragg angle. The x-rays can penetrate in a given crystal up a distance dependent on the absorption coefficient, which in turn depends on the x-ray photon energy and the degree of crystal perfection [221]. The x-ray penetration depth is much smaller for perfect crystals, the diffraction in this case is usually modelled using dynamical diffraction theory [222, 223]. On the other hand, the kinematical approximation is used for modelling the x-ray diffraction from an imperfect crystal.

![Diagram](image)

**Fig. 8.3:** Basic concept of diffraction from the lattices along the x-ray penetration depth in the sample, having contribution of both shocked and unshocked lattices.

In a typical TXRD setup using laser plasma x-ray source, a major part of the laser beam energy is focussed on to a solid target to generate an efficient, high brightness, sub-
picosecond x-ray source of K-α radiation. The K-α line radiation is used as a monochromatic x-ray probe for probing the transient structural modifications in a crystalline sample, induced by the remaining fraction of the laser beam (referred to as the pump laser). The rocking curves of the sample are recorded for different time delays between the pump and the probe pulse. Mostly, the experiment is performed in Bragg geometry and the dynamics of the lattice deformation is studied from the shift / broadening of the diffracted x-ray peak and the change in reflectivity of the sample.

8.2 Description of the experiment

The experiments were conducted using the 10 TW Ti:sapphire laser system. This system (described in Chapter 2) delivers laser pulses at a wavelength of 800 nm. A schematic of the experimental setup is shown in Fig.8.4. The K-α x-ray probe was generated by focusing the 45 fs laser pulses onto a solid target (titanium, iron or copper). The x-ray emission was optimized for its monochromaticity and conversion efficiency by optimizing the laser irradiation parameters [159]. It has been observed that the pre-pulse is a crucial parameter determining both, the conversion efficiency and the monochromaticity [159]. The intensity contrast ratio of the pre-pulses present on nanosecond time scale was measured using a fast photodiode and a digital storage oscilloscope (500 MHz bandwidth). The contrast ratio of the pre-pulse arising due to amplified spontaneous emission (ASE) was about $10^6$. The temporal width of the x-ray pulse from the plasma generated under similar laser irradiation is expected to be of several hundred femtoseconds [74]. The laser irradiation conditions such as energy and angular fluctuations were monitored rigorously to achieve monochromatic and high brightness K-α x-ray radiation. The x-ray conversion i.e. the number of x-ray photons produced versus the number of incoming laser photons are given in Chapter 6.
A part of the stretched (800 nm, 200 ps) pulse was used to irradiate a 500 µm thick flat Si (111) crystal sample (2d = 6.271 Å) at an intensity of 6 GW /cm². The laser beam illuminating the surface of the sample had a spot size of 2 mm diameter. The ablation depth in the crystal is expected to be < 200 nm. The width of the sample participating in the Bragg reflection is ~ 90 µm (in the direction of dispersion). The laser spot size on the sample was approximately twenty two times larger than the x-ray spot size, to ensure probing of a homogeneously excited area. The time delay between the 200 ps pump laser pulse and the probing x-ray pulse was adjusted by an optical delay line. A positive delay here means the pump laser pulse is leading the probe x-ray pulse in time. The zero time was taken as the point where the diffraction signal starts to change. The diffracted x-ray spectrum was recorded on an x-ray CCD camera with an angular resolution better than 0.02°. The pulse
width of the probe x-ray was expected to be sub-ps and the time resolution was about 200 ps, determined by considering the duration of pump pulse.

This is an experiment that involves a challenging task of having spatial overlap between the x-ray beam and the pump beam and temporal synchronization between the x-ray pulse and the laser pulse. Firstly a mechanical alignment of the target, sample and c-ray CCD port was done. We used three He-Ne laser beams from x-ray probe, pump laser and x-ray CCD directions to find the approximate overlap on the crystal. The 800 nm laser beams were ensured to follow the He-Ne beam path during the actual run. To confirm that the overlapped part of the sample is indeed seen by the x-ray CCD, the sample surface was partially blocked with a thin metallic foil strip. This was reflected on the Bragg diffraction pattern as a null region. Once this portion was located by suitably moving the crystal, the pump laser focus was optimized to get maximum deformation of the diffraction at a fixed time delay. The temporal overlap of the beams (identification of “t=0”) was ensured first by monitoring the scattered laser radiation from both the laser beams (pump and probe) from the sample with a photo-diode and fast oscilloscope to locate the temporal overlap. Since the pump pulse duration was 200 ps as compared to 45 fs probe laser pulse, even at the time “t=0”, a deformation of the rocking curve is expected because of the rising edge of the pump pulse. The overlap between the probe x-ray beam and pump beam was optimized by slightly scanning the pump beam over the surface, and looking for the strongest signal change (i.e. largest shift of the Bragg peak), corresponding to the optimal overlap.

The point x-ray source allowed a direct imaging of a part of the crystal surface onto the x-ray CCD camera [87]. This enables simultaneous recording of the diffracted x-ray spectrum from the pristine (un-irradiated) and the laser irradiated area of the crystal. Figure 8.5a shows the space resolved CCD image of the diffracted iron K-α x-rays from laser
irradiated Si (111) surface, at a delay of +600 ps. The lower part of the same picture shows the pristine sample where the two components of the K-α lines (K-α₁ and K-α₂) are clearly identified. The upper part of the picture shows broadening of the K-α lines induced by non-uniform lattice compression attributed to the cumulative effects of the laser induced compression wave and the associated thermal broadening of the lattice.

A computer routine has been developed for reading and analysing of the data files. It includes all required data analysis routines. A user interface has been provided to choose the region of interest. The line profile on the maximally broadened region is taken for analysis. Variation in the width of the rocking curve for the pristine sample at different locations defines the error in measurement. Figure 8.5b shows the fitted line profile of the pristine sample. The line profiles, best fit parameters are saved separately for further analysis.

![Image](image.png)

**Fig. 8.5:** a) Space resolved CCD image of the diffracted iron K-α x-rays from laser irradiated Si (111) surface at a delay of +600 ps, b) fitted line profile of the pristine sample

### 8.3 Measurement of shock-wave profiles

The x-ray source was used for measurement of shock-wave profiles in a silicon crystal by time resolved x-ray diffraction using Ti K-α x-ray line radiation as the probe pulse. A part of the stretched (800 nm, 200 ps) pulse was used as pump to irradiate a 500 μm thick
flat Si (111) crystal sample at an intensity of 6 GW cm\(^{-2}\) determined by considering the duration of pump pulse. The lattice change occurring in the crystal due to shock wave propagation or thermal disordering got manifested as a modification in x-ray diffraction profile integrated over the penetration depth for that photon energy. The broadening of the diffracted signals predominantly towards higher angles indicates shock wave compression of the lattice, whereas the thermal disordering for time delay > 1 ns gives rise to broadening towards the lower angle side [224]. Figure 8.6 shows the broadening of the Ti K-\(\alpha\) line with the time delay between pump and probe pulse. The typical observed diffraction signal gives signature of expansion and compression through the spread in opposite directions resulting in overall broadening. It is observed that the diffraction pattern broadens with increasing delay to reach a maximum. Thereafter, the K-\(\alpha_1\) width decreases and comes close to the pristine value. It can be seen that maximum broadening occurs at 650 ps. It occurs at the time when the shock wave propagating through the sample reaches the x-ray penetration depth. The reduction in the broadening of the K-\(\alpha\) peak is either due to the reduction in compression wave pressure within the penetration depth of probe x-rays in the sample, or due to the passing of the shock wave beyond the maximum probe depth inside the crystal.

![Graph](image.png)

**Fig. 8.6:** Broadening of the FWHM of Ti K-\(\alpha\) line with the time delay between pump and probe pulse.
8.4 Probing of strain propagation in laser shocked crystal with K-α x-ray probe of different photon energies

The irradiation by the pump laser causes formation of plasma and the expansion of this plasma drives a shock wave into the underlying silicon crystal [218, 219]. Probing of the lattice compression as a consequence of the shock wave propagation in a material on a time scale faster than the three dimensional relaxation time scales [225] (few hundreds of picoseconds) can give the information about the shock velocity. The measured rocking curves of Si (111) irradiated by the 200 ps laser pulses at a fluence of 2.3 J cm$^{-2}$, for various delay times between -300 ps and +1800 ps, are shown in Fig.8.7. The diffraction profiles of Fe K$_{α1}$ (6403.8 eV) and K$_{α2}$ (6390.8 eV) are well resolved for zero (and negative) delays. It is observed that the diffraction pattern broadens with increasing the time delay up to +1200 ps. After that, the broadening reduces and finally comes back to the original state for delays larger than +1500 ps. It may be noted that the broadening of the diffracted signals is predominantly towards higher angles, which indicates lattice compression induced by the pump laser beam. The small spreads towards lower angles also appear after 300 ps implying lattice expansion. It is the signature of thermal disordering effect due to heating, indicating a larger role of a thermal wave [224]. The modification of the lattice is either due to the laser ablation of very thin surface of the silicon or due to the stress caused at the front of thermal expansion due to the surface energy deposition. The ablation occurs when the laser fluence is above the threshold of ionization of the ablation vapour and rate of ablation depends on the laser fluence [226]. The pressure wave intensity would decrease monotonically as it propagates in the sample. The lattice change observed is manifested as a modification in x-ray diffraction profile integrated over the penetration depth for that photon energy. By the time the rocking curve is first recorded (the zero time) the shock wave would have penetrated
by about 2 µm. However, this will not affect the measurements because the penetration depth of the Fe K-α x-rays in Si (111) is 11.3 µm, which is much larger 2 µm.

**Fig. 8.7:** Evolution of Si (111) rocking curve for various time delays, at a fixed fluence of 2.3 J cm\(^{-2}\)

We have analysed the dependence of the time evolution of the rocking curves as a function of the pump laser fluence. The laser fluence was varied by changing the laser energy using neutral density filters. Fig. 8.8 shows the evolution of the FWHM of the K-α\(_1\) line as a function of the delay between the pump and the probe pulse, for two different pump laser fluences. It is observed that maximum broadening occurs at a time delay of 1050 ps for a lower laser fluence of 1.2 J cm\(^{-2}\), compared to that at 1160 ps delay observed at a higher fluence of 2.3 J cm\(^{-2}\). The maximum broadening occur at the time when the shock wave propagating through the sample reaches the x-ray penetration depth. The shock pressure is expected to be lower at a lower irradiance and the compression wave will attenuate before reaching a distance equal to the penetration depth. The reduction in the broadening of the K-α peak is either due to the reduction in compression wave pressure within the penetration depth of probe x-rays in the sample, or due to the passing of the shock wave beyond the maximum probe depth inside the crystal. It may be noted that the broadening reduces rapidly for larger
laser fluence indicating a larger thermal expansion and onset of large amplitude rarefaction wave [213, 219], compared to that for the case of smaller laser fluence.

Fig. 8.8: Variation of the FWHM of the K-α₁ line of Fe as a function of the delay between the pump and the probe pulse for two different fluences of 2.3 J cm⁻² (solid squares) and 1.2 J cm⁻² (hollow circles). The curve is to drawn to guide the eye.

The propagation of the thermal wave and the shock wave is manifested through the spread of diffraction signal in opposite sense. The thermal wave propagates typically with a velocity [227] of few times 10⁴ cm/s. The thermal diffusion expected to occur on a time scale of tens of ns after the laser irradiation of the sample. The heating induced by it leads to the lattice expansion and the spread of diffraction signal towards lower angles, and appears when a few micron thick layer of the crystal is heated to a high temperature [218, 224]. On the other hand, the shock wave is launched due to material ablation and its propagation is not limited by the sound velocity. The lattice planes parallel to the shock front propagating into the crystal are compressed. The shift of the diffraction signal towards higher angle side on a time scale of about a ns is observed when the shock wave propagating through the sample reaches the x-ray penetration depth. The typical observed diffraction signal will give signature of expansion and compression through the spread in opposite directions resulting in
overall broadening. Therefore, the differentiation of the shock and thermal waves is not seen clearly.

To bring out the role of probe x-ray region inside the sample on the shock wave profile, the rocking curve of the silicon crystal irradiated at the same laser parameters (200 ps, 2.3 J cm\(^2\)) was also measured with Cu K-\(\alpha\) (8.05 keV, \(\theta_B : 14.2^\circ\)) having larger penetration depth compared to Fe K-\(\alpha\) at 6.4 keV and Ti K-\(\alpha\) (4.5 keV, \(\theta_B : 26.7^\circ\)). The profiles of the rocking curves are similar to those measured with Fe K-\(\alpha\) (4.5 keV, \(\theta_B : 18^\circ\)). Fig. 8.9 shows the FWHM of the K-\(\alpha_1\) line radiation as function of the delay between the pump and the probe pulse, for Fe and Cu. It is observed that the diffraction pattern broadens with increasing delay to reach a maximum. Thereafter, the K-\(\alpha_1\) width decreases and comes close to the pristine value. Maximum broadening occurs at 790 ps, 1160 ps, and 1870 ps for Ti, Fe and Cu respectively. The FWHM of the rocking curve of the irradiated sample shows broadening of 3.2 \(\pm\) 0.3 times, compared to that of the rocking curves of the pristine sample, for both the probe x-ray lines. The changes in diffracted x-ray profile shape are the result of lattice imperfection and results in strain broadening. The strain can be calculated from the width of the diffracted line taking the measured width of the pristine sample as the reference width. This gives a measurement of the strain since the lattice spacing is measured for planes parallel to the shock front [218]. The elastic component of calculated strain profile of the sample is shown in Fig. 8.10. The variation of the FWHM of the rocking curve for the two probes is of similar nature. However, it can be noted from the figure that when sample irradiated at same fluence of 2.3 J cm\(^2\) is probed with Fe K-\(\alpha\) shows maximum strain at 1160 ps whereas it maximum strain at 1870 ps with Cu K-\(\alpha\). Further, the observed maximum strain is \(\sim 0.26\%\), \(\sim 0.4\%\) and \(\sim 0.3\%\) for Ti K-\(\alpha\), Fe K-\(\alpha\) and Cu K-\(\alpha\) respectively. Nevertheless, it is noted that the measurement of evolving shock profile through the sample is carried out using x-ray diffraction with different energy probe pulse can give the depth profiling of the strain.
Fig. 8.9: Variation of the FWHM of the K-α₁ line radiation as function of the delay between the pump and the probe pulse, for Ti, Fe and Cu. The curve is to drawn to guide the eye.

Fig. 8.10: Strain variation as a function of the delay between the pump and the probe pulse, for Fe (hollow circles) and Cu (solid squares).

The diffraction of the x-rays used for recording the rocking curve takes place in a finite volume inside the crystal and the observed diffraction pattern is a weighted sum of the diffraction data from different depths over which the analysis is performed [4]. When the lattice spacing is such that the Bragg condition is satisfied at a particular angle, the x-ray beam is diffracted from the sample within a thin layer of the crystal. The different layers, strained to different extents under the influence of the compression wave, will diffract at slightly different angles leading to the broadening. The x-ray can penetrate in a given crystal
up a distance dependent on the absorption coefficient, which in turn depends on the x-ray photon energy and the degree of crystal perfection [221]. When the crystal is perfect, only the primary extinction (losing intensity as far as diffracted photons will come in) is responsible for the penetration. Primary extinction length is of the order of a few microns [221] e.g., 18 \( \mu \text{m} \) and 15 \( \mu \text{m} \) for Si (111) and (220) at 8 keV, respectively. Conventionally, the attenuation length is defined as the depth into the material measured along the surface normal where the intensity of x-rays falls to 1/e of its value at the surface. Since the x-ray penetration depth is much smaller for perfect crystal, the diffraction in this case is usually modelled using dynamical diffraction theory [222, 223]. On the other hand, the kinematical approximation is used for modelling the x-ray diffraction from an imperfect crystal. However, for the practical case of crystal under moderate shock compression below the Hugonoit elastic limit, x-ray diffraction spectra can be precisely modelled based on the knowledge of x-ray penetration depth [222, 228].

The shock wave propagation [228] in material has been investigated to infer the shock – solid interaction, shock attenuation, variation of shock velocity etc. The shock waves propagate in a material medium in a manner different from that of ordinary acoustic waves. As the shock compression changes the density and temperature of the medium, the shock velocity is normally higher than the sound velocity in the medium in which it propagates. However, at low shocks, due to lower compression, the shock velocity is expected to close to the sound velocity. A study of the time evolution of the rocking curve can be an effective way to understand the propagation of the shock waves inside the crystal. As noted from the Fig. 8.8, maximum broadening occurs for a lower laser fluence of 1.2 J cm\(^{-2}\), at a time delay of 1050 ps compared to 1160 ps observed at higher fluence of 2.3 J cm\(^{-2}\). Ideally, the maximum broadening will occur when all lattice planes with in the x-ray probe length are
compressed and contributing in diffracted x-ray spectrum along the x-ray penetration depth. The penetration depth of Fe K-α at 6.4 keV in Si (111) is 11.3 µm [223]. From the above data, it can be calculated that the shock wave propagates with a speed of $11 \times 10^5$ cm/s at lower irradiance, and $9.7 \times 10^5$ cm/s at higher irradiance. This difference in shock speeds can be either due to the attenuation of the shock wave inside the sample or due to the variation in shock speed in the strained material. From Fig. 4, one can note that the maximum broadening for Cu K-α at 8.05 keV occurs at 1870 ps. The penetration depth of Cu K-α at 8.05 keV in Si (111) is 17.4 µm [229]. The derived shock speed is $9.3 \times 10^5$ cm/s. Similarly, the penetration depth of Ti K-α at 4.5 keV in Si (111) is 6.1 µm. The maximum broadening for Ti K-α occurs at 720 ps and the derived shock speed is $8.5 \times 10^5$ cm/s. The average derived shock speed is $(9.6 \pm 1) \times 10^5$ cm/s. The measured shock speed represents the average speed and there is ~ 10% variation in the shock speed derived with three different photon energy x-ray probe. It can be assigned to the fact that the shock waves are attenuated as they propagate and the onset of the rarefaction wave in the sample makes analysis more complex. Nevertheless, the derived shock wave speed is very close to the sound velocity of $\sim 9.4\times10^5$ cm/s in Si [230]. The derived shock speed values are also in broad agreement with those obtained under similar irradiation conditions.

The experimentally obtained diffraction profile is useful to derive some quantitative knowledge about the non-uniform variation of the inter planar spacing due to the propagating compression front. For this, one requires to carry out computer simulations based on the dynamical x-ray diffraction theory applied to strained and laser-shocked crystals [231]. Nevertheless, some important information such as interaction of the propagating compression front with the solid, which is a function of the penetration depth, can be obtained from the delay time at which maximum broadening occurs in the diffraction profile. As stated earlier,
in the case of Bragg reflection, a large number of layers participate in the process and the diffraction pattern is a cumulative contribution of all the participating layers. From the Bragg’s law, the change in the angle of diffraction is related to the change in the inter-planar spacing. The lattice strain can be estimated using the relation

$$\frac{\Delta d}{d} = - \cot \theta_B \Delta \theta$$

where $d$ is the inter-planar spacing, and $\theta$ is the Bragg angle. The maximum change in the Bragg angle ($\theta - \theta_B$) up to which diffraction signal appears is $0.064^\circ$. The lattice strain estimated from the shift in Bragg angle, corresponds to a compression of 0.4%. Hironaka et al [219] have reported a maximum lattice strain of 1.05% in Si, corresponding to the maximum pressure of 2.18 GPa. The maximum lattice strain of 0.4% in the present experiment corresponds to a pressure of 0.8 GPa.

Many recent studies have used TXRD technique to investigate the strain generated in fs laser excited semiconductor materials. The initial events [227] after fs pulse excitation include the carrier–carrier interaction processes leading to a quasi-equilibrium situation among the electrons on a time scale of few fs. The exchange of energy between the electrons and the phonons takes place in hundreds of fs after the laser excitation peak. The phonon-phonon thermalization time is a few ps after the deposition of the laser energy. Lastly, the thermal diffusion leading to melting (provided sufficient amount of energy has been deposited in the material) can take place on a time scale of the order of tens of ps. Finally, the ablation starts leading to pressure wave generation and propagation on a time scales of hundreds of ps. In the present experimental setup, the time resolution is not sufficient to detect and resolve the initial events after fs pulse excitation. However, using a fs laser as the
probe, phenomena such as photon-electron interaction, electron-phonon coupling, and pressure wave generation and its propagation in the bulk of the crystal can be observed.

### 8.5 Deformation in laser irradiated silicon crystal

The irreversible structural modification in the recovered sample, after the propagation of shock wave, was examined using iron K-α x-ray radiation. Figure 8.11 shows the XRD pattern obtained from a pristine and irradiated part of the sample. The diffracted K-α₁ and K-α₂ lines from the pristine sample are clearly distinguishable. Laser irradiation at a fluence of 2.3 Jcm⁻² results in a clear broadening of the spectrum. The FWHMs of the rocking curves for the irradiated sample is \((0.047 \pm 0.006)°\) compared to the \(0.021°\) for pristine sample.

![Fig. 8.11: XRD pattern obtained from a pristine and irradiated part of the sample.](image)

It is to be noted that this irreversible broadening can be attributed to the cumulative effect of laser induced lattice compression and associated thermal effects resulting in non-uniform dilation. The extent of irreversible broadening of the rocking curve of Si (111) sample for different laser irradiances is shown in Fig. 8.12. A monotonic increase in the residual broadening clearly implies the role of the laser irradiation in modifying the surface patterns of the irradiated sample.
In order to investigate the effect of laser irradiation in near surface region, we have carried out Raman spectroscopy measurements. The results are presented in Fig. 8.13. As can be seen that in the pristine sample Raman peak appears around 520 cm\(^{-1}\), while for the irradiated sample it is found to be shifted towards lower wave numbers and gets broadened. It appears that the short pulse laser irradiation causes anomalous surface transformations in Si crystal, resulting in the formation of localized surface variations during the process of re-crystallization.

**Fig. 8.12:** The extent of irreversible broadening of the rocking curve of Si (111) sample for different laser irradiances.

**Fig. 8.13:** Raman spectroscopy measurements to investigate the effect of laser irradiation in near surface region.
The peak broadening observed in time resolved x-ray diffraction occurs after 1160 ps after the irradiation with laser. The FWHM of K-α₁ was 0.074° reduces to value of 0.047° in the recovered sample primarily due to recrystallization of sample after the propagation of shock or thermal effects. Kishimura *et al* [215] has shown that such deformation of the lattice structure is mainly the formation of mosaic blocks with inclined orientations due to propagation of compression wave in laser ablated samples. The tilting is due to the pressure release after the compression wave is over.

To summarize this chapter, time resolved x-ray diffraction has been carried out to measure the rocking curve of a laser irradiated silicon crystal. The K-α x-ray line emissions from high-intensity ultra-short laser pulse produced plasmas of two different target materials (Fe, and Cu) are used as probe. The dynamics of the strain propagation is studied by measuring the rocking curve of the shocked sample as a function of delay between the pump and the probe pulse. The shock velocity deduced from these measurements is consistent with the predicted velocities. The observed maximum compression is 0.4%, which corresponds to a pressure of 0.8 GPa (8 kbar). The study can be of interest in view of the probing by x-ray pulses of widely different photon energies that can directly give information of the shock penetration depth. This makes this technique promising one for studying the temporal and spatial strain profiles of shocked samples. Such a study is helpful to understand the laser ablation for variety of application such as laser shock treatment and fracture stresses induced during welding etc.