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Probing the pathway of an ultrafast structural phase transition to illuminate the transition mechanism in Cu₂S

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Abstract

Disentangling the primary order parameter from secondary order parameters in phase transitions is critical to the interpretation of the transition mechanisms in strongly correlated systems and quantum materials. Here we present a study of structural phase transition pathways in superionic Cu_2S nanocrystals that exhibit intriguing properties. Utilizing ultrafast electron diffraction techniques sensitive in both momentum-space and the time-domain, we distinguish the dynamics of crystal symmetry breaking and lattice expansion in this system. We are able to follow the transient states along the transition pathway and so observe the dynamics of both the primary and secondary order parameters. Based on these observations we argue that the mechanism of the structural phase transition in Cu_2S is dominated by the electron-phonon coupling. This mechanism advances the understanding from previous results where the focus was solely on dynamic observations of the lattice expansion.

Introduction

Spontaneous symmetry breaking in phase transitions plays a central role in the study of emergent properties in a variety of quantum materials including superconductors, multiferroics, and topological materials. As pointed out by Landau, a phase transition can be described by the corresponding order parameter, a quantity that characterizes the symmetry breaking pattern of the phase transition and that demonstrates singular behavior across the phase boundary. The order parameter utilized in Landau's theory is also known as primary order parameter. In addition to the primary order parameter, in a real material system singular behavior will be seen for other characteristics that are not directly associated with the symmetry breaking. These are associated with secondary order parameters. The secondary order parameters can also be used to

identify the phase boundary and they usually break fewer (or no) symmetry elements in comparison with the primary one. Although primary and secondary order parameters may mark the same phase boundary, they play completely different roles in the phase transition [1, 2]. Specifically, the primary order parameter is the origin of singular behavior across the phase boundary, while singularities in secondary order parameters are subsidiary being induced by their coupling to their attendant primary order parameters.

In many correlated electron systems and quantum materials, the primary and secondary order parameters are intertwined, leading to considerable ambiguity in understanding materials' functionalities that are associated with phase transitions [3-7]. However, recent advancements [8-11] in time-resolved ultrafast observation method using pump-probe techniques offer the ability to track independently the dynamics of both. They are able, in general, to probe both the steady state associated with the phase transition as well as the pathways taken by a material to achieve this steady state. We will demonstrate this here in an ultrafast electron diffraction study of Cu₂S nanocrystals.

Cu₂S is known as a superionic conductor with liquid-like behavior of copper ions above the critical temperature, giving rise to applications in electrochemical, thermoelectric, and battery devices due to its unique electrochemical performance [13-18]. The structural phase transition occurring at a critical temperature close to ambient has been studied intensively in Cu₂S [19-23]. The structural phase transition involves crystal symmetry breaking of the crystalline lattice and a “simultaneous” volume expansion, i.e., Cu₂S is monoclinic (space group $P2_1/c$; hereafter called the “L-phase”) at room temperature and hexagonal (space group $P6_3/mmc$; hereafter called the “H-phase”) at temperatures above 375 K. The structural phase transition in Cu₂S is likely to be a

first-order transition, evidenced by multiple reports of hysteresis during the transition [13, 14, 24, 25].

Previous ultrafast x-ray absorption work on Cu₂S nanocrystals reported a reversible switching behavior between the L-phase and the H-phase with a time-constant of 18 ps [12]. This study however was only able to distinguish the dynamics of the secondary order parameter, the rate of lattice expansion. Here we will add to this prior work. Due to the sensitivity in momentum/reciprocal space of ultrafast electron diffraction, we will be able to report measurements of the transient crystal symmetry breaking (the primary order parameter) and lattice expansion during the phase transition.

In ref. [12] it was suggested that the transition is not governed by electronic mechanisms but by the copper ion self-diffusion rate. However, we will argue that crystal symmetry breaking, i.e. the primary order parameter, plays a key role and is indicative of the underlying physics of the material. The focus on both order parameters brings forth a basic question for a wide range of materials: what are temporal scales governing the two order parameters during the onset of a structural transition? A simplified case illustrating this issue using a 1D assembly of atoms is found in Figure 1, which shows that a material can take multiple pathways on transforming from one phase to another in parameter space. In this letter we will identify which of these pathways Cu₂S takes after being pumped with pulsed laser energy and illuminate the transition mechanism.

Results and Discussions

Cu₂S nanoplates were synthesized (see ref. [24]) that are on the order of 10 nm thick and 100 nm in lateral dimension, and were then deposited on a transmission electron microscope (TEM) grid with β -Si₃N₄ support membrane at the center. The *c* axis of both the L-phase and the

H-phase is perpendicular to the top and bottom surface of the nanoplates [24]. TEM low-mag images show most of the Cu_2S nanoplates lie flat on the $\beta\text{-Si}_3\text{N}_4$ support with their c axes aligned along the electron beam direction (supplementary Figure S2).

The UED experimental settings are the same as in ref. [11] and also can be found in the Methods in the supplementary material. Because the electron probe in the UED experiment is about 200 μm in diameter, the UED patterns were obtained from the scattering from millions of Cu_2S nanoparticles, making the results statistically representative. A typical UED pattern (80 ps after the laser pumping) is shown in supplementary Figure S3 with the integrated radial intensity profile.

As shown in Figure 2a, a comparison of the UED patterns before and after the laser pump indicates that the peak center moves toward the direct beam, which is consistent with the lattice expansion both due to laser heating and the phase transition to the high temperature phase. More significantly, the peaks in the UED patterns become sharper after the laser pumping. This cannot arise from a laser heating effect because heating induces larger atomic vibrations that would affect the intensity in the background and broaden the diffraction peaks, the opposite of what we observed.

It is necessary to understand the formation of the diffraction peaks in the UED patterns during the phase transition. Each diffraction peak in the UED patterns consists of multiple reflections with close q values in the reciprocal space, which is illustrated in Fig. 2b using electron diffraction (ED) patterns obtained from individual Cu_2S nanoplates in transmission electron microscopy (TEM). Firstly, the diffraction peaks in the UED patterns have the average intensity from many individual Cu_2S nanoplates with aligned c axes. Thus the radial position of the diffraction peaks in the UED patterns can be indicated by dash circles in ED patterns in Fig.

2b for the (110) and (120) peaks (using the hexagonal notation). Secondly, due to the instrumental broadening [26], the UED patterns do not have the resolution to distinguish reflections with close q values in reciprocal space, particularly for the L-phase.

To be more specific, for the hexagonal H-phase, the (110) reflections in the ED pattern have single q value of 5.02 nm^{-1} and, similarly, a single q value of 7.67 nm^{-1} is related to the (120) reflections at $325 \text{ }^\circ\text{C}$ [21]. Thus the (110) and (120) peaks in the UED pattern in Fig. 2a are formed by those single- q -valued reflections convoluted with instrument broadening. On the other hand for the monoclinic L-phase, as highlighted by open-green squares (Fig. 2b), the (110) and (120) reflections have multiple q -values due to its lower crystal symmetry. Not only do the single- q -valued (110) and (120) reflections in the H-phase split into multiple q values, but additional reflections also appear (highlighted by open-green triangles in Fig. 2b), giving an additional broadening of the peak intensity profile. A qualitative construction of the intensity profiles of the UED peaks is described in Fig. 2c and 2d for the (110) and (120) peaks. The additional broadening of the UED peaks from the L-phase can be clearly seen from the intensity profiles. We therefore conclude that the observation of the sharpening of the UED peaks after laser pumping is clear evidence of the structural phase transition from L-phase to the H-phase in the Cu_2S nanoplates.

The peak width (reflecting the change of crystal symmetry) and peak center (reflecting the change in molar volume) change as a function of time delay are shown in Figure 3a and 3b for the (110) and (120) peaks, respectively. We note that, the changes of the peak centers for both (110) peak and (120) peak are $\sim 0.8\%$, consistent with previous study reported for the L-phase at room temperature and the H-phase at $325 \text{ }^\circ\text{C}$ [19, 21]. The temporal evolutions of peak center and peak width are obviously very distinct in the ultrafast-time domain. In particular, for

the (110) peak in Figure 3a, the peak width changes from $\sim 0.44 \text{ nm}^{-1}$ to 0.36 nm^{-1} with a time constant of $2.1 \pm 0.2 \text{ ps}$ using exponential fitting, whereas the time constant of peak center position is about $6.7 \pm 0.4 \text{ ps}$. For the (110) peak in UED, the disappearance of the green-triangle-marked reflections (on one side of the (110) green-square reflections in Fig. 2b) affects both the peak width and peak center position. This explains the plot that the peak center measurements change synchronously with the width measurements in the first few ps after the pump. The observation of the (120) peak, shown in Figure 3b, delivers the same message, except that the separation of the temporal evolution of peak width and peak center position is clearer: the time constant is $\sim 2.3 \pm 0.2 \text{ ps}$ for the peak width and $\sim 10.2 \pm 0.3 \text{ ps}$ for the peak center. This even more clear distinction is attributed to the fact that the green-triangle-marked reflections (in Fig. 2b) of the L-phase are located symmetrically around the (120) reflections, and the disappearance of the reflections of the L-phase during the transition affects the peak width measurements but has much less effect on the peak center measurements. In other words, the difference between the time constants ($6.7 \pm 0.4 \text{ ps}$ for the (110) peak and $10.2 \pm 0.3 \text{ ps}$ for the (120) peak) are resulted from the technique with instrument broadening and the characteristics of the crystal structure. Even so, the temporal measurements of the evolution of the (110) peak and (120) peak strongly indicate that the crystal symmetry breaking takes place much faster than the lattice expansion. Thus a pathway similar to the orange route in Figure 1 is indicated by our ultrafast observations in this material. We also provide a theoretical discussion of the dynamics of both the primary and secondary order parameters, based on the theory developed in [1, 27], in the supplementary material.

Other considerations that might affect the measurements here are taken into account. A number of previous studies reported that lattice expansion starts from the surface of a material

and propagates elastically through the material by the speed of sound, which can be calculated by the mass density and bulk modulus [28, 29]. Taking a bulk modulus (B_T) of 50.95 GPa and a mass density (ρ) of 5.6 g/cm³ [15], the speed of sound $v = \sqrt{\frac{B_T}{\rho}}$ is approximately 3016 m/s in bulk Cu₂S. Since the dimension (thickness and the lateral size) of the Cu₂S nanoparticles varies from 10 nm to 100 nm, the time for the propagation of lattice expansion ranges from a few ps to tens of ps, falling into the level of our observation of peak center evolution in time. Thus the evolution of lattice expansion observed here may be a combination of the phase transition and elasticity of the material. Moreover, the shear modulus (G_T) that might affect the symmetry of the structure is significantly smaller than the bulk modulus in Cu₂S ($G_T = 17.77$ GPa) [15]. It means that if the shear modulus could dominate the crystal symmetry change through the elasticity, the process would be strongly correlated with the establishment of mechanical equilibrium, and slower than the observed lattice expansion. That is not the case for Cu₂S in our measurement. Note that the elastic properties could also affect a pressure that is built up through deformation potential at a time scale as fast as phonons are absorbed [30-32] and could drive phase transition in other systems [33]. However, the details of the possible deformation potential in Cu₂S are beyond the scope of this work.

Our dynamic observations of the structural phase transition also settle a longstanding debate of the role of the electronic states in the phase transition of Cu₂S. In particular, based on the time constant (~ 18 ps) of lattice expansion during the structural phase transition using near-edge X-ray spectroscopy reported previously on Cu₂S, it was concluded that the structural phase transition takes place on a time scale that is much longer than the electronic excited states needs to respond to the pumping process; thus the role of the electronic states in the transition mechanism was considered negligible [12]. However, X-ray spectroscopy results come from the

scattering beam with wave vector $q \approx 0$, so the measurements do not directly reflect the process of structural transition. The conclusion of Ref. [12] is inconsistent with other experimental results. For instance, in a recent TEM study, Cu_2S was found to exhibit the surprising characteristic that purely electronic excitations can reversibly manipulate the crystal's structural transformation between its L- and H-phases [24]. Since the observations strongly imply an intimate interplay between electronic degrees of freedom and the lattice, it is difficult to imagine how the modification of the electronic states can be ruled out as the mechanism of the structural transition in this material. Nevertheless as TEM observations cannot trace the structural dynamics through the transition, they cannot pin down the driving force of the transition.

The above ambiguity concerning the phase transition in Cu_2S and other electronic materials has to be addressed by direct probes of the structural evolution using momentum-resolved techniques in the ultrafast time domain. Our measurement of the temporal evolution of lattice expansion (~ 10 ps) is on the same order of the result from the X-ray spectroscopy work on Cu_2S [12]; however, we find that the dynamics of crystal symmetry breaking (~ 2 ps) is faster by 3 - 5 times. Indeed, the time scale of crystal symmetry breaking measured here coincides with the time scale of the carrier population or carrier excited states measured by optical pump-probe spectroscopy in this material [12], directly indicating a key role that electronic states play in the structural transition. In addition, it is accepted that, during a pump-probe process, electron-phonon scattering takes place from hundreds of femtoseconds to a few ps after the laser pumping [34-36]. Governed by electron-phonon coupling, the lattice symmetry changes from monoclinic to hexagonal but the unit-cell maintains the size of the L-phase in Cu_2S for several ps. In the subsequent tens of ps, the lattice continuously expands to the value of the H-phase, resulting

from the diffusion of the copper ions and elastic properties of the material, so completing the transition.

We believe our finding could inspire further study of the structural instability in many superionic conductors such as Cu_2S , CuBr , Ag_2S and AgI by exploring how the perturbation of electronic states affects the bonding situation either locally or collectively. Those ionic conductors share a common feature in their cations having a +1 electronic valence state. In the Cu_2S case, the Cu^+ ions have the d^{10} electronic configuration and the electronic band structure at the Fermi level consists of the Cu $4s$ and $3d$ bands [37]. This points to two following ways for electron-phonon coupling to exert its role in the photoinduced phase transition:

1) A photoexcitation causes a $3d^{10}-3d^94s^1$ transition of the Cu ions. Since $4s$ wide-band electrons are expected to move much faster than $3d$ narrow-band holes, the lag of the latter yields effective $\text{Cu}^{2+} 3d^9$ transient states, which drive the breathing-mode and Jahn-Teller-mode motions of the surrounding sulphur anions.

2) Given the fact that there are noticeable Cu vacancies in the real material Cu_{2-x}S [14-19], Cu ions already exist as Cu^{2+} in small proportions and are likely randomly distributed. Hence, photoexcitation may cause electron transfer between neighboring Cu^{1+} and Cu^{2+} cations (i.e., $\text{Cu}^{1+} \rightarrow \text{Cu}^{2+}$ and $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$), inducing a change in the lattice distortion surrounding the pair of Cu^{1+} and Cu^{2+} ions, in the same spirit as the photoinduced intersite $\text{Mn}^{3+}-\text{Mn}^{4+}$ transition in the manganites [11]. This facilitates the crystal lattice to become more disordered with higher crystal symmetry. These two electron-phonon coupling mechanisms are compatible with each other and can work together.

In summary, our UED-based time-resolved observations of the temporal evolution of the lattice emphasize that both the primary and secondary lattice parameters need to be monitored in

order to come to a complete understanding of the Cu₂S phase transition. Based on our UED results, we conclude that the electron-phonon coupling is strongly suggested to be the fundamental mechanism by which the structural phase transition is mediated. Moreover, knowing the atomic arrangements at each snapshot during the phase transition is essential for characterizing the evolution of lattice energy, making it possible to quantitatively depict the energy pathways of phase transitions for other materials in the future. The capability demonstrated in this study will provide guidelines for phase transitions and will significantly impact research in correlated electron systems and quantum materials.

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Author Contributions

J.T. and Junjie Li designed the project and were the primary interpreter of the resulting data. J.C., L.M. and R.M. synthesized nanomaterials. J.T., Junjie Li., Jun Li., M.B., M.F., C.S., R.M., M.P.

and Y.Z. collected UED data. J.T., Junjie Li. and Jun Li. analyzed UED data. J.T., K.S., Q.M., W-G.Y., R.M.K., R.J.C. and Y.Z. performed the study of the transition mechanism. J.T. Y.L., D.L. and R.J.C. performed the study of crystal structures. All authors contributed to the writing of the paper.

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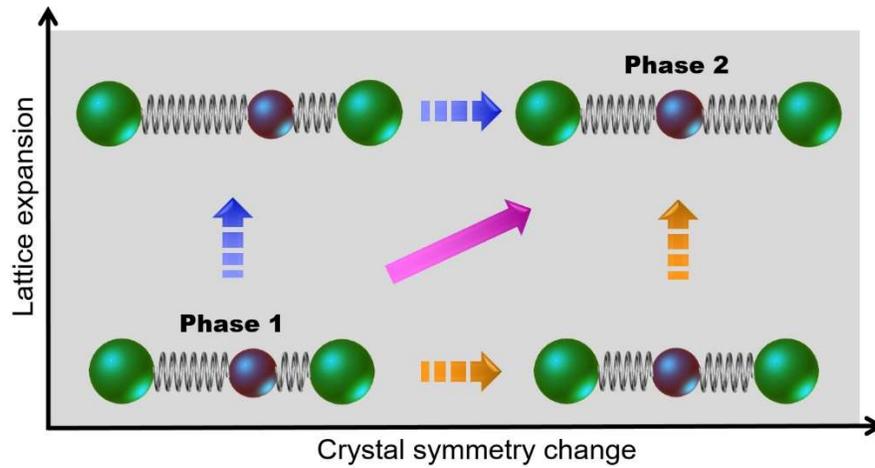


Figure 1. Schematic of a structural phase transition that involves both the crystal symmetry breaking and lattice expansion in a 1D assembly of atoms. Phase 1 has two types of atoms that have unequal spacing. Phase 2 has the same group of atoms with altered lattice symmetry and spacing. Arrows in orange, purple and blue indicate possible transition pathways in the ultrafast time domain.

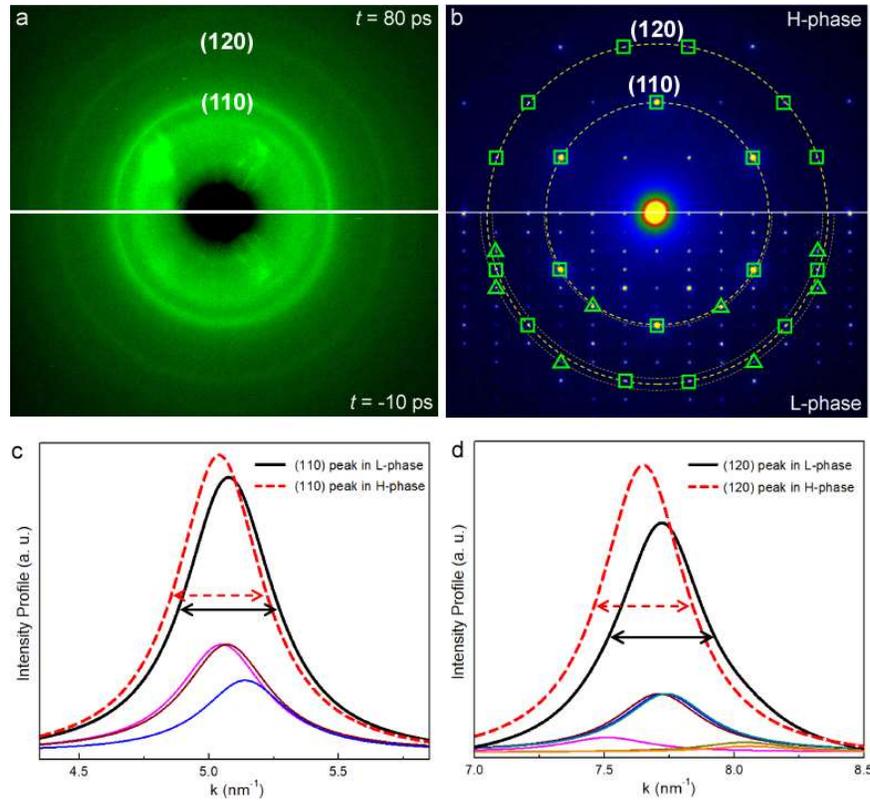


Figure 2. (a) A comparison of UED patterns taken before (bottom) and after (top) laser pump. (110) and (120) reflection rings are indexed using the notation of the hexagonal structure. UED patterns were recorded over an integration of 200 shots, under a pump fluence of 2 mJ/cm^2 . (b) Presented are the electron diffraction (ED) patterns obtained in the L-phase (bottom) and H-phase (top) in transmission electron microscopy (TEM). The open squares mark diffraction peaks that appear in both the L- and H-phases while the open triangles mark peaks that only appear in the L-phase. The UED rings observed in top part of (a) (after the pump) are formed from single diffraction peaks appearing in the TEM image of (b), namely the 5.02 nm^{-1} peak for the (110) ring and the 7.67 nm^{-1} peak for the (120) ring. In contrast the rings in the UED pattern in the bottom part of (a) (before the pump) are formed from reflections at a variety of q values. The (110) ring is formed from reflections at 5.05 nm^{-1} , 5.07 nm^{-1} , and 5.13 nm^{-1} while the (120) ring is composed primarily of reflections at 7.71 nm^{-1} , 7.73 nm^{-1} , and 7.74 nm^{-1} . This latter ring

also sees contributions from reflections close by which however cannot be separately resolved because of instrument resolution. (c) The center and width of the (110) ring before (L-phase) and after (H-phase) the pump are schematically constructed. The black curve marks the ring before the pump when the material is in the L-phase. It is formed from a number of smaller peaks whose intensity profiles are given by the magenta, brown, and blue curves. The red curve gives the peak intensity profile for the H-phase – because of the higher symmetry of the hexagonal phase, this intensity profile is formed from a single ring as explained previously. (d) A similar construction for the intensity profile of the (120) ring is made. Here the intensity profile for the L-phase is composed of four separate intensity profiles (marked by the brown, blue, cyan, magenta, green and orange curves). Details of all these peaks can be found in supplementary Figure S4 and Table S1.

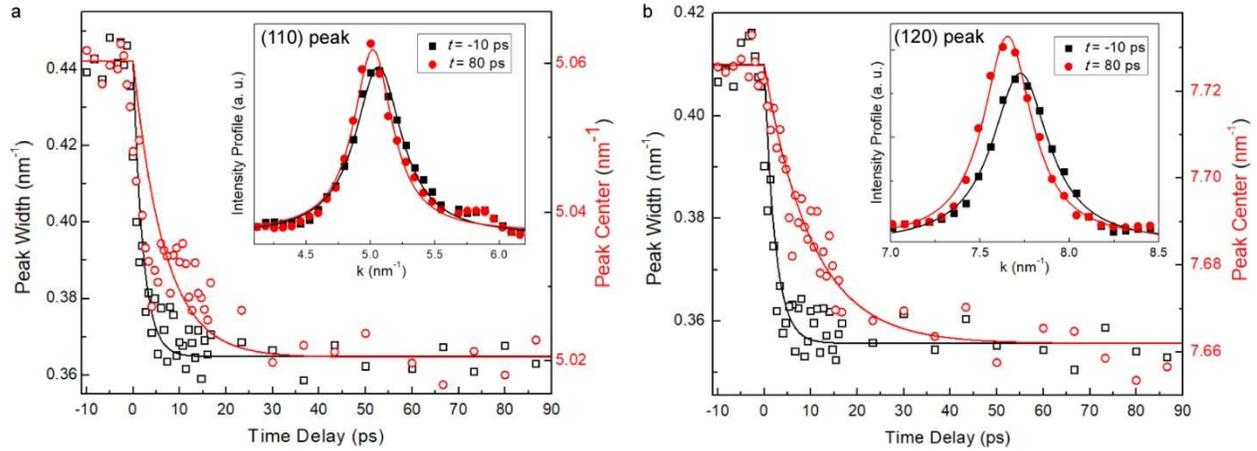


Figure 3. The change of peak width and center position after laser pump are presented. Peak width (plotted by black squares) and peak center position (plotted by red circles) in reciprocal space are given as a function of time delay for the (110) peak in (a) and the (120) peak in (b).

The time constant of peak width change is $\sim 2.1 \pm 0.2$ ps for the (110) peak and $\sim 2.3 \pm 0.2$ ps for the (120) peak, whereas the time constant of the shift in the peak center position is $\sim 6.7 \pm 0.4$ ps for the (110) peak and $\sim 10.2 \pm 0.3$ ps for the (120) peak. Black and red lines are guide for eyes. Peak width was measured using the full width of half maximum of the peak intensity profiles, which are shown as the insets of the plots with a Lorentzian curve fitting. A hump in the shoulder of the (110) peak in the inset of a) is the (200) peak. We checked that this latter peak has a minimal effect on the extraction of the time constants from the presented measurements.