X-ray Intensity Fluctuation Spectroscopy of the Ordering in Cu_3Au

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Abstract

 Cu_3Au is a classic model for the experimental investigation on the transitional process because of its very long relaxation time from the disordered to the ordered state. When Cu_3Au is quenched from higher temperature above its critical temperature (383°C) to some temperature below its critical temperature, the small regions of ordered phase (domains) form in the background of disordered phase. As time evolves, large domains grow at the expense of small domains. X-ray intensity fluctuation spectroscopy (XIFS) is a technique using coherent X-rays to measure the fluctuations of the diffracted intensity (speckle patterns) from the sample. During the ordering process, the structure of the sample changes, so does the speckle pattern.

In this thesis, we use XIFS to investigate the dynamic process of the order-disorder phase transition taking place in the sample Cu_3Au . The sample is quenched from 420°C to three different lower temperatures 378°C, 370°C and 355°C. A CCD detector is used to record the (100) superlattice Bragg peak and the speckle pattern. We analyze the Bragg peak and summarize its properties. The universal scaling law is tested and is observed to be in good agreement with the theory. The average domain size (inverse of Bragg peak width) obeys the power law $t^{1/2}$. This part is referred to as one-time (incoherent) analysis in the thesis. Second, we calculate the two-time correlation functions, also called two-time (coherent) analysis. As expected, twotime correlation function also follows some universal scaling law. In the small time limit, a linear relationship is found between the correlation time T (width of twotime correlation function) and average time $\bar{t} = (t_1 + t_2)/2$. In the large time limit, $T \propto \bar{t}^{1/2}$. The more interesting and exciting results we obtain are that the correlation time has an unpredicted behavior for the first dozens of minutes and the coherent factor (peak height of two-time correlation function) has a dependence on time and on the wave vector. The possible explanations are proposed and discussed.

Résumé

 Cu_3Au est un modèle classique pour effectuer une investigation expérimentale au sujet des processus transitionnels puisque celui-ci possède un temps de relaxation très long d'un état désordonné à un état ordonné. La spectroscopie rayon-X a fluctuations d'intensité (XIFS) est une technique utilisant des rayons-X pour mesurer les fluctuations d'intensité diffractée (patron de speckle) obtenue de l'échantillon.

Dans cette thèse, nous utilisons la XIFS pour investiguer le processus dynamique de la transition de phase ordonné-désordonné qui se produit dans un échantillon de Cu₃Au. La température de l'échantillon est réduite de 420°C au-dessus de sa température critique (383°C) jusqu'à trois températures différentes 378°C, 370°C et 355°C inférieure à sa température critique. Un détecteur CCD est utilisé pour mesurer le pic de Bragg (100) du réseau et le patron de speckle. Nous analysons les pics de Bragg et nous résumons ses propriétés. La loi universelle de changement d'échelle est testée et nous démontrons un bon accord avec la théorie. La grandeur moyenne du domaine (inverse de la largeur du pic de Bragg) obéit la loi de puissance $t^{1/2}$. Dans cette thèse, nous appelons cette partie une analyse un-temps (incoherent). Ensuite, nous calculons les fonctions de corrélation deux-temps, ce que nous appelons une analyse deux-temps (coherent). Comme prévue, les fonctions de corrélation deuxtemps suivent aussi une loi universelle de changement d'échelle. Dans la limite des temps courts, nous trouvons une relation linéaire entre le temps de corrélation T (largeur de la fonction de corrélation deux-temps) et le temps moyen $\bar{t} = (t_1 + t_2)/2$. Dans la limite des temps longs, nous trouvons que $T \propto t^{1/2}$. Les résultats les plus intéressants et excitants que nous obtenons sont que le temps de corrélation démontre un comportement imprévisible pour les premieres douzaines de minutes et le facteur de coherence (hauteur du pic de la fonction de corrélation deux-temps) dépend du temps et du vecteur d'onde. Des explications possibles sont proposées et discutées.

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Introduction

The development of long range order out of a disordered system is a well-known and well studied class of non-equilibrium processes. Via a temperature quench, an Ising system can change from a one-phase region to a disequilibrium state with a globally unstable point in the coexistence region. Ideally, the quench is so rapid that the state of the system (in particular, its order parameter) immediately after the quench is identical to its state immediately before the quench. The order parameter is zero at this point. As time progresses, approximately equal size regions with non-zero order parameter will form. These regions will be separated by domain walls. The characteristic size of domains will grow with time in a process called coarsening.

Binary alloys are convenient model systems for investigating this dynamic phenomena of order-disorder phase transition [1, 2, 3, 4, 5, 6]. Over the past few decades, the numerical studies of scaling theories for the structure functions have been done vastly in systems with a non-conserved order parameter such as binary alloys and binary fluids [7, 8, 9, 10, 11, 12]. Theory predicted that the characteristic length L(t)grows as a power law with the time t: $L(t) = t^a$ [13, 14]. For non-conserved order parameter system, also called model A, a = 1/2. Various Ising systems have been investigated to test the scaling model and good agreement was found between the theories and experiments. For example, Wakabayashi studied the time-dependence kinetics of the order-disorder in Ni₃Mn by neutron scattering techniques [15]. Noda et al. used time resolved X-ray scattering experiments to study the kinetics of ordering process in Cu₃Au alloy in the vicinity of its order-disorder phase transition point [16]. They observed that the X-ray diffraction profiles show universal scaling property in terms of space and time in the later stage of the ordering process. Fig. 1.1 shows one of our results of scaling function for time-dependent structure factors for three temperatures. This data covers three orders of magnitude in intensity and from a few to hundreds of minutes in time. More details will be discussed in this thesis.



Figure 1.1: The scaled intensity vesus scaled wave vector is plotted against the time for two directions: (a) $T_f = 378^{\circ}$ C, (b) $T_f = 370^{\circ}$ C, (c) $T_f = 355^{\circ}$ C. The black lines on the top of image show the contour of rescaled intensity.

All the investigations above only provide information about a configurational average intensity, also called the incoherent intensity, which is the structure factor of the system. Mathematically, this can be written

$$S(\vec{k},\tau) = I_{incoh} = \langle I(\vec{k},\tau) \rangle \tag{1.1}$$

where $\langle \rangle$ denotes an average over the disorder material. But the coherent intensity $I(\vec{k},\tau)$ or the fluctuations in the intensity $I(\vec{k},\tau) - \langle I(\vec{k},\tau) \rangle$ can provide further interesting information about the systems under study. If a sample is illuminated with coherent light, a speckle pattern arises [17, 18, 19, 20, 21], then fluctuations in intensity will be observed. This speckle pattern varies in time as the sample undergoes thermal fluctuations. The time autocorrelation of the speckle pattern yields information about the dynamics of thermal fluctuations and the characteristic times involved [17, 18].

X-ray intensity fluctuation spectroscopy(XIFS) is a new diffraction technique which can measure speckle patterns. It uses a small x-ray beam that is sufficiently coherent to produce speckle patterns characteristic of the specific structural arrangement of the illuminated sample. Such a speckle pattern is uniquely related to the exact spatial arrangement in the sample. It allows us to obtain direct information about the dynamic of atomic-scale fluctuations by measuring the temporal correlations in diffraction intensities. In equilibrium systems, XIFS reduces to measuring one-time correlation functions. In non-equilibrium systems, not only the speckle pattern fluctuates in time, but also the average scattered intensity changes with the dynamic process. Full two-time correlation functions are measured.

G. Brown et al. [22] have done the numerical studies of the statistical properties of coherent radiation scattered from phase-ordering materials with non-conserved order parameter. For such systems it is well established that the standard scaling hypothesis applies, consequently, the average scattering intensity at wave vector \vec{Q} and the time τ is proportional to a scaling function which depends only on a rescaled time, $t \sim |\vec{Q}|^2 \tau$. Considering fluctuations around the average behavior, they also find that the covariance of the scattering intensity for a single wave vector at two different times is proportional to a scaling function with two natural variables $\bar{t} = (t_1 + t_2)/2$ and $\delta t = |t_1 - t_2|$. For small value of \bar{t} this scaling function is linear, only depending on $\delta t/t$. In the large- \bar{t} limit the correlation data collapse onto a universal curve which is a function only of $\delta t/t^{1/2}$.

Cu₃Au is a classical system for studying the properties of first order phase transitions. For over half a century, Cu₃Au has always been and still continues to be a favorite system to study order-disorder transition. If Cu₃Au is heated up to a higher temperature than its critical temperature T_c , the system is in the disordered state. When the system is rapidly quenched to a certain temperature below the ordering temperature T_c , the formation of ordered "droplets" begins due to the fluctuations into the low temperature equilibrium phase. Small domains in the ordered phase then appear here and there throughout the system in the background of disordered phase. The behavior in this stage is often called nucleation [13]. As time evolves, the isolated domains grow in size to reduce the free energy of the system. This process is termed ordering. Eventually the domain walls will meet. The larger domains continue growing by eating up the smaller domains. The evolution to larger domains is called coarsening.

The dynamic process in Cu_3Au is characterized by the formation and growth of antiphase domains. The investigation of the behavior of antiphase domains will provide direct information of the ordering process taking place in the sample. The characteristic length in the scaling law is the average domain size for Cu_3Au , which can be measured as the inverse of the Bragg peak width [23, 24, 25]. Many authors have made clear that there were two types of antiphase domain walls. The type-I antiphase domain wall is expected to be of low energy because the nearest neighbor atoms remain unchanged. The type-II antiphase domain wall causes a chance for two gold atoms to occupy nearest neighbor positions and is expected to be of higher energy than the type-I domain wall.

The non-equilibrium ordering kinetics of Cu_3Au have been studied extensively with incoherent illumination [26, 27, 28]. Recent work [29] using coherent scattering presented the first experimental confirmation of the scaling of the two-time correlation functions in Cu_3Au . The dynamics of the fluctuations are well characterized by the dynamical scaling arguments for calculating these two-time correlations (see Fig. 1.2). One puzzle in these measurements was the presence of delay time before the onset of this scaling behavior. This delay time t_0 , which can be as long as 50 minutes, occurs well after the time at which the system has reached the scaling region as determined by measurements of the average domain size (inverse of the peak width).



Figure 1.2: Rescaled correlation time T versus rescaled average time \bar{t} collapse onto one stationary universal curve with the kink which indicates the transition from linear dependence $T \sim \bar{t}$ to a power law dependence $T \sim \bar{t}^{1/2}$. The dashed line has a slope of 1 and the solid line has a slope of 1/2.

With upgrades to IMMY/XOR side station at the Advanced Photon Source, both the intensity and the coherence factor required to perform XIFS measurements have been improved. This has allowed us to obtain better data and do a deeper investigation of ordering in Cu_3Au . In the thesis, we report on some of our new results and explanations to some unanswered questions.

In chapter 2 we review some basic concepts about X-ray diffraction. It includes the introduction to the properties of X-ray synchrotron sources, geometry of crystal which are the two key elements for X-ray diffraction to take place. In this chapter, we also give an brief introduction to the determination of direction of X-ray diffraction and the calculation of diffracted intensity. In chapter 3 we report the one-time (incoherent) results of the experiments. We summarize the properties of superlattice Bragg peak (100) in Cu₃Au such as the peak height, peak width and peak position. We also test the scaling law and it is found that the functions of the rescaled variables intensity I/Imax versus wave vector/time $dQt^{1/2}$ are time independent and in good agreement with the theory. In chapter 4 the two-time (coherent) results of this thesis are presented. The two-time correlation function is calculated and its line shape is examined. As predicted by the theory, time constants of two-time correlation function can be rescaled to a universal form with rescaled time. Incubation time (up to 50mins) are found as a result of speckle shift. By calculating two-time two-Q correlation functions the correlation functions at the early stage are improved greatly. It is interesting and exciting that we find the dependence of the contrast on the wave vector and time. Some simple models are applied to explain these results. Conclusion and outlook of this thesis are included in Chapter 5.

X-ray Diffraction

Since Von Laue discovered in 1912 that crystals diffract X-rays and that the pattern of the diffraction spots can reveal the structure of the crystal, X-ray diffraction has become an important tool for the investigation of the fine structure of matter. At first, X-ray diffraction was used only for the determination of crystal structures. Later on, however, the applications of this method has been extended to such diverse problems as chemical analysis, the study of phase equilibria, to the determination of the orientation of one crystal or the ensemble of orientations in a polycrystalline material. Lately with the advent of the high brilliance and the high degree of coherence of third generation synchrotron sources, many new types of X-ray experiments become possible. X-ray diffraction is very rich field used by physicists, metallurgists, chemists, ceramists, mineralogists and so on. This chapter just introduces the basic knowledge of this topic related to this thesis. Interested readers can find more details in references [30, 31, 32, 33].

2.1 X-rays and Crystals

2.1.1 Properties of X-ray Synchrotron Radiation Sources

X-rays are produced when any electrically charged particle of sufficient kinetic energy rapidly decelerates. Electrons are usually used for this purpose. If electrons are moving at relativistic velocities in an accelerator such as an electron synchrotron and are deflected along a curved trajectory by a magnetic field, synchrotron radiation is produced. Synchrotron radiation has many advantages over conventional tube sources for X-ray diffraction for several reasons. For example, synchrotron radiation provides the intensity far greater than that of other sources and it can be tuned to the most advantageous X-ray wavelength. Because of the very small divergence of X-ray beam, synchrotron source has an even higher flux (intensity per unit area of source) and brightness (intensity per second per unit source area per unit solid angle per unit spectral bandwidth). Using a pinhole as the spatial filter, synchrotron sources can provide high orders of spatial coherence. Many diffraction experiments like X-ray Intensity Fluctuation Spectroscopy (XIFS) we carried out for this thesis are feasible only with synchrotron radiation.

Several types of devices provide the intense magnetic fields required to produce synchrotron radiation. Initially, sources used synchrotron radiation emanated from the bending magnets of the synchrotron or storage ring. Later, specially designed magnets that wiggles the electrons were placed in the straight section of the storage ring. These wiggler magnets have a magnetic field alternating in polarity along the axial direction, causing the electrons to follow an oscillating trajectory through the device. The output radiation is predominantly in the forward direction and is significantly enhanced in flux and brightness compared to radiation from a bending magnet as radiation is collected from each wiggle.

If the wiggler magnet has only a few periods and the field strength is large, the radiation has the broad-spectrum characteristic of synchrotron radiation. On the other hand, if the magnet has many periods and a weak field, the spectrum exhibits peaks about a fundamental frequency and its harmonic. In this case the device is referred to as an undulator rather than a wiggler. The brightness from the harmonics of an undulator can be several orders of magnitude higher than radiation from a wiggler, which in turn can be several orders of magnitude higher than that from a bending magnet.

The history of synchrotron radiation facilities and their design is commonly classified in terms of generations. The early work carried out on high-energy physics machines is referred to as the first generation. The first generation sources were not optimized for synchrotron radiation applications and often had lower brightness, intensity and stability. The second-generation synchrotron radiation facilities provides higher intensity and brightness because they were optimized for synchrotron radiation. The majority of the experimental beamlines were situated on bending magnets. Although of lower brightness than insertion devices, bending magnets can provide high intensity. The broad spectrum from bending magnets allows easy tuning over a large range of wavelengths. Success at second-generation facilities and the rapid growth of the user community, provided the justification for building third-generation facilities. Much larger numbers of straight sections that use insertion devices provide high-brightness sources. But second-generation facilities continue to be heavily utilized by the many experimental programs that require high flux but only moderate brightness. Brightness and flux available at second- and third-generation facilities are illustrated in Figs. 2.1 and 2.2.



Figure 2.1: Comparison of brightness available at second- and third-generation X-ray synchrotron radiation facilities. [32]



Figure 2.2: Comparison of flux available at second- and third-generation X-ray synchrotron radiation facilities. [32]

2.1.2 Geometry of Crystals

When a crystal grows in a constant environment, the form develops as if identical building blocks were added continuously. The building blocks are atoms or groups of atoms, so that a crystal is a three-dimensional periodic array of atoms. The structure of all crystals can be described in terms of a lattice, with an atom or group of atoms attached to every lattice point. The atom or the group of atoms is called the basis; when repeated in space it forms the crystal structure.

The lattice is defined by three fundamental translation vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ called crystal axes. It is only the magnitude and direction of the repeating displacements $\vec{a}_1, \vec{a}_2, \vec{a}_3$ which are important. In other words, the atomic arrangement looks the same in every respect when viewed from the point \vec{r} as when viewed from the point $\vec{r'}$ which can be expressed as

$$\vec{r'} = \vec{r} + u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3, \tag{2.1}$$

where u_1, u_2, u_3 are arbitrary integers. The set of points $\vec{r'}$ defined by Eq.(2.1) for all u_1, u_2, u_3 defines a lattice. A crystal structure is formed when a basis of atoms is attached identically to every lattice point. The logical relation is

$$lattice + basis = crystal structure$$

The lattice and the crystal axes $\vec{a}_1, \vec{a}_2, \vec{a}_3$ are said to be primitive if any two points $\vec{r}, \vec{r'}$ always satisfy Eq.(2.1) with a suitable choice of the integers u_1, u_2, u_3 . With this definition of the primitive crystal axes, there is no cell of smaller volume that can serve as a building block for the crystal structure. This smallest volume is called primitive unit cell which is designated by the integers u_1, u_2, u_3 .

A lattice translation operation is defined as the displacement of a crystal by the crystal axes

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

Any two lattice points are connected by a vector of this form (see Fig. 2.3).



Figure 2.3: Sketch of portion of a crystal in two dimensions. The atomic arrangement in the crystal looks exactly the same to an observer at $\vec{r'}$ as to an observer at \vec{r} , provided that the vector \vec{T} which connects $\vec{r'}$ and \vec{r} maybe expressed as an integral multiple of the vector \vec{a}_1 and \vec{a}_2 . In this illustration, $\vec{T} = -\vec{a}_1 + 2\vec{a}_2$. The vectors \vec{a}_1 and \vec{a}_2 are primitive translation for the two-dimensional lattice.

Next we define the crystallographic planes hkl which are extremely useful to discuss X-ray diffraction. Integers hkl are called Miller indices. A set of crystallographic planes hkl means a set of parallel equidistant planes, one of which passes through the origin, and the others makes intercepts a_1/nh , a_2/nl , a_3/nk where n is an integer.



Figure 2.4: Representation of the crystallographic planes hkl.

Fig. 2.4 indicates one of the *hkl* planes when n = 1. To determine the Miller indices: a) Find the intercepts on the axes in terms of the lattice constants a_1, a_2, a_3 . b) Take the reciprocals of these numbers and then reduce to three integers having the same ratio, usually the smallest three integers. c) The result is inclosed in parentheses like (*hkl*). For example, the plane whose intercepts are 4, 1, 2, the reciprocals are $\frac{1}{4}$, 1, and $\frac{1}{2}$; the smallest three integers having the same ratio are (142). The indices of some important planes in a cubic crystal are illustrated by Fig. 2.5.

Vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$ define the basis vectors of a three-dimensional lattice. This direct space lattice, however, is not the only way that the periodicity of a given lattice can be represented. A reciprocal lattice \vec{b}_i , i.e. $\vec{b}_1, \vec{b}_2, \vec{b}_3$ in reciprocal space can be defined for every direct space lattice \vec{a}_i , i.e. $\vec{a}_1, \vec{a}_2, \vec{a}_3$ by

$$\vec{b}_{1} = 2\pi \frac{\vec{a}_{2} \times \vec{a}_{3}}{\vec{a}_{1} \cdot \vec{a}_{2} \times \vec{a}_{3}}$$
$$\vec{b}_{2} = 2\pi \frac{\vec{a}_{3} \times \vec{a}_{1}}{\vec{a}_{1} \cdot \vec{a}_{2} \times \vec{a}_{3}}$$
(2.2)



Figure 2.5: Indices of important planes in a cubic crystal. The plane (200) is parallel to (100) to $(\overline{1}00)$. [34]

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

The reciprocal lattice has several important properties. First, the cross-product in the numerator means that \vec{b}_1 is perpendicular to \vec{a}_1 and \vec{a}_2 , that \vec{b}_2 is perpendicular to \vec{a}_1 and \vec{a}_3 and that \vec{b}_3 is perpendicular to \vec{a}_1 and \vec{a}_2 . This relationship means that the reciprocal lattice has the property of orthonormality, i.e.,

$$\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}.\tag{2.3}$$

It can be shown that the volume of the reciprocal lattice unit cell is the reciprocal of the volume of the direct space unit cell scaled by $(2\pi)^3$.

Second, if we define a vector \vec{H}_{hkl} in terms of the reciprocal vectors and the Miller indices:

$$\vec{H}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3, \tag{2.4}$$

we can prove that the vector \vec{H}_{hkl} drawn from the origin of reciprocal space to an point in reciprocal space has the coordinates h, k, l and is perpendicular to the plane

in direct space whose Miller indices are hkl. The length H_{hkl} equals the reciprocal of periodicity of (hkl), i.e., $H_{hkl} = 2\pi/d_{hkl}$.

In defining a lattice with three non-coplanar lattice vectors, depending on the length and orientation of the vectors, unit cells can have various shapes. It turns out that only seven different kinds of cells are necessary to include all the possible point lattices. Seven different point lattices can be obtained simply by putting points at the corners of the unit cells of the seven crystal systems. However, there are other arrangements of points which fulfil the requirements of a point lattice, namely, that each lattice point having identical surroundings. The French crystallographer Bravais demonstrated in 1848 that there are only fourteen possible point lattices which are termed as Bravais lattices. Instead of considering all of the fourteen Bravais lattices we will next consider three crystal structures of cubic symmetry, simple cubic (sc), face-centered cubic (fcc) and body-centered cubic (bcc).

As we know, primitive cells have only one lattice point per cell. To reveal the symmetry of the lattice most of the time it is more convenient to use non-primitive cells, also called conventional cells. There are more than one lattice points per conventional cells. The number of lattice points per unit is given by:

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} + \frac{N_e}{4}, \qquad (2.5)$$

where N_i is the number of lattice points in the interior of a cell which only belong to that cell, N_f lattice points in the faces of a cell are shared by two cells, N_c is the number of lattice points in the corner shared by eight cells, and N_e is the number of lattice points on the edge shared by four cells.

As shown in Fig. 2.6, all the lattice points are located in the corners of cube. The conventional cubic cell of sc lattice is the primitive cell since there is only one lattice point belonging to the cube. The crystal axes coincide with the orthogonal axes. From Eq.(2.3), we can see right away that the reciprocal lattice of sc lattice is also sc lattice.

The conventional cell of fcc lattice is also cubic (see Fig. 2.7). Beside the eight lattice points in the corners of the cube, six lattice points occupy the centers of six



Figure 2.6: Primitive basis vectors of the simple cubic lattice.

faces of cubic. Thus the number of lattice points per cell is four. The primitive crystal axes of the fcc lattice are given by

$$\vec{a}_{1} = \frac{1}{2}a(\hat{y} + \hat{z});$$

$$\vec{a}_{2} = \frac{1}{2}a(\hat{x} + \hat{z});$$

$$\vec{a}_{3} = \frac{1}{2}a(\hat{x} + \hat{y});$$

(2.6)

where a is the side of the conventional cube and $\hat{x}, \hat{y}, \hat{z}$ are orthogonal unit vectors parallel to the cube edges.

Using Eq.(2.3) the primitive translation vectors of the reciprocal lattice for fcc structure can be obtained:

$$\vec{b}_1 = (2\pi/a)(-\hat{x} + \hat{y} + \hat{z});$$

$$\vec{b}_2 = (2\pi/a)(\hat{x} - \hat{y} + \hat{z});$$

$$\vec{b}_3 = (2\pi/a)(\hat{x} + \hat{y} - \hat{z});$$



Figure 2.7: Primitive basis vectors of the face-centered cubic lattice.

We'll see shortly that these are primitive translation vectors of a body-centered cubic (bcc) lattice in the direct space. So the bcc lattice is reciprocal to the fcc lattice.

As shown in Fig. 2.8, the conventional cell of bcc lattice is still cubic. Eight lattice points are in the corners of cubic and one is in the center of cubic. Two lattice point belong to the unit cell. The primitive translation vectors of the bcc lattice (Fig. 2.8) are

$$\vec{a}_{1} = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z});$$

$$\vec{a}_{2} = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z});$$

$$\vec{a}_{3} = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z});$$

Again, the primitive translations of the reciprocal lattice can be calculated from Eq.(2.3)

$$\vec{b}_1 = \frac{2\pi}{a}(\hat{y} + \hat{z});$$



Figure 2.8: Primitive basis vectors of the body-centered cubic lattice.

$$ec{b}_2 = rac{2\pi}{a}(\hat{x} + \hat{z}); \ ec{b}_3 = rac{2\pi}{a}(\hat{x} + \hat{y});$$

Note by comparison with Eq. (2.7) that these are just the primitive vectors of an fcc lattice, so that an fcc lattice is the reciprocal lattice of the bcc lattice.

Other crystal structures are not going to be discussed in this thesis. Further reading can be found in the classical textbook written by C. Kittel [34] and in reference [35].

2.2 X-ray Diffraction

The crystal structure can be studied by X-ray diffraction [36], which depends on the crystal structure and on the wavelength of X-rays. When the wavelength of the radiation is comparable with or smaller than the lattice constant, the incident X-ray beam may be diffracted by the crystal.

2.2.1 The Bragg's Law and Laue's Equations

W. L. Bragg presented a simple explanation of the diffracted beam from a crystal. Consider parallel lattice planes spaced d apart as shown in Fig. 2.9. The radiation is incident in the plane of the paper. The path difference for rays reflected from adjacent planes is $2d \sin \theta$, where θ is measured from the plane. The angle between the diffracted beam and the transmitted beam is always 2θ . This is known as the diffraction angle, and it is this angle, rather than θ , which is usually measured experimentally. Constructive interference of the radiation from successive planes occurs when the path difference is an integral number of n of wavelengths λ , so that

$$2d\sin\theta = n\lambda\tag{2.7}$$

This is the Bragg law. Because $\sin \theta$ can not exceed unity, Bragg reflection can occur only from wavelength $\lambda \leq 2d$. Bragg law is a consequence of the periodicity of the lattice. Although the reflection from each plane is specular, for only certain values of θ the reflections from all parallel planes will add up in phase to give a strong reflected beam.



Figure 2.9: Derivation of the Bragg law $2d\sin\theta = n\lambda$ for the diffraction of X-rays by a crystal. d is the spacing of parallel atomic planes.

Bragg's law describes diffraction in terms of a scalar equation. Crystals are, in general, three-dimensional. To describe the diffracted beam directions, the equations

needed to be expressed in terms of vectors.

We have defined a vector \vec{H} in the reciprocal lattice in terms of the reciprocal axes $\vec{b_1}, \vec{b_2}, \vec{b_3}$

$$\vec{H} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 \tag{2.8}$$

where hkl are Miller indices. Vectors \vec{H}_{hkl} drawn for all values of the indices hkl form the reciprocal lattice with repetition vectors $\vec{b}_1, \vec{b}_2, \vec{b}_3$.

By using the vector \vec{H}_{hkl} it is convenient to express the Bragg law in vector form. If $\vec{k} = 2\pi/\lambda$ and $\vec{k'}$ are the wave vectors of incident and diffracted beams, we construct them making angles θ with the diffracting planes as illustrated by Fig. 2.10. The Bragg law in vector form is then given by

$$\vec{Q} = \vec{k} - \vec{k'} = \vec{H}_{hkl} \tag{2.9}$$



Figure 2.10: Typical scattering geometry showing the incident, diffracted and scattering wave vectors $\vec{k}, \vec{k'}$, and $\vec{Q} = \vec{k} - \vec{k'}$.

To see that Eq.(2.9) is equivalent to the Bragg law, note that $|H_{hkl}| = 2\pi/d_{hkl}$ and $|\vec{Q}| = \frac{4\pi}{\lambda} \sin \theta$ from the geometry of Fig. 2.10. Substitute these two equations into Eq.(2.9), one obtains

$$\frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{d_{hkl}}$$

i.e. $2d\sin\theta = \lambda$ (2.10)

Eq.(2.10) is just the usual form of the Bragg law.

The Eq. (2.9) may be expressed in another way to give what are called the Laue equations. Take the scalar product of both \vec{Q} and \vec{H} successively with $\vec{a}_1, \vec{a}_2, \vec{a}_3$, we get

$$\begin{aligned} \vec{a}_1 \cdot \vec{Q} &= 2\pi h; \\ \vec{a}_2 \cdot \vec{Q} &= 2\pi k; \\ \vec{a}_3 \cdot \vec{Q} &= 2\pi l. \end{aligned}$$

$$(2.11)$$

These equations have a simple geometrical interpretation. The first equation tells us that \vec{Q} lies on a certain cone about the direction of \vec{a}_1 . The second equation tells us that \vec{Q} lies on a certain cone about the direction \vec{a}_2 . The third equation tells us that \vec{Q} lies on a certain cone about the direction \vec{a}_3 . Thus, at a reflection \vec{Q} must satisfy all three equations. It must lie at the common line of intersection of three cones.

2.2.2 Structure-factor Calculation

Bragg's law and Laue's equations give a neat statement of the condition for the constructive interference of waves scattered from the lattice points to determine the direction of diffraction. Notice that they do not refer to the composition of the basis of atoms associated with every lattice point. We shall see, however, that the composition of the basis determines the relative intensity from a given set of parallel planes.

Although X-rays are scattered in all directions by an electron, the intensity of the scattered beam depends on the angle of scattering. J.J. Thomson first demonstrated that the intensity I is given by

$$I = I_0 \frac{K}{R^2} \sin^2 \alpha, \qquad (2.12)$$

where I_0 is intensity of the incident beam, $K = \frac{e^4}{m^2 c^4}$ is a constant, R is the distance between the electron and the point of observation and α is the angle between the scattering direction and the the direction of acceleration of the electron. Suppose the incident beam is traveling in the x direction towards the origin O and encounters an electron at O (see Fig. 2.11). The scattered intensity at P in the xz plane has a scattering angle of 2θ to the incident beam. The unpolarized incident beam can be resolved into two polarized components, having electric vectors \vec{E}_y and \vec{E}_z where



$$E^2 = E_y^2 + E_z^2$$

Figure 2.11: Classical scattering of an unpolarized primary X-ray beam by a single free electron at the origin.

On the average, \vec{E}_y will be equal to \vec{E}_z , since the direction of \vec{E} is perfectly random. Therefore,

$$E_y^2 = E_z^2 = \frac{1}{2}E^2$$

Since \vec{E} measures the amplitude of the wave and the intensity of a wave is proportional to the square of its amplitude. Therefore

$$I_{Oy} = E_{Oz} = \frac{1}{2}I_O$$

The intensity at P arising from y component of the incident beam is found from Eq.(2.12) to be

$$I_{Py} = I_{Oy} \frac{K}{R^2}$$

since $\alpha = \pi/2$. Similarly, the intensity of the scattered z component is given by

$$I_{Pz} = I_{Oz} \frac{K}{r^2} \cos^2 2\theta$$

since $\alpha = \pi/2 - 2\theta$. Therefore the total scattered intensity at P is obtained by summing the intensities of these two scattered components:

$$I_p = I_{Py} + I_{Pz} = I_O \frac{K}{R^2} \left(\frac{1 + \cos^2 2\theta}{2}\right).$$
(2.13)

This is the Thomson equation for the scattering of an X-ray beam by a single electron. The intensity of scattered beam is only a very small fraction of intensity of the incident beam because of small value of $K(=7.94 \times 10^{-30}m^2)$.

When a monochromatic beam of X-rays encounters an atom with a group of electrons confined to the volume of the atom, two scattering processes occur. Tightly bound electrons are set into oscillation and radiate X-rays of the same wavelength as that of the incident beam, which is called coherent or unmodified scattering. More loosely bound electrons scatter part of the incident beam and slightly increase its wavelength in the process, which is called incoherent or Compton modified. It is the unmodified scattering which gives rise to the Bragg reflections. The modified scattering from different electrons is completely incoherent and produces only a diffuse background.

As shown in Fig. 2.12, the incident beam is in the x direction towards O with wave vector k. The electrons are clustered about point O, the position of each represented by a vector r_n . The point of observation P compared with the distance $|r_n|$ has a large distance R from O. It can be shown that the amplitude of the wave at the point of observation diffracted from an atom containing several electrons is given by

$$E = E_0 \frac{\sqrt{K}}{R} \sum_j \exp i(\vec{k'} - \vec{k}) \cdot \vec{r_j}$$

The quantity represented by the summation is called the atomic scattering factor f,

$$f = \sum_{j} \exp i(\vec{k'} - \vec{k}) \cdot \vec{r_j}$$
(2.14)



Figure 2.12: Scattering by a group of electrons at positions r_n .

To find an expression for the intensity of a diffracted beam the coherent scattering must be considered from all the atoms making up the crystal. Since the crystal is merely a repetition of the fundamental unit cell, it is enough to consider the diffracted intensity from a single unit cell. Qualitatively, the effect is similar to the scattering from an atom.

Relative to a crystal origin at O, the position of the atom of type j in unit cell $u_1u_2u_3$ is given by vector $R_j(u_1u_2u_3) = u_1\vec{a}_1 + u_2\vec{a}_2 + u_3\vec{a}_3 + \vec{r}_j$. By summing over j to include all the atoms in a unit cell, and summing over $u_1u_2u_3$ to include all the unit cells, the amplitude of diffracted field at the point of observation is expressed by

$$E \propto \sum_{j} f_{j} e^{(\vec{k'} - \vec{k}) \cdot \vec{r_{j}}} \sum_{u_{1}} e^{(\vec{k'} - \vec{k}) \cdot u_{1} \vec{a}_{1}} \sum_{u_{2}} e^{(\vec{k'} - \vec{k}) \cdot u_{2} \vec{a}_{2}} \sum_{u_{3}} e^{(\vec{k'} - \vec{k}) \cdot u_{3} \vec{a}_{3}}$$

Here we define the structure factor S which involves the positions r_j of the different atoms in the unit cell as

$$S = \sum_{j} f_{j} \exp[(\vec{k'} - \vec{k}) \cdot \vec{r_{j}}]$$
(2.15)

2.2.3 Fourier Series Methods in Structure Determinations

Another method to represent a crystalline structure is to use Fourier analysis to determine the scattering intensity from the basis of atoms. From Eq. (2.2), a crystal is invariant under any translation of the form $\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$. Any local physical property of the crystal is invariant under T. For example, the electron number density

 $n(\vec{r})$ is a periodic function of \vec{r} , with periods $\vec{a}_1, \vec{a}_2, \vec{a}_3$ in the directions of the three crystal axes. Thus

$$n(\vec{r} + \vec{T}) = n(\vec{r})$$
 (2.16)

Such periodicity creates an ideal situation for Fourier analysis. The most interesting properties of crystals are directly related to the Fourier components of the electron density.

We consider first a function n(x) with period a in the direction x, in one dimension. We expand n(x) in a Fourier series of sines and cosines:

$$n(x) = n_0 + \sum_{p>0} [C_p \cos(2\pi px/a) + D_p \sin(2\pi px/a)]$$
(2.17)

where the p's are positive integers and C_p , D_p are real constants, called the Fourier coefficients of the expansion. The factor $2\pi/a$ in the arguments ensures that n(x) has the period a. We say that $2\pi p/a$ is a point in the reciprocal lattice or Fourier space of crystal. The reciprocal lattice points tell us the allowed terms in the Fourier series Eq. (2.17). It is great convenience to write Eq. (2.17) in the compact form

$$n(x) = \sum_{p} n_p \exp(i2\pi p x/a),$$

where the sum is over all integers p: positive, negative, and zero. The coefficients n_p are now complex numbers.

The extension of the Fourier analysis to periodic functions $n(\vec{r})$ in three dimension is straightforward. We must find a set of vectors \vec{H} such that

$$n(\vec{r}) = \sum_{H} n_H \exp(i\vec{H} \cdot \vec{r})$$
(2.18)

is invariant under all crystal translations \vec{T} that leave the crystal invariant. It will be shown below that the set of Fourier coefficients n_H determines the X-ray scattering amplitude. The inversion of Eq. (2.18) gives

$$n_H = V_c^{-1} \int_{cell} dV n(\vec{r}) \exp(-i\vec{H}\cdot\vec{r})$$

Here V_c is the volume of a cell of the crystal.
When the diffraction condition $\delta \vec{k} = \vec{H}_{hkl}$ is satisfied, the scattering amplitude is determined by

$$S_{hkl} = \int dV n(\vec{r}) \exp[i(\vec{k} - \vec{k}') \cdot \vec{r}] = \int dV n(\vec{r}) \exp(-i\vec{H} \cdot \vec{r}).$$
(2.19)

The quantity S_{hkl} is the structure factor and is defined as an integral over a unit cell.

Often it is useful to write the electron concentration $n(\vec{r})$ as the superposition of electron concentration functions n_j associated with each atom j of the cell. If $\vec{r_j}$ is the vector to the center of atom j, then the function $n_j(\vec{r} - \vec{r_j})$ defines the contribution of that atom to the electron concentration at \vec{r} . The total electron concentration at \vec{r} due to all atoms in the cell is the sum

$$n(\vec{r}) = \sum_{j=1}^{n} n_j (\vec{r} - \vec{r}_j)$$

The structure factor defined by Eq. (2.19) may now be written as

$$S_{hkl} = \sum_{j} \exp(-i\vec{H} \cdot \vec{r}_{j}) \int dV n_{j} \Delta \vec{r} \exp(-i\vec{H} \cdot \Delta \vec{r})$$
(2.20)

over the atoms of a cell and $\delta \vec{r} = \vec{r} - \vec{r_j}$. We now obtain the atomic scattering factor as

$$f_j = \int dV n_j \delta \vec{r} \exp(-i\vec{H} \cdot \delta \vec{r}), \qquad (2.21)$$

We combine Eq.(2.20) and Eq.(2.21) to obtain the structure factor of the basis in the form

$$S_{hkl} = \sum_{j} f_j \exp(-i\vec{H} \cdot \vec{r}_j)$$
(2.22)

This is just Eq.(2.15) if the diffraction condition $\delta \vec{k} = \vec{H}_{hkl}$ is applied. The usual form of this result follows on the writing for the atom j:

$$\vec{r_j} = x_j \vec{a_1} + y_j \vec{a_2} + z_j \vec{a_3}$$

as in Eq.(2.1). Then, for the reflection labeled by hkl we have

$$\vec{H} \cdot \vec{r}_{j} = (h\vec{b}_{1} + k\vec{b}_{2} + l\vec{b}_{3}) \cdot (x_{j}\vec{a}_{1} + y_{j}\vec{a}_{2} + z_{j}\vec{a}_{3})$$
$$= 2\pi(hx_{j} + ky_{j} + lz_{j})$$

so that Eq.(2.22) becomes

$$S_{hkl} = \sum_{j} f_j \exp[-i2\pi(hx_j + ky_j + lz_j)].$$
 (2.23)

The structure factor S need not be real. The scattered intensity will involve S^*S , where S^* is the complex conjugate of S.

In a crystal whose Bravais lattice is simple cubic, consider only one atom is attached to each lattice point. Thus an atom belonging to the cubic cell is at postion 000. According to Eq.(2.23), the structure factor can be expressed as

$$S_{hkl} = f.$$

In a crystal whose Bravais lattice is face-centered, the four atoms in the cubic cell are at positions $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$. If the four atoms have the same scattering atomic factor, according to Eq.(2.23), the structure factor can be expressed as

$$S_{hkl} = f(1 + \exp[\pi i(h+k)] + \exp[\pi i(h+l)] + \exp[\pi i(k+l)]).$$

If m is an integer, $exp(\pi im) = (-1)^m$, hence the above equation becomes:

$$S_{hkl} = 4f$$
, when hkl are unmixed (all odd or all even)
 $S_{hkl} = 0$, when hkl are mixed.

It can be seen that $S_{hkl} = 0$ for all diffraction with mixed hkl. Hence the face-centered Bravais lattice is recognized by the fact that all diffractions with mixed indices are missing.

If a crystal's Bravais lattice is body-centered, the two atoms in the cubic cell occupy the positions 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The structure factor is expressed as a sum over two atoms,

$$S_{hkl} = f(1 + \exp\left[\pi i(h+k+l)\right])$$

and hence,

$$S_{hkl} = 2f$$
, when $h + k + l =$ even.
 $S_{hkl} = 0$, when $h + k + l =$ odd.

The body-centered Bravais lattice is recognized from the fact that all diffraction will be missing for h + k + l = odd.

At high temperature above the critical point our sample Cu_3Au is disordered and has a fcc structure. At lower temperature below its critical point the ordered Cu_3Au has a sc structure. For (100) plane, strong scattering is observed for sc structure but no scattering for fcc structure. Thus measuring (100) Bragg peak allows us to monitor the change of structure in the sample.

Assume that the crystal has the shape of a parallelopipedon with edges N_1a_1, N_2a_2, N_3a_3 parallel to the crystal axes $\vec{a}_1, \vec{a}_2, \vec{a}_3$. The intensity at the point of observation is given by

$$I \propto S^2 \frac{\sin^2[(\vec{k'} - \vec{k})/2 \cdot N_1 \vec{a}_1]}{\sin^2[(\vec{k'} - \vec{k})/2 \cdot \vec{a}_1]} \frac{\sin^2[(\vec{k'} - \vec{k})/2 \cdot N_2 \vec{a}_2]}{\sin^2[(\vec{k'} - \vec{k})/2 \cdot \vec{a}_2]} \frac{\sin^2[(\vec{k'} - \vec{k})/2 \cdot N_3 \vec{a}_3]}{\sin^2[(\vec{k'} - \vec{k})/2 \cdot \vec{a}_3]}$$
(2.24)

Incoherent X-ray Studies of Order-disorder Transition in Cu₃Au

3.1 Introduction

3.1.1 Bragg peaks in Cu_3Au

If Cu₃Au is heated up to a higher temperature than its critical temperature T_c , it has an fcc lattice with each site randomly occupied by either a Cu atom or a Au atom as shown in Fig. 3.1(a). The system is in the disordered state. When the system is rapidly quenched to a certain temperature below the ordering temperature T_c , the ordering process begins due to fluctuations into the low temperature equilibrium phase. When the system is in the ordered state, the Au atoms tend to occupy the corner while the Cu atoms will be at the face sites as shown in Fig. 3.1(b).



Figure 3.1: (a) Cu_3Au is the in disordered state with each site randomly occupied by either a Cu atom or a Au atom. (b) Cu_3Au is in the ordered state: the Au atoms tend to occupy the corner while the Cu atoms are at the face sites

There are two types of reflections when Cu_3Au is illuminated by X-rays. One is independent of the degree of order, they are called fundamental reflections, which are measured as the Bragg peaks of disordered phase. The other are called superstructure reflections which vanish when the order vanishes in the system. So measurement of superstructure reflection is one of the approaches to find the long range order parameter in the ordering system.

The sketch of structure factor of Cu_3Au in reciprocal space is shown in Fig. 3.2. The black dots mark the fundamental reflection which are associated with the fcc structure and appear both in the ordered and disordered phases. The superlattice peaks only appear in the scattering pattern from partially ordered Cu_3Au . The superstructure reflections are disk-shaped while the fundamental reflections are sharp spheres.



Figure 3.2: For Cu_3Au , the superstructure reflections like [100] are disk-shaped and the fundamental reflections like [200] are sharp spheres.

The complicated antiphase domain structure present in ordered Cu_3Au not only broadens the superstructure reflection but causes an *hkl*-dependence [30]. More details of anti-phase domains will be discussed in the following section.

3.1.2 Anti-phase domain walls

Fig. 3.3 shows a transmission electron micrograph of a thin foil of Cu_3Au in a highly ordered state [37]. The domain configuration is seen to consist of a network of rectangular blocks. Diffraction analysis of this area shows that the domain boundaries which appear here as dark lines lie essentially on cube planes which are perpendicular to the plane of the figure, whereas the larger dark areas represent (001) domain boundaries which lie in the plane of the foil.



Figure 3.3: Transmission electron micrograph of a thin foil of Cu_3Au in a highly ordered state.

Fig. 3.4 shows a unit cell of the Cu_3Au superlattice, in which the corners are called the type-I sites, the front and back faces are the type-II sites, the left and right side faces are type-III sites while the top and bottom faces are called type-IV sites. If all the gold atoms occupy the type-I sites this type of domain will be designated as type-I domain. Similarly, domains in which all of gold atoms occupy the type II, III and IV sites will be designated as type-II, III and IV domains, respectively.



Figure 3.4: Unit cell of the Cu₃Au superlattice, type-I, II, III, IV sites are shown in the schematic.

When a crystal orders, it is likely that the ordering starts at a large number of positions throughout the crystal. Hence there can be neighboring regions in which there has been a different choice of copper and gold atoms on the four fcc sites. This situation is illustrated schematically by Fig. 3.5. In the left side of the figure, all of gold atoms occupy the corner sites whereas the face centered sites are occupied by copper atoms. Similarly, in the right side of figure, all of gold atoms occupy a face centered site while the other sites are occupied by copper atoms. If a region adjoins another region of different type, an anti-phase boundary is formed between them shown as dashed line in Fig. 3.5.

There exists an infinite variety of anti-phase domain boundary(APDB) configurations as defined by the relation between the plane of the boundary and the displacement vector. However, certain configurations are energetically favorable [23]. There will, in general, be two ways of forming boundaries on cube planes. The first type is formed by the first kind of out-of-step vector, $\frac{1}{2}\vec{a}\langle 110\rangle$, lying in the boundary plane,



Figure 3.5: In the left side and right sides, the copper and gold atoms have different choices of the fcc sites. An anti-phase boundary is formed when those two different regions meet.

as shown in Fig. 3.6(a). This type of boundary is also termed type-I domain wall. On the other hand, the second type is formed by the second kind of out-of-step vector lying in either of the cube planes perpendicular to the boundary plane, as shown in Fig. 3.6(b). There are two possibilities to form second kind of boundary. The out-of-step vector can lie on either of front face or bottom face. The second type of boundary is also called type-II domain walls. [24, 25]

An important feature of the first type of boundary is that gold atoms do not come in contact across the boundary, and thus it is expected to be of lower energy. The second type of boundary, however, causes a chance for two gold atoms to occupy nearest neighbor positions across the boundary and is expected to be of somewhat higher energy than the first type of boundary.

The growing domain structure is often studied by means of the scattering intensity, whose width is proportional to the inverse of the average domain size $R(\tau)$. The dynamics of the system can be characterized by the average domain size $R(\tau)$ in the form of a time-independent scaling function [38]. The time dependence enters only through the characteristic length, which grows with a characteristic power law, $R(\tau) \sim \tau^a$ [13, 39]. This scaling hypothesis has been found to apply to a large range



Figure 3.6: (a) Type-I domain wall: it's formed by a displacement of $\frac{1}{2}\vec{a}\langle 110\rangle$ in the boundary plane. (b) Type-II domain wall is formed by a displacement of $\frac{1}{2}\vec{a}\langle 10\vec{1}\rangle$ in either of the cube planes perpendicular to the boundary plane. The arrows show the directions of the displacements.

of systems. For example, for systems described by a non-conserved order parameter, often called model A, one expects $a = \frac{1}{2}$. Model B refers to systems in which the order parameter is conserved. For this kind of systems, $a = \frac{1}{3}$.

3.1.3 The dynamics of first order phase transition

If a system is rapidly quenched from a one-phase, thermal equilibrium state to a nonequilibrium state inside its coexistence curve (Fig. 3.7), such a quenched system then gradually evolve from this nonequilibrium state to an equilibrium thermodynamic state [40, 41]. Spatial fluctuations develop in time. This process will lead the initially homogeneous system to the final equilibrium state through a sequence of highly in-homogeneous states which are far from equilibrium.

In the classical theory of first-order phase transitions one distinguishes between two different types of instability which characterize the early stages of phase separation in such systems. The first is the initial decay of a metastable state. This kind of instability involves finite amplitude, localized (droplet-like) fluctuations. The rate of birth of such droplets is described by homogeneous nucleation theory [13]. The



Figure 3.7: The solid line is the coexistence curve and the dashed line presents the classical spinodal curve. The two vertial arrows show the typical quenches from some high temperature about the critical temperature T_c into metastable (m) and unstable (u) regions.

second instability is against infinitesimal amplitude, non-localized (long wavelength) fluctuations. This process causes the initial decay of an unstable state. This latter instability is termed spinodal decomposition [13].

To describe the phase transition, a set of macroscopic variables ϕ_i , i=1,2,...,N, whose dynamical evolution is "slow" compared to the remaining microscopic degrees of freedom can be used. The remaining microscopic ("fast") variables enter only in the form of random forces. The choice of this set of variables is an important issue and in general it includes the order parameter ϕ and hydrodynamic variables. At high temperature, there is no order, and the order parameter $\langle \phi \rangle$ is zero. At a critical temperature, T_c , order sets in so that, for temperatures below T_c , $\langle \phi \rangle$ is nonzero. If $\langle \phi \rangle$ rises continuously from zero, as shown in Fig. 3.8(a), the transition is secondorder. If $\langle \phi \rangle$ jumps discontinuously to a nonzero value just below T_c , as shown in Fig. 3.8(b), the transition is a first-order phase transition.

The general dynamical model can be given in terms of nonlinear Langevin equations for the variables ϕ_i . Assume that the system under study depends primarily upon a single thermodynamic-like field or order parameter, which for generality is



Figure 3.8: Order parameter as a funciton of temperature for (a) a second-order and (b) a first-order transiton.

defined as $\phi(\vec{r}, t)$ [14, 42]. Depending on the problem being considered, this field could be concentration, density, molecular order, or one of many other possibilities. In equilibrium, the spatial configuration of order parameter given by

$$\frac{\delta F(\vec{r},t)}{\nabla \phi(\vec{r},t)} = 0 \tag{3.1}$$

where F is the free-energy functional.

If the system is slightly out of equilibrium, it is natural to guess that the rate at which the system relaxes back to equilibrium is proportional to the deviation from equilibrium. In mathematical expression, it's written like:

$$\frac{\partial \phi(\vec{r},t)}{\partial t} = -M \frac{\delta F(\vec{r},t)}{\delta \phi(\vec{r},t)} + \zeta(\vec{r},t)$$
(3.2)

where the constant M is the atomic mobility and $\zeta(\vec{r}, t)$ is the noise term which is assumed to be a Gaussian random function.

The theoretical model introduced above describes the time evolution of a timedependent field. A simple form, called Landau-Ginzburg free-energy functional describing such a process is given by

$$F[\phi] = \int \left(\frac{\kappa \Delta \phi(\vec{r}, t)^2}{2} + f(\phi)\right) d\vec{r}$$
(3.3)

with $f(\phi)$, the potential density, being equal to:

$$f[\phi] = \frac{r\phi^2}{2} + \frac{u\phi^4}{2}$$
(3.4)

An essential feature of this free energy density is that above a critical point it has a single well structure and below a critical point it has a double well structure (see Fig. 3.9). This double well describes the equilibrium situation in which two phases coexist. The Eq.(3.3) and Eq.(3.4) completely define the dynamics of a system in which the final state is doubly degenerate. The binary alloy studied in the thesis, Cu_3Au is a system that can be described by such a model when it undergoes an order-disorder phase transition. The only important particular aspect is the fact that the final, ordered state is not doubly degenerate but four-fold degenerate [43].



Figure 3.9: The free energy density versus the orderparameter for temperature above a critical point (a single well structure) and below the critical point (a double well structure).

3.1.4 X-ray Intensity Fluctuation Spectroscopy(XIFS)

When a laser light illuminates a disordered material the diffraction pattern will show a graininess known as speckle. This is an effect caused by the inherent coherent property of laser light. This leads to a technique called Dynamic Light Scattering or Intensity Fluctuation Spectroscopy. It's been widely used with visible light to study processes such as critical fluctuations near phase transitions in fluids and the diffusion of particles in liquids [44]. But it is not possible to study processes involving length scales less than about 200 nm, or those in opaque materials using visible light. The development of the modern synchrotron X-ray radiation facilities makes it possible to investigate the fluctuations of the structure factor in systems with very small scales. By appropriately collimating an incoherent monochromatic source of high brilliance synchrotron radiation sources one can get sufficient flux to measure the speckle [45, 20]. Now using X-ray intensity fluctuation spectroscopy (XIFS) allows us to obtain direct information about the dynamics of atomic-scale fluctuation of material by measuring the temporal correlations in diffraction intensities [46, 47, 48].

X-ray intensity fluctuation spectroscopy is a diffraction technique. All the knowledge about the conventional X-ray diffraction applies for the this new technique [49, 50]. XIFS adds some new features to the X-ray diffraction and we are now capable to do some experiments which can not be done using conventional X-ray source.

XIFS is an important tool for better understanding the evolution of condensedmatter systems on atomic and nanometer length scales. XIFS examines the temporal evolution of speckle pattern to reveal the underlying structural evolution of the material being studied. In contrast, if the incident beam is not coherent, the speckle is not resolved, and the scattering pattern is determined only by the reflections averaged over a region in the sample.

The prime disadvantage of X-rays over visible light is the much lower intensity levels of x-ray sources. And to eliminate the incoherent average, the scattering volume of the sample has to be restricted to less than the coherence volume of the beam. The experimental difficulty becomes to obtain sufficient diffracted intensity to measure a signal. Fortunately, today's third generation high-brightness synchrotron X-ray sources can be used to meet the requirements. With new synchrotron X-ray sources which are capable of providing coherent X-ray beams many orders of magnitude more intense than previously available, many experiments now are possible to perform.

A unique advantage in scattering with a coherent beam lies in the ability to observe the dynamics of the disorder. It offers the possibility of observing ordering phenomena on length scales as small as 1-10 nm, with no restriction on optical transparency. When the spatial arrangement of the disorder evolves with time, the speckle pattern also changes. The technique of XIFS is simply the observation of the intensity fluctuations at a single point in the speckle pattern to obtain a direct measurement of the dynamics in the system under study.

XIFS can be used to study the dynamics of disorder in systems at equilibrium or nonequilibrium [51]. For equilibrium systems, the exact arrangement of disorder evolves in time but its average distribution does not. The average intensity is constant in time and the fluctuations about this average depend only on the time difference between two measurements. Thus one can use conventional autocorrelation techniques which average over many measurements to obtain the average intensity. In nonequilibrium systems, there is no reason to expect that correlations will depend only on the time difference and so a full two-time correlation function should be used. How to obtain the varied average intensity will be included in chapter 4.

The outline of this chapter is as follows. The experimental set up is described in section 3.2. A brief introduction to the coherent X-rays, the CCD detector and the temperature controller is included. In section 3.3, the main experimental results of incoherent analysis are presented. The details of Bragg peak measured are summerized and the universal scaling law is discussed. Finally this chapter is concluded in section 3.4.

3.2 Experimental details

The experiments reported in this thesis were performed at beamline IMMY/XOR of the Advanced Photon Source at Argonne National Laboratory. A typical experimental setup is shown in Fig. 3.10. A monochromator is used to select the required wavelength. To obtain partially coherent X-rays, the beam is then restricted to a certain size by going though two collimation slits. The slits are chosen to be an aperture of $5\mu m$ in horizontal direction and $10\mu m$ in vertical direction. The X-ray beam illuminated on the sample is monochromatic and has a desired small size. The diffraction pattern is recorded by CCD detector [52, 53] installed on the path of scattered X-rays. This setup provides 7.66 keV X-rays having a relative bandwidth $\Delta \lambda / \lambda = 6.2 \times 10^{-5}$ and a flux of $\sim 2 \times 10^{12}$ photons per second per mm^2 for a storage ring current of



Figure 3.10: A schematic of the coherent X-ray spectrometer. The arrows show the path the X-ray light. The synchrontron X-ray is reflected by two monochromators to select the disired wavelength. The nearly monochromatic X-ray is restricted to a certain size by the apertures to obtain partially coherent X-ray. Then the coherent X-ray is illuminated on the sample and the diffacted X-ray is collected by CCD detector.

A furnace was used to rapidly quench the the sample temperature from 420°C to three final temperatures 378°,C 370°C and 355°C and was held at final temperature for several hours. At the same time X-rays illuminated the sample and the diffraction patterns were recorded by the CCD detector. The two dimensional [100] superlattice Bragg peak was saved as images every eight seconds or every four seconds. This is the continuation of work done by Andrei Fluerasu. See his paper and Ph.D. thesis [54, 55] for detailed description of his work.

3.2.1 Coherent X-rays

As one of the properties of light, there are two types of coherence: longitudinal coherence and transverse coherence [56, 57]. Longitudinal coherence means that the wave of light interferes with a time-delayed copy of itself. This interfering process will produce fringes in a Michelson interferometer. This phenomenon only happens when the wave and its copy are separated from each other by a distance much shorter than the longitudinal coherence length, which is defined as

$$l_l \approx \frac{\lambda^2}{2\delta\lambda},\tag{3.5}$$

where λ is the wavelength of the light, and $\delta\lambda/\lambda$ is the relative bandwidth of the light source. From Eq.(3.5), the longitudinal coherence length increases with the wavelength and inversely with the relative bandwidth of the light source.

In the Young's double-slit experiment, if the two slits are separated much larger than the transverse coherence length, no interference fringes will be seen. If the distance between two slits is comparable to the transverse coherence length, the fringes produced by two copies of the wave is observed in the Young's double-slit experiment. The wave is called transversely coherent. The transverse coherence length is given by

$$l_t = \frac{\lambda R_s}{2d_s} = \frac{\lambda}{2\alpha},\tag{3.6}$$

where R_s is the distance from the light source to the observation point, d_s is the source size, and $\alpha = d_s/R_s$ is the opening angle subtended by the source at the point of observation. From Eq.(3.6), the transverse coherence length diverges for a point source. For a source with finite size, the transverse coherence length increases with the wavelength, which makes it possible to observe interference effects at longer wavelengths.

To quantify the coherence of a light source, we need to calculate the statistical correlation between two points of the light source. The electric fields of the two points can be expressed as $\vec{E}(\vec{r_1}, t_1)$ and $\vec{E}(\vec{r_2}, t_2)$ [17, 18]. The mutual coherence function then can be obtained by

$$\Gamma(\vec{r_1}, \vec{r_2}, \tau) = \langle \vec{E}(\vec{r_1}, t_1) \vec{E}(\vec{r_2}, t_2) \rangle, \qquad (3.7)$$

where the time difference $\tau = t_2 - t_1$ and the average can be considered either over the different coherence regions (space) or over time.

The correlation function above can be considered as only depending on the time difference τ because the incident wave usually have constant intensity. A normalized form of the correlation function $\gamma(\vec{r_1}, \vec{r_2}, \tau)$ can be defined as:

$$\gamma(\vec{r_1}, \vec{r_2}, \tau) = \frac{\Gamma(\vec{r_1}, \vec{r_2}, \tau)}{\Gamma(\vec{r_1}, \vec{r_2}, 0)^{1/2} \Gamma(\vec{r_1}, \vec{r_2}, 0)^{1/2}}$$
(3.8)

which is called the degree of coherence. With $|\gamma| = 1$, it is said the source is perfectly coherent. With $|\gamma| = 0$, the source is incoherent. If $|\gamma|$ has some value between 1 and 0, the source is called partially coherent [58].

The partially transversely coherent X-rays are used for the experiments in this thesis. The selected wavelength λ is ~ 1.8Å. The distance from the sample to the CCD detector (observation point), d_s is set as 1.17m. The source size d_s are $5\mu m \times 10\mu m$ which is the size of slits as mentioned before. From Eq.(3.6), we can calculate the transverse coherence length is ~ $10\mu m$ for our experimental setup.

3.2.2 Charge-coupled devices(CCDs)

CCD is an area detector for X-ray detection in scattering experiments. For more detailed description of CCD detector, see references [52, 53]. An X-ray photon incident generates a distribution of charges in neighboring pixels on the CCD array. In terms of a double distribution $h(\vec{\Delta}, E)$ and of the average number of detected X-rays $\langle n_d(\vec{r} + \vec{\Delta}, t) \rangle_t$, the average voltage measured $\langle V(\vec{r}, t) \rangle_t$ over time (in analog-digital units (ADU)) can be expressed as

$$\langle V(\vec{r},t)\rangle_t = \sum Eh(\vec{\Delta},E)\langle n_d(\vec{r}+\vec{\Delta},t)\rangle_t$$
(3.9)

where the number of charges collected in ADU is proportional to E and $\vec{\Delta}$ is the distance (in pixel units) from the central pixel where the photon strikes the silicon chip. The sum of $h(\vec{\Delta}, \vec{E})$ over all \vec{E} yields the average spatial distribution of total induced charges, and the sum over all $\vec{\Delta}$ gives the distribution of charges induced by an X-ray.

In the absence of X-ray illumination, a leakage current occurs in the CCD, and an offset voltage is introduced in the A/D process. So an estimate of the dark contribution has to be subtracted from measured signal $V_m(\vec{r}, t)$. Thus, the corrected signal is the measured signal minus the detector signal:

$$V_c(\vec{r},t) = V_m(\vec{r},t) - V_d(\vec{r},t)$$
(3.10)

Both the signal and the dark measurements have noise. An estimate of the variance

 $S_d^2(\vec{r}, \delta t)$ of dark can be obtained by making several (N_d) measurements. To reduce the noise introduced by dark correction, and average over a number of dark frames N_d can be performed and the resulting pattern is then subtracted from the data frames. If this dark signal is averaged over N_d readouts of the same duration as V_m , the variance due to electronic noise of $V_c(\vec{r}, t)$ then becomes

$$S_{c}^{2}(\vec{r},\delta t) = S_{m}^{2}(\vec{r},\delta t) + \frac{1}{N_{d}}S_{d}^{2}(\vec{r},\delta t)$$
(3.11)

In this thesis, direct illumination (DI) CCD detector of a 1152×1242 normal silicon (NS) (in unit of pixels) is used to record the scattered X-rays. From DI CCDs, both high spatial resolution and relatively low noise are obtained. This detector has a resolution of slightly longer than one pixel ($20\mu m$), which can give excellent results for the observation of speckles with a typical size of ~ $20\mu m$. To eliminate the dark contribution and reduce the noise caused by dark correction, ten measurements of dark are made. The average of ten measurements is calculated and subtracted from the original data to obtain the signal of X-rays.

3.2.3 Temperature control of sample

As we pointed out before, the sample Cu_3Au undergoes a first-order phase transition when quenched from a higher temperature above the critical temperature to some temperature below it. To study the ordering process in the sample, a temperature controller is required to heat up the sample to some temperature above the critical point and cool it down to some temperature below the critical point rapidly. The final temperature should be reached without any significant oscillations (over or under shooting) to avoid any effects on the kinetic process in the sample. The system will be kept at constant final temperature for long time when the ordering process is going on in the sample. It is also critical to have the final state stable.

A furnace was designed and built by Andrei Fluerasu [55] to control the temperature of the sample as presented schematically in Fig. 3.11. From the left of the figure, the first block stands for the water-cooled copper post as a heat sink. Next to it is a layer of mica which thickness will decide the maximum temperature the furnace can reach with the maximum heating power and the maximum cooling power. The main part of the furnace is a Boron-Nitride coated pyrolytic graphite heater, which is connected to a power supply. Then there is a layer of tungsten buffer block where the sample is mounted. The whole system is placed in a vacuum chamber with a window facing the sample. The X-rays illuminate on the sample through the window. This arrangement can increase the temperature stability and maximum temperature for a given heating power. This furnace is able to cool down the sample at a rate of about 0.2° C/s.



Figure 3.11: The schematic of the furnace used to control the sample temperature. The whole system is mounted in a vacuum chamber with a window to let the X-ray in.

To control the temperature of the sample the Kalman-Predictive-Proportional-Integral-Derivative (KPPID) algorithm is applied. The detailed description of KPPID algorithm can be found in reference [54].

Proportional-Integral-Derivative (PID) algorithm functions well and is used widely in controlling systems. For a good temperature controller, the error function, e(t), which is the difference between the target temperature and the measured temperature, has to be minimized. A PID feedback algorithm is applied to control the heating power P(t) by the formula

$$P(t) = K_p \left(e(t) + \frac{1}{T_i} \int_0^t e(t) dt + T_d \frac{de(t)}{dt} \right)$$
(3.12)

The PID controller thus consists of three components, each with its own distinctive function to fulfill certain control objectives. The coefficient K_p is the gain of the feedback circuit, T_i is the integral time constant, and T_d is the derivative time constant. Together, they control and determine the response of the system. The proportional term (K_p) is the main term which determines the response time, but without an integral correction, it would produce a steady state error. The integral term eliminates the steady-state error but makes the transient response worse. The derivative term improves the transient response by reducing the over or under shooting and reducing the response time. However, the derivative term has to be reduced or canceled in systems with appreciable noise on the temperature readings.

A thermal model for the sample furnace is used to calculate an optimal power profile as the PREDICTIVE power output, also referred as feedforward. By doing this, the corrections made by PID feedback system are small. This will minimize the problems when the PID feedback algorithm attempts to cancel large differences between the set values and the measured values.

To reduce the noise produced by temperature probe and measure the temperature precisely, a Kalman filter is used to estimate the sample temperature. If there are two estimates T_1 , T_2 with standard deviations σ_1 , σ_2 for the sample temperature, then a better estimate for the actual value of temperature is given by the weighted average:

$$T_{kal} = \frac{\sigma_2}{\sigma_1 + \sigma_2} T_1 + \frac{\sigma_1}{\sigma_1 + \sigma_2} T_2$$
(3.13)

This estimate is better because its standard deviation σ_{kal} is smaller than either σ_1 or σ_2 :

$$\frac{1}{\sigma_{kal}} = \frac{1}{\sigma_1} + \frac{1}{\sigma_2} \tag{3.14}$$

The two estimates could be the sample temperature calculated from the thermal model (theoretical value) and the measured value of temperature. Because the calculated temperature is subject to systematic errors. A second Kalman filter is used to compensate the systematic errors. A correction term, ΔT is estimated using the error of the first stage Kalma filtering $(T_{kal} - T_{meas})$. Eventually the temperature is determined as $T = T_{kal} + \Delta T$.

One example of the temperature quench profile is shown in Fig. 3.12. The sample temperature is cooled down from 420°C to 355°C rapidly with little under shooting. The sample temperature is kept at final temperature steadily for over ten hours. The inset figure presents the temperature quench more directly. It can be seen that the quench is finished in about four minutes. The final temperature is reached nearly perfectly and only very small under shooting is observed.



Figure 3.12: One example of the temperature quench profiles from 420° C to 355° C is shown. The inset figure shows the temperature profile for the first twenty minutes with little under or over shooting.

3.2.4 X-ray signals in early time

The experiments we have done benefit greatly from the development of third generation of synchrotron X-ray source. Compared to the conventional X-ray sources, high brilliant synchrotron radiation facility can provide X-ray light which is 10^{13} times brighter. It allows us to study the early stage of the sample when the ordering is low.

In Fig. 3.13, the intensity turn-on is shown for the first twenty minutes whereas the whole ordering process was observed for as long as ten hours. The quench line is the temperature profile. The vertical line marks the time when the critical temperature point (383°C) is crossed. We've selected four different regions from the image of Bragg peak as in Fig. 3.14. The averaged intensity over the four regions is plotted for three final temperatures. There is a clear intensity increase at the critical point for all three temperatures. In other word, the signal is detected at the critical point when the system just starts ordering. Except for the first few minutes after the quench, the sample is at constant temperature for the rest of the measurements as required.

3.3 Experimental results

A two dimensional X-ray scattering scans is presented in Fig. 3.14 when Cu_3Au is in partially ordered state. The x-axis, we often call the longitudinal direction, is in (h00) direction. The y-axis, also called the transverse direction, is in (0k0) direction. It can be seen that a wide range of wave vectors in reciprocal space is covered by the CCD detector. The darks (the background of CCD camera) [52, 53] have been carefully subtracted. The superlattice Bragg peak has the shape of a thin disk as expected. The width is wider in transverse direction while it's narrower in longitudinal direction.

The intensity distribution in terms of the variables $h_1h_2h_3$ for an *hkl*-superstructure reflection can be expressed as [30, 59]:

$$I(h_1h_2h_3) = F^2 \frac{\sin^2[\pi N_1h_1]}{(\pi h_1)^2} \frac{N_2\gamma}{\gamma^2 + (\pi h_2)^2} \frac{N_3\gamma}{\gamma^2 + (\pi h_3)^2}$$
(3.15)

where $(h_1h_2h_3)$ represents the departure of the tip of the diffraction vector from the



Figure 3.13: The quench line is the temperature profile. The vertical line marks the critical temperature point (383°C). The four curves show a clear intensity turn-on at the critical point for all three temperatures. The different color represents the different region in the CCD detector and symbols just lable different curves.



Figure 3.14: Disk-shaped superlattice Bragg peak is shown. The two lines on the top mark the directions in the reciprocal space.

reciprocal lattice point hkl. F is the structure factor as usual. $N_1 N_2 N_3$ are numbers of unit cells in three dimensions respectively. γ is the probability of crossing a domain boundary in the length of lattice constant a.

It's obvious from Eq.(3.15) that h_1 and h_2 are the indices of equal parity. The intensity distribution has the shape of a thin disk, the plane of the disk being the h_1h_2 -plane, which is the longitudinal scan in our data. The thickness of the disk is determined by the crystal dimension N_3a_3 , presented as the transverse scan of our data. The radius of the disk increases with the probability γ of antiphase boundaries.

We see the graininess in Fig. 3.14 as a consequence of partial coherent X-ray scattering. This is called speckle which will be discussed in detail in chapter 4. For one-time (incoherent) analysis we have to average this fluctuating intensity to get a smoothed image, i.e. to smear out the speckle. A couple of approaches were tested to obtain the averaged incoherent X-ray scattering. For two dimensional Gaussian profile the tail is a bit too short while the squared Lorentzian fit profile has a too long tail. A two dimensional Strawitzky-Golay(SG) smoothing filter [60] gave the best estimate of the average scattered intensity.

The two dimensional SG smoothing filter was used by Andrei Fluerasu [55]. The basic idea behind a SG filter is to use a polynomial form in order to least-squares fit the data in a window that is large enough that the fits are not affected by the fluctuations and small enough that the particular polynomial form chosen does not bias the evaluated, fitted, quantity. If the window is too big, we will miss some of the line shape of the Bragg peaks. If the window is too small, the intensity will still look fluctuating. More details about how to choose the box size can be found in the following chapter. In practice, we use a 21×21 or 41×41 pixels window with 3rd order polynomial form to find the incoherent intensity at a particular location of the two-dimensional Bragg peak. This location is in the center of the window. The data in the window is considered to be the incoherent scattered intensity for that particular location.

In this thesis, two methods were applied: 2D Gaussian fits and Strawitzky-Golay smoothing filters. In this chapter, we're only concerned about the peak height(amplitude), peak width(FWHM) and the position of the peak. The 2D Gaussian fit is easy to perform and provides gook values for these quantities. SG filter well describes the average for the tail and is used when the fluctuation of intensity becomes essential as in chapter 4.

The example fits for various times using these two methods are shown in Fig. 3.15. The solid lines on the top of the coherent scattered intensity are the 2D Gaussian fitting profiles. The dashed lines show the averaged intensity fitted by the SG smoothing filter. The fluctuating lines are the central lines of 2D X-ray scans in Fig. 3.14 for early, middle and late times of the ordering process in Cu_3Au . It can be seen that for the early time the two fitting methods provide almost identical average intensity for the whole range of the wave vector. But for the middle and late times, SG smoothing filters average the intensity in the tail much better than the Gaussian fitting whose tail is too low.

It is important to point out that the fluctuations of the intensity are not the noise. It's the contrast of the speckle that we mentioned before, which is larger than the noise. For example, we take the peak value for time = 372mins in the middle row. It is around 5500 counts and converted to about 48 photons. So the noise is ± 7 photons. The contrast of the speckle is 6000(=8000-2000) counts which makes about ± 24 ADU, which is greater than the noise.

3.3.1 Bragg peak

Using averaged intensity obtained from 2D SG filters, the time evolution of Bragg peak for three final temperatures is plotted in Fig. 3.16. We take the center line of all the images of two dimensional Bragg peak recorded by CCD detector and line them vertically in x-axis. In this three dimensional graph, x-axis is time, y-axis is wave vector and color is the intensity of the Bragg peak whose magnitude is shown in different colors. In this way we can see the change of the Bragg peak in time.



Figure 3.15: The fluctuating lines show the coherent intensity of Bragg peak for three different times. The smooth solid lines are the averaged intensity from Gaussian fitting and the smooth dashed lines show the averaged intensity by SG smoothing filter.

As expected, the Bragg peak gets sharper during the ordering process. For all three temperatures, the peak width(FWHM) becomes narrower and the intensity of Bragg peak grows in time. The curves on the top of graphs present the change of peak width(FWHM) from Gaussian fitting in time.

But it's obvious that when the temperature gets closer to the critical temperature a narrower Bragg peak is observed compared with the other two temperatures. As we know, the width of Bragg peak(FWHM), as a measurement of the average domain size, is inversely proportional to the average domain size in the material. In other words, for shallower quenches (higher final temperature) the system has bigger average domains.

This is the consequence of the competition between the diffusion constant and the thermodynamic force, which in this case is the temperature-dependent free energy difference. The two mechanisms have opposite temperature dependence. The higher temperature will increase the diffusion constant but also decrease the thermodynamic force. Our data shows that the average domain size grows faster for shallower quenches, which suggests that the system under study is in the diffusion-dominated regime. For example, at 400 minutes, the widths of the Bragg peak(FWHM) are 0.0025\AA^{-1} for $T_f = 378^{\circ}\text{C}$, 0.0035\AA^{-1} for $T_f = 370^{\circ}\text{C}$ and 0.0048\AA^{-1} for $T_f = 355^{\circ}\text{C}$.

In Fig. 3.17 the width of Bragg peak(FWHM) is plotted over the time when the ordering in the system is in progress. As stated in previous paragraph, the width of Bragg peak(FWHM) is smaller for a shallower quench than for a deeper quench. For all three quenches, the peak width(FWHM) is decreasing with time . In addition, at the beginning there is a fast change of the peak width(FWHM) while in the late stage the peak width(FWHM) decreases very slowly. It is natural to conclude that the ordering process is much faster in early time but getting slower when the system is closer to the ordered state. After more than five hundreds minutes the system is still not one hundred percent ordered according that the peak width(FWHM) is still decreasing very slowly.

The ratio of peak widths(FWHM) in the longitudinal and transverse directions



Figure 3.16: The center slice of disc-shaped superllattice Bragg peak is plotted against time to show the growing of the Bragg peak. The curves on the top of graphs present the change of peak width(FWHM) from Gaussian fitting in time.



Figure 3.17: The change of peak width is plotted against time for three final temperatures. The solid lines are the peak widths from the fits and the symbols are just to label the curves.

against time is plotted in Fig. 3.18. At the first glance, we can see this ratio is higher for lower final temperature. For all three temperatures, the data shows a quick change of ratio in early time. It's longer for shallow quench and up to fifty minutes for the highest final temperature. After the sudden change of ratio, it can be seen that the ratio is decreasing slowly in time for the two deeper quenches, while the ratio is steadily constant for the shallow quench.

As we know, the ratio of peak width(FWHM) in the longitudinal and transverse directions is a measure of the ratio of type-II and type-I domain walls densities in the sample. We can conclude that the type-I domain walls are predominant as expected because of its relative lower energy than the type-II domain walls. The different behavior between the higher final temperature and lower final temperatures suggests that the formation of domain walls may have different mechanism in two cases. It seems that it is more complicated process for lower temperatures because there is a different time behavior for the type-II and type-I domain walls. For the higher temperature, only the growth of the domains is involved by sacrificing the small



Figure 3.18: The ratio of peak widths(FWHM) in the longitudinal and transverse directions against time is plotted. The solid lines are the peak widths from the fits and the symbols are just to label the curves.

domains.

Another highly related and interesting property is the integrated intensity. From Fig. 3.14, we know that the Bragg peak is disk-shaped with two identical transverse scans and one longitudinal scan. So the integrated intensity is calculated by the product of the fitted amplitude, the fitted longitudinal width and the fitted transverse width squared. In this way, we can partially compensate the missing counts in the tail which are not measured by the CCD detector when the Bragg peak is wide and out of the range of the CCD detector. In Fig. 3.19, the integrated intensity is plotted again the evolution of the time. Here we see again the difference between the higher final temperature and lower final temperatures. For higher final temperature, the integrated intensity is constant through the ordering process except for the very short early stage. For the two lower final temperatures, the integrated intensity shows obvious decreasing tendency in time. This intensity change appears to be related to the relative amount of type-I and type-II domain walls changing as in Fig. 3.18. For



all three temperatures, integrated intensity increases rapidly to the highest value in ten to twenty minutes.

Figure 3.19: The integrated intensity is calculated by the product of the fitted amplitude, the fitted longitudinal width and the fitted transverse width squared and plotted against the time. The symbols are just to label the curves.

From the simple mean-field theories for an Ising model, Monte Carlo simulation of the ordering process and the experimental data [39, 61, 62, 27], it may be argued that the integrated intensity should be constant. The sudden increase of integrated intensity in early time can be explained as follows. In the early time, the Bragg peak is very broad and out of the measurement range of CCD detector. Even though we've tried to correct this by using the product of the fitted peak height(amplitude), the fitted longitudinal width and the fitted transverse width squared instead of summing all the counts in CCD detector, because of the very low intensity at the beginning, it is difficult to obtain the good fitting results including the amplitude and peak widths in longitudinal and transverse directions. After the abrupt change of intensity in early time, the intensity starts decreasing for the two lower temperatures while the intensity is constant for the higher temperature. This is very similar to the results in Fig. 3.18 of the ratio of the Bragg peak widths, which suggests that the ratio of peak widths affects the results of integrated intensity. In other words, as we pointed out above, it might be related to the evolution of the two types of domain walls in the sample during the ordering process.

It also worth while to discuss the change of the peak position during the ordering process in the system. The move of the peak position in time is plotted in Fig. 3.20. The behavior is similar for three quenches. There is a dramatic change of peak position in the early time. The move of the peak position becomes steady after one hundred minutes. The change of peak position (referred as $q - q_0$ in the figure) is increasing all the time for our measurement. This is the the direction where the Bragg angle increases in our experiments. As we know the Bragg angle θ is inversely proportional to the lattice constant a,

$$2a\sin(\theta) = n\lambda\tag{3.16}$$

It can be concluded that the lattice constant of Cu_3Au is shrinking in some way. In other words the distance between the atoms is getting slightly smaller during the ordering process.



Figure 3.20: The move of the peak position in time is plotted for three final temperatures.

The change of peak position was explained by Andrei Fluerasu [55] in his Ph.D. thesis. He interpreted it as a change in the average lattice constant caused by the domain walls. The volume fraction associated with the domain walls is proportional to the increase of the lattice constant. During the ordering process, the domains get bigger and the domain walls get thinner, which will decrease the volume fraction of the domain walls. Hence the average lattice constant approaches its nominal value. He actually proposed an equation to calculate the distorted lattice constant as:

$$\tilde{a} = a \frac{D}{D + (a - L)} \tag{3.17}$$

with the following notations: *a*-lattice constant, D-average domain size, L-average domain wall thickness(see Fig. 3.21).



Figure 3.21: The schematic of the domain in Cu_3Au with the following notations: *a*-lattice constant, D-average domain size, L-average domain wall thickness. The polygon in the center stands for a domain and the black dots are atoms. [55]

From Eq.(3.17), a value L = a would let the lattice undisturbed, $\tilde{a} = a$, a value L < a would "push" the atoms closer together and as a consequence would reduce the lattice constant $\tilde{a} < a$, while a value L > a would increase the lattice constant $\tilde{a} > a$. For our data the lattice constant gets smaller in time which suggests that the domain walls push the atoms closer to each other as time evolves. This means that the domain walls are thinner than the lattice constant.

3.3.2 One-time scaling

It's well known that universal laws exist for the development of long-range order in a system approaching equilibrium after a quench. Scaling describes well the evolution of dynamic process. If scaled by a single length scale, which contains all the time-dependence, the system looks invariant in time. For our sample Cu₃Au which has the nonconserved-order-parameter system (model A), one expect that the characteristic length $L(t) \sim t^{1/2}$ [22].

The characteristic length for Cu_3Au is the average domain size of ordered domains. This value is inversely proportional to the peak width (FWHM) of the Bragg peak in our measurement. As already mentioned in the previous section, 2D Gaussian fit is used to obtain the peak width(FWHM) for the dynamic process.

To test the power scaling law, the average domain size, i.e. the inverse of the peak width (FWHM) is fitted to the equation

$$D = R_g t^{1/2} + R_0 \tag{3.18}$$

The parameter $R_g[\frac{A}{min^{1/2}}]$ is a measure of the speed of growth of the ordered domains and R_0 can be interpreted as a droplet size at which the scaling description starts being accurate.

In Fig. 3.22, $(1/FWHM - R_0)$ is plotted against the time in a log scale. The straight line on the top is the fitted data. It can be seen that the data has a slope of 1/2 through the ordering process. The parameter R_g decreases when temperature goes down. This is saying that the process of domains growing is slower at lower temperature. Here the data shows again the diffusion is playing a major role in the ordering process of Cu₃Au.

The structure factor also exhibits scaling of the form[14]

$$S(Q,t) = [L(t)]^{d} \tilde{S}_{\hat{e}}(qL(t))$$
(3.19)

where $\vec{\delta Q} = \vec{Q} - \vec{Q_0}$, $\vec{Q_0}$ is the ordering wave vector, d is the spatial dimensionality, and $\hat{e} = \vec{\delta Q}/\delta Q$. The scaling function \tilde{S} is in general anisotropic, and reflects the structure of the domains and the formation of the domain walls.



Figure 3.22: Scaling law: domain size $t^{1/2}$. The average domain size, i.e. the inverse of the peak width (FWHM) is plotted against the time in a log scale. The straight line on the top is the fitted data from Eq.(3.18).
In Fig. 3.23 the scaled scattered intensity(structure factor squared) is plotted again scaled wave vector in semi-log scale for a few selected times in both longitudinal and transverse directions. Because our data has more than ten percent fluctuation (speckle), the average intensity obtained from SG smoothing filters, instead of coherent intensity was used for the analysis of scaling. It can be seen in Fig. 3.23 that for three final temperatures the scaled intensity is independent of time. Even for the longest Q's where the intensity is low, the scaling law applies very well as seen on a log scale.

In a three dimensional graph, full data of the scaled intensity versus scaled wave vector is plotted against the time in Fig. 3.24. The black lines on the top of image show the contours of rescaled intensity. We can see that the rescaled intensity which has the same value are at the same position over all the time. For the small Q's the black line is perfectly straight. For bigger Q's the lines are although noisy, also straight. This shows the whole line shape scales very precisely.

As of our knowledge, none of the previous data has shown such a beautiful scaling for large range of time, wave vector and temperature. Shannon et. al. [26, 27] studied ordering kinetics in single-crystal bulk Cu₃Au using time-resolved X-ray scattering. Their results showed that the line shape of the scattering function exhibits a crossover from a Gaussian to a Lorentzian squared as the system evolves. There is no such a crossover of the line shape for our data. The normalized intensity $\frac{I}{I_{max}}$ against the rescaled scattering vector $\frac{Q_x}{width_x}$ collapsed on a nearly perfect stationary line shape for our data. We believe the crossover shown in their data comes from the relative low resolution of the scattering geometry they used. Since our resolution is given by the speckle size, around a CCD pixel (22 μm), it has no effect on our diffraction patterns.

3.4 Conclusion

In this chapter, we reported the experimental results of order-disorder phase transition in Cu_3Au using incoherent X-ray. The information about the Bragg peak of Cu_3Au , such as peak height (amplitude), peak widths(FWHM) and peak position, is



Figure 3.23: The scaled scattered intensity(structure factor squared) is plotted again scaled wave vector in semi-log scale for a few selected times (shown as different colors) in both longitudinal and transverse directions.



Figure 3.24: Full data of the scaled intensity vesus scaled wave vector is plotted against the time: (a) $T_f = 378^{\circ}$ C, (b) $T_f = 370^{\circ}$ C, (c) $T_f = 355^{\circ}$ C. The black lines on the top of image show the contour of rescaled intensity.

summarized for three final temperatures. The (100) superlattice Bragg peak has the shape of a thin disk with two long identical longitudinal diffractions and one short transverse diffraction. The Bragg peak gets sharper in time when the ordering is in process in the sample. The amplitude increases, peak widths(FWHM) get narrower and there is slight change of peak position when the time evolves. As a measurement of the ratio of type-I and type-II domain densities formed in the sample, the ratio of peak widths(FWHM) in longitudinal and transverse directions was discussed. The integrated intensity of the three dimensional Bragg peak in time is calculated and discussed for three final temperatures.

The single-time scaling law is tested for our data. It's well known that universal laws exist for the development of long-range order in a system approaching equilibrium after a quench. For Cu₃Au which has the nonconserved-order-parameter(model A), one expect that the characteristic length $L(t) \sim t^{1/2}$. Our data shows that the average domain size (the inverse of the peak width(FWHM)) follows the $t^{1/2}$ line through the whole ordering process for all three final temperatures. The intensity of Bragg peak also shows the beautiful scaling in time for the full range of wave vector and final temperatures we have covered. Coherent X-ray Studies of Order-disorder Transition in Cu₃Au

4.1 Introduction

4.1.1 Speckle pattern in the X-ray spectroscopy

Speckle can be observed when coherent light reflects or scatters diffusely off disordered material. It is well known that laser is the natural coherent source of light [44]. Taking advantage of high-brilliance synchrotron X-ray sources, M. Sutton et al. [45] first demonstrated that one can get sufficient coherent X-ray flux to observe speckle in the diffraction pattern from the system which contains some randomness.

The intensity at each point in the scattering pattern is the sum of light from many different points in the disordered materials with randomly distributed phases. However, since the light is coherent, the phase at each point ends up having a definite value. Where the phases add destructively, it results in a dark spot and where they add constructively a bright spot is seen. Fig. 4.1 is an example of the speckle pattern observed when the partially coherent X-ray beam illuminates on the partially order single crystal of the binary alloy Cu_3Au . If the light is incoherent, the speckle smears and we only see the average of the intensity.

The following argument is based on the section 3.3 of the chapter written by M. Sutton [17]. More details can be found in the reference [17, 18]. The principal result of the section is the intensity-intensity correlation $G^{(2)}$ between two points on the detector \vec{Q} and $\vec{Q} + \delta \vec{Q}$:

$$G^{(2)}(\vec{Q},\vec{Q}+\delta\vec{Q},\tau) = \langle I(\vec{Q},t)I(\vec{Q}+\delta\vec{Q},t+\tau) \rangle$$



Figure 4.1: Speckle pattern in the diffuse scattering from randomly distributed antiphase domain walls in a $\rm Cu_3Au$ single crystal

$$= \langle I(\vec{Q}) \rangle^2 + \beta(\delta \vec{Q}) \mid G^{(1)}(\vec{Q},\tau) \mid^2$$
(4.1)

Where $\beta(\delta \vec{Q})$ is called the coherence factor. $G^{(1)}(\vec{Q},\tau)$ is the electric field-field correlation function for the scattered waves,

$$G^{(1)}(\vec{Q},\tau) = \langle E_s^*(\vec{Q},t)E_s(\vec{Q},t+\tau)\rangle$$
$$= \langle E_s^*(0,0)E_s(0,\tau)\rangle e^{-i\omega_0\tau}S(\vec{Q},\tau)$$
(4.2)

Where the structure factor $S(\vec{Q}, \tau) = \int e^{i\vec{Q}\cdot\vec{r}} \langle \delta\rho(\vec{r_1}, 0)\delta\rho(\vec{r_2}, \tau) \rangle d\vec{r}$ and constants have been ignored for convenience.

Eq.(4.1) and Eq.(4.2) describe how the speckle pattern is produced and how the intensity varies. It is useful to discuss several limits of the Eq.(4.1). First with $\tau = 0$ and $\delta \vec{Q} = 0$, one gets

$$\langle I^2(\vec{Q},t)\rangle - \langle I(\vec{Q},t)\rangle^2 = \beta(0)\langle I(\vec{Q},t)\rangle^2$$
(4.3)

which shows that the variance of the scattering intensity is proportional to the square of the scattering intensity.

According to M. Sutton [17, 18], $\beta(0)$ can be approximated as the ratio of the coherence volume to the scattering volume. Approximately $\beta(\delta \vec{Q})$ is the Fourier transform of the scattering volume V. Thus the speckle size can be estimated as the inverse of the appropriate projection of the beam size, i.e., $d_{det}\lambda/d_{beam}$. d_{beam} is the size of the beam on the sample and d_{det} is the distance to the detector. To obtain the coherent light, the scattering volume has to be comparable to the coherence volume which is usually small. The restriction of scattering volume requires sufficient counts in the light beam which is impossible for the conventional X-ray sources to provide.

Another limit is for $\delta \vec{Q} = 0$ (measuring a single speckle) then Eq.(4.1) can be written as

$$G^{(2)}(\vec{Q},\vec{Q},\tau) = \langle I(\vec{Q}) \rangle^2 + \beta(0) \mid G^{(1)}(\vec{Q},\tau) \mid^2$$
(4.4)

or by defining $g^{(1)} = G^{(1)}(\vec{Q}, \tau) / \langle I(\vec{Q}) \rangle$ and $g^{(2)} = G^{(2)}(\vec{Q}, \vec{Q}, \tau) / \langle I(\vec{Q}) \rangle^2$, Eq.(4.4) becomes:

$$g^{(2)}(\vec{Q},\tau) = 1 + \beta(0) \mid g^{(1)}(\vec{Q},\tau) \mid^2$$
(4.5)

Eq.(4.5) relates the normalized autocorrelations of the intensity measurements $g^{(2)}$ to the normalized autocorrelations of the density $g^{(1)}$. In other words, by measuring $G^{(2)}(\vec{Q},\tau)$ (the speckle intensity as a function of time) the statistical mechanics of the system under study can be investigated. Using X-ray Intensity Fluctuation Spectroscopy, experiments can be done to measure the covariance of intensity readily. Thus XIFS becomes a powerful technique to probe the dynamics of the materials.

4.1.2 Studies on the kinetics of phase transition

As pointed out above, for coherent diffraction, the scattering from an inhomogeneous material displays a characteristic speckled scattering pattern. For instance, when a disordered homogeneous material is rapidly brought to a new set of conditions, corresponding to the coexistence of two equilibrium phases, a spatial pattern of domains of the two phases develops. The random distribution of domains results in the speckle pattern in the scattered intensity. As the domains change shape, the speckle pattern changes and this time dependence of the speckle offers a unique method for studying the evolution of inhomogeneous materials.

The Fourier transform of the order parameter $\phi(\vec{R}, \tau)$, the scalar field describing the inhomogeneity of a specific sample, is related to the scattering intensity by

$$I(\vec{k},\tau) = |\hat{\phi}(\vec{k},\tau)|^2$$
(4.6)

where we ignore the proportionality constant for convenience. The average of $I(\vec{k}, \tau)$ over an ensemble of initial conditions is the structure factor,

$$S(\vec{k},\tau) = \langle I(\vec{k},\tau) \rangle \tag{4.7}$$

Where the ensemble average expresses the distinction between coherent scattering, given by I, and incoherent scattering, given by S.

G. Brown et al. [22] have made simulations and a theoretical study of the fluctuations in the scattering intensity from a nonequilibrium system undergoing phase ordering by domain growth, in which case the order parameter is not constrained by any conservation laws (model A). The relationship between an individual speckle at two different times τ_1 and τ_2 is, on average, described by the intensity covariance,

$$Cov_k(\vec{k},\tau_1,\tau_2) = \langle I(\vec{k},\tau_1)I(\vec{k},\tau_2) \rangle - \langle I(\vec{k},\tau_1) \rangle \langle I(\vec{k},\tau_2) \rangle$$
(4.8)

For random systems, the covariance is maximum in the equal-time limits, $\tau_1 = \tau_2$. As the two measurement times become widely separated, the values of the intensity become stochastically independent and the covariance decays to zero. The normalized analog of the covariance is the correlation function,

$$Corr(\vec{k},\tau_1,\tau_2) = \frac{\langle I(\vec{k},\tau_1)I(\vec{k},\tau_2)\rangle - \langle I(\vec{k},\tau_1)\rangle\langle I(\vec{k},\tau_2)\rangle}{\sqrt{\langle I^2(\vec{k},\tau_1)\rangle - \langle I(\vec{k},\tau_1)\rangle^2}\sqrt{\langle I^2(\vec{k},\tau_2)\rangle - \langle I(\vec{k},\tau_2)\rangle^2}}$$
(4.9)

By choosing a scaled time t given by $t(\vec{k}, \tau) = [kR(\tau)]^2$, the covariance $Cov_k(\vec{k}, \tau_1, \tau_2)$ changes to $Cov(t_1, t_2)$.

A more natural set of variables, the average time $\bar{t} = (t_1 + t_2)/2$ and the time difference $\delta t = |t_1 - t_2|$ are used to express the two-time correlation functions [22]. A constant value of \bar{t} corresponds to a line perpendicular to the $t_1 = t_2$ diagonal and δt measures the distance from the equal time diagonal along a line with constant \bar{t} . The characteristic time difference δt required for the scaled intensity covariance $Cov(t_1, t_2)$ to decay to half its maximum value can be found as a function of \bar{t} . For small value of \bar{t} the relationship between two natural variables is linear $\delta t \sim \bar{t}$ and at large values of \bar{t} , $\delta t \sim \bar{t}^{1/2}$.

An analytic theory is developed by C. Yeung and D. Jasnow [63], which is an extension of the analysis by T. Ohta, D. Jasnow and K. Kawasaki [64, 65]. They predict the form of the correlation function as:

$$F(\delta t, \bar{t}) = \frac{2}{\pi} (2\pi)^{d/2} \int_0^\infty du u^{d/2} J_{d/2-1}(u) \times \arcsin\left\{ \left[1 - \left(\frac{\delta t}{2\bar{t}}\right)^2 \right]^{d/4} \exp\left(\frac{-u^2}{2\bar{t}}\right) \right\}$$
(4.10)

The asymptotic early-time form is,

$$F(\delta t, \bar{t}) \approx \frac{2}{\pi} (2\pi)^{d/2} \left[1 - \left(\frac{\delta t}{2\bar{t}}\right)^2 \right]^{d/4} exp\left(-\frac{\bar{t}}{2}\right)$$
(4.11)

A more useful result in the limit of large \bar{t} is well approximated as:

$$F(z,\bar{t}) \approx \bar{t}^{-1/2} \pi^{(d-3)/2} 2^{(d+3)/2} \left(z \sqrt{\frac{d}{8}} \right)^{(d+1)/2} \times K_{(d+1)/2} \left(z \sqrt{\frac{d}{8}} \right)$$
(4.12)

Where $z = \delta t/\sqrt{t}$, K_n is a modified Bessel function of the second kind. We note that the full result Eq.(4.10) as well as the early-time approximation Eq.(4.11) depends on δt only through the scaling combination $\delta t/\bar{t}$. However, in the asymptotic latetime approximation Eq.(4.12), the natural scaling combination is $z = \delta t/\sqrt{\bar{t}}$. This analytical result is in excellent agreement with G. Brown's numerical simulations.

Similar work for a conserved case (model B) was done by G. Brown et al. [66] to investigate the speckled intensity patterns created by scattering coherent radiation from materials undergoing spinodal decomposition after a rapid change in a thermodynamic parameter such as temperature. For binary systems which obey a local conservation law, the characteristic domain size is known to grow in time τ as $R \sim \tau^a$ with a = 1/3. With two variables $\delta t = k^{1/a} | \tau_2 - \tau_1 |$ and $\bar{t} \sim k^{1/a}(\tau_1 + \tau_2)/2$ the two-time intensity covariance at wave vector \vec{k} can be collapsed onto a scaling function $Cov(\delta t, \bar{t})$, which was found to depend on δt only through $\delta t/\bar{t}$ in the small \bar{t} limit and $\delta t/\bar{t}^{1-a}$ in the large- \bar{t} limit.

The results of the experimental study on the systems with conserved order parameter are consistent with the prediction from theory. A. Malik et al. [10] reported the observation of the dynamics of the speckle pattern during phase separation in a sodium borosilicate glass. Non-equilibrium fluctuation in the structure factor were analyzed using a two-time correlation function to obtain the correlation time. The scaling function W was found to follow a power law $W \sim x^{(1-a)}$, where $(1-a) = 0.65 \pm 0.04$, which agrees with the predicted scaling law $\delta t/\bar{t}^{1-a}$ with a = 1/3 in the large- \bar{t} limit. F. Livet et al. [9] studied AlLi single crystal during the evaporation-condensation coarsening process. Two-time correlation functions were measured. The scaled correlation times versus \bar{t} closely collapse quite well onto the universal form predicted by the theory. At early times, the correlation time grows linearly with time and at late times the correlation time grows as $\bar{t}^{2/3}$ roughly. Other experiments have been performed by K. Ludwig [7] to examine the coarsening kinetic in the classic long-period superlattice Cu-Pd alloy. The evolution of the speckle intensity were measured near the centres of both a superlattice peak and a satellite peak. The decay of the two-time correlation function was independent of the direction examined and was similar for the superlattice and satellite peaks. The correlation time δt increases linearly with average time \bar{t} . However, the power law $\delta t \sim \bar{t}^{1/2}$ was not observed in the large \bar{t} limit. This was interpreted as δt increases much more slowly with increasing \bar{t} than expected. A. Fluerasu et al. [29] has studied order-disorder phase transition and measured the two-time correlation functions in Cu₃Au using X-ray intensity fluctuation spectroscopy. They have found that the scaling form of two-time correlation functions crosses over from linear in \bar{t} to $\bar{t}^{1/2}$.

In this chapter we introduce some theoretical and numerical approaches involved in the data analysis in section 4.2. The line shape of correlation function is discussed and the sizes of box used to obtain the average intensity are examined in this section. In Section 4.3 the main experimental results are presented. Two-time correlation function is calculated and the universal scaling law is tested. Two interesting features, speckle shift and speckle contrast dependence are discussed in detail. This chapter is concluded in section 4.4.

4.2 Theoretical and numerical approaches

4.2.1 Line shape of two-time correlation function

As we mentioned above, Yeung and Jasnow proposed the functional forms of the correlation function Eq.(4.10), Eq.(4.11) and Eq.(4.12) in terms of two natural variables, $\bar{t} = (t_1 + t_2)/2$ and $\delta t = |t_1 - t_2|$. Since the upgrade of IMMY/XOR beamline in Argonne National Lab (more details about the beamline can be found in the experimental method section of chapter 3), we have obtained much better data for Cu₃Au. Accordingly the result of two-time correlation function has been improved greatly. Now it is possible and also worth while to test the line shape of two-time correlation function.

First we programmed Eq.(4.10) for full result and Eq.(4.12) for large- \bar{t} limit to calculate the correlation function. In Fig. 4.2(a), the normalized correlation function $F(\delta t, \bar{t})/F_{max}$ is plotted against δt for several selected \bar{t} . As it is shown in the figure the dashed line corresponds to the full result Eq.(4.10) and the solid line represents the large- \bar{t} limit Eq.(4.12). From the inside to outside, \bar{t} are 2, 10, 20, 30, 60 respectively in the same units as the paper [22]. It can be seen that the two equations give the different results if $\bar{t} < 20$ but the two curves collapse onto each other when $\bar{t} > 20$. So the large- \bar{t} limit is meant to be $\bar{t} > 20$ in the paper [22]. This value is consistent with where the crossover from linear to $\bar{t}^{1/2}$ happens in Fig. 5 of Brown's paper [22]. To see the line shape of the two equations δt is rescaled by dividing the value of δt when the normalized correlation function $F(\delta t, \bar{t})/F_{max}$ falls to 1/2. The rescaled results for the full result Eq.(4.10) and for the large- \bar{t} limit Eq.(4.12) are plotted in Fig. 4.2(b) and (c). From Fig. 4.2(b), the correlation functions have different shapes for the small- \bar{t} and large- \bar{t} limits. The correlation function has a longer tail for large- \bar{t} limit. In Fig. 4.2(c) for large- \bar{t} , the correlation functions collapse onto one curve as expected.

Now we know the correlation functions have different line shapes for the small- \bar{t} and large- \bar{t} limits. Next we want to test how they agree with our data. The experimental data is fitted by Eq.(4.10) in the small- \bar{t} limit, large- \bar{t} limit and Gaussian function as well for comparison. In Fig. 4.3 the experimental and three fitting results are plotted for three different \bar{t} s. The dashed line corresponds to Eq.(4.12) in the small- \bar{t} limit, the solid corresponds to Eq.(4.12) in the large- \bar{t} limit (or Eq.(4.10)), and the dotted line corresponds to the Gaussian fit. All figures show that the form of small- \bar{t} limit fits the data better than the form of the large- \bar{t} limit. Surprising, the Gaussian function almost exactly matches the form of small- \bar{t} limit. Fig. 4.3(b) ($\bar{t} = 295$ mins) is the biggest \bar{t} we can get in order that the correlation function has the tail to test the line shape. Since at this value of \bar{t} the form of small- \bar{t} limit provides the better fitting result than the form of large- \bar{t} limit, the data at this moment is in the range of



Figure 4.2: (a) Normalized correlation function $F(\delta t, \bar{t})/F_{max}$ is plotted against δt for several selected \bar{t} . The dashed line corresponds to the full result Eq.(4.10) and the solid line represents the large- \bar{t} limit Eq.(4.12). From the inside to outside, \bar{t} are 2, 10, 20, 30, 60 respectively in the same time unit as the paper [22]. Normalized correlation function $F(\delta t, \bar{t})/F_{max}$ versus rescaled time difference $\delta t/\delta t_{1/2}$ for the full result Eq.(4.10) in (b) and for the large- \bar{t} limit Eq.(4.12) in (c).

the small- \bar{t} limit discussed in the paper [22]. Because of the small difference between the line shapes of two limits, detailed test of Eq.(4.10) will require even better data.

4.2.2 Estimate of average (incoherent) intensity

One of the main problems for two-time analysis is to calculate the ensemble average of the scattered intensity. In an equilibrium system $\langle I(\vec{Q},t)\rangle$ is expected to be constant in time and can be evaluated simply by averaging $I(\vec{Q},t)$ over a long-enough time interval. However, in a non-equilibrium system $\langle I(\vec{Q},t)\rangle$ changes with time and separating the intensity fluctuations from this changing average is not always straightforward. If the scattering is isotropic, $\langle I(\vec{Q},t)\rangle$ can be evaluated by averaging over intensities at constant Q. This is not our case because of the anisotropy of the superlattice scattering. The other option to calculate the average intensity $\langle I(\vec{Q},t)\rangle$ is least-square fitting.

As we have pointed out in chapter 3, A. Fluerasu in his Ph.D. thesis [55] tested several analytical forms to obtain the average intensity and pointed out that SG smoothing filters provide the best estimate of the average intensity in the tails of the Bragg peak than other fitting profile. Since in this chapter it is important that the fluctuating intensity $I(\vec{Q}, t)$ is well averaged everywhere. SG smoothing filters give an excellent estimate of the average intensity in the whole region of Bragg peak and will be applied in this chapter.

The SG filter uses a polynomial form in order to least-squares fit the data. In practice, a box has to be chosen that is large enough that the fits are not affected by the fluctuations and small enough that the the particular polynomial form does not bias the fitted quantity. To find out what's the best choice of box size, a couple of box sizes are examined.

In Fig. 4.4 two slices of average intensity of Bragg peak using different sizes of box are plotted. Fig. 4.4(a) and (b) correspond to some early time and some late time of the ordering process respectively. Both of them show similar features. In the regions where the intensity is low, the box size doesn't have a big affect on the



Figure 4.3: Experimental and fitting results of correlation functions are plotted for three different \bar{t} : 145mins, 295mins and 442mins. The dashed line corresponds to Eq.(4.12) in the small- \bar{t} limit, the solid corresponds to Eq.(4.12) in the large- \bar{t} limit (or Eq.(4.10)), and the dotted line corresponds to the Gaussian fit.

average intensity. But around the center of Bragg peak the box size 11×11 is too small because from the reported experimental results [27] the incoherent intensity is supposed to be smooth with no fluctuation. We can see the fluctuation remain in the average intensity curve. Box size 21×21 seems still too small and not good enough either. Both of box sizes 31×31 and 41×41 smear out the fluctuation and give similar results. In practice box sizes 41×41 is applied.

4.3 Experimental results

As we pointed out before, the observation of the speckles is the consequence of the partially coherent X-rays. To see the speckle in the scattering pattern, two conditions apply. First the X-ray source has to be coherent or partially coherent. By confining the X-ray beam to finite size so that the transverse coherence length is comparable to the diffraction volume in the sample, we are able to obtain the partially coherent X-rays. Second, because of the small size of the X-ray beam, the X-ray source has to be bright enough so that sufficient scattered X-rays can be collected. Taking advantage of the third generation of brilliant synchrotron X-ray source, the required brightness is provided. Under the two conditions, speckles can be observed.

A closer view of the speckle is shown in Fig. 4.5(a). This is the center region of Fig. 3.14. We can see the bright spots which represent higher intensity and darker spots which represent lower intensity are distributed uniformly in the image. In other words, the intensity is fluctuating over the detector. In Fig. 4.5(b), the average intensity obtained from SG smoothing filters is plotted. There are no bright or dark spots appearing in the image. The intensity changes smoothly over detector. The deviation of the fluctuating intensity $I(\vec{Q},t)$ around average intensity $\langle I(\vec{Q},t) \rangle$ can be seen directly in Fig. 4.5(c) where the center lines of (a) and (b) are plotted. The fluctuating line is the coherent intensity with speckles from (a) and the smoother line is the average intensity from (b). To show the degree of the fluctuation of the



Figure 4.4: Average intensity obtained from SG smoothing filters using different sizes of box. Black lines are original fluctuating intensity. (a) Time=140mins (b) Time=560mins. Box sizes 11×11 and 21×21 are too small and do not provide smooth average intensity. Box sizes 31×31 and 41×41 smear out the fluctuation and give the best estimate of average intensity.

intensity, the normalized intensity $D(\vec{Q},t)$ given by,

$$\frac{I(\vec{Q},t) - \langle I(\vec{Q},t) \rangle}{\langle I(\vec{Q},t) \rangle}$$
(4.13)

is plotted in Fig. 4.5(d). As expected, it looks similar to Fig. 4.5(a) and has the bright spots and dark spots at the same places. The fluctuating line on the top shows the center line of Fig. 4.5(d). It has been rescaled to fit in the image. It can been seen that the normalized intensity is fluctuating up and down about zero. The crests correspond to the bright spots in the image while the troughs are the positions of dark spots.

To demonstrate the time evolution of the speckles during the ordering process, we take the center lines from the two dimensional images at different times and plot them against the time as shown in Fig. 4.6 (waterfall plot). In Fig. 4.6(a), the fluctuating intensity is plotted. We see the straight bright lines and the straight dark lines of speckles are distributed alternately. We know from Fig. 4.5, the bright spots and dark spots represent the crests and the troughs of the fluctuating intensity respectively. In Fig. 4.6(a), the bright or dark lines stay straight in time, which means the speckles mostly stay at the same position during the ordering process. We have seen the time evolution of the average intensity obtained from SG smoothing filter in the chapter 3. It is plotted again in Fig. 4.6(b). The normalized intensity, $D(\vec{Q}, t)$ is plotted in Fig. 4.6(c), also referred to the waterfall plot. It shows the same features as in (a). But Fig. 4.6(c) is just the result of $\frac{(a)-(b)}{(b)}$ or $\frac{(a)}{(b)}-1$, which emphasizes on the deviation of the fluctuating intensity around average intensity. For the early times or larger wave vectors where the intensity is low, we don't see the traces of the speckles in (a) because of the high intensity in the center but still see them (bright or dark lines) follow straight lines in (c). By plotting in this way, we can see that the fluctuations slow down as the system evolves. This phenomenon will be discussed in details in the following section.



Figure 4.5: (a) Fluctuating intensity $I(\vec{Q}, t)$ with speckles uniformly distributed (b) Average intensity $\langle I(\vec{Q}, t) \rangle$ obtained from SG smoothing filters (c) Center lines of (a)(the fluctuating line) and (b)(the smoother line) for comparison (d) Normalized intensity $\frac{I(\vec{Q},t) - \langle I(\vec{Q},t) \rangle}{\langle I(\vec{Q},t) \rangle}$, the fluctuating line on the top is the center line of image(d).



Figure 4.6: (a) Time evolution of the fluctuating intensity. Alternately distributed bright lines and the dark lines show the traces of the speckle. (b) Time evolution of the average intensity obtained from SG smoothing filter. No speckles can be seen. The curves on the top of graph present the change of peak width from Gaussian fitting in time. (c) Normalized intensity, $D(\vec{Q},t)$ (waterfall plot). The traces of speckles stay at the same position during the ordering process.

4.3.1 Two-time correlation functions

The incoherent (average) intensity $\langle I(\vec{Q},t)\rangle$ measures the ensemble average structure factor of the sample. Using partially coherent X-ray beam the speckles are detected as a direct measurement of the exact structure factor of the sample. When the sample gets ordering after the temperature quench, the domains form and grow in time. The dynamics in the sample change during the ordering process. So does the speckles. Measuring the time evolution of the speckles will provide valuable insight about the dynamics of fluctuations in the system under study.

The way to analyze the speckle (the fluctuations in scattered intensity) was proposed by G. Brown et al. [22, 66]. The intensity correlation functions measure twotime correlation functions of the order parameter which is the density of the ordered material. The intensity covariance correlation functions measures the two-time correlations of the density fluctuations. Following their analysis, a correlation function can be defined by,

$$C(\vec{Q}, t_1, t_2) = \langle D((\vec{Q}, t_1)D^*((\vec{Q}, t_2)) \rangle$$
(4.14)

Where the normalized intensity $D(\vec{Q}, t)$ can be expressed as:

$$D(\vec{Q},t) = \frac{I(\vec{Q},t) - \langle I(\vec{Q},t) \rangle}{\langle I(\vec{Q},t) \rangle}$$
(4.15)

With the average intensity estimated from SG smoothing filters, the normalized intensity over time is calculated.

According to Eq.(4.14), the two-time correlation functions for every pair of the times are calculated. To improve statistics, the functions are averaged over a relatively small area (41 × 41 pixels). One typical example of two-time correlation function contour for $T_f = 378^{\circ}$ C is plotted in Fig. 4.7. It is symmetric about the $t_1 = t_2$ diagonal line as expected. The correlation function is the same if the order is switched. The color is brighter, i.e., the correlation is greater when nearer to the diagonal line. This is not surprising because the speckles are more related when the two times are closer to each other. It can also be seen that the correlation time becomes longer when the time evolves, which can be interpreted as the ordering process in the sample is

slowing down with time. You may notice that the correlation time does not increase at the moment that the critical temperature is reached (t=0) but after around fifty minutes. This time delay is actually the consequence of the shift of the speckle position in the early time. We'll discuss in detail the shift of the speckle position and how to correct this in the following section.



T_f=378°C

Figure 4.7: Two-time correlation function contour for $T_f = 378^{\circ}$ C. It is symmetric about the $t_1 = t_2$ diagonal line. The correlation is greater when nearer to the diagonal line. The correlation time becomes longer when the time evolves. Incubation time is as long as around 50 minutes.

In Fig. 4.8, the two-time correlation function are plotted for three selected wave vectors and for the three final temperatures. The row (a) is for $T_f = 378^{\circ}$ C. The row (b) is for $T_f = 370^{\circ}$ C. And the row (c) is for $T_f = 355^{\circ}$ C. Accordingly, each vertical column corresponds to a different wave vector, $dQ = 0.002 \text{\AA}^{-1}$, $dQ = 0.011 \text{\AA}^{-1}$ and $dQ = 0.021 \text{\AA}^{-1}$, respectively. All graphs are plotted with the same scale in the third dimension which means the same color corresponds to the same value even for the different graphs. As a whole, all the graphs have similar features. The two-time correlation functions are symmetric about the diagonal line and the correlation is greater when nearer to the diagonal line. The correlation time becomes longer when the time evolves. But we can also see the difference between the different wave vectors and the different final temperatures. First, there is a temperature-dependence. For the shallower quench ($T_f = 378^{\circ}$ C) the edges of the two-time correlation functions are more rounded while the edges for the other two lower final temperatures are more sharp and straight. Aside from the shape, the correlation also increases as the final temperature decreases. Second, for the two lower final temperatures the correlation has an obvious dependence on the wave vectors and on the time. The correlation increases with the time and decreases with the wave vectors. More details and explanation will be given in the following section.

Similar to the incoherent analysis that the rescaled scattered intensity or the width of the Bragg peak obeys the universal scaling law, the two-time correlation function can also be rescaled to follow an universal form. To test this for our data, two natural variables, the average time $\bar{t} = (t_1 + t_2)/2$ and the time difference $\delta t = |t_1 - t_2|$ are used to express the two-time correlation functions [22].

The two-time correlation function can be expressed in functional forms [22]. We have discussed the line shape of the correlation function in detail in section 4.2.1. For a three-dimensional system, the measured correlation functions are fitted to the form

$$C(\delta t, \tau) = \beta C_{norm}(z_{1/2} * \frac{\delta t}{T})$$
(4.16)

Where the two parameters β is the coherence factor and T, FWHM of the correlation function is the correlation time. The value of z for which C_{norm} falls to 0.5 can calculated numerically, $C_{norm}(z_{1/2} = 1.2597) = 0.5$.

Several cross sections of two-time correlation function in Fig. 4.7 and the fitting results are plotted in Fig. 4.9. The different symbols are for different average time \bar{t} . The curves are the fitting results from Eq.(4.16). It can be seen that the coherence



Figure 4.8: Contours of two-time correlation function for three selected wave vectors and for the three final temperatures. (a) $T_f = 378^{\circ}$ C, (b) $T_f = 370^{\circ}$ C and (c) $T_f = 355^{\circ}$ C. Accordingly, each vertical column corresponds to a different wave vector, $dQ = 0.002 \text{\AA}^{-1}$, $dQ = 0.011 \text{\AA}^{-1}$ and $dQ = 0.021 \text{\AA}^{-1}$, respectively.

factor, i.e., the degree of coherence of the X-ray beam is roughly 12.5%. So the speckle contrast (square root of the coherence factor) is $\sqrt{12.5\%} \approx 36\%$. This is a much higher contrast than 10% that A. Fluerasu [55] reported in his Ph.D. thesis.



Figure 4.9: Cross sections of two-time correlation function for selected average time \bar{t} . The curves are the fitting results from Eq.(4.16). Two variables correlation time T and coherence factor are obtained from the fitting procedure.

The fitted correlation time T versus the average time \bar{t} for several selected wave vectors is plotted in Fig. 4.10. As we stated before, the correlation time increases with the average time. It also can be seen that for the larger average time, the correlation time decreases when the wave vector increases. We can conclude that the ordering process in the system is not uniform everywhere at the same time. The process is faster in the centre of the Bragg peak where the wave vector is small while in the tails of the Bragg peak the process is slow.

To rescale the two variables, the correlation time T and the average time \bar{t} , they



Figure 4.10: The fitted correlation time T versus the average time \bar{t} for several selected wave vectors. Correlation time increases with the average time and decreases when the wave vector increases.

are multiplied by the wave vector squared [22, 55]. According to the Brown et al. [22], the rescaled correlation times follows an universal curve with a slope of 1 in the small \bar{t} asymptotic limit and with a slope of 1/2 in the large \bar{t} asymptotic limit. The rescaled correlation time T against the average time \bar{t} is plotted in Fig. 4.11. We can see the rescaled correlation time T and the average time \bar{t} collapse onto one stationary universal curve with the kink which indicates the transition from linear dependence $T \sim \bar{t}$ to a power law dependence $T \sim \bar{t}^{1/2}$. The dashed line has a slope of 1 and the solid line has a slope of 1/2. In the Figure, a constant value t_0 is subtracted from the average time \bar{t} . t_0 is the delay time as we mentioned earlier and will be explained in the following section. Without the shift of the time origin, the scaling law didn't work. This indicates that the scaling law starts working after the delay time. During the delay time, there might be other mechanism dominant we do not fully understand yet.

In Fig. 4.12, our results on the rescaled correlation time T versus the average time \bar{t} in two directions and for all final temperatures are summarized. The dashed lines



Figure 4.11: Rescaled correlation time T versus rescaled average time \bar{t} collapse onto one stationary universal curve with the kink which indicates the transition from linear dependence $T \sim \bar{t}$ to a power law dependence $T \sim \bar{t}^{1/2}$. The dashed line has a slope of 1 and the solid line has a slope of 1/2.

with a slope of 1 shows that all the data obeys the scaling law for the small- \bar{t} limit. In this data, we only see a little data which follows the solid lines with the slope of 1/2 in longitudinal direction. In transverse direction, the cross over probably happens even later so that we barely see anything. It seems that our experiments do not get to the large average time \bar{t} limit.

The theoretical scaling laws: correlation time T versus \bar{t} from reference [22] is replotted in Fig. 4.13. Two scaling laws for the small- \bar{t} and large- \bar{t} limits are also plotted. The dashed line corresponds to $T \sim \bar{t}$ and the solid line corresponds to $T \sim \bar{t}^{1/2}$. The transition from linear relationship $T \sim \bar{t}$ to $T \sim \bar{t}^{1/2}$ takes place at $\bar{t} \approx 20$ time units as we pointed out before. Our data for $T_f = 378^{\circ}$ C, the crossover happens $\bar{t} * dQ^2 = 0.02$. Because all scaled variables are normalized, one might expect that the crossover is universal. But this is not true for our data. More theoretical work should be carried out to explore the universality of the crossover.

4.3.2 Shift of speckle positions in the early time

We have mentioned that we didn't see any correlations for the early time in Fig. 4.7 because the position of the speckle changed. Assuming the speckles do not change position, it makes sense that we only correlate the speckles at the same position (wave vector), also called the 1Q-2t method. If the speckle moves its position, we are trying correlate the two different speckles which are at the same position at different times. The correlation function will be found to be much smaller than its actual value. To recover the loss of the correlate every pair of the wave vectors and find the maximum of the correlation functions and the position where the maximum is as well. In this way we can not only compensate the speckle contrast but obtain the change of the speckle position.

The correlation functions for a few pairs of times along the line $\bar{t} = 140$ mins are calculated using 2Q-2t method and plotted in Fig. 4.14. In the longitudinal direction (see Fig. 4.14(a)), the position of speckle shifts with time. If the 1Q-2t



Figure 4.12: Rescaled correlation time T versus the average time \bar{t} in two directions and for all final temperatures are summarized. The dashed lines with a slope of 1 shows that all the data obeys the scaling law for the small- \bar{t} limit.



Figure 4.13: Theoretical scaling laws: correlation time T versus \bar{t} from reference [22]. The dashed line corresponds to $T \sim \bar{t}$ and the solid line corresponds to $T \sim \bar{t}^{1/2}$. The transition from linear relationship $T \sim \bar{t}$ to $T \sim \bar{t}^{1/2}$ takes place at $\bar{t} \approx 20$.

method is applied to calculate the correlation functions, the values at dQ = 0 shown as the crosses in the figure are taken as the speckle contrast. It is obvious that these values are much smaller than the true values at the peaks. For the $t_1 = 71$ mins, $t_2 = 69$ mins pair, there is no shift of the speckle position, so the two methods give the same result. From Fig. 4.14(b), it can be seen that no speckle shift is observed in transverse direction.

The waterfall plot is plotted for this quench ($T_f = 378^{\circ}$ C) in Fig. 4.15. We can clearly see the shift of speckle position in the early time. The change of the speckle position obtained from 2Q-2t method is plotted as solid line in Fig. 4.15. It matches with the waterfall plot. The dashed line on the right is the change of the Bragg peak position. Bragg peak position changes at a much smaller scale and it is not clear if it is accounted for the speckle shift. Since the scaling law did not work during the delay time, the ordering process or the formation of domains obeys some unknown law which is different from the predicted scaling law at later times.

The shift of speckle is only longitudinal which is the \vec{Q} direction, so can be inter-



Figure 4.14: Speckle shift in the early time for the shallower quench. Solid lines are the fits. Correlation functions for a few pairs of times along the line t = 140 mins are calculated using 2Q-2t method to compensate the speckle contrast and obtain the change of the speckle position. (a) Longitudinal direction: speckles shift the positions. (b) Transverse direction: no shift of speckle postions.



Figure 4.15: Waterfall plot to show the speckle shift in the early time for shallower quench. Solid line is the change of the speckle position obtained from 2Q-2t method. Dashed line on the right is the change of the Bragg peak position for reference.

preted as the dilation of the domains. Assuming that the original number density is $C(\vec{r})$, the structure factor is given by

$$S(\vec{Q}) = \int C(\vec{r}) \exp(-i\vec{Q}\cdot\vec{r}) d\vec{r}$$

After dilation, the number density becomes $C'(\vec{r}) = C(\lambda \vec{r})$ so that the structure factor for the new structure is given by

$$S'(\vec{Q}) = \int C'(\vec{r}) \exp(-i\vec{Q}\cdot\vec{r})d\vec{r}$$
$$= \int C(\lambda\vec{r}) \exp(-i\frac{\vec{Q}}{\lambda}\cdot\lambda\vec{r})d\lambda\vec{r}/\lambda^{3}$$
$$= \frac{1}{\lambda^{3}}S(\frac{\vec{Q}}{\lambda})$$

It can be seen that after the dilation the wave vector slightly changed by a factor of λ .

The values of the delay time for different final temperatures are plotted in Fig. 4.16. From Fig. 4.16, it is not surprising that the delay time has a temperaturedependence since it exists in every aspect of our analysis. It is interesting that the delay time gets longer as we approach the critical temperature. If we look back the incoherent data, some evidence is in agreement with this observation. First, in Fig. 3.19, the data shows the steep increase of the integrated intensity at the beginning. However, the slope of the curve, i.e., the rate of this increase is the steepest for the lowest temperature and less steep for the highest temperature. This suggests that the ordering process is slower for shallower quench which is consistent with that the delay time is longer for shallower quench. Second, in Fig. 3.13, the measurement of intensity at the the critical point was presented. From this figure, it can be clearly seen that the intensity turn-on takes place later for lower final temperature. In other words, it shows again that the ordering process in early time is slower for higher final temperature. Since time constants for the order parameter get slower near the phase transition, the delay time appears to be related to phase transition kinetics. Further experimental and theoretical work needs to be done to further study this effect.



Figure 4.16: Incubation time for different final temperatures. The origin of time is shifted by the amount of delay time for each final temperature to make the scaling form work. Dash-dotted line is just the guide to the eyes.

The two-time correlation functions calculated using 2Q-2t method is plotted in the upper-left corner of Fig. 4.17. In the lower-right corner, the two-time correlation functions calculated using 1Q-2t method is plotted for comparison. First, most importantly, during the delay time, the result has been improved greatly. The two-time correlation functions is measured and the correlation time starts increasing at the moment that the critical temperature is reached (t=0). Second, we can see that the data is smoother in the upper-left corner than in the lower-right corner. So the 2Q-2t method gives less noisy results than the 1Q-2t method. This is not surprising because more pixels now contribute to the calculation of two-time correlation function.

It is worth to point out that even though a correlation time is now resloved during the delay time, the curvature is still quite different than after the delay time. An obvious bending is seen at the crossover. The correlation time is measured at a smaller scale. This is another evidence that the correlation time during the dalay time is much faster than after the delay.



Figure 4.17: Two-time correlation functions calculated using 1Q-2t method in the lower-right corner and two-time correlation functions calculated using 2Q-2t method in the upper-left corner. Correlation function is recovered during the delay time.

4.3.3 Discussion on the contrast of speckle

The most striking and interesting result is that the contrast of two-time correlation function shows a dependence on the evolution time and wave vector. And it is not surprising that it is temperature-dependent as well. One typical graph showing this dependence is plotted in Fig. 4.18. In this graph, we plot the coherence factor (contrast) versus the average time $\bar{t} = (t_1 + t_2)/2$ for different wave vectors. In general, the contrast increases with time for smaller wave vectors while decreases with time for larger wave vectors. A bump can be seen either obvious or less obvious for each curve. At early times, the contrast does not change much for different wave vectors. But at late times, there is a significant change of contrast when the wave vectors change. For bigger wave vectors, the contrast is as high as 23% which is twice big as the normal contrast (around 12%). For smaller wave vectors, the lowest contrast is 7% which is much less than the normal contrast. The big question is why we sometimes get extra contrast and why sometimes lose the contrast?



Figure 4.18: Wave vector dependence of two-time correlation function in transverse direction for $T_f = 378^{\circ}$ C. At early times, the contrast does not change much for different wave vectors. But at late times, there is a significant change of contrast when the wave vectors change. The symbols simply label the data curves.
The sample Cu₃Au we are investigating has a fcc lattice as shown in Fig. 4.19. The positions of the four atoms 1,2,3 and 4 in the unit cell of the lattice are $\vec{r_j} = (000)$, $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$ respectively. For the (001) Bragg peak, if the wave vector is slightly away from the center in the z direction, i.e. $Q = 2\pi \cdot (0, 0, 1 + \delta l)$, the contribution of the scattered electric field for one unit cell can be expressed as:

$$\vec{E} = \sum_{i=1}^{4} \exp(i\vec{Q} \cdot \vec{r}_{j})$$

= 2 + 2 exp[\pi i(1 + \delta l)]
= 2 exp[i(\frac{\pi}{2} + \varphi)] \{exp[-i(\frac{\pi}{2} + \varphi)] + exp[i(\frac{\pi}{2} + \varphi)] \}, (4.17)

where $\varphi = \frac{\pi}{2} \cdot \delta l$ and the constants are ignored for convenience.



Figure 4.19: Unit cell of Cu₃Au and the positions of the four atoms 1,2,3 and 4 in the unit cell of the lattice: (000), $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}0\frac{1}{2})$ and $(\frac{1}{2}\frac{1}{2}0)$.

In Eq.(4.17), there are two possible phases: $-(\frac{\pi}{2}+\varphi)$ or $\frac{\pi}{2}+\varphi$ varying from domain to domain. These have the same value for cosine and opposite signs for sine. If we introduce some variable $T(x) = \pm 1$, Eq.(4.17) becomes

$$\vec{E}(x) = 2\exp[i(\frac{\pi}{2}+\varphi)][\cos(\frac{\pi}{2}+\varphi) + iT(x)\sin(\frac{\pi}{2}+\varphi)].$$
(4.18)

Therefore the mean intensity can be calculated from Eq.(4.18):

$$\langle I \rangle = \int 2[\cos^2(\frac{\pi}{2} + \varphi) + \langle T(x)T(x')\rangle \sin^2(\frac{\pi}{2} + \varphi)] \exp(i\vec{Q} \cdot xdx).$$
(4.19)

The calculation of mean-square intensity $\langle I^2 \rangle$ is straightforward but tedious and will not be shown here.

Jakeman et al. [67] proposed a theoretical model to investigate the statistical properties of electromagnetic radiation scattered by a randomly grooved surface as shown in Fig. 4.20. They called such a wave a telegraph wave. They calculated the contrast of the intensity pattern for both near- and the far-field geometries. For far-field calculation, they used the following expression of normalized version as the scattered electric field:

$$E = \frac{1}{L} \int_{-L/2}^{L/2} \exp[ik(x\sin\theta + h_0T(x)\cos\theta)]dx$$

= $\cos(kh_0\cos\theta) + \frac{i}{L} \int_{-L/2}^{L/2} T(x)\sin(kh_0\cos\theta)\exp(ikx\sin\theta)dx,$ (4.20)

where L is the dimension of the hard aperture, h_0 is the height of the rectangular grooves. This will directly apply to our scattering.



Figure 4.20: Sketch of a randomly grooved surface from Jakeman's model.

The scattered field is thus expressed as the sum of a constant or unscattered component and a fluctuating part of zero mean. The mean and mean-square intensity for a random telegraph wave with Poisson-distributed crossings are calculated. In the forward direction where $\theta=0$, the results reduce to

$$\langle I \rangle = \cos^2 k h_0 + \sin^2 k h_0 [1/\bar{N} - 1/2\bar{N}^2 + \exp(-2\bar{N})/2\bar{N}^2],$$
 (4.21)

$$\langle I^2 \rangle = \cos^4 k h_0 + \frac{\sin^2 k h_0 \cos^2 k h_0}{\bar{N}^2} [2\bar{N} + \exp(-2\bar{N}) - 1] + \frac{\sin^4 k h_0}{\bar{N}^4} \left[3\bar{N}^2 - 6\bar{N} + \frac{9}{2} - (3\bar{N} + \frac{9}{2}\exp(-2\bar{N}) \right], \qquad (4.22)$$

where $\bar{N} = \bar{R}L$. The normalized second intensity moments $\langle I^2 \rangle / \langle I \rangle^2$ calculated from Eq.(4.21) and Eq.(4.22) are shown in Fig. 4.21. The phase distribution of the telegraph wave is not well approximated by a Gaussian in which case the second intensity moments $\langle I^2 \rangle / \langle I \rangle^2$ would be 2 instead of 3 as shown in Fig. 4.21. For partially coherent diffraction, we would expect the consequently coherent factor to be $1 + 2\beta$ as opposed to $1 + \beta$. It can be seen that Fig. 4.21 has similar features to our experimental results Fig. 4.18. The mean-square intensity increases as \bar{N} for larger values of kh_0 and decreases as \bar{N} for smaller values of kh_0 . In the limit of small \bar{N} , the mean-square intensity changes slightly for different values of kh_0 . In larger \bar{N} limit, the mean-square intensity falls quickly with kh_0 . Only in the special case when $kh_0 = (2n+1)\pi/2$, the mean-square intensity saturates at a value of 3 for large \bar{N} .



Figure 4.21: The normalized second intensity moments $\langle I^2 \rangle / \langle I \rangle^2$ calculated from Eq.(4.21) and Eq.(4.22) for different values of $k_0 h$.

In Jakeman's Eq.(4.20), let $\theta = 0$. Eq.(4.20) will reduce to

$$\vec{E} = \cos(kh_0) + iT(x)\sin(kh_0)$$
 (4.23)

Comparing it with our calculation Eq.(4.18), it is clear that $kh_0 = \frac{\pi}{2} + \varphi$ for our case.

So Jakeman's results Eq.(4.21) and Eq.(4.22) can be used to explain our data (see Fig. 4.18).

According to Eq.(4.21) and Eq.(4.22), the mean and mean-square intensity for varied dQ in Fig. 4.18 are calculated. The second moment of intensity which has been normalized to be comparable with our data are shown in the upper figure of Fig. 4.22. The circles on the graph indicates the experimental values of coherence factor for each k_0h or dQ. The vertical dashed line marks the average \bar{N} for the six different dQ. The intersections are considered as the theoretical values of coherence factor for different dQ. The experimental and theoretical values versus dQ are plotted in the lower graph of Fig. 4.22. We can see that they agree with each other quite well.

In conclusion, Jakeman's model explained very well the extra contrast and the nearly zero contrast observed in the experiments for late times. But Jakeman's model does not show the feature of normal contrast in the early time. The physical reason is that the Jakeman's telegraph wave model is a non-Gaussian model. We suggest that in the early time the fluctuating scattered electric field is more Gaussian distributed as would be the case for diffused domain walls. The normal contrast is the result of averaging over the Gaussian distributed intensity.

Features in telegraph model depend on a well defined phase at each point having only two values. This model is valid when the scattering from each domain is centered at $\vec{Q_0}$ and has a width of $2\pi/L$. At the late times the domains are large and well registered so that the telegraph wave model applies. At the early time, the domains are small and could have different orientations. Also a diffuse or spread out domain wall could form and would lead to a more Gaussian-like phase distribution. As we know, for a given pixel in the detector, the random phase of each domain that contributes to it leads to the speckle pattern. A small mosaic or distribution of angles will lead to a range of dQ and thus phases, at each pixel so that the telegraph model is not a good approximation any more. The data for three temperatures in two directions is summarized in Fig. 4.23. These results for contrast dependence on wave vector or temperature show some interesting features. Not surprising, the behaviour



Figure 4.22: Upper: The rescaled second moment of intensity from the model. The circles on the graph indicates the experimental values of coherence factor for each k_0h or dQ. The vertical dashed line marks the average \bar{N} for six different dQ. Lower: The experimental and theoretical values versus dQ.

is different between the shallower quench and the deeper quenches. For the shallower quench, the contrast seems to remain constant and there is little dependence on the wave vector. For deeper quenches, as described before, in the early time the normal contrast is obtained while at late times the contrast changes with the different wave vector. The contrast can be twice as big as the normal value for small wave vector or smaller than the normal value for bigger wave vector. Further work requires to be done to come up some more complex model to fully explain this phenomenon.

4.4 Conclusion

In this chapter, we presented the coherent X-ray studies of order-disorder transition in Cu₃Au. We measured the autocorrelation function of the scattered intensity which is a description of the evolution of the density-density correlation functions. The twotime correlation functions can be expressed with two natural variables, the average time $\bar{t} = (t_1 + t_2)/2$ and the time difference $\delta t = |t_1 - t_2|$. The correlation times T versus the average time \bar{t} was found to follow some scaling forms as predicted by the theory. The scaling forms cross over from $T \sim \bar{t}$ to $T \sim \bar{t}^{1/2}$.

The correlation time is found to start increasing only after 10, 15 up to 50 minutes (delay time) depending on different temperature quenches. The loss of speckle contrast during the delay time was caused by a shift of the speckle position. 2Q-2t method instead of 1Q-2t was applied to compensate the speckle contrast and the results have been improved greatly.

Finally we reported that the significant change of speckle contrast was observed for different wave vector and different temperature quenches in the sample. At late times the contrast was twice big as expected for small wave vector and the contrast was much smaller than expected value for large wave vector. A telegraph wave model was applied and well explained the extra contrast and loss of the contrast. The model didn't show the feature that the contrast was same for all wave vectors in the early time. The explanation of this result is under investigation.



Figure 4.23: The data for three temperatures in two directions is summarised, (a) $T_f = 378^{\circ}$ C, (b) $T_f = 370^{\circ}$ C, (c) $T_f = 355^{\circ}$ C,. For shallower quench, the contrast seems remain constant and there is no dependence on the wave vector. For deeper quenches, as described before, in the early time the normal contrast is obtained while in the late time the contrast changes with the different wave vector.

Conclusion and Outlook

In conclusion, this thesis is a summary of a study on the order-disorder phase transition in the classic sample Cu_3Au . Using traditional incoherent X-ray sources, one can only measure the averaged intensity and obtain the averaged behavior of the sample under study. With the synchrotron X-ray sources, coherent X-rays can be produced and the speckle patterns can be observed to reveal the exact information of the illuminated sample. The results of this thesis are then divided into two parts and are reported as incoherent (one-time) analysis in Chapter 3 and coherent (two-time) analysis in Chapter 4.

In chapter 3, we present the experimental results of order-disorder phase transition in Cu₃Au using incoherent X-rays. The information about the (100) superlattice Bragg peak of Cu₃Au is summarized for three temperature quenches. The (100) superlattice Bragg peak has the shape of a thin disk with two long identical longitudinal diffractions and one short transverse diffraction. The Bragg peak gets sharper and narrower in time when the ordering is in process in the sample. Slight change of peak position with time is interpreted as the result of distortion of lattice due to the growth of the domains in the sample. The universal scaling law is tested for the incoherent data. Our data shows that the average domain size (the inverse of the peak width) follows the $t^{1/2}$ line through the whole ordering process for the three temperature quenches. The rescaled intensity of Bragg peak also looks invariant in time when plotted against the wavevector rescaled by the peak width.

In chapter 4, we present the coherent X-ray studies of order-disorder transition

in Cu₃Au. The fluctuation of the scattered intensity, speckle patterns are measured as the evolution of time. The information about the change of exact structure in the sample can be obtained from the speckle patterns. Though for non-equilibrium system separating the averaged intensity $\langle I \rangle$ from the fluctuating intensity I is not straightforward, SG filters provide a good estimate to the averaged intensity. The twotime correlation functions of the normalized intensity $(I - \langle I \rangle)/\langle I \rangle$ are then calculated. They can be expressed with two natural variables, the average time $\bar{t} = (t_1+t_2)/2$ and the time difference $\delta t = |t_1 - t_2|$. The correlation times T versus the average time \bar{t} is found to follow some scaling forms as predicted by the theory. The scaling forms cross over from $T \sim \bar{t}$ to $T \sim \bar{t}^{1/2}$. The crossover happens earlier for shallower temperature quench, which suggests a faster ordering process in the sample. This is the first clue that the dynamics of sample have a dependence on the quench temperature.

Though the crossover for shallower temperature quench is quite obvious, they are not so convincing for deeper quenches. To improve the results, the first thought is to increase the time of the experiments or use a bigger CCD detector. This is not very doable for two reasons. First, because of the technological limits of XIFS method [68], longer experiments are not feable at present. Second, for our sample Cu₃Au, the (100) Bragg peak is already very sharp at the end point of present data. Even though we can measure larger wave vectors not much signal will be received. Another difficulty is that the graph is in log-log scale. The time or the wave vector has to be increased by the order of ten to see the effect. Actually, one alternative option is to choose a different sample which has a faster dynamic. The crossover will be reached earlier and enough data can be used to test the latter scaling form $T \sim \bar{t}^{1/2}$. So far, the transition of two scaling laws in systems with non-conserved order parameter has not been observed in other systems. The results obtained by A. Fluerasu [29] for Cu₃Au did not clearly show this transition. The work done by K. Ludwig et. al. [7] investigated a Cu-Pd alloy and their results only showed the linear part of the scaling laws. However, the study of systems with conserved order parameter did not encounters this difficulty. F. Livet [9] observed both the linear scaling law and $T \sim \bar{t}^{2/3}$ in AlLi single crystal. A. Malik et. al. [10, 9] measured two-time correlation functions in a sodium borosilicate glass undergoing phase separation and also obtained $T \sim \bar{t}^{2/3}$ relationship between the correlation time and the average time.

The correlation time T is found to start increasing only after 10, 15 up to 50 minutes (incubation time) depending on temperature quench. The loss of speckle contrast during the incubation time is a consequence of the shift of speckle position. Instead of using the same wave vector for each pair of times (1Q-2t method), the speckles are paired for different wave vectors (2Q-2t method) to compensate the speckle contrast and the results have been improved greatly. The physical explanation is that the growth of domains in the sample causes a slight change of structure and the small dilation of wave vector. Here the incubation time is longer for shallower quenches, second evidence that ordering process in the sample has a dependence on quench temperature.

We also reported the very interesting result that the significant change of speckle contrast is observed depending on evolution time and on wave vector. At late times the contrast is twice as big as expected for smaller wave vectors and the contrast is very small for larger wave vectors. At early times, the contrast is same for different wave vectors. A telegraph wave model is applied and well explains the extra contrast and loss of the contrast at late times. But this model does not show the same behavior for the early times. Telegraph wave model assumes that the domain walls are rectangular grooved and have a well defined phase with only two values. At the late times, the domains are big and packed tightly hence the domain walls are well characterized by the telegraph model. At the early times, the domains are small and it is possible to have different orientations. The phases of domain walls may be better described by Gaussian distribution. A more complex model to combine the characters of telegraph wave model and Gaussian model is actually under investigation.

In the previous paragraph, we only discussed the speckle contrast for the deeper quench. For shallower quench, the speckle contrast actually remains constant and is independent of the wave vector and time. This is another observation which suggests that the sample shows different behaviors between shallower quench and deeper quench. This temperature dependence might be the consequence of some different relaxation mechanisms between different quenches which are not understood yet. Our shallower quench is only 5°C below the critical point and the deeper quench is 28°C below the critical point. Because of this significant difference between the final temperatures, we already observe that the domains are formed at the different rate and the ordering process is faster for shallower quench. This mostly will affect the shape and orientation of the domain walls and results in different speckle pattern. It is worth further investigation on this interesting phenomenon both theoretically and experimentally.

On the other hand, the temperature dependence is only observed in the coherent analysis but not in incoherent analysis. This is one example to show the power of the new technique XIFS we use to carry out the experiments in this thesis. The results obtained in this thesis present that XIFS provides new information and brings new insight into the investigation on the system under study. The applications of XIFS will offer a lot possibilities in studying numerous systems with different dynamics. With the new generation of synchrotron X-ray sources, the dynamics in the systems can be studied on the time scales ranging from minutes to tens of nano seconds and space scales of nanometers.

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