



Pair distribution function analysis of diffuse scattering from high- T_c superconductor $\text{Na}_{0.25}\text{Ba}_{0.75}\text{Fe}_2\text{As}_2$

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Abstract

Two-dimensional difference pair distribution function of single crystal $\text{Na}_{0.25}\text{Ba}_{0.75}\text{Fe}_2\text{As}_2$ was studied by analysing the diffuse scattering profiles extracted from the total scattering data. Diffuse scattering intensities were obtained from two-dimensional diffraction map by subtracting a background fit with a two-dimensional Lorentzian function and by using an inward interpolation method.

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1. Introduction

Superconductors transport electricity without dissipation and have an important role in various applications. Materials with higher transition temperatures are urgently needed in order to make superconductors practical and beneficial. Consequently, high temperature superconductors such as BaFe₂As₂-based materials have been developed and modified [1]. The properties of materials are normally influenced by their crystal structures. If they are grown as a well-ordered single crystal, we can determine the structures by conventional crystallographic methods based on Bragg scattering. In reality, most crystals are not perfectly ordered or disordered. To understand structure-property relations in deep detail, considering only Bragg crystallography is not enough since it provides merely the average structure of crystals. On the other hand, real crystals contain information beyond the average structure. By the diffuse scattering analysis, subtle details of the real crystals can be extracted; for example, vibration in the crystals due to thermal excitation and disorders [2].

2. Theory

X-ray scattering of materials is caused by the electron density ρ . The scattering amplitude is the summation of a scattering wave from each electron and the intensity is proportional to the square of the amplitude.

Difference pair distribution function

In kinematic theory, multiple scattering is neglected. The scattering from a single crystallite is written as the Fourier transform of its electron density:

$$F(\mathbf{h}) = FT[\rho(\mathbf{r})]$$

The scattering intensity is captured by the x-ray detector:

$$I(\mathbf{h}) = FT[< \rho(\mathbf{r}) * \rho(\mathbf{r}) >]$$

The bracket $< >$ denotes averaging over exposure time and scattering mosaic blocks. The term $\rho(\mathbf{r}) * \rho(\mathbf{r})$ is the autocorrelation function of the electron density. The structure factor of the Bragg peaks can be calculated as the Fourier transform of the average structure:

$$F_{Bragg}(\mathbf{hkl}) = FT[< \rho(\mathbf{r}) >]$$

Diffuse scattering is all scattering from a single crystal apart from Bragg scattering. Therefore, the diffuse scattering is the difference between total and Bragg scattering:

$$I_{diffuse}(\mathbf{h}) = I(\mathbf{h}) - I_{Bragg}(\mathbf{h})$$

Similarly,

$$\begin{aligned} I_{diffuse}(\mathbf{h}) &= FT[< \rho(\mathbf{r}) * \rho(\mathbf{r}) >] \\ &\quad - FT[< < \rho(\mathbf{r}) > * < \rho(\mathbf{r}) > >] \\ &= FT[P_{\Delta}(\mathbf{r})] \end{aligned}$$

The function $P_{\Delta}(\mathbf{r})$ is called Difference Pair Distribution Function. Applying Fourier transform to both sides of the equation, we get a spatially reversed version of the function:

$$FT[I_{diffuse}(\mathbf{h})] = P_{\Delta}(-\mathbf{r})$$

As the positions of the reflections on the reciprocal lattice are related by a center of symmetry through the reciprocal lattice origin, the Difference Pair Distribution Function is therefore centrosymmetric:

$$P_{\Delta}(-\mathbf{r}) = P_{\Delta}(\mathbf{r})$$

Fourier transform of the diffuse intensity provides the autocorrelation discarding phase information. Only the power is returned. It is therefore an irreversible operation. However, it allows us to measure the relative positions of atoms or disorders in crystals and to make a distance map of finding two atoms or disorders separated by distance values in real space [3].

3. Methods and analysis

3.1 Data collection

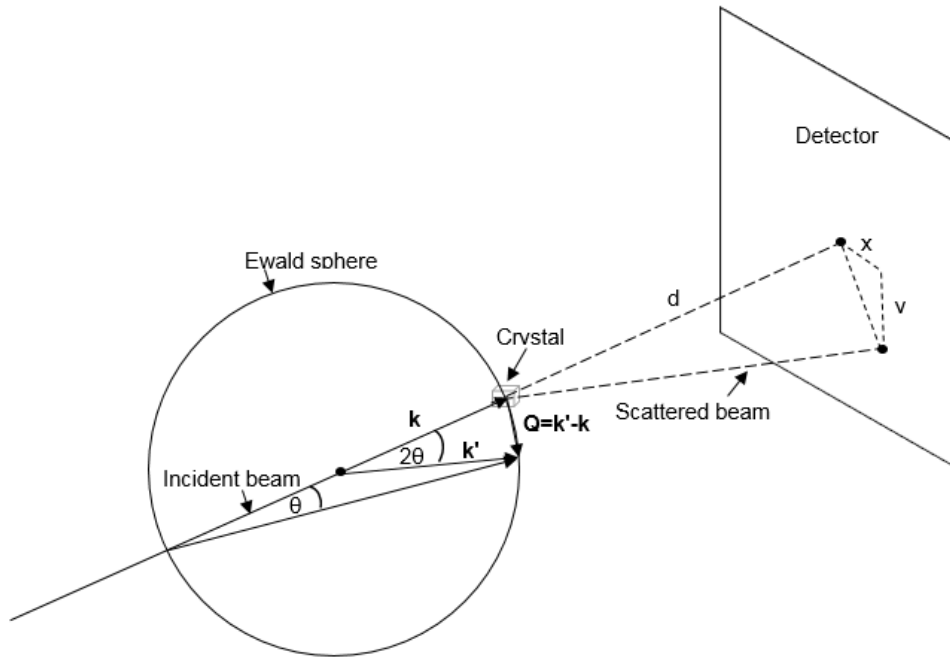


Fig. 1: Experimental scattering geometry

The scattering geometry for the diffraction experiments is illustrated in Fig. 1. The crystal sample is placed far from the detector in length d . The wave vectors of the incident beam and the scattered beam are \mathbf{k} and \mathbf{k}' respectively where 2θ is the angle between the beams.

3.2 Image scaling

Q measures the change in wave vector and is called the scattering vector which can be expressed in terms of the 2-dimensional experimental parameters as follows:

$$|Q_x| = \frac{kx}{\sqrt{x^2 + y^2 + d^2}}$$

$$|Q_y| = \frac{ky}{\sqrt{x^2 + y^2 + d^2}}$$

$$k = \frac{2\pi}{\lambda}$$

k and λ are the magnitudes of wave number and wave length of X-ray. In elastic scattering, the photon energy is conserved. Thus, the magnitude satisfies $|k|=|k'|$. The set of reciprocal lattice vectors **G** determines the possible X-ray reflections. When **Q** is equal to a particular reciprocal lattice vector:

$$\mathbf{Q} = \mathbf{G}$$

Or,

$$\mathbf{k} + \mathbf{G} = \mathbf{k}'$$

With taking the square of both sides of the previous equation, the diffraction condition is written as:

$$2\mathbf{k} \cdot \mathbf{G} + \mathbf{G}^2 = 0$$

This particular expression is often used as the condition for diffraction which is another statement of the Bragg condition:

$$2l\sin\theta = \lambda$$

Where l is the spacing between adjacent parallel planes. λ is the wave length of X-ray. θ is the Bragg angle. The result of diffraction theory, namely that $\mathbf{Q} = \mathbf{G}$ is possibly expressed in another way to give the Laue equations:

$$\mathbf{a}_1 \cdot \mathbf{Q} = 2\pi h$$

$$\mathbf{a}_2 \cdot \mathbf{Q} = 2\pi k$$

$$\mathbf{a}_3 \cdot \mathbf{Q} = 2\pi l$$

\mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are real lattice vectors. h , k and l are the Miller indices denoting planes orthogonal to the reciprocal lattice vector. If h , k and l have rational ratios, then the planes can be written in terms of integer indices (hkl) by scaling \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 appropriately. In this work, a suitable fit of the unit cell parameters was found, they were used as a starting point for indexing the planes of Bragg reflections [4].

3.3 Image processing

Separation of Bragg and diffuse data

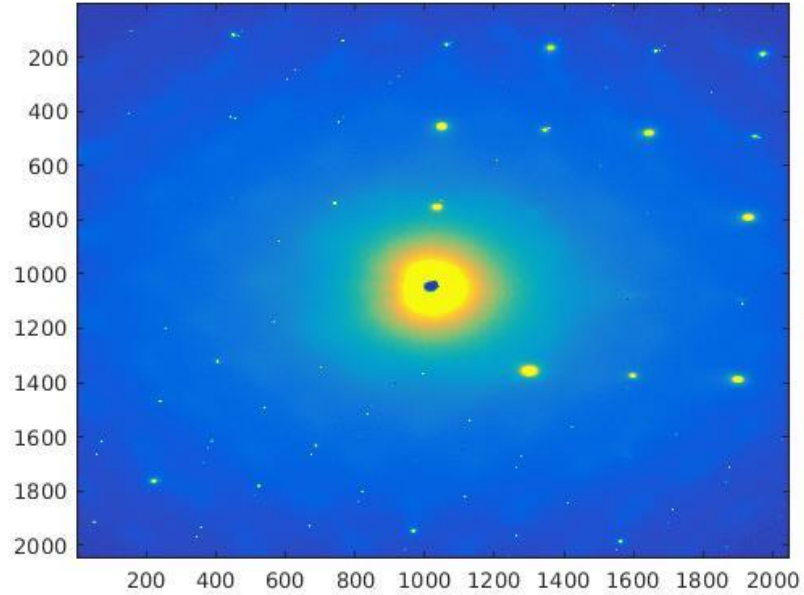


Fig. 2 The original image

The original image which shows total scattering profiles is shown in Fig.2 Separation of Bragg and diffuse scattering is straightforward, because the signal of diffuse scattering is by far broader than the Bragg profiles and interpolation of the diffuse intensities beneath the Bragg scattering provides a reasonable approximation to the real diffuse intensities. In this work, the intensities of many pixels in the image center region are higher than some Bragg scattering intensities far from the center, they make the difficulty to separate the bright spots from diffuse profiles. As can be seen from the one-dimensional curves at the origin along vertical (Fig.3) and horizontal axes (Fig. 4), the curve shapes distribute like a Lorentzian function although the highest intensity in the center could not be seen due to the fact that the center intensity peak is blocked by the beam stop in the experimental setup.

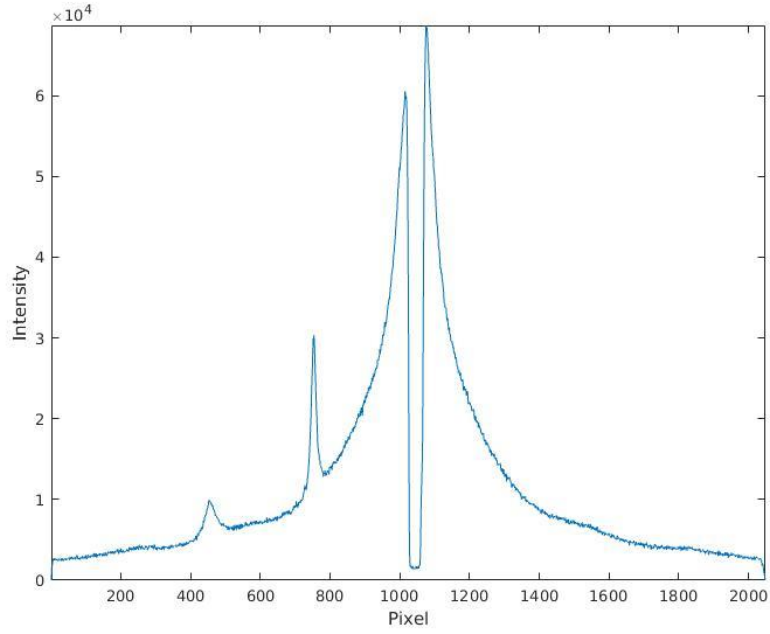


Fig. 3: One dimensional intensity distribution along the horizontal axis at $x=0$

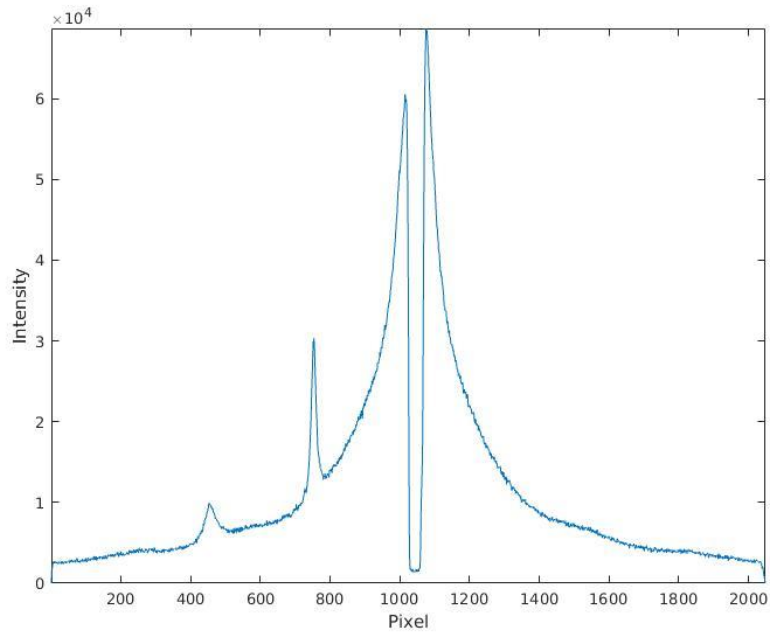


Fig. 4: One dimensional intensity distribution along the vertical axis at $y=0$

A two dimensional Lorentzian function fit of the intensities is made (Fig.5). Then, it is subtracted from the real image to remove background (Fig.6). The negative values from the subtraction are set to zero.

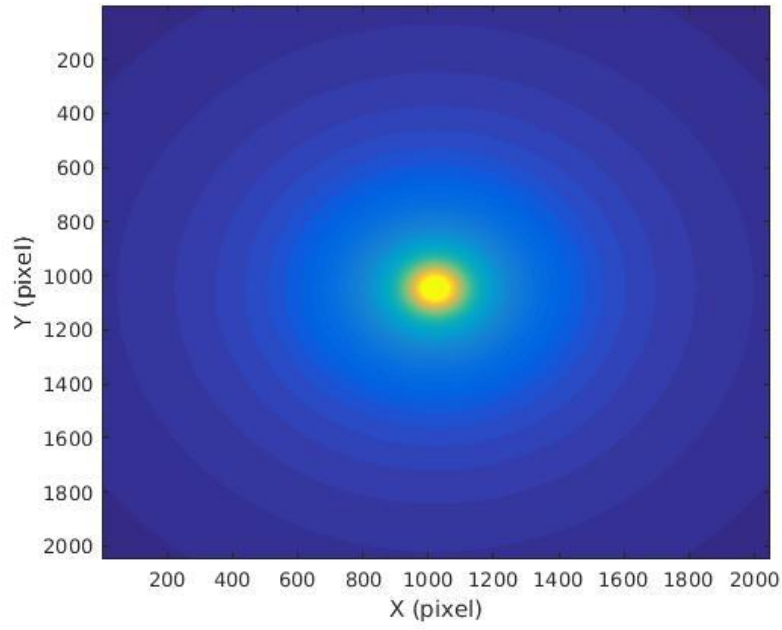


Fig. 5 Two-dimensional intensity distribution generated by Lorentzian function fitting

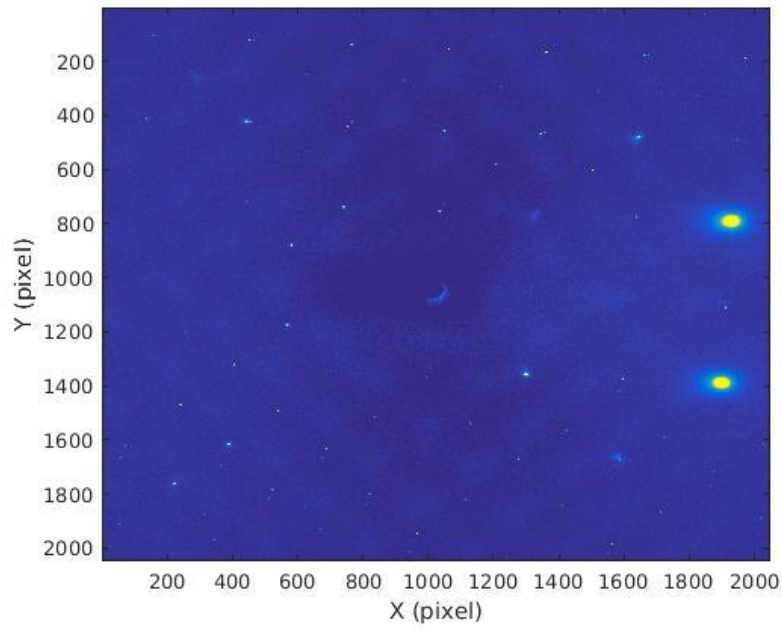


Fig. 6: The subtracted image

Now, the bright spots, Bragg scattering profiles, are clearly visualized. From this stage, we can rescale the image from pixel axes to h and k axes by considering Bragg profiles. After, the inward interpolation technique, which computes the discrete Laplacian over the bright Bragg scattering regions and solves the Dirichlet boundary value problem, is applied, the original spot intensities are substituted by the reasonable diffuse scattering intensities shown in Fig. 7.

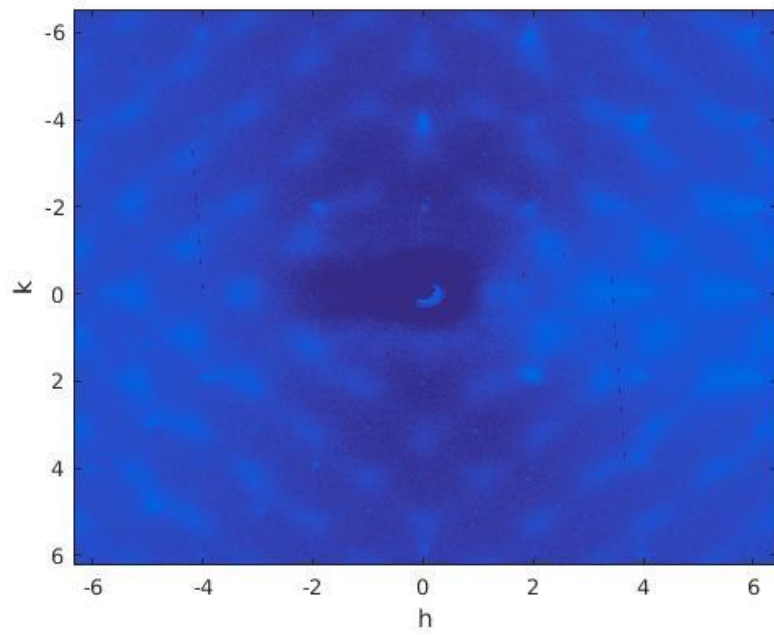


Fig. 7: The image with inward interpolation treatment

The spots are not completely disappeared yet but their intensities are in the level of their pixels around which is reasonable enough to use as approximate intensities of real diffuse scattering as inspection by subtracting Fig.7 from Fig. 1 resulting clear Bragg scattering (Fig. 8).

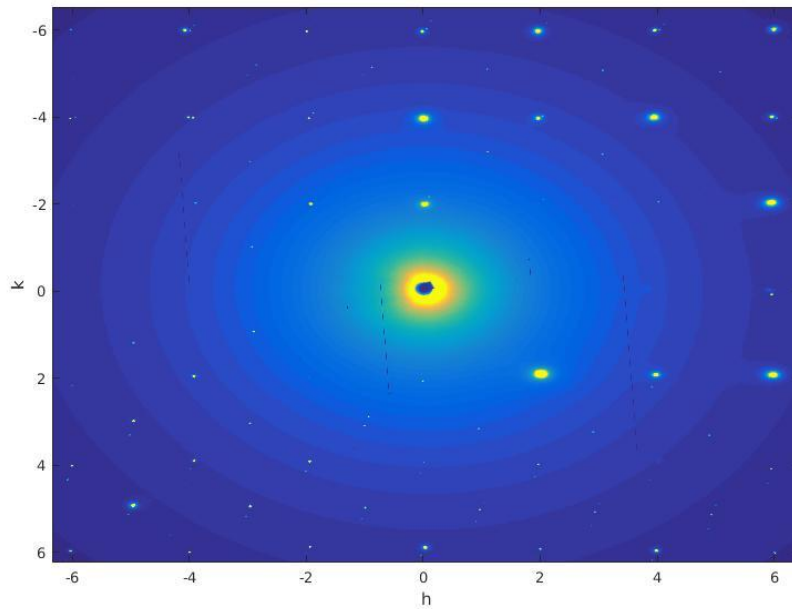


Fig. 8: The clear image of Bragg scattering

3.4 Difference pair distribution function

To illustrate the relation between a reciprocal space data and a number of pixels in real space in a simple way, the function $f(x)=1+\cos(x)$ where $-5\pi < x < 5\pi$, is generated as seen in Fig.9 showing there are 5 periods of the oscillation with no values along y axis lower than zero. The curve characteristic is periodic and positive which seems similar to one-dimensional intensities of X-ray diffraction patterns. As seen from Fig. 9, there are five peaks which can be compared that there are five Bragg peaks in one dimension. We use Fourier transform to find the frequency components of the signal and shift them to a center (Fig. 10) to easily consider. The calculation result is as follows:

$$FT(f(x)) = \delta c + \frac{1}{2}\{\delta(c - c_0) + \delta(c + c_0)\} \quad (\text{eq. i}).$$

Where $FT(f(x))$ is Fourier transform of $f(x)$, δ is a Dirac delta function, c and c_0 are constant.

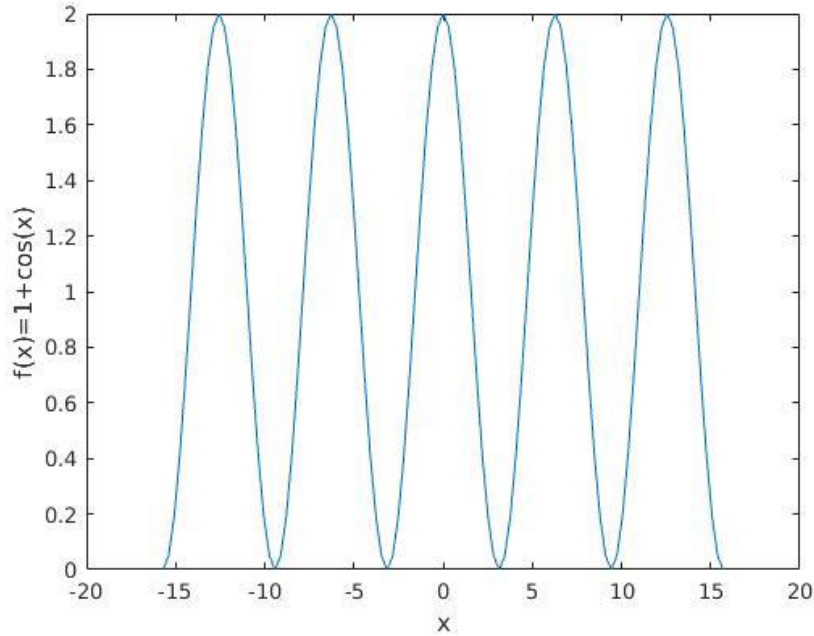


Fig. 9: The plot of $f(x)=1+\cos(x)$ where $-5\pi < x < 5\pi$

By considering the number of pixels counted from the center peak to each side peak in Fig.10, we can see that it is equal to the number of peaks in Fig. 9 which is supposed to be the value of c_0 and the position of the center peak for c (eq. i). Consequently, we can similarly apply this relation using the real space distances of the average structure, which is strongly confined at reciprocal lattice points, as constraints to scale the approximate distances of diffuse scattering profiles. The two-dimensional Fourier transform of the diffuse scattering image is performed by using the MATLAB fft2 function. It returns the two-dimensional discrete Fourier transform computed with a fast Fourier transform algorithm as shown in Fig. 11. The Fourier transform map of the Bragg profiles (Fig. 12) is also created to make a comparison about relative distances of finding atoms or disorders along a and b directions.

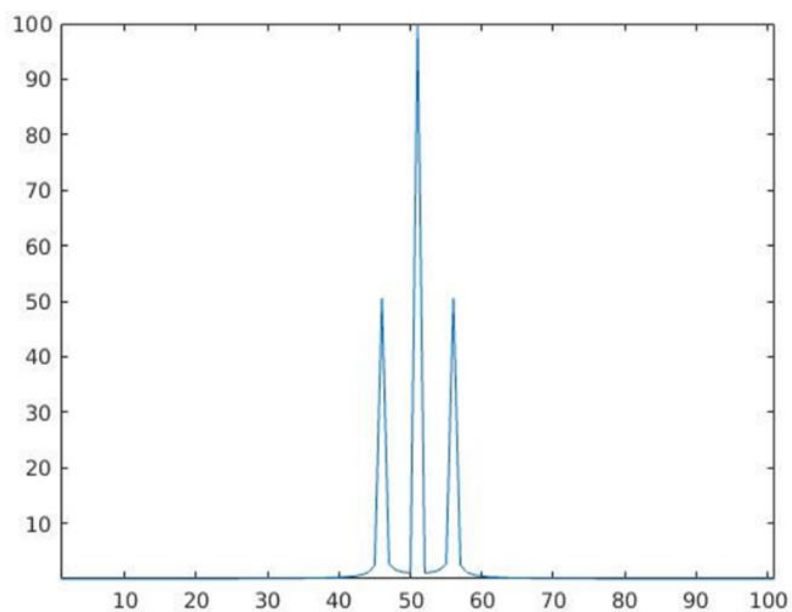


Fig. 10: The plot of Fourier transform of $f(x)$

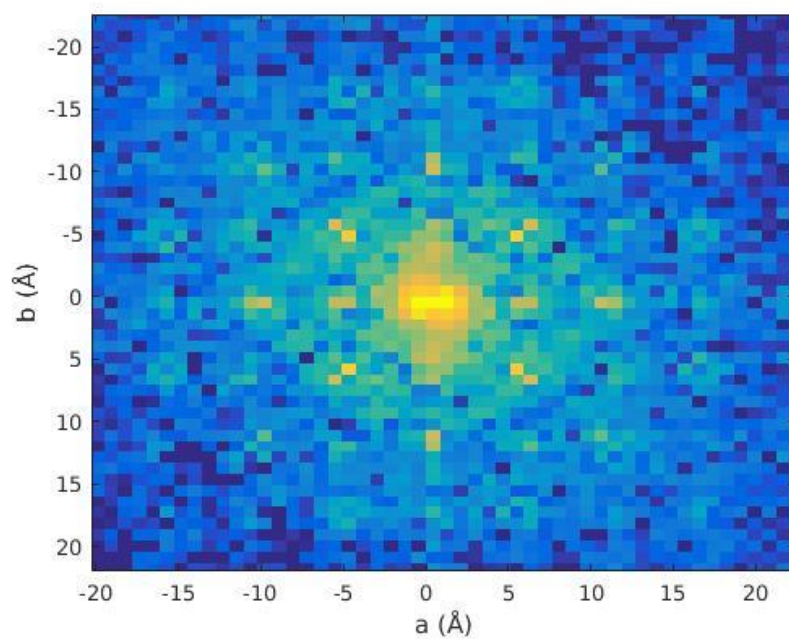


Fig. 11: Fourier transform of diffuse scattering

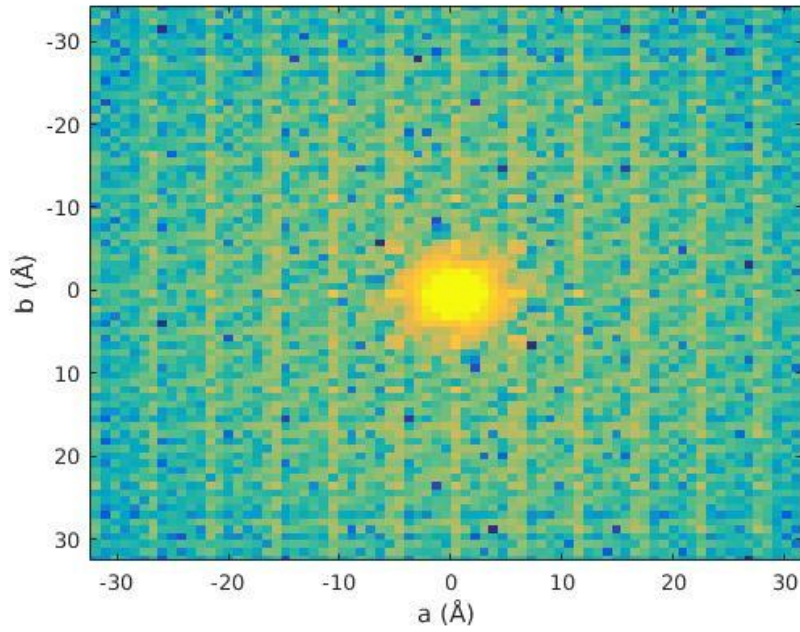


Fig. 12: Fourier transform of Bragg scattering

Fig. 11 depicts the difference distribution function map of diffuse scattering. The yellow dots show the high possibility of finding atoms or disorders in a distance value related to the other atoms or disorders. Along b direction the yellow dots are considerably sharp. The nearest dot distance from the center on the horizontal axis is approximately equal to the length between the planes of Bragg profiles on a direction in Fig. 12. Conversely, on b direction in Fig. 11, the yellow dots are not sharp but diffuse from the center to the distance about the distance between planes in b direction of Bragg scattering (Fig.12). Interestingly, the second nearest yellow dots form the center on b direction in Fig. 11 are sharp at the similar distance of the second nearest yellow dots on b direction in Fig.12. Moreover, There are yellow dots between a and b directions. The difference pair distribution function result is able to be further discussed. In this case, the diffuse scattering is likely to be from Na-doping making distortion in the crystal. As considering the lengths of the spots along a and c axes from the center spot, the distance in real space of diffuse scattering profiles is relevant to the distance of Bragg scattering profiles (Fig. 12). However, this is not confirmed and diffuse scattering profiles are possibly from various factors.

4. Conclusions

The diffuse scattering data can be extracted from total scattering data captured in experiments by image processing methods. The difference pair distribution function map can be generated from the data which have been scaled by Q -range obtained from Bragg profiles.

5. Acknowledgements

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6. References

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