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Supporting information for article:

Solving the disordered structure of β-Cu$_{2-x}$Se using the three-dimensional difference pair distribution function

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# Supporting information

S1. Interpretation of the 3D-ΔPDF peak amplitudes

Starting from the equation given for the 3D-ΔPDF given in the introduction and partitioning the electron density into a sum of atomic electron densities, the 3D-ΔPDF can be rewritten as

$$\text{3D-}\Delta\text{PDF}(\boldsymbol{r}) = \sum_{ij} \delta\rho_j(\boldsymbol{r}) * \delta\rho_i(\boldsymbol{r}) * \delta(\boldsymbol{r} - \boldsymbol{r}_{ij})$$

Where $\delta\rho_i(\boldsymbol{r})$ is the difference between the real and average electron density of the i'th atom, $\delta(\boldsymbol{r})$ is the Dirac-delta function, $\boldsymbol{r}_{ij}$ is the vector between atom i and atom j, and $*$ is the convolution operator. For every pair of atoms there will be a peak in the 3D-ΔPDF given by $\delta\rho_j(\boldsymbol{r}) * \delta\rho_i(\boldsymbol{r})$ at the position $\boldsymbol{r}_{ij}$. Because of the Fubini-Tonelli theorem, the integral of such a peak will be given by the product of the integral of the two functions, and therefore just as the product of the difference in number of electrons:

$$\text{peak amplitude} \propto \int_{peak} \text{3D-}\Delta\text{PDF}\,(\boldsymbol{r})\,d\boldsymbol{r} = \sum_{(i,j)|r_{ij}=r} \int \delta\rho_j(\boldsymbol{r})\,d\boldsymbol{r} \cdot \int \delta\rho_i(\boldsymbol{r})\,d\boldsymbol{r}$$

$$= \sum_{(i,j)|r_{ij}=r} \delta Z_j \cdot \delta Z_i$$

where δZ_i is the difference in number of electrons in the real and average structure for atom i (e.g. if the atom is occupied 1/3 in the average structure, δZ will be $\frac{+2}{3} Z$ if the site is occupied and $\frac{-1}{3} Z$ if the site is unoccupied, where Z is the atomic number). The sum runs over all pairs of atoms (i,j) separated by the same vector $\boldsymbol{r}$.
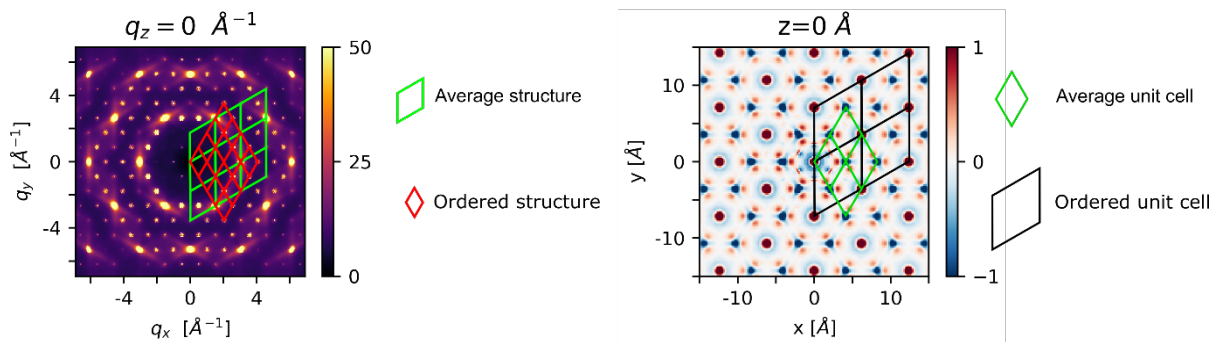
Figure S1 Reciprocal and direct lattice of $Cu_{2-x}Se$ for the average and ordered structures. Left: $q_z = 0$ plane for the scattering, with the average reciprocal lattice in green and the ordered reciprocal lattice in red. Right: $Z = 0$ Å plane of the measured 3D-ΔPDF with the average unit cell in green and the ordered unit cell in black.

S2. Solving the structure of β-Cu₂₋ₓSe "by hand"

The ordered structure needs to have a periodic structure in the plane with unit cell vectors $a_{layer} = a_{avg} - b_{avg}$ and $b_{layer} = 2b_{avg} + a_{avg}$, as this gives rise to the positions of the sharp "superstructure" lines in the scattering, as shown in Figure S1. The same can be seen in the 3D-ΔPDF which is periodic in two dimensions. The unit cell of the average structure is marked by a green box and the ordered unit cell as a black box in the right part of Figure S1. It is seen that the average unit cell vectors have negative peaks in the 3D-ΔPDF while the ordered unit cell vectors are at positive peaks, validating the dimensions of the ordered unit cell.

Each layer in the average structure contains two sub-layers of each type (Se, Cu1a, Cu1b, Cu2). In Figure S2 one such layer is shown with marked sub-layers for reference. First the individual layers are evaluated. Each of the three types of Cu layers together with the 3D-ΔPDF for z = 0 Å are shown in Figure S3. To find the ordered structure for each layer it is first assumed that the atom marked "O" is occupied (The choice of a different "O" would give the same structure, just with a shifted origin). The vectors to atoms with marked numbers are marked by the same numbers in the 3D-ΔPDF. The solution for the layers are shown with red-tinted atoms. The solution for the Cu2 layer is given in the main text. The Cu1a layer is 1/3 occupied and the Cu1b layer 2/3 occupied. For each of these layers there is only one possible solution in agreement with the ordered unit cell size. The solution to the Cu1a layer is also clearly in agreement with the 3D-ΔPDF, where the vectors between occupied sites have positive peaks while the vectors from occupied to non-occupied have negative peaks. The agreement of the Cu1b layer with the 3D-ΔPDF is less clear. We look at vector to the nearest neighbor (e.g. O-1). When going through the sites, one third of the time this vector separates two occupied sites (e.g. 5 and 8) while two thirds of the time the vector separates an occupied and an unoccupied site (e.g. O and 1). This gives a peak amplitude proportional to

$$\delta Z_{occ}^2 + 2\,\delta Z_{occ}\,\delta Z_{unocc} = \left(\left(\frac{1}{3}\right)^2 + 2\frac{1}{3}\frac{-2}{3}\right)Z_{Cu}^2 = \frac{-1}{3}Z_{Cu}^2\,.$$

This is in agreement with the observed negative feature for vector 1.

Now that the ordered structures for all layer types has been identified, the inter-layer orderings can be found. Only three inter-layer orderings are needed to construct the full layer: Cu1a to Cu1b, Cu1b to Cu2 and Cu2 to Cu2. Table S1 gives the vertical distances between all different sub-layers within the layer, where the notation for the sublayers is given in Figure S2. The ordering of these sublayers to each other can then be found from the 3D-ΔPDF for the vertical distance between the layers. Figure S4 shows one such layer for z=0.97Å.

First we look at the ordering between the close Cu1a and Cu1b layers (e.g. Cu1a_1 and Cu1b_1 in Figure S2). As the Cu1a and Cu1b sites are only 0.95 Å apart, it is not possible for a Cu1a site right next to a Cu1b site to both be filled at the same time. As 1/3 of the Cu1a sites and 2/3 of the Cu1b sites are filled, either the Cu1a or the Cu1b site is filled for every pair of sites. As we know how each of these layers order, there is only one possibility to combine the two, which is illustrates in Figure S5.
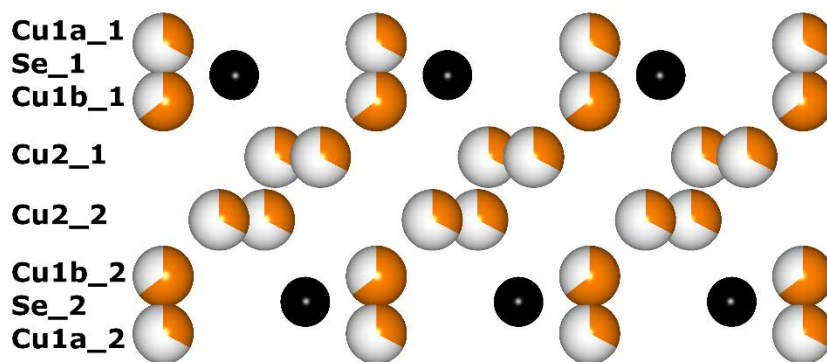
Figure S2 Average layer structure. Partially filled atoms show the degree of occupancy. Black is Se and orange is Cu.
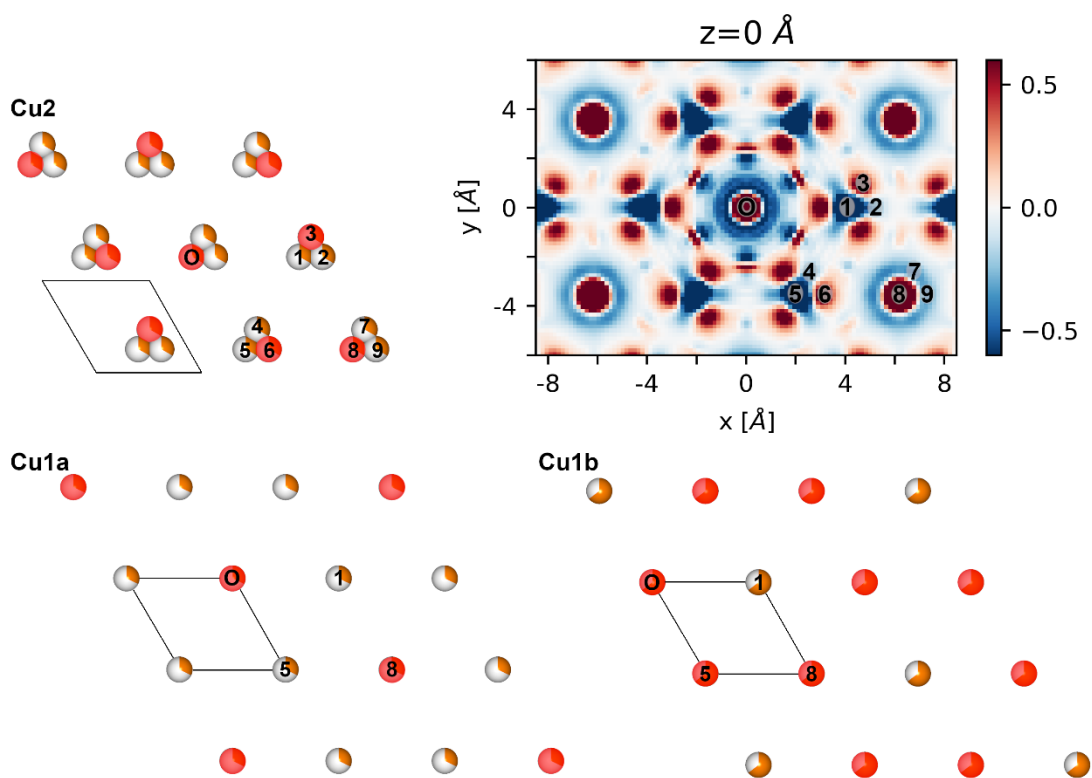
Figure S3 Structure of Cu layers and the 3D-ΔPDF for the z=0Å plane. The ordered structure for each layer is marked with red-tinted circles. Vectors O-n for the numbers, n, marked in the structures are marked by the same numbers in the 3D-ΔPDF. The black lines mark the unit cell of the average structure

The same is seen in the 3D-ΔPDF for the z = 97Å layer in Figure S4 (with the grid size used here, 0.97Å is the closest layer of the obtained 3D-ΔPDF to 0.95Å). For the vector (x,y,z) = (0, 0, 0.97Å) there is a negative feature, showing there to be no Cu1a and Cu1b sites filled right on top of each other as expected. For the vectors corresponding to the six surrounding atoms in the other layer (marked 1), positive features are observed, showing the Cu1a site to be surrounded by filled Cu1b sites. For the vectors corresponding to the ordered unit cell in the xy-plane, there are negative features in the 3D-ΔPDF for this z-coordinate, again showing that the Cu1a and Cu1b sites right on top of each-other are not filled at the same time.

We then look at the coupling from Cu1b to Cu2 layers next to each other (e.g. Cu1b_1 and Cu2_1 in Figure S2). These have a vertical distance of 0.94 Å. These layers are shown in Figure S6. As the ordering within these two layers are known, again only the relative positon of the layers is needed. First the layer of Cu1b site is filled with the known ordered pattern, shown by the blue-tinted atoms. There are two types of occupied Cu1b sites, marked O and O' and one unoccupied type of Cu1b site, marked O*. The vectors from O to site 3, 4 and 5 are identical to the vectors from O' to 3', 4' and 5' and O* to 3*,4* and 5*. The 3D-ΔPDF for the vector 3 is negative, showing that site 3 and 3' are not occupied. If just one of 3 or 3' were occupied, the 3D-ΔPDF would have been positive. If e.g. 3 was occupied, the O-3, O'-3' and O*-3* would contribute to the 3D-ΔPDF as $\delta Z_O \delta Z_3 + \delta Z_{O'} \delta Z_{3'} + \delta Z_{O^*} \delta Z_{3^*}$

$$= \left(1 - \frac{2}{3}\right)\left(1 - \frac{1}{3}\right) Z_{Cu}^2 + \left(1 - \frac{2}{3}\right)\left(0 - \frac{1}{3}\right) Z_{Cu}^2 + \left(0 - \frac{2}{3}\right)\left(0 - \frac{1}{3}\right) Z_{Cu}^2 = \frac{1}{3} Z_{Cu}^2$$

As the ordered structure of the Cu2 layer is known, there is only one possible combination of the two layers that gives 3 and 3' not occupied. This ordering is marked by the red tinted atoms in Figure S6. The vectors 4 and 5 in the 3D-ΔPDF have positive features, in agreement with the O-4 and O'-5' occupied sites.

Finally we look for the relation between two Cu2 layers (e.g. Cu2_1 and Cu2_2 in Figure S2). Figure S7 show these layers. It is first assumed that the lower layer has the blue-tinted sites occupied. We look at the occupied site O and the two unoccupied sites O' and O*. We then look at the vector O-6 which is identical to O'-6' and O*-6*. The 3D-ΔPDF has a negative feature for this vector, which is only possible if there are no atoms separated by that vector, meaning that site 6 has to be empty. If site 6 was occupied the 3D-ΔPDF for this vector would be positive as $\delta Z_O \delta Z_6 + \delta Z_{O'} \delta Z_{6'} + \delta Z_{O^*} \delta Z_{6^*}$

$$= \left(1 - \frac{1}{3}\right)\left(1 - \frac{1}{3}\right) Z_{Cu}^2 + \left(0 - \frac{1}{3}\right)\left(0 - \frac{1}{3}\right) Z_{Cu}^2 + \left(0 - \frac{1}{3}\right)\left(0 - \frac{1}{3}\right) Z_{Cu}^2 = \frac{2}{3} Z_{Cu}^2$$

There are two possible arrangements that leave site 6 empty. These are shown in Figure S7 by the red-tinted atoms. In one of the possibilities site 7 is empty while site 8 is occupied and vice versa in the other possibility. In the 3D-ΔPDF it is seen that vectors 7 and 8 both have positive peaks. There is a negative peak for vector 9, showing that site 9 needs to be empty. Positive peaks are observed for vectors 10 and 11, where one of the

possible arrangements has 10 occupied and the other has 11 occupied. This shows that both possibilities are present in the real structure. The two possibilities are the mirror image of each other. This is where one of the modes of disorder in the structure is introduced.

The full layer can now be constructed as each sublayer is known as well as the ordering between these. Two types of layers are needed, one for each of the possible orderings between two Cu2 layers, as shown in Figure S7. These two types of layers are related through a mirror plane.
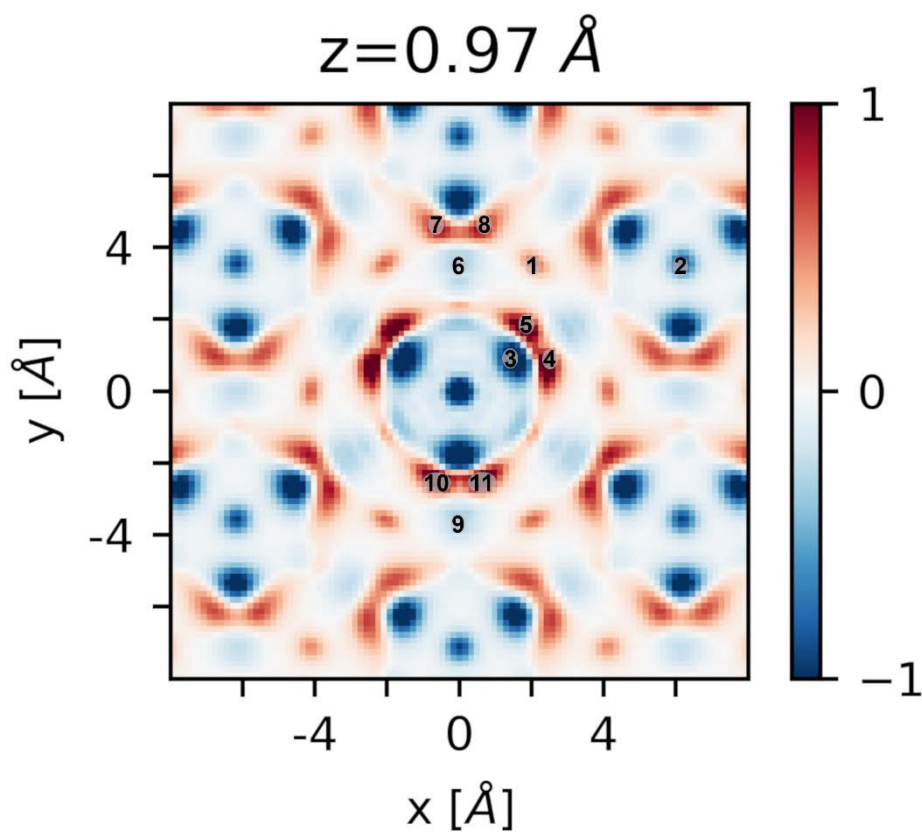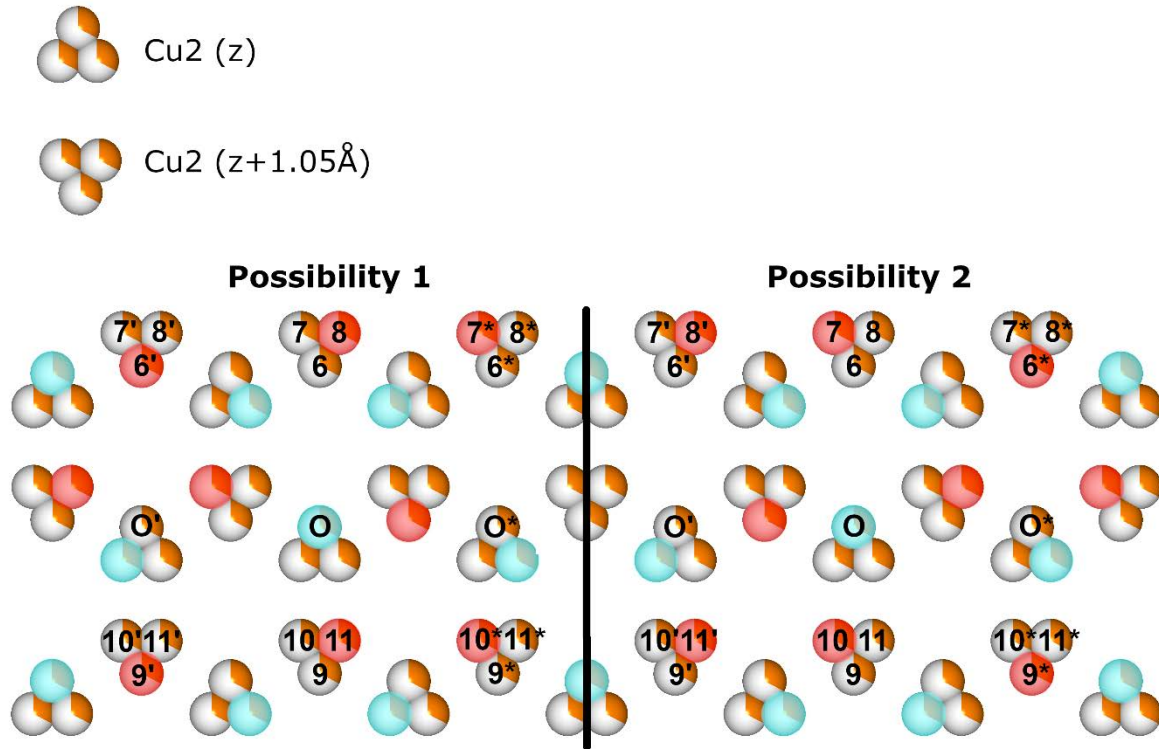

Figure S4 3D-ΔPDF for the z=0.97Å layer.
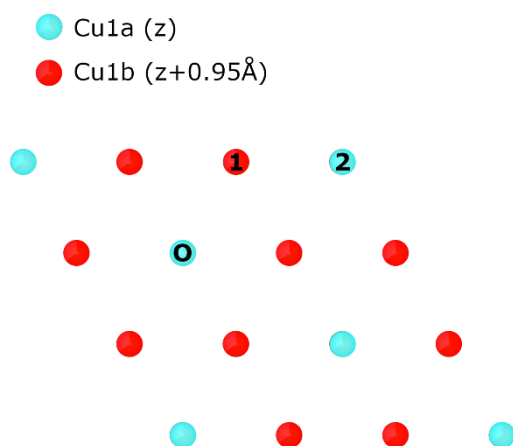
Figure S5 Ordering of close-contact Cu1a and Cu1b layers. The Cu1a and Cu1b layer are separated in z by 0.95Å.
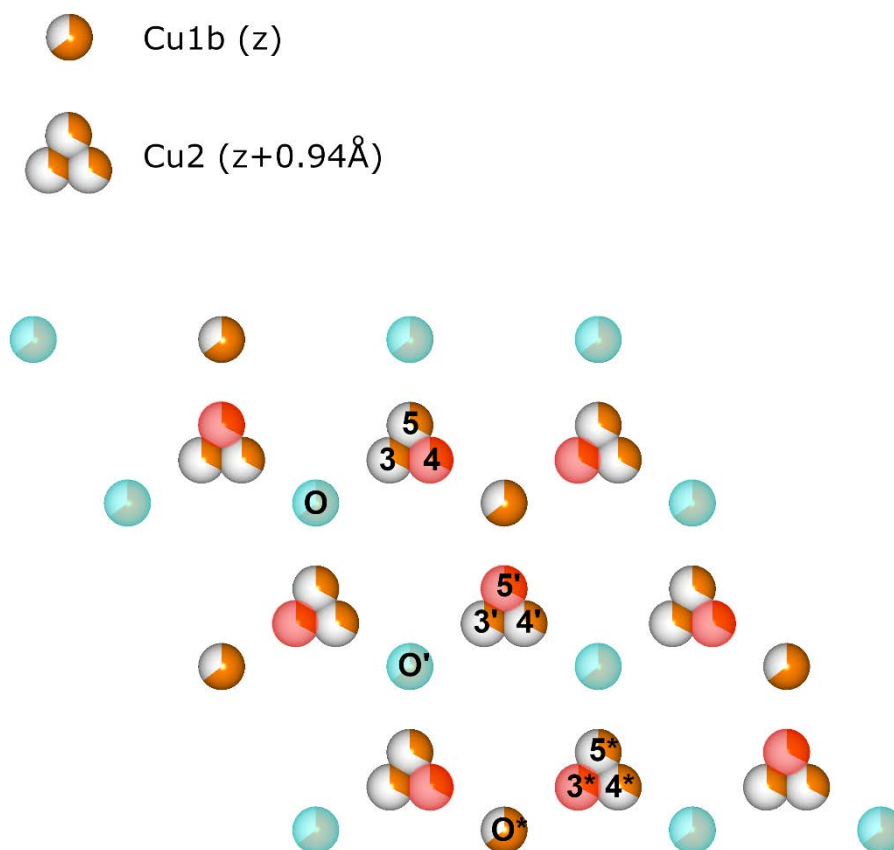
Figure S6 Ordering of close Cu1b and Cu2 layers. The Cu1b and Cu2 layer are separated in z by 0.94Å. Blue and red tinted atoms mark the occupied sites in the Cu1b and Cu2 layer, respectively.

Figure S7 Ordering of close Cu2 layers. The layers are separated in z by 1.05 Å. Blue and red tinted atoms mark the occupied sites in the lower and upper layer, respectively.

S3. Simulations for different models.

Simulations were also made for models where only of the two modes of disorder (mirror/non-mirror layers and inter-layer vectors) were used.

If the simulation is made only using the disorder in the stacking vectors and all layers are the same mirror image, 3D-ΔPDF it not in agreement with experiment. The simulated 3D-ΔPDF for the z = 0.97Å layer for this model is shown in Figure S8 and should be compared to the experiment in Figure S4.

Likewise if only the disorder in whether each layer is mirrored or not is used, the 3D-ΔPDF is also not in agreement with experiment. For this model the 3D-ΔPDF for the y = 0Å layer is shown in Figure S9. In this case strong features are seen for every 20.4 Å, corresponding to 3 layers in the structure. This should be compared to the experimental 3D-ΔPDF as shown in Figure 4 in the main text, where the features quickly disappear along the z direction.

Table S1   Distances between sub-layers in the ordered layer stack.

Vertical distance [Å]	1st layer	2nd layer
0.42	Cu1b_1	Se_1
0.53	Cu1a_1	Se_1
0.94	Cu1b_1	Cu2_1
0.95	Cu1a_1	Cu1b_1
1.05	Cu2_1	Cu2_2
1.36	Cu2_1	Se_1
1.89	Cu1a_1	Cu2_1
1.99	Cu1b_1	Cu2_2
2.41	Cu2_1	Se_2
2.93	Cu1b_1	Cu1b_2
2.94	Cu1a_1	Cu2_2
3.34	Cu1b_1	Se_2
3.88	Cu1a_1	Cu1b_2
4.30	Cu1a_1	Se_2
4.83	Cu1a_1	Cu1a_2
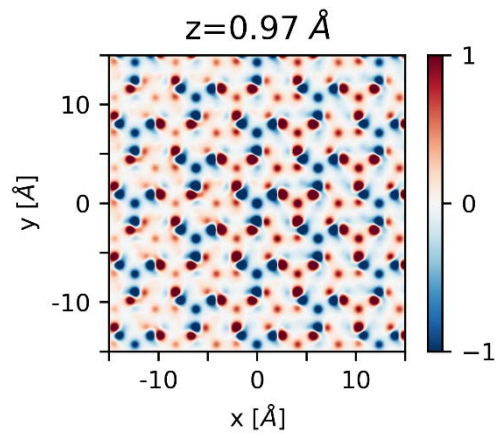
Figure S8 Simulated 3D-ΔPDF for the model where the mirror image disorder of the layer is not used.
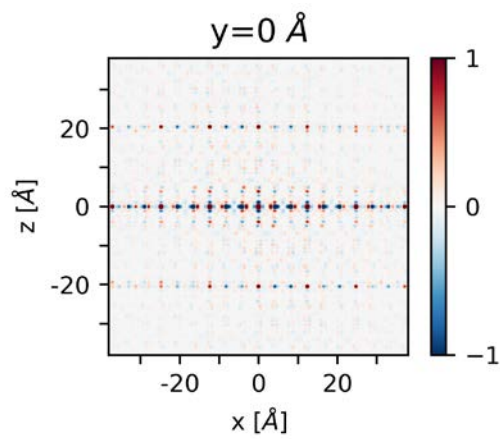
Figure S9 Simulated 3D-ΔPDF for the model where only the mirror image disorder of the layer is used.