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

Nikolaj Roth and Bo B. Iversen*

Center for Materials Crystallography, Department of Chemistry, Aarhus University, Aarhus 8000, Denmark.

*Correspondence e-mail: bo@chem.au.dk

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High-performing thermoelectric materials such as Zn₄Sb₃ and clathrates have atomic disorder as the root to their favorable properties. This makes it extremely difficult to understand and model their properties at a quantitative level, and thus effective structure–property relations are challenging to obtain. Cu_{2-x}Se is an intensely studied, cheap and non-toxic high performance thermoelectric, which exhibits highly peculiar transport properties, especially near the β -to- α phase transition around 400 K, which must be related to the detailed nature of the crystal structure. Attempts to solve the crystal structure of the low-temperature phase, β -Cu_{2-x}Se, have been unsuccessful since 1936. So far, all studies have assumed that β -Cu_{2-x}Se has a three-dimensional periodic structure, but here we show that the structure is ordered only in two dimensions while it is disordered in the third dimension. Using the three-dimensional difference pair distribution function (3D- Δ PDF) analysis method for diffuse single-crystal X-ray scattering, the structure of the ordered layer is solved and it is shown that there are two modes of stacking disorder present which give rise to an average structure with higher symmetry. The present approach allows for a direct solution of structures with disorder in some dimensions and order in others, and can be thought of as a generalization of the crystallographic Patterson method. The local and extended structure of a solid determines its properties and Cu_{2-x}Se represents an example of a high-performing thermoelectric material where the local atomic structure differs significantly from the average periodic structure observed from Bragg crystallography.

1. Introduction

The discovery of disorder effects in crystal structures, which were previously believed to be ordered, has made it possible to explain properties of solids that could not previously be understood. This has been especially important to the field of thermoelectrics, where disorder effects have clarified the fundamental origin of the low thermal conductivity in, for example, clathrates and Zn₄Sb₃ (Christensen *et al.*, 2010; Snyder *et al.*, 2004). Ordered crystal structures are solved through analysis of either X-ray or neutron diffraction data, where the periodicity of the crystal leads to sharp and intense Bragg peaks in the diffraction pattern. Disorder on the other hand gives rise to weak diffuse scattering, which is broad in reciprocal space. In crystals with an average order and local disorder, the scattering will contain both sharp Bragg peaks as well as weak diffuse scattering, making it difficult to measure the diffuse scattering accurately, as it is often more than three orders of magnitude weaker than the Bragg diffraction. In recent years, the measurement of diffuse scattering from single crystals has been made easier because of improvements in detector technology as well as improved X-ray and neutron sources.

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Cu_{2-x}Se is a promising thermoelectric material as it is cheap, non-toxic and has a high thermoelectric figure of merit (zT) (Eikeland *et al.*, 2017; Liu, Yuan *et al.*, 2013; Lu *et al.*, 2015; Qiu *et al.*, 2016; Nguyen *et al.*, 2013; Brown *et al.*, 2016; Brown, Day, Caillat & Snyder, 2013; Brown, Day, Borup *et al.*, 2013; Dalgaard *et al.*, 2018; Liu, Shi *et al.*, 2013; Liu *et al.*, 2012; Miyatani, 1973; Vučić *et al.*, 1984, 1981; Vucic *et al.*, 1982; Yu *et al.*, 2012; Chi *et al.*, 2014; Mahan, 2015; Sirusi *et al.*, 2015; Sun *et al.*, 2015; Kang *et al.*, 2016). The compound has a phase transition at 350–410 K depending on the degree of Cu deficiency (Brown, Day, Caillat & Snyder, 2013; Chi *et al.*, 2014; Eikeland *et al.*, 2017; Liu, Shi *et al.*, 2013; Liu, Yuan *et al.*, 2013; Vučić *et al.*, 1984). Both low- and high-temperature phases have been studied for their thermoelectric properties, while the high-temperature phase is also a superionic conductor (Miyatani, 1973; Vucic *et al.*, 1982; Mahan, 2015; Sirusi *et al.*, 2015; Kang *et al.*, 2016). The compound has been described as a phonon-liquid electron-crystal material because of its good electrical conductivity and low thermal conductivity (Liu *et al.*, 2012). There is much interest in the highly peculiar behavior of the transport properties around the phase transition, where a large enhancement in zT is observed (Brown, Day, Borup *et al.*, 2013; Brown *et al.*, 2016; Liu, Yuan *et al.*, 2013).

There is some confusion in the literature about the nomenclature for the low- and high-temperature phases of Cu_{2-x}Se . Here we use the original labeling by Rahlfs (1936), which names the low-temperature phase $\beta\text{-Cu}_{2-x}\text{Se}$ and the high-temperature phase $\alpha\text{-Cu}_{2-x}\text{Se}$. The high-temperature $\alpha\text{-Cu}_{2-x}\text{Se}$ has the cubic anti-fluorite structure with the Cu atoms distributed in a disordered way on the corners and center of tetrahedra between the layers of the face-centered-cubic (f.c.c.) Se lattice (Dalgaard *et al.*, 2018; Eikeland *et al.*, 2017; Danilkin *et al.*, 2011, 2012).

The structure of $\beta\text{-Cu}_{2-x}\text{Se}$ has been discussed since 1936 (Rahlfs, 1936), and more than ten different unit cells for the structure have been proposed, some of which were collected in the 1987 article by Milat *et al.* (Milat *et al.*, 1987). The crystal systems of these proposed unit cells span triclinic, monoclinic, orthorhombic, tetragonal, trigonal and cubic. In 2011, Gulay *et al.* claimed to have solved the structure of $\beta\text{-Cu}_{2-x}\text{Se}$ from X-ray diffraction data (Gulay *et al.*, 2011), but their model had a very low agreement with the data and was later shown to be incorrect (Eikeland *et al.*, 2017). Later studies by Brown *et al.* attempted to find the structure using pair distribution function and density functional theory (DFT) analysis (Brown, Day, Borup *et al.*, 2013; Brown, Day, Caillat & Snyder, 2013; Brown *et al.*, 2016). Even with all this effort to understand the structure of $\beta\text{-Cu}_{2-x}\text{Se}$, there is still wide acknowledgement that a sufficient structural model has not yet been found (Brown *et al.*, 2016; Dalgaard *et al.*, 2018; Eikeland *et al.*, 2017; Frangis *et al.*, 1991; Gulay *et al.*, 2011; Liu, Yuan *et al.*, 2013; Lu *et al.*, 2015; Milat *et al.*, 1987; Nguyen *et al.*, 2013; Yamamoto & Kashida, 1991; Brown, Day, Caillat & Snyder, 2013; Kashida & Akai, 1988; Qiu *et al.*, 2016; Rahlfs, 1936). One reason for this lack of structural information is the difficulty in synthesizing high-quality single crystals of the β phase. As the high-temperature α phase is cubic, the low-temperature phase can

easily become twinned. However, this difficulty is not enough to explain the problem of solving the structure. In 2017, Eikeland *et al.* showed that the diffraction pattern of a very high quality single crystal of $\beta\text{-Cu}_{2-x}\text{Se}$ can be divided into strong main reflections and weak superstructure reflections and was able to solve the average structure from the main peak intensities only (Eikeland *et al.*, 2017). This average structure contains ordered Se sites and Cu on disordered sites. The information about the Cu ordering is then contained in the weak reflections.

Fig. 1(a) shows the $hk0$ plane of the scattered X-ray intensity from $\beta\text{-Cu}_{2-x}\text{Se}$ at 300 K, where the strong main reflections and weak superstructure reflections can be seen. Several superstructures for the Cu ordering have been proposed, of which most have very small differences in energy (Eikeland *et al.*, 2017; Gulay *et al.*, 2011; Liu, Yuan *et al.*, 2013; Lu *et al.*, 2015; Nguyen *et al.*, 2013; Qiu *et al.*, 2016). However, none of these have so far been in good agreement with experimental X-ray scattering data. We show here that the previously reported superstructure reflections are not Bragg reflections, but instead diffuse-scattering rods, showing the structure to have a two-dimensional ordered superstructure and one-dimensional disorder. These diffuse rods along the l direction of reciprocal space can be seen in Figs. 1(b) and 1(c). We analyze these diffuse-scattering data using the three-dimensional difference pair distribution function (3D- Δ PDF) method (Canut-Amorós, 1967; Schaub *et al.*, 2007; Weber *et al.*, 2007; Weber & Simonov, 2012), which makes it possible to directly construct the two-dimensional superstructure of the layers as well as identify the one-dimensional disorder of the layer stacking. The 3D- Δ PDF is defined as the inverse Fourier transform of the scattered diffuse intensity, which is equal to the autocorrelation of the difference between the total electron density and the average periodic electron density (Weber & Simonov, 2012):

$$3\text{D-}\Delta\text{PDF} = \mathcal{F}^{-1}(I_{\text{diffuse}}) = \langle \delta\rho \otimes \delta\rho \rangle,$$

where $\delta\rho(\mathbf{r}) = \rho_{\text{total}}(\mathbf{r}) - \rho_{\text{periodic}}(\mathbf{r})$ is the difference electron density, $\langle \dots \rangle$ is the experiment time average and $\otimes$ is the cross-correlation operator. The autocorrelation of the difference density will have positive peaks for vectors separating more electron density than in the average periodic structure, and negative peaks for vectors separating less electron density than the average periodic structure. As the 3D- Δ PDF gives a direct-space three-dimensional view of the correlations in the system, it provides an intuitive way to understand the information contained in the scattering data. It can be thought of as a generalized Patterson function for diffuse scattering. Unlike the frequently used one-dimensional PDF technique (Billinge & Egami, 2003), the 3D- Δ PDF method separates interactions at equal distances but different spatial directions, and it also makes observations of weak disorder possible in systems with a superimposed average order.

From the 3D- Δ PDF analysis, we find that the structure consists of ordered layers which are stacked in a disordered way. There is only one type of layer, which can be described using layer-group symmetry, whereby only coordinates for five

Figure 1

Experimental (a)–(c) and calculated (d)–(f) X-ray scattering for β -Cu_{1.95}Se at 300 K. (a) $q_z = 0$ plane with strong reflections which give an average structure with space group $R\bar{3}m$, while weak reflections are seen between the main reflections. (b) $q_x = 0$ plane where rows of Bragg peaks are seen with lines of diffuse scattering between them. (c) $q_y = 1.00$ Å^{−1} plane which only has diffuse-scattering lines. (d), (e) and (f) are the corresponding layers of the calculated scattering. The calculation is based on a random stacking of layers generated with both a random order of mirrored and non-mirrored layers as well as a random order of the three possible inter-layer vectors (see text). The calculation does not take atomic vibrations into account.

atoms are needed. We then find that there is a disordered stacking sequence of this layer and its mirror image as well as disorder in three possible inter-layer vectors. We then compare the found structure with suggested structures in the literature and show that many of the previously proposed structures are periodic repetitions of units that will be found in the real disordered structure.

2. Methods

Single crystals of β -Cu_{2−x}Se were grown using chemical vapor transport with iodine as a transport agent as previously reported by Eikeland *et al.* (2017). The average structure was studied at 300 K on a SuperNova diffractometer from Agilent Technologies using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). Diffracted intensities were collected on a CCD detector and the data were integrated and corrected for absorption using *CrysAlisPro* (Agilent, 2010). The structure solution and refinement were carried out with *SHELXS* and *SHELXL*, respectively, using the *OLEX2* GUI (Dolomanov *et al.*, 2009; Sheldrick, 2015*a,b*). The occupancies of all Cu sites were allowed to refine freely, while the occupancy of Se was fixed to 1. The diffuse scattering experiment was carried out at the 15-ID-D beamline at the Advanced Photon Source. A single crystal of Cu_{2−x}Se (90 µm octahedron) was glued to the end of a thin glass pin using epoxy and mounted on a Huber kappa-geometry goniometer. Data were measured using 40 keV X-rays with a sample-to-detector distance of 120 mm on a Dectris Pilatus 1M CdTe detector. As the detector has gaps between the detector modules, three runs were measured with different detector positions to avoid any missing data. Each run was a 360° omega rotation with phi and kappa at 0. Each

frame was measured every 0.1° during a continuous rotation. After the experiment the crystal was removed and the background air scattering was measured separately for later subtraction. The data were converted to reciprocal space using a Matlab script written by Martin von Zimmerman (Zimmermann, 2019). During this process the data were corrected for Lorentz and polarization factors, the background scattering from air was subtracted, and a solid-angle correction was applied as the detector is flat. The resulting data were symmetrized using the $\bar{3}m$ point symmetry of the Laue group. The resulting scattering data were reconstructed on a $901 \times 901 \times 901$ point grid with each axis spanning ± 19.5 Å^{−1}. In order to obtain the 3D- Δ PDF, the Bragg peaks were removed and replaced by interpolated values using a punch-and-fill method, as previously described in the supporting information of Roth *et al.* (2018). The resulting data containing only the diffuse scattering were then Fourier transformed to give the 3D- Δ PDF.

The theoretical scattering pattern based on the found model for the structure was calculated using a Python script. First, the atomic scattering factors for Cu and Se are calculated on a $501 \times 501 \times 501$ point grid for the same range as the experimental data using the parametrized scattering factors from Doyle & Turner (1968). The scattering for one unit cell of the ordered layer structure is then calculated using the structure-factor equation $F_{\text{cell}}(\mathbf{q}) = \sum_j f_j(\mathbf{q}) \exp(i\mathbf{r}_j \cdot \mathbf{q})$, where $\mathbf{q}$ is the scattering vector and $\mathbf{r}_j$ is the coordinate of the j th atom in the layer unit cell based on the model in Table 2. The scattering of one ordered layer is calculated by $F_{\text{layer}}(\mathbf{q}) = \sum_j F_{\text{cell}}(\mathbf{q}) \exp(i\mathbf{t}_j \cdot \mathbf{q})$, where $\mathbf{t}_j$ is the translational vector to the j th unit cell in two dimensions. The scattering of the mirrored layers is given by the mirror of F_{layer} . The scattering for a sequence of layers is

Table 1
Crystallographic data for the average structure.

Chemical formula	Cu _{1.95} (₂)Se
Space group	<i>R</i> 3 <i>m</i> , hexagonal
Temperature (K)	300
<i>a</i> (Å)	4.1217 (3)
<i>c</i> (Å)	20.435 (3)
<i>V</i> (Å ³)	300.65 (7)
<i>Z</i>	6
ρ_{calc} (g cm ⁻³)	6.726
μ (mm ⁻¹)	38.35
<i>F</i> (000)	544
(sin θ/λ) _{max} (Å ⁻¹)	0.74
<i>N</i> _{Tot,obs}	2127
<i>N</i> _{Uniq,obs}	157
<i>N</i> _{Parameters}	19
GOF	1.107
<i>R</i> _{int}	0.0797
<i>R</i> ₁	0.0404
<i>wR</i> ₂	0.0804

	Position [<i>x/a</i> , <i>y/b</i> , <i>z/c</i>]	Wyckoff position	Occupancy
Se	[0, 0, 0.24097 (7)]	6c	1
Cu1a	[0, 0, 0.1181 (6)]	6c	0.328 (14)
Cu1b	[0, 0, 0.0715 (4)]	6c	0.648 (14)
Cu2	[0.2624 (6), 0.5248 (6), 0.02557 (16)]	18 <i>h</i>	0.325 (5)

then calculated as $F_{\text{model}}(\mathbf{q}) = \sum_j F_{\text{layer}_j}(\mathbf{q}) \exp(i\mathbf{s}_j \cdot \mathbf{q})$, where $\mathbf{s}_j$ is the vector to the *j*th layer and F_{layer_j} is the scattering factor for the *j*th layer. Finally, the intensity is obtained through $I = |F_{\text{model}}|^2$. To calculate the 3D- Δ PDF based on the found model, the calculated intensity for the average structure is subtracted from the calculated intensity for the model and the Fourier transform is taken.

3. Average structure

The average structure, which was solved and refined from the Bragg diffraction data, is identical to the one previously reported (Eikeland *et al.*, 2017) and is shown in Fig. 2. Structural data are given in Table 1. The structure is built up from hexagonally-close-packed Se layers stacked in a distorted f.c.c. pattern along the *c* axis in the hexagonal unit cell. The Cu atoms are disordered over three different sites. Two of these sites, marked Cu1a and Cu1b in Fig. 2(a), are very close and have occupancies of 1/3 and 2/3, respectively, within two standard deviations. From chemical considerations, it is expected that when a Cu1a site is filled, the Cu1b right next to it will be empty and vice versa. The last Cu site, marked Cu2, forms small triangles with each corner 1/3 filled as seen in Fig. 2(b). Also, for this site it is expected that only one Cu position in each of the triangles will be occupied in the real structure. The structure can be seen as layered, where each layer consists of two Se layers, two Cu1a layers, two Cu1b layers and two Cu2 layers. One such layer is marked with a curly bracket in Fig. 2(a), and Fig. 2(b) shows one such layer from above. Between these layers are gaps of ~ 3 Å, and the interactions between the layers are expected to be weak. From the structural refinement, the composition is found to be Cu_{1.95}(₂)Se, in quantitative agreement with refinements on a previous crystal

from the same synthesis batch (Eikeland *et al.*, 2017), which suggests that there is a $\sim 2.5\%$ deficiency of Cu. However, it should be mentioned that the present refinements, like the previous in the literature, used the independent-atom model with neutral Cu and Se species. Since the structure probably contains species closer to Cu⁺ and Se²⁻, the real Cu content may in fact be closer to the stoichiometric Cu₂Se.

4. Two-dimensional order and one-dimensional disorder

The diffuse scattering contains information on the local deviations from the average structure. In Figs. 1(b) and 1(c) strong diffuse features are seen as thin lines along the *l* direction of reciprocal space. This one-dimensional diffuse scattering reveals the presence of two-dimensional ordering and one-dimensional disorder. From the average structure, it is expected that the one-dimensional disorder may arise

Figure 2
Average structure of β -Cu_{1.95}Se. (a) The layered structure with the different sites marked. (b) A single layer seen from above. The black atoms are Se, and the orange are Cu. The partly filled colors show the occupancy of the site.

from stacking faults of layers that have a two-dimensional ordered superstructure. To confirm this and to find the exact ordering and disorder, we use the 3D- Δ PDF which is obtained as the Fourier transform of the diffuse scattering. The amplitude of a peak in the 3D- Δ PDF for a vector $\mathbf{r}$ is given by $\sum_{(i,j)|\mathbf{r}_{ij}=\mathbf{r}} \delta Z_i \delta Z_j$, where δZ_i is the difference in the number of electrons between the real and average structure for atom i (see supporting information for more details). The summation runs over all pairs of atoms (i, j) separated by the same vector $\mathbf{r}$.

To illustrate the method by which the two-dimensional ordered structure can be solved, a layer of Cu₂ sites is shown in Fig. 3 together with a small part of the 3D- Δ PDF for the $z = 0$ plane. The Cu₂ layers are perpendicular to the c direction of the unit cell of the average structure and contain small triangles of Cu sites, with each corner of the triangles having 1/3 occupancy in the average structure.

We start by assuming that the site marked 'O' is occupied by a Cu atom. The two immediate neighbors in the same triangle are separated from 'O' by a distance of 0.88 Å and cannot be occupied at the same time as 'O'. This is confirmed by the 3D- Δ PDF, where there is a positive peak at the origin surrounded immediately by a negative ring. Positive peaks in the 3D- Δ PDF show vectors for which the real structure has more electron density separated by that vector compared with the average structure. In the same way, a negative peak occurs for vectors which separate less electron density

compared with the average structure. As all atoms are always separated from themselves by the zero vector, which is different to the average structure, a positive peak will always be found at the zero vector in the 3D- Δ PDF. The average structure gives electron density separated by the vectors between the Cu sites within one triangle. As this does not occur in the real structure, these vectors show negative regions in the 3D- Δ PDF. To find the ordering of Cu between the triangles, we then look at longer vectors in the 3D- Δ PDF. Some of the sites in Fig. 3 are marked by numbers. The vectors from 'O' to the numbered sites are marked in the 3D- Δ PDF using the same numbers. It is found that for vectors from 'O' to each corner of a triangle, only one will be in a positive region of the 3D- Δ PDF, and the remaining two in the negative regions. This shows that there is a unique ordering of the Cu₂ layers. The red-tinted sites in Fig. 3 show the occupied Cu sites

Figure 3

Two-dimensional ordering of the Cu₂ layers in β -Cu_{1.95}Se. (Left) A layer of Cu₂ sites in the average structure, which form triangles with each triangle 1/3 occupied. Red-tinted atoms mark the ordered structure if a Cu atom occupies the position marked 'O'. (Right) The $z = 0$ plane of the 3D- Δ PDF for short-range correlations. Numbers, n , marked in the left figure give vectors O- n which are marked by the same number in the right figure.

Figure 4

3D- Δ PDF for Cu_{2-x}Se at 300 K. (a, b, c) are the measured 3D- Δ PDF while (d, e, f) are the corresponding calculated 3D- Δ PDF from the simulated model of perfect two-dimensional order and one-dimensional disorder. The simulated 3D- Δ PDF has been broadened by a Gaussian function to emulate the effect of isotropic thermal vibration.

assuming that 'O' is occupied. Longer correlations can then be seen in Fig. 4, where larger cuts through the 3D- Δ PDF are shown. The same method for finding the ordered structure of a layer with the same z coordinate is then used for the other Cu layers in the structure. The correlations between layers are then found for the $z \neq 0$ Å parts of the 3D- Δ PDF. Fig. 4(b) shows one such layer with $z = 0.97$ Å. In this way, the ordered superstructure can be solved, as the possible sites and amounts of filling is known from the average structure. A detailed step-by-step guide through the structure solution is given in the supporting information.

The one-dimensional disorder can also be seen from the 3D- Δ PDF when looking at longer correlations in the z direction. Fig. 4(c) shows the $y = 0$ Å plane. The ordering of the layers is seen as strong features in the xy plane, while the stacking disorder is seen by the fast decay of features in the z direction. The longest distance in the z direction with strong features is seen to be around 5 Å. This is also the thickness of the layers in the structure and thus there is disorder in the stacking of layers. It is therefore meaningful to describe the structure by perfectly ordered two-dimensional layers with stacking disorder.

The ordered-layer superstructure that was found is shown in Fig. 5. The layer is three-dimensional with translational symmetry in two dimensions and point symmetry in the third. This type of symmetry is best described using the subperiodic layer groups (Kopsky & Litvin, 2002), and the layer has $p\bar{3}$ layer-group symmetry. The new unit cell and symmetry elements of the layer are shown in Fig. 5(b). Using this description, only one Se site and four Cu sites are needed. The unit-cell dimensions, atomic coordinates, Wyckoff positions and their related sites in the average structure are given in Table 2. Note that the coordinates x and y are given as relative

Table 2

Structure of ordered layer in β -Cu_{1.95}Se.

Note that x and y coordinates are given relative to the unit-cell axis, while the z coordinates are in Å. The layer related by the mirror operation $(x, y, z) \rightarrow (y, x, z)$ is also permitted.

Layer group	$p\bar{3}$ (No. 66)		
Temperature (K)	300		
a (Å)	7.1389 (5)		
	$x/a, y/b, z$	Wyckoff position	Corresponding site in average structure
Se	1/3, 1/3, 1.888 Å	6e	Se
Cu1	1/3, 2/3, 2.415 Å	2c	Cu1a
Cu2	0, 0, 1.463 Å	2b	Cu1b
Cu3	2/3, 1/3, 1.463 Å	2c	Cu1b
Cu4	0.596, 2/3, 0.523 Å	6e	Cu2

coordinates with respect to the unit-cell axis, while the z coordinates are given in Å. In the supporting information we show that the 3D- Δ PDF requires two types of layers which have the same structure but are related by the mirror operation $(x, y, z) \rightarrow (y, x, z)$ in the layer coordinate system. As the layer itself has an inversion center this mirror is the same as turning the layer upside-down by rotating the layer 180° around $[1\bar{1}0]$.

The one-dimensional disorder along the c direction can be explained through the symmetry relation between the average structure and the ordered layer structure. The unit cell of the ordered layer structure is a superstructure in the ab plane with $a_{\text{layer}} = a_{\text{avg}} - b_{\text{avg}}$ and $b_{\text{layer}} = 2b_{\text{avg}} + a_{\text{avg}}$, which makes $|a_{\text{layer}}| = \sqrt{3}|a_{\text{avg}}|$, as shown in the supporting information. As the ordered layer symmetry is $p\bar{3}$ while the average structure has symmetry $R\bar{3}m$, the disorder in stacking gives the average structure its mirror plane and the R centering as well as a smaller unit cell. The mirror plane gives the possibility of two types of layers in the structure, one which is the mirror image of the other, also identified from the 3D- Δ PDF (see the supporting information). In the average structure, the relation from one layer to the next is given by the R -centering vector $(2/3, 1/3, 1/3)$ which, by symmetry, is equivalent to $(-1/3, 1/3, 1/3)$ and $(-1/3, -2/3, 1/3)$. In the ordered layer structure, these are no longer equivalent because of the lower symmetry. In the coordinate system of the ordered layer these vectors are $(-1/3, 0, 6.81 \text{ Å})$, $(0, -1/3, 6.81 \text{ Å})$ and $(1/3, 1/3, 6.81 \text{ Å})$. This means that there are two modes of disorder in the c direction of Cu_{2-x}Se. One is whether each layer is mirrored or not and the other is which of the three inter-layer vectors relate one layer to the next. Both of these disorder modes are needed to construct the average structure. From the 3D- Δ PDF along the z direction, as seen in Fig. 4(c), there are no strong features at lengths corresponding to inter-layer vectors, meaning that the stacking of layers is highly disordered.

To check the validity of the proposed model, the scattering and resulting 3D- Δ PDF has been calculated for a model with a random stacking of layers, where both the sequence of mirrored and non-mirrored layers is random as well as a random order of the three inter-layer vectors connecting one

Figure 5

Two-dimensional layer superstructure of β -Cu_{1.95}Se. (a) Layer observed from the side. (b) A single layer observed from above with the layer-group symmetry marked. The black atoms are Se and the orange are Cu. A triangle marks a threefold axis and a circle marks an inversion center.

Figure 6

Local coordination in Cu_{2-x}Se with color coding of different sites. (a) Two layers stacked on top of each other, here using the same mirror image and the inter-layer vector $(-1/3, 0, 0.681 \text{ \AA})$. The gray box marks half of one layer, which is shown in (b). (b) A close-packed Se layer together with close-contact Cu. (c) Trigonal pyramidal coordination of Cu1, Cu2 and Cu3 sites. (d) Trigonal pyramidal coordination of two Cu4 sites forming a dimer. The site labels used here refer to Table 2.

layer to the next. The 3D- Δ PDF from this model is shown in Figs. 4(d), 4(e) and 4(f), and a good agreement with the measured 3D- Δ PDF is found. The calculated scattering for three reciprocal-space planes is shown together with the experimental data in Fig. 1. Both the strong Bragg peaks and thin diffuse lines are recreated in the scattering pattern calculated from the model. Theoretical scattering patterns were also calculated from structural models where only one of the modes of disorder (mirror or inter-layer translation) were used, but these patterns are not in agreement with experimental data (shown in the supporting information). When comparing the experimental and calculated scattering, it is seen that although both the strong Bragg peaks and weak diffuse-scattering rods are reproduced by the calculated model, there are a few very weak features in the experiment that are not reproduced by the model. In the experiment, a small number of weak peaks can be found halfway between some of the Bragg peaks in the q_z direction. This suggests that there is a small modulation of the average structure, doubling the c axis. However, these peaks are around three orders of magnitude weaker than Bragg peaks, showing this modulation to be very small. Likewise the diffuse-scattering rods in the experiment show a slight modulation of intensity along q_z not seen in the calculated data, suggesting that there might be weak correlations in the highly disordered stacking order of layers. The experimental data also show a very weak broad diffuse-scattering term, which is not reproduced by the calculation. This diffuse term is three-dimensional and slowly varying, which means that it gives information about very short range correlations within the ordered layers. This is most likely thermal diffuse scattering from correlated atomic motion as the measurement was carried out at 300 K. It could

also be related to the slight Cu deficiency of the structure. The result of this is also seen in 3D- Δ PDF for the $z = 0$ layer close to the origin (Fig. 4), where there are a few weak features not reproduced in the model 3D- Δ PDF. Further analysis of this very weak secondary diffuse term as a function of temperature might give insight into the mechanism of the Cu diffusion in the material.

5. Local coordination and dimer formation

Fig. 6 shows two of the ordered layers stacked on top of each other where the different crystallographic sites are color-coded. Here, the same mirror image of the layer is used with an inter-layer vector of $(-1/3, 0, 6.81 \text{ \AA})$, but all the different stacking types will give the same local coordination of the atoms. The site labels used here are the ones given in Table 2.

The structure of Cu_{2-x}Se consists of a rhombohedrally distorted face-centered cubic packing of Se with alternating short (3.04 Å) and long (3.78 Å) distances between the close-packed layers. Figs. 6(c) and 6(d) show the coordination of the different Cu sites. The Cu1 sites (blue) are placed in tetrahedral holes in the short gap, pointing out of the ordered layer. The Cu2 (red), Cu3 (green) and Cu4 (orange) sites all have trigonal pyramidal coordination to Se, where Cu2 and Cu3 sites point into octahedral holes in the ordered layer, while the Cu4 sites point into tetrahedral holes. The Cu2 sites form pairs pointing into the same octahedral hole from each side of the ordered layer while the Cu3 sites are adjacent to Cu1 sites. The Cu4 sites form dimers which share two Se atoms. The Cu4–Cu4 distance in these dimers is shorter (2.32 Å) than the Cu4–Se distance (2.56 Å). The formation of Cu–Cu dimers with short Cu–Cu distances down to 2.30 Å have previously been

observed in molecular Cu–Se clusters (Dehnen *et al.*, 2002). Some of the largest of the reported molecular clusters with a 2:1 ratio of Cu:Se, *e.g.* $\text{Cu}_{140}\text{Se}_{70}(\text{PET}_3)_{34}$, have three layers of Se stacked ABA [as in the hexagonal close-packed (h.c.p.) structure] with Cu in trigonal and tetrahedral coordination to Se. This is very similar to the structure for bulk Cu_2Se found here, although the bulk structure has f.c.c. stacking of the Se layers. These molecular clusters might be seen as precursor phases to the bulk structure and could give insight into the formation of Cu_2Se .

Fig. 6(b) shows half of one of the ordered layers, as viewed from above. As seen in the figure, the Cu4 sites are displaced away from the ideal tetrahedral sites toward the Cu1 sites. As the Cu1 site is above the Se layer while the Cu2, Cu3 and Cu4 sites are below, there is more room underneath the Cu1 sites than the Cu2 and Cu3 sites.

6. Comparison with structures suggested in the literature

A number of structures for $\beta\text{-Cu}_{2-x}\text{Se}$ have been suggested in the literature. However, none of them are in good agreement with the measured scattering data. Common to all of the proposed models is the assumption of a periodic structure in three dimensions in contrast to the real structure reported here, which is ordered in two dimensions and has stacking disorder in the third dimension. However, many of the suggested structures are periodic repetitions of structural units that also occur in the real disordered structure. Gulay *et al.* suggested a monoclinic structure (space group $C2/c$) with four layers going through the unit cell (Gulay *et al.*, 2011). The layers themselves are in fact equivalent to the two-dimensional layer shown in Fig. 5, but the stacking sequence is given by two identical layers, then two mirrored layers and so on. Liu *et al.* suggested two different structures based on DFT calculations (Liu, Yuan *et al.*, 2013), one being a monoclinic structure (space group $C2/c$) and the other triclinic ($P\bar{1}$). Both of these also have approximately the same ordered two-dimensional layers as shown in Fig. 5. The triclinic structure has a stacking of identical layers, whereas the monoclinic structure has a stacking of alternating mirrored and non-mirrored layers. It was noted that these two structures were very close in energy. Lu *et al.* suggested another triclinic structure (space group $P1$), which has stacking of only one slightly distorted layer. They suggested that several of the proposed structures form together based on electron microscopy (Lu *et al.*, 2015). Qiu *et al.* suggested three additional structures with very small energy differences, and based on electron microscopy measurements they also suggested that the structures coexist. They suggested two triclinic structures (space group $P\bar{1}$) and one monoclinic structure (space group $C2/c$), which all have slightly distorted layers compared with those found here (Qiu *et al.*, 2016). Both the triclinic structures have stacking of one layer type (no mirrored layers) and the monoclinic structure has alternating mirrored and non-mirrored layers. Nguyen *et al.* suggested a monoclinic structure ($P2_1/c$), which does not resemble the real structure

reported here (Nguyen *et al.*, 2013). Eikeland *et al.* proposed a monoclinic superstructure ($C2/c$) with two types of layers stacking in an alternating sequence. One of the layer types is the correct ordered layer while the other does not resemble the correct ordered layer (Eikeland *et al.*, 2017).

Several of the suggested structures found in the literature having the correct layer types, but periodic stacking sequences, were noted to have very similar enthalpies of formation. It seems reasonable that the stacking disorder found in the real structure is caused by the almost identical enthalpy of the different stacking types together with a higher entropy term from the disorder.

7. Concluding remarks

The use of high-energy synchrotron radiation with low-noise detectors has made it possible to measure weak diffuse-scattering signals from advanced materials in large volumes of reciprocal space. From such data it is becoming increasingly evident that structural disorder is present, *e.g.* in key thermoelectric materials such as PbTe and Cu_{2-x}Se , and, moreover, that this disorder is critical for giving the materials their desirable properties. The apparent disorder is not fully random, but correlated, and by using 3D- Δ PDF analysis of single-crystal diffuse X-ray scattering we show that it is possible to solve structures that are ordered in some dimensions but disordered in others. Correlated disorder means that there is a local order in regions of the crystal dictated by specific chemical bonding interactions. The term local order might therefore be more descriptive than correlated disorder.

Here we have studied the thermoelectric material $\beta\text{-Cu}_{2-x}\text{Se}$ for which the structure has been discussed since 1936 without any structural models being able to explain the measured scattering data satisfactorily (Eikeland *et al.*, 2017; Frangis *et al.*, 1991; Gulay *et al.*, 2011; Kashida & Akai, 1988; Liu, Yuan *et al.*, 2013; Lu *et al.*, 2015; Milat *et al.*, 1987; Nguyen *et al.*, 2013; Qiu *et al.*, 2016; Rahlfs, 1936; Yamamoto & Kashida, 1991). The reasons for this failure have been that all previous structural models have assumed three-dimensional periodicity and it has been difficult to synthesize high-quality single crystals. The real structure of $\beta\text{-Cu}_{2-x}\text{Se}$ consists of two-dimensional ordered layers, which stack in a highly disordered sequence. Using the 3D- Δ PDF, the structure of the ordered two-dimensional layer could be determined by methods related to crystallographic Patterson analysis. In addition, the precise modes of stacking disorder could be identified. Two disorder modes are present in the stacking, one being the sequence of mirrored and non-mirrored layers and the other being the sequence of three possible inter-layer vectors. The disordered stacking gives rise to an average structure with higher symmetry. Several of the previously suggested structures in the literature, which have been noted to have very small differences in enthalpy, in fact have the correct two-dimensional layer structure, but they all assume various periodic stacking sequences (Gulay *et al.*, 2011; Liu, Yuan *et al.*, 2013; Lu *et al.*, 2015; Qiu *et al.*, 2016). The stacking disorder found in the real structure is caused by the almost identical

enthalpy of the different stacking types together with a higher entropy term from the disorder. This underlines the importance of considering non-periodic structures in materials science. In general, the crystal structure induces the specific physical properties of a material, and any kind of quantitative modeling of real materials therefore must use the correct crystal structure. We have constructed the new structural model for Cu_{2-x}Se based on a combination of standard crystallographic analysis of Bragg diffraction data, giving the average structure, and 3D- Δ PDF analysis of the diffuse scattering, providing the deviations from the average structure. The 3D- Δ PDF gives an intuitive and direct method for structural solution of disordered systems without the need for reverse Monte Carlo simulation or energy minimization calculations.

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