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Crystal structure of incommensurate η'' -Cu_{1.235}Sn intermetallic

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Abstract: The crystallographic parameters of the incommensurately ordered phase η'' of the composition Cu_{1.235}Sn are reported. This phase belongs to the group of ordered Ni₂In/NiAs-type phases, with a NiAs-type arrangement Cu(1) Sn and additional Cu(2) atoms partially occupying trigonal-bipyramidal interstices in an ordered fashion, leading to the formula Cu(1)Cu(2)_{0.235}Sn = Cu_{1.235}Sn. The structure model, afterward refined on the basis of powder X-ray diffraction data, has been derived on the basis of the slightly Cu-poorer commensurately ordered η' -Cu₆Sn₅ (=Cu_{1.2}Sn) phase but also on previously reported commensurate structure models η^8 -Cu_{1.25}Sn and η^{4+1} -Cu_{1.243}Sn derived from selected area electron diffraction data. In line with a recent work (Leineweber, Wieser & Hgel, *Scr. Mater.* 2020, 183, 66–70), the incommensurate η'' phase is regarded as a metastable phase formed upon partitionless ordering of the η high-temperature phase with absent long-range ordering of the Cu(2) atoms. The previously described η^8 and η^{4+1} superstructure are actually of the same phase, and the corresponding superstructure models can be regarded as approximant structures of the η'' phase.

The refined structure model is described in 3+1 dimensional superspace group symmetry $C2/c(q_1 0 - q_3)00$ with a unit cell of the average structure with lattice parameters of $a_{av} = 4.21866(3)$ Å, $b_{av} = 7.31425(5)$ Å, $c_{av} = 5.11137(3)$ Å and $b_{av} = 90.2205(5)^\circ$ and a unit cell volume $V = 157.717(2)$ Å³. The modulation vector is with $q_1 = 0.76390(4)$, $q_3 = 1.51135(5)$, and governs the spatial modulation of the occupancy of the Cu(2) atoms described by a Crenel function. The occupational ordering is accompanied by

displacive modulations of the atoms constituting the crystal structure, ensuring reasonable interatomic distances on a local level. In particular, the spatial requirements of pairs of edge-sharing Cu(2)Sn₅ trigonal bipyramids (Cu(2)₂Sn₈) lead to a measurable splitting of some fundamental reflections in the powder diffraction data. This splitting is considerable smaller in η' -Cu_{1.20}Sn, which lacks such pairs due to the lower Cu content.

Keywords: incommensurate structures; intermetallic compounds; Rietveld refinement; soldering.

1 Introduction

The phase equilibria and the intermetallic phases of the binary Cu–Sn system [1–4] are relevant for the field of Sn-containing bronzes but also for the field of joining of Cu alloys using Sn solders. Upon soldering, typically the intermetallic compounds (IMCs) Cu₃Sn and Cu₆Sn₅ develop. It is, however, already known since the 1910–1920s [5–9] that, what we will further on refer to as Cu₆Sn₅ IMC *as a whole*, consists of different phases. The crystal structures of all these phases derive from the hexagonal Ni₂In/NiAs-type structure (*Strukturbericht* designation B8₂/B8₁), see Figure 1a. In this structure, Cu(1) and Sn form an NiAs substructure with Cu(2) in interstices formed by trigonal bipyramids with five Sn atoms on the corners (including the six surrounding Cu(1) atoms a so-called Edshamar₁₁ polyhedron results, like it is used in the structure description of some works, e.g., [10]). The Cu(2) sites are only occupied with an occupancy of δ . The composition implied by the formula Cu₆Sn₅ corresponds to $\delta = 1/5$. In the present work, compositions of Cu₆Sn₅ IMC will be given by a formula of the form Cu_{1+ δ} Sn.

Most Cu–Sn phase diagrams show two distinct Cu₆Sn₅ phases, an η high-temperature phase and an η' low-temperature phase. While the η phase is reported to be disordered with respect to Cu(2) (e.g., Ref. [11]; $P6_3/mmc$ space group symmetry), there have been many reports about superstructure reflections (e.g., [12]) characteristic for an ordered η' phase. The monoclinic superstructure of this phase was reported in 1994 from a twinned crystal specimen and found to be of monoclinic $C2/c$ symmetry [13]. The basis

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Figure 1: (a) Ni₂In/NiAs-type crystal structure of disordered Cu_{1+δ}Sn = Cu(1)Cu(2)_δSn with conventional hexagonal unit cell (basis vectors with index h) as well as the C-centered (pseudo-) orthorhombic unit cell (index av) used for the monoclinic modulated ordered structures considered in the present work. The partial occupancy of the Cu(2) sites is indicated by the partial black filling of the circles representing the atoms. (b) A schematic featuring the partially occupied Cu(2) sites projected on a ($\bar{1}10$)_h/(010)_{av} plane, where the Cu(2) sites are located at different y_{av} coordinates. Such a scheme is employed to depict the Cu(2) ordering in Figures 3 and 6. Note that, for convenience, the starting points of the basis vectors has been shifted to the Cu(2) sites in (b).

vectors $\mathbf{a}_m$, $\mathbf{b}_m$ and $\mathbf{c}_m$ of the supercell can be related with $\mathbf{a}_h$, $\mathbf{b}_h$ and $\mathbf{c}_h$ spanning the hexagonal unit cell of disordered η phase according to

$$\begin{pmatrix} \mathbf{a}_m \\ \mathbf{b}_m \\ \mathbf{c}_m \end{pmatrix} = \mathbf{A} \begin{pmatrix} \mathbf{a}_h \\ \mathbf{b}_h \\ \mathbf{c}_h \end{pmatrix} = \begin{pmatrix} 1 & 1 & -2 \\ -1 & 1 & 0 \\ 2 & 2 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_h \\ \mathbf{b}_h \\ \mathbf{c}_h \end{pmatrix}. \quad (1)$$

Crystallographic features of the η and η' phases and of the further discussed commensurate superstructures are summarized in Table 1. Such further superstructures have been reported following to Ref. [13]: η^8 [14], η^6 [14] and η^{4+1} [15]. Common to the intermetallic phases investigated in these works is that they had been heat treated considerably above 200 °C and cooled. The compositions derived for these supercells, Cu_{1.25}Sn for η^8 and η^6 as well as Cu_{1.243}Sn for η^{4+1} , are more Cu-rich than the η' phase (Cu_{1.20}Sn). These more Cu-rich compositions are compatible with the compositional range of the η phase field, which appears to shift to more Cu-rich composition with increasing temperature according to the majority of phase diagrams in the literature [2, 4]. Figure 2 shows the phase boundaries according to Ref. [2] in form of dashed gray lines.

In recent experimental works involving the present authors [16–18], some new insight has been obtained on differently ordered Cu_{1+δ}Sn phases making up of Cu₆Sn₅ IMC:

- i. A method has been devised quantifying the characteristic monoclinic distortion present in the η' superstructure in terms of a strain tensor calculated from the lattice parameters of the η' phase [16].

- ii. Composition dependences of the unit cell volumes for ordered and disordered Cu₆Sn₅ IMC [17, 18] were derived, allowing determination of compositions/ δ values on the basis of sufficiently accurate lattice parameter data. This allowed identification of the extent of a two-phase region $\eta' + \eta$ in a narrow temperature range [17] but also the shape of homogeneity range of the η high-temperature phase [18]. The correspondingly obtained Cu–Sn phase diagram is contained in Figure 2 as black boundaries.
- iii. An incommensurately modulated η'' phase for Cu-rich compositions was reported. That phase was produced when Cu-rich η phase obtained at elevated temperature, was brought to long-range order by annealing at 438 K [18]. In view of other observations, this η'' phase as well as an apparent extension of the η' phase to $\delta > 0.2$ was proposed to be metastable; see red phase boundaries in Figure 2. Upon order formation of the η'' from the η phase occurring partitionless (i.e., without composition change), the volume decrease was marginal, i.e., in the order of 0.12–0.14%.
- iv. It has been made likely that the previously reported η^8 and η^{4+1} superstructures are likely approximant structures of the η'' phase [18].

The present work presents details of the crystal structure analysis of the η'' only briefly reported in Ref. [18]. In particular, it is shown how the interrelation between the η' , η^8 , and η^{4+1} superstructures can be used to arrive at a general structure model serving as the basis for Rietveld refinements of η'' phase's atomic structure. Selected details of the refined atomic structure are analyzed.

Table 1: Overview over previously reported commensurate structures for Cu₆Sn₅ IMC and a hypothetical η' superstructure and their relation with the general modulated structure model according to $C2/c(q_1, 0 - q_3)00$ symmetry described in Section 3.1. Original description with space group and transformation matrices **A** according to Eq. (1) and **A'** as defined below Eq. (2), trying to keep different **A** matrices compatible with previous works [10, 16]. For the description according to Section 3.1, modulation vector **q** according to Eqs. (3) and (5), the parameter t_0 defining the section of the modulated structure description through the superspace and $r/(r+s)$ referring to the definition of the basis vector in agreement with Eq. (6), for which also a corresponding **A'** matrix defining the supercell is given. The space group refers to a correspondingly formulated supercell.

Structure	Ref.	Ideal composition	Original description	Description according to Section 3.1		
			Space group	A	A'	q , t_0 , $r/(r+s)$ Space group A' in agreement with Eq. (6) Disordered high-temperature phase
η	e.g., [11]	Cu _{1+δ} Sn	$P6_3/mmc$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$		
(average)		Cu _{1+δ} Sn	$C2/c$	$\begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	
η'	[13]	Cu _{1.20} Sn	$C2/c$	$\begin{pmatrix} 1 & 1 & -2 \\ -1 & 1 & 0 \\ 2 & 2 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & -2 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$	Common average structure of modulated structure descriptions of η' , η^8 , η^{4+1} , and η^x
η^8	[14]	Cu _{1.25} Sn	$P2_1/c$	$\begin{pmatrix} 2 & 2 & -1 \\ -1 & 1 & 0 \\ 2 & 2 & 1 \end{pmatrix}$	$\begin{pmatrix} 2 & 0 & -1 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$	$\frac{4}{3}\mathbf{a}_{AV}^* - \frac{8}{3}\mathbf{c}_{AV}^*$ As on the left 0 1
η^6	[14]	Cu _{1.25} Sn	$C2$	$\begin{pmatrix} 3 & 3 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} 3 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\frac{3}{4}\mathbf{a}_{AV}^* - \frac{3}{2}\mathbf{c}_{AV}^*$ $B2_1/c^d$ $1/16$ 0.5 Does not fit into scheme $\begin{pmatrix} 2 & 0 & -3 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$
η^{4+1}	[15]	Cu _{1.243} Sn ^a	$P1^c$	$\begin{pmatrix} 19 & 19 & -9 \\ -1 & 1 & 0 \\ 2 & 2 & 1 \end{pmatrix}$	$\begin{pmatrix} 19 & 0 & -9 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$	$\frac{28}{37}\mathbf{a}_{AV}^* - \frac{56}{37}\mathbf{c}_{AV}^*$ $C2/c$ 0 0.556 $\frac{3}{4}\mathbf{a}_{AV}^* - \frac{3}{2}\mathbf{c}_{AV}^*$ $I2/c^d$ 0 0
η^x		Cu _{1.333} Sn ^b				$\begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$

^a $\delta = 9/37$.
^bHypothetical end-member of structure series.
^cThe Cu(2) atom ordering reported implies $I2/c^d$ symmetry.
^dUnconventional settings of space group no. 14 and 15.

Figure 2: Phase diagram Cu–Sn in the composition–temperature range relevant for this work, modified after Ref. [18]. The grey lines depict the phase boundaries according to an older work [2]. The black lines are due to assuming a stoichiometric η' line compound coexisting at a certain temperature range with η high-temperature phase [17] and due to assessing the homogeneity ranges of η at higher temperatures from the lattice parameters [18]. The red lines delimit the approximate ranges of an extended (to higher Cu contents/higher δ) η' and of the η'' region resulting from partitionless ordering of quenched η phase [18].

2 Methods

For sake of brevity, the detailed structure analysis presented in the present work solely relies on the diffraction data of the most Cu-rich η'' -phase material from Ref. [18], using the same diffraction data.

Five gram alloy was produced with 57 at.% Cu and 43 at.% Sn (Cu: Wieland, plate, K09 grade, 99.99; Sn: Alfa Aesar 99.999 %). The alloy composition was chosen to be located in the (ϵ) -Cu₃Sn + η two-phase field of the Cu–Sn system. Hence, at least upon annealing above 500 K, the corresponding equilibrium was established, leading to an η phase of a Cu content reflecting the high-Cu/low-Sn boundary of the η phase field. The metal pieces were sealed under argon into a fused silica tube. Melting occurred for 24 h at 1073 K. The following heat-treatment step occurred at 653 K for 315 h. After this treatment step, the alloy was quenched in water including crushing of the tube. The alloy piece was fragmented, and one fragment was resealed to be heat treated at 438 K for 72.5 h, followed by quenching.

For X-ray diffraction analysis, the alloy pieces were crushed and ground in an agate mortar. Coarse particles were removed by use of a 50 μ m/mesh sieve. A powder layer was produced on a (510) cut Si crystal from a slurry produced with ethanol, which evaporated prior diffraction analysis. Powder X-ray diffraction (PXRD) data

were recorded on a Bruker D8 ADVANCE diffractometer equipped with a Co tube and using a quartz-crystal Johansson monochromator in the primary beam providing monochromatic Co-K α_1 radiation and an LYNXEYE position-sensitive detector in the diffracted beam. Evaluation of the diffraction data was done using the JANA2006 software [19].

3 Results

3.1 Development of the modulated structure model

The previously reported superstructures for Cu₆Sn₅ IMC listed Table 1 all have in common a translation vector $\mathbf{b}_m = -\mathbf{a}_h + \mathbf{b}_h$, as indicated by the 2nd row of the matrix **A** according to Eq. (1). Hence, in accordance with Refs. [13–15], a projection along that direction can be employed to unambiguously depict the Cu(2) distribution (see right side of Figure 1). Such a projection is used in Figure 3 for the η' , η^8 , and η^{4+1} superstructures, keeping the drawings in agreement with the **A** matrices from Table 1. The η^6 structure is not considered further but only noted for completeness, since it cannot be described by the modulated structure model to be outlined in the following. The alloys with the applied heat treatments investigated in our own studies have given no indication for η^6 type of order.

The η' , η^8 , and η^{4+1} superstructures have, apart from the translation vector $\mathbf{b}_m = -\mathbf{a}_h + \mathbf{b}_h$, further features in common, which partially have been also referred to in previous works [13–15], and which are visible from inspecting Figure 3. In particular, all Cu(2) atoms are assembled on planes parallel to $(11\bar{4})_h$. The trace of such a plane is illustrated by a dashed green line in Figure 3. These planes are spanned by $\mathbf{b}_m$ and by a further translation vector $\mathbf{c}_m = 2\mathbf{a}_h + 2\mathbf{b}_h + \mathbf{c}_h$ (third row of the **A** matrices in Table 1). Assembling the Cu(2) on some of these planes and leaving others empty explains occurrence of superstructure reflections perpendicular to such planes (see analysis of diffraction patterns in Ref. [18]). Taking the positions of these superstructure reflections as modulation vectors, it succeeded to arrive at a general structure model featuring one-dimensional modulations, which is able

- to describe the η' , η^8 , and η^{4+1} superstructures as commensurately modulated structures, and
- to act as a starting model for Rietveld refinement based on X-ray powder diffraction data from the η'' phase.

The modulated structures have at maximum a monoclinic symmetry due to the symmetry breaking

associated with selecting one set of $(11\bar{4})_h$ planes on which the Cu(2) atoms are assembled. Hence, in line with the conventions to formulate one-dimensionally modulated structures an *average structure* is used in the following as a basis to describe the structures. This average structure has a unit cell spanned by the basis vectors $\mathbf{a}_{av}$, $\mathbf{b}_{av}$, $\mathbf{c}_{av}$ obtained using the transformation matrix $\mathbf{A}_{av}$:

$$\begin{pmatrix} \mathbf{a}_{av} \\ \mathbf{b}_{av} \\ \mathbf{c}_{av} \end{pmatrix} = \mathbf{A}_{av} \begin{pmatrix} \mathbf{a}_h \\ \mathbf{b}_h \\ \mathbf{c}_h \end{pmatrix} = \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{a}_h \\ \mathbf{b}_h \\ \mathbf{c}_h \end{pmatrix}. \quad (2)$$

The unit cell of the average structure has close-to orthorhombic shape with $a_{av} \approx a_h$, $b_{av} \approx 3^{1/2}a_h$, $c_{av} \approx c_h$, $\beta_{av} \approx 90^\circ$. With respect to this average structure, $\mathbf{A}$ from Eq. (1) can be reformulated as $\mathbf{A} = \mathbf{A}'\mathbf{A}_{av}$ (see Table 1) and $(11\bar{4})_h$ becomes $(20\bar{4})_{av}$. The matrices $\mathbf{A}'$ have been included in Table 1, too.

The modulation vector selected here to describe the modulated structure is of the type

$$\mathbf{q} = q_1 \mathbf{a}_{av}^* - q_3 \mathbf{c}_{av}^* \quad (3)$$

with positive q_1 and q_3 ,¹ and with * designating the basis vectors of the reciprocal lattice. The $\mathbf{q}$ vector leads to Bragg reflections at

$$\mathbf{g} = h\mathbf{a}_{av}^* + k\mathbf{b}_{av}^* + l\mathbf{c}_{av}^* + m\mathbf{q}. \quad (4)$$

Thereby, h , k , l are the conventional Laue indices and m is the order of the satellite reflection. The Cu(2) distribution of the η' , η^3 , and η^{4+1} superstructures is reproduced correctly with the following structure features:

- 3+1 dimensional superspace group symmetry is taken as $C2/c(q_1 0 - q_3)00$ [20]
- the Cu(2) distributions is described by a Crenel type occupation modulation with a fractional length of the occupied region equal to the value of δ of the respective superstructure
- q_1 and q_3 in Eq. (3) fulfill

$$q_3 = 2q_1 = 2(1 - \delta) \quad (5)$$

and there is an appropriate t_0 value describing the position of the section of the three-dimensional structure through

¹ In Ref. [18] $\mathbf{q} = q_1 \mathbf{a}_{av}^* + q_3 \mathbf{c}_{av}^*$ was adopted instead as modulation vector. In order to keep maximum agreement with the descriptions of the superstructures in [10], as also used in Ref. [16], the modulation vector is modified here. Both descriptions, of course, imply the same atomic structures. The convention used ensures, in particular, direct comparability of the signs of the components in the strain tensors in Eqs. (7) and (8).

the 3+1 dimensional superspace structure. The t_0 determines the actual superstructure and its 3-dimensional space group symmetry.

Using the tools implemented into the Jana2006 software [19], atomic coordinates pertaining to the three η' , η^3 , and η^{4+1} superstructures can be derived in the modulated structure description and as conventional superstructures. The basic parameters pertaining to these descriptions have been added to the lower part of Table 1. Thereby, a uniform type of $\mathbf{a}_m$ basis vector of

$$\begin{aligned} \mathbf{a}_m' &= r(\mathbf{a}_h + \mathbf{b}_h - 2\mathbf{c}_h) + s(\mathbf{a}_h + \mathbf{b}_h - \mathbf{c}_h) \\ &= r(\mathbf{a}_{av} - 2\mathbf{c}_{av}) + s(\mathbf{a}_{av} - \mathbf{c}_{av}) \\ &= (r + s)(\mathbf{a}_{av} - 2\mathbf{c}_{av}) - (2r + s)\mathbf{c}_{av}, \end{aligned} \quad (6)$$

with integer valued r and s was adopted, as given in the first row of the $\mathbf{A}'$ matrices on the right part of Table 1, where the original description of the η' phase already adopts that setting. The accordingly generated atomic arrangement of the η^{4+1} structure shows $C2/c$ symmetry, whereas the space group pertaining to the original unit cell appears to be $I2/c$ instead of $P1$ given in Ref. [15]. This higher symmetry is also confirmed when applying the findsym software tool [21] with very high tolerances to the fractional coordinates reported in Ref. [15].

There is, in fact, an infinite number of superstructures which can be derived based on the present ideal scheme with validity of Eq. (5), in the range $0 \leq r/(r + s) \leq 1$. The η' -Cu_{1.20}Sn superstructure constitutes the endmember superstructure with $r/(r + s) = 1$, whereas $r/(r + s) = 0$ corresponds to a structure included as η^x -Cu_{1.333}Sn in Table 1 and in Figure 3.

3.2 Rietveld refinement

According to Ref. [18] the heat treatment step at 438 K produced the η'' ordering from η at constant composition (i.e., partitionless) assessed as Cu_{1.235}Sn on the basis of the lattice parameters. Rietveld refinement on the basis of the PXRD data from this alloy (see Figure 4) succeeded based on an incommensurately modulated structure model, which is based on the structure description outlined in Section 3.1.

Upon starting to do full-pattern based refinements on the basis of the PXRD data, it first succeeded to get convincing fits to the fundamental reflections using the average structure. Thereby, it turned out that, against original expectation from the evaluation of PXRD patterns of the η' phase [16, 17], visible reflection splitting occurred for some of the fundamental reflections (see Figure 4c). In terms of the monoclinic lattice parameters of the average structure, it turned out that the lattice angle β_{av} deviated

Figure 3: Distribution of the Cu(2) atoms in various ordered Cu_{1+δ}Sn superstructures listed in Table 1 (primed basis vector refer to Eq. (6)) by projecting the Cu(2) atoms on a plane parallel to (010)_{av} in accordance with Figure 1.

from 90° by a significant amount of $\pm 0.2^\circ$. Both directions correspond to equivalent structures and, hence, equivalent qualities of fit. Upon trying to establish q_1 and q_3 parameters for the modulation vector according to Eq. (3), performing a fit considering the satellite reflections, however, it turned out to be important to get the correct choice of the direction of the deviation from $\beta_{av} = 90^\circ$, which turned out to be positive ($90.2 \dots^\circ$) for a $\mathbf{q}$ vector according to Eq. (3). The q_1 and q_3 values calculated via Eq. (5) for the η^{4+1} structure (see also lower part of Table 2) constituted a suitable starting point for a converging refinement of q_1 and q_3 , but these values deviated significantly from the starting values. In any case, freely refined q_1 and q_3 values according to Eq. (3) appeared necessary, since the restriction according to Eq. (5), even with only imposing $q_3/q_1 = 2$ ends with remaining misfits between observed and calculated

peak positions. Displacive modulation parameter were required for all sites to get reasonable satellite reflection intensities.

The refinement model further included a second, hexagonal phase used to describe the relevant reflections due to the Cu₃Sn phase and having a crystal structure according to Ref. [22, 23]. That phase was present due to the overall alloy composition corresponding to 43 at.% Sn and this phase was also visible in optical micrographs of the microstructure, see supplementary material of Ref. [18]. A simplified hexagonal close packed structure was adopted to keep the Rietveld refinement stable, which was well possible because the orthorhombic distortion due to the long-period superstructure is apparently negligible, and the superstructure reflections are very weak (one superstructure reflection is discernible at $2\theta = 32.4^\circ$, see Figure 4b). Note that slight preferred orientation has been adopted for both phases, which might be related with anisotropic cleavage of the crystallites and an orientation relationship of the Cu₃Sn crystallites in the Cu₆Sn₅ matrix.

The final parameters of the Rietveld refinement are listed Table 2. The final choice of the parameters to be refined, in particular the selected orders of the modulation functions, was a compromise between improving the residuals and keeping stability of the refinement as determined by the correlations between the refined modulation parameters.

4 Structure discussion

4.1 Properties of the ideal superstructures

The ordered superstructures which are basis for the general modulated structure model derived in Section 3.1 (see Figure 3) feature very specific close distances between Cu(2) atoms. In the context of this work these distances can be described in terms of different types of connectivities between Cu(2)Sn₅ trigonal bipyramids via common Sn atoms. Possible close connectivities are depicted in Figure 5. It is directly evident from an inspection of the superstructures depicted in Figure 3 that only ac type edge-sharing of Cu(2)Sn₅ trigonal pyramids occurs, which are shown in Figure 5c.

Quite naturally the degree of connectivity between Cu(2)Sn₅ trigonal bipyramids should increase with increasing Cu(2) content, i.e., with increasing δ . In case of the η' superstructure at $\delta = 0.2$ the Cu(2)Sn₅ trigonal bipyramids are isolated in the sense that there are no Sn atoms in common to two or more of such trigonal

Figure 4: Powder-X-ray diffraction data of η'' -Cu_{1.235}Sn with some Cu₃Sn impurity (Co-K α_1 radiation; black data points) together with calculated profile (red) and difference curve (black, bottom) as a result of Rietveld refinements. Reflection markers for the two phases are indicated with black reflection markers, which in the case of η'' pertain to fundamental reflections and green ones to satellite reflections up to order of two: (a) overview with square-root intensity scale, (b) zoomed low-angle region and (c) magnified region of the main fundamental reflections revealing the reflection splitting.

bipyramids. This has to change for $\delta > 0.2$. Until, $\delta = 0.25$, this edge sharing occurs in the form of isolated ac-type edge-sharing *pairs* of Cu(2)Sn₅ trigonal bipyramids (isolated Cu(2)₂Sn₈ units). All Cu(2) atoms in the η^8 superstructure belong to such pairs. The η^{4+1} superstructure consists of both the isolated Cu(2)Sn₅ trigonal bipyramids (composing the η' superstructure) and the Cu(2)₂Sn₈ units. Strikingly the compositional range of the Cu₆Sn₅ IMC, especially when considering the disordered η high-temperature phase (see Figure 2), is approximately confined to the range $0.2 \leq \delta \leq 0.25$. Limiting the homogeneity range to $\delta \leq 0.25$ allows avoiding likely unfavorable

higher connectivities between Cu(2)Sn₅ trigonal bipyramids as, e.g., expected for the hypothetical η^x -Cu_{1.33}Sn superstructure (see Figure 3). Note, however, that disordered η phase with $\delta < 0.2$ appears to exist at relatively low temperatures implying existence of Sn having no direct Cu(2) neighbors atoms at some low temperatures [17].

4.2 Refined atomic structure of the η'' phase

The q_1 and q_3 parameters resulting from Rietveld refinement (Table 2) determining the modulation vector $\mathbf{q}$

Table 2: Results of the Rietveld refinement of the crystal structure of η'' -Cu_{1.235}Sn with $\delta = 0.235$ are assessed based on the lattice parameters [18], which are based on the PXRD data shown in Figure 4. Numbers in parentheses indicate standard deviations pertaining to the Rietveld refinement process.

Diffractometer	Bruker D8 ADVANCE			
Radiation	Co-K _{α1} (λ = 1.78897 Å, quartz primary beam monochromator)			
Diffraction angle range, stepwidth	20–152°, 0.012°			
Background parameters, sample displacement parameter	8, 1			
Residual parameters	profile parameters: $R_{wp} = 0.1018$, $R_p = 7.52$ Bragg R value for the η'' phase over all reflections up to 2nd order satellites: 0.0556			
Profile function	Pseudo Voigt [24], using only two Lorentzian parameters for each phase			
Phase 1				
η''-Cu _{1.235} Sn				
Average structure, space group $C2/c$, Superspace group $C2/c(q_1 0 - q_3)00$, Phase fraction (mass fractions) 0.919(6)				
Lattice parameters and unit cell volume				
$a_{av} = 4.21866(3)$ Å, $b_{av} = 7.31425(5)$ Å, $c_{av} = 5.11137(3)$ Å, $\beta_{av} = 90.2205(5)^\circ$, $V = 157.717(2)$ Å ³				
Modulation vector $\mathbf{q} = q_1 \mathbf{a}_{av}^* - q_3 \mathbf{c}_{av}^*$ with $q_1 = 0.76390(4)$, $q_3 = 1.51135(5)^d$				
atomic displacement parameter ^b for all sites: $\langle u^2 \rangle = -0.0045(2)$ Å ²				
one preferred orientation parameter				
site M	x_{av}^M	y_{av}^M	z_{av}^M	Occupancy
Sn	0	0.3313(2)	1/4	1 Sn
Cu(1)	0	0	0	1 Cu
Cu(2)	0	0.66667(–) ^a	1/4	0.229(2) Cu, see below
Final coordinates				
Sn	x^{Sn}	y^{Sn}	z^{Sn}	1
$x^{Sn} = x_{av}^{Sn} + u_{x,s,1}^{Sn} \sin 2\pi x_4 + u_{x,s,2}^{Sn} \sin 4\pi x_4 + u_{x,s,3}^{Sn} \sin 6\pi x_4$ $y^{Sn} = y_{av}^{Sn} + u_{y,c,1}^{Sn} \cos 2\pi x_4 + u_{y,c,2}^{Sn} \cos 4\pi x_4 + u_{y,c,3}^{Sn} \cos 6\pi x_4$ $z^{Sn} = z_{av}^{Sn} + u_{z,s,1}^{Sn} \sin 2\pi x_4 + u_{z,s,2}^{Sn} \sin 4\pi x_4 + u_{z,s,3}^{Sn} \sin 6\pi x_4$ $u_{x,s,1}^{Sn} = 0.0252(4)$, $u_{x,s,2}^{Sn} = -0.0304(5)$, $u_{x,s,3}^{Sn} = 0.0238(9)$ $u_{y,c,1}^{Sn} = -0.0158(2)$, $u_{y,c,2}^{Sn} = -0.0184(2)$, $u_{y,c,3}^{Sn} = 0.0061(7)$ $u_{z,s,1}^{Sn} = 0.0330(3)$, $u_{z,s,2}^{Sn} = 0.0018(4)$, $u_{z,s,3}^{Sn} = -0.0152(7)$				
Cu(1)	$x^{Cu(1)}$	$y^{Cu(1)}$	$z^{Cu(1)}$	1
$x^{Cu(1)} = x_{av}^{Cu(1)} + u_{x,s,1}^{Cu(1)} \sin 2\pi x_4 + u_{x,s,2}^{Cu(1)} \sin 4\pi x_4$ $y^{Cu(1)} = y_{av}^{Cu(1)} + u_{y,s,1}^{Cu(1)} \sin 2\pi x_4 + u_{y,s,2}^{Cu(1)} \sin 4\pi x_4$ $z^{Cu(1)} = z_{av}^{Cu(1)} + u_{z,s,1}^{Cu(1)} \sin 2\pi x_4 + u_{z,s,2}^{Cu(1)} \sin 4\pi x_4$ $u_{x,s,1}^{Cu(1)} = 0.0301(8)$, $u_{x,s,2}^{Cu(1)} = -0.0037(11)$ $u_{y,s,1}^{Cu(1)} = -0.0128(5)$, $u_{y,s,2}^{Cu(1)} = 0.0225(5)$ $u_{z,s,1}^{Cu(1)} = -0.0027(7)$, $u_{z,s,2}^{Cu(1)} = 0.0023(8)$				
Cu(2)	$x^{Cu(2)}$	$y^{Cu(2)}$	$z^{Cu(2)}$	according to Crenel function
Crenel function: refined length of the occupied domain: $\delta = 0.229(2)$				
$x^{Cu(2)} = x_{av}^{Cu(2)} + u_{x,s,1}^{Cu(2)} \sin 2\pi x_4$ $y^{Cu(2)} = y_{av}^{Cu(2)} + u_{y,c,1}^{Cu(2)} \cos 2\pi x_4$				

Table 2: (continued)

$$z^{\text{Cu}(2)} = z_{\text{av}}^{\text{Cu}(2)} + u_{z,s,1}^{\text{Cu}(2)} \sin 2\pi x_4$$
$$u_{x,s,1}^{\text{Cu}(2)} = 0.068(5), u_{y,c,1}^{\text{Cu}(2)} = -0.0059(9), u_{z,s,1}^{\text{Cu}(2)} = -0.045(4)$$

Phase 2: ϵ -Cu₃Sn

Average structure, space group $P6_3/mmc$, Phase fraction 0.081(3)

Lattice parameters and unit cell volume

$a = 2.75866(5) \text{ \AA}$, $c = 4.32935(16) \text{ \AA}$, $V = 28.5331(6) \text{ \AA}^3$

atomic displacement parameter^b $\langle u^2 \rangle = 0.026(2) \text{ \AA}^2$

site	x_{av}^M	y_{av}^M	z_{av}^M	Occupancy
M	1/3	2/3	1/4	1/4 Sn, 3/4 Cu

^aheld constant due to severe correlation with $u_{y,c,1}^{\text{Cu}(2)}$.

^bThe negative atomic displacement parameter for the η'' phase may be caused by surface roughness effects or residual transparency of the specimen, whereas the relatively large value for the Cu₃Sn phase might be attributed to static atomic displacements present in the neglected superstructure.

^cSimplified structure model to stabilize refinement [22, 23].

^dCalculated reflections up to satellite reflection order of $|m| = 2$

according to Eq. (3) do not fulfill the relation $q_3/q_1 = 2$ implied by Eq. (5), which is fulfilled for all the ideal superstructures. Moreover, neither q_1 nor q_3 exactly fulfills the relation with the parameter δ , neither if the latter value is taken as assessed from the lattice parameters as described in Ref. [18] nor taking the refined value of δ , which is by 3 standard deviations smaller than the assessed parameter (0.229 vs. 0.235). Hence, the Cu(2) ordering must be defective as compared to the ideal structure model derived in Section 3.1 if Eq. (5) would prevail. An approximant structure has been derived based on the refined structure parameters using the tools by Jana2006 and is depicted schematically in Figure 6, highlighting the types of defects occurring in the ordering in terms of dislocation dipoles in the projected modulated structure (double “T”s).

The occurrences of such disturbances in the modulated Cu(2) distribution originate from the deviations from $q_3/q_1 = 2$. These dipoles, on a larger spatial scale can be conceived to form boundaries between more well-ordered regions, and thereby resemble (albeit being geometrically different) domain boundaries showing up in approximant structures of incommensurate Ni₂In/NiAs type Cu_{1+ δ} In phase with $\delta > 0.5$ [25]. It has to be emphasized that the diffraction data available here and the refinement unlikely contain significant information about the exact way in which the deviations from the ideal structural model are realized on a local level, in particular at the dislocations dipoles in Figure 6.

Deviations from ideal occupational ordering as observed here and also previously in related

Figure 5: Type of close Cu(2)–Cu(2) distances depicted (a) schematically as in Figure 3 with solid circles as the Cu(2) atoms and (b, c, d) as illustrated in terms of connected Cu(2)Sn₅ trigonal bipyramids. Only the ac type of edge-sharing according to (c) occurs in the superstructures depicted in Figure 3.

Figure 6: Approximant structure of η'' -Cu_{1.235}Sn calculated using the refined parameters resulting from Rietveld refinement as depicted by the arrangement of Cu(2) atoms in the projection described in Figure 1 and as used in Figure 3 and Figure 5 above. Due to deviation of the refined values of q_1 and q_3 from $q_3/q_1 = 2$, disturbances in the modulated structure occur, which are highlighted as double-“T”s, indicating that in the projection these disturbances can be regarded as edge dislocation dipoles in the ordered arrangement.

intermetallics (e.g., [26, 27]) might originate from peculiarities of the electronic structure. They will, however, in the present case more likely originate from a dependence of the energy of the modulated structure from the degree of ordering. Onset of spatially modulated occupational order can generally be described in terms of static concentration waves [28], which modulate the occupancies of the ordering sites. While the optimum, composition(δ)-adapted ordered superstructures according Section 3.1 and Eq. (5) might indeed be of lowest-energy if perfectly established, incomplete ordering, e.g., during the onset of ordering might deviate from the restrictions of Eq. (5). That argument has already been used in Refs. [26, 27], where the order was definitely incomplete, as also demonstrated by the observed temperature dependence of the degree of order [26]. But also in the present case, where the Crenel function appears suitable to describe the ordering, the early stage of ordering or the short-range order in the short-range ordered η phase may cause onset of ordering with q_1 and q_2 deviating from Eq. (5). During further improving the state of ordering, approaching order in accordance with Eq. (5), would require longer-range redistribution of Cu(2) atoms in order to accomplish the required changes of q_1 and q_3 . Hence, it is expected that the degree of ordering will first improve with

“somewhat incorrect” q_1 and q_3 values, while only a very long-time annealing might bring about changes in q_1 and q_3 toward values in accordance with Eq. (5). Annealing experiments at different temperatures and different durations and analysis of changes in q_1 and q_3 with the annealing program, may yield information about these ideas. Note, however, that according to the current ideas about the phase diagram [18] (see Figure 2), the η'' phase is in any case metastable with respect to unmixing, which might obstruct an analysis of structure changes of the ordering of the η'' phase by means of long-term annealing experiments.

In any case, disregarding the disturbances of the order due to the dislocation dipoles, the Cu(2) ordering in Figure 6 strongly resembles the ordering pattern of the ideal η^{4+1} superstructure, which contains both pairs of ac edge-sharing Cu(2)Sn₅ trigonal bipyramids (Cu(2)₂Sn₈) and isolated Cu(2)Sn₅ trigonal bipyramids.

The refined parameters from Table 2 can be used to calculate interatomic distances, which are most conveniently depicted for an incommensurate structure as a function of the internal coordinate t given by $t = x_4 - \mathbf{q} \cdot (\mathbf{T} + \mathbf{r}_0)$, while $\mathbf{T}$ is a translation vector of the average structure and $\mathbf{r}_0$ the position vector in the average structure. Figure 7 focusses on the distances from the Cu(2)

atoms to other atoms. Especially, when comparing these distances with the “unmodulated” distances shown as dashed lines, the following can be concluded from Figure 7:

- i. The Cu(2)–Sn distances get expanded, in particular, for the equatorial triangles surrounding the Cu(2) atoms in the a_{av} – b_{av} plane. This agrees with the trends described previously in similar Ni₂In/NiAs structures [13, 26, 27, 29, 30]. Minor t ranges of short Cu(2)–Sn distances are likely insignificant in view of the limited orders of satellite reflections visible for evaluation.
- ii. The Cu(2)–Cu(1) distances get somewhat contracted, which is also in agreement with previous observations [13, 26, 29].
- iii. Cu(2)–Cu(2) get strongly expanded. This is the distance between the two Cu(2) atoms in the centers of two ac edge-sharing Cu(2)Sn₅ trigonal bipyramids (Cu(2)₂Sn₈) as shown in Figure 5c. This distance increase is a consequence of the increase of the lengths of the Cu(2)–Sn distances for the Sn atoms bridging the two trigonal bipyramids.

mentioned in Section 3.2 and which has highlighted in Figure 4c. The type of distortion will now be worked out in terms of special types of strain tensors. In Ref. [16], it was shown how the symmetry breaking distortions of a superstructure can be expressed in terms of a symmetric strain tensor following the idea of the Aizu strain [31]. Such a strain tensor fulfills the symmetry restrictions of the crystal class of the analyzed crystal structure. Apart from a zero trace, which is generally required, further restrictions are imposed depending on the crystal class of the parent structure, with respect to which the distortion is considered. Upon describing a 2nd rank tensor like the Aizu strain tensor, it has to refer to a Cartesian coordinate system defined in a specific way with respect to the crystallographic coordinate system of the high-symmetry structure. In case of the monoclinic η' superstructure derived from the hexagonal η , the Cartesian basis vectors were $\mathbf{e}_1$ parallel to $\mathbf{a}_h + \mathbf{b}_h$, $\mathbf{e}_2$ parallel to $-\mathbf{a}_h + \mathbf{b}_h$ and $\mathbf{e}_3$ parallel to $\mathbf{c}_h$. For that the strain tensor has been determined on the basis of the lattice parameters determined for the η' phase [16]:

4.3 Metrical distortion of the η'' phase

The Cu(2)–Cu(2) pairs from the pairs ac edge-sharing trigonal bipyramids Cu(2)₂Sn₈, which do not occur in the η' superstructure, may be made responsible for the metrical distortion of the η'' -Cu_{1.235}Sn structure which has been

$$\begin{aligned} \boldsymbol{\varepsilon}_{\eta \rightarrow \eta'} &= \begin{pmatrix} \varepsilon_{m11} & 0 & \varepsilon_{m13} \\ 0 & -\varepsilon_{m11} & 0 \\ \varepsilon_{m13} & 0 & 0 \end{pmatrix} \\ &= \begin{pmatrix} -0.00080 & 0 & -0.00026 \\ 0 & 0.00080 & 0 \\ -0.00026 & 0 & 0 \end{pmatrix} \quad (7) \end{aligned}$$

Figure 7: {two columns} Plot of the interatomic distances Cu(2)–Sn, Cu(2)–Cu(1) and Cu(2)–Cu(2) as full lines versus the internal coordinate t as results from the Rietveld refinement on the basis of PXRD data from η'' -Cu_{1.235}Sn. The distances only occur in a certain range of t , in which the Cu(2) sites are occupied. Since for Cu(2)–Cu(2) pairs both sites have to be occupied, the t range for which such pairs occur, is smaller than the ranges for Cu(2)–Sn and Cu(2)–Cu(1). Dashed lines are obtained from setting all displacement modulation parameters u (see Table 2) equal to zero.

Thereby, the chosen Cartesian basis vectors $\mathbf{e}_1$ – $\mathbf{e}_3$ are also parallel with the basis vectors of the undistorted average unit cell used for the modulated structure description of the η' and also compatible with the $\mathbf{q}$ vector listed in the lower part of Table 1.

Applying the same procedure to the refined cell parameters of the average structure of the η'' (see Table 2), one obtains (technically following the somewhat more compact but equivalent procedure described in Ref. [32]):

$$\boldsymbol{\varepsilon}_{\eta \rightarrow \eta''} = \begin{pmatrix} -0.00050 & 0 & -0.00192 \\ 0 & 0.00050 & 0 \\ -0.00192 & 0 & 0 \end{pmatrix} \quad (8)$$

As already emphasized in Ref. [16], the components of $\boldsymbol{\varepsilon}_{\eta \rightarrow \eta'}$ are very small, which can explain the not directly detectable peak splitting in PXRD patterns of η' -Cu_{1.20}Sn, at least not in view of the resolution of the diffraction pattern, which largely corresponds to that in the current case. In comparison to this the 7 fold larger ε_{m13} component of $\boldsymbol{\varepsilon}_{\eta \rightarrow \eta''}$ (which is simply $\frac{1}{2}\cos\beta_{av}$) brings about a visible splitting of some reflections (see Figure 4c). Figure 8 compares the tensor surfaces of $\boldsymbol{\varepsilon}_{\eta \rightarrow \eta'}$ and $\boldsymbol{\varepsilon}_{\eta \rightarrow \eta''}$. The green lobes point into the direction of expansion approximately in the $(+\mathbf{e}_1 - \mathbf{e}_3)$ direction, which is about parallel to the Cu(2)–Cu(2) pairs in the modulated structure. Evidently these pairs and the ac edge-sharing trigonal bipyramids Cu(2)₂Sn₈ act as elastic dipoles [33] with very anisotropic space requirement. The density of such dipoles determines the overall extent of the symmetry breaking strain. In fact, checking the lattice parameters of the alloys showing diffraction patterns from Cu₆Sn₅ IMC with η''

phase ordering imply that the deviation from β_{av} decreases with increasing Sn content/decreasing δ .

5 Conclusions

The crystallographic details of the Ni₂In/NiAs type η'' -Cu_{1.235}Sn phase, being one of the ordered states of the Cu₆Sn₅ intermetallic compound, have been worked out based on powder X-ray diffraction data evaluated by Rietveld analysis:

- The partially occupied Cu(2) exhibit monoclinic incommensurate spatial occupational order which was successfully described by a Crenel function. The ordering of these Cu(2) sites is closely related with the commensurate ordering in the more Sn-rich monoclinic η' -Cu_{1.20}Sn (Cu₆Sn₅) superstructure.
- The occupational modulations are accompanied by characteristic displacive modulations, in particular ensuring the geometric requirements of the Cu(2) in interstices formed by five Sn atoms, forming characteristic Cu(2)Sn₅ trigonal-bipyramids.
- Whereas the Cu(2)Sn₅ trigonal-bipyramids occur as isolated units in the η' -Cu_{1.20}Sn (Cu₆Sn₅) superstructure, the higher content of Cu(2) atoms leads to occurrence of pairs of edge-sharing Cu(2)Sn₅ trigonal pyramids (Cu(2)₂Sn₈). The anisotropic space requirements of these pairs and their uniform orientation in the ordered structure cause a detectable monoclinic spatial distortion of the crystal structure of η'' -Cu_{1.235}Sn.

The present structure data will ease adequate phase identification in Cu₆Sn₅ intermetallic compound. Moreover, the structural observations will also contribute to a better understanding of the general ordering trends within the large group of Ni₂In/NiAs type phases.

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Figure 8: {single column} Tensor surfaces (green lobes: positive, red lobes: negative) depicting the direction dependence of symmetry-breaking strain for η'' -Cu_{1.235}Sn (Eq. (8), this work) and for η' -Cu_{1.20}Sn (Eq. (7), [16]), revealing, in view of the common scale (bottom), a much more pronounced distortion for the case of η'' -Cu_{1.235}Sn. That distortion is also visible by splitting of fundamental reflections in the powder diffraction pattern (see Figure 4c).

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