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The Superstructure of Domain-Twinned η'-Cu₆Sn₅

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Abstract

The cell of the low-temperature modification of Cu_6Sn_5, the η-phase, has been determined by means of electron diffraction of single domains. The basic hexagonal NiAs (B8) type cell is pentupled, reflected in the reciprocal lattice by a fivefold superstructure running along $[11\bar{2}1]^*$. The extensive domain-twinning macroscopically gives rise to perfect hexagonal symmetry, which explains the previously proposed hexagonal cell [$a = 5a_{NiAs}$, $c = 5c_{NiAs}$; Bernal (1928), *Nature*, **122**, 54]. The structure was solved by occupying every fifth trigonal bipyramidal site of the NiAs-type structure and shifting the atoms surrounding these additional Cu atoms to form Edshammar₁₁ polyhedra with Cu—Sn and Cu—Cu distances in the range 2.60–2.74 Å. The supercell reflections from the different domains of the twinned crystals are not superimposed, which facilitated the crystal structure refinement [space group $C2/c$; $a = 11.022$ (5), $b = 7.282$ (4), $c = 9.827$ (2) Å, $\beta = 98.84$ (4)° and $Z = 4$], by means of single-crystal X-ray diffraction on a domain-twinned specimen. The Edshammar₁₁ polyhedra form corner-connected zigzag chains along [001]. The structure of η'-Cu_6Sn_5 is hence a new superstructure-type belonging to the NiAs–Ni₂In structure group. The projections of this structure along the axes of the NiAs-type base cell are void of superstructure.

Introduction

This work is part of a series of investigations on structures of and structural relations between M—Sn intermetallic phases, where M are first-row transition metals. Apart from the theoretical importance, there is a vast technical interest in these systems. This investigation concerns the Cu–Sn phase diagram, which is also important in more complex systems since when Cu is present in a Sn melt, crystals of Cu_6Sn_5 easily grow. This phase (together with Cu_3Sn) is the phase growing in Sn/Pb solders of copper leads. Cu_6Sn_5 grows in certain amalgams; it forms in the processing of wires of the superconducting phase Nb_3Sn and in brass.

In this report, the domain crystal structure of one modification of Cu_6Sn_5, the low-temperature modification η', is studied. The high-temperature modification η-Cu_6Sn_5 was first reported to be of the NiAs structure type ($P6_3/mmc$, $a = 4.190$ Å and $c = 5.086$ Å) by Westgren & Phragmen (1928). Bernal (1928) found a superstructure of the low-temperature ordered modification η'. He suggested a fivefold superstructure along all axes yielding a hexagonal cell of the approximate dimensions $a = 20.8$, $c = 25.4$ Å. The same supercell of η' was also reported by Carlsson & Hägg (1932) and Gangulee, Das & Bever (1973). In the present investigation the cell is found to be monoclinic, but the domain-twinned

structure which builds up the macroscopic crystals has a reciprocal lattice corresponding to the cell of Bernal (1928). Goria (1956) reports another super-structure of η' that runs only along the c direction ($a = 4.18$, $c = 25.20$ Å). This is not the same phase as in the present paper and we have not seen any diffraction compatible with this cell. Electron diffraction of the high-temperature η phase has, however, revealed two additional types of superstructures. No superstructure has so far been detected in the corresponding powder diffraction patterns, but in single-crystal work, reflections can be detected. This investigation will be presented elsewhere.

The present paper describes how the structure of η'-Cu_6Sn_5 was solved and refined. The investigation was carried out in four distinct steps.

(1) A preliminary single-crystal X-ray diffraction investigation of a macroscopic crystal, the results of which led us to suspect twinning.

(2) An electron diffraction study to elucidate the twinning. This enabled us to build a probable model of the structure.

(3) An X-ray powder diffraction study that confirmed the model and enabled us to refine the atomic positions.

(4) A final single-crystal X-ray diffraction refinement of a domain-twinned specimen.

Preparation

Cu was mixed with an excess of Sn (1:4) and sealed in a quartz ampoule under vacuum. The mixture was heated to 773 K for 20 h and allowed to cool slowly. The resulting ingot was leached in HCl (12 mol l^{-1}) for several days and the residue contained long hexagonal rods. These were annealed for several weeks at 453 K before being subjected to the X-ray or electron diffraction experiments.

The NiAs-Ni$_2$In-type structures

The NiAs structure type consists of a hexagonal close-packed array of the larger atomic species with the smaller atoms in the octahedral interstities. There is a substantial variation of the axial ratio of the NiAs structures, but in the M—B intermetallics the c/a ratio is 1.2–1.3 (Villars & Calvert, 1985). This means that the octahedra are compressed about 25% along the c-axis compared with ideal octahedra, $i.e.$ there are Ni–Ni connections along the c-axis. The Ni atoms form trigonal prisms around As. The space group of NiAs is $P6_3/mmc;$ The Wyckoff position $2(c)$ ($\frac{1}{3},\frac{2}{3},\frac{1}{4}; \frac{2}{3},\frac{1}{3},\frac{3}{4}$) is occupied by the larger atom (As) and $2(a)$ ($0,0,0; 0,0,\frac{1}{2}$), $i.e.$ the octahedral site, is occupied by Ni(1).

This type of NiAs structure may be stuffed by filling the trigonal bipyramidal sites, the Wyckoff

position $2(d)$ ($\frac{1}{3},\frac{2}{3},\frac{3}{4}; \frac{2}{3},\frac{1}{3},\frac{1}{4}$). The structure type is then Ni$_2$In, which has In in a hexagonal close-packed array and Ni in all octahedral and trigonal bipy-ramidal interstices. M—B intermetallics assigned to either the NiAs- or the Ni$_2$In-type structure commonly have a composition between MB and M_2B, which leads to a partial filling of the trigonal bipyramid interstities. If this is accomplished in an ordered manner, a superstructure is formed. Co$_3$Sn$_2$ (Brand, 1967; Larsson, Stenberg & Lidin, 1994) and Ni$_3$Sn$_2$ (Nial, 1947) are examples of this. The η'-Cu_6Sn_5 structure which will be described here is another example.

The polyhedron around the extra Ni(2) in Ni$_2$In can be described as an Edshammar$_{11}$ polyhedron (Edshammar, 1969; Hyde & Andersson, 1989). The Edshammar$_{11}$ polyhedron (Fig. 1) was originally described as the 11-polyhedron, formed by pulling a cube apart along the [111] axis and recombining the apices after rotating one half $2\pi/6$ (Edshammar, 1969; Lidin, Somer, Popp & van Schnering, 1992). The Edshammar$_{11}$ polyhedron coordinating Ni(2) in Ni$_2$In is also described by the combination of the Ni$_6$ trigonal prism and the In$_5$ trigonal bipyramid. Ni$_2$In is then described as a close-packed array of Ni-centered Edshammar$_{11}$ polyhedra (consisting of Ni and In), while NiAs in this parlance is described as a close-packed array of $empty$ Edshammar$_{11}$ polyhedra. To understand the types of NiAs–Ni$_2$In superstructures that η'-Cu_6Sn_5 represents, the Edshammar$_{11}$ polyhedron is an important concept.
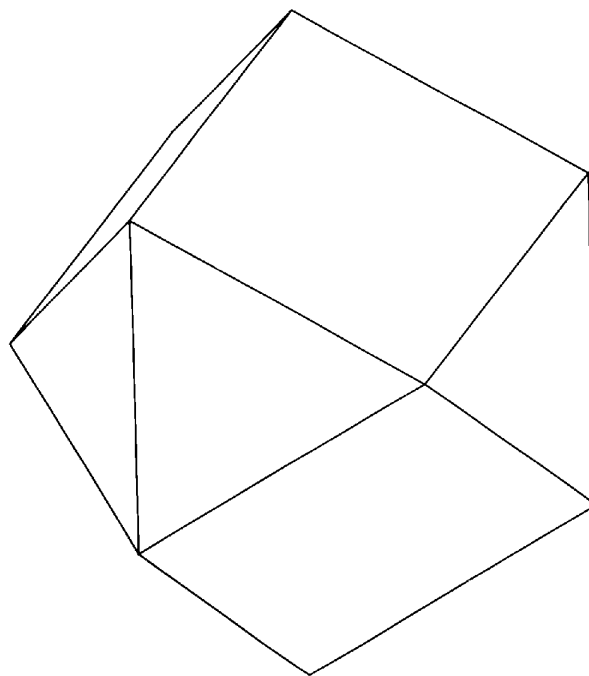

Fig. 1. The Edshammar$_{11}$ polyhedron.

Preliminary X-ray investigation

In a first attempt to determine the structure, well crystallized specimens, with clear-cut morphology, were investigated with a Weissenberg camera. The apparent cell was found to be in agreement with the earlier reports; a basic NiAs-type with all axes pentupled [*i.e.* $a = 20.870$ (2), $c = 25.081$ (2) Å; Gangulee, Das & Bever, 1973]. One of these crystals was investigated by synchrotron radiation at the EMBL in Hamburg. The reciprocal lattice planes containing the reflections $hk0$ and $h0l$, referred to the NiAs-type cell, together with their symmetry equivalents were found to be void of superstructure reflections, suggesting that the projection of the structure onto the base planes is perfectly homogeneous with respect to the NiAs (or the Ni$_2$In) structure. The five constraints set up by the size of the cell ($a = 5a_h$, $c = 5c_h$, the index h referring to the NiAs-type cell), the stuffed NiAs model, hexagonal symmetry, systematic absences and composition are, however, incompatible. The stoichiometry calls for 50 extra Cu$'$ atoms (in Edshammar$_{11}$ polyhedra) and the homogeneity conditions imposed by the systematic absences in the ($hk0$) and {$h0l$} planes demands that these should be distributed among the available Cu$'$ sites according to strict rules. The available sites are given by the combinations of five x-values, five y-values and ten z-values, yielding in all 250 sites. Each x-value and each y-value must be represented ten times, and each z-value must be represented five times. This cannot be combined with hexagonal or trigonal symmetry (or even with orthorhombic symmetry) and twinning was, therefore, suspected. To corroborate the assumption that the superstructure of η'-Cu$_6$Sn$_5$ is caused by regularly filled Edshammar$_{11}$ polyhedra in the base NiAs-type lattice, the average structure was refined using only the base NiAs-cell reflections. 30 unique reflections from the data collected in Hamburg were refined to an R value of 20% using the pure NiAs model. When copper was added in 1/5 of the Edshammar positions, *i.e.* adding 1/5 occupancy of the $2d$ position in the averaged model, the R value decreased to 6%.

Electron diffraction of domains

The electron diffraction studies were performed on well shaped crushed crystals with a JEOL 2000 FX microscope. Diffraction patterns clearly show that the structure is not hexagonal but built up from monoclinic domains. The hexagonal symmetry of the NiAs type cell is broken by a fivefold superstructure along one of the $\langle 11\bar{2}1 \rangle^*$ directions.

Figs. 2(a–f) show examples of electron diffraction patterns from η'-Cu$_6$Sn$_5$. In Figs. 2(a) and (b), the result from the preliminary single crystal work is

verified; the projections along the principal NiAs axes are void of superstructure. A typical diffraction pattern from a crystal fragment aligned along the zone axis $[0\bar{1}1]_h$ is shown in Fig. 2(c). In this single domain crystallite the superlattice spots are only running in the $[11\bar{2}1]_h^*$ direction. This means that the hexagonal symmetry is broken; there is a mirror plane in the hexagonal NiAs lattice but not in the superlattice. After examining a great number of crystallites, many in several directions, the conclusion was that this superstructure could explain all diffraction patterns recorded. The C-centered monoclinic cell chosen to explain the superstructure (*vide infra* and Fig. 5) is generated from the NiAs cell by the transformation matrix $1\bar{1}2/\bar{1}10/221$. The diffraction patterns are indexed in both the base NiAs-type cell and the monoclinic supercell. In some cases, moving the beam across a fragment in diffraction mode causes additional superstructure reflections to appear, as in Fig. 2(c). These are running along another $\langle 11\bar{2}1 \rangle^*$ direction, *i.e.* $[\bar{2}111]^*$. This is caused by the superposition of diffraction from two distinct domains, *cf.* Fig. 2(d). Note that only diffraction spots originating from the NiAs base lattice are superimposed. Figs. 2(e) and (f) show examples of diffraction from other zone axes. In Fig. 2(e), the zone axis referring to the NiAs base cell is $[1\bar{3}2]$. Diffraction from two domains with the fivefold superstructure running along different $\langle 11\bar{2}1 \rangle^*$ directions can be seen. The superstructure along $[11\bar{2}1]^*$ is seen directly in the diffraction pattern. The extra reflections running in the $[3\bar{1}2\bar{3}]^*$ direction originate from a domain with the superstructure running along another $\langle 11\bar{2}1 \rangle^*$ direction, *i.e.* $[\bar{1}2\bar{1}1]^*$.

It was not possible to produce any good quality high-resolution images in the 2000 JEOL microscope used and there is, at this point, little information available on the nature of the domain twinning. The size of the domains is hard to estimate since single domain areas are only found at thin edges of crystallites and even there only scarcely. One single domain crystallite was, however, found roughly of size 700 × 200 Å. Preliminary investigations indicate that the crystals are more stable in a higher voltage instrument (400 KeV) and it is possible that more information about the domains can be extracted from further investigations.

A model of η'-Cu$_6$Sn$_5$ from the reciprocal lattice

Considering the fivefold superstructure along $[11\bar{2}1]^*$, a model for the structure can be constructed, assuming that the superstructure is caused by alternating copper-filled and empty Edshammar$_{11}$ polyhedra in a NiAs structure. One fifth of all Edshammar$_{11}$ positions in the NiAs-type cell are to
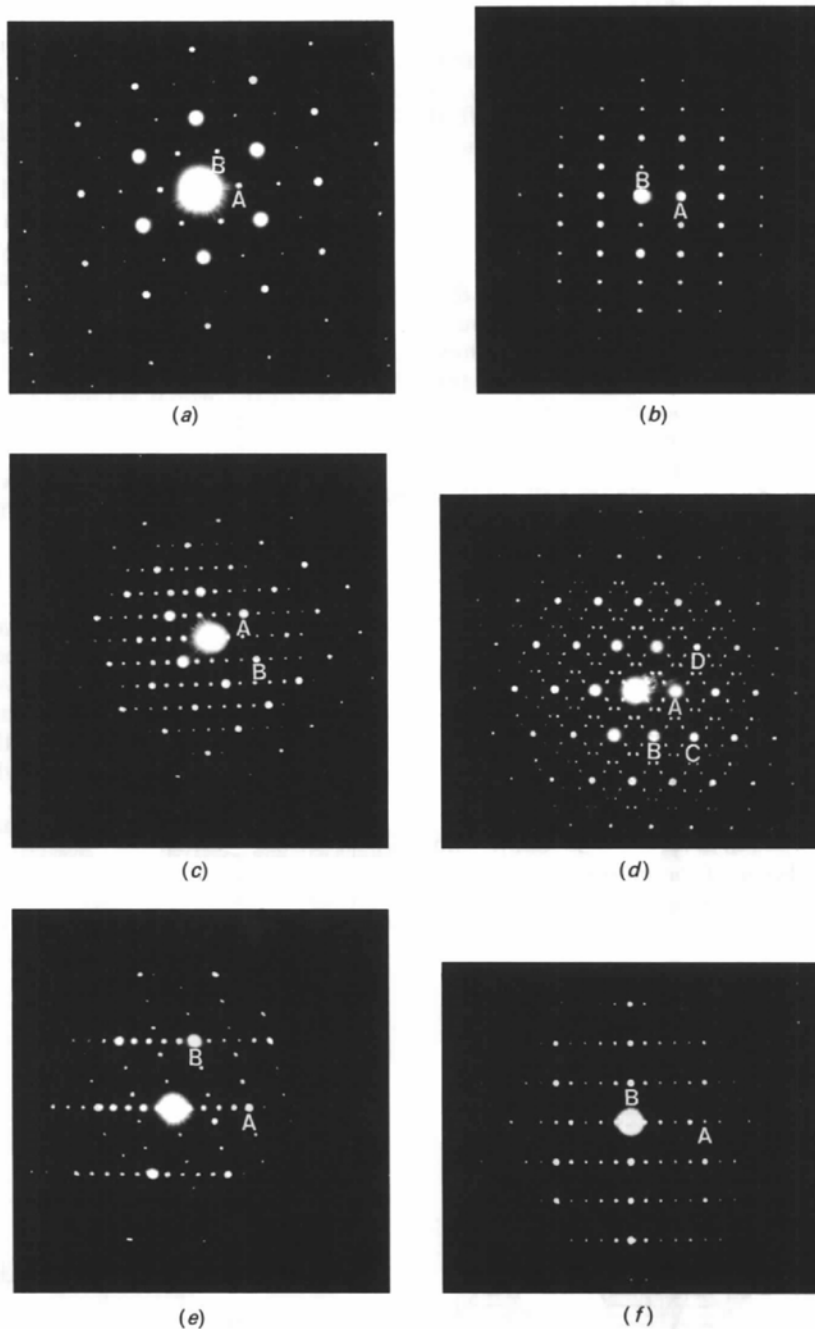
Fig. 2. Electron diffraction of η'-Cu_6Sn_5. The zone axes and the indexes are given, refering to both the NiAs-type system and the monoclinic system, in order to facilitate the overview. The strong reflections indexed are the NiAs reciprocal lattice points and the fivefolding superstructure reflections are running along different $\langle 11\bar{2}1 \rangle_h^*$ directions. (a) The lack of superstructure in the $(hk0)_h$ plane. Zone axis: $[201]_m$ $(=[001]_h)$; (A) $1\bar{1}2_m$ $(=10\bar{1}0_h)$, (B) 112_m $(=01\bar{1}0_h)$. (b) The lack of superstructure in the $\{h0l\}$ reciprocal planes. Zone axis: $[152]_m$ $(=[010]_h)$; (A) $1\bar{1}2_m$ $(=10\bar{1}0_h)$, (B) $20\bar{1}_m$ $(=0001_h)$. (c) The diffraction pattern originating from one single domain; the superstructure reflections are running along $[11\bar{2}1]^*$. Zone axis: $[110]_m$ $(=[0\bar{1}1]_h)$; (A) $1\bar{1}2_m$ $(=10\bar{1}0_h)$, (B) $\bar{1}13_m$ $(=01\bar{1}\bar{1}_h)$, (C) 005_m $(=11\bar{2}1_h)$. (d) The diffraction pattern originating from two domains with the superstructure running along the two directions $[11\bar{2}1]_h^*$ and $[\bar{2}111]_h^*$. Referring to domain 1, cf. Fig. 2(c): zone axis: $[110]_m$ $(=[0\bar{1}1]_h)$. (A) $1\bar{1}2_m$ $(=10\bar{1}0_h)$, (B) $\bar{1}13_m$ $(=01\bar{1}1_h)$, (C) 005_m $(=11\bar{2}1_h)$, (D) $33\bar{1}_m$ $(=1\bar{1}1\bar{1}_h)$. Referring to domain 2 (indexed by keeping zone axis and index for A unchanged), (B) $22\bar{1}_m$ $(=1\bar{1}0\bar{1}_h)$, (D) 005_m $(=11\bar{2}1_h)$. (e) Diffraction from two domains. The superstructure is running along $[111]_h^*$ and $[\bar{1}21]_h^*$. Domain 1, zone axis: $[120]_m$ $(=[1\bar{3}2]_h)$; (A) 005_m $(=11\bar{2}1_h)$, (B) $4\bar{2}3_m$ $(=20\bar{2}\bar{1}_h)$, (C) $8\bar{4}1_m$ $(=3\bar{1}2\bar{3}_h)$. Domain 2, zone axis: $[312]_h$ $(=[34\bar{2}]_m)$; (A) $\bar{1}33_m$ $(=2\bar{1}1\bar{1}_h)$, (B) $24\bar{1}_m$ $(=2\bar{2}0\bar{1}_h)$, (C) $5\bar{5}5_m$ $(=2\bar{3}1\bar{3}_h)$. (f) The $[11\bar{2}1]_h^*$ direction is pentupled. Notice the modulation in the $[11\bar{2}1]_h^*$ axis; every second supercell reflection is weaker. Zone axis: $[100]_m$ $(=[11\bar{2}]_h)$; (A) 005_m $(=11\bar{2}1_h)$, (B) $0\bar{2}0_m$ $(=1\bar{1}00_h)$.

be filled to obtain the composition $Cu_2Cu_{2/5}Sn_2$, which is the average content in the base unit cell. There are two symmetrically equivalent Edshammar positions in NiAs, referred to here as E_a and E_b. A set of $(11\bar{2}1)$ planes of the NiAs cell can, by a shift of the origin, be made to cut the E_a or the E_b positions in *every unit cell* (Fig. 3). Filling all E_a positions in every fifth $(11\bar{2}1)$ plane causes a fivefold superstructure in the $[11\bar{2}1]^*$ direction of the reciprocal lattice. Half of the extra Cu' has been placed in the structural model. The $(11\bar{2}1)$ planes exactly half the distance between the set of E_a (1121) planes cut through the E_b position in NiAs. This positioning of the next set of filled planes will spread out the filled Edshammar polyhedra as evenly as possible, complying with the homogeneity conditions for the projections on the NiAs-type axes as stated earlier. Filling up planes half way between the first filled planes will weaken every second (supercell) reflection along the $[11\bar{2}1]^*$ reciprocal NiAs axis. Multiple diffraction and atomic displacements will diminish this effect in electron diffraction patterns, but it is still clearly discernable as an intensity modulation, making every second supercell reflection stronger [Fig. 2(*f*)]. The resulting model is a structure where the filled Edshammar$_{11}$ polyhedra are evenly distributed throughout the structure. Filled Edshammar$_{11}$ polyhedra sharing corners form zigzag chains along $[001]_{mono}$. Projections of this model along the $\langle 100 \rangle$ and $[001]$ directions of the base NiAs-type cell show no superstructure. The choice of the monoclinic cell was made from the model; the space group of the model being $C2/c$.
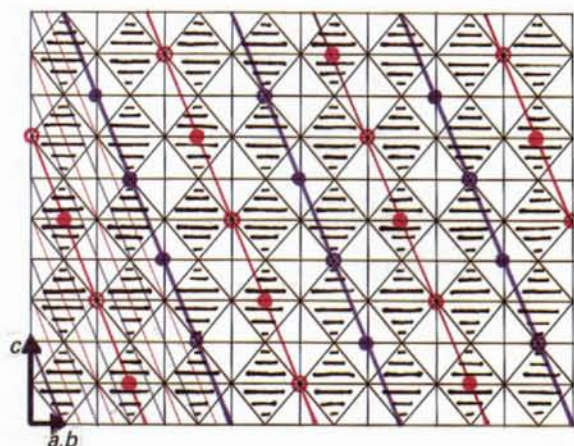
Powder diffraction and improvement of the model

To refine the cell parameters a Guinier–Hägg camera with Cu $K\alpha$ radiation was used with silicon as an external standard. Only the NiAs-type reflections were used in the first stages of the work. It is not possible to detect any splitting of reflections, which would indicate that the base cell is distorted. The calculated structure factors from the single-crystal experiment were later used to fully index the powder pattern and a least-squares refinement on 23 (of 36) lines with a contribution from only one unique reflection was made.* The cell parameters received are $a = 11.033$ (3), $b = 7.294$ (3), $c = 9.830$ (4) Å and $\beta = 98.82$ (3)°, which should be compared with the cell calculated from the data from the single crystal work (*vide infra*). Z is 4 for the formula Cu_6Sn_5.

A powder diffraction pattern was recorded using Cu $K\alpha$ radiation with an Inel diffractometer and compared with calculated data using the Powder Diffraction Package of Calligaris & Geremia (1990). The main difference between the recorded pattern [Fig. 4(*a*)] and the pattern calculated from the above model [Fig. 4(*b*)] is the appearance of peaks at 2θ below 20°. The model was improved by shifts of the atomic positions. The improvement of the model is based on the surroundings of the additional Cu atom, *i.e.* the Edshammar$_{11}$ polyhedron. The base

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* Lists of powder diffraction data, anisotropic displacement parameters and observed and calculated structure factors have been deposited with the IUCr (Reference: AB0319). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
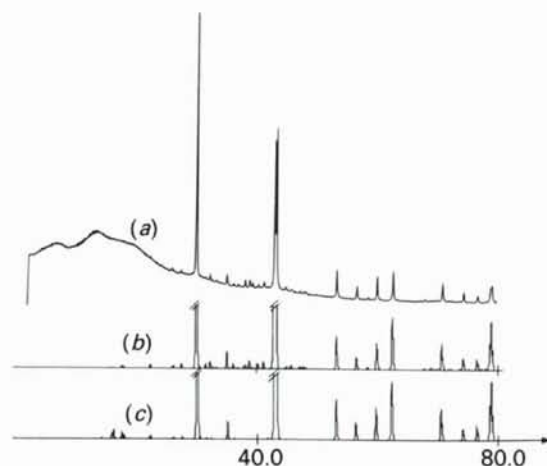

Fig. 3. The $(11\bar{2}1)_h$ planes are viewed along $[\bar{1}10]_h$. In every fifth (111) plane, marked with the thicker blue lines, all the trigonal bipyramidal sites in the hexagonal close packing are filled with Cu (filled and empty circles are on a different height in the projection, 1/2 and 0). The plane half distances between these planes are also filled (red atoms on different heights from the blue, 1/4 and 3/4).

Fig. 4. X-ray powder patterns of η'-Cu_6Sn_5. (*a*) Recorded powder pattern; (*b*) simulated pattern using the first undistorted model; (*c*) simulated pattern using coordinates derived by manual shifts of the atoms. The Sn atoms are shifted away from the center in the Edshammer polyhedron (0.2 Å for the triangle and 0.15 Å for the top and bottom) and the Cu atoms that are free to move are shifted 0.1 Å in the NiAs *xy*-plane to shorten the Cu—Cu' distances.

triangle of Sn, around the additional Cu gives short Cu—Sn distances. Hence, some models were constructed where the atoms were shifted in such a way as to give a more normal distribution of Cu—Sn and Cu—Cu distances in the Edshammar$_{11}$ polyhedron. In Fig. 4(c), a theoretical diffraction pattern is shown from a model where the three Sn atoms forming a triangle around Cu' are moved 0.2 Å from the center. The Sn forming the top and bottom of the Edshammar polyhedron are moved 0.15 Å away and the Cu atoms not occupying a center of symmetry are moved 0.1 Å to shorten the Cu'—Cu distances in the Edshammar$_{11}$ polyhedron.

Refinement of single-crystal diffraction data

The properties of the reciprocal lattice made it possible to perform reliable least-squares refinements on the domain-twinned crystal structure without the use of special twin programs. The superstructure reflections from the different domains never overlap and since they constitute 80% of the complete diffraction material, the other 20% (the NiAs reflections) could be ignored. The reciprocal lattice of the crystal used is built up of about equal contributions from all six possible domain orientations, originating from the fivefold superstructure along different $\langle 11\bar{2}1 \rangle^*$ directions of the base NiAs-type lattice. Fig. 5 shows the decomposition of the reciprocal lattice into six domains. It is clear that the reciprocal lattice points of the base NiAs lattice includes contributions from all six unique domain orientations, while the superstructure reflections, constituting 4/5 of the total material, do not overlap. The refinement was carried out on the unique 957 non-overlapping superstructure reflections only. Table 1 gives the experimental details.

The data was corrected for absorption. Since the domains are small and assumed to be evenly distributed throughout the crystal, normal numerical absorption correction was used. The whole crystal absorbs X-rays, but only 1/6 of the crystal contributes to the diffraction; the effect of the diluted diffracting power of the crystal is accounted for by a simple scaling included in the overall scale factor.

The refinements were made gradually starting from the model from the powder diffraction work. Finally, anisotropic refinement was carried out to
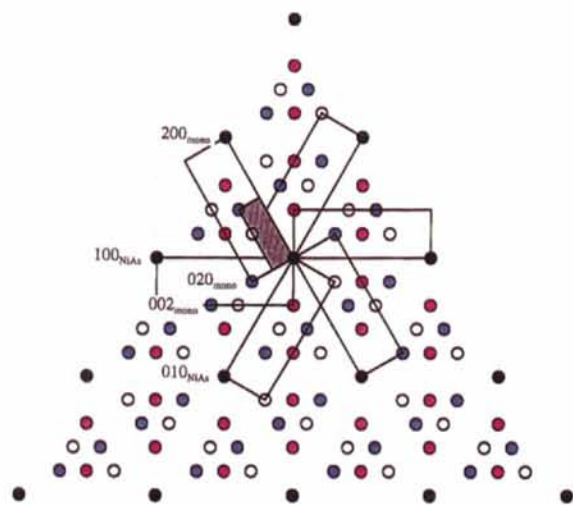

Fig. 5. A projection along c^*_{hex} of the reciprocal lattice of the domain twin decomposed into six individual lattices (red, blue and white). The overlapping base-cell reflections are marked as black circles. Each color represents two sublattices, at different levels along c^*_{hex}. Due the the C-centering of the monoclinic lattice, reflections with $h + k = 2n + 1$ are extinguished. In the blue sublattice, the a^*b^*-plane of the monoclinic unit cell is hatched. The unit cells of the six monoclinic sublattices share a common origin and the points $(200)_{\text{mono}}$ are in the $[hk\bar{4}]_{\text{hex}}$-plane, the points $(020)_{\text{mono}}$ are in the $[hk0]_{\text{hex}}$-plane and the points $(002)_{\text{mono}}$ are in the $[hk2]_{\text{hex}}$-plane. Note how the overlap affects only 1/5 of the reflections.
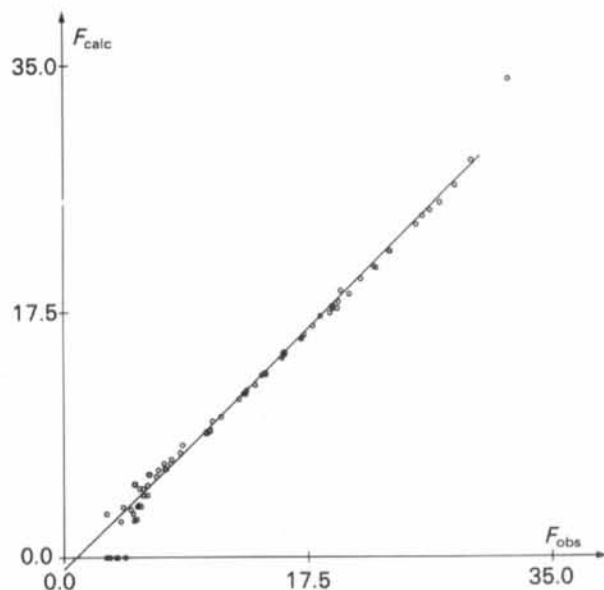

Fig. 6. A plot of F_{obs} against F_{calc} for the overlapping hexagonal base reflections. The axes are labelled in arbitrary units.
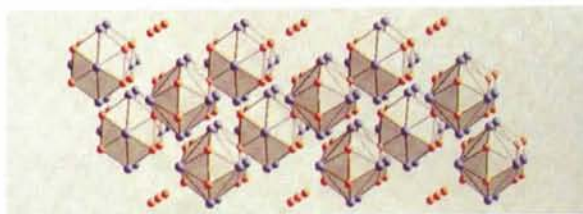

Fig. 7. The structure of η'-Cu$_6$Sn$_5$ viewed roughly along the $\langle 1\bar{1}0 \rangle$ direction. Blue spheres represent Sn and red spheres denote Cu.

Table 1. *Crystal data, data collection and refinement parameters*

Crystal data

Chemical formula	Cu_6Sn_5
Molecular weight	974.83
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	11.022 (5)
b (Å)	7.282 (4)
c (Å)	9.827 (2)
β (°)	98.84 (4)
V (Å³)	779.4 (5)
Z	4
D_x (Mg m⁻³)	8.27
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71069
No. of reflections for cell parameters	25
θ range for cell parameters (°)	6.03–16.99
μ (mm⁻¹)	31.8
Temperature (K)	293
Crystal color	Grey metallic
Crystal form	Hexagonal rod
Crystal size (mm)	0.035 diameter × 0.30 length
Crystal source	Tin melt

Data collection

Diffractometer	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans
Absorption correction	Analytical by integration from crystal shape
T_{min}	0.2180
T_{max}	0.3945
No. of measured reflections	3906
No. of independent reflections	957
No. of observed reflections	796
Observation criterion	$[I > 3\sigma(I)]$
R_{int}	0.0551
θ_{max} (°)	30
Range of h, k, l	$-15 \rightarrow h \rightarrow 15$
	$-10 \rightarrow k \rightarrow 10$
	$-13 \rightarrow l \rightarrow 13$
No. of standard reflections	2
Frequency of standard reflections (min)	120
Intensity variation (%)	± 1.1

Refinement

Refinement on	F
R	0.0279
wR	0.0400
S	1.15
No. of reflections used in refinement	796
No. of parameters used	53
Weighting scheme	$w = 1/[\sigma^2(F_o) + (0.03F_o^2)^2]$
$(\Delta/\sigma)_{max}$	0.03
$\Delta\rho_{min}$ (e Å⁻³)	−1.29
$\Delta\rho_{max}$ (e Å⁻³)	1.16
Source of atomic scattering factors	International Tables for X-ray Crystallography (1974, Vol. IV,)

Table 2. *Atomic site parameters for* η'-Cu_6Sn_5

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å²)
Sn1	0.39106 (6)	0.16250 (12)	0.52867 (11)	0.0100 (2)
Sn2	0.28518 (8)	0.65499 (13)	0.35792 (6)	0.0088 (2)
Sn3	0.0	0.79892 (17)	1/4	0.0102 (2)
Cu1	0.10096 (9)	0.47297 (26)	0.20236 (10)	0.0106 (4)
Cu2	0.30620 (10)	0.50404 (13)	0.60972 (12)	0.0103 (4)
Cu3	0.0	0.0	0.0	0.0121 (5)
CuA	0.0	0.16020 (16)	1/4	0.0094 (4)

check the stability of the structure solution; R/wR decreased from 3.8/5.2 to 2.8/4.0% and the atoms showed only small distortions from spherical displacement; see Table 2 for final atomic parameters.* After the final refinement, the intensities of the base reflections were calculated and added together to 90 unique base reflections, according to the assumption of equal volume for each domain orientation. The observed and calculated structure factors from the

* See deposition footnote.

base NiAs lattice are plotted in Fig. 6. The unweighted R-value is 10.0%, and there are no systematic deviations from the least-squares line. Hence, the model based on a structure solution from only the weak super cell reflections agrees well with the total data set, *i.e.* the superstructure describes the whole crystal well and the degree of disorder of the filled Edshammar$_{11}$ positions is low.

We would like to emphasize that the difference of the final model from the starting model is relatively small, which means that the model from the powder investigation described the structure faily well. Thus, the method used here may be useful in solving other similar problems, even if it is not possible to grow good quality single crystals or if the super reflections from different domains overlap.

Structural description of η'-Cu_6Sn_5

In η'-Cu_6Sn_5, 1/5 of the Edshammar$_{11}$ polyhedra (the 'trigonal bipyramidal sites' of a closed-packed array) are filled in an ordered way (Fig. 7). The Edshammar$_{11}$ polyhedron is regular with respect to Cu—Cu and Cu—Sn distances (Table 3) and the distribution of the polyhedra in the structure is spread out. Two Sn triangles sharing corners are never both centered by Cu since there is then no possibility of expanding the centered triangle at the cost of the noncentered triangle. All atoms belong to this Edshammar$_{11}$ polyhedron and there is a twofold axis cutting through the base. The Edshammar$_{11}$ polyhedra share the corners corresponding to centers of symmetry (Cu3), forming zigzag chains along $\langle 001 \rangle_{mono}$. Two different types of coordination polyhedra exist around the other three unique Cu atoms. Cu3 is ten-coordinated by six Sn atoms in the octahedron, two Cu atoms capping the top and bottom (as in NiAs), and a further two CuA atoms which are centering Edshammar$_{11}$ polyhedra. The Cu1 and Cu2 atoms are nine-coordinated by an octahedron capped at the top and bottom and by one further CuA atom. All Sn atoms are seven-coordinated by Cu atoms, forming capped trigonal prisms. Sn2 has a triangular face of the prism capped, while Sn1 and Sn3 are capped on a square face.

Table 3. *Contact distances* (Å) < 3.2 Å *for each atom in* η'-Cu_6Sn_5

The cell and coordinates from the single-crystal experiment are used.

Sn1—CuA	2.653 (1)
Sn1—Cu1	2.670 (2)
Sn1—Cu2	1.672 (2)
Sn1—Cu3	2.769 (2)
Sn1—Cu1	2.810 (2)
Sn1—Cu2	2.815 (2)
Sn1—Cu1	2.833 (2)
Sn2—Cu2	2.685 (1)
Sn2—Cu1	2.695 (2)
Sn2—Cu2	2.716 (2)
Sn2—CuA	2.739 (1)
Sn2—Cu	2.742 (2)
Sn2—Cu2	2.742 (1)
Sn2—Cu3	2.795 (2)
Sn3—CuA	2.631 (2)
Sn3—2Cu1	2.693 (2)
Sn3—2Cu2	2.760 (2)
Sn3—2Cu3	2.860 (1)
Cu1—Cu1	2.544 (2)
Cu1—Cu2	2.570 (2)
Cu1—CuA	2.609 (2)
Cu1—Sn1	2.670 (2)
Cu1—Sn3	2.693 (2)
Cu1—Sn2	2.695 (2)
Cu1—Sn2	2.742 (2)
Cu1—Sn1	2.810 (2)
Cu1—Sn1	2.833 (2)
Cu2—Cu3	2.537 (2)
Cu2—Cu1	2.570 (2)
Cu2—CuA	2.644 (2)
Cu2—Sn1	2.672 (2)
Cu2—Sn2	2.685 (1)
Cu2—Sn2	2.716 (2)
Cu2—Sn2	2.742 (1)
Cu2—Sn3	2.760 (2)
Cu2—Sn1	2.815 (2)
Cu3—2Cu2	2.537 (2)
Cu3—2CuA	2.720 (1)
Cu3—2Sn1	2.769 (2)
Cu3—2Sn2	2.795 (2)
Cu3—2Sn3	2.860 (1)
CuA—2Cu1	2.609 (2)
CuA—Sn3	2.631 (2)
CuA—2Cu2	2.644 (2)
CuA—2Sn1	2.653 (1)
CuA—2Cu3	2.720 (1)
CuA—2Sn2	2.739 (1)

Concluding remarks

The superstructure is formed by additional atoms in one fifth of the trigonal bipyramidal sites of the NiAs-type base structure. All atoms in the structure belong to the Edshammar polyhedra, which form zigzag chains by corner sharing. The resulting structure is a new type of superstructure related to the Ni$_2$In–NiAs structure types.

The highly regular 11-configuration of the extra Cu atom indates the Edshammar$_{11}$ polyhedron as an important concept in understanding the structure of η'-Cu_6Sn_5 and it is worth while exploring the construction of other distributions of self-avoiding filled Edshammar$_{11}$ polyhedral packings in the quest for ordered NiAs–Ni$_2$In intermediate structures.

It is noteworthy that the coordination number of all atoms increases in comparison to that in pure NiAs, without disrupting the homogeneity of the structure. Summing over the Pauling bond orders (Pauling, 1960) for the base structure Cu yields a value ranging between 7.45 and 7.51 and for Sn and Cu' between 8.38 and 8.44.

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