

Table 2. Selected geometric parameters (Å)

Mo(1)—Mo(2)	2.6905 (6)	Sr—O(3)	3.219 (4)
Mo(1)—Mo(4)	2.7507 (6)	Mo(1)—O(5)	2.034 (4)
Mo(1)—Mo(5)	2.7672 (6)	Mo(1)—O(7)	2.036 (4)
Mo(1)—Mo(3)	2.7740 (7)	Mo(1)—O(4)	2.104 (4)
Mo(1)—Mo(1)*	2.7651 (9)	Mo(1)—O(8)	2.106 (4)
Mo(1)—Mo(2)*	3.0380 (6)	Mo(1)—O(8)	2.117 (4)
Mo(1)—Mo(3)*	3.0869 (6)	Mo(2)—O(1)	1.902 (4)
Mo(2)—Mo(5)	2.7196 (6)	Mo(2)—O(6)	1.953 (4)
Mo(2)—Mo(4)	2.7413 (7)	Mo(2)—O(4)	2.040 (4)
Mo(2)—Mo(3)	2.8263 (6)	Mo(2)—O(8)	2.117 (4)
Mo(3)—Mo(4)	2.6034 (6)	Mo(2)—O(7)	2.145 (4)
Mo(3)—Mo(5)	2.6950 (6)	Mo(3)—O(3)	2.042 (4)
Mo(3)—Mo(5)	2.7494 (6)	Mo(3)—O(2)	2.058 (4)
Mo(4)—Mo(5)	2.7389 (6)	Mo(3)—O(4)	2.065 (4)
Mo(4)—Mo(5)	2.7715 (7)	Mo(3)—O(6)	2.087 (4)
Mo(5)—Mo(5)	2.8324 (9)	Mo(3)—O(8)	2.148 (4)
Sr—O(1)	2.529 (4)	Mo(4)—O(3)	2.061 (4)
Sr—O(1)	2.552 (4)	Mo(4)—O(7)	2.062 (4)
Sr—O(4)	2.597 (4)	Mo(4)—O(1)	2.070 (4)
Sr—O(7)	2.648 (4)	Mo(4)—O(5)	2.071 (4)
Sr—O(2)	2.718 (4)	Mo(4)—O(2)	2.087 (4)
Sr—O(5)	2.750 (4)	Mo(5)—O(5)	2.023 (4)
Sr—O(3)	2.764 (4)	Mo(5)—O(6)	2.039 (4)
Sr—O(8)	2.770 (4)	Mo(5)—O(2)	2.063 (4)
Sr—O(2)	2.930 (4)	Mo(5)—O(3)	2.065 (4)
Sr—O(6)	2.935 (4)		

* Intercluster distance.

Single crystals were obtained by heating a stoichiometric mixture (starting materials SrMoO₄, MoO₃ and Mo) in a sealed molybdenum crucible at ca 2220 K for 15 min. The crucible was then cooled at the rate of 100 K h⁻¹ to 1300 K and finally furnace-cooled to room temperature.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71430 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU1050]

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Sn_{8.7}(Ni_{0.5}Zn_{0.4}Cu_{0.1})_{10.4}, a New Tin-Based Alloy from a Complex Metallic Mixture

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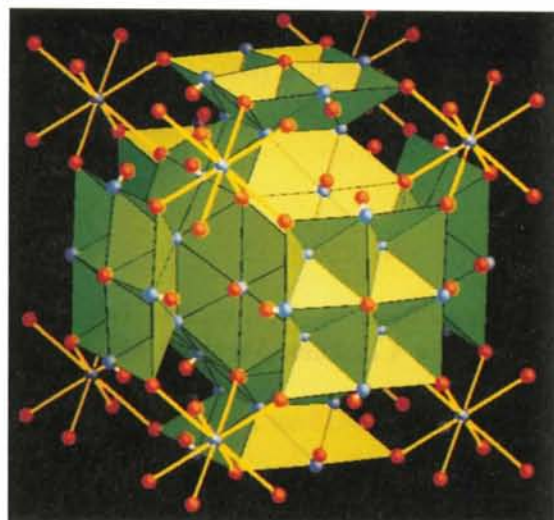
Abstract

The title alloy has a complicated composition, Sn_{8.7}(Ni_{0.5}Zn_{0.4}Cu_{0.1})_{10.4}, and was synthesized from the elements. It is a new structure type consisting of primitive cubic (p.c.), body-centred cubic (b.c.c.) and face-centred cubic (f.c.c.) blocks. It is related to γ -brass and to BaHg₁₁. The compound undergoes a phase transition to a CsCl-type structure when subjected to the electron beam of a high-resolution electron microscope.

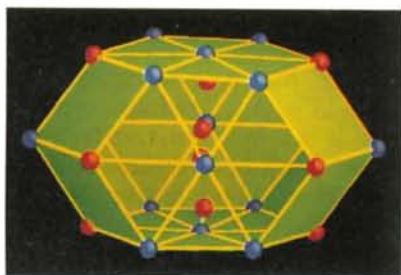
Comment

Tin-based alloys are of vast technological importance and include materials such as soft solder, type metal, fusible metal, pewter, bronze, bell metal, Babbitt's metal, white metal, die-casting alloy and phosphor-bronze. As tin can act as both metal and non-metal, the compounds of tin exhibit a rich and varied structural chemistry of great theoretical interest.

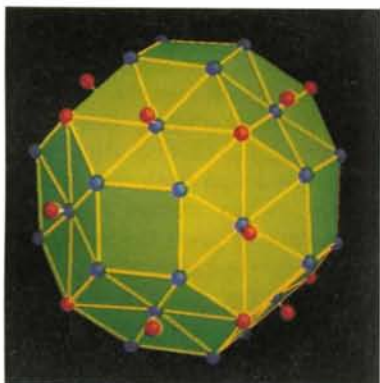
In search of new tin-based alloys, equal amounts of Al, Zn, Cu, Ni, Co, Fe, Mn, Cr, V, Mg and Ti were mixed together with a large excess of Sn. The mixture was heated under Ar in a sealed stainless-steel ampoule to 1073 K for 5 h and then cooled to room temperature at a rate of approximately 100 K h⁻¹. After leaching the ingot in hydrochloric acid (6 M) for 3 days, the residue consisted of crystals of mainly three different habits, one being dull-greyish thin hexagonal rods and needles, the other two silvery metallic cuboctahedra or fat rods. The thin hexagonal rods were of the CoSn type and are discussed elsewhere (Larsson & Lidin, 1994). The latter two habits proved to come from the same cubic phase.



(a)



(b)



(c)

Fig. 1. Sn atoms are represented by red spheres and (Ni, Zn, Cu) are represented by blue spheres. (a) The structure of $\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$ represented as an intergrowth of f.c.c., b.c.c. and p.c. blocks. (b) The void in $\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$; note how the shift in the split position may fill this void. (c) The structure of $\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$ represented by interpenetrating rhombic dodecahedra. In (a) and (c), the origin is in the centre of the image. In (c), the top and bottom vertices are at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.



(a)



(b)

Fig. 2. Electron diffraction patterns (EDP) of $\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$ at an acceleration voltage of 200 kV. (a) Initial EDP. (b) EDP after 15 min; note the slight expansion of the reciprocal lattice that accompanies the disappearance of the superstructure as the lattice converts to the CsCl type.

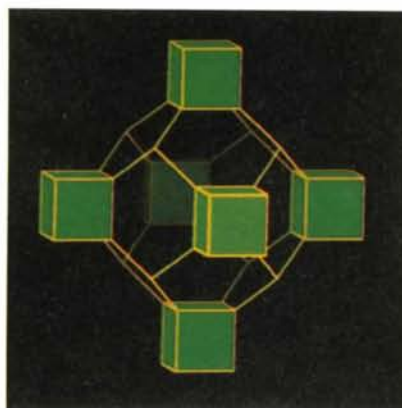


Fig. 3. A hypothetical zeolite structure based on truncated-rhombic dodecahedra.

The composition of the silvery crystals was determined by means of microprobe analysis (scanning electron microscopy) and a preliminary X-ray diffraction investigation was carried out according to the precession method. The elemental analysis gave the composition $\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$, while the preliminary X-ray analysis indicated a structure based on a trebling of a b.c.c. lattice.

The structure is a defect superstructure of the CsCl type. Just like the γ -brass structure, the basic unit cell is trebled, and the cubic unit cell has an edge around 9 Å, but the vacancies and deformations are different, and the resulting structures are quite distinct. In γ -brass, the number of vacancies is 2 [at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$], leaving 52 atoms in the unit cell. In the present structure, the vacant positions are $(\frac{1}{6}, \frac{1}{6}, \frac{1}{6})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{6})$, leaving only 40 atom sites in the unit cell (partial occupancy of some sites leaves an average of 38.3 atoms per cell). As a result of the differences in occupancy, the deviations from ideal CsCl positions are also distinct from those of γ -brass.

The structure consists of f.c.c., b.c.c. and p.c. blocks, all coexisting. A 27-atom p.c. block surrounds the origin. This block shares faces with 22-atom f.c.c. slabs, and in the position $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$, single b.c.c. cubes are formed (Fig. 1a). The structure contains large cavities in the shape of the elongated dodecahedron of von Fedorov (1904) around the positions $(0, \frac{1}{2}, \frac{1}{2})$. These voids are partially filled by the split position (Fig. 1b). An alternative description has all atoms except (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ on interpenetrating rhombic dodecahedra. The interpenetration in turn gives rise to an interesting polyhedron, a truncated rhombic dodecahedron, (TRD; Fig. 1c). This representation clearly shows the relationship between this structure and that of BaHg_{11} (Peyronel, 1952), which has been described by means of the von Fedorov polyhedron (Nyman & Andersson, 1979). The networks of TRD and von Fedorov polyhedra are similar in the two structures, but the contents of the polyhedra are quite different. The von Fedorov polyhedron is centered by a Ba atom in BaHg_{11} ; in $\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$ the polyhedron is empty while its hexagonal faces are centred. In this structure, the TRD is filled by a primitive cubic arrangement, while in BaHg_{11} it contains a network of cubes and square antiprisms reminiscent of that in tveitite ($\text{Ca}_{14}\text{Y}_5\text{F}_{43}$; Bevan, Strähle & Greis, 1982) and the metallic carbide Cr_{23}C_6 (Bowman, Arnold, Storms & Nereson, 1972). The atomic positions on the rhombic dodecahedra are the vertices, the face centres and the edges at the points of intersection between two rhombic dodecahedra. In Table 1 the idealized positions for the two descriptions are compared to the real atomic positions in space group $Pm\bar{3}m$ (although

this is not the space group used in the final refinement, the actual differences in atomic positions are slight). Note the one split position in the actual structure.

Single crystals were ground and studied in a JEOL 2000 FX transmission electron microscope. The electron diffraction pattern of the $hk0$ zone (Fig. 2a) clearly shows the trebling of the cell axes. The crystals were not stable in the electron beam and after a few minutes of irradiation the superstructure was destroyed (Fig. 2b), resulting in a structure with a unit cell having an edge slightly smaller than that of the substructure of the original cell. The open packing, in conjunction with the fact that the superstructure is destroyed upon irradiation in the electron beam, suggests that the super-cell ordering is electronic in nature, *i.e.* caused by electron localization. The delocalization upon electron-beam irradiation then causes a contraction of the sublattice to yield a CsCl-type structure.

In the structure of the title compound, the TRDs share square faces. It is possible to arrange the TRDs to share hexagonal faces instead and this yields a space-filling arrangement of TRDs and cubes. This f.c.c. arrangement is strongly reminiscent of molecular sieve silicates (Fig. 3). The TRD has indeed been depicted (van Koningsveld, 1991) as an intermediate step in the σ transformation from α -cages to β -cages in zeolites, but we have found no attempt in the literature to use it in a space-filling arrangement. Apart from the f.c.c. arrangement, it is possible to combine the TRD with α - and β -cages to form a plethora of tetragonal, orthorhombic and lower symmetry zeolitic structures as well. The f.c.c. arrangement would have a cubic unit cell with a 13.57 Å edge assuming an Si—Si distance of 3.15 Å (as in sodalite).

Experimental

Crystal data

$\text{Sn}_{8.7}(\text{Ni}_{0.5}, \text{Zn}_{0.4}, \text{Cu}_{0.1})_{10.4}$
 $M_r = 1676$ (1)
 Cubic
 $P\bar{4}3m$
 $a = 8.854$ (7) Å
 $V = 694$ (2) Å³
 $Z = 2$
 $D_x = 8.02$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å

Cell parameters from 17 reflections
 $\theta = 6.9\text{--}23.3^\circ$
 $\mu = 31.0$ mm⁻¹
 $T = 293$ K
 Rod
 $0.25 \times 0.06 \times 0.06$ mm
 Grey metallic
 Crystal source: Sn melt

Data collection

Enraf-Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans

355 observed reflections
 $[F_o^2 > 3\sigma(F_o^2)]$
 $R_{\text{int}} = 0.05142$

Absorption correction: $\theta_{\max} = 40^\circ$
 by integration from crystal shape
 $T_{\min} = 0.018$, $T_{\max} = 0.225$
 2591 measured reflections
 487 independent reflections

$h = 0 \rightarrow 15$
 $k = 0 \rightarrow 16$
 $l = 0 \rightarrow 16$
 2 standard reflections
 frequency: 120 min
 intensity variation: 3%

Refinement

Refinement on F
 $R = 0.0535$
 $wR = 0.0752$
 $S = 1.01$
 355 reflections
 35 parameters
 $w = 1/(\sigma^2 + 0.07F_o)^2$

$(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 4.7 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -3.9 \text{ e } \text{Å}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. A comparison between the real structure of Sn_{8.7}(Ni_{0.5},Zn_{0.4},Cu_{0.1})_{10.4} and the two idealized models

The position $x \times 0$, $x = 0.3704(5)$, is partly filling the von Fedorov elongated dodecahedron.

Position in $Pm\bar{3}m$	Value of the free parameter in the model		
	Real structure	TRD	p.c., b.c.c., f.c.c.
0 0 0			
$\frac{1}{2} \frac{1}{2} \frac{1}{2}$			
$x \ x \ x$	0.3270 (3)	0.326	0.293
$x \ 0 \ 0$	0.2892 (2)	0.250	0.293
$x \ x \ \frac{1}{2}$	0.1523 (2)	0.151	0.146
$x \ x \ 0$	0.3193 (10)	0.326	0.293
$x \ x \ 0$	0.3704 (5)	-	-

Table 2. Atomic positions in Sn_{8.7}(Ni_{0.5},Zn_{0.4},Cu_{0.1})_{10.4}

The M positions denote Ni, Zn or Cu, refined according to the scattering power of copper. Note that Sn4 and $M4$ occupy the same disordered position. The occupancy of Sn2 refined as Sn 0.83 (3) which could be interpreted as full occupancy by 60% Sn and 40% M .

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_j a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Wyckoff position	x	y	z	$U_{eq} (\text{Å}^2)$	Occupancy
Sn1 4(e)	0.3270 (3)	0.3270 (3)	0.3270 (3)	0.0077 (4)	1.00
Sn2/ M 4(e)	0.6737 (4)	0.6737 (4)	0.6737 (4)	0.0139 (6)	0.60/0.40
Sn3 6(f)	0.2892 (2)	0.0000	0.0000	0.0094 (3)	0.97(2)
$M1$ 1(a)	0.0000	0.0000	0.0000	0.0023 (9)	0.87(4)
$M2$ 1(b)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.0020 (9)	0.75(4)
$M3$ 12(i)	0.1523 (2)	0.1523 (2)	0.5061 (5)	0.0038 (4)	0.86(2)
Sn4 12(i)	0.3704 (5)	0.3704 (5)	0.0066 (8)	0.0103 (7)	0.44(1)
$M4$ 12(i)	0.3193 (10)	0.3193 (10)	0.9969 (15)	0.0150 (14)	0.52(2)

The structure was determined from a rod-shaped specimen, the rod axis being the $\langle 011 \rangle$ axis of the unit cell. The rod-shaped crystal form could indicate a discrepancy from cubic symmetry but no evidence of this was found. The structure was solved by considering the CsCl base structure, a Patterson map and direct methods (*MULTAN80*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Once a starting model was found, a large number of $\Delta\rho$ map syntheses followed by small changes in the model and least-squares refinements led to the final model. All computer programs used are described by Lundgren (1982). It was not possible to distinguish Ni, Zn and Cu unambiguously, since the scattering powers of these elements are similar; hence

the M sites were refined as Cu. The atomic parameters of the final structure are given in Table 2. The main contribution to the deviation from the centrosymmetric space group is not the coordinates but the difference in occupancy of Sn1 and Sn2. In the corresponding centrosymmetric space group $Pm\bar{3}m$, these occupy the same position. Least-squares refinement in $Pm\bar{3}m$, anisotropically and with variable occupancies, gave the final R/wR values 6.20/11.54, respectively, and $S = 1.11$, which are considerably higher than the values in the non-centrosymmetric space group (5.35/7.52 and 1.01, respectively). It was not possible to refine any model without invoking a split of the $M4/Sn4$ position along the direction $\langle 110 \rangle$. The sum of the occupancies of the split position is close to unity when the position partly filling the von Fedorov elongated dodecahedron is refined as tin and the position completing the TRD is refined as M (Cu). When calculating formal Z and D_x , we assumed that 40% of the Sn2 position is occupied by M and 60% by Sn, as suggested by the relationship $0.6 + (0.4 \times 29/50) = 0.83$ (see Table 2). This assumption fits well with energy dispersive X-ray analysis.

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Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71428 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1035]

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