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The CoSn Type Structure of $(Fe_{0.6},Cr_{0.2},Ni_{0.2})Sn$

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Abstract

The structure of $(Fe_{0.6},Cr_{0.2},Ni_{0.2})Sn$ is of the CoSn structure type with Fe, Cr and Ni disordered in the Co position. The structure contains a void surrounded by a 20-vertex polyhedron. The coordination polyhedra for Sn are hexagons and edge-capped trigonal prisms, and for Fe, ten-vertex polyhedra.

Comment

In the pursuit of new stable tin-based alloys we prepared complex mixtures of mainly the third-row transition metals with tin, the idea being to grow alloys from the dilute tin solution. This method has formerly been employed to grow single crystals of Cu_6Sn_5 (Carlsson & Hägg, 1932). Crystals of the approximate composition (microprobe determination) $(Fe_{0.6},Cr_{0.2},Ni_{0.2})Sn$ were obtained as a by-product in these experiments (Larsson, Lidin & Jacob, 1994). The crystals are dull-greyish hexagonal rods and needles of the CoSn structure type.

The structure of CoSn has been reported from powder data only (Nial, 1938). It is isostructural with PtTl, FeSn, FeGe, InNi, $Pb_{12}Rh_{13}$ and various mixed phases (Villars & Calvert, 1985). In the title compound, Fe, Cr and Ni are disordered in the Co position. The present compound is thus described by the CoSn structure.

The easiest way to visualize CoSn is to consider close-packed Co_3Sn *A* layers where Sn1 is hexagonally coordinated by Co in an Sn-centred Co-kagome net. The close-packed layers are connected *via* Sn2 *B* layers consisting of simple hexagonal nets (half atom density). The Co atoms form the bases of trigonal bipyramids while Sn2 atoms connect the apices. Thus chains of corner-sharing trigonal bipyramids run along the **c** direction. If a coordination distance of 2.7 Å is considered, Sn2 is six-coordinated by Co in the form of a trigonal prism expanded along the *c* axis. The next-nearest neighbours are three other Sn2 in the same layer which cap the edges of the trigonal prism. The Sn1 atom in the *A* plane is six-coordinated in a planar hexagon. Co is surrounded by a ten-vertex polyhedron that can be visualized as a hexagon of Co and Sn1 and a rectangle of Sn2 interpenetrating at right angles. The Co and Sn2 atoms in the chains of corner-sharing trigonal bipyramids form undulating hexagonal channels; Sn1 is located at the narrowest portion of these (Fig. 1). Hence, there is a large void between two Sn1 atoms in adjacent layers. This empty 20-vertex polyhedron is a hexagonal prism of Co, capped at all six rectangular faces by Sn2 and centred at the top and bottom by Sn1 (Fig. 2). Because of the substantial difference in coordination between Sn1 and Sn2, the chemical formula of CoSn is really Co_3SnSn_2.

Two other structure types are built from the same kind of undulating channels as CoSn: $CaCu_5$ (Haucke, 1940) and Zr_4Al_3 (Wilson, Thomas & Spooner, 1960). Both have the same basic arrangement of the corner-sharing trigonal bipyramids, but Ca in $CaCu_5$ (corresponding to Sn1) is shifted by $\frac{1}{2}$ along the *c* axis. Ca then occupys a 6 + 12 polyhedron of Cu which can be described as a hexagonal prism, centred at the six rectangular faces. Zr in Zr_4Al_3 occupys the channels at $\frac{1}{4}$ and the cell is expanded by about 10% in the **c** direction. This structure may also be described in terms of tetraedersterns (Hyde & Andersson, 1989).

The void in CoSn, being unusually large for an alloy structure, could be explained by stereoactive electrons. Computation of electron localization functions (ELF) has been carried out for metallic systems (*e.g.* Savin, Becke, Flad, Nesper, Preuss & von Schnering, 1991), but in a system like this with open *d* shells, such a calculation is difficult. It is, however, noteworthy that the structure does not change when subjected to high pressure (270 kBar; Schwarz, Larsson & Lidin, 1992) as would be expected for such a loosely packed structure. This suggests that the void may be stabilized by localized electrons.

Experimental

Crystal data

$(Fe_{0.6},Cr_{0.2},Ni_{0.2})Sn$
Hexagonal
P6mm
$a = 5.3311\ (3)$ Å
$c = 4.4332\ (3)$ Å
$V = 109.11$ Å^3
$Z = 3$
$D_x = 7.94$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Cell parameters from 50 reflections
$\theta = 5$–$44°$
$\mu = 30.8$ mm^{-1}
$T = 300$ K
Hexagonal rod
0.25 × 0.02 × 0.02 mm
Grey, metallic
Crystal source: Sn melt

Data collection

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

214 observed reflections $[F_o^2 > 3\sigma(F_o^2)]$
$R_{\rm int} = 0.087$

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Absorption correction:
by integration from crystal shape
$T_{\min} = 0.049$, $T_{\max} = 0.359$
2179 measured reflections
217 independent reflections

$\theta_{\max} = 45°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 8$
2 standard reflections
frequency: 60 min
intensity variation: 3%

Refinement

Refinement on F
$R = 0.0243$
$wR = 0.0299$
$S = 1.11$
214 reflections
11 parameters
$w = 1/[\sigma^2 + (0.025F_o)^2]$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 2.5$ e Å^{-3}
$\Delta\rho_{\min} = -2.8$ e Å^{-3}

Extinction correction: Becker & Coppens (1975)
Extinction coefficient: 4.024×10^3
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sn1	0.0	0.0	0.0	0.0099 (2)
Sn2	0.333	0.666	0.5070 (8)	0.0083 (1)
Fe	0.5	0.0	0.0051 (14)	0.0079 (2)

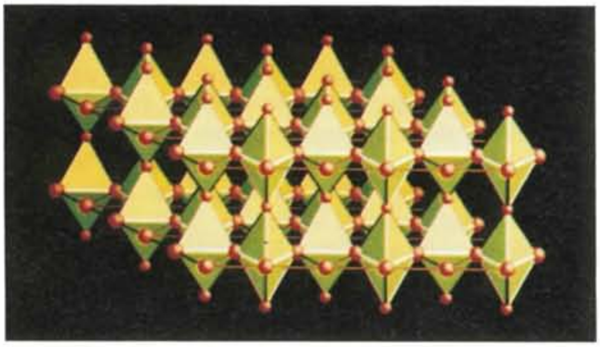

Fig. 1. The structure of CoSn. Spheres at the bases of the trigonal bipyramids are Co.

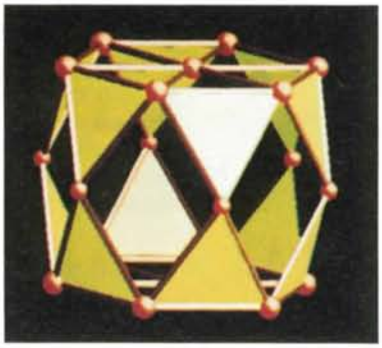

Fig. 2. The empty 20-vertex polyhedron.

Table 2. *Selected geometric parameters* (Å)

Sn1—Fe	2.6656 (2)	Fe—Fe*	2.6655 (2)
Sn2—Fe	2.692 (6)	Fe—Sn1	2.6656 (2)
Sn2—Fe	2.705 (6)	Fe—Sn2	2.692 (6)
Sn2—Sn2*	3.0779 (2)	Fe—Sn2	2.705 (6)

The crystals were grown from a tin melt containing equal amounts of Mg, Ti, V, Cr, Mn, Fe, Co, Cu, Zn and Al at 1073 K for 5 h, and then cooled at a rate of 100 K h^{-1}. The composition was determined by means of energy dispersive X-ray analysis with a Jeol 840A scanning electron microscope. The internal R value of the intensity material is relatively high, particularly when compared with the low final R value of the structure determination. This is attributed to the shape of the specimen. The thin hexagonal rod shape in combination with a fairly high absorption coefficient make some reflections unobservable, and this cannot be amended simply by absorption correction. However, the data used is of higher quality than the internal R value implies, since reflections with high standard deviations contribute little to the averaged intensity. Since Cr and Ni are next-nearest neighbours to the left and right of Fe in the periodic table and occur in equal amounts in the compound, the mixed (Fe,Cr,Ni) position was refined as pure Fe [all programs used are described by Lundgren (1982)]. Changing the occupancy of this position to 3:1:1 gave exactly the same result in the refinement. The microprobe analysis indicates a small excess of Sn in the compound: 9, 9, 27 and 55 mol% for Ni, Cr, Fe and Sn, respectively. The value for Sn is less reliable than the others since the crystals were grown from an Sn melt and residual Sn could contaminate the crystal faces. If the occupancy factors are refined, there is indeed a tendency for a rise in occupancy of the Fe position, and a decrease in the occupancy of the Sn1 position. This is in agreement with a disorder where Fe is partially replaced by Sn. The extreme values of the final $\Delta\rho$ map were at the positions of the atoms or close to them. No residual electron density was found in the empty 20-vertex polyhedra.

The deviations in the coordinates from the centrosymmetric space group $6/mmm$ are small. The anisotropic temperature factors do not change drastically, but the final R values increase significantly ($R/wR = 2.6/3.6$) and $\Delta\rho_{\max}$ increases to 5.5 e Å^{-3}.

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Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71362 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1040]

References

Becker, P. J. & Coppens, P. (1975). *Acta Cryst.* A**31**, 417–425.

Carlsson, O. & Hägg, G. (1932). *Z. Kristallogr.* **83**, 308–317.

Haucke, W. (1940). *Z. Anorg. Allg. Chem.* **244**, 17–22.

Hyde, B. & Andersson, S. (1989). In *Inorganic Crystal Structures*. New York: Wiley.

Larsson, A.-K., Lidin, S. & Jacob, M. (1994). *Acta Cryst.* C**50**. 9–12.

Lundgren, J.-O. (1982). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.

Nial, O. (1938). *Z. Anorg. Allg. Chem.* **238**, 287–296.

Savin, A., Becke, A. D., Flad, J., Nesper, R., Preuss, H. & von Schnering, H. G. (1991). *Angew. Chem.* **30/4**, 409–412.

Schwarz, U., Larsson, A.-K. & Lidin, S. (1993). In preparation.

Villars, P. & Calvert, L. D. (1985). In *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*. Ohio: ASM.

Wilson, C. G., Thomas, D. K. & Spooner, F. J. (1960). *Acta Cryst.* **13**, 56–57.