

The Crystal Structure of AuNi₂Sn₄

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SAMPLE PROVENANCE

A hitherto unknown, virtually stoichiometric phase with composition AuNi₂Sn₄ has been identified in the Au–Ni–Sn system, and its structure has been determined by direct methods. The unit cell is rhombohedral (space group: $R\bar{3}m$) with dimensions $a = 422.6(1)$ pm and $c = 2656.6(4)$ pm in the hexagonal setting and $a = 918.2(2)$ pm and $\alpha = 26.60(1)^\circ$ in the rhombohedral setting. According to the hexagonal description Au is in $3b$ and Ni, Sn(I), and Sn(II) are in $6c$ with $z = 0.40091(6)$, $0.29965(3)$, and $0.11204(3)$, respectively. AuNi₂Sn₄ proves to be isostructural with the mineral smythite (Fe₃S₄–s). The Fe₃S₄–s-type structure belongs to the NiAs-type family and certain aspects of the structural relationships are briefly discussed. © 1995 Academic Press, Inc.

Samples were prepared by melting together weighed amounts of the [$>99.95\%$ pure] elements in sealed, evacuated silica-glass tubes (1). After quenching in ice water the samples were annealed for 4–5 days at 400°C. However, it proved difficult to prepare a batch of phase pure AuNi₂Sn₄ large enough for, say, density measurements by this simple approach. Instead a large-scale sample with nominal composition Au₁₆₇Ni₁₆₇Sn₆₆₇ was treated according to the above procedure. At this composition and at 400°C there is established an equilibrium AuNi₂Sn₄ + L, and on cooling L gives AuSn₄ and minor amounts of AuSn₂. The thus-obtained sample was then treated with 8 M HCl, which reacted with AuSn₄ and (although more slowly) also with AuSn₂, but not with AuNi₂Sn₄. After this treatment the solid gold is left behind as very finely dispersed particles. Almost all the gold can be separated from the AuNi₂Sn₄ phase by ultrasound agitation in ethanol and sucking off the gold–ethanol suspension by a drop pipette. A brown–yellow surface tint of the AuNi₂Sn₄ sample and a pycnometric density, too large by about 3% (9.83 g cm^{–3} at 25.00°C with kerosene as displacement liquid), show that the separation is not quite complete.

This procedure gave a large number of good quality single crystals of AuNi₂Sn₄ (as judged by the Weissenberg technique) suitable for structure determination.

X-RAY DATA AND STRUCTURE DETERMINATION

Crystal and experimental data are given in Table 1. Unit cell dimensions were calculated from diffractometer setting angles for 25 reflections with $23 < 2\theta < 44^\circ$. Intensities were recorded for a quadrant of reciprocal space and corrected for Lorentz and polarization effects. The structure was determined by direct methods (2) and refined by full-matrix least-squares calculations (3) using isotropic thermal parameters. The data were corrected for absorption by empirical methods [(4); minimum and maximum absorption correction were 0.810 and 1.280, respectively]. The intensities of equivalent reflections were then averaged (R for merging 0.036). The positional

INTRODUCTION

The charting (1) of the phase relations in the Au–Ni–Sn system has shown that there exists a hitherto unknown ternary phase with the virtually stoichiometric composition AuNi₂Sn₄. The composition was established by microprobe analyses of the phase in question for three samples with nominal formulae: Au₁₀₀Ni₂₅₀Sn₆₅₀, Au₁₀₀Ni₃₅₀Sn₅₅₀, and Au₂₀₀Ni₂₅₀Sn₅₅₀. The thus-obtained analytical formulae, AuNi_{1.97}Sn_{4.07}, AuNi_{1.95}Sn_{4.04}, and AuNi_{1.88}Sn_{3.97}, respectively, agree within the estimated error limits with AuNi₂Sn₄ and document, moreover, the stoichiometric nature of the phase. (Additional evidence of the lack of a homogeneity range for AuNi₂Sn₄ comes from the invariable unit cell dimensions derived for samples with different nominal compositions.) Thermal analysis show that AuNi₂Sn₄ is stable up to ca. 420°C, at which temperature it undergoes the peritectic reaction



(Au₂₃Ni₂₅Sn₅₂ belongs to the continuous homogeneity range of the solid solution phase between AuSn and Ni₃Sn₂ with regular to partially filled up NiAs-type structure), and Au₀₁Ni₄₁Sn₅₈ to the homogeneity range of Ni₃Sn₄.) This paper concerns the crystal structure of AuNi₂Sn₄.

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TABLE 1
Crystal and Experimental Data for AuNi₂Sn₄

Diffractometer	NICOLET P3/F
Crystal dimensions (mm)	0.05 × 0.02 × 0.02
Radiation	MoK α (λ = 71.069 pm)
Crystal system	Trigonal
<i>a</i> (hex) (pm)	422.6(1)
<i>c</i> (hex) (pm)	2656.6(4)
<i>a</i> (rhom) (pm)	918.2(2)
α (rhom) (°)	26.60(1)
<i>V</i> (hex) (pm ³)	4.109(1) × 10 ⁸
Space group	<i>R</i> $\bar{3}m$
Formula weight	789.15
<i>Z</i> (hex)	3
<i>D_x</i> (g cm ⁻³)	9.567
<i>D_m</i> (g cm ⁻³)	9.83
μ (MoK α) (cm ⁻¹)	623.4
Scan mode	$\omega/2\theta$
Scan speed (θ) (°min ⁻¹)	2.0
Scan range (θ) (°)	1.9
Maximum sin θ/λ (pm ⁻¹)	8.0 × 10 ⁻³
Stability monitoring	3 test reflections/135 observations
Total no. of measured reflections	532
Independent reflections with <i>I</i> > 3.0 σ (<i>I</i>)	261
Structure determination	Mithril
Refinement	Full-matrix least-squares
Weighting scheme	$w = [\sigma^2(F)]^{-1}$
No. of parameters refined	13
$R = \sum F_o - F_c / \sum F_o $	0.026
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$	0.028
$S = [\sum w(F_o - F_c)^2 / (n - m)]^{1/2}$	2.00
Max. $\Delta\rho$ (e pm ⁻³)	4.83 × 10 ⁻⁶
Min. $\Delta\rho$ (e pm ⁻³)	-2.53 × 10 ⁻⁶

and anisotropic thermal parameters as well as the isotropic extinction parameter were finally refined by least-squares calculations (3). Figures of merit are listed in Table 1 and final parameters are given in Table 2. Observed and calculated structure factors can be obtained from the authors upon request.

TABLE 2
Fractional Coordinates and Thermal Parameters with E.S.D.'s in Parentheses

Atom	Position	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₃₃
Au	3 <i>b</i>	$\frac{1}{2}$	0.0058(3)	0.0030(3)
Ni	6 <i>c</i>	0.40091(6)	0.0033(5)	0.0042(6)
Sn(I)	6 <i>c</i>	0.29965(3)	0.0026(2)	0.0065(4)
Sn(II)	6 <i>c</i>	0.11204(3)	0.0026(3)	0.0065(4)

Note. Space group *R* $\bar{3}m$. Fixed occupation number 1 for all positions.

DISCUSSION

Illustrations of the AuNi₂Sn₄ crystal structure in perspective and projection are shown in Fig. 1 and relevant interatomic distances are listed in Table 3. A search in Pearson's Handbook (7) under *hR7* revealed that AuNi₂Sn₄ is isostructural with the mineral smythite [Fe₃S_{4-s} (5)].² So far Fe₃S_{4-s}, as opposed to other similarly composed iron sulfides, is not obtained by synthesis, and AuNi₂Sn₄ is, in fact, the first man-made phase with the structure type in question. [The values for the parameters in the structures of Mo₂B₅ (8), and Li₇Si₃ (9) are so different from those for Fe₃S_{4-s} and AuNi₂Sn₄ that it is unnatural to include them as isostructural phases.]

The Fe₃S_{4-s}-type structure belongs to the NiAs-type family. However, it differs from the structures of other family members with metal vacant NiAs-like structures (cf. the deviation from 1 : 1 stoichiometry in composition). In the Fe₃S_{4-s}-type structure the (ordered) vacancies are confined to every fourth metal layer (along *c* in the hexagonal setting), whereas they are arranged (ordered or disordered) in alternating layers in the other metal vacant, NiAs-like structures (10). Another distinction concerns the stacking sequence of the nonmetal atoms, which is *ABABCACABCBC...* and *AB...* in the Fe₃S_{4-s}- and NiAs-type structures, respectively. It may also be mentioned that AuNi₂Sn₄ has two phases with NiAs-like structures as neighbors in the Au-Ni-Sn phase diagram, viz., Au_{1-t}Ni_{t+Δt}Sn (0 ≤ *t* ≤ 1, Δt varying systematically between ~0 and ~0.5) with regular to partially filled up NiAs-type structure (1) and Ni₃Sn₄ with Ni₃Sn₄-type (Fe₃Se₄-like) structure (11).

In order to assess the coordination numbers (CN) for the four crystallographic different kinds of atoms in the structures of AuNi₂Sn₄ and Fe₃S_{4-s} the Frank-Kasper [F-K(6)] approach has been used. The results of this analysis are included in Table 3 and show that the coordination situation is appreciably different in the two phases. For each interatomic distance in the first coordination sphere around a given atom Table 3 lists the associated relative F-K area. This quantity, which we define as the size of the appropriate F-K plane relative to the total surface area of the F-K polyhedron, serves as an indicator of the space-filling efficiency of the pair of atoms concerned. It is instructive to compare the F-K polyhedron of Ni versus Fe(II) and of Sn(I) versus S(I) in Fig. 2. Although all eight atoms in the first coordination sphere of Ni are of equal importance, the significance of the seventh Fe(I) atom in the close surrounding of Fe(II)

² It may be argued that AuNi₂Sn₄ and Fe₃S_{4-s} should be classified as isopuntal rather than isostructural. However, although *c/a* differs by ~58%, the close conformity in the variable positional parameters makes it more natural to choose the latter classification.

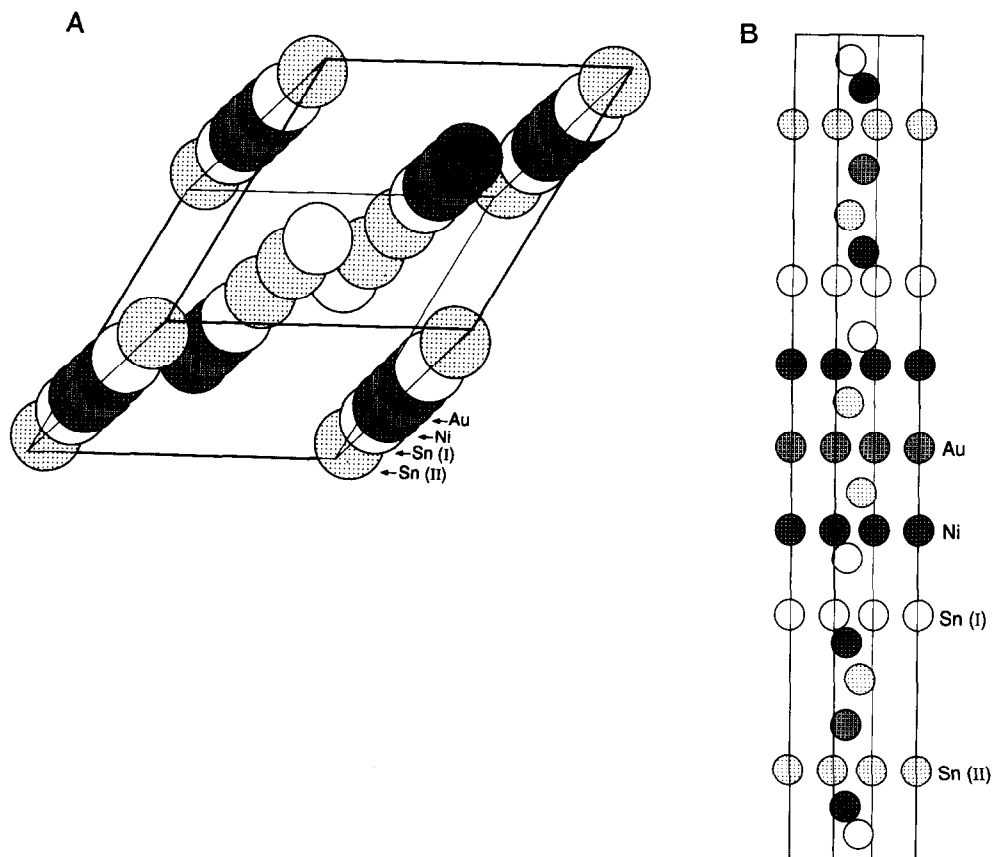


FIG. 1. The $[\text{Fe}_3\text{S}_4\text{-s}$ type (5)] crystal structure of AuNi_2Sn_4 in hexagonal setting [Au, Ni, Sn(I), and Sn(II) corresponds to Fe(I), Fe(II), S(I), and S(II), respectively], viewed in (A) perspective and (B) projection. The legend to the symbols for the atoms is given on the illustrations.

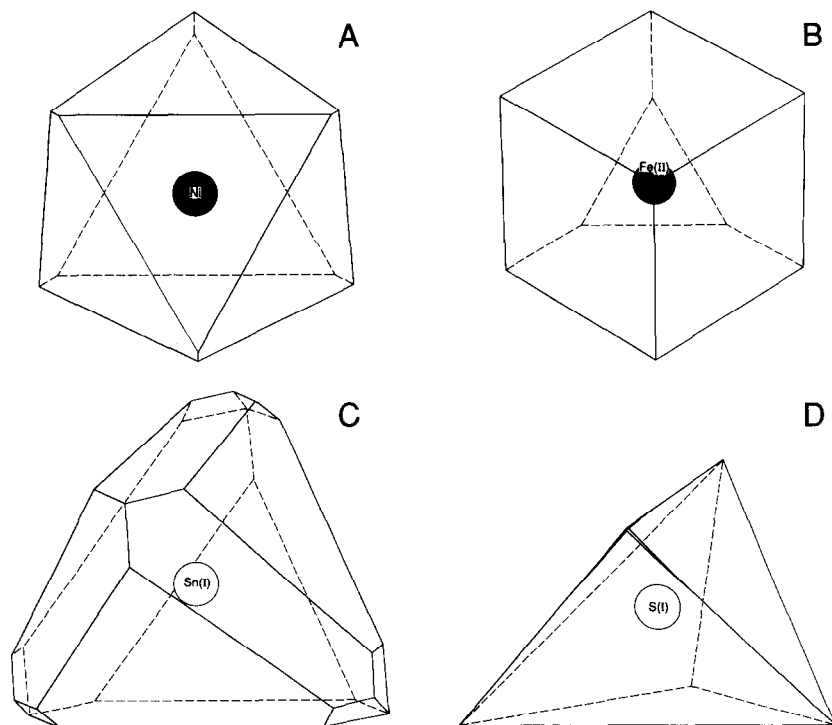


FIG. 2. Selected Frank-Kasper [F-K (6)] polyhedra from the structures of AuNi_2Sn_4 and of $\text{Fe}_3\text{S}_4\text{-s}$. Compare the corresponding pairs: (A) Ni versus (B) Fe(II) and (C) Sn(I) versus (D) S(I). Relative sizes of the planes are listed in Table 3.

TABLE 3
Interatomic Distance Data for AuNi₂Sn₄ and Fe₃S₄-s (5)

AuNi ₂ Sn ₄				Fe ₃ S ₄ -s				
Specification	Distance	F-K area	CN	Specification	Distance	F-K area	CN	
Au-Ni	263.2(2)	2 × 18.6	2	Fe(I)-Fe(II)	286	2 × 3.8	2	
	-Sn(II)	6 × 10.5	6		-S(II)	244	6 × 15.4	6
	283.9(1)	100.2	8			100.0	8	
Ni-Au	263.2(2)	1 × 10.6	1	Fe(II)-Fe(I)	286	1 × 3.4	1	
	-Sn(I)	3 × 11.2	3		-S(I)	241	3 × 17.4	3
	-Sn(I)	1 × 11.0	1		-S(I)	441	0	0
	-Sn(II)	3 × 14.9	3		-S(II)	247	3 × 14.8	3
	271.1(1)	99.9	8			100.0	7	
Sn(I)-Ni	260.1(1)	3 × 12.4	3	S(I)-Fe(II)	241	3 × 23.9	3	
	-Ni	1 × 9.4	1		-Fe(II)	441	0	0
	-Sn(I)	3 × 9.4	3		-S(I)	365	3 × 9.1	3
	-Sn(I)	6 × 0.6	6		-S(I)	347	0	0
	-Sn(I)	3 × 7.2	3		-S(II)	345	3 × 0.3	3
	-Sn(II)	320.7(1)	100.0		16			99.9
Sn(II)-Au	283.9(1)	3 × 13.1	3	S(II)-Fe(I)	244	3 × 16.2	3	
	-Ni	3 × 9.9	3		-Fe(II)	247	3 × 0.6	3
	-Sn(I)	3 × 7.3	3		-S(I)	345	3 × 0.3	3
	-Sn(I)	3 × 3.0	3		-S(II)	344	99.9	12
	-Sn(II)	379.2(1)	99.9		12			

Note. Interatomic distance (in pm, number in parenthesis corresponds to e.s.d.'s in axes and positional parameters), the associated area on the Frank-Kasper [F-K (6)] polyhedron (as a percentage of the total surface area), and the coordination number (CN). The data for Fe₃S₄-s are calculated from: $a = 347$, $c = 3450$ pm, and $z = 0.417$, 0.289, and 0.126 for Fe(II), S(I), and S(II), respectively.

is more marginal (see also Table 3). The changes in the F-K polyhedron from Sn(I) to S(I) are much more extensive, the development being perhaps best appreciated on considering the information in Fig. 2 and Table 3 together. Since the values of the positional parameters for AuNi₂Sn₄ and Fe₃S₄-s (see Tables 2 and 3) are rather similar, the differences in interatomic distances and coordinations originate almost exclusively from the unit cell dimensions.

The stipulation of estimated interatomic distances for

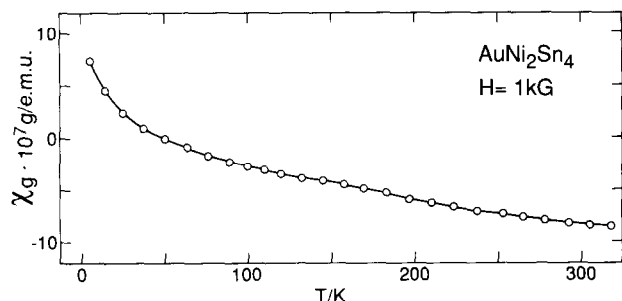


FIG. 3. The temperature variation in the magnetic susceptibility of AuNi₂Sn₄.

AuNi₂Sn₄ is based on the actual CN's in Table 3. The CN = 12 radii for Au, Ni, and Sn (for valence 1, 4, and 6, respectively) then give 258.8, 293.7, 278.4, 274.1, 317.0, 313.0, and 309.0 pm for the Au-Ni, Au-Sn(II), Ni-Sn(I), Ni-Sn(II), Sn(I)-Sn(I), Sn(I)-Sn(II), and Sn(II)-Sn(II) distances, respectively (12). Comparison of the observed values in Table 3 with these estimates shows deviations of -105.6 and -70.2 to 7.7 pm, the large negative discrepancies referring to the long distances Sn(I)-Sn(I) [-105.6 pm] and Sn(II)-Sn(II) [-70.2 pm]. The obvious inference of the latter finding is that these long separations in the first coordination spheres of the atoms concerned are consequences of the packing of spheres of unequal size. In other words, the requirement of complete space filling is the sole reason why the F-K approach includes the atoms in question in CN. Neglecting the long distances just considered, the remaining differences between observed and estimated distances (-18.3 to 7.7 pm) fall in the usual range of match/mismatch for similar comparisons. It should be noted that the basis for such comparisons is the hard-sphere model for atoms, and only rather moderate adjustments in the atomic shapes are needed to account for the latter discrepancies.

The magnetic susceptibility data in Fig. 3 (collected with a Quantum Design SQUID magnetometer) show that AuNi_2Sn_4 changes from weakly paramagnetic to weakly diamagnetic at some 50 K. AuNi_2Sn_4 thus definitely carries no unpaired electrons, and we moreover suggest that it is a metallic- or semimetallic-type conductor.

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