

BRIEF COMMUNICATIONS

The Crystal Structure of $\text{Ni}_{21}\text{In}_2\text{P}_6$

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The crystal structure of $\text{Ni}_{21}\text{In}_2\text{P}_6$ has been determined and refined from single crystal diffractometer data. $\text{Ni}_{21}\text{In}_2\text{P}_6$ is isostructural with Cr_{23}C_6 . It crystallizes in space group $Fm\bar{3}m$ (No. 225) with $a = 11.1120(4)$ Å and 4 formula units in the unit cell. $\text{Ni}_{21}\text{In}_2\text{P}_6$ is the first phosphide representative of the Cr_{23}C_6 structure type to be reported. © 1990 Academic Press, Inc.

Introduction

This work is part of a series of studies concerning phases and reactions in transition metal-indium-phosphorus ternary systems, presently in progress in our laboratory. During the investigation of the Ni-In-P system a new ternary phase with the composition $\text{Ni}_{21}\text{In}_2\text{P}_6$ was found. A complete single-crystal structure refinement of this compound is reported in the present paper. A more detailed account of the phase relationships in the system will be reported later.

Experimental

Preparation

Starting materials were turnings of nickel (purity 99.999%, Johnson Matthey Chemicals Ltd, England), indium phosphide (semiconductor grade, gift from the Swedish Institute of Microwave Technique), and

red phosphorus with a claimed purity better than 99.9%. A sample with the approximate composition $\text{Ni}_{75}\text{In}_{10}\text{P}_{15}$ was prepared by heating nickel, indium phosphide, and phosphorus in an evacuated silica tube. The temperature was raised from room temperature to 1000°C and after a few days it was slowly cooled to 800°C and kept there for a month.

X-ray Powder Diffraction Work

Powder diffraction patterns were obtained with a focusing Guinier-Hägg-type camera using $\text{CuK}\alpha_1$ radiation and silicon ($a = 5.43106$ Å) as internal calibration standard. The positions and intensities of the diffraction peaks were measured using a film scanner and the unit cell dimension was refined using a local least-squares program (CELLKANT). The sample contained $\text{Ni}_{21}\text{In}_2\text{P}_6$ ($a = 11.1120(4)$ Å) and small amounts of nickel and Ni_2In . After several attempts a fragment was found

which proved to be a single crystal when examined in a Weissenberg camera.

Single Crystal Diffraction Work

The single crystal diffraction data were recorded at room temperature on a Stoe four-circle diffractometer with a graphite monochromator using $\text{MoK}\alpha$ radiation. The intensities were measured using the ω - 2θ technique up to a maximum of 60° in 2θ . Five standard reflexions were measured every 3rd hour in order to check the stability of the experimental conditions. The crystal shape was approximated to a distorted tetrahedron with the base edges 23.0, 15.0, and $12.5 \mu\text{m}$ and the height $25.0 \mu\text{m}$. Corrections were made for absorption and L_p effects. The absorption correction was performed using the computer program CAMEL JOCKEY (1-3). The calculated linear absorption coefficient was 300 cm^{-1} . The intensities of 3142 reflections, out of which 111 were nonequivalent, were used in the refinement. Their indices were $-14 \leq h, k, l \leq 14$. The calculations were performed using computer programs described by Sheldrick (4) and Lundgren (5). Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography (6).

Structure Analysis

Using the information from Weissenberg photographs the space group could be determined by the method described by Crowfoot (7). Initial positions for nickel, indium, and phosphorus were determined by the direct method program SHELXS86 (4). A difference Fourier map was made to verify that all atoms had been located. The structural parameters were refined by least-squares methods.

The refinements were based on F_0^2 data and weights were assigned to the reflections according to the formula $w = 1/\sigma^2(F_0^2)$. As

the observed structure factors were consistently lower than the calculated ones for the strongest reflections, an isotropic extinction correction was applied including the whole material. The correction was made according to the Becker-Coppens model (8, 9, 10). 753 strong reflections with an extinction correction exceeding 20% were omitted because the conditions required from the kinematical extinction theory used were not fulfilled. All subsequent refinements were based on the averaged extinction-corrected F^2 data. The possibility of a deviation from the ideal composition was tested by refining the occupation factors for the different atomic positions but no significant changes were obtained.

The agreement factors finally obtained for 90 independent reflections with $F_0^2 > 3\sigma_c(F_0^2)$ were $R(F) = 0.086$, $R(F^2) = 0.087$, and $R_w(F^2) = 0.126$. Errors in the geometrical description of the crystal are probably responsible for the relatively high final values obtained for the agreement factors.

Description and Discussion of the Structure

Final structure data for $\text{Ni}_{21}\text{In}_2\text{P}_6$ are presented in Table I and interatomic distances are listed in Table II.

$\text{Ni}_{21}\text{In}_2\text{P}_6$ crystallizes in space group $Fm\bar{3}m$ and is isostructural with Cr_{23}C_6 . The structure can be described as cubo-octahedral nickel atom clusters in a face-centered arrangement, with cubic nickel atom clusters filling the octahedral interstices be-

TABLE I
POSITIONAL PARAMETERS WITH ESDs FOR $\text{Ni}_{21}\text{In}_2\text{P}_6$

Atom	Position	x	y	z	$B(\text{\AA}^2)$
Ni(1)	48h	0	0.1740(1)	0.1740(1)	0.76(8)
Ni(2)	32f	0.3842(1)	0.3842(1)	0.3842(1)	0.42(8)
Ni(3)	4a	0	0	0	0.5(1)
P(1)	24e	0.2623(5)	0	0	0.3(1)
In(1)	8c	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.49(8)

TABLE II
INTERATOMIC DISTANCES LESS THAN 4.0 (Å)

In(1)	-	4 Ni(2)	2.5830	Ni(2)	-	In(1)	2.5830
	-	12 Ni(1)	3.0239		-	6 Ni(1)	2.7442
	-	12 P(1)	3.9311		-	3 Ni(2)	3.6394
Ni(1)	-	2 P(1)	2.1680	P(1)	-	4 Ni(1)	2.1680
	-	Ni(1)	2.3890		-	4 Ni(2)	2.2687
	-	5 Ni(1)	2.7342		-	Ni(3)	2.9144
	-	4 Ni(2)	2.7442		-	4 Ni(1)	3.6912
	-	2 In(1)	3.0239		-	4 P(1)	3.7358
	-	2 P(1)	3.6912		-	4 In(1)	3.9311
	-	2 Ni(1)	3.8667		-	4 Ni(1)	3.9962
	-	2 P(1)	3.9962	Ni(3)	-	12 Ni(1)	2.7342
Ni(2)	-	3 P(1)	2.2687		-	6 P(1)	2.9144
	-	3 Ni(2)	2.5734				

Note. All ESDs are smaller than 0.0002 Å.

tween the cubo-octahedra. Each cubo-octahedron is centered by a nickel atom. The indium atoms are located at the corners of cubes with an edge length of half the unit cell a -axis. These atoms are surrounded by nickel atoms forming a CN 16 Friauf polyhedron (a truncated tetrahedron). The phosphorus atoms are surrounded by eight nickel neighbors at the corners of a square antiprism.

The structure of Cr_{23}C_6 was originally determined by Westgren from X-ray diffraction data (11) and confirmed later from neutron diffraction data by Meinhard and Krisement (12) and Bowman *et al.* (13). The only additional binary representative of this structure type seems to be Mn_{23}C_6 (11) while several ternary carbides and a very large number of ternary borides have been reported to crystallize with the Cr_{23}C_6 -type structure. Stadelmaier has provided major contributions to the knowledge of ternary borides ("tau-borides") and discussed their crystal chemistry at length (14).

The occurrence of $\text{Ni}_{21}\text{In}_2\text{P}_6$ with the Cr_{23}C_6 -type structure further substantiates the close structural relationships between metal-rich transition metal phosphides on one hand and transition metal carbides and

borides on the other. Another recent example of this crystal-chemical feature is provided by the kappa-phase structure family, exhibiting numerous isostructural borides, carbides, and phosphides (15). In the present study, some attempts were made to prepare isostructural phosphide counterparts to $\text{Ni}_{21}\text{In}_2\text{P}_6$ by replacing nickel by cobalt or copper. These efforts were, however, without success.

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References

1. H. D. FLACK, *Acta Crystallogr. A* **30**, 569 (1974).
2. H. D. FLACK, *J. Appl. Crystallogr.* **8**, 520 (1975).
3. H. D. FLACK, *Acta Crystallogr. A* **33**, 890 (1977).
4. G. M. SHELDRIK, in "Crystallographic Computing 3" (G. M. Sheldrick, C. Kruger, and R. Goddard, Eds.), pp. 175-189, Oxford Univ. Press, London/New York (1985).
5. J. O. LUNDGREN, in "Crystallographic Computer Programmes", Internal Report, UUI-C-B13-4-05, Dept. of Inorganic Chem., Univ. of Uppsala (1982).
6. "International Tables for X-ray Crystallography", Kynoch Press, Birmingham (1974).
7. D. CROWFOOT, *Z. Kristallogr.* **90**, 215 (1935).
8. P. J. BECKER AND P. COPPENS, *Acta Crystallogr. A* **30**, 129 (1974).
9. P. J. BECKER AND P. COPPENS, *Acta Crystallogr. A* **31**, 417 (1975).
10. P. BECKER, *Acta Crystallogr. A* **33**, 243 (1977).
11. A. WESTGREN, *Jernkontorets Ann.* **117**, 501 (1933).
12. D. MEINARD AND O. KRISEMENT, *Z. Naturforsch.* **15a**, 880 (1960).
13. A. L. BOWMAN, G. P. ARNOLD, E. K. STORMS, AND N. G. NERESON, *Acta Crystallogr. B* **28**, 3102 (1972).
14. H. H. STADELMAIER, in "Developments in the Structural Chemistry of Alloy Phases" (B. C. Giessen, Ed.), pp. 161-180, Plenum, New York/London (1969).
15. A. HÅRSTA AND S. RUNDQVIST, *J. Solid State Chem.* **70**, 210 (1987).