

08.3-3 X-RAY INVESTIGATION OF CRYSTALLIZATION AND THERMAL EXPANSION OF AuSn₄, PdSn₄ AND PtSn₄.

By R. Kubiak and M. Wołczyrz, Institute for Low Temperature and Structure Research, Polish Academy of Sciences Wrocław, Poland.

Isomorphic crystal structures of AuSn₄, PdSn₄ and PtSn₄ are described by the orthorhombic space group Aab2 (Schubert & Roesler, Z. Metallkd. (1950) 41,298; Kubiak & Wołczyrz, J. Less-Comm. Met. (1984) 97,265). The investigation of crystallization process of AuSn₄ (Kubiak, J. Less-Comm. Met. (1981) 80, P53) revealed the existence of the relationship between the speed of crystallization and the formation of superstructure (with 6-fold extension of *c*-parameter).

In the present work the single crystals of all the three compounds were obtained in order:

- (i) to check whether crystallization process of PdSn₄ and PtSn₄ can also lead to the superstructure formation,
- (ii) to compare the thermal expansion of all three compounds.

The results are following:

- (i) Contrary to AuSn₄, attempts to obtain PdSn₄ and PtSn₄ single crystals from stoichiometric alloys were unsuccessful. Therefore, single crystals of PdSn₄ and PtSn₄ were obtained by the fast cooling of the melted mixtures of the pure metals with the excess of tin, which then was etched. As a result of this procedure, single crystals were obtained with a shape of rectangular plates. X-ray photographs were taken but gave no evidence of the superstructure.
- (ii) Thermal expansion coefficients were calculated on the basis of precise lattice parameters measurements performed with a Bond-type diffractometer (Łukasiewicz et al., Krist. Tech (1978) 13,561) equipped with the high- and low-temperature attachment. Lattice parameters are almost linear vs. temperature. Numerical values of the linear (α_L) and volume (β_V) thermal expansion coefficients calculated at T=298 K are presented below.

	lattice param. at 298 K	temp. range T [K]	α_L [10 ⁻⁵ K ⁻¹]	β_V [10 ⁻⁵ K ⁻¹]
AuSn ₄	a 6.5124(1)	300 - 473	2.292	5.904
	b 6.5162(1)		2.212	
	c 11.7065(1)		1.400	
PdSn ₄	a 6.3888(1)	194 - 500	1.281	5.391
	b 6.4415(1)		1.292	
	c 11.4462(2)		2.818	
PtSn ₄	a 6.3823(1)	295 - 499	1.265	4.920
	b 6.4190(1)		1.241	
	c 11.3666(2)		2.414	

The results presented above show distinctly different behaviour of AuSn₄ in comparison with the two other compounds. For AuSn₄ the difference between the lattice parameters *a* and *b* is much less than for PdSn₄ and PtSn₄. Therefore in AuSn₄ stacking faults can appear relatively easy and possibility of superstructure formation does exist. This leads probably also to the different character of the thermal expansion of AuSn₄.

As it was stated, in the case of the fast crystallization AuSn₄ shows superstructure which disappears when the sample is heated and homogenized. This phenomenon can be a reason of different superconduction critical temperatures measured for the thin film of AuSn₄ obtained by sputtering of tin and gold on the cooled substrate (Klokholm & Chion, Acta Met. (1966) 14,565) and for the bulk and homogenized sample (Raub, Z. Metallkd. (1964) 55,195).

08.3-4 ANOMALOUS SCATTERING PHENOMENA APPLIED TO THE STUDY OF SHORT-RANGE ORDER IN TERNARY ALLOYS.

By H. Iwasaki, S. Hashimoto and Y. Watanabe, The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, J. Harada, K. Ohshima and M. Sakata, Faculty of Engineering, Nagoya University, Nagoya, H. Terauchi, Faculty of Science, Kwansai Gakuin University, Nishinomiya, T. Matsushita, T. Nakajima and T. Ishikawa, KEK, National Laboratory for High Energy Physics, Ibaraki, Japan.

Intensity measurement of diffuse scattering from a short-range-ordered Cu-20at%Ni-24at%Zn alloy single crystal has been carried out using a monochromatic radiation selected from a band of continuous spectrum of synchrotron orbital radiation now available at KEK. A simple mathematical treatment of the three sets of intensity data obtained with the three wavelengths lying near the absorption edges of the component atoms enables one to divide the observed intensity into the partial intensities arising from the spatial correlation of the three different pairs of atoms, Cu-Ni, Ni-Zn and Zn-Cu. It has been found that a specific pair of atoms in ternary alloy does not behave in the same manner as it does in binary alloy. Attempts have also been made to divide the diffuse scattering intensity around a fundamental reflection into components arising from displacements of atoms and from clustering of atoms.

08.3-5 THE STRUCTURE OF THE TERNARY CARBIDE Ho₂Cr₂C₃. By R.K. Behrens and W. Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany.

The new compounds R₂Cr₂C₃ with R = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu were prepared by arc melting the stoichiometric mixtures of the elemental components and subsequent annealing at 900°C. They crystallize with a new structure type which was determined from single crystal X ray data of Ho₂Cr₂C₃. It has monoclinic symmetry, space group C2/m and the lattice constants: a = 10.480(2) Å, b = 3.3623(5) Å, c = 5.533(1) Å, $\beta = 106.37(1)^\circ$, V = 187.1 Å³, Z = 2. The least squares refinement resulted in a residual of R = 0.027 for 24 variables and 739 independent F values. The structure may be derived from a body centered cubic metal lattice by distortion and ordering of the metal atoms (Fig. 1). One fourth of the (distorted) octahedral voids is filled with carbon atoms. The refinement of the occupancy factors of the two independent carbon positions resulted in almost the ideal values (occupancy parameters of 97 ± 4 and 94 ± 3 %). Each Ho atom is surrounded by 6 Ho (at distances from 3.36 to 3.59 Å), 5 Cr (3.00 to 3.15 Å) and five carbon atoms (2.41 to 2.63 Å). The Cr atoms have coordination number 11 (5 Ho, 2 Cr, and 4 C atoms). The two different carbon atoms have 2 Cr + 4 Ho and 3 Cr + 3 Ho neighbors with Cr-C distances varying between 1.91 and 2.03 Å. The structure is closely related to that of orthorhombic UMoC₂ (Cromer, Larson & Roof, Acta Cryst. (1964) 17, 272). The latter structure can also be derived from a body centered cubic metal lattice by ordering of the metal atoms and filling (in this case one third) of the octahedral voids by carbon

atoms. However, besides the higher C content of UMoC_2 , the C positions of $\text{Ho}_2\text{Cr}_2\text{C}_3$ do not all correspond to the occupied positions in UMoC_2 , although the arrangements of the metal atoms correspond in the two structures. The compounds $\text{U}_2\text{Mo}_2\text{C}_3$ and $\text{U}_2\text{W}_2\text{C}_3$ are isotypic with $\text{Ho}_2\text{Cr}_2\text{C}_3$. This also appears to be the case for the compound $\text{PuWC}_{1.75}$ (Ugajin, Abe, J. Nucl. Mater. (1973) 47, 117).

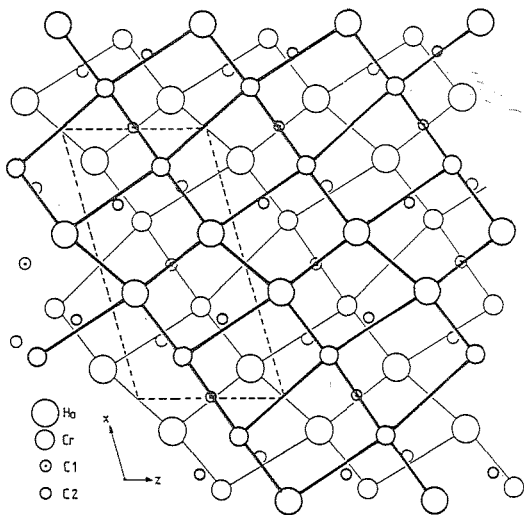


Fig. 1. Crystal structure of $\text{Ho}_2\text{Cr}_2\text{C}_3$. Atoms connected by thick and thin lines are at $y = 0$ and $y = 1/2$ respectively.

08.3-6 $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$, A COMPLEX CARBIDE WITH FILLED $\text{Th}_2\text{Zn}_{17}$ STRUCTURE. By G. Block and W. Jeitschko, Anorganisch-Chemisches Institut, Universität Münster, D-4400 Münster, West Germany.

The title compound was prepared by reaction of the elemental components in a high frequency furnace with subsequent annealing at 800°C . It crystallizes with a rhombohedral cell, space group $R\bar{3}m$ and the hexagonal lattice constants: $a = 8.8714(7) \text{ \AA}$, $c = 12.783(2) \text{ \AA}$, $V = 871.2 \text{ \AA}^3$, $Z = 3$. The structure was determined from single crystal X ray data and refined to a residual of $R = 0.023$ for 25 variable parameters and 414 independent structure factors. The structure can be derived from that of $\text{Th}_2\text{Zn}_{17}$ (Makarov and Vinogradov, Sov. Phys. Crystallogr. (1956) 1, 499) with the Pr and Mn positions corresponding to those of Th and Zn. The carbon atoms fill octahedral voids formed by a square of Mn atoms (Mn-C distances of 1.94 \AA (2x) and 1.95 \AA (2x)) and two Pr atoms at 2.57 \AA . The ideal composition with all octahedral voids filled is represented by the formula $\text{Pr}_2\text{Mn}_{17}\text{C}_3$. The refinement of the occupancy parameter of the carbon positions, however, showed that these positions are only occupied to $57 \pm 3\%$ in the crystal picked for the structure determination. The Pr atoms are situated in a coordination polyhedron formed by three carbon atoms at 2.57 \AA , 19 Mn atoms (at distances varying between 3.19 and 3.43 \AA) and one Pr atom at 3.95 \AA . The four crystallographically different Mn atoms have coordination numbers 12, 13 and 14 with zero or one C neighbor, one, two or three Pr neighbors and between 9 and 13 Mn neighbors (Fig. 1).

The new compound $\text{La}_2\text{Mn}_{17}\text{C}_{3-x}$ is isotypic with $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$. A compound reported by Stadelmaier and Park (Z. Metallk. (1981) 72, 417) with the composition $\text{Gd}_4\text{Fe}_{31}\text{C}_3$ most likely is isotypic with $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$. The structure will be discussed together with other recent examples of ternary carbides which can be derived from binary structure types by filling of interstitial voids.

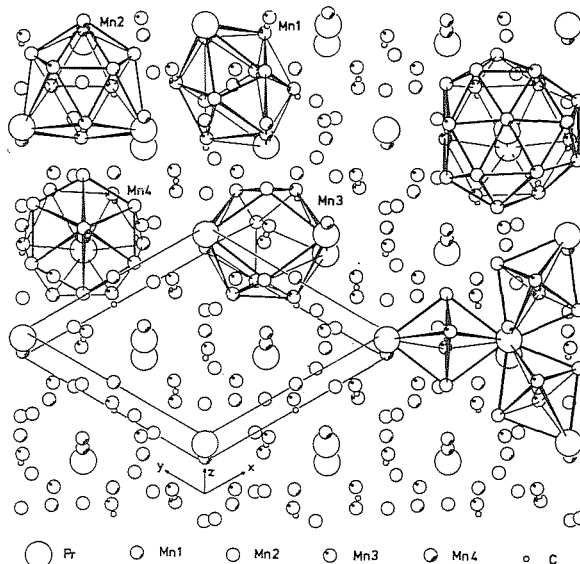


Fig. 1. Coordination polyhedra in $\text{Pr}_2\text{Mn}_{17}\text{C}_{3-x}$. Only one half of the structure between $z = 0$ and $z = 1/2$ is shown.

08.3-7 TEMPERATURE DEPENDENCE OF THE LATTICE CONSTANTS AND THE CRYSTAL STRUCTURE OF $\text{Mn}_{11}\text{Ge}_8$ AT 295 K AND 116 K. By T. Ohba, N. Watanabe and Y. Komura, Faculty of Science, Hiroshima University, Naka-ku, Hiroshima, Japan.

Four intermetallic compounds were reported in Mn-Ge system according to Elliot. Among them Mn_3Ge_2 was found to be antiferromagnet at low temperature and it transforms to weak ferromagnet at 160 K , then changes to a paramagnet at 300 K [Zavadskii and Fakidov; Soviet Physics JETP 24, 887 (1967)].

Israiloff et al. [Monatsh. Chem. 105, 1387 (1974)] studied the crystal structure and concluded that Mn_3Ge_2 is isotypic with $\text{Cr}_{11}\text{Ge}_8$ by a comparison of the powder pattern. In this paper, the crystal structure of $\text{Mn}_{11}\text{Ge}_8$ is refined by a single crystal X-ray diffraction method at 295 K and 116 K . Crystal Data: Orthorhombic, Pnam, $a = 13.214(2)$, $b = 15.880(3)$ and $c = 5.0905(5) \text{ \AA}$, $Z = 4$ at 295 K .

The temperature dependence of the lattice constants is measured using a single crystal. Fig. 1 shows a curve for lattice constant a vs temperature for an example. A kink appears at the transition temperature (160 K). Kinks are also observed on curves for b - and c -axis at the same temperature.

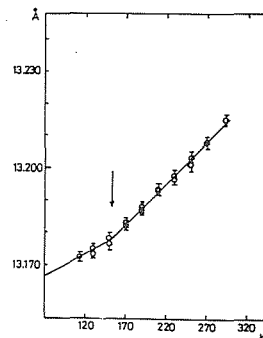


Fig. 1