

The refinement of the structure was made at 295 K and 116 K using a program RADIEL [Coppens et al.; Acta Cryst. A35, 63 (1979)]. The final weighted R(F) values are 0.0292 and 0.0260 at 295 K and 116 K, respectively. Although the crystal symmetry does not change, the positional parameters above and below the transition temperature show non-uniform changes of the interatomic distances. The histograms of the change of the interatomic distances ($\Delta d = d_{295} - d_{116}$) for Ge-Ge, Mn-Ge and Mn-Mn are shown in Fig. 2. Changes of the Mn-Mn distances are greater than those of Mn-Ge and Ge-Ge, and some of Mn-Mn distances are even expanded at 116 K. Such features of the interatomic distances suggest that the contribution of Mn-Mn distances to the magnetic property is fairly large in $Mn_{11}Ge_8$. The deformation densities along Mn-Mn bonds, which are expanded at 116 K, vary considerably from 295 K to 116 K.

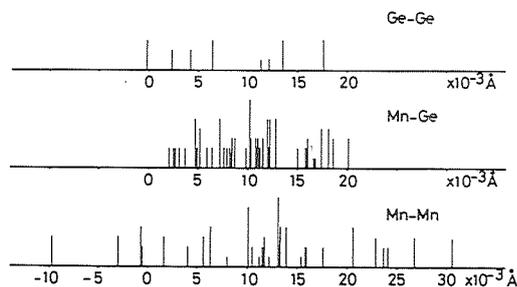


Fig. 2

08.3-8 CRYSTAL STRUCTURE OF $Pr_6Ni_7Si_4$, AN INTERGROWTH OF THREE SIMPLER STRUCTURAL SLABS. By E. Hovestreydt and E. Parthé, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Genève 4 (Switzerland).

$Pr_6Ni_7Si_4$ crystallizes with an orthorhombic unit cell (oP68, Pbcm, $a = 5.888(1)$, $b = 7.4265(9)$, $c = 29.558(8)$ Å). Its structure corresponds to a new structure type which can be described as an intergrowth of three types of slabs. One has an arrangement of Ni centered trigonal Pr prisms as in the Fe_3C type, which is already found with Pr_2Ni . The second slab can be described as a segment of a $ThSi_2$ type structure also with trigonal Pr prisms which are centered by Ni atoms. The $ThSi_2$ type has not yet been found with binary rare earth transition metal compounds, however, a ternary variant occurs with $PrNiSi$. The third slab which is only 3 Å thick and contains Pr, Ni and Si atoms lies between the $ThSi_2$ and the Fe_3C type slabs. The atom arrangement in the thin slab has similarities with the $TiNiSi$ type, a $PbCl_2$ derivative type, which is found for example with $PrNiGa$. However, the coordination polyhedra of the Ni and Si atoms in this thin slabs include Pr atoms from the neighbouring slabs. All Ni and Si atoms are thus found to be in the centers of strongly deformed trigonal Pr prisms.

An isotypic phase seems to exist in the system Ce-Ni-Si where M.G. Mis'kiv (thesis, Ivano Franko Univ., Lvov, USSR, 1973) found a compound with similar lattice constants and space group, however, the composition given there was $Ce_{10}Ni_{12}Si_3$.

A detailed account of this structure determination will be published in Acta Crystallographica.

08.3-9 THE CRYSTAL STRUCTURE OF $Co_2P(h)$ AND ITS

STRUCTURAL RELATIONSHIP TO THE $Co_2P(r)$.

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In the system Co-P, the following compounds are known: Co_2P (Ni_2Si type), CoP (MnP type) and CoP_3 ($CoAs_3$ type). The metallographic investigation showed that the compound Co_2P undergoes a phase transformation. The X-ray powder investigation confirms the polymorphism of Co_2P . The since known compound Co_2P isostructural to Ni_2Si (Nowotny, Z. anorg. Chem. (1947) 254, 349; Rundquist, Acta Chem. Scand. (1960) 14, 1961) is the low-temperature form $Co_2P(r)$. The new high-temperature phase $Co_2P(h)$ stable at above 1400K is isostructural to Fe_2P . The crystal powder data of the high-temperature phase are:

$Co_2P(h)$, $P\bar{6}2m$, Fe_2P type, $a = 5.722(1)$, $c = 3.476(1)$ Å

Among all the homologous phases isostructural to Fe_2P , $Co_2P(h)$ shows the highest axial ratio $c/a = 0.607$.

The other crystal chemical data of compounds isostructural to Fe_2P , and Ni_2Si will be compared with the data of $Co_2P(h)$ and $Co_2P(r)$. The structural relationship between the Fe_2P and Ni_2Si type structure will be discussed.

08.3-10 $Zr_2Ru_3Si_4$, A NEW STRUCTURE TYPE CONTAINING COLUMNS OF SHARED Si-CENTERED ANTIPRISMS AND OF SHARED Ru-CENTERED OCTAHEDRA. By B. Chabot†, E. Parthé† and H.F. Braun††. †Laboratoire de Cristallographie aux Rayons X, Université de Genève, ††Département de Physique de la Matière Condensée, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Genève 4, Switzerland.

$Zr_2Ru_3Si_4$ crystallizes with a monoclinic unit cell (mC72, $C2/c$) with $a = 18.992(3)$, $b = 5.3476(8)$, $c = 13.289(3)$ Å and $\beta = 127.73(1)^\circ$. Its structure corresponds to a new structure type which is characterized by

- columns of Si-centered face-shared square antiprisms formed by Zr and Ru atoms
- columns of Ru-centered face-shared Si-octahedra.

Columns of centered antiprisms and columns of centered octahedra are structural features which are found in other ternary compounds $R_xT_yM_2$ where R is an early transition element (Sc, Ti, Zr, Hf) or a small rare-earth (Lu); T is a transition element of the Cr, Mn, Fe or Co group and M is Si or Ge atom. The compositions of these structures can be related to :

- the composition of the M-centered antiprism columns ($R_4T_4M_2$ or $R_6T_2M_2$ or R_8M_2)
- the type of linkage of the T-centered M-octahedron columns (isolated column : M_6T_2 ; edge-linked to two other columns : $M_2M_4/2T_2$, or edge-linked to three other columns : $M_{6/2}T_2$)
- the presence or not of additional Si atoms inbetween the antiprism columns.

In the table, calculated stoichiometries and formulae of known structure types are shown as a function of anti-

prism composition and type of linkage of the octahedron columns. Formulae framed by rectangles with full lines correspond to structures containing only columns of antiprisms and octahedra, those by rectangles with dashed lines to structures containing additional M atoms in between the antiprisms columns. In this latter case the additional atoms assure that the T elements participating in the antiprisms have an octahedral M surrounding; these M-octahedra, however, do not form face-shared octahedron columns.

antiprism composition / linkage	$(R_4T_4)M_2$ antiprism columns	$(R_6T_2)M_2$ antiprism columns	R_8M_2 antiprism columns
M_6T_2 isolated octahedron columns	$R_4T_6M_8$ $Zr_2Ru_3Si_4$	$R_6T_4M_8$	$R_8T_2M_8$
$2(M_2M_{4/2})T_2$ octahedron columns edge-connected with 2 others	$R_4T_8M_{10}$ $Sc_2Cr_4Si_5$	$R_6T_6M_{10}$ $ZrFeSi_2$ $ZrMnSi_2$ $LuMnGe_2$	$R_8T_4M_{10}$
$4(M_{6/2})T_2$ octah. columns edge-connected with 3 others	$R_4T_{12}M_{14}$	$R_6T_{10}M_{14}$	$R_8T_8M_{14}$ $Zr_4Co_4Ge_7$

The structure of $Zr_2Ru_3Si_4$ will be compared with $ScRe_2Si_3$ and $Sc_3Re_2Si_3$. The latter has a similar unit cell and identical atom sites (except for one unoccupied Si position). A detailed account of this work will be published in Acta Crystallographica.

08.3-11 A NEUTRON POWDER DIFFRACTION INVESTIGATION OF LANTHANUM HEXABORIDE. By M.M. Korsukova, V.N. Gurin, A.F. Ioffe Physical-Technical Institute, Academy of Sciences of the USSR, Leningrad, USSR

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It has been established that the cell dimensions of LaB_6 do not vary with composition (Storms, Mueller, J. Phys. Chem. (1978) 82, 51). Nevertheless, the chemical analyses indicate that a relatively extensive range of homogeneity occurs. Several explanations have been presented as regards the atomic mechanism behind this composition variation. The most obvious suggestion is the occurrence of vacancies at the lanthanum position for boron-rich compositions. Another explanation (Storms, Mueller, J. Phys. Chem. (1978) 82, 51) anticipates the occurrence of separate phases with different compositions (LaB_6 and LaB_9) but with identical unit cells as well as identical diffraction intensities.

In the present study an attempt was made to evaluate the occurrence of vacancies in the La- or B-sublattice using the neutron powder diffraction technique.

The crystals were prepared by solution growth from an Al melt using a ^{11}B -enriched (93-96%) boron. The B/La ratio in the melt was 9/1. The neutron powder diffraction study was made using the Rietveld-type profile refinement technique.

The results of these investigations will be presented and discussed.

08.3-12 CRYSTAL STRUCTURE OF NEW PHASES IN THE Ca-Au, Sr-Au AND Ba-Au SYSTEMS

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About the existence and the crystal structure of intermetallic compounds in the systems formed by Ca, Sr and Ba with Au a few data are available in the literature. Concerning the range 0-50% at. of gold, three phases were reported in the Ca-Au diagram and five in the Sr-Au diagram, all of these with unknown structure. For the same range in the Ba-Au system no information are given (M. Hansen & K. Anderko, "Constitution of Binary Alloys", McGraw-Hill, 1958; R.P. Elliott, "Constitution of Binary Alloys, 1st Supplement", McGraw-Hill, 1965). Recently CaAu was found to be isotypic with the CrB type (F. Merlo, J. Less-Comm. Met. 86, 1982, 241-6).

In this work we present the crystal structure determination of the intermetallic compounds Ca_7Au_3 , Ca_5Au_3 , Ca_5Au_4 , Sr_7Au_3 , Sr_3Au_2 , SrAu and BaAu.

They were identified by single crystal methods and the structures determined and refined by single crystal diffractometer data.

Ca_7Au_3 , oP80, orthorhombic, Pbcu, $a=20.742(8)$, $b=18.036(8)$, $c=6.665(2)$ Å, $Z=8$, is a new structure.

It can be derived from the hexagonal Th_7Fe_3 - type, with the following relationships:

$$a = 2 a_{Th_7Fe_3} ; b = \sqrt{3} a_{Th_7Fe_3} ; c = c_{Th_7Fe_3}$$

The structure is built up by packing four layers along the short axis. Two of these, formed by Ca atoms only, are identical to those formed by Th atoms in Th_7Fe_3 ; two other layers containing both Ca and Au are rearranged, so that the calcium octahedra assume two possible orientations, one rotated 60° about the short axis relative to the other.

Ca_5Au_3 , tI32, tetragonal, $I4/mcm$, $a=7.867(3)$, $c=14.39(1)$ Å, $Z=4$, is isotypic with Cr_5B_3 .

Ca_5Au_4 , mP18, monoclinic, $P2_1/c$, $a=8.028(3)$, $b=8.019(6)$, $c=7.727(3)$ Å, $\beta=109.16(6)^\circ$, $Z=2$, is a new structure. It is closely related to the Pu_5Rh_4 -type.

Sr_7Au_3 , hP20, hexagonal, $P6_3mc$, $a=11.07(1)$, $c=7.161(4)$ Å, $Z=2$, is isotypic with Th_7Fe_3 .

Sr_3Au_2 , hR15, rhombohedral, $R\bar{3}$, $a=9.604(4)$, $c=18.36(1)$ Å, $Z=9$, is isotypic with Er_3Ni_2 .

SrAu, mP40, monoclinic, $P2_1/m$, $a=40.13(3)$, $b=4.697(1)$, $c=6.192(4)$ Å, $\beta=94.21(6)^\circ$, $Z=20$, is a new structure. It belongs to the family of the stacking variants of the CrB-FeB types, with stacking symbol hch_2ch_2chc and Zhdanov notation $(2)21(2)12$.

BaAu, oP8, orthorhombic, Pnma, $a=8.338(8)$, $b=4.925(3)$, $c=6.390(7)$ Å, $Z=4$, is isotypic with FeB.

In these structures gold is always surrounded by a trigonal prism formed by alkaline earth atoms. Through the lateral faces of the prism other waist contacts with alkaline earth or gold atoms are also possible, so that we find Au-Au pairs in Ca_5Au_3 , Ca_3Au_4 and Sr_3Au_2 , and Au zig-zag chains in $SrAu_5$ and BaAu.