08.3-08   STRUCTURES OF NEW TERNARY PHASES IN THE Sc-Rh-Si SYSTEM. By B. Chabot, N. Engel and E. Parthé, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Genève 4, Switzerland.

The presence of at least nine ternary phases in the Si-rich part of the Sc-Rh-Si system has been established by Braun, Burri & Rinderer (J. Less-Common Met. 68, P1-P8 (1979)) using microprobe analysis. The structures of four of these phases have been studied in our laboratory, three of them crystallizing with new structure types.

$Sc_5Rh_4Si_{10}$: P4/mbm, a = 12.325, c = 4.032 Å, Z = 2 was studied by Braun, Yvon & Braun (Acta Cryst. B36, 2397-2399 (1980)). This structure is characterized by Si-centered trigonal prisms $SiSc_6$ and by Rh-centered tetragonal antiprisms $RhSc_4Si_4$.

$ScRhSi_2$: Pnma, a = 6.292, b = 4.025, c = 9.517 Å, Z=4 (Chabot, Braun, Yvon & Parthé, Acta Cryst. in the press) crystallizes with an ordered YZn_3 type. In this structure all Si atoms have a trigonal prismatic surrounding.

$ScRh_3Si_7$: R3̄c, a = 7.5056, c = 19.691 Å, Z = 6 (Chabot, Engel & Parthé, Acta Cryst. in the press) has no trigonal prisms. This new structure type is stabilized by strong Si-Rh interactions. The Sc atoms are at the centres of octahedra formed by an hexagonal close packed array of the Rh atoms.

ScRhSi : Pnma, a = 6.4736, b = 4.0500, c = 7.2483 Å is isotypic, or closely related, to the TiNiSi type.

These structures, together with the phases which are being studied at the present time, will be discussed from a crystal-chemical point of view.

08.3-09   THE CRYSTAL CHEMISTRY OF PHASES OF THE NiAs FAMILY CONTAINING NICKEL, PALLADIUM AND PLATINUM. By M. Ellner, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, Seestr. 75, D-7000 Stuttgart 1, FRG

The crystal chemical parameters of the phases of the NiAs family containing nickel, palladium and platinum were studied in the entire range of homogeneity for each phase. The number of atoms in the unit cell, N_A^C, of the partially filled Ni_2In type structure and some superstructure phases related to the Ni_2In type structure were determined by means of X-ray diffraction and macroscopic density measurements. The experimentally obtained values of the number of atoms in the unit cell were compared with the ideal value, $(N_A^C)'$, calculated from the relation $(N_A^C)' = N_B^C/x_B$, where N_B^C = number of atoms of the element of the B sub-group in the unit cell (= number of B atoms) and x_B = molar fraction of the element of the B sub-group. For the Ni_2In, NiAs and CdJ type structures, it will be assumed $N_B^C = 2$, and thus $(N_A^C)' = 2/x_B$. The results of the experimental measurements on the partially filled phases of the Ni_2In type structure show that, for the molar fraction $x_B > 0.375$, a number of atoms larger than 2 can be found. This anomalous filling of the Ni_2In type structure will be discussed.

It has been observed that the axial ratio c/a and the degree of filling of the phases having the same valence electron concetration (isovalent compounds) of the NiAs family is dependent upon the atomic radii ratio of the transition metal and the B element, r_T/r_B. The isovalent partially filled phases of the Ni_2In type structure with a smaller B atom tend to be more filled than the phases containing some large atom of the same B sub-group. For some phases with the NiAs type structure containing atoms of the VB and VIB sub-groups, it is known that the axial ratio c/a of the phases with a higher valence electron concentration is lower than that of the phases with a lower electron concentration. This fact can be observed by great volume difference of the elements of the VB and VIB sub-groups. Such anomalous behaviour of these phases can be explained by average valence electron density calculated by formula $D_V = N_V^C/V$, where N_V^C = number of valence electrons in the unit cell, and V = volume of the unit cell. For the phases of the Ni_2In and NiAs type structure, a linear correlation between the axial ratio c/a and the average valence electron density was found.

08.3-10   THE CRYSTAL STRUCTURE OF ζ-$Mn_{2.6}$Ge. By Y. Komura and H. Hirayama, Faculty of Science, Hiroshima University, Hiroshima, Japan and T. Tagai, Inst. für Kristallographie der Universität, Frankfurt am Main, BRD.

Mn-Ge system has many intermetallic phases such as ε- and $ε_1$-$Mn_{3.25}$Ge, ζ- and κ-Mn_5Ge_2, η-Mn_5Ge_3 and Mn_3Ge_2 according to Elliott (Constitution of Binary Alloys, First Supplement, 1965). The high temperature ζ-Mn_5Ge_2 phase was described firstly by Zwicker et al. (Z. Metallkd. 40, 433 (1949)) as a closely related compound with Ni_2In ($B8_2$) type structure.

Although Ohoyama (J. Phys. Soc. Jpn. 16, 1995 (1961)) proposed a hexagonal cell of a=7.186, c=13.08Å, the structure has not yet been solved. The structure was analysed using a single crystal specimen which was kindly supplied by Ohoyama. Weissenberg photographs and automated counter-diffractometer with MoKα radiation were used for the analysis.

The ζ-$Mn_{2.6}$Ge is trigonal, a_h=7.185, c_h= 39.17Å, 128 atoms per unit cell, space group P3c1. Intensity distribution shows following remarkable characteristics : (1) hkℓ reflections are strong only when ℓ=3n, n being integer, specially ℓ=30n reflections are very strong. (2) Only hk0 reflections with h,k=3n are very strong and the other hk0 reflections are rather weak. A structural model was derived based on the above characteristics and the three dimensional Patterson function. The direct method also leads to the same model. The model contains 30 sublayers of c/30 apart,

3 atoms being placed on each layer with the rotation of 60° in successive layers as shown in the figure. These sublayers contain 90 atoms altogether in the unit cell. The other 38 atom positions as well as the configuration in the sublayers were refined by Fourier synthesis and full-matrix least-squares to R(F)=0.095, based on 1337 observed reflections. The ζ-phase structure comes out as the following : Ge atoms occupy every fifth layer in the 30 sublayers, and the other layers are occupied by Mn atoms. Remaining 38 atoms are located on the three fold axes of
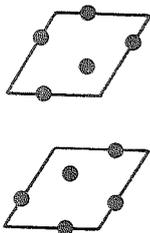
$00z$, $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}z$. Positions of Mn atoms on these axes are above and below the Ge sublayers, and Ge atoms on the axes are settled in between these Ge sublayers.

Coordination numbers for the atoms on three fold axes are mainly 10 and 11, and the atoms on sublayers have coordinations from 11 to 13. Interatomic distances range from 2.43 to 3.20Å except for a few shorter distances of 2.21Å. The structure has similarity with the ones of Mn_5Ge_3 ($D8_8$) and MnGeNi ($B8_2$) with respect to the layer structure and the atomic arrangements in the sublayers.

08.3-11   IS THE SPHERE-PACKING MODEL APPROPRIATE FOR THE SIGMA PHASE?
By Clara Brink Shoemaker and David P. Shoemaker, Oregon State University, Corvallis, OR 97331, USA.

C. G. Wilson and F. J. Spooner [Acta Cryst. (1973). A29, 342] have used a sphere-packing model of the sigma phase to predict the cell dimensions by averaging three estimates for a and c derived from different "panels" of atoms in the structure. The sphere radii are derived from the occupancy and the CN12 radii of the atoms. Their individual estimates from different panels in the same structure differ (in the case of random order, $\bar{R} = 1.35$ Å) by as much as 0.72 Å in c and 1.27 Å in a, although the averages, perhaps fortuitously, agree well with the observed values. This model has been discussed recently by L. M. Alte da Veiga et al. [Acta Cryst. (1981), to be published.]

In our study of 14 sigma-phase related "tcp" phases we have found that atoms with coordinations higher than 12 are much better represented by "dimpled spheres" having two radii rather than one. With such radii we obtain estimates for a and c for the different panels that are in much better agreement. Even more reliable predictions can be made by using all the distances, calculated from these radii by our 1969 procedure (C. B. Shoemaker and D. P. Shoemaker in: Developments in the structural chemistry of alloy phases. B. C. Giessen, Ed., Plenum Press, p. 133). In view of our finding that radii for a given CN type in a given compound are insensitive to occupancy, and in view of the crudeness of the sphere model, we regard the latter's predictions of ordering as unreliable.

08.3-12   INTERMETALLIC PHASES ON THE Ga RICH SIDE OF THE R-Ga SYSTEMS(R=RARE EARTH METAL).
By G.Kimmel,J.Pelleg and L.S.Zevin,Materials Engineering Department,Ben Gurion University of the Negev,Beer Sheva, Israel.

The existence of intermetallic compounds hitherto unidentified, on the Ga-rich side of the R-Ga systems, such as for example Nd-Ga, has already been reported and later confirmed by the present authors(J.Less-Common Met.(1978) 61,293; J.Less Common Met.(1980) 75,133). One of these compounds,the RGa_6, has a tetragonal symmetry, $PuGa_6$ type, and it is a common feature of all R-Ga systems. $Nd-Ga_6$, one of such compounds, is formed by a peritectic reaction at 617°C. It undergoes a transition at 463°C probably of an allotropic nature.Details of this transition will be discussed.
RGa_2 type compounds show a wide homogeneity range of about 10-15 at.%Ga in some R-Ga systems investigated. The systems belong to the light lanthanides. The lattice parameters of the hexagonal RGa_2 compounds (AlB_2 type) increase on addition of Ga. A model is presented to explain the increase in lattice parameters.

08.3-13   STRUCTURAL PRINCIPLES OF LITHIUM-GROUP III-COMPOUNDS.
By J. Stöhr, W. Müller and H. Schäfer, Abt. II für Anorganische Chemie der Technischen Hochschule Darmstadt, West-Germany.
Single crystals of the following Li-GroupIII-compounds were prepared and the structures determined. Li_5Ga_4:trigonal,P3m1,a=437.5 pm,c=825.7 pm. The Ga-atoms form undulating hexagonal double sheets, which are separated by layers of Li-atoms. Li_3Ga_2:trigonal,R3m,a=436.7 pm,c=1389.6 pm. The simple undulating hexagonal sheets of Ga-atoms are separated by layers of Li-atoms. Li_2Ga:orthorhombic,Cmcm, a=456.2 pm,b=954.2 pm,c=436.4 pm.The Ga-atoms form zig-zag-chains. Li_5In_4:trigonal,P3m1,a=478 pm,c=888 pm, isostructural to Li_5Ga_4. Li_3In_2:trigonal,R3m,a=474.8 pm,c=1474.0 pm, isostructural to Li_3Ga_2. Li_2In:orthorhombic, Cmcm,a=476.3 pm,b=1001.7 pm,c=473.5 pm, isostructural to Li_2Ga. $Li_{13}In_3$:cubic, Fd3m,a=1355.6 pm. Isolated In-atoms are observed,i.e. they have only Li-atoms as neighbours. Li_2Tl: orthorhombic,Cmcm,a=474.1 pm,b=1002.3 pm,c=478.6 pm, isostructural to Li_2Ga. Li_5Tl_2: trigonal,R3m,a=471.6 pm,c=2039.9 pm. This structure, which is isostructural to Li_5Sn_2, is characterized by Tl_2-units. Li_3Tl:cubic,Fm3m, a=667,1 pm. Isolated Tl-atoms are observed, isostructural to Li_3Bi. $Li_{22}Tl_5$:cubic,F43m,a=2000.3 pm. Isolated Tl-atoms, isostructural to $Li_{22}Pb_5$. Li_5InTl:trigonal, R3m,a=472.2 pm,c=2029.5 pm, isostructural to Li_5Tl_2.

These compounds are interpreted as Tungsten variants and their structural relationship to the Li-Al-compounds are discussed.