

**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<sub>5</sub>Rh<sub>4</sub>Si<sub>10</sub>: 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<sub>6</sub> and by Rh-centered tetragonal antiprisms RhSc<sub>4</sub>Si<sub>4</sub>.

ScRhSi<sub>2</sub>: 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<sub>3</sub> type. In this structure all Si atoms have a trigonal prismatic surrounding.

ScRh<sub>3</sub>Si<sub>7</sub>: R $\bar{3}$ c, 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<sub>2</sub>In type structure and some superstructure phases related to the Ni<sub>2</sub>In 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<sub>2</sub>In, 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<sub>2</sub>In 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<sub>2</sub>In 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 concentration (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<sub>2</sub>In 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<sub>2</sub>In 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  $\zeta$ -Mn<sub>2.6</sub>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  $\epsilon$ - and  $\epsilon_1$ -Mn<sub>3.25</sub>Ge,  $\zeta$ - and  $\kappa$ -Mn<sub>5</sub>Ge<sub>2</sub>,  $\eta$ -Mn<sub>5</sub>Ge<sub>3</sub> and Mn<sub>3</sub>Ge<sub>2</sub> according to Elliott (Constitution of Binary Alloys, First Supplement, 1965). The high temperature  $\zeta$ -Mn<sub>5</sub>Ge<sub>2</sub> phase was described firstly by Zwicker et al. (Z. Metallkd. **40**, 433 (1949)) as a closely related compound with Ni<sub>2</sub>In (B8<sub>2</sub>) type structure.

Although Ohoyama (J. Phys. Soc. Jpn. **16**, 1995 (1961)) proposed a hexagonal cell of  $a = 7.186$ ,  $c = 13.08$  Å, 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 MoK $\alpha$  radiation were used for the analysis.

The  $\zeta$ -Mn<sub>2.6</sub>Ge is trigonal,  $a_h = 7.185$ ,  $c_h = 39.17$  Å, 128 atoms per unit cell, space group P3c1. Intensity distribution shows following remarkable characteristics: (1)  $hk\ell$  reflections are strong only when  $\ell = 3n$ , n being integer, specially  $\ell = 30n$  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,