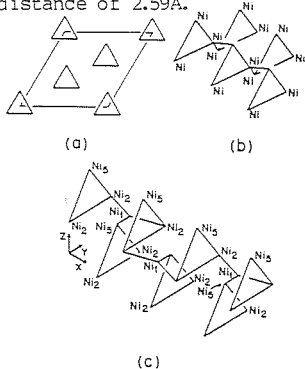


08.3-01 A SUPERSTRUCTURE OF α -Ni₇S₆ AND ITS RELATIONSHIP TO HAZELWOODITE (Ni₃S₂) AND MILLERITE (NiS). By John B. Parise, Dept. Earth & Space Sci., SUNY at Stony Brook NY11794, USA. and Frank H. Moore, AINSE, Sutherland, NSW2120, AUSTRALIA.

The distribution of vacancies in a 2A2B2C superstructure of α -Ni₇S₆ quenched from 500°C, has been determined using the partial Patterson function. The unit cell is monoclinic with $a=6.525(7)\text{Å}$, $b=32.388(24)\text{Å}$, $c=22.730(20)\text{Å}$ and $\gamma=90.05(5)$. Coordination spheres in the structure contain features common to those of the intermetallic sulphides, Ni₃S₂ (tetrahedral) and NiS (square pyramidal). Vacancies are ordered so as to maximize the distance between Ni atoms and to preserve the Ni₃ clusters which also occur in Ni₃S₂ and NiS. In these three structures the average Ni-Ni distance within the trinuclear cluster is 2.5Å, approximately equal to that found in Ni metal. The Ni₃ clusters in 2A2B2C-Ni₇S₆ (Fig. c) are connected via a fourth Ni atom at a distance of 2.59Å.

This compares with the independent clusters found in NiS (Fig. a) and the interconnected clusters found in Ni₃S₂ (Fig. b). This suggests that delocalization of electrons over a Ni-Ni bonded network as well as the minimizing of repulsive forces by forming an ordered arrangement of vacancies, are responsible for the stability of the 2A2B2C-Ni₇S₆ superstructure.



08.3-02 CRYSTAL CHEMISTRY OF RT₅H(D)_x, RT₂H(D)_x AND RT₃H(D)_x HYDRIDES ON THE BASE OF INTERMETALLIC COMPOUNDS WITH THE CaCu₅, PuNi₃, MgCu₂ and MgZn₂ STRUCTURE TYPES. By V.V. Burnasheva, N.V. Fadeeva, K.N. Semenenko, S.P. Solov'ev and V.A. Yartisi, L. Ya. Karpov Physico-Chemical Institute, Moscow, USSR.

The main results of our systematic X-ray and neutron diffraction investigations of hydrides on the base of intermetallic compounds (IMC) can be summarized as follows:

1. Crystal structures of hydride phases on the base of IMC with the CaCu₅, PuNi₃, MgCu₂ and MgZn₂ type structures retain the symmetry of the parent IMC. Absorption of hydrogen by IMC results in increasing their unit-cell volumes by 7-29% or (2.5 - 3.0 Å³) per absorbed H atom.
2. Results of neutron diffraction analysis of LaNi₅D_{6.0}, LaNi₄AlD_{4.1}, HoNi₃D_{1.8}, ZrCr₂D_{3.5} and ZrMoFeD_{2.6} reveal the dominant tendency to the location of the H atoms at tetrahedral sites surrounded by R₂T₂ polyhedra. This is the case in ZrMoFeD_{2.6} and ZrCr₂D_{3.5}. In LaNi₅D_{6.0}, LaNi₄AlD_{4.1} and HoNi₃D_{1.8} the sites are surrounded by RT₃ polyhedra. The easy occupation of R₂T₂ voids is governed by their effective dimensions, the number of surrounding active R atoms and the smallest decrease of interatomic Me-Me distances on deuteration of IMC.
3. In all the studied IMC hydrides, interatomic distances Me-H are as a rule longer than $r_{Me} + (0.2 - 0.3)\text{Å}$ and the H-H distances are longer than (1.8 - 2.0) Å.
4. In most cases, hydrogen atoms are displaced from the centres of the voids. As an example, in LaNi₅D_{6.0} this decreases the coordination number from 4 to 3 and correspondingly changes the coordination polyhedron from tetrahedron La₂Ni₂ to triangle LaNi₂.

08.3-03 NEUTRON DIFFRACTION INVESTIGATION OF LaNiD_{3,7}. V.V. Burnasheva, N.V. Fadeeva, K.N. Semenenko, S.P. Solov'ev and V.A. Yartisi, L. Ya. Karpov Physico-Chemical Institute, Moscow, USSR.

It is known that the hydrogenation of ZrNi and ZrCo intermetallic compounds (IMC) gives rise to ZrNi(Co)H(D)_{3,0} phases in which hydrogen (or deuterium) atoms occupy 4c (0y 1/4; y ~ 0,94) and 8f (0yz; y ~ 0,30, z ~ 0,51) crystallographic sites.

We have shown that the deuteration of LaNi IMC, which have the structure of CrB type (Cmcm; $a=3,81\text{Å}$; $b=10,53\text{Å}$; $c=4,37\text{Å}$), results in the LaNiD_{3,7} compound having the same symmetry with $a=3,98\text{Å}$; $b=11,94\text{Å}$; $c=4,87\text{Å}$. Crystal structure of this compound was proposed to be similar to that of above-mentioned IMC except for deuterium atoms in excess of D/LaNi=3,0 must be located at 4b (0,1/2,0), 8e (x,0,0; x ~ 0,26) or 8g (x,y,1/4; x ~ 0,23; y ~ 0,83) sites.

To verify this proposition the neutron diffraction study of LaNiD_{3,7} has been carried out using polycrystalline samples. Final value of R-factor was found to be 0,066. As a result it was shown that the deuterium atoms occupy expected 4c (D(1)), 8f (D(2)) and at the same time 4b (D(3)) sites.

Coordination polyhedra for D(1) and D(2) atoms are La₃Ni₂ and La₃Ni tetrahedra respectively. For the D(3) atoms the coordination was found to be linear (Ni₂) which is the first discovered example of such a type among all IMC compounds studied.

08.3-04 THE CRYSTAL STRUCTURES OF INTERMETALLIC R₅Rh₃ and R₅Ir₃ (R = Rare earth). By J.M. Moreau, J. Le Roy and D. Paccard, Laboratoire Structure de la Matière, Université de Savoie, Annecy-le-Vieux, 74019, France.

The structure of Ho₅Rh₃ was refined by full-matrix least squares, using the Mn₅Si₃ structure parameters. The refinement was based on a set of $\theta=2\theta$ scan of 170 intensities. The value of $R(\sum|\Delta F|/\sum|Fo|)$ was 0.09 with isotropic temperature factors. The X-ray powder diagrams of the crushed melts for R₅Rh₃ (R = Dy, Ho, Tm, Lu) showed the existence of a phase isotypic with Ho₅Rh₃ (R = Gd, Tb, Er) using Guinier films. Previously the structure of R₅Rh₃ (R = Gd, Tb, Er) isotypic with Mn₅Si₃ has been identified from powder diagrams (Raman and Ghassem, J. Less Comm. Met. (1973) 30, 185).

Two structures were obtained with R₅Ir₃. For R = La, Ce, Pr, Nd, Sm, Gd the Pu₅Rh₃ structure type has been observed (Paccard, Le Roy and Moreau, Acta Cryst. (1979) B35, 1315). For R = Tb, Dy, Ho, Er, Tm, Lu the Pu₅Rh₃ type has been observed only after annealing the crushed melt and was identified as a low temperature form (Le Roy, Moreau, Paccard and Parthé, J. Less Comm. Met. (1980) 76, 131). This structure is a member of a structural series with the formula R_{5n+6}T_{3n+5}. A high temperature form was identified for R = Tb, Dy, Ho, Er, Tm, Lu. The powder diagrams taken with Guinier camera ($\lambda\text{CuK}\alpha$) showed a phase isotypic with Mn₅Si₃. However, Weissenberg films of Lu₅Ir₃ and Er₅Ir₃ single crystals have shown weak and diffuse superstructure reflexions.

Indexing of these reflexions gave space group P622 with a unit cell related to the Mn_5Si_3 cell by $cs = 3c$, $as = a-b$, $bs = a+2b$. Intensities were collected on Lu_5Ir_3 single crystal. Fourier maps have shown disorder along the c axis. Using the fact that hko data did not contain any superstructure reflexions, atoms should be split with different z values as it has been made for Eu_5As_3 (Wang, Calvert, Gabe and Taylor, Acta Cryst. (1978) B34, 2281).

08.3-06 FRAMEWORK DESCRIPTION OF INTERMETALLIC COMPOUNDS LIKE α -Mn, γ -BRASS, Ni_2Ti . By E. Hellner, E. Koch and A. Reinhardt, Institute of Mineralogy, University of Marburg, Lahnberge, D-3550 Marburg/L., Germany.

The cluster concept of Bradley and Jones (J. Inst. Met. <1933> 51, 131) applied e. g. by Pearson et al. (Z. Krist. <1976> 143, 387), and by Chabot et al. (Acta Cryst. <1980> B36, 2202) hinders the recognition of three-dimensional connected basic frameworks which are important for the discussion of relations between structures of intermetallic compounds. $W^*[4t_c]$, the framework of the oxygen atoms

in sodalite $Na_4(AlSiO_4)_3Cl$, is also the basic framework of α -Mn, γ -brass, Tl_7Sb_2 , Ag_8Ca_3 , and with its 8. order of Cu_4Sn_{11} , $Li_{22}Si_5$, Mg_6Pd , Na_6Tl , and $Sm_{11}Cd_{45}$. The large voids in $W^*[4t_c]$ are filled up by different sets of "nested polyhedra" in different structure types to form heterogeneous frameworks. Several other frameworks appear as well in structures of intermetallic as in those of inorganic compounds. Examples are: D[60], the framework of the fluorine atoms in $RbNiCrF_6$, is the basic one of $NiTi_2$ and F_3W_3C . In $Mn_{23}Th_6$ and Ir_4Sc_{11} a heterogeneous framework is built up by F(60), F(8c), and F'(8c). F[12co], and F'[8c] together are the heterogeneous basic framework in $Cr_{23}C_6$, and also the framework of fluorine atoms in KTh_3F_{10} . (4t), (6o), (8c), and (12co) stand for tetrahedron, octahedron, cube and cuboctahedron, respectively.

08.3-05 $Ce_2Ga_{10}Ni$ - A MEMBER OF $R_mX_{4m+2n}X_n$ SERIES OF NONHOMOGENEOUS LINEAR STRUCTURES. By Ya.P. Yarmolyuk, Yu.N. Hryn, O.A. Usov, A.M. Kuzmin, I.V. Rozhdestvenskaya, V.A. Bruskov, E.I. Hladyshevsky, Physical Technical A.F. Ioffe Institute, 194021 Leningrad, USSR.

The crystal structure study of $Ce_2Ga_{10}Ni$ compound is part of investigation of some crystallographic properties of nonhomogeneous linear structure series $R_mX_{4m+2n}X_n$. The structure

is tetragonal (I4/mmm, $a=4.262$, $c=26.391$, $Z=2$).

Atomic coordinates are as follows:

	4Ce	4Ga	8Ga	4Ga	2Ni
x	0.	0.	0.	0.	0.
y	0.	0.5	0.5	0.	0.
z	0.3539	0.25	0.4509	0.1065	0.1968

The coordination numbers of atoms are: Ce-20, Ga-9, Ni-8. The structure is solved by means of crystallographic relationships with known structures and by direct methods (MULTAN - XTLM10) and refined in anisotropic approximation to $R=0.11$ for 408 reflections (SYNTEX P₂, MoK α) using XTLM10 crystallographic program system (O.A. Usov et al, Abstracts of 6th Europ. Cryst. Meeting, Barcelona, 1980, p.150). The $Ce_2Ga_{10}Ni$ structure consists of layers of structure types $BaAl_4(RX_4)$, $CaF_2(X_2X)$ and is a real member of $R_mX_{4m+2n}X_n$ series with $m=4$, $n=2$. The $BaAl_4$ and CaF_2 fragments enter also the structures of $R_{m+n}X_{4m+2n}$ series; $HfCuSi_2$ ($m=n=1$), $SrZnSb_2$, $SrZnBi_2$ ($m=n=2$), but CaF_2 fragments have RX_2 composition.

08.3-07 Gd_3NiSi_2 - A NEW TERNARY SILICIDE WITH BRANCHED Ni-Si CHAINS. By K. Klepp & E. Parthé, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland.

Ternary silicides of the rare earths with the late transition metals are attracting an increasing interest because of their peculiar structural features. In contrast to the great diversity of phases which is generally found in these ternary systems only a few compounds have so far been reported for the pseudobinary sections RSi-RT. Gd_3NiSi_2 , which is part of a study of these sections is orthorhombic, Pnma with $a = 11.398$, $b = 4.155$, $c = 11.310$ Å, $Z = 4$. The crystal structure is characterized by Ni and Si centered trigonal prisms. The arrangement of the Gd and Si atoms is related to that of Hf and P in the structure of Hf_3P_2 . While the P-atoms are isolated in the latter structure, the occupation of a further trigonal prismatic site in Gd_3NiSi_2 gives rise to the formation of isotactic -Si-Ni(Si)- chains with an average Ni-Si distance of 2.45 Å. The relationship with $Ce_7Ni_2Si_5$ and $R_{10}Co_7Ga_3$ will be discussed.

