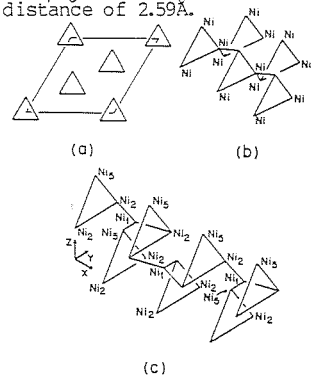
08.3-01 A SUPERSTRUCTURE OF α-Ni_7S_6 AND ITS RELATIONSHIP TO HAZELWOODITE(Ni_3S_2) AND MILLERITE (NiS). By John B. Parise, Dept. Earth & Space Sci., SUNY at Stony Brook NY11794, USA. and Frank H. Moore, AINSE, Sutherland, NSW2120, AUSTRALIA.

The distribution of vacancies in a 2A2B2C superstructure of α-Ni_7S_6 quenched from 500°C, has been determined using the partial Patterson function. The unit cell is monoclinic with a=6.525(7)Å, b=32.388(24)Å, c=22.730(20)Å and γ=90.05(5). Coordination spheres in the structure contain features common to those of the intermetallic sulphides, Ni_3S_2 (tetrahedral) and NiS(square pyramidal). Vacancies are ordered so as to maximize the distance between Ni atoms and to preserve the Ni_3 clusters which also occur in Ni_3S_2 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 Ni_3 clusters in 2A2B2C-Ni_7S_6 (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 Ni_3S_2 (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-Ni_7S_6 superstructure.



08.3-02 CRYSTAL CHEMISTRY OF $RT_5H(D)_x$, $RT_2H(D)_x$ AND $RT_3H(D)_x$ HYDRIDES ON THE BASE OF INTERMETALLIC COMPOUNDS WITH THE $CaCu_5$, $PuNi_3$, $MgCu_2$ and $MgZn_2$ STRUCTURE TYPES. By V.V. Burnasheva, N.V. Fadeeva, K.N. Semenenko, S.P. Solov'ev and V.A. Yartis', 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 $CaCu_5$, $PuNi_3$, $MgCu_2$ and $MgZn_2$ 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 A^3) per absorbed H atom.
2. Results of neutron diffraction analysis of $LaNi_5D_{6.0}$, $LaNi_4AlD_{4.1}$, $HoNi_3D_{1.8}$, $ZrCr_2D_{3.5}$ and $ZrMoFeD_{2.6}$ reveal the dominant tendency to the location of the H atoms at tetrahedral sites surrounded by R_2T_2 polyhedra. This is the case in $ZrMoFeD_{2.6}$ and $ZrCr_2D_{3.5}$. In $LaNi_5D_{6.0}$, $LaNi_4AlD_{4.1}$ and $HoNi_3D_{1.8}$ the sites are surrounded by RT_3 polyhedra. The easy occupation of R_2T_2 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) 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 $LaNi_5D_{6.0}$ this decreases the coordination number from 4 to 3 and correspondingly changes the coordination polyhedron from tetrahedron La_2Ni_2 to triangle $LaNi_2$.

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. Yartis'. 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 Å; b=10,53 Å; c=4,37 Å), results in the $LaNiD_{3,7}$ compound having the same symmetry with a=3,98 Å; b=11,94 Å; c=4,87Å. Crystal structure of this compound was proposed to be similar to that of above-mentioned IMC exept 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 forD(1) and D(2) atoms are La_3Ni_2 and La_3Ni tetrahedra respectively. For the D(3) atoms the coordination was found to be linear (Ni_2) which is the first discovered example of such a type among all IMC compounds studied.

08.3-04 THE CRYSTAL STRUCTURES OF INTERMETALLIC R_5Rh_3 and R_5Ir_3 (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 Ho_5Rh_3 was refined by full-matrix least squares, using the Mn_5Si_3 structure parameters. The refinement was based on a set of θ-2θ scan of 170 intensities. The value of R ($\Sigma|\Delta F|/\Sigma|Fo|$) was 0.09 with isotropic temperature factors. The X-ray powder diagrams of the crushed melts for R_5Rh_3 (R = Dy, Ho, Tm, Lu) showed the existence of a phase isotypic with Ho_5Rh_3 (R = Gd, Tb, Er) using Guinier films. Previously the structure of R_5Rh_3 (R = Gd, Tb, Er) isotypic with Mn_5Si_3 has been identified from powder diagrams (Raman and Ghassem, J. Less Comm. Met. (1973) 30, 185).

Two structures were obtained with R_5Ir_3. For R = La, Ce, Pr, Nd, Sm, Gd the Pu_5Rh_3 structure type has been observed (Paccard, Le Roy and Moreau, Acta Cryst. (1979) B35, 1315). For R = Tb, Dy, Ho, Er, Tm, Lu the Pu_5Rh_3 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 (λCuKα) showed a phase isotypic with Mn_5Si_3. However, Weissenberg films of Lu_5Ir_3 and Er_5Ir_3 single crystals have shown weak and diffuse superstructure reflexions.