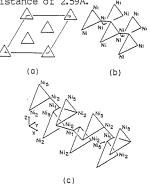**08.3-01   A SUPERSTRUCTURE OF α-Ni$_7$S$_6$ AND ITS RELATIONSHIP TO HAZELWOODITE(NI$_3$S$_2$) AND MILLERITE (NIS).** By <u>John B. Parise</u>,Dept. Earth & Space Sci., SUNY at Stony Brook NY11794, USA. and Frank H. Moore, AINSE, Sutherland, NSW2120, AUSTRALIA.

The distribution of vacancies in a 2A2B2C superstructure of α-Ni$_7$S$_6$ 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$_3$S$_2$ (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$_3$S$_2$ 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$_7$S$_6$ (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$_3$S$_2$ (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$_7$S$_6$ superstructure.

(a)   (b)

(c)

08.3-02   CRYSTAL CHEMISTRY OF RT$_5$H(D)$_x$, RT$_2$H(D)$_x$ AND RT$_3$H(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 <u>V.A. Yartis'</u>, 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$_5$D$_{6.0}$, LaNi$_4$AlD$_{4.1}$, HoNi$_3$D$_{1.8}$, ZrCr$_2$D$_{3.5}$ and ZrMoFeD$_{2.6}$ reveal the dominant tendency to the location of the H atoms at tetrahedral sites surrounded by R$_2$T$_2$ polyhedra. This is the case in ZrMoFeD$_{2.6}$ and ZrCr$_2$D$_{3.5}$. In LaNi$_5$D$_{6.0}$, LaNi$_4$AlD$_{4.1}$ and HoNi$_3$D$_{1.8}$ the sites are surrounded by RT$_3$ polyhedra. The easy occupation of R$_2$T$_2$ 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$_5$D$_{6.0}$ this decreases the coordination number from 4 to 3 and correspondingly changes the coordination polyhedron from tetrahedron La$_2$Ni$_2$ to triangle LaNi$_2$.

08.3-03   NEUTRON DIFFRACTION INVESTIGATION OF LaNiD$_{3,7}$. V.V.Burnasheva, N.V.Fadeeva, K.N.Semenenko, <u>S.P.Solov'ev</u> 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 for D(1) and D(2) atoms are La$_3$Ni$_2$ and La$_3$Ni 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$_5$Rh$_3$ and R$_5$Ir$_3$ (R = Rare earth). By <u>J.M. Moreau</u>, J. Le Roy and D. Paccard, Laboratoire Structure de la Matière, Université de Savoie, Annecy-le-Vieux, 74019, France.

The structure of Ho$_5$Rh$_3$ was refined by full-matrix least squares, using the Mn$_5$Si$_3$ 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$_5$Rh$_3$ (R = Dy, Ho, Tm, Lu) showed the existence of a phase isotypic with Ho$_5$Rh$_3$ (R = Gd, Tb, Er) using Guinier films. Previously the structure of R$_5$Rh$_3$ (R = Gd, Tb, Er) isotypic with Mn$_5$Si$_3$ has been identified from powder diagrams (Raman and Ghassem, J. Less Comm. Met. (1973) <u>30</u>, 185).

Two structures were obtained with R$_5$Ir$_3$. For R = La, Ce, Pr, Nd, Sm, Gd the Pu$_5$Rh$_3$ structure type has been observed (Paccard, Le Roy and Moreau, Acta Cryst. (1979) <u>B35</u>, 1315). For R = Tb, Dy, Ho, Er, Tm, Lu the Pu$_5$Rh$_3$ 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) <u>76</u>, 131). This structure is a member of a structural series with the formula R$_{5n+6}$T$_{5n+5}$. 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$_5$Si$_3$. However, Weissenberg films of Lu$_5$Ir$_3$ and Er$_5$Ir$_3$ single crystals have shown weak and diffuse superstructure reflexions.