s7.m26.p4   **Hydrogen-induced structure transition in LaNi₃B.** Y. Filinchuk and K. Yvon, *University of Geneva, Switzerland. E-mail: Yaroslav.Filinchuk@cryst.unige.ch*

Keywords: Metal hydride; Structure transition; Bonding

A new $LaNi_3B$ phase of novel structure appears after annealing at 800°C of an arc-melted sample. Thermal gravimetrical analysis of the hydrogen absorption revealed that a solid-solution hydride $LaNi_3BH_{2.5-3}$ forms at near ambient conditions. We have carried out single-crystal X-ray diffraction studies (Stoe IPDS II diffractometer) of the alloy and hydride structures, using the same single crystal, measured before and after hydrogen treatment. The initial orthorhombic structure undergoes a transition that can be described by a group-subgroup sequence: $Imma \rightarrow Pmma \rightarrow Cmcm$. Apart from a unit cell doubling along *a* and *b* the structure expands in the *a-b* plane (by up to ~8%) and contracts along *c* (by ~3%). A pronounced anisotropy of the thermal displacements is observed for one of the two Ni atoms in the alloy structure. The elongated shape of the thermal displacement ellipsoid preludes a site-symmetry degeneration which is actually observed in the structure of the hydride. To be sure that weak superstructure peaks have not been overlooked, we have studied the alloy and its hydride with high-resolution synchrotron powder diffraction (BM1 beamline at ESRF). This confirms our observations of the structure transition, resulting in a single-crystal-like quality of the structural parameters derived by Rietveld refinement. It is highly satisfactory that the anisotropic thermal displacement ellipsoids in the alloy structure display the same features as those from the single-crystal X-ray diffraction.

To understand the role of the hydrogen in the structure transition, we have studied deuterided samples on the high-resolution neutron powder diffractometer HRPT at SINQ, PSI (Switzerland). Four deuterium positions, which tend to be fully occupied in stoichiometric $LaNi_3BD_3$, were located and shown to have the following environments: tetrahedral La_2Ni_2 for D1 and D2, trigonal-prismatic La_3Ni_3 for D3 and trigonal-bipyramidal La_2Ni_3 for D4. From a bonding point of view a more satisfactory description is in terms of a quasi two-dimensional [NiD] framework, possibly made up by 2-centre 2-electron and 3-centre 2-electron bonds as shown below.
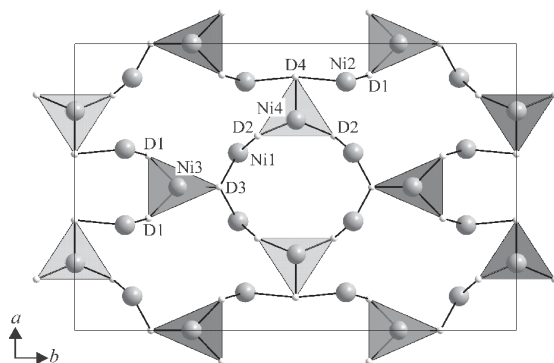
Such a framework would be unique in metal hydride structures. The Ni-D distances are in the range 1.61–1.97 Å, while the La-D contacts are 2.4-2.9 Å. The La-B planes do not accommodate hydrogen, the B-D and D-D interactions appearing to be repulsive: shortest B–D and D-D contacts are 2.52(2) and 2.33(1) Å respectively.

s7.m26.p5   **The perils of large 'small' molecules - successful refinement of metallosupramolecular grid-like assemblies.** Peter Horton,[a] Michael Hursthouse[a] and Craig Matthews[b], [a]*University of Southampton, UK, and* [b]*Nottingham Trent University, UK. E-mail: pnh@soton.ac.uk*

Keywords: Supramolecular; Large cells; Difficult structures

With recent advances in diffractometers and as computers grow ever more powerful, it is possible to collect and solve several data sets every day. Thus the technique is now being used as alternative form of characterisation. This also has meant that the size of crystals required to obtain data has decreased, and the size of the molecules involved has increased, which can lead to a severe shortfall in data to parameter ratio. A recent area which has gained from these advancements is that of molecular grid and tape structures, although the successful solution and refinement may often be problematic due to the generally large asymmetric units. As chemists design and prepare these larger structures, the composition is generally known, but the geometry is still vital to determine. Most programs for full structure determinations were designed for small molecules with up to 100 non-hydrogen atoms. Although they can cope with larger numbers, quite a few crash once more than 500 atoms become involved. This does cause problems not only in attempts to solve structures, but also (especially for the chemist) when trying to visualise them later. Through our work with the UK National Service it has been necessary to address some of the problems described. For example the application of focussing mirrors to a rotating anode generator significantly increases the number of observed reflections for small crystals and for those of the above type of compound which are often weakly diffracting. This increase in quantity of experimental data coupled with the large number of variables provides a real test for the software. Generally, of the initial solution refinement programs, it is often only Shelxs-97 which produces a reasonable solution, although the assignment of the atoms is tedious. Most of the 'brute-force' programs give a nonsensical solution, if at all. For refinements Shelxh-97 does work, although sometimes the source code needs to be tweaked to cope with the largest structures (4000 parameters might be ample for most systems but 8000 is often a better limit). This poster will present successful structure determination of a number of these cases and the pitfalls and method of treatment will be outlined.