

(8f) $x = 0.211$, $y = 0.299$, $z = 0.304$; deuterium(2) in (8f) $x = 0.136$, $y = 0.316$, $z = 0.881$; deuterium(3) in (8f) $x = 0.010$, $y = 0.287$, $z = 0.054$; deuterium(4) in (8f) $x = 0.131$, $y = 0.995$, $z = 0.081$; average Ni–D bond length = 1.54 Å, average D–Ni–D bond angle = 109.4°. These results contrast sharply with previously reported deuterium atom configurations in this compound (square planar [2], disordered [3]). For a detailed account of this work see ref. 4 (X-ray results) and ref. 5 (neutron results).

- 1 J. M. Cowley and A. Y. Au, *Acta Cryst.*, A34 (1978) 738.
- 2 D Noréus and P. E. Werner, *J. Less-Common Met.*, 97 (1984) 215.
- 3 J. L. Soubeyrou, D. Fruchard, A. Mikou, M. Pezat and B. Darriet, *Mat. Res. Bull.*, 19 (1984) 1119.
- 4 P. Zolliker, K. Yvon and Ch. Baerlocher, *J. Less-Common Met.*, 115 (1986) 68.
- 5 P. Zolliker, K. Yvon, J. D. Jorgensen and F. Rotella, *Inorg. Chem.*, to be published.

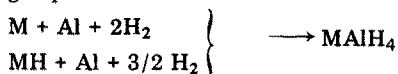
Hydridoaluminates of alkaline metals*

J. P. BASTIDE, J. C. BUREAU, P. CLAUDY, J. M. LETOFFE and J. EL HAJRI

Laboratoire de Thermochimie Minérale, Institut National des Sciences Appliquées de Lyon, Bâtiment 401, 20 avenue A. Einstein 69621 Villeurbanne Cedex (France)

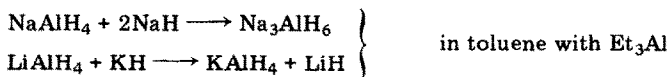
Compounds with general formula $MAIH_4$, M_3AlH_6 , $M_2M'AlH_6$ ($M, M' \equiv Li, Na, K$) have been studied for several years in our laboratory, especially from a fundamental point of view. We present here an overall picture of our research work concerning preparation, thermodynamic and structural properties of these complex hydrides.

Preparation. Hydridoaluminates can be obtained by different methods: under hydrogen pressure:



These reactions are generally performed in a dispersing medium (toluene) using triethylaluminum as an "activator" ($T < 150^\circ C$, $P_{H_2} < 150$ bar). Higher yields are obtained with the second process. In this case, the simple hydride MH is prepared under mild conditions by direct synthesis in presence of a catalyst such as phenanthrene ($T < 100^\circ C$, $P_{H_2} < 15$ bar).

In organic liquid media (preparative chemistry in glove boxes):
non-solvating medium = addition or exchange



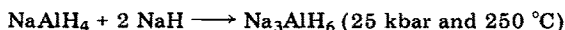
($T < 110^\circ C$ at atm. pressure)

solvating media = exchange



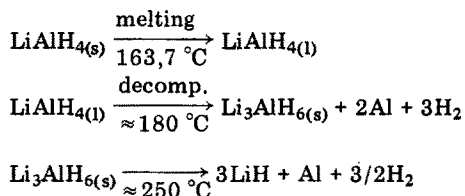
*Abstract of a paper presented at the International Symposium on the Properties and Applications of Metal Hydrides V, Maubuisson, France, May 25 - 30, 1986.

Solid state reactions (piezochemistry in a belt-type apparatus):



Purification. Unsolvated microcrystalline powder of pure LiAlH_4 (or LiAlD_4) is obtained by precipitation from diethylether solution using toluene.

Thermal behaviour and thermodynamics. Thermodynamic properties were investigated by calorimetric measurements. We also performed thermogravimetric analysis and differential scanning calorimetry studies with special attention to phase transformations. LiAlH_4 exhibits the following thermal behaviour:



At the melting point, $\Delta H = 16.6 \pm 0.5 \text{ kJ mol}^{-1}$ and $\Delta S = 38.0 \text{ J K}^{-1} \text{ mol}^{-1}$. For Na_3AlH_6 a polymorphic transition is observed (see below) at 525 K just before melting.

Structural aspects. There is no evidence that the tetrahydridoaluminates belong to the same structural family. LiAlH_4 possesses a monoclinic structure in which the coordination number (CN) of lithium and aluminium is respectively 5 and 4. Study of the P - T phase diagram shows the formation of a dense form in which the CN of aluminium is 6. NaAlH_4 crystallizes with a scheelite-type structure (tetragonal CaWO_4) with CN for sodium of 8 and for aluminium of 4. The ionic environment of Al^{3+} has been studied by Raman spectroscopy. Work on KAlH_4 is now in progress; this compound probably possesses a barite-type structure (orthorhombic BaSO_4) with CN for potassium of 12 and CN for aluminium of 4.

Except for Li_3AlH_6 , the hexahydridoaluminates crystallize with a cryolite (Na_3AlF_6) or elpasolite (K_2NaAlF_6) structure, generally pseudocubic. Under high temperature and/or high pressure conditions they may exhibit polymorphic transitions to more symmetrical structures. Neutron diffraction studies are in progress (for the deuterated compound) to try to elucidate the structure of Li_3AlH_6 which seems to be more complex.

Studies of the Mg_2Ni - Mg_2NiH_4 system*

D. NOREUS

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm (Sweden)

A quantum chemical description of the transition metal-hydrogen complexes in Mg_2NiH_4 and Mg_2FeH_6 has been made aiming at a fundamental understanding of the bonding in these systems. The low temperature phase of Mg_2NiH_4 has been studied by electron microscopy. In this investigation the microtwinning, responsible for the earlier confusion in structural work was clearly seen. Finally, the $\alpha\text{-Mg}_2\text{NiH}_{0.3} + \text{H}_2 \rightarrow \beta\text{-Mg}_2\text{NiH}_4$ reaction was studied using a volumetric method.

*Abstract of a paper presented at the International Symposium on the Properties and Applications of Metal Hydrides V, Maubuisson, France, May 25 - 30, 1986.