ESRF	**Experiment title:** EQUATION OF STATE AND PHASE-TRANSITION BEHAVIOUR IN METAL CARBIDES, HYDRIDES AND CLOSE-PACKED STRUCTURES IN THE 100 GPa PRESSURE RANGE	**Experiment number:** HC 104
Beamline: ID9/BL3	**Date of Experiment:** from: 12/7/95 to: 17/7/95	**Date of Report:** 9 October, 1995
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Report:

Summary: Feasibility of very high-pressure powder-diffraction experiments (100-200 GPa) using straightforward white beam energy-dispersive diffraction (EDX) in diamond-anvil cell (DAC). Equation-of-state (EOS) studies of metal carbides and hydrides to moderate pressures (50 GPa). DAC sample stability limited success on very high-pressure runs (all entailed confined gas/solid and will require further attempts on stable loading, together with new anvil geometries). Pure aluminium was compressed to ≈70 GPa with Pt as pressure standard. At 120 GPa the diffracted intensity from Al was too weak for acceptable exposure time: At small beam size (of order 10pm edge) thinned samples of low-atomic number elements may require focused radiation for powder studies. New EOS data were obtained on AlH_3 and AlD_3 in He media (see below) and indicating a strong isotope effect in the volume under pressure.

$A1H_3$ and AID_3: The metal hydrides under high pressures are of interest in relation to their connection with the problem of metallisation of pure hydrogen (see for example [1 ,2]). At ambient pressure stoichlometric aluminium hydride AlH_3 has dielectric properties and forms a number of metastable structure modifications, the most stable of which (called α-AlH_3) has a rhombohedral unit cell (S.G. $R\bar{3}c$) with a=4.4493 A and c=ll.8037 Å in hexagonal axes [3].

Aluminium hybride has been studied by x-ray diffraction at pressures up to 35 GPa [5]. On the basis of the equation of state obtained it was predicted that at 46 GPa the effective volume of each hydrogen atom should become equal to that characteristic of the transitional metal hydrides (V_H=2.8-2.9 Å^3/H atom) which have metallic properties. Visual observations have shown that in exactly the same pressure range (between 43 and 47 GPa) the transparency of AIH_3 sample disappears, that could be considered an indication of a dielectric-t-metal transition.

The experiment was carried out on powder sample under near hydrostatic conditions using diamond anvil cell with the helium as a pressure transmitting medium and EDX techniques.

From 10 to 18 diffraction peaks at different pressures belonging to the Al sublattice were clearly observed. No structure changes in the Al subsystem was observed at pressures up to 54 GPa. Hence, data available now provide insufficient evidence to associate the loss of transparency of the sample at 45 GPa with the transition to the metallic state caused by a structural transformation.

Fig.1 shows pressure-volume relations for AlH_3 and AlD_3 as well as p-v curve for Al [6] to which the value 3 V_H has been added. Within errors our data coincide with the data for AlH_3 obtained earlier in the range 0-35 GPa [5] but at higher pressures aluminium hydride proved to be less compressible then it was predicted. There is some scatter in the data, but new estimates show that the pressure at which one can expect the effective hydrogen volume to become equal to the value characteristic of the transitional metal hydrides is around 0.9-1 Mbar.

Previous studies [4] have shown the specific volume difference between AlH_3 and AlD_3 increases with the pressure and saturates near 4 GPa. Such behaviour of ΔV was related to the transformation of the deuterium sublattice to the close-packed structure which takes place at around 5 GPa. The isotope effect was observed in our experiment is similar to that found by neutron diffraction, that is the volume difference ΔV between AlH_3 and AlD_3 increases with pressure (Fig.1), but no sign of saturation is found up to 16 GPa.

References

[1] B. Baranowski,et *al.* in ***Molecular Systems under High Pressures,*** R. Pucci and G. Piccitto, Eds. (Elsevier, Amsterdam, 1991), pp. 139-156; [2] N. Ashcroft, ***Phys. Wor/d,*** July 1995, pp.43-47; K. Ghandehari et al., Phys. ***Rev. Lett., 74, 2264-2267 (1995) [3]*** J. W. Turley, H. W. Rinn.,lnorg. ***Chem. 8, 18-22 (1969) [4]*** I. N. Goncharenko et al., ***Physics B,*** 174, 117-120 (1991) [5] B. Baranowksi, H. D. Hochheimer, K. Stösner, and W. Hönle, ***J. Less-Common Met. 113, 341-347 (1985). [6]*** R. Greene et ***al., Phys. Rev. Lett. 73, 2075-2078 (1994)***

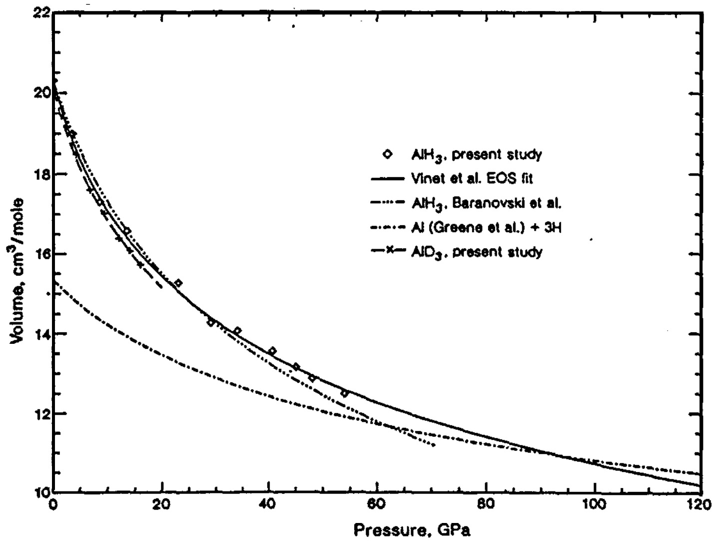

Fig.1. Molar volumes of AlH_3 and AlD_3 and sum of molar volumes of Al (recent data [6]) plus threefold effective volume of hydrogen (3×1.8 cm^3/mole H) in metallic hydrides as function of pressure. The crossover gives a point (near 94 GPa) at which the transition to the metallic state could be expected (l].

Other: Pure cementite (Fe_3C) is not stable under most synthesis conditions and a preliminary study was carried out on chilled iron-carbon alloy containing Fe-Fe_3C intergrowths. Several of the nine diffraction lines expected between 1.9- 2.4Å were observed at low pressure. Isolated Cohenite has now been obtained from meteoritic samples, but higher resolution monochromatic studies are likely to be required for this material.