YCu$_3$Al$_2$, an example of an AB_5 structure type

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Yttrium tricopper dialuminium, YCu$_3$Al$_2$, is isostructural with hexagonal CaCu$_5$, in which each Cu atom at the $3g(\frac{1}{2},0,\frac{1}{2})$ position in space group $P6/mmm$ (No. 191) is partially replaced by an Al atom. The hydrogen-uptake properties are usually enhanced in other AB_5 structures by aluminium substitution. YCu$_5$ does not show any hydrogen absorption, and the goal of the present work is to investigate whether aluminium substitution could expand the metal-atom lattice enough to provide better interstitial positions for hydrogen storage. However, no enthalpy change was observed up to 773 K under 3 MPa static H$_2$ pressure by differential thermal analysis (DTA) for the title compound. The compound does not show any significant hydrogen absorption/desorption in the pressure-composition isotherms (P–C–T diagrams) in the temperature range 298–673 K under 3.3 MPa H$_2$ pressure.

Comment

Previous investigations have shown that the light rare-earth elements, and incidentally also some heavy rare-earth elements, form hexagonal compounds of the AB_5 system (CaCu$_5$ type), as reported in the literature (Dwight, 1961; Wernick & Geller, 1959; Haszko, 1960). The stoichiometric composition of these hexagonal phases does not seem well established, as some rare-earth elements have the CaCu$_5$ structure in compounds of composition RCu$_4$ as well as in compounds of composition RCu$_5$ (Gschneidner, 1961).

Studies of the intermetallic AB_5 system (CaCu$_5$ type) has shown that several properties, *e.g.* the hydrogen-absorption properties of the phases, can be easily varied over a wide range by the partial replacement of A or B atoms by other metals (Lanker *et al.*, 1982; Van Vucht *et al.*, 1970). Relatively large differences in the metallic radii of the A and B metals favors the stability of the AB_5 phases, making them so-called 'line compounds' in their binary-phase diagrams. This stability may be essential in order to obtain a homogeneous composition of the intermetallic compound.

Pure RCu$_5$ is not stable and crystallizes in the BaAl$_4$-type structure. It is noted that aluminium substitution stabilizes the hexagonal CaCu$_5$-type structure for RCu$_4$Al compounds (R = La–Sm; Takeshita *et al.*, 1978).

The investigation of the present compound is part of a larger project aimed at finding alternative intermetallic AB_5 compounds for hydrogen absorption, based on both elements lighter than lanthanides (for example, R = Y) and cheap elements (for example, substitution of a B atom in RB_5-type structures by Cu and Al).

YCu$_5$ and YNi$_5$ did not show any hydrogen uptake and it was therefore of interest to study the influence of metal-atom replacement in YCu$_5$ (Wernick & Geller, 1959; Buschow & Goot, 1971) by aluminium, as the atomic radius of Al (1.432 Å) is larger than that of Cu (1.278 Å; Teatum *et al.*, 1960), thus expanding the metal-atom lattice and possibly also providing interstitial positions for hydrogen.

The YCu$_5$ structure (Wernick & Geller, 1959) is built from alternate layers of the CaCu$_5$ type, *viz.* each Y atom is surrounded by six Cu atoms in one plane (at 2.88 Å) and by two further sets of six Cu atoms in adjacent planes (at 3.23 Å).
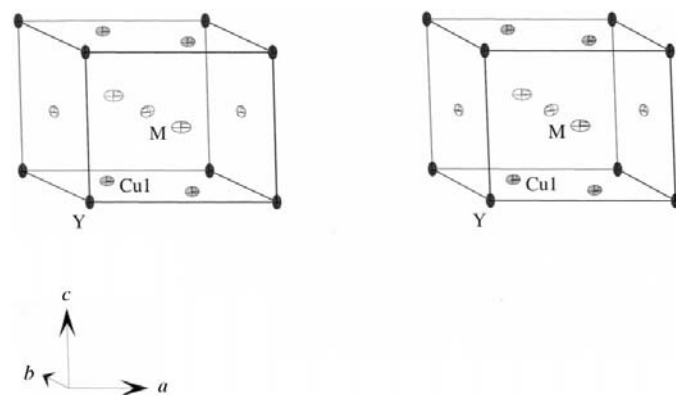

Figure 1
Stereoview of the unit-cell contents with ellipsoids plotted at the 90% probability level. Position M is a mixed position of Cu2 (31%) and Al2 (69%).

The same planes exist in YCu$_3$Al$_2$, but at slightly different distances (Fig. 1). The average nearest-neighbour Cu1—Cu2 distances are increased compared with those of YCu$_5$ (2.49 and 2.51 Å; Wernick & Geller, 1959). The Cu—Cu distances in the present compound are close to those of a normal close-packed Cu atom with coordination number (CN) 12 (average nearest-neighbor distance = 2.56 Å; Wernick & Geller, 1959).

This compound does not show any hydrogen absorption/ desorption in the pressure-composition isotherms (P–C–T diagrams) in the temperature range 298–673 K under 3.3 MPa H$_2$ pressure using an automated Sieverts-type apparatus. No enthalpy change was observed up to 773 K under 3 MPa static H$_2$ pressure by differential thermal analysis (DTA) for the present compound. No disproportion of the alloy was observed by X-ray diffraction after DTA and P–C–T.

inorganic compounds

Experimental

The purity of the starting materials was 99.99% for Cu and Al, and 99.9% for Y. A pressed tablet of a mixture of suitable weight% ratio of finely powdered starting materials was sintered at 773 K under 0.6 MPa argon-gas pressure for 1 h, followed by higher temperature annealing at 1023 K for 1 h, with subsequent rapid cooling to room temperature. The sample was crushed and reheated directly to 1023 K under the same conditions as above, followed by cooling at 20 K min^{-1} to 673 K and then rapid cooling to room temperature. Upon optical microscopic examination, the alloy exhibited regular metallic hexagons. Some of the crystallites were isolated and crushed to powder form for identification by Guinier–Hägg X-ray powder diffraction. The atomic composition was verified by EDX (energy dispersive X-ray) analysis with a Jeol 820 scanning electron microscope equipped with a LINK elemental analysis system.

Crystal data

YCu$_3$Al$_2$	Mo $K\alpha$ radiation
$M_r = 332.03$	Cell parameters from 50
Hexagonal, $P6/mmm$	reflections
$a = 5.172 (3)$ Å	$\theta = 18$–$22°$
$c = 4.141 (2)$ Å	$\mu = 31.38$ mm^{-1}
$V = 95.93 (9)$ Å^3	$T = 293 (2)$ K
$Z = 1$	Metallic prism, grey
$D_x = 5.747$ Mg m^{-3}	$0.29 \times 0.07 \times 0.06$ mm

Data collection

Stoe AED-2 diffractometer	$R_{int} = 0.099$
θ–2θ scans	$\theta_{max} = 44.9°$
Absorption correction: multi-scan	$h = -10 \rightarrow 10$
($XABS$2; Parkin et al., 1995)	$k = -10 \rightarrow 10$
$T_{min} = 0.062$, $T_{max} = 0.152$	$l = -8 \rightarrow 7$
2818 measured reflections	4 standard reflections
196 independent reflections	frequency: 120 min
182 reflections with $I > 2\sigma(I)$	intensity decay: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.021$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.38$	$\Delta\rho_{max} = 1.86$ e Å^{-3}
196 reflections	$\Delta\rho_{min} = -2.21$ e Å^{-3}
10 parameters	Extinction correction: $SHELXL$97
	Extinction coefficient: 0.167 (16)

The highest peak in the residual density map, 1.86 e Å^{-3} at (0, 0, 0.1241), is 0.51 Å from the Y-atom position. The absorption correction was carried out with $XABS$2 (Parkin et al., 1995) using reflection data from the whole sphere.

Data collection: AED-2 (Stoe & Cie, 1988); cell refinement: DIF4 (Stoe & Cie, 1988); data reduction: $REDU$4 (Stoe & Cie, 1988); program(s) used to solve structure: $SHELXS$97 (Sheldrick, 1990); program(s) used to refine structure: $SHELXL$97 (Sheldrick, 1997); molecular graphics: $DIAMOND$ (Bergerhoff, 1996).

Table 1
Selected bond lengths (Å).

Y—Cu1	2.9861 (17)	Cu1—Cu2^i	2.5527 (10)
Y—Cu2	3.3128 (13)	Cu2—Cu2^{ii}	2.5860 (15)

Symmetry codes: (i) $-y, x - y, z$; (ii) $1 - y, x - y, z$.

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