average N—H—Cl angle is 111°. It is interesting to note that most of the hydrogen atoms are involved in a strong hydrogen bond. The average N···Cl distance amounts to 3·350 (6) Å, which is in good agreement with that in NH_4Cl (3·27 Å for the high-temperature form and 3·34 Å for the low-temperature form). In view of the above results, the packing of the double chains is determined by the ammonium ions. Fig. 2 shows the unit cell.

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Neutron Powder Diffraction Study of Titanium Copper Deuteride $TiCuD_{0\cdot90}$

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Abstract. $TiCuD_{0\cdot90}$, tetragonal, $P4/nmm$, a = 3·020 (1), c = 6·837 (3) Å (parameters determined by X-ray powder diffraction), Z = 2. The structure has been refined by the method of total-profile analysis of a neutron diffraction powder pattern. The composition obtained from the refinement corresponds to the formula $TiCuD_{0\cdot90(1)}$ ($TiCuD_{0\cdot96}$ by thermal analysis). The D atoms are located at the centers of distorted tetrahedra of Ti atoms, with a Ti—D distance of 1·927 (4) Å.

Introduction. The title compound was prepared by absorption of D_2 in γ-TiCu. The sample of γ-TiCu was prepared by arc melting (Maeland, 1978) and contained small quantities of the δ phase (Karlsson, 1951). Initially, γ-TiCu was exposed to D_2 at a pressure of 177·5 p.s.i. at room temperature (23 °C), and then heated to 200 °C over a period of 1·5 h, without apparent absorption of D_2. After 1 h at 200°C, however, absorption started and the D_2 pressure decreased 124 p.s.i. in 0·5 h. The sample was cooled to room temperature over a period of 20 h and then reheated to 200 °C to homogenize it. After 2 h at 200 °C it was cooled again to room temperature over a period of 24 h. The D_2 pressure after this treatment was 37 p.s.i. From the pressure change, the volume of the system and the sample weight, a composition corresponding to the formula $TiCuD_{0\cdot99}$ was calculated. Thermal analysis of the powdered sample gave $TiCuD_{0\cdot96}$.

X-ray powder patterns were consistent with the symmetry of space group $P4/nmm$. The lattice parameters determined from these patterns by least-squares analysis are in agreement with the results obtained for $TiCuH_{0\cdot97(3)}$ (Maeland, 1978).

Table 1. *Experimental conditions used to measure the powder pattern of* $TiCuD_{0\cdot9}$

Monochromatic beam: reflection 220 of a Cu monochromator
Mean neutron wavelength: $\lambda = 0\cdot925$ (1) Å
Horizontal divergences
  (*a*) in pile collimator: 20′ arc
  (*b*) monochromatic beam collimator: 23′ arc
  (*c*) diffracted beam collimator: 24′ arc
Monochromator mosaic spread: ~20′ arc
Sample container: vanadium can of ~1 cm diameter
$2\theta_{\text{initial}} = 5\cdot0°$, $2\theta_{\text{final}} = 90\cdot0°$, step = 0·1°
Number of independent Bragg reflections: 102
Number of observations above background: 601

Neutron diffraction measurements were made at room temperature on a powder diffractometer at the National Bureau of Standards Reactor, using the experimental conditions given in Table 1. An inspection of the powder pattern showed the presence of weak lines which could not be indexed on the basis of the tetragonal unit cell determined by X-rays. The presence of these extra lines, noted also in the X-ray patterns, is not surprising, as the original sample of γ-TiCu contained small quantities of the δ phase. The regions of the pattern clearly affected by the impurities were therefore excluded from all subsequent calculations.

The refinement of the structure was based on space group *P*4/*nmm* and was carried out with the method of total-profile analysis (Rietveld, 1969). The neutron scattering amplitudes were $b(\mathrm{Ti}) = -0{\cdot}34$, $b(\mathrm{Cu}) = 0{\cdot}76$ and $b(\mathrm{D}) = 0{\cdot}667 \times 10^{-12}$ cm (Bacon, 1972). The contribution to the profile from the background was estimated in the regions of the powder pattern free from diffraction lines and it was extrapolated from these regions to the scattering angles where overlapping was severe. The initial values of the lattice parameters were those determined by X-ray diffraction and the profile parameters *U*, *V*, *W* were calculated theoretically (Caglioti, Paoletti & Ricci, 1958). The Ti and Cu atoms were placed in the special positions 2(*c*) with values of the *z* coordinates of 0·65 and 0·10 respectively, *i.e.* the same values determined for these atoms in the structure of γ-TiCu (Karlsson, 1951). The D atoms can be located in positions 2(*c*), 2(*b*), and 2(*a*). Spatial considerations suggest position 2(*b*), and, in fact, refinements carried out with the D atoms located at 2(*c*) and 2(*a*) gave *R* factors of the order of 50% or more and meaningless structural parameters. The final refinement was therefore done with the D atoms located in the special positions 2(*b*). Individual temperature factors were not refined, in view of the uncertainty in the determination of background, especially at high scattering angles. A total of 11 profile, lattice and structural parameters were allowed to refine simultaneously until all shifts were less than 0·3 times the standard deviation σ. The results of the refinement are given in Table 2 and the observed and calculated profiles are shown in Fig. 1.

In order to check for possible small shifts of the D atoms from the locations imposed by the symmetry of space group *P*4/*nmm*, refinements were also carried out in space groups *Pmmn* [Cu and Ti atoms in positions 2(*a*) and D atoms in 2(*b*)] and *Pmm*2 [Cu and Ti atoms in positions 1(*c*) and 1(*b*) and D atoms in positions 1(*d*) and 1(*a*)]. These calculations did not improve the *R* factors and, perhaps more importantly, did not reveal significant variations of the *z* coordinates of the D atoms from $z = 0{\cdot}5$.

Discussion. Recently, hydrides of intermetallic compounds have received considerable attention as poten-

Table 2. *Results of the total-profile refinement of the structure of* $TiCuD_{0.9}$

Numbers in parentheses are standard deviations in the last decimal figure.

$U = 8{\cdot}6\ (6)$, $V = -3{\cdot}7\ (4)$, $W = 0{\cdot}79\ (6)\ \mathrm{deg}^2$*

$a = 3{\cdot}033\ (1)$, $c = 6{\cdot}847\ (2)$ Å†

Atomic coordinates

	x	*y*	*z*
Ti	$\frac{1}{4}$	$\frac{1}{4}$	0·6751 (9)
Cu	$\frac{1}{4}$	$\frac{1}{4}$	0·0933 (5)
D	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$

Overall temperature factor = 0·65 (2) Å^2

Occupancy factor for deuterium = 0·90 (1)

$R = 100[\sum|I(\mathrm{obs.}) - I(\mathrm{calc.})|/\sum I(\mathrm{obs.})] = 8{\cdot}78$

$R_p = 100[\sum|y(\mathrm{obs.}) - y(\mathrm{calc.})|/\sum y(\mathrm{obs.})] = 12{\cdot}75$

$R_w = 100\,\{\sum w[y(\mathrm{obs.}) - y(\mathrm{calc.})]^2/\sum w[y(\mathrm{obs.})]^2\}^{1/2} = 14{\cdot}05$

$R_E = 100\,\{(N - P + C)/\sum[y(\mathrm{obs.})]^2\}^{1/2} = 7{\cdot}11$

In the above formulas *N* is the number of statistically independent observations, *P* the number of parameters refined, *C* the number of constraints, *I* the integrated intensities, *y*(obs.) and *y*(calc.) the profile intensities and *w* the weights associated with the data points *y*(obs.).

* The theoretical values of the full width at half maximum parameters are $U = 0{\cdot}72$, $V = -0{\cdot}47$, $W = 0{\cdot}24\ \mathrm{deg}^2$. These parameters have been calculated with the expressions given by Caglioti, Paoletti & Ricci (1958).

† Cell-dimension errors do not include the error in the neutron wavelength. The X-ray cell parameters ($a = 3{\cdot}020$, $c = 6{\cdot}837$ Å) were used for calculating the interatomic distances.

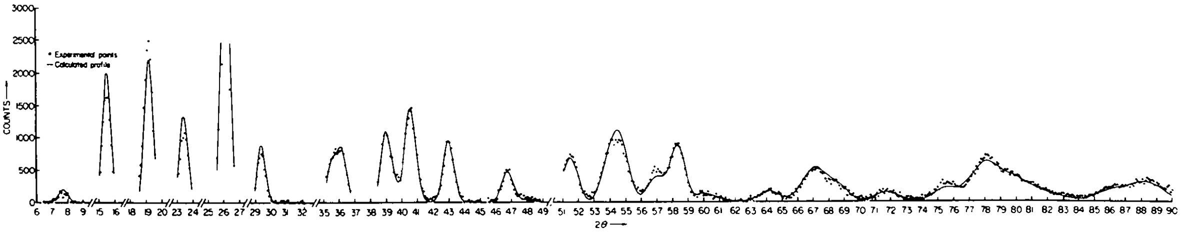

Fig. 1. Comparison of the calculated and observed neutron diffraction profiles for $TiCuD_{0.9}$. The truncations of the tails of some of the peaks are caused by the presence in the pattern of extra lines due to impurities.

tial energy-storage media (Reilly, Hoffman, Strickland & Wiswall, 1974; Libowitz, 1976). The compounds most promising from a practical point of view are those containing an element (such as Ti, Mg, *etc.*) capable of forming a stable hydride, and a second element (such as Fe, Cu, *etc.*) which forms hydrides with difficulty or not at all.

The function of the metal elements in these compounds is still poorly understood. It is presumed that the role of Fe, Cu, *etc.*, is to destabilize the hydrides, thus lowering their dissociation temperature. The rule of reversed stability (van Mal, Buschow & Miedema, 1974), states that, within a given series of intermetallic compounds, the greater the stability of the intermetallic compound, the less stable is its hydride. This rule, however, does not hold in all cases (Maeland, 1978).

A better understanding of the chemical behavior of intermetallic hydrides can be obtained if their crystal structure is known. In particular, the location of the H atoms permits one to determine the metal species to which the H is bonded and the type of bonding.

The neutron diffraction analysis of titanium copper deuteride has been carried out as part of a study of metal hydrides of potential value in practical applications.

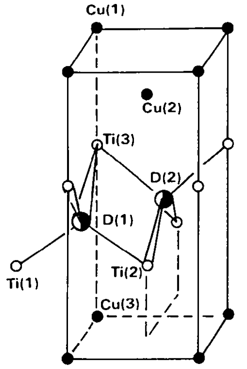

Fig. 2. Schematic view of the structure of $TiCuD_{0\cdot 9}$.

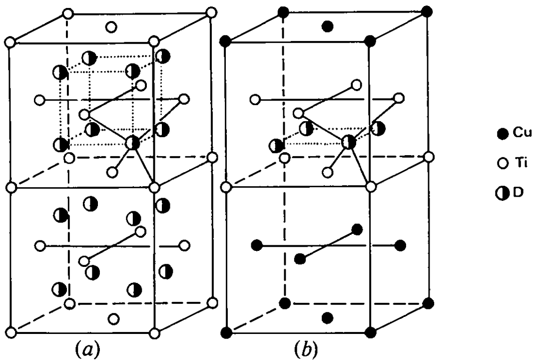

Fig. 3. Comparison between the structures of (*a*) TiD_2, and (*b*) TiCuD (idealized). For clarity the unit cell of TiCuD is doubled.

The occupancy factor determined by neutron diffraction corresponds to the formula $TiCuD_{0\cdot 90(1)}$. The difference between this composition and that determined by thermal analysis [$TiCuD_{0\cdot 96(3)}$] cannot be considered significant. However, a small loss of D_2 with time may well have occurred.

The values of the profile parameters U, V and W obtained in the refinement (Table 2) vary considerably from those calculated theoretically. This difference is larger than the discrepancy between theoretical predictions and experimental results observed previously (Caglioti & Ricci, 1962) and can be attributed to a number of causes, most probably to broadening of the diffraction peaks due to crystallite size.

The difference between the lattice constants determined by X-ray and neutron diffraction may be due to the uncertainty with which the neutron wavelength is known. The X-ray parameters, therefore, have been used for calculating the interatomic distances reported in this paper.

The structure of $TiCuD_{0\cdot 90}$ is illustrated in Fig. 2. In Table 3 are indicated the relevant interatomic distances and these are compared, where applicable, with the corresponding distances found in γ-TiCu (Karlsson, 1951) and in $TiD_{1\cdot 97}$ (Sidhu, Heaton & Zauberis, 1956). The D atoms are located at the centers of distorted tetrahedra of Ti atoms (Ti—Ti distances are 3·020 and 3·208 Å) and are bonded to the Ti atoms (Ti—D is 1·927 Å; the shortest Cu—D distance is 3·164 Å). The arrangement of the Ti and D atoms is the same as that found in $TiD_{1\cdot 97}$, with the same Ti—D distances (Fig. 3).

Recent inelastic-scattering measurements on $TiCuH_{0\cdot 9}$ (Maeland, Rush & Rowe, 1978) show a single peak due to optical vibrations of the H atoms whose frequency is very close to that observed in γ-TiH_x. Thus, these results provide further evidence that the H atoms in titanium copper hydride are surrounded by almost regular tetrahedra of Ti atoms, with metal—hydrogen bonds quite similar to those in γ-TiH_x.

Table 3. *Interatomic distances* (Å) *in* $TiCuD_{0\cdot 9}$

Atoms are labelled as in Fig. 2.

	$TiCuD_{0\cdot 9}$	TiCu*	$TiD_{1\cdot 97}$†
Ti(1)–Ti(2)	3·020 (1)	3·139	3·140
Ti(2)–Ti(3)	3·208 (7)	2·820	
Cu(1)–Cu(2)	2·487 (3)	2·494	
Ti(3)–Cu(1)	2·859 (7)	2·650	
Ti(3)–Cu(2)	2·659 (4)	2·645	
Ti(3)–Cu(3)	3·978 (7)	3·237	
Ti(1)–D(1)	1·927 (4)		1·923
Cu(2)–D(2)	3·164 (3)		
D(1)–D(2)	2·136 (1)		2·220

* Karlsson (1951).
† Sidhu, Heaton & Zauberis (1956).

The structure of $\mathrm{TiCuD}_{0\cdot9}$ can be thought of as formed by slices of TiD_2 and slices of Cu atoms (Fig. 3). In light of this structural property it becomes understandable why titanium hydride precipitates so easily when $\mathrm{TiCuD}_{0\cdot9}$ is heated at relatively low temperatures (>200 °C). The introduction of the D atoms into the structure has the effect of increasing significantly the Ti—Cu distances, as compared with the corresponding distances in γ-TiCu, but does not alter the general configuration of the Ti and Cu atoms. As pointed out by Maeland (1978), this particular feature of the structure may well explain the failure of the rule of reversed stability in the series Ti*R* (*R* = Fe, Cu, Ni, Co). This rule is derived on the assumption that the Ti—D bonds are formed at the expense of the Ti—*R* bonds. This may be true for those structures in which the H is located between the atoms of the two metal species, but it is certainly not true for $\mathrm{TiCuD}_{0\cdot9}$ in which the D atoms are entirely surrounded by Ti atoms and interfere little with the Ti—Cu bonds.

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Cadmium Hydroxyapatite

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Abstract. $\mathrm{Cd_5(PO_4)_3OH}$, hexagonal, $P6_3/m$, a = 9·335 (2), c = 6·664 (3) Å, Z = 2, D_x = 5·694 g cm^{-3}. Crystals were grown by a hydrothermal reaction; 0·5 g of $\mathrm{Cd_5H_2(PO_4)_4.4H_2O}$ in 50 ml of distilled water with an initial pH of 3·3, controlled by adding 2·5 *M* $\mathrm{H_3PO_4}$ solution, were heated at 200 °C for two weeks The final pH was 2·8. A comparison of interatomic distances and bond angles with those of Ca and Sr hydroxyapatites is presented.

Introduction. Cadmium hydroxyapatite is isostructural with calcium hydroxyapatite (Sudarsanan & Young, 1969), and $\mathrm{Cd^{2+}}$ has the possibility of substitution for $\mathrm{Ca^{2+}}$ in bone tissue. As part of a study of the apatite group compounds, single crystals of cadmium hydroxyapatite [$\mathrm{Cd_5(PO_4)_3OH}$] were synthesized, and the crystal structure was investigated. The crystals were colourless, transparent, hexagonal prisms. Their sizes were 0·1–0·2 mm in length and 0·03–0·06 mm in diameter.

From Weissenberg and precession photographs, the crystal was found to have the hexagonal Laue symmetry 6/*m*. Since the systematic absences were 00*l* for *l* odd, the space groups were determined to be $P6_3/m$ (centrosymmetric) or $P6_3$ (non-centrosymmetric).

Intensities were measured on an automated four-circle diffractometer (Philips PW 1100) with graphite-monochromated Mo $K\alpha$ radiation, by the ω–2θ scan technique with a scan speed of 4° min^{-1} in ω, using a crystal of length 0·1 mm and diameter 0·03 mm. A total of 524 independent reflexion data ($F_o > 3\sigma$) were obtained in the range $2\theta \leq 70°$.

Intensities were corrected for Lorentz and polarization factors. Absorption corrections (μ = 108·8 cm^{-1}, Mo $K\alpha$) were made with the program *ACACA* (Wuensch & Prewitt, 1965). The structure was solved by three-dimensional Patterson and difference Fourier syntheses. Two OH groups in the unit cell statistically occupy the four crystallographically