LETTER TO THE EDITOR

The low-temperature orthorhombic structure of YCu

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Abstract. Neutron diffraction results on the intermetallic compound YCu show that the low-temperature phase is of orthorhombic FeB type, space group *Pnma* with $a = 7.0936$ Å, $b = 4.5254$ Å, $c = 5.4030$ Å. The copper coordination is sevenfold and the overall structure may be regarded as a vestige of the cubic high-temperature CsCl modification.

Intermetallic compounds of type RCu where R stands for rare-earth elements adopt the FeB-type orthorhombic structure for the light rare earths (La–Eu) and the cubic CsCl structure for the heavy ones (Gd–Lu), respectively [1, 2]. Exceptions to these rules are SmCu which exists in both structural modifications and FeB-type YbCu, this latter case being attributed to the divalent nature of ytterbium in this compound [3]. ScCu and YCu are cubic at room temperature. However, YCu undergoes a martensitic crystal-structure transformation at about 140 K to an orthorhombic phase. Balster *et al* [4], who first discovered this transition, did not assign a structure type although they did explicitly exclude FeB and CrB structures for this new YCu orthorhombic phase. The existence of similar martensitic phase transitions was subsequently found for GdCu and TbCu [3, 5, 6].

In order to address the problem of whether the magnetoelastic energy serves as the mechanism for the structural and the magnetic para- to antiferromagnetic transition observed in TbCu [5] at the same temperature, neutron diffraction experiments were performed on the $Y_x Tb_{1-x} Cu$ series [7–9]. It was found that increasing the Y content lowers the magnetic transition temperature while the structural transition appears at higher temperatures and comprises a larger volume fraction of the sample. The structural transition—but not the magnetic one—is strongly dependent on the heat treatment of the sample and a large hysteresis is found. Using powdered samples the same magnetic but not structural transition can be found; we conclude that the internal stress induced in the sample by the crushing or filling of the bulk sample hinders the martensitic transformation. The phase diagram of the system $Y_x Tb_{1-x} Cu$ can be found in [8], details of the magnetic structure in [10].

The structure of the low-temperature orthorhombic phase of YCu and TbCu has not been described up to now. We report here on the structure of YCu and $Y_{0.9} Tb_{0.1} Cu$ using neutron diffraction results obtained on D1B at the ILL in Grenoble
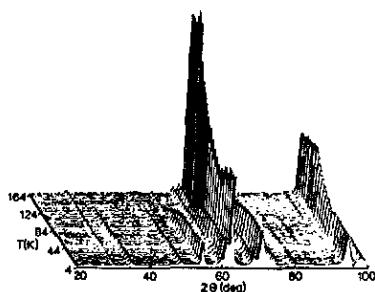
Figure 1. Evolution of the neutron diffraction spectra (λ = 2.52 Å) of YCu between 240 and 5 K.
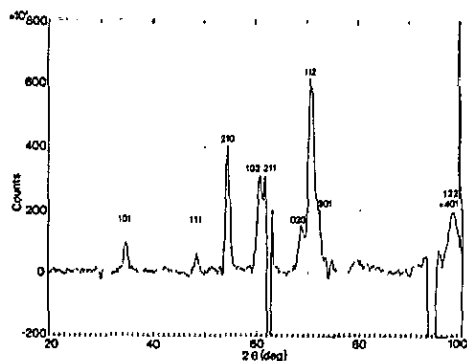
**Figure 2.** Difference plot 54–140 K showing the orthorhombic FeB-type peaks.

and on POLARIS [11], the medium-resolution high-intensity powder diffractometer at ISIS, the UK spallation source.

Details of the sample preparation are given elsewhere [9]. Figure 1 shows a three-dimensional thermogram as obtained on D1B of the phase transition occurring in YCu on lowering the temperature. As can be observed the transition does not propagate through the whole sample. Figure 2 is a difference plot from 54 to 140 K suppressing several small impurity peaks and showing the additional lines appearing at low temperature which correspond to the orthorhombic phase. The two negative peaks indicate the fraction of the cubic YCu phase which underwent the transition. Starting with lattice parameters approximately equal to those published by Larson and Cromer [12] for FeB-type CeCu and Walline and Wallace [13] for FeB-type SmCu, NdCu and PrCu, attempts to index these additional lines were unsuccessful. However, on changing the orthorhombic b and c parameters in such a way as to permute the order of several indices we succeeded in refining the low-temperature phase in the space group *Pnma*. A multiphase Rietveld refinement program [14] was used in fitting the fraction of non-transformed CsCl-type YCu and a third phase identified as YCu_2 as impurity phases. The resulting lattice constants of the orthorhombic phase: a = 7.07 Å, b = 4.51 Å and c = 5.38 Å deviate significantly from the values found for isostructural FeB-type RCu phases where $a \simeq 7.2$ Å, $b \simeq 4.3$ Å and $c \simeq 6.2$ Å [12, 13]. In fact, following the work of Hohnke and Parthé [15] the present orthorhombic phase is found to resemble closely the FeB-type structured compounds LaCu, CeCu, PrCu and NdCu as published by Dwight *et al* [16]. The lattice constants found there are similar to ours found for FeB-type YCu and raise the question whether there exist two different orthorhombic modifications for some RCu compounds. Hohnke and Parthé have, however, already pointed out that in the context of AB compounds with FeB or CrB structure the results of Dwight *et al* [16] seemed to be more consistent with the general trend than those of Larson and Cromer [12] and Walline and Wallace [13]. Using the lattice constants and atom positions resulting from refinement of the D1B data as a starting model, data collected at 5 K on POLARIS on $Y_{0.9}Tb_{0.1}Cu$, over a more extensive d-spacing range, were used for a final refinement. Table 1 gives the results of this fit and the most important interatomic distances. The structure can be regarded as a sequence of trigonal prisms formed by the R atoms, stacked side by side along the direction of the b-axis through the centre of which pass zigzag chains

of Cu atoms. The Cu–Cu distance within the chains is, at 2.69 Å, significantly lower than the value found for the Cu–Cu separation in CsCl-type YCu.

Table 1. Results of the Rietveld refinement for $Y_{0.9}Tb_{0.1}Cu$ at 5 K in the space group *Pnma* and most important interatomic distances.

		$a = 7.09362(29)$Å	$b = 4.52541(18)$Å	$c = 5.40303(22)$Å
		x	y	z
Cu		0.03305(50)	0.25	0.62818(90)
Y		0.18279(49)	0.25	0.13931(96)
Tb		0.18279(49)	0.25	0.13931(96)
Cu–Cu	(2x)		2.6941(36) Å	
Cu	(2x)		3.7832(53) Å	
Y			2.8470(69) Å	
Y			2.8744(56) Å	
Y			2.9589(64) Å	
Y	(2x)		3.0070(39) Å	
Y	(2x)		3.0309(33) Å	
Y–Y	(4x)		3.6506(56) Å	
Y	(2x)		3.7431(52) Å	
Y	(2x)		3.7565(48) Å	
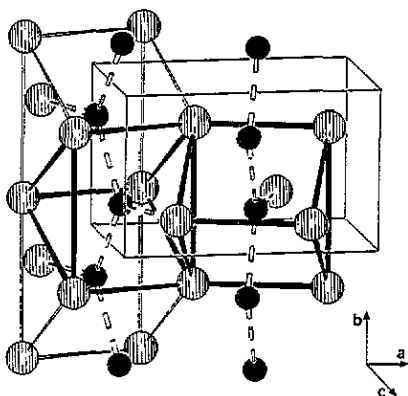
Figure 3. The structure of YCu at low temperature *showing the Cu chains surrounded by seven Y* atoms in one-cap trigonal prism coordination.
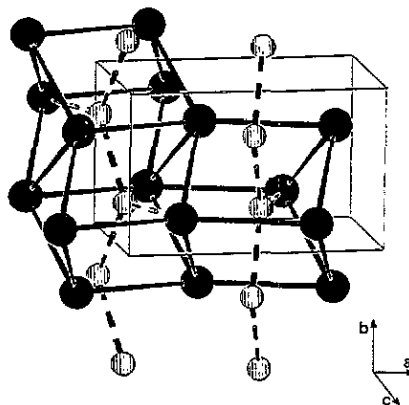
Figure 4. The structure of YCu at low temperature *indicating the existence of distorted Y cubes* reminiscent of the parent CsCl-type structure.

The orthorhombic YCu structure is illustrated in figure 3. It is apparent that besides the six neighbouring R atoms forming the trigonal prism there is a further nearest neighbour for every Cu atom (see table 1). The seventh atom, approximately centred above the basal plane of the trigonal prism, gives rise to a one-cap trigonal prism coordination polyhedron and may be regarded as a vestige of the parent cubic CsCl coordination where each Cu has eight nearest-neighbour Y atoms. Figure 4 illustrates how the orthorhombic FeB can be built up from distorted Y cubes and indicates thereby the relationship to the parent CsCl structure.

Comparing the volume of the formula units one sees that the low-temperature FeB structure has a volume larger by about 3% than the high-temperature CsCl

structure. The resulting internal pressure may explain why the martensitic phase transition is of a gradual and incomplete character.

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