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A single-crystal x-ray and HRTEM study of the heavy-fermion compound $YbCu_{4.5}$

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Abstract. The title compound crystallizes with monoclinic symmetry. Its structure derives from the cubic $AuBe_5$-type structure via the introduction of planar defects parallel to $\{hhh\}$ which lead to a nearly orthogonal $\approx 7 \times 7 \times 6.5$ supercell having the cell parameters $a^s = 48.961(20)$ Å, $b^s = 48.994(4)$ Å, $c^s = 45.643(4)$ Å, $\beta = 91.24(1)^\circ$. A four-dimensional structural analysis reveals a quasi-linear modulation of the atomic positions and occupancies of ytterbium and copper along c^s. On the basis of this result and the electron microscopy images, a three-dimensional model of the superstructure was constructed in space group $C2$. The model contains 7448 atoms per unit cell which are distributed over 350 Yb sites and 1519 Cu sites. It has the overall composition $YbCu_{4.43}$, contains short Yb–Yb distances, and is consistent with the chemical and physical properties.

1. Introduction

The intermetallic compound $YbCu_{4.5}$ shows heavy-fermion properties which are attributed [1, 2] to a valence instability of ytterbium. The magnetic properties suggest [3] a nearly trivalent state, and Mössbauer data [4] suggest the presence of at least two different crystallographic Yb sites. Its crystal structure has so far not been determined. In 1971 Iandelli and Palenzona [5] investigated the compound by x-ray powder diffraction and suggested tetragonal symmetry, cell parameters of $a = 4.96$ Å, and $c =$ multiple of 6.92 Å, and an atom arrangement related to the cubic $PdBe_5$ structure type (which is commonly called the $AuBe_5$ structure type). According to the authors, isostructural $RCu_{4.5}$ compounds (R = rare-earth element) also form with R = Gd, Dy, Tm, Lu and Hf. Previous studies by Buschow *et al* [6, 7] had shown that R elements having small atomic size (R = Gd–Lu) favoured RCu_5 phases crystallizing with the $AuBe_5$-type structure (space group $F\bar{4}3m$) while those having large atomic size (R = La–Sm) favoured phases crystallizing with the

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hexagonal $CaCu_5$-type structure (space group $P6/mmm$). For R = Yb a compound with '$YbCu_5$' stoichiometry does not seem to exist [8]. There does exist, however, a phase of composition $YbCu_{6.5}$ [8] which crystallizes with the hexagonal $TbCu_7$-type structure, a substitutional variant of the $CaCu_5$-type structure, which is also adopted by other R elements such as R = Gd, Tb, Dy and Y [7]. Ytterbium in that compound is presumably divalent. In this paper we present the results of an x-ray single-crystal and a high-resolution transmission electron microscopy (HRTEM) study of $YbCu_{4.5}$. It will be shown that the compound crystallizes with monoclinic symmetry and has the overall composition $YbCu_{4.43}$. Its atom arrangement is one of the most complex found among intermetallic compounds so far, consisting of 7448 atoms per unit cell which are distributed over 350 sites occupied by ytterbium and 1519 sites occupied by copper.

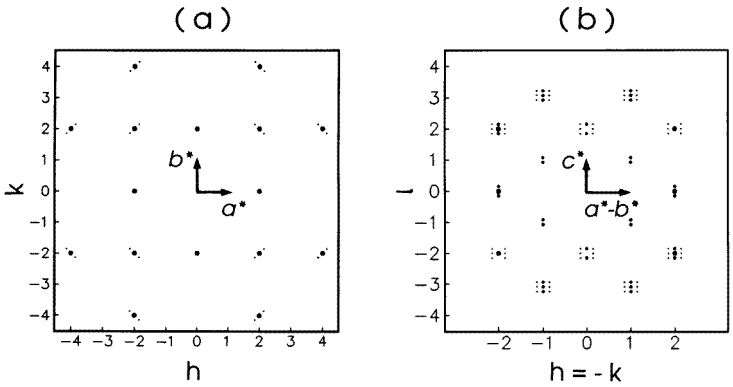

Figure 1. Reproductions of precession photographs of (a) $(h, k, 0)$ and (b) $(h, -h, l)$ reciprocal-lattice planes in the pseudo-cubic average cell a, b, c of $YbCu_{4.5}$.

2. Experimental details

2.1. Synthesis

Ytterbium (3N) and copper (5N) were melted at a molar ratio of 1:4.5 by resistive heating in a tantalum tube of which both ends were sealed. The tube was passed three times through a high-frequency vertical zone-melting furnace. The sample was single phase as judged by metallographic inspection. X-ray powder diffraction patterns (Guinier diffractometer Huber 645, Cu Kα_1 radiation) showed a mixture of sharp and broad diffraction profiles which were consistent with the assumption of a strongly deformed $AuBe_5$-type derivative structure. The chemical composition, $YbCu_{4.5(1)}$, was determined by electron probe microanalysis. The pycnometrically determined density, $D_{exp} = 9.60(2)$ g cm^{-3}, was significantly higher than that stated previously ($D_{exp} = 9.27$ g cm^{-3} [5]).

2.2. X-ray study

Single crystals were isolated from the alloy and investigated using a precession camera (Ni-filtered Cu Kα radiation) in order to determine the space group symmetry. Photographs of the $(h, k, 0)$ and $(h, -h, l)$ reciprocal-lattice planes are reproduced in figure 1. They show various types of reflection which can be classified as main reflections and satellite

reflections. The main reflections can be indexed with a monoclinically distorted cubic face-centred $AuBe_5$-type structure having pseudo-cubic cell parameters of $a, b, c \sim 7$ Å. The distortion away from orthogonality is relatively small. The angle between the vectors $\boldsymbol{a}^* - \boldsymbol{b}^*$ and $\boldsymbol{c}^*$ is 90.8°, corresponding to a monoclinic angle of $\beta \approx 91.2°$. There are two types of satellite reflection which differ with respect to intensity and position. Satellites of the first type are situated along the $\boldsymbol{c}^*$-direction of the monoclinic cell. Their intensities are strong, and they can be indexed on a supercell with $c^s \approx 6.5c$. Satellites of the second type are situated along the diagonal directions $\boldsymbol{a}^* - \boldsymbol{b}^*$ and $\boldsymbol{a}^* + \boldsymbol{b}^*$ and their intensities are rather weak and diffuse. They can be indexed on a supercell with $a^s = 7a$ and $b^s = 7b$. The systematically absent reflections and symmetry-equivalent intensities are consistent with the space groups $C2$, Cm and $C2/m$.

For the structure analysis a plate-like crystal of dimensions $0.108 \times 0.102 \times 0.032$ mm^3 was mounted on a CAD4 four-circle diffractometer and investigated with Cu Kα radiation (graphite monochromator). Fourteen reflections, selected in the range $35° < 2\Theta < 100°$, were used to determine the monoclinic cell parameters of the average structure, $a = 7.002(3)$ Å, $b = 7.005(1)$ Å, $c = 7.028(1)$ Å, $\beta = 91.24(1)°$. The cell parameters of the monoclinic supercell were refined from 10 main and 15 satellite reflections and found to be $a^s = 48.961(20)$ Å, $b^s = 48.994(4)$ Å, $c^s = 45.643(4)$ Å, $\beta = 91.24(1)°$. Integrated intensities for 13 844 main and satellite reflections were collected in the angular range $5° < 2\Theta < 60°$.

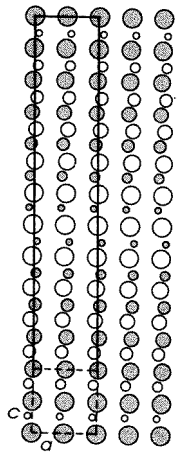

Figure 2. A projection of the modulated structure solution along the monoclinic axis $\boldsymbol{b}$. Only Yb atoms are shown. The sizes of the circles indicate their occupation probabilities. Filled and empty circles belong to two mutually shifted $AuBe_5$-type fragments (see the text). Full lines are drawn as a guide to the eye, indicating 6.5-times repetition of the average cell (dashed line) along [001].

In a first step the average structure of $YbCu_{4.5}$ was refined on the basis of the monoclinic subcell a, b, c, β and space group $C2$, a subgroup of $F\bar{4}3m$. The relatively low consistency index $R = 0.087$ (145 main reflections, 14 parameters) confirmed that the average positions of ytterbium and copper were close to the corresponding positions in $AuBe_5$. Three copper positions (out of five) showed partial occupancy. The programs used for data treatment and structure refinement were those contained in the Xtal3.2 system [9]. In a second step, an attempt was made to describe the superstructure by using a modulated-structure approach in $(3 + 3)$-dimensional superspace [10]. Unfortunately, all satellites of the second type ($hklmnp$, $m \neq 0, n \neq 0$) had strong diffuse tails along $\boldsymbol{c}^*$ which made it difficult to use these reflections during structure solution. Therefore, only main reflections and satellites of the first type ($hkl00p$) were used. This limitation reduced the analysis to the $(3 + 1)$-dimensional superspace, which represents a projection of the $(3 + 3)$-dimensional structure

along monoclinic $\boldsymbol{a}$ and $\boldsymbol{b}$. The modulation vector used was $(\alpha, 0, \gamma) = (0, 0, 1/13)$. The structure was finally solved by the Patterson method and refined from 512 observed main and satellite reflections in a non-standard setting of the superspace group $P2\,(\alpha, 1/2, \gamma)$, yielding a consistency index of $R = 0.080$ for 119 parameters. The calculations were performed by using the program system JANA93 [11]. The results are represented in figure 2 which shows a projection of the $(3 + 1)$-dimensional structure along $\boldsymbol{b}$. The modulations involve both positional coordinates and occupancy factors of ytterbium and copper sites. They proceed along $\boldsymbol{c}$ and suggest the presence of two $AuBe_5$ structural fragments (see the shaded and non-shaded sites). Their thickness along $\boldsymbol{c}$ corresponds to 6.5 subcells, and they are mutually shifted by the monoclinic subcell vector $(-0.0685, -0.4315, 0.2678)$.

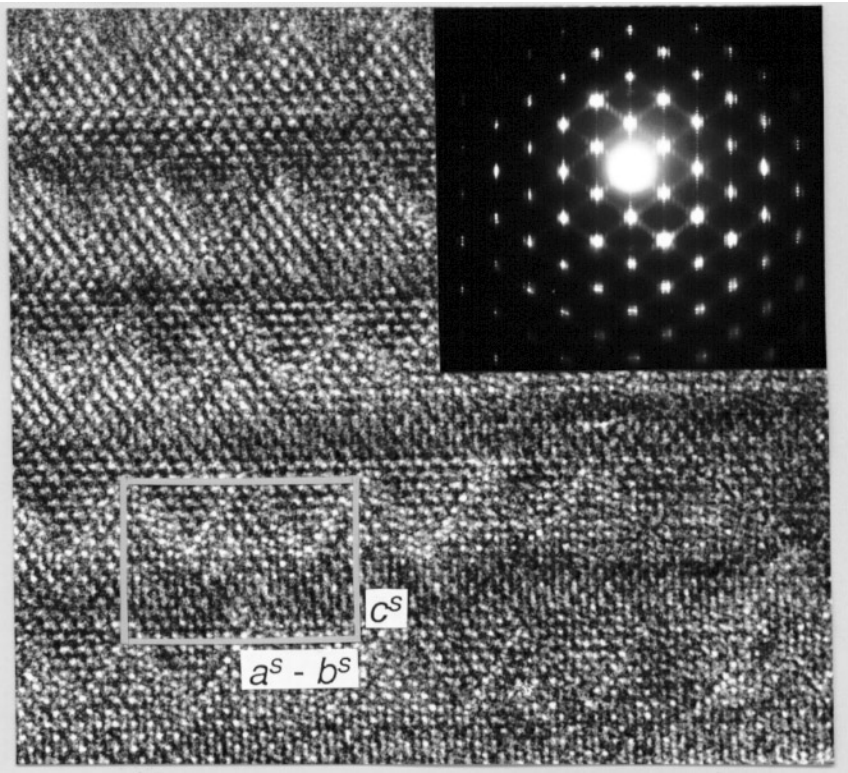

Figure 3. A HRTEM image of $YbCu_{4.5}$ viewed along [110], and the corresponding selected-area diffraction pattern.

2.3. HRTEM study

Crystal slabs of a few mm thickness were isolated from a large crystal block by using a diamond saw, and subsequently thinned down to the required thickness by argon-ion thinning, using a Gatan DuoMill device. In this way, suitably prepared specimens oriented with their plate surface parallel to the (110) and the (010) plane, respectively, could be obtained. Selected-area electron diffraction patterns as well as the corresponding HRTEM micrographs were made by using a Philips CM30ST microscope operated at 300 kV accelerating voltage. The typical contrast of the defect structure is shown in figures 3 and

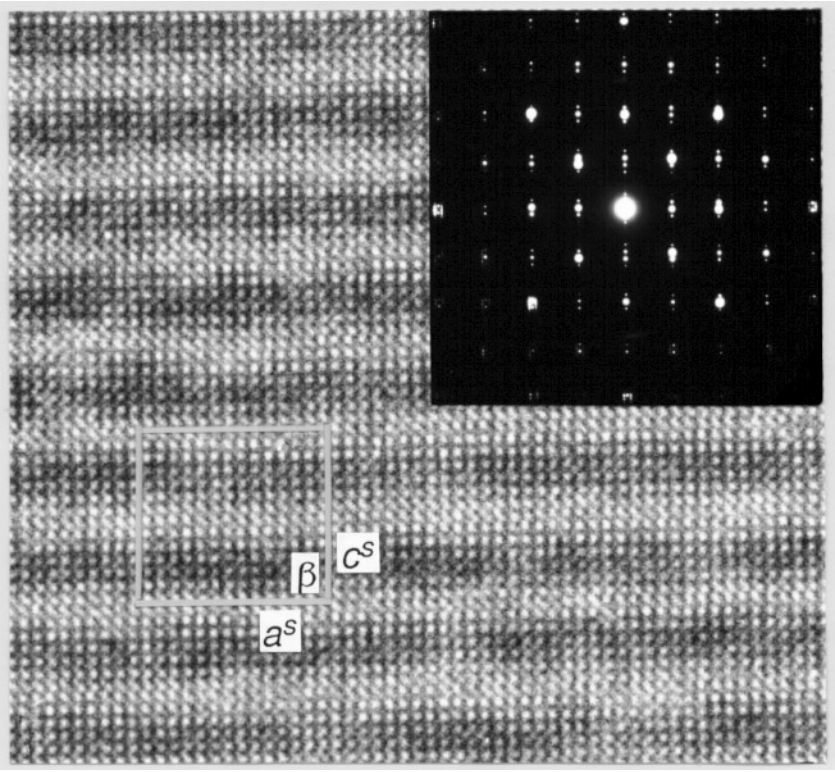

Figure 4. A HRTEM image of $YbCu_{4.5}$ viewed along [010], and the corresponding selected-area diffraction pattern.

4 (viewed along [110] and [010], respectively). The most prominent features in figure 3 are the triangle-shaped regions of dark contrast which have straight and sharp boundaries compared to the surrounding brighter regions. These features are rather unusual and can be interpreted as planar defects which run parallel to the $\{hhh\}$ planes in the cubic $AuBe_5$-type average structure (see below). Such features do not occur in micrographs taken along [100], [010] and [001]. Notice that the triangular regions are not strictly periodic but consist of 'big' and 'small' triangles which repeat more or less randomly along $\boldsymbol{a}^s - \boldsymbol{b}^s$. This violates the periodicity along $\boldsymbol{c}^s$ and could explain why the satellite spots, especially those of the second type, have diffuse streaks along $\boldsymbol{c}^*$ in both the x-ray and electron diffraction patterns.

3. Results

Based on the above findings, a three-dimensional model for the monoclinic superstructure was constructed as follows. First, a pseudo-cubic supercell was created by repeating the cubic $AuBe_5$-type subcell (Pearson symbol $cF24$, $a = 7$ Å, one Yb and two Cu sites) seven times along all three crystal directions. The supercell was then divided with planar defects running parallel to $\{hhh\}$ into three types of region, marked I, II and III, as shown in figure 5. The atom sites within the various regions were then derived from the following symmetry operations:

(i) *region I:* the positions of the $AuBe_5$-type subcell were left unchanged;

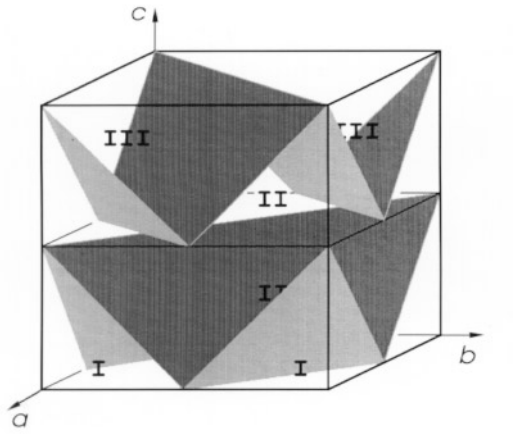

Figure 5. Planar defects in $YbCu_{4.5}$, leading to a sevenfold monoclinic supercell of the cubic $AuBe_5$-type subcell ($a = 7$ Å) along all crystal directions. Regions I, II and III consist of a $AuBe_5$-type structure.

(ii) *region II:* the positions of the $AuBe_5$-type subcell were rotated around a twofold axis running along $x, x, 0$ (this symmetry operation does not belong to space group $F\bar{4}3m$) and subsequently shifted by (0, 0.5, 0.25) and then by (−0.0685, −0.0685, 0.0178); and

(iii) *region III:* the positions of the $AuBe_5$-type subcell were first rotated and shifted as in region II, then shifted by (0, −0.5, 0.25), and finally shifted by (−0.0685, 0.0685, 0.0178).

All shift vectors are expressed in terms of the cubic subcell and correspond to the result of the modulated structure refinement (see figure 2). The signs of the shift components along $\boldsymbol{a}$ (the same in regions II and III) and $\boldsymbol{b}$ (opposite in regions II and III) are consistent with a monoclinic cell angle of $\beta = 91.24^\circ$. The signs of the shift components along $\boldsymbol{c}$ (the same in regions II and III) and the separation and orientation of the planar defects $\{hhh\}$ are consistent with translational periodicities of about 7 times those of the cubic subcell along $\boldsymbol{a}$ and $\boldsymbol{b}$, and 6.5 times those of the cubic subcell along $\boldsymbol{c}$.

A representation of the atom distribution along the viewing directions [110] and [010] is given in figure 6. The various regions having a $AuBe_5$-type atom arrangement and their separation with planar defects are clearly visible. The triangle-shaped regions (the upper part to the left) as viewed along [110] correspond to regions II and III as shown in the upper part of figure 5, and the triangular pattern in the HRTEM image as shown in figure 3. The planar defects delimiting the triangular regions I and II in the lower part of figures 5 and 6 are not visible in that direction, and they are not observed in the HRTEM image (figure 3). By contrast, the separation between the triangular patterns as viewed along [010] is clearly visible in both the model (see the dotted line in figure 6) and the HRTEM image (see the contrast with periodicity $\boldsymbol{c}^s/2$ in figure 4).

A closer inspection of the planar defects separating regions II and III (or regions I and II) shows that they are of two types; one corresponds to anti-phase boundaries (see the full lines in figure 6) and the other to shear planes (see the shaded bands in figure 6). Both influence in their vicinity the $AuBe_5$-type atom arrangement, and in particular the copper atom substructure which clearly suffers from steric hindrance. Assuming an exclusion distance of 2.0 Å for Cu–Cu and Yb–Cu contacts, all Cu atoms near anti-phase boundaries

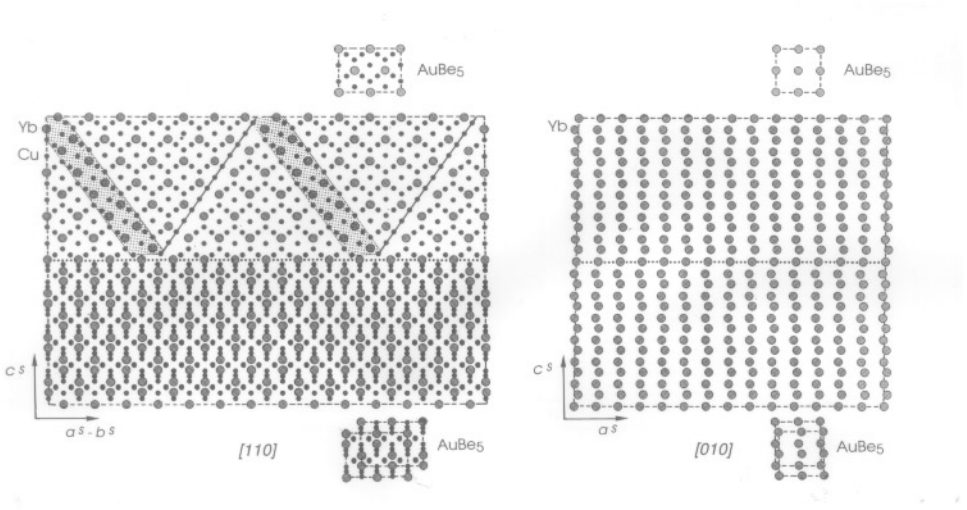

Figure 6. A structure model of $YbCu_{4.43}$, viewed along [110] and [010], and corresponding projections of the cubic $AuBe_5$-type structure. Only Yb (Au) atoms are shown in [010] projections. Full lines indicate anti-phase boundaries between regions I and II (or II and III), dotted lines separate the upper from the lower half of the supercell, and shaded bands indicate the Cu-deficient regions near the shear planes.

can be relocated, thus maintaining locally the $YbCu_5$ stoichiometry. However, the Cu atoms situated near the shear planes cannot all be relocated. Structure modelling suggests that one third of the Cu atoms lying inside the shaded bands have to be taken out. This leads to a local composition of $YbCu_2$ inside the bands, and to an overall composition of $YbCu_{4.43}$ of the crystal. As expected, these compositions (and the atom distribution near the shear planes) depend critically on the exclusion distance. A relatively short value of 2.0 Å (rather than a longer one as suggested from the sums of metallic radii) was chosen because it gave the best compromise between a very homogeneous distribution of atom coordinations (see below) and a low concentration of short Yb–Cu and Cu–Cu contacts. During the atom-elimination procedure, Yb–Cu and Cu–Cu contacts as short as 2.1 Å were tolerated for those atom pairs which could be anticipated to relax to greater distances during a full structure refinement. Unfortunately, the resolution of our data and the complexity of the structure model prevented us from performing such a refinement, and thus from characterizing the regions of the planar defects further. However, it is obvious from the model that the atom coordinations near the planar defects are rather different from those inside the $AuBe_5$-type regions, and that the fraction of atoms affected is very large. For example, the fraction of ytterbium atoms affected by the planar defects is about 50%. Those in the vicinity of anti-phase boundaries have 14 copper neighbours while those in the vicinity of shear planes have 14 copper and 2 ytterbium neighbours, as compared to those in the $AuBe_5$-type regions which have 16 copper neighbours. Thus, roughly speaking, there occur three types of ytterbium site in the structure, and their frequencies of occurrence are about 25%, 25% and 50%, respectively. One site is of particular interest (the one in the vicinity of shear planes) because it shows Yb–Yb contact distances (≈3.6 Å), which are close to those in elemental ytterbium (3.8 Å), and much shorter than the Yb–Yb distances in the $AuBe_5$-type regions (≈4.9 Å) and across the anti-phase boundaries (≈4.4 Å). Interestingly, the coordinations of the Cu atoms lying near the shear planes (i.e. inside the shaded band) and

on the anti-phase boundaries are similar, i.e. they consist of eight copper and four ytterbium neighbours, as compared to nine copper and three ytterbium neighbours in the $AuBe_5$-type regions. This feature can be considered as a merit of the model which justifies the choice of the exclusion distance.

In order to check the model for consistency with the diffraction data, x-ray structure factors were calculated for the monoclinic supercell a^s, b^s, c^s, β based on space group $C2$. Ytterbium was distributed on 336 4*c* sites, 7 2*b* sites and 7 2*a* sites, while copper was distributed on 1519 4*c* sites, corresponding to a total number of 7448 atoms per unit cell†. The calculated and observed structure factors agreed to a consistency factor of $R = 12\%$ for those 512 reflections which were used in the modulated structure refinement.

Finally, it is worthwhile to point out that our model has many of the characteristics of a so-called crystallographic shear (CS) structure [12, 13]. The shear vector for the Yb sites, for example, is equal to the shift vector between regions I and II (or II and III). The shear vectors for the Cu sites are different. In contrast to typical CS structures, however, the topology of $YbCu_{4.5}$ is more complex than a simple sequence of shifted slabs.

4. Conclusions

The crystal structure of $YbCu_{4.5}$ has monoclinic symmetry and is derived from the cubic $AuBe_5$ structure via the introduction of anti-phase boundaries and copper-deficient shear planes. This creates a strong structural anisotropy and lifts the degeneracy of the ytterbium site. Three types of ytterbium site occur in the structure: those in the $AuBe_5$-type regions; those near anti-phase boundaries; and those near shear planes. Their relative abundancies are 2:1:1 and their local environments differ. The ytterbium sites near the shear planes show Yb–Yb distances of the order of 3.6 Å which are presumably related to formation of shear planes, and might be of relevance for the interpretation of the magnetic properties. The composition of the model, $YbCu_{4.43}$, is consistent with chemical analysis, $YbCu_{4.5(1)}$, and the refined composition of the average structure, $YbCu_{4.61(6)}$. The calculated density, $D_x = 9.46$ g cm^{-3}, is consistent with the experimental density, $D_{exp} = 9.60(2)$ g cm^{-3}. The observed and calculated x-ray intensities agree well, and the correspondence between the x-ray diffraction results and the HRTEM micrographs is satisfactory, in particular with respect to the supercell dimensions, the orientation, the separation and shifts of the planar defects, and the appearance of triangle-shaped, slightly disordered structure regions. Finally, it is worth pointing out that the model is consistent with observed Mössbauer spectra which were originally interpreted as the superposition of two quadrupole spectra originating from two different crystallographic ytterbium sites having about equal populations in the structure, and finally reinterpreted as the superposition of three spectra with the population 2:1:1 [4].

Acknowledgments

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† The list of atomic coordinates can be obtained from the authors.

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