

Communication

Y_3Ru_{2-x} —A Representative of a Composite Modulated Family of Intermetallics

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Abstract: The compound Y_3Ru_{2-x} was synthesized from the elements and the structure was solved from single crystal synchrotron data. The high quality of the data allowed the determination of the incommensurate ordering of the compound, previously reported as disordered, with respect to the second subsystem. The compound crystallizes in the super space group $X-3(00\gamma)0$ with the q -vector axial along c^* , $q = 00\gamma$, $\lambda = 0.4276(7)$ and the centering vectors $(1/3\ 2/3\ 0\ 1/3)$, $(2/3\ 1/3\ 0\ 2/3)$.

Keywords: incommensurate; composite; intermetallic

1. Introduction

Ruthenium forms a number of interesting binary compounds with rare earth metals, as reported by Palenzona and Canepa [1]. The phase RE_3Ru_2 ($RE =$ Rare Earth element) is reported for the heavier rare earths, Dy, Ho, Er, Tm, Lu and for Y. The structure of Er_3Ru_2 has been reported [2] to crystallize in the space group $P6_3/m$ with the cell parameters $a = 7.875\ \text{\AA}$, $c = 3.931$ and contains a motif of Ru-centered trigonal prisms of Er and octahedral channels of Er that host Ru atoms that appear to be unconnected to the surrounding structure. In a separate paper, the arrangement of Ru in the octahedral channels is described as “... having one of the ruthenium atoms arranged in strings of unknown translational period along the c -axis that are not commensurate with the rest of the structure [3].”

2. Materials and Methods

Ruthenium shot (99.9%, ABCR) was degassed according to the procedure described by Palenzona and Canepa [1] and pressed into pellets together with a small superstoichiometry of yttrium (99.9%, STREM). The pellets were homogenized by repeated arc-melting. Weighing the resulting ingot revealed a slight loss of Y due to vaporization and the over-all composition changed from the nominal 36% Ru to 38% Ru. After sealing the ingot in an evacuated silica ampoule, it was annealed at 770 °C for 12 days. The challenge in the synthesis is to achieve a relatively homogeneous sample with high melting Ru (melting point 2334 °C) without significant loss of the volatile Y (melting point 1523 °C). This is a challenge for all binary Ru-Y compounds, but in particular for the relatively low melting Y_3Ru_{2-x} , that additionally has a very close companion in $Y_{44}Ru_{25}$. Since the real composition of Y_3Ru_{2-x} is $Y_3Ru_{1.787}$ (62.7% Y), the difference to $Y_{44}Ru_{25}$ (65.7%) is indeed small and balancing the Y content with evaporation is finicky business. Crushing the ingot yielded a Y_3Ru_{2-x} single crystal of good quality, but the sample also contained $Y_{44}Ru_{25}$ and traces of the high melting YRu_2 (melting point 1950 °C). Interestingly, the compositionally close $Y_{44}Ru_{25}$ is also a composite structure, but structurally very different from Y_3Ru_{2-x} .

The single crystal was mounted on a glass fibre and a first X-ray experiment on in-house equipment (XCaliburE, Oxford diffraction) exhibited a diffraction pattern with clear incommensurate satellites.

The number of these was however limited and therefore the sample was taken to the synchrotron Soleil, where a measurement was carried out at the beamline Cristal.

Single crystal data were collected using radiation of the wavelength $\lambda = 0.42484 \text{ \AA}$ in a single 360° scan with the detector set at an angle of 30° . The unit cell was found to have the parameters $a = 7.9986(5) \text{ \AA}$, $c = 3.9840(3) \text{ \AA}$, in excellent agreement with reported data [1] ($a = 8.004$, $c = 3.998$) and a \mathbf{q} vector given by $\mathbf{q} = (1/3 \ 1/3 \ \gamma)$, $\gamma = 0.4276(7)$. A second \mathbf{q} vector $\mathbf{q}_2 = (2/3 \ 2/3 \ \gamma)$ indicates that the structure most likely is twinned and diffuse scattering was discernible, forming planes perpendicular to \mathbf{c}^* and enveloping the strong first order satellites (conf Figure 1). Second order satellites were clearly discernible, but on integration, few were above a 3σ threshold, therefore second order satellites were not used in the refinement (confer Table 1).

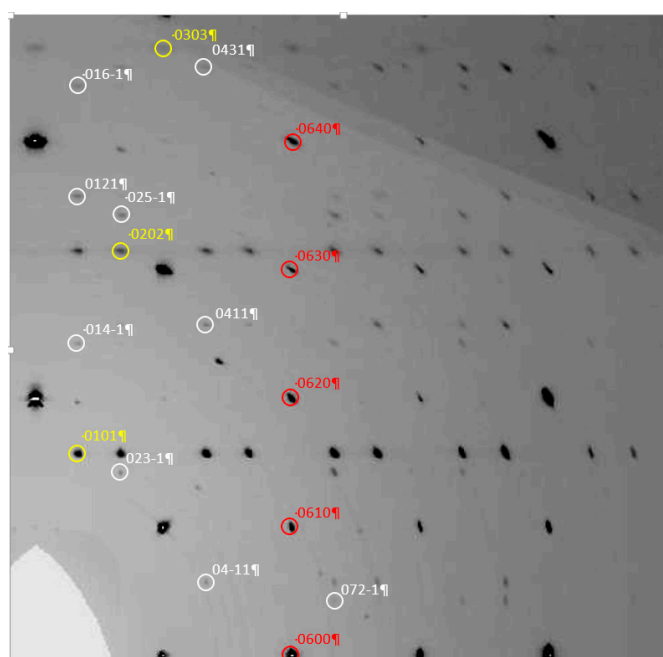


Figure 1. Reconstructed 0klm layer from the single crystal experiment. Sublattice reflections up to hk03 (yellow) and hk40 (red) are visible, as are mixed satellites (white). Diffuse scattering is visible for the hk01 layer and more prominent for the hk02 layer.

Table 1. Crystallographic data for Y3Ru2.

Refined Formula	Y ₃ Ru _{1.787}
Formula Weight M _r	447.4
Crystal size (mm)	
Color	
Crystal System	Trigonal
Superspace group	X-3(00γ)0
Centering vectors	1/3 2/3 0 1/3; 2/3 1/3 0 2/3
Lattice parameters	a = 13.842 c = 3.9855
Modulation vector (γ)	1.574
Formula units	6
Twinning fractions	1: 0.5331(10) 2: 0.4669(10)
R _{int} (%)	4.77
R _{obs} (%)	7.05
wR _{obs} (%)	6.07
R _{main} (%)	2.85
R _{sat} (%)	9.54
GOF	1.39
No of parameters	24
CCDC No	

For the final treatment of the data, integration was carried out in the augmented unit cell $a = 13.842$ $c = 3.9855$ and an axial q -vector, $\mathbf{q} = (0\ 0\ \gamma)$, $\gamma = 1.574$. In this cell, the following $3 + 1$ dimensional extinction condition applies: $hklm$, $h - k + m = 3n$, which is compatible with the centring vectors $(1/3\ 2/3\ 0\ 1/3)$ and $(2/3\ 1/3\ 0\ 2/3)$. The intensity distribution of the satellites indicates that a composite structure is probable, and the structural solution supports this, placing one Ru position and one Y position in the original unit cell and a second Ru position in a unit cell given by the transformation matrix W . Since reflections of the type $hklm$ with both l and m being non-zero are observable, there is data to support intersystem modulation.

$$W = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

This yields a second unit cell with the c' parameter $2.5321\ \text{\AA}$ and the \mathbf{q}' vector γ component $\gamma = 0.6353$.

The structure was solved by charge flipping [4] in superspace, as implemented in JANA2006 [5]. Three atomic positions were easily identified and one of them was clearly best described as a second component of the structure. Refinement progressed smoothly and convergence was achieved for a model using first order harmonic modulations for the positional parameters of all atoms. Introduction of anisotropic displacement parameters led to strong correlations between the modulation parameters and displacement parameters for the single atom in the second composite cell, Ru2. The atomic positions in the first composite cell, Y1 and Ru1, were stable and essentially spherical. In the final refinement, the displacement parameters for Ru2 were left as isotropic. Final agreement parameters R_1 for the converged model were 0.029 for 532 independent, observed, main reflections and 0.096 for 2332 first order satellites in a model with 24 refined parameters. The twin ratio was refined to slightly less than 50% for the individual for which satellite data was used. Conversely the merging R -values for trigonal and hexagonal symmetry were indistinguishable, indicating that the volume of both possible rhombohedral individuals (obverse/reverse) should be equal. Using a smaller twin ratio for the modulated twin is corroborated by the observation of diffuse scattering perpendicular to the c^* -axis. Satellites being replaced by diffuse scattering may be interpreted as proof of the presence of a significant number of regions in the crystal where no correlation between the first and second composite part can be found. All structural figures in the paper were prepared using the software Diamond [6].

3. Discussion

The amplitudes of the positional modulations are small, and hence the structure is essentially that described by Fornasini and Palenzona [2], with the exception of Ru2, which is perfectly ordered in the present model. In Figure 2, the backbone of the structure, the first subcell, is shown. Ru1 atoms centre tri-capped trigonal prisms of Y1 and these polyhedra share faces and edges to form a network with hexagonal tunnels running along the c -direction of the trigonal cell. In the centre of the hexagonal tunnels reside the Ru2 atoms that have a different repeat along c . This causes a continuously changing environment for the Ru2 atoms, shifting between planar trigonal coordination and octahedral coordination. This is shown in Figure 3.

In Figure 4, the variation in bond distances is shown. The slight modulation serves to even out the small differences in coordination caused by the composite nature of the structure.

The overall composition of the single crystal is $Y_3Ru_{1.79}$ as defined by the unit cell and the q -vector. The content of the first sub cell is $Y_{18}Ru_6$, while that of the second subcell is Ru_3 . Since the ratio between the sub cell volumes is given by the ratio of the c -axes, and the second sub cell hence is 1.572 times smaller (and consequently denser), the combined cell content is given by $Y_{18}Ru_6 + 1.572^* Ru_3 = Y_{18}Ru_{10.72}$. The difference in electronegativity between Y and Ru is close to unity and the compound must be considered to be polar, albeit not strongly so.

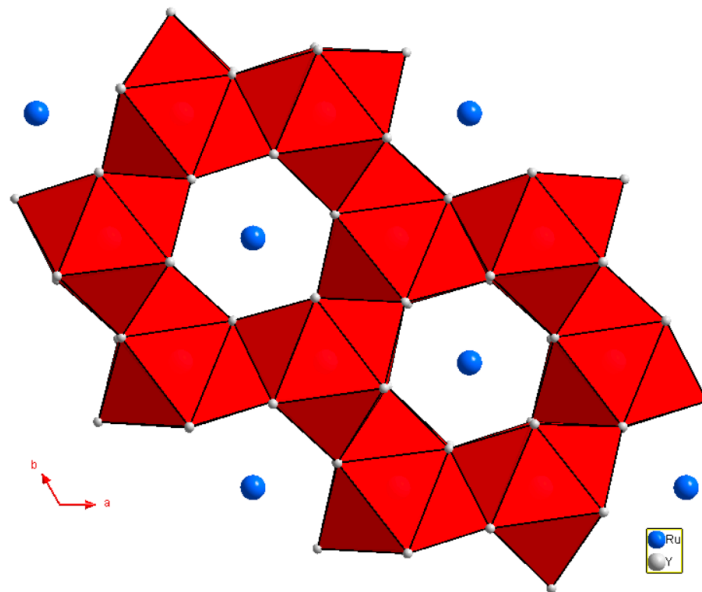


Figure 2. The structure of Y_3Ru_{2-x} may be described as constructed from Ru-centred tri-capped trigonal prisms of Y (RuY_9). These entities share faces along the c -axis and edges in the perpendicular direction so that each Y atom is shared between three RuY_9 polyhedra yielding a structure in the first sub cell with the composition RuY_3 . The Ru atom in the second sub cell (Ru_2 , blue) resides in the trigonal antiprismatic tunnels formed by the first sub structure.

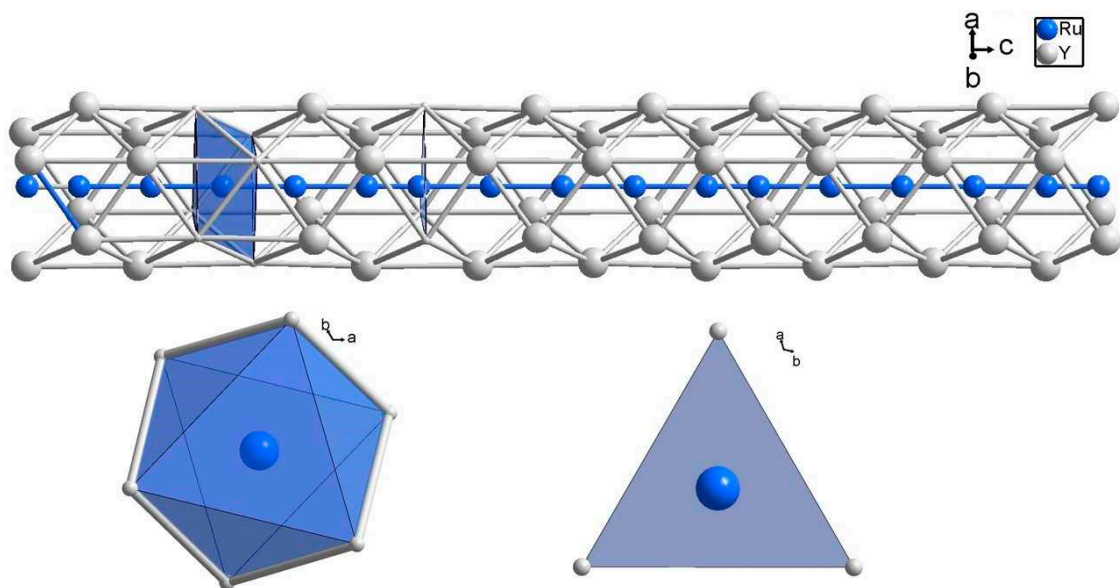


Figure 3. The chain formed by the Ru atoms of the second sub cell (Ru_2 , blue) in the trigonal antiprismatic surroundings of the Y atoms from the first sub cell. Note the continuous change of local environment for Ru_2 from planar trigonal to compressed octahedral.

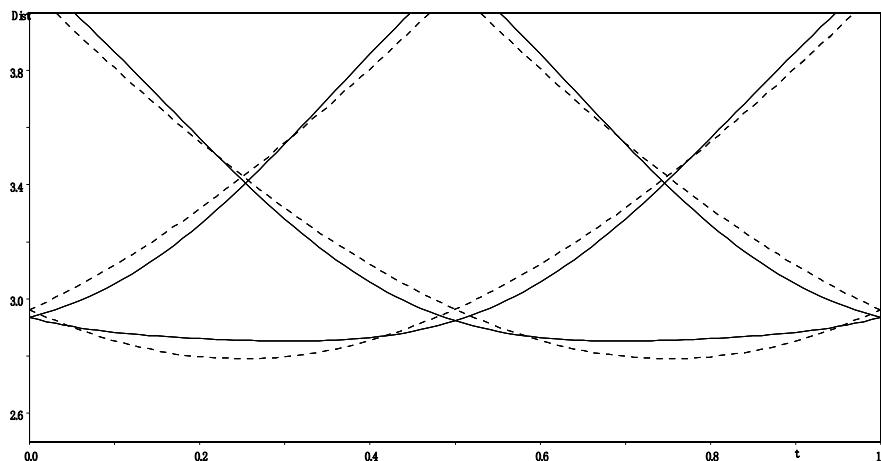


Figure 4. Caption: Distances Ru2 (second sub cell)—Y1 (first sub cell) as a function of position in internal space. Solid lines represent the modulated structure, while dashed lines show distances in a rigid, unmodulated composite structure. Note the tendency towards a more homogeneous surrounding for Ru2 as a result of even very slight modulation. For reasons of symmetry, each line represents three interatomic distances, so that the graph shows variation in coordination number for Ru2 between three and six, if a bonding cut-off is set at 3.2 Å

4. Conclusions

Y_3Ru_{2-x} is a modulated incommensurate composite structure. A detailed structural investigation shows that an intersystem modulation is present, although weak. The compound has been reported as isostructural to the corresponding rare earth compounds with Dy, Ho, Er, Tm and Lu. It would be interesting to study the magnetic properties of these systems to probe the effect of magnetic ordering in geometrically incommensurate systems.

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