Communication

Y₃Ru₂₋ₓ—a Representative of a Composite Modulated Family of Intermetallics

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Received: 11 March 2019; Accepted: 29 March 2019; Published: 1 April 2019

Abstract: The compound Y₃Ru₂₋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(00γ)0 with the q-vector axial along c*, q = 00γ, λ = 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 RE₃Ru₂ (RE = Rare Earth element) is reported for the heavier rare earths, Dy, Ho, Er, Tm, Lu and for Y. The structure of Er₃Ru₂ has been reported [2] to crystallize in the space group P6₃/m with the cell parameters a = 7.875 Å, 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 Y₃Ru₂₋ₓ, that additionally has a very close companion in Y₄₄Ru₂₅ (65.7%) is indeed small and balancing the Y content with evaporation is finicky business. Crushing the ingot yielded a Y₃Ru₂₋ₓ single crystal of good quality, but the sample also contained Y₄₄Ru₂₅ and traces of the high melting YRu₂ (melting point 1950 °C). Interestingly, the compositionally close Y₄₄Ru₂₅ is also a composite structure, but structurally very different from Y₃Ru₂₋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 $\lambda = 0.42484$ Å in a single 360° scan with the detector set at an angle of 30°. The unit cell was found to have the parameters $a = 7.9986(5)$ Å, $c = 3.9840(3)$ Å, in excellent agreement with reported data [1] ($a = 8.004$, $c = 3.998$) and a $q$ vector given by $q = (1/3 1/3 \gamma)$, $\gamma = 0.4276(7)$. A second $q$ vector $q_2 = (2/3 2/3 \gamma)$ indicates that the structure most likely is twinned and diffuse scattering was discernible, forming planes perpendicular to $c^*$ and enveloping the strong first order satellites (conf Figure 1). Second order satellites were clearly discernible, but on integration, few were above a $3\sigma$ 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.](image_url)

| Table 1. Crystallographic data for Y3Ru2. |
|------------------------------------------|
| **Refined Formula** | Y$_3$Ru$_{1.787}$ |
| **Formula Weight Mr** | 447.4 |
| **Crystal size (mm)** |  |
| **Color** |  |
| **Crystal System** | Trigonal |
| **Supercell group** | X-3(00y) |
| **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 ($\gamma$)** | 1.574 |
| **Formula units** | 6 |
| **Twinning fractions** | 1: 0.5331(10), 2: 0.4669(10) |
| **Rint (%)** | 4.77 |
| **Robs (%)** | 7.05 |
| **wRobs (%)** | 6.07 |
| **Rmain (%)** | 2.85 |
| **Rsat (%)** | 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, $q = (0 0 \gamma)$, $\gamma = 1.574$. 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 Å and the $q'$ vector $\gamma$ 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 in 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 Ru3. 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 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.

**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.** 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.
Acknowledgments:
The authors contributed equally to the manuscript.

Funding:
Putz, H.; Brandenburg, K. Diamond—Crystal and Molecular Visualization, Crystal Impact. Available online: https://www.crystalimpact.com/diamond/ (accessed on 10 January 2019).

Conflicts of Interest:
The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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4. Conclusions

Y3Ru2−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.

Author Contributions: The authors contributed equally to the manuscript.

Funding: Financial support from the Swedish Research Council, VR and the Royal Physiographical Society is gratefully acknowledged.

Acknowledgments: Beamtime for this study was provided at the Synchrotron Soleil and assistance from beamline scientist Pierre Fertey is gratefully acknowledged. We are thankful to Alfred Goe Carlsson for help with the synthesis.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.